ICMS

Instituto de Ciencia de Materiales de Sevilla

Memoria de Actividades
Annual Report

Consejo
Superior de
Investigaciones
Científicas

Universidad
de Sevilla

Junta de
Andalucía

2018

Consejo Superior de Investigaciones Científicas
Universidad de Sevilla
Junta de Andalucía

INSTITUTO DE CIENCIA DE MATERIALES DE SEVILLA

Memoria de Actividades
Annual Report
2018

Centro de Investigaciones Científicas "Isla de la Cartuja" (cicCartuja)
c/ Americo Vespucio, nº 49
41092 Isla de la Cartuja SEVILLA
Tfno.: +34 954 48 95 27
Fax: +34 954 46 01 65
http://www.icms.us-csic.es
buzon@icmse.csic.es

Edita
Instituto de Ciencia de Materiales de Sevilla (ICMS)
Centro Mixto entre el Consejo Superior de Investigaciones
Científicas y la Universidad de Sevilla
Centro de Investigaciones Científicas Isla de la Cartuja (cicCartuja)
c/ Americo Vespucio, 49
41092 Isla de la Cartuja, Sevilla
http://www.icms.us-csic.es

Diseño y Maquetación
José Carlos Rivero Cabello

Comisión Memoria-ICMS
Gerardo Colón Ibáñez - Francisco José Gotor Martínez - Hernán R. Míguez García

Fotografías de Portada
Edificio CicCartuja I y II

INDICE

TABLE OF CONTENTS

El ICMS en 2018
ICMS in 2018

Presentación Presentation

A través de esta Memoria 2018, el Instituto de Ciencia de Materiales de Sevilla (ICMS) pretende comunicar lo mejor de las actividades científicas realizadas a lo largo de pasado año. El ICMS es un centro mixto del Consejo Superior de Investigaciones Científicas (CSIC) y la Universidad de Sevilla (US), cofinanciado por la Junta de Andalucía. Fue creado en 1986 y está integrado por personal científico de la Universidad de Sevilla y el CSIC, A finales de 2018, contaba con 98 empleados, de los cuales 49 eran científicos permanentes.

De acuerdo con la estructura establecida en el vigente Plan Estratégico 2018-2021, nuestro centro se organiza en torno a 5 departamentos, cuyos miembros abordan temáticas tanto fundamentales como aplicadas. Así, nuestras investigaciones abordan problemas candentes de la Química y Física del Estado Sólido, la Catálisis Heterogénea, la Cerámica, la Óptica, la Ciencia de Superficies, las Energías Renovables y el Medio Ambiente, etc. Entre ellas, podemos resaltar el aprovechamiento de las energías solar y de biomasa, la generación de H_2 y otros combustibles limpios y de origen renovable, el aprovechamiento y conversión química del CO_2, la depuración de efluentes químicos, el secuestro de residuos radioactivos, la mejora de la selectividad y rendimiento de reacciones químicas básicas, el aumento de la eficiencia de los dispositivos generadores de energía renovable (celdas fotovoltáicas, electrodos, celdas de combustible o baterías) y de los emisores de luz (LEDs), el desarrollo y la mejora de sensores químicos y agentes de contraste radiológico, de materiales biocompatibles para implantes quirúrgicos, de pigmentos cerámicos, y un largo etcétera.

Nuestros principales empeños para los años venideros son realizar investigaciones que se sitúen en la vanguardia de la Ciencia e Ingeniería de Materiales y que éstas sirvan de apoyo al desarrollo en Andalucía de un nuevo sistema económico, en el que las bases científica y tecnológica pasen a ser pilares fundamentales.

Through this Activity Report 2018, the Institute of Materials Science of Seville (ICMS) is communicating the best of its scientific activities carried out for the last year. The ICMS is a joint center of the Spanish Research Council (CSIC) and the University of Seville (US), also funded by the Junta de Andalucia. It was founded in 1986, and integrated by scientific staff of the University of Seville and the CSIC. At the end of last year, it includes 98 people, 49 of them as permanent scientific staff.

The current Strategic Plan 2018-2021 organizes our Center in 5 departments, which personnel address both fundamental and applied research. Thus, our researchers address hot topics related with disciplines of Solid State Chemistry and Physics, Heterogeneous Catalysis, Ceramics, Optics, Surface Science, Renewable Energy and Environment, etc, Among them, we could mention the exploitation of solar energy and biomass, the generation of H_2 and other clean and renewable fuels, the exploitation and chemical conversion of CO_2, the removal of pollutans, the storage of radioactive wastes, the improvement of the selectivity and yield of basic chemical reactions, the efficiency of renewable energy generators (photvoltaic cells, electrodes, fuel cells and batteries) and light emitting devices (LEDs), the development and improvement of chemical sensors and radiological contrast agents , the production of biocompatible scafolds for surgical implants, the production of ceramic pigments, and a long et cetera.

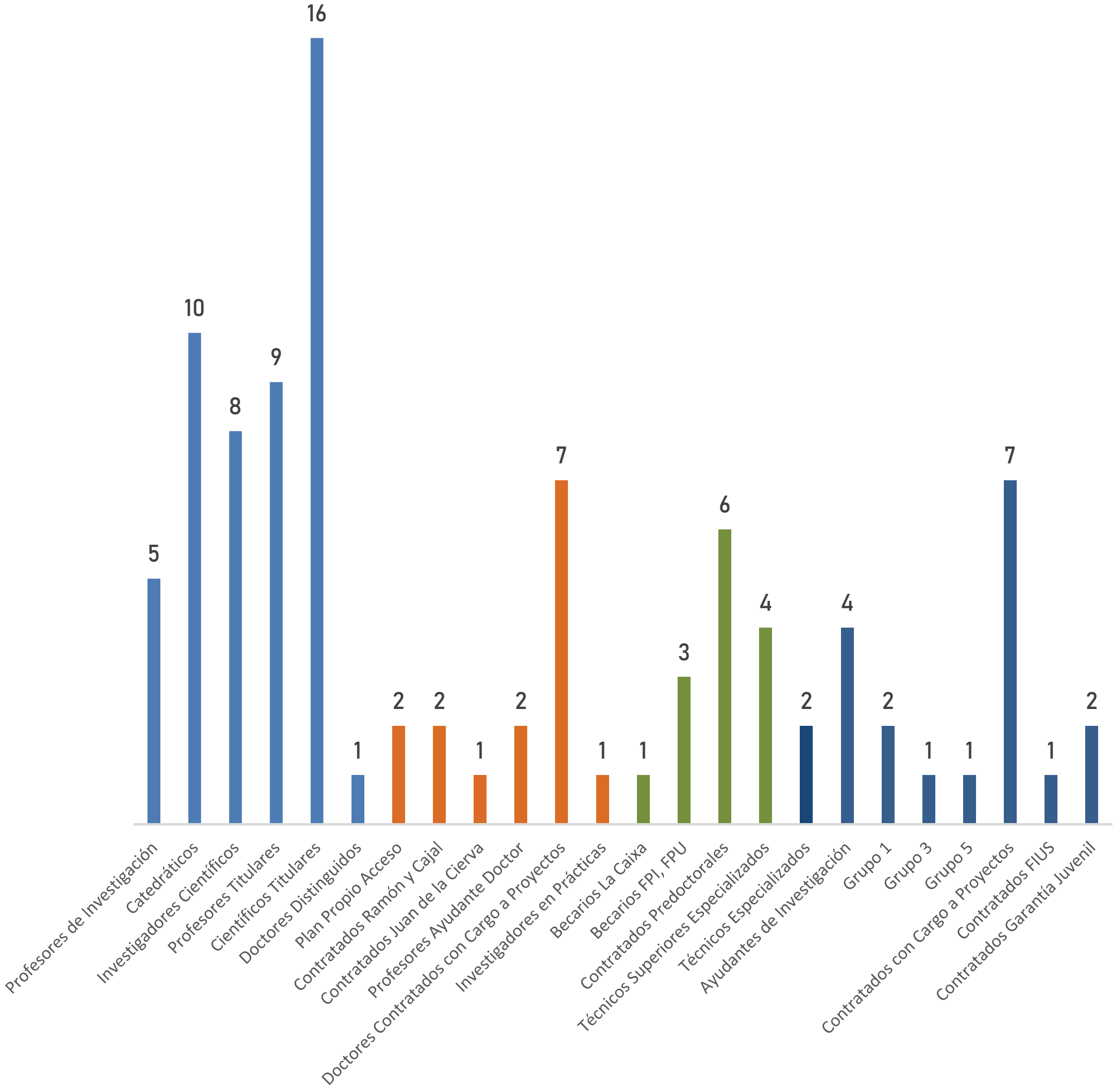
Our main efforts for near future are to cover the most modern and innovative aspects of the current Material Science and Material Engeeniring, as well as to support in the region of Andalusia, the development of a new economic system, in which scientific and technological basis should become fundamental pillars.

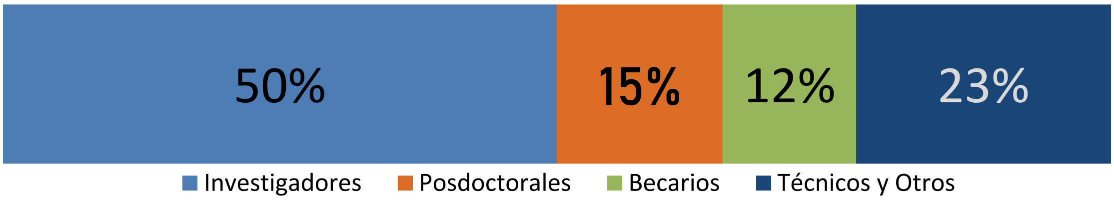
Dr. Juan Pedro Espinós Manzorro
Director del Instituto de Ciencia de Materiales de Sevilla

Datos Estadísticos del ICMS
Statistical Data of ICMS

RECURSOS HUMANOS / HUMAN RESOURCES

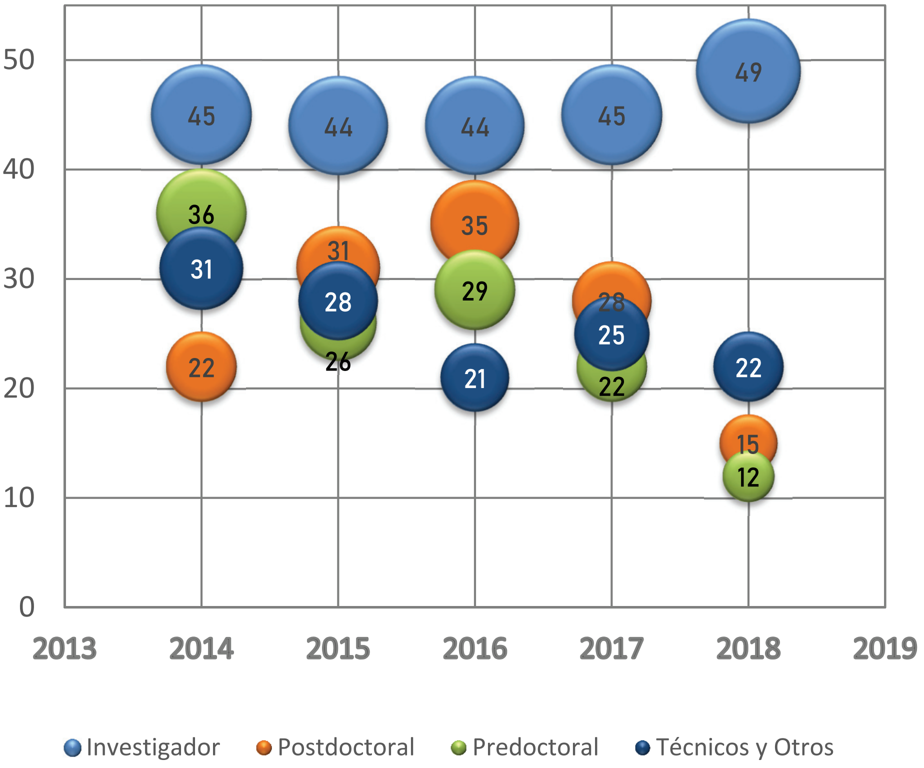
Distribución del personal por categorías – 2018*
Distribution by professional category – 2018



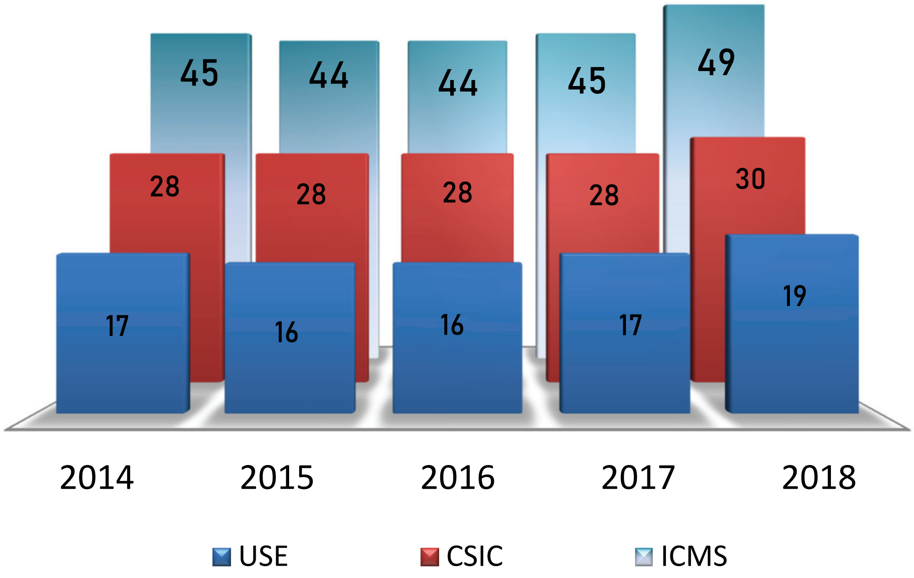


* Datos a 31 de Diciembre de 2018

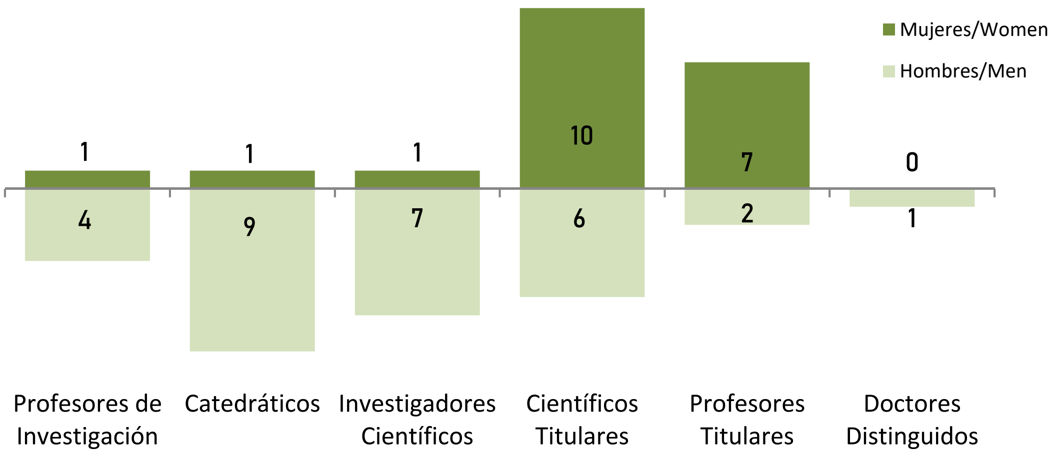
Evolución 2014-2018 del personal
Evolution of Staff

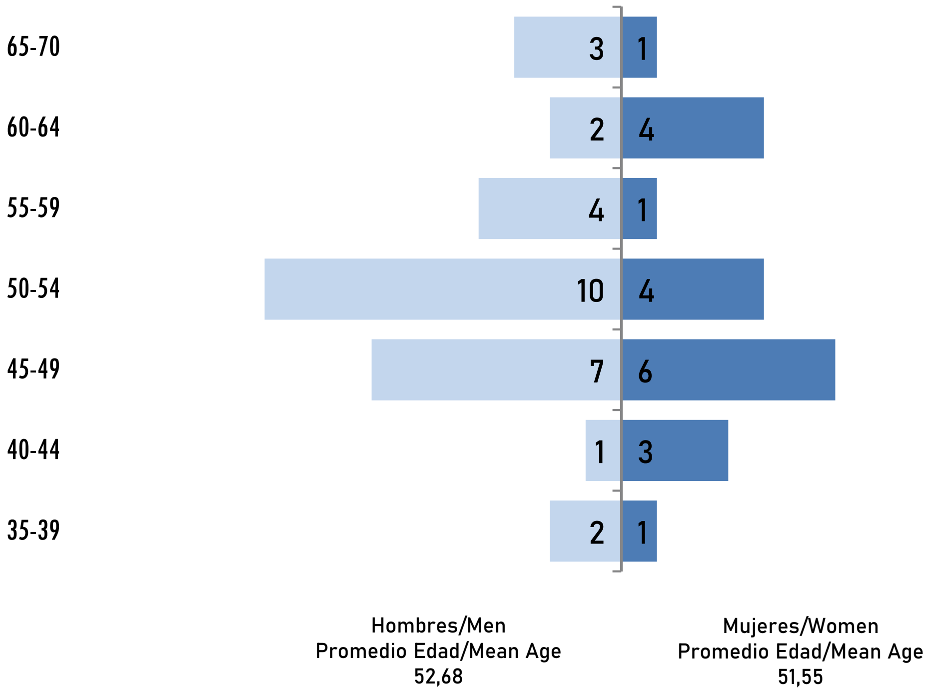


Evolución 2014-2018 del personal investigador
Evolution of Research Staff



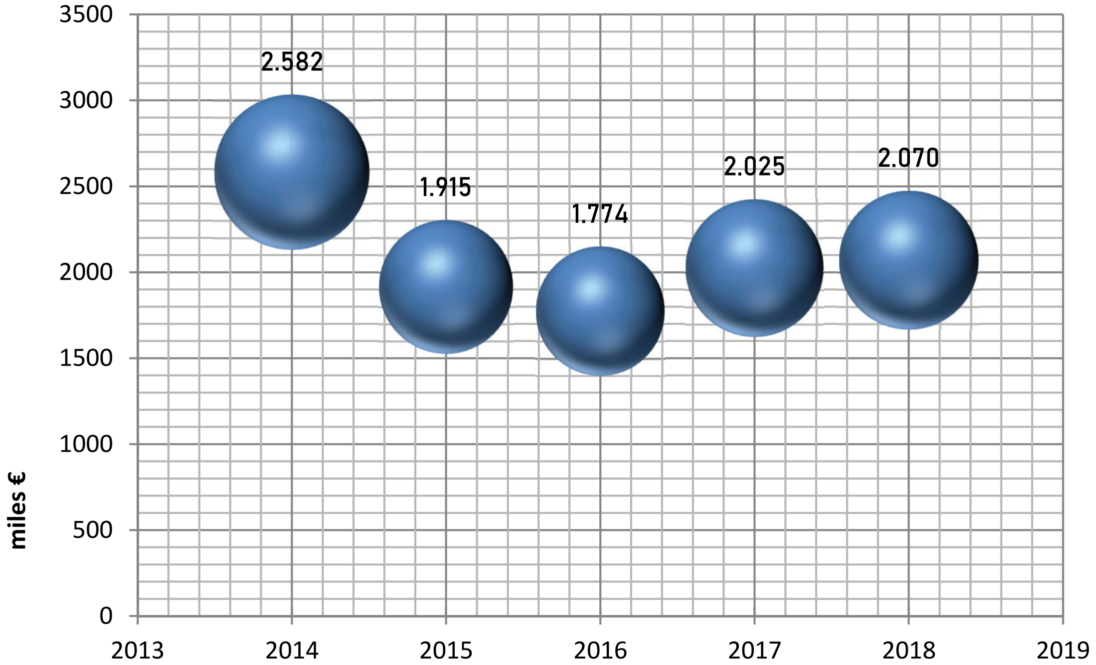
Distribución del personal Investigador (sexo y edad)
Distribution by Scientific staff (gender and age)



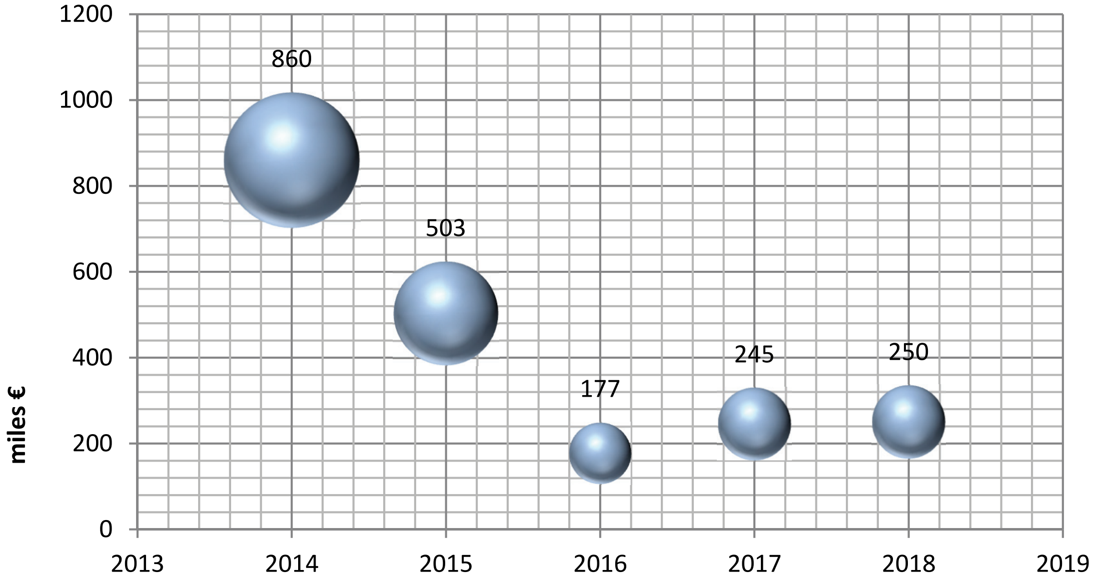


FINANCIACIÓN / FUNDING

Evolución 2014-2018 de la Financiación conseguida por año (miles€)(PCO)
Evolution of the funding of the ICMS



Investigación Contratada



PRODUCCIÓN CIENTÍFICA / SCIENTIFIC PRODUCTION

Revistas SCI en las que se ha publicado algún artículo, por orden de Factor de Impacto
Number of Scientific Papers published in a Specific Journal Arranged by Their Impact Factor (SCI)

REVISTA JOURNAL	ARTÍCULOS PAPERS	FACTOR DE IMPACTO IMPACT FACTOR (*)	Mejor PCT
ENERGY & ENVIRONMENTAL SCIENCE	1	33,250	D1
MATERIALS HORIZONS	1	14,356	D1
APPLIED CATALYSIS B-ENVIRONMENTAL	9	14,229	D1
ANGEWANDTE CHEMIE-INTERNATIONAL EDITION	1	12,257	D1
ACS CATALYSIS	2	12,221	D1
JOURNAL OF MATERIALS CHEMISTRY A	2	10,733	D1
CHEMISTRY OF MATERIALS	1	10,159	D1
GREEN CHEMISTRY	1	9,405	D1
GLOBAL CHANGE BIOLOGY	1	8,880	D1
ACS APPLIED MATERIALS & INTERFACES	2	8,456	D1
APPLIED ENERGY	1	8,426	D1
CHEMICAL ENGINEERING JOURNAL	2	8,355	D1
CHEMSUSCHEM	1	7,804	D1
JOURNAL OF CATALYSIS	2	7,723	D1
JOURNAL OF PHYSICAL CHEMISTRY LETTERS	4	7,329	D1
ACS PHOTONICS	1	7,143	D1
ADVANCED OPTICAL MATERIALS	1	7,125	D1
ACS SUSTAINABLE CHEMISTRY & ENGINEERING	3	6,970	D1
JOURNAL OF MATERIALS CHEMISTRY C	1	6,641	Q1
ACTA BIOMATERIALIA	1	6,638	D1
JOURNAL OF CLEANER PRODUCTION	1	6,395	D1
SENSORS AND ACTUATORS B-CHEMICAL	1	6,393	D1
JOURNAL OF COLLOID AND INTERFACE SCIENCE	1	6,361	Q1
COMPOSITES PART A-APPLIED SCIENCE AND MANUFACTURING	1	6,282	D1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	1	6,019	Q1
MATERIALS & DESIGN	1	5,770	Q1

REVISTA JOURNAL	ARTÍCULOS PAPERS	FACTOR DE IMPACTO IMPACT FACTOR (*)	Mejor PCT
ELECTROCHIMICA ACTA	1	5,383	Q1
JOURNAL OF CO2 UTILIZATION	3	5,189	D1
CHEMISTRY-A EUROPEAN JOURNAL	1	5,160	Q1
APPLIED SURFACE SCIENCE	1	5,155	D1
FUEL	2	5,128	D1
CATALYSIS TODAY	5	4,888	Q1
BUILDING AND ENVIRONMENT	1	4,820	D1
ADVANCED MATERIALS INTERFACES	2	4,713	Q1
APPLIED CATALYSIS A-GENERAL	2	4,630	Q1
JOURNAL OF PHYSICAL CHEMISTRY C	1	4,309	Q1
ELECTROCHEMISTRY COMMUNICATIONS	1	4,197	Q1
MICROPOROUS AND MESOPOROUS MATERIALS	1	4,182	Q1
JOURNAL OF ALLOYS AND COMPOUNDS	8	4,175	D1
CRYSTAL GROWTH & DESIGN	1	4,153	D1
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	1	4,084	Q2
DALTON TRANSACTIONS	1	4,052	Q1
JOURNAL OF THE EUROPEAN CERAMIC SOCIETY	6	4,029	D1
APPLIED THERMAL ENGINEERING	1	4,026	D1
SCIENTIFIC REPORTS	4	4,011	Q1
APPLIED CLAY SCIENCE	1	3,890	Q1
POLYMER	1	3,771	Q1
PHYSICAL CHEMISTRY CHEMICAL PHYSICS	1	3,567	Q1
OPTICS EXPRESS	1	3,561	Q1
CERAMICS INTERNATIONAL	9	3,450	D1
CATALYSTS	2	3,444	Q2
JOURNAL OF MATERIALS SCIENCE	1	3,442	Q2
CRYSTENGCOMM	1	3,382	Q1
JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY A-CHEMISTRY	4	3,261	Q2
ADVANCED POWDER TECHNOLOGY	1	3,250	Q2
MATERIALS CHARACTERIZATION	1	3,220	Q1
SURFACE & COATINGS TECHNOLOGY	4	3,192	Q1
JOURNAL OF THE AMERICAN CERAMIC SOCIETY	1	3,094	D1
CHEMPHYSCHEM	1	3,077	Q2

REVISTA JOURNAL	ARTÍCULOS PAPERS	FACTOR DE IMPACTO IMPACT FACTOR (*)	Mejor PCT
CHEMICAL ENGINEERING RESEARCH & DESIGN	1	3,073	Q2
MATERIALS LETTERS	4	3,019	Q2
MATERIALS	2	2,972	Q2
MOLECULAR CATALYSIS	3	2,938	Q2
JOURNAL OF PHYSICAL CHEMISTRY B	2	2,923	Q2
ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH	2	2,914	Q2
INTERNATIONAL JOURNAL OF REFRACTORY METALS & HARD MATERIALS	2	2,794	Q1
SENSORS AND ACTUATORS A-PHYSICAL	1	2,739	Q2
ELECTROANALYSIS	1	2,691	Q2
MICROSCOPY AND MICROANALYSIS	1	2,673	D1
JOURNAL OF PHYSICAL CHEMISTRY A	1	2,641	Q2
AMERICAN MINERALOGIST	2	2,631	Q2
JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY	2	2,471	Q2
INORGANICA CHIMICA ACTA	1	2,433	Q2
CATALYSIS LETTERS	1	2,372	Q3
JOURNAL OF SOLID STATE CHEMISTRY	1	2,291	Q2
THERMOCHIMICA ACTA	2	2,251	Q2
JOURNAL OF MATERIALS IN CIVIL ENGINEERING	1	1,984	Q2
JOURNAL OF CULTURAL HERITAGE	1	1,955	Q3
COLLOID AND INTERFACE SCIENCE COMMUNICATIONS	1	1,870	Q3
REVIEWS ON ADVANCED MATERIALS SCIENCE	1	1,828	Q3
CHEMISTRYSELECT	1	1,716	Q3
MICRON	1	1,530	Q3
APPLIED RADIATION AND ISOTOPES	1	1,343	Q2
SURFACE AND INTERFACE ANALYSIS	1	1,319	Q4
JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING+	1	0,875	Q1
REVISTA DE LA CONSTRUCCION	1	0,468	Q4
Total	**155**	**5,337**	

(*) Factor de Impacto correspondiente al año 2018
Journal Citation Reports of 2018

COMPOSICIÓN Y ESTRUCTURA

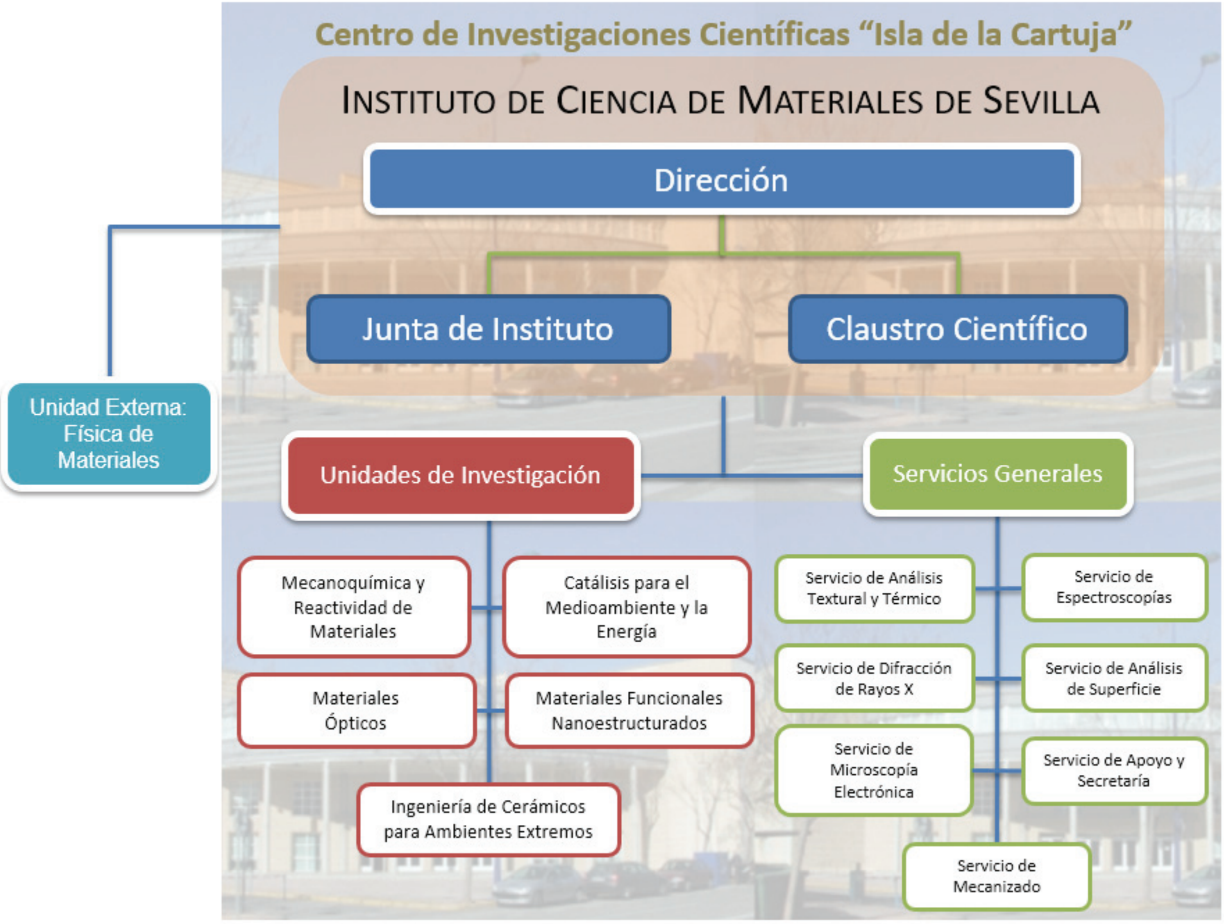
STRUCTURE AND ORGANISATION

EL INSTITUTO / THE INSTITUTE

El Instituto de Ciencia de Materiales de Sevilla (ICMS) fue creado en 1.986. En 1996 se trasladó a unos nuevos locales en la Isla de la Cartuja, integrándose, junto con otros dos Institutos Mixtos, en el Centro de Investigaciones Científicas Isla de la Cartuja (Junta de Andalucia -Consejo Superior de Investigaciones Científicas - Universidad de Sevilla). El ICMS se estructura en cinco Unidades de Investigación ubicadas en el edificio de la Isla de la Cartuja y una Unidad Externa en el campus de Reina Mercedes, Facultad de Física. En la actualidad, el Instituto está formado por grupos de investigación del CSIC y de la Universidad de Sevilla. Estos grupos tratan de aunar sus esfuerzos en diversas áreas de la física y química del estado sólido, físico-química de superficies y otras disciplinas relacionadas en la Ciencia de Materiales. Esta actividad persigue contribuir al desarrollo científico dentro de los Planes de Investigación tanto Autonómicos como Nacionales en el área de la Ciencia y Tecnología de Materiales, así como de las equivalentes de la UE.

The Institute of Materials Science of Seville (ICMS) was created in 1986. In 1996, it moved to new premises at the Isla de la Cartuja, combining with two other Mixed Institutes to make up the Isla de la Cartuja Scientific Research Centre (Junta de Andalucia - Consejo Superior de Investigaciones Científicas - Universidad de Sevilla). The Institute comprises three research units housed in the building at the Isla de la Cartuja and an external unit at the Physics Faculty on the Reina Mercedes campus. Today it incorporates research groups of CSIC and the University of Seville. The aim of these groups is to unite efforts in various areas of solid-state physics and chemistry, physical chemistry of surfaces, and other related disciplines of materials science. Such activity seeks to contribute to scientific development within the Research Plans of both regional and state authorities, and their EU equivalents, in the field of materials science and technology.

ORGANIGRAMA / ORGANIZATION CHART



DIRECCIÓN / DIRECTORATE

Director / Director:	D. **Alfonso Caballero Martínez**
Vicedirector / Vicedirector:	Dª **Ana Isabel Becerro Nieto**

JUNTA DE INSTITUTO / INSTITUTE BOARD

Presidente / Chairman:	D. **Alfonso Caballero Martínez**
Vicedirector / Vicedirector:	Dª **Ana Isabel Becerro Nieto**

Vocales / Members:

D. **Juan Pedro Holgado Vázquez**
Representante U.I. Catálisis para el Medioambiente y la Energía
Dª **Maria Dolores Alba Carranza**
Representante U.I. Ingeniería de Cerámicos para Ambientes Extremos
D. **Luis A. Pérez Maqueda**
Representante U.I. Mecanoquímica y Reactividad de Materiales
D. **Juan Pedro Espinós Manzorro**
Representante U.I. Materiales Funcionales Nanoestructurados
D. **Hernán R. Míguez García**
Representante U.I. Materiales Ópticos
Dª **Angela Gallardo López**
Representante U.E.I. Física de Materiales
Dª **Svetlana Ivanova Lyubomirova**
Representante del Profesorado de plantilla de la Universidad de Sevilla
D. **Juan Carlos Sánchez López**
Representante del Personal Científico de plantilla del CSIC
D. **Juan Carlos Martín Sánchez**
Representante del Personal No Científico y No Profesorado de Plantilla

CLAUSTRO CIENTÍFICO / SCIENTIFIC BOARD

Presidente / Chairman: D. Alfonso Caballero Martínez

Vocales
Members

Alba Carranza, María Dolores
Alcalá González, María Dolores
Alvarez Molina, Rafael
Avilés Escaño, Miguel Angel
Ayala Espinar, María Regla
Barranco Quero, Angel
Becerro Nieto, Ana Isabel
Benítez Jiménez, José Jesús
Bobadilla Baladrón, Luis Francisco
Borrás Martos, Ana Isabel
Borrego Moro, Josefa
Bravo León, Alfonso
Calio, Laura
Calvo Roggiani, Mauricio
Castro Arroyo, Miguel Angel
Centeno Gallego, Miguel Angel
Clauss Klamp, Caroline
Colón Ibáñez, Gerardo
Conde Amiano, Clara F.
Córdoba Gallego, José Manuel
Cotrino Bautista, José
Diánez Millán, María Jesús
Díaz Cuenca, María Aranzazu
Domínguez Leal, María Isabel
Domínguez Rodríguez, Arturo
Espinós Manzorro, Juan Pedro
Estrada de Oya, María Dolores
Fernández Camacho, Asunción
Fortio Godinho, Vanda C.
Franco García, Victorino
Galisteo López, Juan Francisco
Gallardo Cruz, Carmen
Gil Rostra, Jorge
Gómez García, Diego
Gómez Ramírez, Ana María
Gotor Martínez, Francisco José
Hidalgo López, M. Carmen
Holgado Vázquez, Juan Pedro
Ivanova, Svetlana Lyubomirova
Jiménez de Haro, M. Carmen
Jiménez Melendo, Manuel
Laguna Espitia, Oscar Hernando
López Santos, M. Carmen
Lozano Barbero, Gabriel
Malet Maenner, Pilar
Martínez Blanes, José María
Martínez Fernández, Julián
Martínez Tejada, Leidy Marcela
Míguez García, Hernán Ruy
Muñoz Bernábé, Antonio
Navío Santos, José Antonio
Núñez Alvarez, Nuria
Ocaña Jurado, Manuel
Odriozola Gordón, José Antonio
Palmero Acebedo, Alberto
Pavón González, Esperanza
Penkova, Anna Dimitrova
Perejón Pazo, Antonio
Pereñíguez Rodríguez, Rosa
Pérez Maqueda, Luis Allan
Poyato Galán, Rosalía
Ramírez de Arellano-López, Antonio
Ramírez Rico, Joaquín
Real Pérez, Concepción
Rico Gavira, J. Victor
Rodríguez González-Elipe, Agustín
Rojas Ruiz, T. Cristina
Romero Sarria, Francisca
Sánchez Jiménez, Pedro E.
Sánchez López, Juan Carlos
Sánchez Soto, Pedro José
Sánchez Valencia, Juan Ramón
Sarrión Aceytuno, Beatriz
Sayagués De Vega, M. Jesús
Vattier Lagarrigue, Florencia
Yubero Valencia, Francisco

UNIDADES DE INVESTIGACIÓN / RESEARCH UNITS

CATÁLISIS PARA EL MEDIOAMBIENTE Y LA ENERGÍA / CATALYSIS FOR ENVIROMENT AND ENERGY

PERSONAL / PERSONNEL

Catedráticos

Dr. Alfonso Caballero Martínez
Dr. José Antonio Navío Santos
Dr. José Antonio Odriozola Gordón

Investigadores Científicos

Dr. Miguel Angel Centeno Gallego
Dr. Gerardo Colón Ibáñez

Científicos Titulares

Dra. M. Carmen Hidalgo López
Dr. Juan Pedro Holgado Vázquez

Profesores Titulares

Dra. María Isabel Domínguez Leal
Dra. Svetlana Lyubomirova Ivanova
Dra. Anna Dimitrova Penkova
Dra. Francisca Romero Sarria

Investigadores Contratados

Dr. Luis Bobadilla Baladrón
Dr. Oscar Hernando Laguna Espitia

Profesores Contratado Doctor

Dra. Rosa Pereñíguez Rodríguez

Profesores Ayudante Doctor

Dra. Leidy Marcela Martínez Tejada

Becarios Predoctorales

Ldo. Lola de las Aguas Azancot Luque
Ldo. José Luis Santos Muñoz

Personal Contratado

Lda. Laura Blandón Évora
Ldo. Gabriel Delgado Martín
Lda. Ángeles María López Martín
Ldo. Francisco Jesús Platero Moreno

INGENIERÍA DE CERÁMICOS PARA AMBIENTES EXTREMOS
ENGINEERED CERAMICS FOR EXTREME ENVIRONMENTS

PERSONAL / PERSONNEL

Catedráticos

Dr. Miguel Angel Castro Arroyo
Dr. Manuel Jiménez Melendo
Dra. Pilar Malet Maenner
Dr. Julián Martínez Fernández
Dr. Antonio Ramírez de Arellano-López

Científicos Titulares

Dr. José Jesús Benítez Jiménez
Dra. María Dolores Alba Carranza

Profesores Titulares

Dr. Alfonso Bravo León
Dra. Caroline M. Clauss Klamp
Dr. Joaquin Ramírez Rico

Becarios Predoctorales

Ldo. Rafael Cabezas Rodríguez
Lda. María del Pilar Orihuela Espina
Ldo. Francisco J. Osuna Barroso

Personal Contratado

Dra. Esperanza Pavón González

MECANOQUÍMICA Y REACTIVIDAD DE MATERIALES
MECHANOCHEMISTRY AND REACTIVITY OF MATERIALS

PERSONAL / PERSONNEL

Catedráticos
Dr. Diego Gómez García

Investigadores Científicos
Dr. Luis Allan Pérez Maqueda
Dra. Concepción Real Pérez
Dr. Pedro José Sánchez Soto

Científicos Titulares
Dra. María Jesús Diánez Millán
Dr. Francisco José Gotor Martínez
Dra. Rosalía Poyato Galán
Dra. María Jesús Sayagués de Vega

Profesores Titulares
Dra. María Dolores Alcalá González
Dra. María Regla Ayala Espinar

Investigadores Contratados
Dr. José Manuel Córdoba Gallego
Dr. Antonio Perejón Pazo
Dr. Pedro E. Sánchez Jiménez
Dra. Beatriz Sarrión Aceytuno

MATERIALES FUNCIONALES NANOESTRUCTURADOS
NANOSTRUCTURED FUNCTIONAL MATERIALS

PERSONAL / PERSONNEL

Profesores de Investigación

Dr. Juan Pedro Espinós Manzorro
Dr. Agustín Rodríguez González-Elipe
Dra. Asunción Fernández Camacho

Catedráticos

Dr. José Cotrino Bautista

Investigadores Científicos

Dr. Angel Barranco Quero
Dr. Francisco Yubero Valencia
Dr. Juan Carlos Sánchez López

Científicos Titulares

Dra. Ana Isabel Borrás Martos
Dr. Alberto Palmero Acebedo
Dra. María Aránzazu Díaz Cuenca
Dra. T. Cristina Rojas Ruiz

Investigadores Contratados

Dr. Rafael Álvarez Molina
Dr. Jorge Gil Rostra
Dra. M. Carmen López Santos
Dra. Vanda C. Fortio Godinho
Dra. Ana María Gómez Ramírez
Dr. Juan Ramón Sánchez Valencia

Becarios Predoctorales

Ldo. Aurelio García Valenzuela
Ldo. José Manuel Obrero Pérez

Personal Contratado

Ldo. Dirk Hufschmidt
Ing. Tec. M. Rocío García Gil

MATERIALES ÓPTICOS / OPTICAL MATERIALS

PERSONAL / PERSONNEL

Profesores de Investigación

Dr. Hernán R. Míguez García
Dr. Manuel Ocaña Jurado

Científicos Titulares

Dra. Ana Isabel Becerro Nieto
Dr. Mauricio E. Calvo Roggiani
Dr. Gabriel Lozano Barbero
Dra. Nuria O. Núñez Álvarez

Doctores Distinguidos

Dr. Juan F. Galisteo López

Investigadores Contratados

Dra. Laura Calio

Becarios Predoctorales

Lda. Victoria Esteso Carrizo
Ldo. Daniel González Mancebo
Ldo. José María Miranda Muñoz
Ldo. Andrea Rubino

Personal Contratado

Lda. Elena Cabello Olmo
Lda. Lucía T. Castillo Flores
Lda. M. Carmen Gutiérrez Lázaro
Ldo. Mariano Laguna Moreno

SERVICIOS GENERALES / GENERAL SERVICES

Servicio de Apoyo y Secretaría
Dª Margarita Adorna Muñoz
Dª Ana García Martín

Informática – Apoyo Dirección
D. José Carlos Rivero Cabello

Servicio de Análisis Textural y Térmico
Dª Cristina Gallardo López

Servicio de Análisis de Superficie
Dra. Florencia Vattier Lagarrigue

Servicio de Difracción de Rayos X
Ldo. José María Martínez Blanes

Servicio de Espectroscopías
Dr. Miguel Angel Avilés Escaño

Servicio de Microscopía Electrónica
Dra. M. Carmen Jiménez de Haro
Lda. Olga Montes Amorín (cicCartuja)
Dª M. Inmaculada Rosa Cejudo

Servicio de Mecanizado
D. Juan Carlos Martín Sánchez

Unidad "Mecanoquímica y Reactividad de Materiales"
Lda. Belinda Sigüenza Carballo

Unidad "Materiales Funcionales Nanoestructurados"
Dr. Victor J. Rico Gavira

FÍSICA DE MATERIALES (UNIDAD EXTERNA DE INVESTIGACIÓN)
PHYSICS OF MATERIALS (EXTERNAL UNIT)

PERSONAL / PERSONNEL

Catedrático

Dr. Alejandro Conde Amiano
Dra. Clara F. Conde Amiano
Dr. Alberto Criado Vega
Dr. Arturo Domínguez Rodríguez
Dr. Luis M. Esquivias Fedriani
Dr. Victorino Franco García
Dr. Antonio Muñoz Bernabé

Profesor Titular

Dr. Javier S. Blázquez Gámez
Dra. Josefa María Borrego Moro
Dra. María Dolores Estrada de Oya
Dra. M. del Carmen Gallardo Cruz
Dra. Angela Gallardo López
Dr. Felipe Gutiérrez Mora
Dr. José María Martín Olalla
Dra. Ana Morales Rodríguez
Dr. Francisco Javier Romero Landa

Investigador Contratado

Dr. Jhon J. Ipus Bados
Dr. Victor Morales Flórez

Becario Predoctoral

Ldo. Luis M. Moreno Ramírez

UNIDADES DE INVESTIGACIÓN
RESEARCH UNITS

CATÁLISIS PARA EL MEDIOAMBIENTE Y LA ENERGÍA
CATALYSIS FOR ENVIRONMENT AND ENERGY

GRUPOS DE INVESTIGACIÓN

Fotocatálisis Heterogénea: Aplicaciones
Heterogeneus Photocatalysis: Applications [642005]

Materiales y Procesos Catalíticos de Interés Ambiental y Energético
Materials and catalytic processes for environment and energy [642004]
http://matproner.icms.us-csic.es

Química de Superficies y Catálisis
Surface Chemistry and Catalysis [642006]

PERSONAL / PERSONNEL

Catedráticos

Dr. Alfonso Caballero Martínez
Dr. José Antonio Navío Santos
Dr. José Antonio Odriozola Gordón

Investigadores Científicos

Dr. Miguel Angel Centeno Gallego
Dr. Gerardo Colón Ibáñez

Científicos Titulares

Dra. M. Carmen Hidalgo López
Dr. Juan Pedro Holgado Vázquez

Profesores Titulares

Dra. María Isabel Domínguez Leal
Dra. Svetlana Lyubomirova Ivanova
Dra. Anna Dimitrova Penkova
Dra. Francisca Romero Sarria

Investigadores Contratados

Dr. Luis Bobadilla Baladrón
Dr. Oscar Hernando Laguna Espitia

Profesores Contratado Doctor

Dra. Rosa Pereñíguez Rodríguez

Profesores Ayudante Doctor

Dra. Leidy Marcela Martínez Tejada

Becarios Predoctorales

Ldo. Lola de las Aguas Azancot Luque
Ldo. Rafael Castillo Barrero (hasta septiembre)
Lda. Sara Navarro Jaén (hasta septiembre)
Ldo. José Luis Santos Muñoz

Personal Contratado

Lda. Laura Blandón Évora
Ldo. Gabriel Delgado Martín
Lda. Ángeles María López Martín
Ldo. Juan Carlos Navarro De Miguel (hasta mayo)
Ldo. Francisco Jesús Platero Moreno

Proyectos de Investigación / Research Projects

"Una manera de hacer Europa"

Desarrollo de nuevos materiales nanoestructurados para la valorización de metano a hidrógeno y olefinas C2-C4 Development of new nanostructured materials for methane valorization to C2-C4 olefins

Código/Code:	ENE2017-82451-C3-3-R
Periodo/Period:	01-01-2018 / 31-12-2020
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	205.700 €
Investigador responsable/Research head:	Alfonso Caballero Martínez y Gerardo Colón Ibáñez
Componentes/Research group:	Rosa María Pereñiguez Rodríguez, Francisco Jesús Platero Moreno, Angeles María López Martín, Juan Pedro Holgado Vázquez

RESUMEN / ABSTRACT

El desarrollo de nuevos materiales con propiedades singulares en distintos campos de aplicación se ha convertido en las últimas décadas en una prioridad en multitud de áreas de la ciencia y la tecnología. Entre ellas, además de materiales micro y mesoporosos de composición variable, pueden destacarse los sólidos basados en estructura perovskita ABO_3. La versatilidad que presentan estos últimos mediante la sustitución parcial en las posiciones A y B por distintos metales alcalinos, alcalino-terreos y de transición los convierte en una alternativa interesante, y de hecho tienen aplicaciones en campos relacionados con sus propiedades electricas, ópticas, térmicas, catalíticas y como adsorbentes. En el presente proyecto coordinado se plantea la preparación de un conjunto de materiales, entre ellos algunos con estructura perovskita (Fe, Co, Mn, Cu y Bi en posiciones B; Ca, Mg, Ce y La en posiciones A), y estudiar su aplicación en distintos procesos de catálisis heterogénea y de adsorción de contaminantes. Para ello se emplearán una serie de técnicas de preparación recientemente descritas (Cristalización por Microondas, Proceso de Autocombustión, Mesoestructuración por Nanocasting y Porosidad Jerarquizada) que permiten obtener sistemas de alta superficie específica y nanoestructura controlada. De esta forma, y combinando los metales en posiciones A y B para que actuen tanto como agentes promotores como precursores de aleaciones metálicas en los sistemas reducidos, se obtendrán sistemas con propiedades muy variadas y versatiles. Asi, en el subproyecto 1 se estudiarán sus propiedades catalíticas en procesos de enorme interés para la valorización de metano, principal componente del gas natural y una de las fuentes de energía más abundantes en la actualidad. En concreto, y junto con sistemas soportados en materiales mesoporosos y otros, se estudiará en primer lugar la actividad de perovskitas de niquel para la reacción de reformado seco de metano con el fin de obtener gas de síntesis. El objetivo será obtener sistemas activos y sobre estables frente a los fenómenos de desactivación habituales por deposición de coque. En segundo lugar, se estudiarán sistemas basados principalmente en Fe y Co para la reacción de Fisher-Tropsch a olefinas C2-C4, productos de gran interés económico por ser precursores de

una gran cantidad de otros productos de alto valor añadido. Por otro lado, los trabajos propuestos en el subproyecto 2 están relacionados con la aplicación de estos sólidos de estructura perovskita para el desarrollo de procesos de eliminación de contaminantes emergentes, un nuevo tipo de desechos que suelen ser resistentes a los procesos de degradación biológico convencionales, constituyendo por tanto un problema medioambiental de primer orden. En concreto, el proyecto pretende desarrollar tratamientos integrados de depuración (adsorción-POA), utilizando perovskitas para la eliminación de contaminantes emergentes (Ibuprofeno, Salicílico, Ciprofloxacina, Cafeína, Gemfibrozil y Benzafibrato), optimizando parámetros como el rendimiento, la reciclabilidad de los catalizadores, la aplicabilidad y la sostenibilidad. De especial relevancia en este tipo de procesos es la utilización de procesos de fotocatálisis heterogénea, por lo que el desarrollo de nuevos óxidos semiconductores como las perovskitas, con características fisicoquímicas y estructurales superiores a las del TiO_2, es un objetivo de primer orden del presente subproyecto.

In the present project the preparation of a set of materials, including some with perovskite structure (Fe, Co, Mn, Cu and Bi in positions B; Ca, Mg, Ce and La in positions A), and the study of its application in different processes of heterogeneous catalysis and adsorption of pollutants has been proposed. For this purpose, a number of recently described preparation techniques will be used to obtain high surface specific and controlled nanostructure systems. In this way, and combining the metals in positions A and B to act both as promoters and precursors of metal alloys in the reduced systems, systems with very varied and versatile properties will be obtained.

Thus, we will study its catalytic properties in processes of great interest for the valorization of methane, the main component of natural gas and one of the most abundant energy sources today. In particular, and together with systems supported on mesoporous materials and others, the activity of nickel perovskites for the dry methane reforming reaction will be studied first in order to obtain synthesis gas. The aim will be to obtain active and above all stable systems in the face of the usual deactivation phenomena by deposition of coke. Secondly, systems based mainly on Fe and Co for the Fisher-Tropsch reaction to C2-C4 olefins will be studied, products of great economic interest as precursors to a large number of other high added value products.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Aprovechamiento de biomasa y producción sostenible de energía mediante (foto)catalizadores y reactores estructurados basados en materiales carbonosos Biomass valorization and sustainable energy production over (photo)catalysts and structured reactors based on carbonaceous materials

Código/Code:	ENE2017-82451-C3-3-R
Periodo/Period:	01-01-2018 / 31-12-2020
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad

Importe total/Total amount:	193.600 €
Investigador responsable/Research head:	Miguel Angel Centeno Gallego y Svetlana Ivanova
Componentes/Research group:	Leidy Marcela Martínez Tejada, María Isabel Domínguez Leal, Regla Ayala Espinar, Carlos López Cartes

RESUMEN / ABSTRACT

El objetivo principal del presente proyecto coordinado entre la U. de Zaragoza, el ICMS y la U. de Cádiz, es el desarrollo de catalizadores multifuncionales y estructurados basados en materiales catalíticos carbonosos, tanto de carácter biomórfico, como grafénico-grafítico. Estos materiales catalíticos han de ser activos, selectivos y estables en reacciones directamente relacionadas con el aprovechamiento de la biomasa lignocelulósica (producción de 5-HMF, ácido levulínico, FDCA, o γ-valerolactona) y la producción sostenible de energía (producción de H2), así como la valorización química y fotoquímica de CO2 (hidrogenación de CO2, descomposición de biogás, foto-reformado de bio-alcoholes), usando H2 de origen renovable ("water splitting"). Este proyecto trata de mejorar procesos actualmente implementados que están relacionados con la producción de energía, y otros más novedosos, como el aprovechamiento de la luz solar, que sin lugar a dudas están llamados a tener un papel importante en este campo. De hecho, la utilización de la energía solar haría más viable energéticamente, por ejemplo, la reacción de metanación de CO2 al usar H2 de origen (foto)renovable producido por "water splitting". Se busca también la generación de productos de alto valor añadido por procesos de biorefinería, que sustituyan los obtenidos actualmente a partir de fuentes fósiles. Se pretende conseguir un conjunto de sólidos carbonosos con propiedades estructurales (porosidad jerárquica meso/micro), hidrofilicidad-hidrofobicidad, funcionalidades químicas, composición superficial etc. diseñados ad hoc para cada una de las reacciones consideradas por los distintos subproyectos, incluyendo la implementación de procesos en continuo mediante la utilización de reactores estructurados a partir de los catalizadores más eficientes. El desarrollo y utilización de sistemas catalíticos estructurados aumenta la viabilidad e intensificación de los procesos y por tanto la eficiencia energética y medioambiental. La complementariedad de los tres grupos proponentes abre la posibilidad de abordar en un solo proyecto todos estos objetivos, permitiendo aplicar distintas metodologías emergentes para la síntesis de nuevos materiales carbonosos, como son la mineralización biomórfica, la expansión/funcionalización de compuestos intercalados de grafito, grafitos especiales (e.g. "graphite nanolayers" o "nanoflakes"), uso de plantillas inorgánicas para generación de carbones mesoporosos, su funcionalización avanzada y su aplicación en procesos de alto impacto en el área de la energía, tecnología química y tecnologías ambientales.

The main goal of ENERCARB, project coordinated among the U. of Zaragoza, the ICMS and the U. of Cádiz, is the development of multifunctional and structured catalysts based on carbonaceous catalytic materials of biomorphic and/or graphenic-graphitic character. These materials must be active, selective and stable in catalytic reactions related to i) the production and use of chemicals derived from lignocellulosic biomass, i.e. 5-HMF, levulinic acid, FDCA and g-valerolactone; ii) to sustainable energy vector production (H2), and iii) to chemical and photochemical utilization of CO2 (CO2 hydrogenation), biogas decomposition, photo-reforming of bio-alcohols) using H2 of renewable origin ("water splitting"). This project tries to improve currently implemented processes for energy production, and to propose other more innovative processes, such as use of sunlight, undoubtedly called to play an important role in this field. In fact, the use of solar energy would make more energy-efficient, the CO2 methanation reaction by using H2 of (photo)renewable origin produced by "water splitting". ENERCARB also intends to generatre high added value products by bio-refinery processes, as alternative to currently obtained chemicals from fossil sources. A set of carbonaceous solids with tunned structural properties (meso/micro hierarchical porosity), hydrophilicity-hydrophobicity, chemical functionalities, surface composition, etc., will be designed ad hoc for each of the reactions considered by the different subprojects. The implementation of continuous processes through the use of structured reactors is the next logical step to increase the efficiency of the the proposed proceses. The development and use of structured catalytic systems increases the viability and intensifies the processes, and therefore leads to higher energy and environmental efficiency. The complimentary nature of the three participating groups opens the possibility of addressing all these objectives in one single project. It will allow the application of different emerging methodologies for the synthesis of new carbonaceous materials, such as biomorphic mineralization, the expansion-functionalization of graphite intercalation compounds, special graphites (e.g. graphite nanolayers or nanoflakes), use of inorganic templates for the generation of mesoporous carbons, and also its advanced functionalization and its application in processes of high impact in the area of energy, chemical and environmental technologies.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Diseño racional de fotocatalizadores altamente eficientes mediante control nivel atómico Rational design of highly effective photocatalysts with atomic-level control

Código/Code:	PCIN-2017-056)
Periodo/Period:	02-10-2017 / 01-10-2020
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad. Unión Europea
Importe total/Total amount:	97.000 €
Investigador responsable/Research head:	Gerardo Colón Ibañez
Componentes/Research group:	Alfonso Caballero Martínez, Angeles Martín

RESUMEN / ABSTRACT

El uso de la energía solar para la generación de hidrógeno a partir de agua es probablemente uno de procesos más limpios y sostenibles para la obtención de energía. Sin embargo, los catalizadores que dan mejores rendimientos son demasiado caros para ser económicamente viables. El proyecto RATOCAT tiene como objetivo el desarrollo de materiales fotocatalíticos optimizados. De esta forma las prestaciones fotocatalíticas de sistemas basados en TiO2 y gC3N4 podrían optimizarse mediante el diseño de su superficie con nanoestructuras de composición, nanoarquitectura, tamaño y estado químico altamente controladas. Se empleará para ello estudios de simulación teórica para proponer la nanoestructuras óptimas que serán depositadas de forma controlada y precisa mediante atomic layer deposition (ALD).

Los test de actividad fotocatalítica tanto a escala de laboratorio como en planta piloto (Plataforma Solar de Almería).

Using the sun's energy to generate hydrogen from water is probably the cleanest and most sustainable source of fuel that we can envisage. Unfortunately, catalysts that do this are currently too expensive to be commercially viable. The RATOCAT project aims to develop improved photocatalyst materials, along with the processes for their production. The catalytic performance of cheap TiO2 and C3N4 powders will be improved by tailoring their surface with nanostructured oxides as co-catalysts of highly-controlled composition, nanoarchitecture, size and chemical state. First principles simulations will be used to design the optimum nanostructures, which will then be deposited onto powders with the required precision using atomic layer deposition, again supported by simulation. Lab-scale tests of photocatalytic activity will provide feedback for the optimisation of the material and process, before the most promising materials are tested in the field on both pure water and wastewater.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Desarrollo de Materiales Foto-Funcionales para Aplicaciones Medioambientales Development of photo-functional materials for environmental applications

Código/Code:	CTQ2015-64664-C2-2-P
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	76.320,75 €
Investigador responsable/Research head:	José Antonio Navío Santos
Componentes/Research group:	Maria del Carmen Hidalgo López, Manuel Macías Azaña

RESUMEN / ABSTRACT

La fotocatálisis heterogénea es un proceso avanzado de oxidación que ha sido objeto de una enorme cantidad de estudios relacionados con la purificación de gases y del agua. La mayoría de estos estudios se han realizado para el tratamiento de aguas y utilizando el TiO2 o materiales basados en este óxido y más recientemente, aunque en una clara minoría, se han estudiado otros óxidos inorgánicos binarios, ternarios y cuaternarios, predominando en todo caso los estudios de estos últimos materiales para el tratamiento de aguas. En cuanto al catalizador (base del proceso fotocatalítico) que es el responsable de la eficacia o fracaso del proceso, en la última década se han desarrollado numerosos y variados métodos de síntesis que han sido principalmente probados en procesos de degradación fotocatalítica en fase acuosa. Sin embargo, pocos estudios se han realizado con óxidos mixtos (binarios, binarios-acoplados, ternarios y cuaternarios) y menos en fase gasesosa.

En base a estas consideraciones y a la dilatada y reconocida experiencia que el grupo de este Subproyecto#2 tiene el campo de la síntesis y caracterización de materiales foto-funcionales (en el UV y UV/Vis), y debido al reducido número de estudios fotocatalíticos en fase

gas, en su mayoría estudiando un sólo componente, se plantea en este Subproyecto#2, el desarrollo de materiales foto-funcionales que conduzcan a materiales basados no sólo en TiO2 con propiedades mejoradas sino a otros materiales basados en este óxido y a otros óxidos inorgánicos binarios, los obtenidos por acoplamientos de óxidos binarios y ternarios, que se obtengan por procedimientos de síntesis distintos (o modificados) a los ya recogidos en la bibliografía, y cuya fotoactividad sea evaluada por el grupo del Subproyecto#1, sin que se descarte ensayos previos de actividad fotocatalítica en agua por el grupo del Subproyecto#2.

Entre los materiales que se pretenden sintetizar en el Subproyecto#2 (empleando métodos no-hidrotermales, hidrotermales y sol-gel) se contemplan: óxidos binarios (TiO2, ZnO, ZnO2, Fe_2O_3, WO_3, Bi_2O_3, Ta_2O_5 , La_2O_3), óxidos binarios acoplados (TiO_2-WO_3, TiO_2-ZnO, TiO_2-ZnO_2; TiO_2-Ta_2O_5, TiO_2-La_2O_3, ZnO-Fe_2O_3 y ZnO_2-Fe_2O_3), óxidos ternarios (Bi_2WO_6, Bi_2WO_6-ZnO, Bi_2WO_6-ZnO_2, Bi_2WO_6-Fe_2O_3, $Bi_2Ti_2O_7$, $ZnWO_4$, $La_2Ti_2O_7$), contemplando la foto-deposición de metales (Pt, Ag, Au) en los sistemas que muestren una actividad fotocatalítica considerable (Semiconductores/Metal).

Los mejores sistemas evaluados se remitirán al grupo del Subproyecto#1 para el estudio de la viabilidad fotocatalítica en la eliminación de NOx,COVs, CO, CO_2 y SO_2 presentes en emisiones gaseosas.

Heterogeneous photocatalysis is an advanced oxidation process which has been the subject of a huge amount of studies related to gas and water purification. Most of these studies have been performed for the treatment of water mainly by using the TiO2-based materials and more recently, although in a clear minority, by using other inorganic oxides binary, ternary and quaternary, predominating in all cases, the studies of the latter materials for water treatment. In terms of the photocatalyst, which is responsible of the efficiency of the photocatalytic processse, in the last decade have been developed numerous and varied methods of synthesis that have mainly been tested on processes of degradation in aqueous phase. However, few studies have been conducted with mixed oxides (binary, binary-coupled, ternary or quaternary) and less in gas phase.

Based on the above considerations and given the long and recognized experience that members of this Subproject# 2 have in the field of synthesis and characterization of photo-functional materials (UV and UV/Vis), an due also due to the small number of photocatalytic studies in the gas phase , most of them by studying a single component, the work arises in this Subproject # 2 is the development of photo-functional materials that lead to materials based, not only on TiO2 with improved properties but other materials based on this oxide and other binary inorganic oxides, those obtained by coupling of binary oxides and ternary, which are obtained by processes of different synthesis to those already reported in the literature, and whose photoactivity will be evaluated by the group of Subproject # 1, without discarding a prior testing photocatalytic activity in water by the group of Sub-group # 2.

Among the materials that are to be synthesized in the Subproject # 2 (by using non-hydrothermal, hydrothermal and sol-gel methods) are contemplated: binary oxides (TiO_2, ZnO, WO_3, Fe_2O_3, Bi_2O_3, Ta_2O_5, La_2O_3), coupled binary oxides (TiO_2-WO_3, TiO_2-ZnO, TiO_2-ZnO_2, TiO_2-Ta_2O_5, TiO_2-La_2O_3, ZnO-Fe_2O_3 y ZnO_2-Fe_2O_3), ternary oxides (Bi_2WO_6, Bi_2WO_6-ZnO, Bi_2WO_6-ZnO_2, Bi_2WO_6-Fe_2O_3, $Bi_2Ti_2O_7$, $ZnWO_4$,$La_2Ti_2O_7$) studying the photo-deposition of single metals (Pt, Ag, Au) on those prepared systems that exhibit significant photocatalytic activity (Semiconductor /Metal). Best evaluated systems will be forwarded to the Subprojet 1 for the feasibility study on the photocatalytic removal of NOx, VOCs, CO, CO_2 and SO_2 present in gaseous emissions.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Sistemas Catalíticos Estructurados para la Producción de Biocombustible

Structured Catalytic Systems for Biofuel Production

Código/Code:	ENE2015-66975-C3-2-R
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	302.500 €
Investigador responsable/Research head:	José Antonio Odriozola Gordón
Componentes/Research group:	Anna Dimitrova Penkova, María Isabel Domínguez Leal, Francisca Romero Sarria

RESUMEN / ABSTRACT

La dependencia de nuestro actual sistema energético de las fuentes de combustibles fósiles y sus adversos efectos medioambientales están potenciando el desarrollo de fuentes de energía de origen renovable. Este es el caso de los biocombustibles de segunda generación. Los procesos de producción de combustibles a partir de biomasa lignocelulósica y residuos orgánicos son habitualmente catalíticos y se caracterizan por la necesidad de un intenso intercambio de calor asociado al elevado efecto térmico de las reacciones químicas implicadas, dificultad para minimizar simultáneamente las limitaciones difusionales y la caída de presión en los reactores convencionales de lecho fijo y, en ocasiones, por necesitar tiempos de contacto extremadamente cortos. Todo ello hace que las tecnologías catalíticas convencionales trabajen en condiciones no óptimas.

Los sistemas catalíticos estructurados, catalizadores estructurados y reactores de microcanales ofrecen excelentes oportunidades para superar estas limitaciones ya que permiten minimizar simultáneamente las limitaciones difusionales y la caída de presión, mejorar los flujos radiales de calor y materia y permitir tiempos de contacto muy cortos con elevadas eficiencias. Los monolitos de canales paralelos longitudinales, las espumas de porosidad abierta y las mallas metálicas son sustratos que pueden fabricarse a partir de numerosas aleaciones metálicas y con diferentes densidades de celda o poro. También pueden ser recubiertas de cualquier catalizador de interés, adaptándose así a los diferentes requerimientos de cada proceso. Por otro lado, los reactores de microcanales pueden proporcionar una intensificación del proceso sin igual que va acompañada de un excelente control de la temperatura, de la calidad de producto y con mejoras sustanciales en la seguridad del proceso.

El objetivo del proyecto es estudiar sistemas catalíticos estructurados para la producción de energía de origen renovable. En concreto, se estudiarán la síntesis de Fischer-Tropsch, la síntesis directa de dimetiléter y la producción del gas de síntesis que alimentará estos procesos mediante reformado de biogás y "producer gas".Además se estudiará la reacción de desplazamiento del gas de agua que resulta clave para el ajuste de la relación H2/CO en el gas de síntesis.

Se hará especial hincapié en la influencia de las características térmicas de los sistemas estructurados en su comportamiento catalítico. Para ello se estudiará el efecto de la densidad de celdas en monolitos, densidad de poros en espumas, luz de malla en mallas apiladas, tipo de aleación metálica, espesor del recubrimiento catalítico y geometría del sustrato (incluyendo en

algunos casos reactores de microcanales).Se considerarán como fases activas catalizadores muy próximos al estado del arte.

El desarrollo de estos estudios se hará con el apoyo de tres tareas transversales lideradas por cada uno de los tres grupos participantes, pero en las que participarán todos ellos: la preparación de los sistemas catalíticos estructurados, la caracterización mediante técnicas avanzadas y los estudios de modelado y simulación. Mediante este proyecto se pretende generar un conocimiento que contribuya a expandir el actual campo de aplicación de los sistemas catalíticos estructurados hacia aplicaciones energéticas sostenibles que se verían beneficiadas por las ventajas que ofrecen estos sistemas en línea con el reto Energía segura, eficiente y limpia.

The dependence of our current energy system on fossil fuels and their harmful effects on the environment are strengthen the development of renewable energy sources. This is the case of the second generation biofuels. The production of fuels from lignocellulosic biomass and wastes very often involve catalytic processes that are characterized by strong heat exchange requirements due to the high thermal effect of the chemical reactions involved, as well as by the difficulty for simultaneously minimizing transport limitations and pressure drop in conventional fixed-bed reactors. Sometimes, extremely short contact times are also required. As a result, the conventional catalytic technologies operate under non-optimal conditions. The structured catalytic systems, structured catalysts and microchannel reactors offer excellent opportunities for overcoming those limitations because they efficiently allow to minimize simultaneously both the transport limitations and pressure drop while improving the radial fluxes of mass and heat and allowing very short contact times. The monoliths with parallel channels, open cell foams and stacked wire meshes can be made of a variety of metallic alloys and cells or pore densities. They can be also coated with any convenient catalyst thus becoming appropriate for the process of interest. On the other hand, the microchannel reactors are capable of providing an incomparable intensification of the process with an excellent temperature control, and improved product quality and process safety. The objective of this project is the investigation of the application of structured catalytic systems for the production of renewable fuels. The reactions investigated will be the Fischer-Tropsch synthesis, the direct dimethyl ether synthesis and the production of the syngas that will be fed to these processes through the reforming of biogas and producer gas. The water-gas shift reaction will be investigated as well due to its important role for adjusting the H2/CO ratio of the syngas. Special attention will be paid to the study of the effect of the thermal properties of the structured systems on their catalytic performance. To this end, the effects of the cells density of monoliths, pore density of foams, mesh of metallic wire meshes, type of metal alloy, thickness of the catalytic coating and substrate geometry (including in some cases microchannel reactors) will be investigated. Catalyst close to the state-of-the-art will be considered as the active phases. The development of these investigations will be supported by three transversal tasks led by each of the three participating research groups but in which all the groups will be involved: preparation of the structured catalytic systems, characterization using advanced techniques and modeling and simulation studies. This proposal aims at generating knowledge that helps to expand the current range of applications of the structured catalytic systems towards the field of sustainable energy applications that will benefit from the advantages of these systems in line with the challenge Safe, efficient and clean energy.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Desarrollo de procesos catalíticos y fotocatalíticos para la valorización del gas natural: activación y transformación de metano e hidrocarburos ligeros Development of catalytic and photocatalytic processes for natural gas valorization: Activation and transformation of methane and light hydrocarbons

Código/Code:	CTQ2014-60524-R
Periodo/Period:	01-01-2015 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	194.810 €
Investigador responsable/Research head:	Alfonso Caballero Martínez
Componentes/Research group:	Juan Pedro Holgado Vázquez, Gerardo Colón Ibáñez, Rosa María Pereñiguez Rodríguez, Alberto Rodríguez Gómez

RESUMEN / ABSTRACT

En el presente proyecto se pretenden realizar diversos estudios y desarrollos relacionados con distintos procesos de activación y transformación de metano en moléculas de más valor añadido. Con este fin se estudiarán tanto procesos bien establecidos de conversión indirecta, a través de reacciones de reformado (RM) para la obtención de gas de síntesis, como distintos procesos de conversión directa, en concreto la oxidación directa a metanol (DOM) y la aromatización de metano (DAM).

En lo que respecta a la reacción de reformado, se plantea el desarrollo de sistemas catalíticos con resistencia mejorada a los procesos de desactivación. Para ello se prepararán y caracterizarán nuevos catalizadores bimetálicos nanoestructurados de niquel depositados en soportes como ceria, alumina y alumina/ceria, así como soportes mesoporosos de tipo SBA-15, dopados con ceria y alumina. Como segundo metal se utlizarán cobalto o hierro. Paralelamente, se realizará un estudio de la reacción de reformado por vía fotocatalítica utilizando sistemas de Cu, Pt y Ni depositados en soportes activos clásicos como titania o ceria, así como otros de más reciente desarrollo, como son Ga_2O_3, nitruro de carbono o grafeno. En este caso, se pretende igualmente explorar las posibilidades de la activación fotoquímica para la reacción de oxidación preferencial de CO (foto-PROX) en presencia de hidrógeno, de utilidad en los procesos de purificación de hidrógeno procedente del gas de síntesis. Se incidirá en la preparación de sistemas con una estructura de de bandas apropiada para el control de esta oxidación selectiva de CO.

En cuanto a los procesos de conversion directa, se estudiará la reacción de DOM usando O_2, H_2O_2 o N_2O como activadores de la reacción, en combinación con sistemas basados en Au/Pd, Fe, Cu y/o Ni depositados en soportes como zeolitas ZSM-5, grafeno y TiO_2. En este último caso, utilizando Au/Pd como fase metálica activa en presencia de H_2O_2 como especie oxidante se planteará la posibilidad de combinar la síntesis in situ de agua oxigenada con la posterior oxidación directa de metano. Igualmente, se explorará el proceso de oxidación fotocatalítica de metano a metanol como una alternativa novedosa y altamente atractiva. En

este caso, el uso de nuevos fotocatalizadores de oxidación como el BiVO4 así como la presencia de mediadores redox permitirán controlar la oxidación selectiva a metanol.

Algunos sistemas estrechamente relacionados con los anteriores, y en particular los basados en Mo soportados en zeolitas ZSM-5 y MCM-22, se utilizarán para el estudio de la reacción de aromatización de metano. La proporción de aluminio, el porcentaje de molibdeno y su activación en la estructura microporosa del soporte, así como la adición de promotores como Ga, Tl o Pb serán algunas de las variables a optimizar para esta reacción. De forma paralela se podrá estudiar el proceso de aromatización fotoinducido, recientemente descrito por algunos autores.

The present project intends to study and develop different methane activation and transformation processes to obtain high value added molecules.

For this scope we propose to study well established processes of indirect conversion, through reforming reactions (RM) for syngas production, as well as those direct conversion ones, particularly the direct oxidation to methanol (DOM) and aromatization of methane (DAM).

Regarding to the methane reforming reaction, we propose the development of catalytic systems with improved resistance against deactivation processes. In this case, we would prepare and characterize new nanostructured bimetallic catalysts based on nickel supported on ceria, alumina, or alumina/ceria, as well as mesoporous SBA-15 supports, doped with ceria and alumina. As a second metal we would use cobalt or iron. At the same time, we would perform the study of the reforming reaction by a photocatalytic process using Cu, Pt and Ni doped photoactive systems such as titania or ceria, and others recently proposed as Ga2O3, carbon nitride or graphene. In this case, we propose to explore the possibility of the photochemical activation for the preferential oxidation of CO (photo-PROX) in the presence of hydrogen, a very usefulness process for hydrogen purification from syngas synthesis. We will focus our attention in the preparation of systems with the appropriate band structure for the control of the selective oxidation of CO.

Concerning to direct conversion processes, we would study the direct oxidation of methane (DOM) using O2, H2O2, or N2O as reaction activators, in combination with systems based on Au/Pd, Fe, Cu and/or Ni deposited on different supports as ZSM-5, graphene and TiO2. In this later case, using Au/Pd as the active metallic phase in the presence of H2O2, we propose the possibility to combine the synthesis of H2O2 in situ with the subsequent direct oxidation of methane.

Moreover, we would explore the photocatalytic oxidation of methane to methanol as a novel and highly attractive alternative. In this case, the use of new photocatalytic materials as BiVO4 and the presence of redox mediators would allow us to control the selective photo-oxidation to methanol.

Other catalytic systems closely related to above mentioned, and in particular those based on Mo supported on ZSM-5 and MCM-22 zeolites, would be used for the methane aromatization reaction study. The aluminiun ratio, Mo loading and its activation in the microporous structure of the suport, as well as the addition of certain promoters as Ga, Tl or Pb would be some of the parameters to be optimized for this reaction. At the same time, recently reported photoinduced aromatization process would be studied.

Desarrollo de catalizadores biomórficos obtenidos a partir de biomasa residual para producción de hidrógeno y refino de bio-oil Development of Biomorphic Catalysts from Residual Biomass for Hydrogen Production and Bio-oil Refining

Código/Code:	ENE2013-47880-C3-2-R
Periodo/Period:	01-01-2014 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	225.060 €
Investigador responsable/Research head:	Miguel Angel Centeno Gallego
Componentes/Research group:	María Isabel Dominguez Leal, Carlos López Cartes, Leidy Marcela Martínez Tejada, Svetlana Ivanova

RESUMEN / ABSTRACT

El objetivo principal del presente proyecto coordinado entre las universidades de Zaragoza y el Instituto de Ciencias de Materiales de Sevilla es el desarrollo de catalizadores metálicos soportados en carbones biomórficos (CB), para su posterior aplicación a procesos de producción de hidrógeno y de refino de bio-oil. La técnica de Mineralización Biomórfica es una innovadora herramienta capaz de sintetizar materiales inorgánicos funcionales utilizando como plantilla diversas estructuras formadas en procesos biológicos. Así, a partir de materiales lignocelulósicos (biomasa) se puede preparar una gran variedad de materiales cerámicos microestructurados. No obstante, la replicación de los distintos niveles jerárquicos existentes en los tejidos biológicos sigue siendo un gran reto a día de hoy. Para avanzar en esta línea, en este proyecto se va a abordar el estudio de la síntesis, caracterización y aplicación de catalizadores metálicos soportados en carbón biomórfico (Me/CB), con distribuciones de tamaño homogénea y porosidad jerarquizada.

La preparación de estos materiales se realiza mediante descomposición térmica en atmósfera reductora (o inerte) a alta temperatura, y elevadas velocidades de calentamiento, de un material lignocelulósico (e.g. celulosa, lignina, papel) impregnado con los precursores metálicos catalíticos. De esta manera, en una sola etapa, se obtiene un soporte carbonoso biomórfico con nanopartículas de metal dispersas en su superficie. Este método de síntesis presenta una extraordinaria versatilidad, puesto que además de poder utilizar diferentes materias primas de partida, se pueden obtener catalizadores de muy distintas composiciones y contenidos metálicos, así como su estructuración en dispositivos monolíticos y espumas. Como materias primas, además de celulosa, lignina o papel, se van estudiar biomasas agrícolas residuales.

Los catalizadores tipo Me/CB se pretenden aplicar en procesos de producción de hidrógeno (descomposición de hidrocarburos ligeros, de amoniaco y deshidrogenación de ácido fórmico), en la reacción de Water-Gas-Shift (WGS), y en distintas reacciones test de refino de

bio-oil (conversión de acético a acetona, hidrogenación de vainillina y ciclohexeno y conversión de m-cresol a fenol).

The main goal of this coordinated project among the Universities of Zaragoza and the Institute of Material Science of Seville is the development of supported metal catalysts on biomorphic carbons (CB) for their subsequent application in the hydrogen production and in the refining of bio-oil processes. Biomimetic mineralization is a powerful tool that takes structures formed by a biological process as templates to synthesize inorganic functional materials. It offers the advantage to fabricate materials that are difficult to produce by top-down fabrication methods and that have chemical compositions which cannot be produced by self-assembly. Given that the wood is a multifunctional material that is structured on several levels of hierarchy, a large variety of ceramic microstructured materials can be prepared using lignocellulosic materials (biomass). However, the replication of the different hierarchical levels present in vegetal tissues still remains as great challenge today. In order to get a deeper acknowledgement in this subject, this proposal is going to study the synthesis, characterization and application of metallic catalysts supported on biomophic carbons (Me/CB), prepared with uniform size distributions, and hierarchical porosity.

The preparation of the biomorphic materials will be carried out by thermal decomposition in a reducing (or inert) atmosphere, at high temperature, and high heating rates, of several lignocellulosic components (eg cellulose, lignin, paper) impregnated with catalytic metallic precursors. In this way, in a single step, it is possible to obtain a biomorphic carbonaceous support with the metallic nanoparticles dispersed on its surface. This method of synthesis of catalysts has an outstanding versatility because allows the use of different lignocellulose raw materials, with a large variety of compositions and metal contents. In addition they can be easily structured in monolithic devices or foams. As raw materials, besides cellulose, lignin or paper, it is going to be studied several types of waste agricultural biomass.

The obtained Me/CB catalysts will be applied in hydrogen production processes (light hydrocarbons and ammonia decomposition, dehydrogenation of formic acid), water-gas-shift reaction, and in several reactions test of refining of bio-oil (conversion of acetic in acetone, hydrogenation of vanillin and cyclohexene, and conversion of m-cresol into phenol).

UNIDAD ASOCIADA / ASSOCIATED UNIT

Grupo de Fotocatálisis y Electroquímica Aplicada al MedioAmbiente
Laboratory of Photocatalysis and Electrochemistry Applied to the Environment

La Junta de Gobierno del CSIC, en su reunión de fecha 22 de diciembre de 2004, aprobó la propuesta de reconocimiento de la Unidad Asociada denominada "Grupo de Fotocatálisis y Electroquímica aplicada al Medio Ambiente" de la Universidad de Palmas de Gran Canaria (ULPGC) a través del Instituto de Ciencia de Materiales de Sevilla, con el Grupo de investigación del Profesor Dr. José Antonio Navío Santos. Actualmente, el responsable de esta Unidad Asociada, por parte de la ULPGC es el Prof. Dr. Óscar Manuel González Díaz y por parte del CSIC la Dra. M. Carmen Hidalgo.

Las líneas principales de actuación son:
"Fotocatálisis en procesos ambientales"
"Espectro-electroquímica aplicada al medio ambiente"
"Materiales para tratamientos de aguas residuales y de gases contaminados"

Entre las acciones propuestas destacar los objetivos de preparación de nuevos mate-riales fotocatalizadores, así como la caracterización de los mismos y su estudio en aplicaciones de fotocatálisis solar para descontaminación y tratamiento de aguas residuales y de gases.

The CSIC's Board in its meeting from the 22nd December 2004, approved the proposal to recognize the Associated Unit titled "Laboratory of Photocatalysis and Elec-trochemistry Applied to the Environment", of the University of Las Palmas de Gran Canaria (ULPGC) through the Institute of Materials Science of Seville.

The actual person in charge of this Associated Unit is Prof. Dr. Óscar Manuel González Díaz, from ULPGC and Dr. M. Carmen Hidalgo from the CSIC.

The main research lines are:
"Photocatalysis for environmental processes"
"Spectroscopical-electrochemistry applied to environment"
"Materials for the treatment of waste water and polluted gases"

Among the proposed actions, it may be emphasized the objectives of preparation of new photocatalysts materials, their characterization and the study of their applications in solar photocatalysis and treatment of water.

The CSIC's Board of Governors, in its meeting from the 22nd December 2004, passed the proposal to recognize the Associated Unit titled "Laboratory of Photocatalysis and Electrochemistry Applied to the Environment", of the University of Las Palmas de Gran Canaria through the Material Science Institute of Seville.

The actual person in charge of the of this Associated is Prof. Dr. Óscar Manuel González Díaz, from the University of Las Palmas de Gran Canaria and Dr. José Antonio Navío Santos from the CSIC's Institute.

The main research lines of working are:
“Photocatalysis for environmental processes”
“Spectroscopical-electrochemistry applied to environment”
“Natural processes for the treatment of waste water”

Among the proposed actions we may emphasize the objectives of preparation of new photocatalysts materials, their characterisation and the study of their applications in solar photocatalysis and treatment of waste water.

Experimentos en Grandes Instalaciones / Large Facility Experiments

Sincrotrón ALBA / ALBA Synchrotron

Influence of surface dynamics on the catalytic properties of a PtCu model catalyst for PrOx reaction

Código/Code:	2017092458
Periodo/Period:	01-03-2018 / 04-03-2018
Organismo Financiador/Financial source:	ALBA Synchrotron
Instalación Científica:	ALBA CIRCLE Line (NAP-XPS), Barcelona (España)
Investigador principal/Research head:	José Antonio Odriozola Gordón
Investigadores/Researchers:	Rafael Castillo Barrero, José Luis Santos Muñoz, Juan Carlos Navarro de Miguel

Artículos Publicados en Revistas SCI / Papers In SCI Journals

Solar pilot plant scale hydrogen generation by irradiation of Cu/TiO_2 composites in presence of sacrificial electron donors

Maldonado, MI; Lopez-Martin, A; Colon, G; Peral, J; Martinez-Costa, JI; Malato, S
Applied Catalysis B: Enviromental, **229** (2018) 15-23
Agosto, 2018 | **DOI:** 10.1016/j.apcatb.2018.02.005

A Cu/TiO_2 photocatalyst has been synthesised by reducing a Cu precursor with $NaBH_4$ onto the surface of a sulphate pretreated TiO_2 obtained by a sol-gel procedure. The catalyst, that shows a clearly defined anatase phase with high crystallinity and relatively high surface area, and contains Cu_2O and CuO deposits on its surface, has been used to produce hydrogen in a solar driven pilot plant scale photocatalytic reactor. Different electron donor aqueous solutions (methanol, glycerol, and a real municipal wastewater treatment plant influent) have been tested showing similar or even higher energy efficiency than those obtained using more expensive noble metal based photocatalytic systems. The glycerol solutions have provided the best reactive environments for hydrogen generation.

Selective CO methanation with structured RuO_2/Al_2O_3 catalysts

Munoz-Murillo, A; Martinez, LM; Dominguez, MI; Odriozola, JA; Centeno, MA
Applied Catalysis B: Environmental, **236** (2018) 420-427
Noviembre, 2018 | **DOI:** 10.1016/j.apcatb.2018.05.020

Active and selective structured RuO_2/Al_2O_3 catalysts for CO methanation using a flow simulating CO_2-rich reformate gases from WGS and PROX units (H-2 excess, CO_2 presence and 300 ppm CO concentration) were prepared. Both, the RuO_2/Al_2O_3 powder and the slurry prepared from it for its structuration by washcoating of the metallic micromonolithic structure, were also active and selective. Both the slurry (S-RuAl) and micro monoliths (M-RuAl) were able to completely and selectively methanate CO at much lower temperatures than the parent RuAl powder. The optimal working temperature in which the CO conversion is maximum and the CO2 conversion is minimized was determined to be from 149 degrees C to 239 degrees C for S-RuAl and from 165 degrees C to 232 degrees C for M-RuAl, whilst it was from 217 degrees C to 226 degrees C for RuAl powder. TPR, XRD and TEM measurements confirmed that the changes in the activity and selectivity for CO methanation among the considered catalysts can be related with modifications in the surface particle size of ruthenium and its reducibility. These were ascribed to the metallic substrate, the presence of PVA and colloidal alumina in the slurry preparation, the aqueous and acidic media and the thermal treatment used, resulting in a more active and selective catalysts than the parent powder.

Enhanced photocatalytic removal of phenol from aqueous solutions using ZnO modified with Ag

Vaiano, V.; Matarangolo, M.; Murcia, J.J.; Rojas, H.; Navío, J.A.; Hidalgo, M.C.
Applied Catalysis B: Environmental, **225** (2018) 197-206
Enero, 2018 | **DOI:** 10.1016/j.apcatb.2017.11.075

Different photocatalysts based on commercial ZnO modified by silver photodeposition were prepared in this work. The samples were characterized by X-ray fluorescence spectrometry (XRF), specific surface area (SSA), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and UV–vis diffuse reflectance (UV–vis DRS). XRD and XPS showed that Ag/ZnO samples are composed of metallic Ag (Ag0) and ZnO structure was identified. Furthermore, TEM analysis evidenced that the number of silver particles increased with the Ag content. At last, UV–vis DRS results revealed a reflectance band for Ag/ZnO samples, ascribed to the surface plasmon resonance (SPR) absorption of metal silver particles. Commercial ZnO and Ag/ZnO samples were evaluated in the phenol removal under UV light irradiation. It was observed an enhancement of photocatalytic phenol removal from aqueous solutions by silver addition in comparison to commercial ZnO. In particular, the phenol removal increased with the silver content from 0.14 to 0.88 wt%, after this content (i.e 1.28 wt%) the phenol degradation significantly decreased indicating that the optimal Ag content was equal to 0.88 wt%. The influence of the best photocatalyst dosage and the change of the initial phenol concentration in solution were also investigated in this work and the best photocatalytic performance was obtained by using 50 mg L−1 of phenol initial concentration and 0.15 g L−1 of photocatalyst dosage. Finally, the optimized Ag/ZnO photocatalyst was employed for the treatment of a real drinking wastewater containing phenol in which the almost total phenol removal was achieved after 180 min of UV irradiation time.

New concept for old reaction: Novel WGS catalyst design

Garcia-Moncada, N; Gonzalez-Castano, M; Ivanova, S; Centeno, MA; Romero-Sarria, F; Odriozola, JA

Applied Catalysis B: Environmental, **238** (2018) 1-5

Diciembre, 2018 | **DOI:** 10.1016/j.apcatb.2018.06.068

The viability of water gas shift catalytic system for mobile application passes through obligatory reactor volume reduction, achieved normally by using less charge of more efficient catalyst. Completely new concept for catalyst design is proposed: a catalytic system including classically reported WGS catalysts of different nature or active phase (Cu, Pt or Au) mechanically mixed with an ionic conductor. The influence of the later on catalyst activity is studied and discussed, more precisely its effect on the rate of the reaction-limiting step and catalysts' efficiency. It is demonstrated with this study, that the presence of an ionic conductor in contact with a WGS catalyst is essential for the water supply (dissociation and transport), thereby potentiating the water activation step, whatever the mechanism and catalyst overall performance.

Chemical CO_2 recycling via dry and bi reforming of methane using Ni-Sn/Al_2O_3 and Ni-Sn/CeO_2-Al_2O3 catalysts

Stroud, T; Smith, TJ; Le Sache, E; Santos, JL; Centeno, MA; Arellano-Garcia, H; Odriozola, JA; Reina, TR

Applied Catalysis B: Environmental, **224** (2018) 125-135

Mayo, 2018 | **DOI:** 10.1016/j.apcatb.2017.10.047

Carbon formation and sintering remain the main culprits regarding catalyst deactivation in the dry and bi-reforming of methane reactions (DRM and BRM, respectively). Nickel based catalysts (10 wt.%) supported on alumina (Al_2O_3) have shown no exception in this study, but can be improved by the addition of tin and ceria. The effect of two different Sn loadings on this base have been examined for the DRM reaction over 20 h, before selecting the most appropriate Sn/Ni ratio and promoting the alumina base with 20 wt.% of CeO_2. This catalyst then underwent activity measurements over a range of temperatures and space velocities, before undergoing experimentation in BRM. It not only showed good levels of conversions for DRM, but exhibited stable conversions towards BRM, reaching an equilibrium H-2/CO product ratio in the process. In fact, this work reveals how multicomponent Ni catalysts can be effectively utilised to produce flexible syngas streams from CO_2/CH_4 mixtures as an efficient route for CO_2 utilisation.

CO/H-2 adsorption on a Ru/Al_2O_3 model catalyst for Fischer Trospch: Effect of water concentration on the surface species

Jimenez-Barrera, E; Bazin, P; Lopez-Cartes, C; Romero-Sarria, F; Daturi, M; Odriozola, JA
Applied Catalysis B: Environmental, **237** (2018) 986-995
Diciembre, 2018 | **DOI:** 10.1016/j.apcatb.2018.06.053

Water presence and concentration strongly influence CO conversion and CS+ selectivity in the Fischer Tropsch reaction. In this work, the influence of the water concentration was investigated using a model Ru/Al_2O_3 (5 wt. %) catalyst. The surface species formed after CO and H-2 adsorption in dry and wet (different water concentrations) conditions were analyzed by FTIR. Firstly, water adsorption was carried out up to complete filling of the pores and then CO was put in contact with the catalyst. The absence of adsorbed CO species in these conditions evidences that CO diffusion in water controls the access of the gas to the active sites and explains the negative effect of high water concentrations reported by some authors. Moreover, the adsorption of a mixture of CO + H-2 + H2O, being the water concentration close to that needed to have a monolayer, and a dry mixture of CO + H-2 were carried out and compared. Results evidence that water in this low concentration, is able to gasify the surface carbon species formed by CO dissociation on the metallic sites. This cleaning effect is related to the positive effect of water on CO conversion detected by some authors.

Tailoring structured WGS catalysts: Impact of multilayered concept on the water surface interactions

Gonzalez-Castaño, M; Le Sache, E; Ivanova, S; Romero-Sarria, F; Centeno, MA; Odriozola, JA
Applied Catalysis B: Environmental, **222** (2018) 124-132
Marzo, 2018 | **DOI:** 10.1016/j.apcatb.2017.10.018

A novel multilayer approach for designing structured WGS catalyst is employed in this study as a response to the lack of new strategies in the literature. The approach proposes the use of two successive layers with different functionalities on metallic micromonolith substrate. The WGS catalyst behavior is modulated by the nature of the inner layer which determines the active species surface population by acting on the water activation step. The catalytic promotion attained by introducing inner ceria containing solids with increasing number of oxygen defects is intensely analyzed through FT-IR and H2O-TPD. Several evidences about the participation of the oxygen vacancies, as key sites, for water absorption processes are established. Besides, remarkable relationships between the water absorption strengths and the water splitting processes within their influence on the catalyst performance are also discussed.

A direct in situ observation of water-enhanced proton conductivity of Eu-doped ZrO_2: Effect on WGS reaction

Garcia-Moncada, N; Bobadilla, LF; Poyato, R; Lopez-Cartes, C; Romero-Sarria, F; Centeno, MA; Odriozola, JA
Applied Catalysis B: Environmental, **231** (2018) 343-356
Septiembre, 2018 | DOI: 10.1016/j.apcatb.2018.03.001

Eu-doped ZrO_2 solid solutions have been synthesized in order to prepare proton conductors as water-enhancer additives for the WGS reaction. Elemental characterization has been carried out revealing homogeneous dopant distribution resulting in fluorite-type solid solutions for Eu_2O_3 contents up to similar to 9 mol.%. Representative samples of the Eu-doped ZrO_2 series have been analysed by Impedance Spectroscopy (IS) in inert, oxygen and wet conditions. The solid solution with 5 mol.% of Eu_2O_3 has presented the highest conductivity values for all tested conditions indicating an optimal amount of dopant. Moreover, the presence of vapour pressure results in an increment of the conductivity at temperatures lower than 300 degrees C, meanwhile at higher temperatures the conductivity is the same than that in inert conditions. To elucidate these results, in situ DRIFTS studies were carried out. These experiments evidenced the existence of water dissociation at oxygen vacancies (band at 3724 cm(-1)) as well as the presence of physisorbed water at temperatures up to similar to 300 degrees C where the band at 5248 cm(-1) characteristic of these species disappeared. These results points to a layer model where the physisorbed water interacts with surface hydroxyls generated by dissociated water that improves the proton conductivity through Grotthuss' mechanism in the RT-300 degrees C temperature range. These samples were successfully tested in WGS reaction as additive to a typical Pt-based catalyst. The presence of the mixed oxide reveals an increase of the catalyst' activity assisted by the proton conductor, since improves the water activation step.

Phase-Contact Engineering in Mono- and Bimetallic Cu-Ni Co-catalysts for Hydrogen Photocatalytic Materials

Munoz-Batista, MJ; Meira, DM; Colon, G; Kubacka, A; Fernandez-Garcia, M
Angewandte Chemie-International Edition, **57** (2018) 1199-1203
Enero, 2018 | **DOI:** 10.1002/anie.201709552

Understanding how a photocatalyst modulates its oxidation state, size, and structure during a photocatalytic reaction under operando conditions is strongly limited by the mismatch between (catalyst) volume sampled by light and, to date, the physicochemical techniques and probes employed to study them. A synchrotron micro-beam X-ray absorption spectroscopy study together with the computational simulation and analysis (at the X-ray cell) of the light-matter interaction occurring in powdered TiO2-based monometallic Cu, Ni and bimetallic CuNi catalysts for hydrogen production from renewables was carried out. The combined information unveils an unexpected key catalytic role involving the phase contact between the reduced and oxidized non-noble metal phases in all catalysts and, additionally, reveals the source of the synergistic Cu-Ni interaction in the bimetallic material. The experimental method is applicable to operando studies of a wide variety of photocatalytic materials.

Unravelling the Role of Oxygen Vacancies in the Mechanism of the Reverse Water-Gas Shift Reaction by Operando DRIFTS and Ultraviolet-Visible Spectroscopy

Bobadilla, LF; Santos, JL; Ivanova, S; Odriozola, JA; Urakawa, A
ACS Catalysis, **8** (2018) 7455-7467
Agosto, 2018 | **DOI:** 10.1021/acscatal.8b02121

The reaction mechanism of the reverse water gas shift (RWGS) reaction was investigated using two commercial gold-based catalysts supported on Al_2O_3 and TiO_2. The surface species formed during the reaction and reaction mechanisms were elucidated by transient and steady-state operando DRIFTS studies. It was revealed that RWGS reaction over Au/Al_2O_3 proceeds through the formation of formate intermediates that are reduced to CO. In the case of the Au/TiO_2 catalyst, the reaction goes through a redox mechanism with the suggested formation of hydroxycarbonyl intermediates, which further decompose to CO and water. The Ti-3+ species, the surface hydroxyls, and oxygen vacancies jointly participate. The absence of carbonyl species adsorbed on gold particles during the reaction for both catalysts indicates that the reaction pathway involving dissociative adsorption of CO_2 on Au particles can be discarded. To complete the study, operando ultraviolet visible spectroscopy was successfully applied to confirm the presence of Ti3+ and to understand the role of the oxygen vacancies of TiO_2 support in activating CO_2 and thus the subsequent RWGS reaction.

Understanding the Role of the Acid Sites in 5-Hydroxymethylfurfural Oxidation to 2,5-Furandicarboxylic Acid Reaction over Gold Catalysts: Surface Investigation on $Ce_xZr_{1-x}O_2$ Compounds

Megias-Sayago, C; Chakarova, K; Penkova, A; Lolli, A; Ivanova, S; Albonetti, S; Cavani, F; Odriozola, JA

ACS Catalysis, **8** (2018) 11154-11164

Diciembre, 2018 | DOI: 10.1021/acscatal.8b02522 DEC 2018

A series of $Ce_xZr_{1-x}O_2$ supports with different Ce/Zr molar ratios were utilized for the preparation of gold catalyst used in the selective oxidation of 5-hydroxymethyl-2-furfural to 2,5-furandicarboxylic acid. The used method of gold deposition allows the preparation of gold particles with homogeneous size and shape distribution, a formulation very useful for studies dedicated to revealing the support participation in the reaction. The supports are characterized by Fourier transform infrared spectroscopy using CO as probe molecule, and the sample catalytic activity is thereafter correlated to the support acid site distribution. The possible participation of its Lewis/Bronsted acidity in the reaction mechanism is also proposed.

Pt/$CePO_4$ catalysts for the WGS reaction: influence of the water-supplier role of the support on the catalytic performance

Navarro-Jaen, S; Centeno, MA; Laguna, OH; Odriozola, JA

Journal of Materials Chemistry A, **6** (2018) 17001-17010

Septiembre, 2018 | **DOI:** 10.1039/c8ta04603d

For Pt catalysts which have demonstrated great activity for the WGS reaction, the activation of water is described as the rate-limiting step. Such limitation could be overcome through the design of supports able to supply water. In this study, the hexagonal and monoclinic phases of $CePO_4$ have been evaluated as supports for Pt WGS catalysts. The hexagonal structure presents channels containing water, absent in the monoclinic structure. The presence of these channels in the hexagonal phase increases the interaction with the water molecules, leading to an enhancement of the WGS catalytic performance. DRIFTS results showed that dissociation of water does not occur on these supports, while calculated apparent activation energies present values similar to those reported in the literature for the dissociation of water in Pt (111). These results suggest that cerium phosphates act as water suppliers, increasing the number of available species to be dissociated on the Pt surface.

Epimerization of glucose over ionic liquid/phosphomolybdate hybrids: structure-activity relationship

Megias-Sayago, C; Alvarez, E; Ivanova, S; Odriozola, JA
Green Chemistry, **20** (2018) 1042-1049
Marzo, 2018 | **DOI:** 10.1039/c7gc03738d

The influence of the crystal structure and chemical nature of some ionic liquid/ phosphomolybdate hybrids on their catalytic activity in the epimerization of glucose was studied. A clear evidence of structure-activity relationship was found. The inorganic part of the hybrid ensured the availability of active sites for the reaction, while the organic cation part organized the structure and controled the diffusion of the reactants. This study can be used as a first approach to predict the symmetry, long range order and availability of active sites in the presented class of imidazolium based polyoxometalate hybrids.

High {0 0 1} faceted TiO_2 nanoparticles for the valorization of oxygenated compounds present in aqueous biomass-derived feedstocks

Fernández-Arroyo, A.; Lara, M.A.; Domine, M.E.; Sayagués,M.J.; Navío, J.A.; Hidalgo, M.C.
Journal of Catalysis, **358** (2018) 266-276
Febrero, 2018 | **DOI:** 10.1016/j.jcat.2017.12.018

{0 0 1} faceted TiO_2 catalysts are hydrothermally synthesized by using titanium(IV) isopropoxide and butoxide precursors (ISO and BUT TiO_2 samples) together with HF addition. Their activity and stability are evaluated in the catalytic condensation of light oxygenated organic compounds present in an aqueous model mixture simulating a real bio-refinery effluent, under moderate operation conditions. High {0 0 1} faceted TiO_2 catalysts show organic products yields superior to those attained with other TiO_2 samples (anatase, rutile, and P25). This enhanced catalytic activity relates to their physico-chemical and textural properties, such as high surface area (≈100 m2/g), regular morphology (platelets conformed by partially agglomerated TiO_2 nanoparticles), and adequate Lewis acidity. XRD and Raman measurements evidence the unique presence of anatase crystalline phase in both ISO and BUT materials, in which the use of HF during synthesis produces the preferential growth of TiO_2 crystals mainly exposing the {0 0 1} plane. This effective {0 0 1} facet exposition directly determines catalytic results. Moreover, TiO_2 ISO catalyst shows outstanding stability under reaction conditions, maintaining practically unaltered their activity after several re-uses. In particular, Lewis acid sites present in TiO2 faceted materials are more stable in the presence of organic acids under aqueous environments. This opens new possibilities for the application of these materials in the valorization of light oxygenated compounds present in biomass-derived aqueous effluents.

Revealing the substitution mechanism in Eu^{3+}:$CaMoO_4$ and Eu^{3+},Na^{+}:$CaMoO_4$ phosphors

Becerro, AI; Allix, M; Laguna, M; Gonzalez-Mancebo, D; Genevois, C; Caballero, A; Lozano, G; Nunez, NO; Ocaña, M

Journal of Materials Chemistry C, **6** (2018) 47

Diciembre, 2018 | **DOI:** 10.1039/c8tc04595j

Eu^{3+}-Doped calcium molybdate is an excellent phosphor for lighting and display devices due to the very intense pure red emission after UV excitation. It has been reported in the literature that the $CaMoO_4$ unit cell volume expands after Eu3+ doping, in spite of the smaller Eu^{3+} ionic radius compared with Ca^{2+}. Likewise, several studies found that the emission intensity of the phosphor could be improved by codoping with alkaline ions like Li+, Na+ or K+. None of these studies correlated the apparent volume expansion and luminescence enhancement with the crystal structural details. This paper analyses the aliovalent substitution mechanism and crystal structure of Eu^{3+}:$CaMoO_4$ and Eu^{3+},Na^{+}:$CaMoO_4$ phosphors using complementary techniques like Raman spectroscopy, EXAFS and SPD. We found that the substitution mechanism was different for both systems, with Ca site vacancies forming in the Eu^{3+}:$CaMoO_4$ phosphors and leading to Ca1-3xEu2xxMoO4 compositions, while the Eu^{3+},Na^{+}:$CaMoO_4$ phosphors formed Ca1-2xEuxNaxMoO4. SPD showed that the cell volume expansion observed with increasing Eu^{3+} content is related to the increase of the Mo-O bond distance due to the higher electronegativity of Eu^{3+} compared with Ca^{2+}. Finally, it was shown that the luminescence properties, i.e. lifetime values and quantum yields (the latter reported here for the first time), do not depend on the presence of monovalent ions in the crystal structure but, exclusively, on the Eu^{3+} content of the phosphor. The integral and detailed analysis of the materials presented in this paper, ranging from crystal structure to luminescent properties including elemental composition, allows a full picture of the structure-property relationships that had never been addressed before for $CaMoO_4$-based phopshors.

Multicomponent Ni-CeO_2 nanocatalysts for syngas production from CO_2/CH_4 mixtures

Le Sache, E.; Santos, J. L.; Smith, T. J.; Centeno, M. A.; Arellano-Garcia, H.; Odriozola, J. A.; Reina, T. R.

Journal of CO2 utilization, **25** (2018) 68-78

Mayo, 2018 | **DOI:** 10.1016/j.jcou.2018.03.012

The dry reforming of methane with CO_2 is a common route to transform CO_2/CH_4 mixtures into added value syngas. Ni based catalysts are highly active for this goal but suffer from deactivation, as such promoters need to be introduced to counteract this, and improve performance. In this study, mono- and bi-metallic formulations based on 10 wt.% Ni/CeO_2-Al_2O_3 are explored and compared to a reference 10 wt.% Ni/gamma-Al_2O_3. The effect of Sn and Pt as promoters of Ni/CeO_2-Al_2O_3 was also investigated. The formulation promoted with Sn looked especially promising, showing CO_2 conversions stabilising at 65% after highs of 95%. Its increased performance is attributed to the additional dispersion Sn promotion causes. Changes in the reaction conditions (space velocity and temperature) cement this idea, with the Ni-Sn/CeAl material performing superiorly to the mono-metallic material, showing less deactivation.

However, in the long run it is noted that the mono- metallic Ni/CeAl performs better. As such the application is key when deciding which catalyst to employ in the dry reforming process.

CO_2 reforming of methane over Ni-Ru supported catalysts: On the nature of active sites by operando DRIFTS study

Alvarez, A; Bobadilla, LF; Garcilaso, V; Centeno, MA; Odriozola, JA
Journal of CO2 utilization, **24** (2018) 509-515
Marzo, 2018 | **DOI:** 10.1016/j.jcou.2018.01.027

The present paper addresses the nature of the active sites of a bimetallic Ni-Ru supported catalyst on the dry reforming of methane (DRM). The structural characterization by XRD and Raman spectroscopy, along with the reducibility study (TPR-H-2) of the samples, evidenced the existence of a strong Ni-Ru interaction in the bimetallic system. We have assumed that Ru atoms block the most reactive Ni sites (step-edge sites) leaving less reactive centers for methane activation (terraces). In this way, operando DRIFTS measurements revealed that Ru decreases the catalytic activity but favors the carbon gasification and prevents the CO dissociation.

Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel

Navajas, A; Campo, I; Moral, A; Echave, J; Sanz, O; Montes, M; Odriozola, JA; Arzamendi, G; Gandia, LM
Fuel, **211** (2018) 173-181
Enero, 2018 | **DOI:** 10.1016/j.fuel.2017.09.061

There is still a need for active, selective and stable heterogeneous catalysts for the synthesis of biodiesel. In this work, magnesium-aluminium hydrotalcites with Mg/Al molar ratios within the 1.5-5 range were synthesized by coprecipitation and used as transesterification catalysts for the synthesis of biodiesel. The mixed oxides obtained after calcination recovered the hydrotalcite structure in the form of meixnerite after rehydration in boiling water. The solids were characterized by XRD, TGA, N-2 adsorption-desorption, and SEM. Basic properties were assessed by means of Hammett indicators and CO_2-TPD. Rehydrated materials with the highest Mg/Al ratios showed some distinctive features: low surface area, well defined flake-like crystals, high basicity and strong basic sites with H_ values above 11. They were also the most active catalysts allowing to achieve 51-75% sunflower oil methanolysis conversion after 8 h of reaction under mild conditions (60 degrees C, 1 atm), methanol/oil molar ratio of 12 using between 2 and 6 wt% of catalyst. The conversion increased up to 96% (92% fatty acid methyl esters yield) using 2 wt% catalyst and methanol/oil molar ratio of 48. Catalyst leaching was not a serious problem with these solids that could be reutilized maintaining very good activities. A general accordance between solids basic properties and their catalytic performance has been observed. These results are among the best reported in the literature for heterogeneous methanolysis catalysts and have been attributed to the high basicity of the rehydrated solids and the presence of strong and accessible basic sites probably consisting in interlayer hydroxide anions at the edges of the crystals.

Understanding the differences in catalytic performance for hydrogen production of Ni and Co supported on mesoporous SBA-15

Rodriguez-Gomez, A; Pereñiguez, R; Caballero, A
Catalysis, **307** (2018) 224-230
Junio, 2018 | **DOI:** 10.1016/j.cattod.2017.02.020

Three mono and bimetallic NixCo1-x/SBA-15 catalysts (x = 1, 0.5 and 0) with a total metallic content of 10 wt% have been prepared by a deposition-precipitation (DP) method. The catalytic performances on the dry reforming of methane reaction (DRM) have been determined and correlated with their physical and chemical state before and after the catalytic reaction. So, while the nickel monometallic system presents a high activity and stability in the DRM reaction, the Co/SBA-15 catalytic system turns out completely inactive. For its part, the Ni0.5Co0.5/SBA-15 has initially a catalytic performance similar to the Ni/SBA-15 monometallic system, but rapidly evolving to an inactive system, therefore resembling the behavior of the cobalt-based catalyst. The characterization by TEM and in situ XPS techniques has allowed us to ascribe these differences to the initial state of metallic particles after reduction and their different evolution under reaction conditions. So, while after reduction both nickel containing NixCo1-x/SBA-15 catalysts (x = 1 and 0.5) present a well dispersed metallic phase, the cobalt monometallic catalyst yields big metallic particles with a heterogeneous distribution of sizes. Additionally, unlike the Ni/SBA-15, the NiCo/SBA-15 system increases during reaction the metallic particle sizes.
Besides indicating that the particle size is a major reason determining the catalytic performances, these results suggest that in the Ni-Co system both metals form after reduction a bimetallic phase mainly located inside the mesoporous channels of SBA-15 support. Under DRM reaction conditions, the cobalt is segregated to the surface of the bimetallic particles, which seems to determine the interaction with the support surface SBA-15. This feature gives rise to a much less stable metallic phase which suffers an important sintering process under DRM catalytic conditions.

Gold catalyst recycling study in base-free glucose oxidation reaction

Megias-Sayago, C.; Bobadilla, L. F.; Ivanova, S.; Penkova, A.; Centeno, M. A.; Odriozola, J. A.
Catalysis Today, **301** (2018) 72-77
Marzo, 2018 | **DOI:** 10.1016/j.cattod.2017.03.022

This work is devoted to the study of viability of immobilized gold colloids on carbon as catalysts for the base-free glucose oxidation reaction with a special emphasis made on catalysts' recycling, operational life and possible routes for deactivation/reactivation under batch conditions. The observed catalytic behavior is related to all possible manners of deactivation, like gold metal state changes (particle size agglomeration or leaching), support modifications or active sites blocking by intermediates. In an attempt to recover the initial catalytic activity, the samples are subjected to different treatments such as H_2O and NaOH washings and calcination. The failure of the regeneration procedures to recover the initial activity and after detailed catalyst' characterization allows us to find out the main cause of deactivation.

Influence of gold particle size in Au/C catalysts for base-free oxidation of glucose

Megias-Sayago, C; Santos, JL; Ammari, F; Chenouf, M; Ivanova, S; Centeno, MA; Odriozola, JA
Catalysis Today, **306** (2018) 183-190
Mayo, 2018 | **DOI:** 10.1016/j.cattod.2017.01.007

A series of gold colloids were prepared and immobilized on commercial activated carbon. The influence of the colloid preparation and stability were studied and related to the gold particle size in the final catalyst. The catalysts show an important activity in the glucose to gluconic acid oxidation reaction, leading to gluconic acid yield close to 90% in base free mild conditions (0.1 MPa O-2 and 40 degrees C). The size-activity correlation and probable mechanism were also discussed. Finally, the viability of the catalyst was tested by recycling it up to four times.

ZnO and Pt-ZnO photocatalysts: Characterization and photocatalytic activity assessing by means of three substrates

Jaramillo, C; Navio, J.A.; Hidalgo, M.C.; Macías, M.
Catalysis Today, **313** (2018) 12-19
Septiembre, 2018 | **DOI:** 10.1016/j.cattod.2017.12.009

ZnO nanoparticles have been previously synthesized by a facile precipitation procedure by mixing aqueous solutions of Zn(II) acetate and dissolved Na_2CO_3 at pH ca. 7.0 without the addition of a template. The as-prepared ZnO material was anealed at 400 °C in air for 2 h. The Pt-ZnO catalysts (0.5 or 1.0 Pt wt.%) were obtained by photochemical deposition method on the surface of the prepared ZnO sample, using hexachloroplatinic acid (H_2PtCl_6). It has been shown that Zn^{2+} is lost from the photocatalyst to the medium and a replacement of the cationic vacancies of Zn^{2+} by Pt^{4+} cations occurs during the platinization process of the ZnO samples, regardless of whether the platinum metal photodeposition process. The as-prepared catalysts were characterized by XRD, BET, FE-SEM, TEM, XPS and diffuse reflectance spectroscopy (DRS). Three different probe molecules were used to evaluate the photocatalytic properties under UV-illumination: Methyl Orange and Rhodamine B were chosen as dye substrates and Phenol as a transparent substrate. High conversion values (ca. 100%) and a total organic carbon (TOC) removal of 90–96%, were obtained over these photocatalysts after 160 min of UV illumination. In general, it was observed that the presence of Pt on ZnO affects the lattice parameters and the crystallite size. Although ZnO can completely degrade RhB, MO and Phenol totally in ca. 60 min, the process is more efficient for Pt–ZnO photocatalysts.

Synthesis of Pd-Al/biomorphic carbon catalysts using cellulose as carbon precursor

Cazana, F; Galetti, A; Meyer, C; Sebastian, V; Centeno, MA; Romeo, E; Monzon, A
Catalysis Today, **301** (2018) 226-238
Marzo, 2018 | **DOI:** 10.1016/j.cattod.2017.05.026

This work presents the results obtained with novel Pd and Pd-Al catalysts supported on carbon, which have been prepared using a biomorphic mineralization technique. The catalyst synthesis procedure includes a stage of thermal decomposition under reductive atmosphere of cellulose previously impregnated with the metallic precursors. We have studied the influence of the temperature and time of decomposition, and of the Al precursor addition, on the textural and catalytic properties. The characterisation results indicate that the preparation method used leads to the formation of carbonaceous supports with a high microporosity (up to 97% micropore volume) and values of the BET surface up to 470 m2/g while maintaining the original external structure. The use of low temperatures (ca. 600 °C) during the decomposition step allows the preparation of highly dispersed catalysts with narrow Pd particle size distributions. However, the thermal decomposition at elevated temperatures (ca. 800 °C) increases the Pd particle size due to the sintering of the metallic phase. This phenomenon is augmented with the decomposition time and is not affected by the presence of Al. Consequently, the catalytic activity of these materials in cyclohexene hydrogenation is strongly affected by the operational conditions used during the thermal decomposition step. Unexpectedly, the more sintered catalysts, i.e. those prepared at 800 °C, show the highest activity. According to the characterization results, this fact can be explained considering that the smaller Pd particles obtained after preparation at e.g. 600 °C are quite inactive because they are confined in the internal structure of the micropores of the support and/or embedded inside the carbon matrix. In contrast, after decomposition at 800 °C, the larger Pd particles formed are placed at the external surface of the catalyst, being accessible to the reactants. In addition, for the specific conditions under which the Pd is accessible, the presence of Al favours the cyclohexene conversion due to the enhancement of the adsorption on the Pd surface as a consequence of a charge transfer phenomenon. These results can serve as a guideline for the preparation of these catalysts based on raw lignocellulosic materials in order to maximize their catalytic performance.

Multicomponent Au/Cu-ZnO-Al_2O_3 catalysts: Robust materials for clean hydrogen production

Santos, JL; Reina, TR; Ivanov, I; Penkova, A; Ivanova, S; Tabakova, T; Centeno, MA; Idakiev, V; Odriozola, JA
Applied Catalysis A-General, **558** (2018) 91-98
Mayo, 2018 | **DOI:** 10.1016/j.apcata.2018.04.002

Clean hydrogen production via WGS is a key step in the development of hydrogen fuel processors. Herein, we have designed a new family of highly effective catalysts for low-temperature WGS reaction based on gold modified copper-zinc mixed oxides. Their performance was controlled by catalysts' composition and the Au-Cu synergy. The utilization of hydrotalcite precursors leads to an optimal microstructure that ensures excellent Au and Cu dispersion and favors their strong interaction. From the application perspective these materials succeed to overcome the major drawback of the commercial WGS catalysts: resistance towards start/stop operations, a mandatory requisite for H-2-powered mobile devices.

Hydrodeoxygenation of vanillin over carbon supported metal catalysts

Santos, JL; Alda-Onggar, M; Fedorov, V; Peurla, M; Eranen, K; Maki-Arvela, P; Centeno, MA; Murzin, DY
Applied Catalysis A-General, **561** (2018) 137-149
Julio, 2018 | **DOI:** 10.1016/j.apcata.2018.05.010

Different carbon supported metal catalysts were synthesized, and characterized with various physico-chemical methods and tested in vanillin hydrodeoxygenation under 30 bar total pressure in water as a solvent at 100 degrees C. The catalysts exhibited high specific surface area and the metal dispersion decreased in following order: Pt/ C > Pd/C > Au/C > Rh/C > Ru/C. The most active catalyst was Pd/C followed by Ru/C. Vanillin hydrodeoxygenation proceeded via hydrogenation forming vanillyl alcohol further to its hydrogenolysis forming p-creosol. Both hydrogenation and hydrogenolysis were promoted by Pd/C, which exhibited rather high dispersion. The highest selectivity to p-creosol, 95% at complete vanillin conversion, was obtained with Pd/C. Kinetic modelling of vanillyl alcohol selectivity as a function of vanillin conversion was performed.

Improving the activity of gold nanoparticles for the water-gas shift reaction using TiO_2-Y_2O_3: an example of catalyst design

Plata, JJ; Romero-Sarria, F; Suarez, JA; Marquez, AM; Laguna, OH; Odriozola, JA; Sanz, JF
Physical Chemistry Physics, **20** (2018) 22076-22083
Septiembre, 2018 | **DOI:** 10.1039/c8cp03706j

In the last ten years, there has been an acceleration in the pace at which new catalysts for the water-gas shift reaction are designed and synthesized. Pt-based catalysts remain the best solution when only activity is considered. However, cost, operation temperature, and deactivation phenomena are important variables when these catalysts are scaled in industry. Here, a new catalyst, Au/TiO_2-Y_2O_3, is presented as an alternative to the less selective Pt/oxide systems. Experimental and theoretical techniques are combined to design, synthesize, characterize and analyze the performance of this system. The mixed oxide demonstrates a synergistic effect, improving the activity of the catalyst not only at large-to-medium temperatures but also at low temperatures. This effect is related to the homogeneous dispersion of the vacancies that act both as nucleation centers for smaller and more active gold nanoparticles and as dissociation sites for water molecules. The calculated reaction path points to carboxyl formation as the rate-limiting step with an activation energy of 6.9 kcal mol(-1), which is in quantitative agreement with experimental measurements and, to the best of our knowledge, it is the lowest activation energy reported for the water-gas shift reaction. This discovery demonstrates the importance of combining experimental and theoretical techniques to model and understand catalytic processes and opens the door to new improvements to reduce the operating temperature and the deactivation of the catalyst.

$LaFeO_3$ ceramics as selective oxygen sensors at mild temperature

Jaouali, I; Hamrouni, H; Moussa, N; Nsib, MF; Centeno, MA; Bonavita, A; Neri, G; Leonardi, SG
Ceramics International, **44** (2018) 4183-4189
Marzo, 2018 | **DOI:** 10.1016/j.ceramint.2017.11.221

In this study, an investigation about the oxygen sensing properties of lanthanum orthoferrite ($LaFeO_3$) ceramics is reported. $LaFeO_3$ nanoparticles were synthesized by using tartaric sol-gel route and annealed in air at different temperatures (500, 700 and 900 degrees C). The samples have been characterized by using thermal analysis (TA), BET surface area and porosity, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Results of sensing tests indicate that $LaFeO_3$ nanoparticles exhibit good response to oxygen at mild temperatures (300-450 degrees C). The effect of annealing temperature on gas sensing performance was investigated, demonstrating that $LaFeO_3$ ceramics obtained after annealing at 500 degrees C display better characteristics with respect to others. The oxygen sensor developed shows also high stability in humid environment and excellent selectivity to oxygen over other interfering gases such as CO, NO_2, CO_2, H-2 and ethanol.

Metal Micro-Monoliths for the Kinetic Study and the Intensification of the Water Gas Shift Reaction

Garcia-Moncada, N; Groppi, G; Beretta, A; Romero-Sarria, F; Odriozola, JA
Catalysts, **8** (2018) art. 594
Diciembre, 2018 | **DOI:** 10.3390/catal8120594

A kinetic study of the water gas shift (WGS) reaction has been carried out on a Pt-based catalyst promoted by a Zr-based proton conductor. The investigation was first performed on powders with diluted feed mixtures and then extended to more severe and representative conditions by using a catalyst coated metallic micromonolith. Temperature measurements reveal that isothermal conditions were obtained along the micromonolith during the tested conditions. In addition, the very thin catalytic layer allows for the discarding of intraporous resistances, providing excellent conditions to analyse the kinetics of the WGS reaction under the integral regime. The proposed rate expression accounts for independence on CO concentration, an inhibiting effect of H-2 and a promoting effect of H_2O; kinetic orders on CO and H-2 are in line with those reported in the literature for the Pt-based catalyst. Instead, the obtained reaction order of water (0.36) is significantly lower than that reported for unpromoted catalysts (typically 0.77-1.10) in good agreement with the proposed water-enhancer effect of the proton conductor on the rate-limiting step. Metallic micromonoliths turn out to be a powerful tool for the kinetic investigation, due to the absence of mass and heat transport limitations and represent a strategy for the intensification of the WGS unit for future applications of fuel processors in small mobile devices.

Policies and Motivations for the CO_2 Valorization through the Sabatier Reaction Using Structured Catalysts. A Review of the Most Recent Advances

Navarro, JC; Centeno, MA; Laguna, OH; Odriozola, JA
Catalysts, **8** (2018) art. 578
Diciembre, 2018 | **DOI:** 10.3390/catal8120578

The current scenario where the effects of global warming are more and more evident, has motivated different initiatives for facing this, such as the creation of global policies with a clear environmental guideline. Within these policies, the control of Greenhouse Gase (GHG) emissions has been defined as mandatory, but for carrying out this, a smart strategy is proposed. This is the application of a circular economy model, which seeks to minimize the generation of waste and maximize the efficient use of resources. From this point of view, CO_2 recycling is an alternative to reduce emissions to the atmosphere, and we need to look for new business models which valorization this compound which now must be considered as a renewable carbon source. This has renewed the interest in known processes for the chemical transformation of CO_2 but that have not been applied at industrial level because they do not offer evident profitability. For example, the methane produced in the Sabatier reaction has a great potential for application, but this depends on the existence of a sustainable supply of hydrogen and a greater efficiency during the process that allows maximizing energy efficiency and thermal control to maximize the methane yield. Regarding energy efficiency and thermal control of the process, the use of structured reactors is an appropriate strategy. The evolution of new technologies, such as 3D printing, and the consolidation of knowledge in the structing of catalysts has enabled the use of these reactors to develop a wide range of possibilities in the field. In this sense, the present review presents a brief description of the main policies that have motivated the transition to a circular economy model and within this, to CO2 recycling. This allows understanding, why efforts are being focused on the development of different reactions for CO_2 valorization. Special attention to the case of the Sabatier reaction and in the application of structured reactors for such process is paid.

A facile shape-controlled synthesis of highly photoactive fluorine containing TiO_2 nanosheets with high {001} facet exposure

Lara, M. A.; Sayagues, M. J.; Navio, J. A.; Hidalgo, M. C.
Journal of Materials Science, **53** (2018) 435-446
Enero, 2018 | **DOI:** 10.1007/s10853-017-1515-6

Surface-fluorinated TiO_2 materials with high {001} facet exposure were prepared by a simple and high-yield preparation procedure. Faceted/fluorinated samples showed a high photocatalytic performance not only in oxidation processes, tested in phenol and methyl orange degradation, but also in a reduction process as Cr(VI) photoreduction. Reaction rates for these materials greatly exceeded the ones obtained for materials prepared without fluorine addition and for commercial TiO_2 Degussa (Evonik) P25 used as reference photocatalyst. A broad characterisation of the samples allowed us to estimate the percentages of different facets and the amount and form in which the fluorine is found on the surfaces. Good photocatalytic behaviour can be ascribed to both high {001} facet exposure and adsorbed fluorine on the photocatalysts surfaces.

Silver-modified ZnO highly UV-photoactive

Jaramillo-Páez, C.; Navío, J.C.; Hidalgo, M.C.
Journal of Photochemistry and Photobiology A: Chemistry, **356** (2018) 112-122
Abril, 2018 | **DOI:** 10.1016/j.jphotochem.2017.12.044

ZnO nanoparticles were successfully synthesized by a controlled precipitation procedure by mixing aqueous solutions of Zn(II) acetate and dissolved Na2CO3 at pH ca. 7.0 without template addition and ulterior calcination at 400 °C for 2 h. The Ag-ZnO catalysts (ranging from 0.5 to 10 Ag wt.-%) were obtained by photochemical deposition method at the surface of the prepared ZnO sample, using AgNO3 as precursor. The as-prepared catalysts (with and without silver) were characterized by XRD, BET, FE-SEM, TEM, and XPS and diffuse reflectance spectroscopy (DRS). The effect of Ag-phodeposition on the photocatalytic properties of ZnO nanoparticles was investigated. Three different probe molecules were used to evaluate the photocatalytic properties under UV-illumination and visible illumination: Methyl Orange and Rhodamine B were chosen as hazardous dyes and Phenol as a transparent substrate. For each of the chosen substrates, it was observed that the UV-photocatalytic properties of ZnO improved with the amount of Ag deposited, up to an optimum percentage around 1–5 wt.-% Ag, being even better than the commercial Evonik-TiO2(P25) in the same conditions. Above this amount, the UV-photocatalytic properties of the Ag-ZnO samples remain unchanged, indicating a maximum for Ag-deposition. While ZnO and Ag-ZnO catalysts can photodegrade Rhodamine B, Methyl Orange and Phenol totally within 60 min under UV-illumination, the process is slightly faster for the case of Ag–ZnO nanoparticles. Under Vis-illumination, the silver-metalized samples did not present photocatalytic activity in the degradation of Methyl Orange. However, a very low photoactivity was present for phenol degradation (10% conversion) and a moderate conversion of ca. 70% for Rhodamine B degradation, after 120 min of Visible-illumination. High conversion values and a total organic carbon (TOC) removal of 86–97% were obtained over the Ag-ZnO photocatalysts after 120 min of UV-illumination, suggesting that these Ag-modified ZnO nanoparticles may have good applications in wastewater treatment, due to its reuse properties.

Photocatalytic H_2 production from glycerol aqueous solutions over fluorinated Pt-TiO_2 with high {001} facet exposure

V. Vaiano; M.A. Lara; G. Iervolino; M. Matarangolo; J.A. Navío; M.C. Hidalgo

Journal of Photochemistry and Photobiology A: Chemistry, **365** (2018) 52-59

Octubre, 2018 | **DOI:** 10.1016/j.jphotochem.2018.07.032

An optimized fluorinated TiO_2 catalyst with high {001} facet exposure loaded with platinum (TiO_2-PtFAC) was tested in the photocatalytic hydrogen production from glycerol solution under UV light irradiation. The samples were synthesized by direct hydrothermal treatment starting from two different types of precursors that are titanium tetraisopropoxide (I) or titanium butoxide (B), while platinisation was performed by photodeposition method. The obtained catalysts were characterised by different techniques (XRD, FESEM, TEM, BET, UV–vis DRS, XRF and XPS) and the results evidenced that anatase is the only crystalline phase present in all TiO_2 samples. The morphology of the samples was seen as rectangular platelets particles where Pt particles were was observed all over the surface. The presence of Pt and F in the platinised samples was also confirmed by XRF and XPS analysis. The photocatalytic results have shown that the presence of Pt on TiO_2{001}facet surface remarkably enhanced the hydrogen production from aqueous solution at 5 wt % of glycerol. Comparing the results obtained from the photocatalysts prepared by the two different precursors, it was found that the best performances in terms of H2 production was achieved with TiO_2-PtFAC(I) (about 13 mmol L−1 after 4 h of irradiation time), while the H_2 production was lower for TiO_2-PtFAC(B) (about 9 mmol L−1 after 4 h of irradiation time). The effect of the operating conditions using TiO_2-PtFAC(I) evidenced that the highest H_2 production was obtained with a photocatalyst dosage equal to 1.5 g L−1, initial glycerol concentration at 5 wt% and a pH value equal to 7. Finally, a photocatalytic test was also performed on glycerol solution prepared with a real water matrix. Despite the presence of ions scavengers (chlorides and carbonates) in solution, TiO_2-PtFAC(I) was able to reach a photocatalytic H2production of about 6 mmol L−1 after 4 h of UV light irradiation.

Study of the effectiveness of the flocculation-photocatalysis in the treatment of wastewater coming from dairy industries

Murcia, J.J., Hernández-Laverde, M., Rojas, Muñoz, E., Navío, J.A., Hidalgo, M.C.
Journal of Photochemistry and Photobiology A: Chemistry, **358** (2018) 256-264
Mayo, 2018 | **DOI:** 10.1016/j.jphotochem.2018.03.034

The aim of the present work was to evaluate the effectiveness of flocculation-photocatalysis as combined processes in the treatment of dairy industries wastewater. Different commercial and lab prepared flocculants and photocatalysts were evaluated. All the materials prepared were extensively characterized. Commercial materials presented the best physicochemical properties and performance in the treatment of the studied wastewater. On one hand, all the photocatalysts evaluated showed bactericidal activity for E. Coli, total coliforms and other enterobacteriaceae. Total elimination of E. coli was obtained by using commercial TiO_2 P25 Evonik, under 120 W/m2 of UV–vis light intensity and 5 h of total illumination time. Other species of bacteria remained after treatment under these conditions. It was also found that the highest light intensity of 120 W/m^2 led to increase the Chemical Oxygen Demand and Total Organic Carbon in the samples treated, it can be due to the faster formation of new organic compounds as intermediaries during the photocatalytic reactions at the highest photonic flux. Flocculation pre-treatment of the wastewater samples led to improve the effectiveness of the photocatalytic treatment; thus, the combination of flocculation-photocatalysis treatments at low light intensity of 30 W/m^2 leads to achieve the total elimination of E. coli, and under this intensity the elimination of total coliforms and other enterobacteriaceae increased 5.48% compared to the photocatalytic treatment alone. These treatment conditions led to comply the Colombian regulations for dairy wastewater.

Photo-induced processes on Nb_2O_5 synthesized by different procedures

Jaramillo-Páez, C., Sánchez-Fernández, F.J., Navío, J.A., Hidalgo, M.C.
Journal of Photochemistry and Photobiology A: Chemistry, **358** (2018) 40-52
Mayo, 2018 | **DOI:** 10.1016/j.jphotochem.2018.03.040

The properties of Nb_2O_5 strongly depend on its synthesis procedure as well as the conditions of ulterior thermal treatment. We report the synthesis of Nb_2O_5 powders prepared by sol-gel precipitation method using niobium(V) ethoxide as precursor. Two chemical routes were chosen: the presence of tryethyl amine (TEA) as precipitant/template agent, or the oxidant peroxide method. In addition, microwave-assisted activation was also used. The as-prepared samples by the above procedures were amorphous. Structural changes upon heating from room temperature up to 800 °C were investigated by X-ray powder diffraction technique combined with thermogravimetric analysis. The sequential thermal treatment up to 800 °C promotes the crystallization of hexagonal phase to orthorhombic phase whereas the ulterior cooling to room temperature lead to a mixture of both phases. Samples calcined at selected temperatures of either 600 °C or 800 °C for 2 h, were characterized by XRD, SEM, N_2-adsorption and diffuse reflectance spectroscopy (DRS). The synthetic approach routes as well as the combined microwave activation followed by ulterior thermal treatment lead to changes not only on particle size but also on the textural properties of the synthesized catalysts. The catalysts synthesized have been evaluated using Rhodamine B (RhB) as a substrate, under both UV and visible lighting conditions. None of the catalysts synthesized showed activity in the visible. Under

UV-illumination conditions, some of the catalysts exhibited a relatively low photoactivity in the degradation of RhB, which is associated with a photo-sensitizing effect. However, the addition of Ag^+ ions considerably increased the activity of all the catalysts in the degradation of RhB under UV-illumination conditions. A mechanism is proposed to explain the photo-induced processes obtained, leaving the door open to the possible implications of the observed results in relation to the interaction of RhB dye with noble metal nanoparticles such as silver.

Structural Reversibility of $LaCo_{1-x}Cu_xO_3$ Followed by In Situ X-ray Diffraction and Absorption Spectroscopy

Pereñiguez, Rosa; Ferri, Davide

Chemphyschem, **19** (2018) 1876-1885

Agosto, 2018 | **DOI:** 10.1002/cphc.201800069

Combinations of perovskite-type oxides with transition and precious metals exhibit a remarkable self-regenerable property that could be exploited for numerous practical applications. The objective of the present work was to study the reversibility of structural changes of perovskite-type oxides under cyclic reducing/oxidizing atmosphere by taking advantage of the reducibility of $LaCoO_3$. $LaCoO_3$ +/- and $LaCo_{0.8}Cu_{0.2}O_3$ +/- were prepared by ultrasonic spray combustion and were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and temperature-programmed reduction (TPR). XRD and XAS data confirmed that copper adopted the coordination environment of cobalt at the B-site of the rhombohedral LaCoO3 under the selected synthesis conditions. The structural evolution under reducing atmosphere was studied by insitu XRD and XANES supporting the assignment of the observed structural changes to the reduction of the perovskite-type oxide from ABB'O-3 (B'=Cu) to B'(0)/ABO(3) and to B'B-0(0)/A(2)O(3). Successive redox cycles allowed the observation of a nearly complete reversibility of the perovskite phase, i.e. copper was able to revert into $LaCoO_3$ upon oxidation. The reversible reduction/segregation of copper and incorporation at the B-site of the perovskite-type oxides could be used in chemical processes where the material can be functionalized by segregation of Cu and protected against irreversible structural changes upon re-oxidation.

Numerical study of the accuracy of temperature measurement by thermocouples in small-scale reactors

Blay, V; Bobadilla, LF

Chemical Engieering Research & Design, **131** (2018) 545-556

Marzo, 2018 | **DOI:** 10.1016/j.cherd.2017.06.003

Proper temperature measurement is imperative in any laboratory study if reliable data are to be obtained, particularly in the field of chemical kinetics. In this paper we analyze in silico some typical thermowell configurations used in small-scale reactors by coupling computational fluid dynamics (CFD) with conjugated heat transfer phenomena. This allows us to identify deviations in measurements arising from thermal radiation and self-conductivity in mid and high temperature ranges, in addition to radial temperature gradients. A novel design is proposed and optimized by additional simulation, showing potential for faster and more accurate temperature measurements.

Improving the direct synthesis of hydrogen peroxide from hydrogen and oxygen over Au-Pd/SBA-15 catalysts by selective functionalization

Rodriguez-Gomez, A; Platero, F; Caballero, A; Colon, G
Molecular Catalysis, **445** (2018) 142-151
Febrero, 2018 | **DOI:** 10.1016/j.mcat.2017.10.034

A series of gold-palladium catalysts supported in a mesoporous surface functionalized silica SBA-15 was studied for H_2O_2 direct synthesis. Support functionalization was performed using different organic groups (namely-SO_3H, -NH_2 and-SH) while metal was then supported by an ion exchanged method. Different Au-Pd/SBA-15 catalysts were tested in the Direct Synthesis of Hydrogen Peroxide (DSHP). Organic functional groups (-SH, -SO_3H and-NH_2) with acid-base properties acted as anchoring sites controlling both the dispersion of the metallic active phase and the chemical state of gold and palladium species as Au^+ and Pd^{2+}, respectively. Compared to a Au-Pd/SBA-15 system prepared by incipient wetness impregnation over non-functionalized SBA-15, catalytic performance is improved upon functionalization, increasing hydrogen peroxide rate in sulfonic-SBA-15 systems and reducing the hydrogenation/decomposition activity by adding amine groups. The occurrence of amine groups clearly suppresses the support microporosity and probably condition the metal cluster size. The analysis of particle size by TEM showed that sulfonated samples lead to a Pd size compromise which improves the H_2O_2 production hindering the competitive side reactions, particularly suppressed by the presence of amine groups.

Analysis of the variables that modify the robustness of Ti-SiO_2 catalysts for alkene epoxidation: Role of silylation, deactivation and potential solutions

Plata, JJ; Pacheco, LC; Remesal, ER; Masa, MO; Vega, L; Marquez, AM; Odriozola, JA; Sanz, JF
Molecular Catalysis, **459** (2018) 55-60
Noviembre, 2018 | **DOI:** 10.1016/j.mcat.2018.08.010

Catalytic epoxidation of alkenes plays an essential role in the transformation and synthesis of many organic chemicals. Ti atoms grafted on mesoporous silica, silylated on the surface, is considered the most active and selective catalyst for these reactions. However, the durability and robustness of the active centers remain as the main drawback in industry. In this paper, the characterization of industrial samples is combined with DFT calculations to rationalize the deactivation process of the catalyst and improve its performance. Silylating agents are characterized by experimental and simulated 29Si-NMR and their role in the catalytic mechanism is analysed. Potential deactivation processes are identified before, during and after the reaction. Modifications of the silylating agents and of the active center are proposed to improve the durability of the catalyst.

Bimetallic Ni-Co/SBA-15 catalysts for reforming of ethanol: How cobalt modifies the nickel metal phase and product distribution

Rodriguez-Gomez, A; Caballero, A
Molecular Catalysis, **449** (2018) 120-130

Abril, 2018 | **DOI:** 10.1016/j.mcat.2018.02.011

In this study, five mono and bimetallic xNi-(10-x)Co/SBA-15 catalysts (x = 10, 8, 5, 2 and 0, with a total metallic content of 10 wt%) have been synthesized using a deposition-precipitation (DP) methodology. Catalytic performances on the steam reforming of ethanol reaction (SRE) have been determined and correlated with their physical and chemical state. A nickel content of 5% or higher yields catalytic systems with good activity, high selectivity to hydrogen and a low production of acetaldehyde (less than 5%). However, in the systems where the cobalt is the main component of the metallic phase (8-10%), the selectivity changes, mainly due to the production of an excess of acetaldehyde, which is also reflected in the larger H-2/CO2 ratio. In agreement with previous findings, this important modification in the selectivity comes from the formation of a cobalt carbide phase, where only takes place in the cobalt enriched systems, and is inhibited with nickel content larger than 5%. The formation of this carbide phase seems to be responsible for the decrease of cobalt particle size during the SRE reaction. Even though this cobalt carbide phase is thermodynamically metastable against decomposition to metallic cobalt and graphite carbon, our results have shown that it only reacts and decomposes after a hydrogen treatment at 600 degrees C.

Nickel Particles Selectively Confined in the Mesoporous Channels of SBA-15 Yielding a Very Stable Catalyst for DRM Reaction

Rodriguez-Gomez, A; Pereniguez, R; Caballero, A
Journal of Physical Chemistry B, **112** (2018) 500-510
Enero, 2018 | **DOI:** 10.1021/acs.jpcb.7b03835

A series of four Ni catalysts supported on SBA-15 and on a high SiO2 surface area have been prepared by modified impregnation (ImU) and deposition-precipitation (DP) methods. The catalysts have been extensively characterized, including in situ XAS (bulk sensitive) and XPS (surface sensitive) techniques, and their catalytic activities evaluated in the dry reforming reaction of methane (DRM). The combined use of XPS and XAS has allowed us to determine the location of nickel particles on each catalyst after reduction at high temperature (750 degrees C). Both Ni/SiO2-DP and Ni/SBA-15-DP catalysts yield well-dispersed and homogeneous metallic phases mainly located in the mesoporosity of both supports. On the contrary, the Ni/SiO2-ImU and Ni/SBA-15-ImU catalysts present a bimodal distribution of the reduced nickel phase, with nickel metallic particles located out and into the mesoporous structure of SiO2 or the SBA-15 channels. The Ni/SBA-15-DP catalyst was found the most stable and performing system, with a very low level of carbon deposition, about an order of magnitude lower than the equivalent ImU catalyst. This outstanding performance comes from the confinement of small and homogeneous nickel particles in the mesoporous channels of SBA-15, which, in strong interaction with the support, are resistant to sintering and coke deposition during the demanding reaction conditions of DRM.

Design of Ag/ and Pt/TiO_2-SiO_2 nanomaterials for the photocatalyti degradation of phenol under solar irradiation

Matos, J; Llano, B; Montana, R; Poon, PS; Hidalgo, MC
Environmental Science and Pollution Research, **25** (2018) 18894-18913

Julio, 2018 | **DOI:** 10.1007/s11356-018-2102-3

The design of hybrid mesoporous TiO_2-SiO_2(TS1) materials decorated with Ag and Pt nanoparticles was performed. The photocatalytic degradation of phenol under artificial solar irradiation was studied and the activity and selectivity of the intermediate products were verified. TiO_2-SiO(2)was prepared by sol-gel method while Ag- and Pt-based photocatalysts (TS1-Ag and TS1-Pt) were prepared by photodeposition of the noble metals on TS1. Two series of photocatalysts were prepared varying Ag and Pt contents (0.5 and 1.0 wt%). An increase in the photocatalytic activity up to two and five times higher than TS1 was found on TS1-Ag-1.0 and TS1-Pt-1.0, respectively. Changes in the intermediate products were detected on Ag- and Pt-based photocatalysts with an increase in the catechol formation up to 3.3 and 6.6 times higher than that observed on TS1, respectively. A two-parallel reaction mechanism for the hydroquinone and catechol formation is proposed. A linear correlation between the photocatalytic activity and the surface concentration of noble metals was found indicating that the electron affinity of noble metals is the driven force for both the increase in the photoactivity and for the remarkable changes in the selectivity of products.

Photo/Electrocatalytic Properties of Nanocrystalline ZnO and La–Doped ZnO: Combined DFT Fundamental Semiconducting Properties and Experimental Study

Ahsaine, A.H.; Slassi, A.; Naciri, Y.; Chennah, A.; Jaramillo-Páez, C.; Anfar, Z.; Zbair, M.; Benlhachemi, A.; Navío, J.A.
Chemistry Select, **3** (2018) 7778-7791
Julio, 2018 | **DOI:** 10.1002/slct.201801729

This work reports the synthesis of nanocrystalline ZnO and 5% La-doped ZnO (La/ZnO) materials for photo/electrocatalytic degradation of Rhodamine B. The samples were characterized by X-Ray diffraction, scanning and transmission electron microscopy, X-Ray photoelectron spectroscopy and diffuse reflectance spectra. The effect of La doping on electronic structure was investigated using density functional theory calculations (DFT), La-doped ZnO showed an n-type metallic nature compared to pristine ZnO and La doping creates occupied states within the band gap edge. Under UV light, La/ZnO showed higher kinetic constant and efficiency than ZnO. A possible mechanism was elaborated on the basis of DFT and active trapping measurements. Different initial Rhodamine B concentration were studied to assess the electro-oxidation of RhB. The electrochemical degradation of RhB over La/ZnO spindles electrode was pronounced with three time's high kinetic constant. The superior electro/photoactivity of La/ZnO was due to its unique morphology, high charge separation of the charge carriers and higher conductivity induced by La-doping (intermediary levels). Superoxide ions and holes were the main active species for the photodegradation. Whereas, synergetic effect of hydroxyl radicals and hypochlorite ions were responsible of the high RhB electrocatalytic degradation.

A comparative assessment of the UV-photocatalytic activities of ZnO synthesized by different routes

Jaramillo-Paez, C; Sanchez-Cid, P; Navio, JA; Hidalgo, MC
Journal of Environmental Chemical Engineering, **6** (2018) 7161-7171
Diciembre, 2018 | **DOI:** 10.1016/j.jece.2018.11.004

ZnO was synthesized by a precipitation procedure, free of template agent, by mixing aqueous solutions of Zn (OAc)(2) and dissolved Na2CO3 at pH ca. 7. This material was calcined at different temperatures (200-600 degrees C for 2 h). In two other alternative procedures, after the precipitation, the suspension was taken to hydrothermal treatments or to microwave treatments, subjecting them to calcination treatments at the same temperatures as the previous material. All materials were characterized using various techniques. The photocatalytic activity was assessed in the degradation of methyl orange and phenol using UV-illumination and evaluating the corresponding percentages of conversion and mineralization. A minimal difference between the relative intensities of the exposed faces (I100I002) related to XRD for the synthesized samples seems to be an important factor in obtaining good photocatalytic properties. This minimum, was achieved with a calcination treatment at 400 degrees C for 2 h. With this calcination treatment, no significant variations were observed in the photocatalytic activities of ZnO obtained by the three procedures, although in all cases the zinc oxides obtained exhibited, for each substrate, higher UV-photocatalytic activities than those obtained with TiO2 (P25) used as a reference catalyst. In all cases, the samples showed no photocatalytic activity in the visible region of the spectrum.

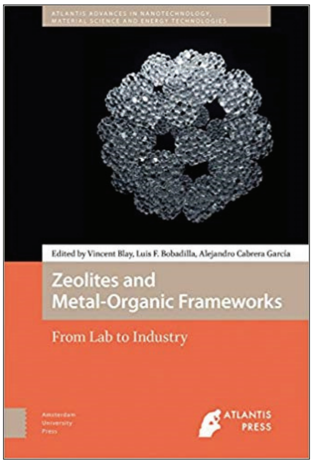
ARTICULOS PUBLICADOS EN REVISTAS (NO SCI) / PAPERS IN NON-SCI JOURNALS

Operando DRIFTS-MS Study of WGS and rWGS Reaction on Biochar-Based Pt Catalysts: The Promotional Effect of Na

Santos, J.L.; Bobadilla, L.F.; Centeno, M.A.; Odriozola, J.A.
C-Journal of Carbon Research, **4** (2018) UNSP47
Septiembre, 2018 | **DOI:** 10.3390/c4030047

Biochar-based Pt catalysts, unpromoted and Na-promoted, were prepared by an incipient wetness impregnation method and characterised by Inductively coupled plasma mass spoectrometry (ICP-MS) analysis, X-ray diffraction, N-2 adsorption and transmission, and scanning electron microscopy. It was demonstrated that a sodium promoter modifies the acid-base properties of the support, altering the Pt-support interaction. An operando Diffuse reflectance infrared fourier transform spectroscopy-mass spectrometry (DRIFTS-MS) study was performed to gain insights into the reaction pathways and the mechanism of the Water-Gass-Shift (WGS) and the Reverse Water-Gass-Shift (rWGS) reactions. It was demonstrated that the addition of Na enhances the catalytic performance due to the changes induced by the alkali in the electronic structure of the Pt active sites. This effect favours the activation of H2O molecules during the WGS reaction and the dissociation of CO2 during the rWGS reaction, although it may also favour the consecutive CO methanation pathway.

LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS



Zeolites and Metal-Organic Frameworks: From Lab to Industry (Atlantis Advances in Nanotechnology, Material Science and Energy Technologies)
Vicent Blay, Luis F. Bobadilla y Alejandro Cabrera-García
Editor: Amsterdam University Press, Netherlands
Número de Páginas: 342
ISBN10: 9462985561

Zeolites are natural or synthetic materials with porous chemical structures that are valuable due to their absorptive and catalytic qualities. Metal-Organic Frameworks (MOFs) are manmade organometallic polymers with similar porous structures. This introductory book, with contributions from top-class researchers from all around the world, examines these materials and explains the different synthetic routes available to prepare zeolites and MOFs. The book also highlights how the substances are similar yet different and how they are used by science and industry in situations ranging from fueling cars to producing drugs.

Spectroscopic Methods of Characterization for Zeolites and MOFs
L.F. Bobadilla, L. Oliviero, F. Romero-Sarria, M. Daturi
Zeolites and Metal-Organic Frameworks. From Lab to Industry (342 páginas). CAPITULO: 3, PÁGINAS: 53-87. 1ª Edicion Abril 2018. Atlantis Press / Amsterdam University Press, Amsterdam. Vincent Blay, Luis F. Bobadilla, Alejandro Cabrera-García (editores). ISBN: 978 94 6298 556 8, E-ISBN 978 90 4853 671 9 (doi 10.5117/9789462985568). Series: Atlantis Advances in Nanotechnology, Material Science and Energy Technologies. ISSN: 2352-0655 (Series Editor: Dr. Christian Ngô)

Synthesis and Identification Methods for Zeolites and MOFs
L.M. Martínez T., S. Ivanova, B. Louis, J.A. Odriozola
Zeolites and Metal-Organic Frameworks. From Lab to Industry (342 páginas). CAPITULO: 3, PÁGINAS: 25-52. 1ª Edicion Abril 2018. Atlantis Press / Amsterdam University Press, Amsterdam. Vincent Blay, Luis F. Bobadilla, Alejandro Cabrera-García (editores). ISBN: 978 94 6298 556 8, E-ISBN 978 90 4853 671 9 (doi 10.5117/9789462985568). Series: Atlantis Advances in Nanotechnology, Material Science and Energy Technologies. ISSN: 2352-0655 (Series Editor: Dr. Christian Ngô)

Biomass Transformation into Chemicals Using Zeolites and MOFs
O.H. Laguna, S.M. Coman, M.A. Centeno,V.I. Parvulescu
Zeolites and Metal-Organic Frameworks. From Lab to Industry (342 páginas). CAPITULO: 5, PÁGINAS: 117-147. 1ª Edicion Abril 2018. Atlantis Press / Amsterdam University Press, Amsterdam. Vincent Blay, Luis F. Bobadilla, Alejandro Cabrera-García (editores). ISBN: 978 94 6298 556 8, E-ISBN 978 90 4853 671 9 (doi 10.5117/9789462985568). Series: Atlantis Advances

in Nanotechnology, Material Science and Energy Technologies. ISSN: 2352-0655 (Series Editor: Dr. Christian Ngô)

Special Issue "Structured and Micro-Structured Catalysts and Reactors"
Catalysts (ISSN 2073-4344) Open Access Journal
Editor Invitado: José Antonio Odriozola Gordón
MDPI Suiza

Special Issue "Preferential Oxidation of Carbon Monoxide"
Catalysts (ISSN 2073-4344) Open Access Journal
Editores Invitados: Miguel Angel Centeno Gallego y Oscar H. Laguna
MDPI Suiza

Special Issue "Catalysis by Precious Metals, Past and Future"
Catalysts (ISSN 2073-4344) Open Access Journal
Editoras Invitadas: Marcela Martínez Tejada y Svetlana Ivanova
MDPI Suiza

CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

PARTICIPACIÓN EN LA ORGANIZACIÓN DE CONGRESOS Y REUNIONES / PARTICIPATION IN ORGANISING AND MEETINGS

XXVI Congreso Iberoamericano de Catálisis | CICAT2018
9 – 14 septiembre [Coimbra, Portugal]
José Antonio Odriozola [Miembro del Comité Científico)

3rd Fundamentals and Applications of cerium dioxide in Catalysis
25 – 27 junio [Barcelona, España]
José Antonio Odriozola Gordón [Miembro del Comité Científico)

COMUNICACIONES / COMMUNICATIONS

XI International Workshop on Oxide Surfaces
22 – 26 enero [Granada, España]

XPS Studies of the Surface Dynamics of Au/ZnO-CeO_2 Catalysts Pretreated under Reductant and Oxidizing Atmospheres
O.H. Laguna, M.A. Centeno, G. Munuera, J.A. Odriozola
Comunicación oral

Engineering Solutions for CO_2 Conversion, International Workshop, Department of Chemical and Process Engineering, University of Surrey

25 – 26 enero [Guildford, Gran Bretaña]

CO_2 utilisation enabled by michochannel reactors
J.A. Odriozola
Conferencia Invitada

6th International Congress on Operando Spectroscopy

15 – 19 abril [Málaga, España]

A new approach for monitoring the Fischer-Tropsch synthesis by operando DRIFTS-MS studies at moderated pressures
L.F. Bobadilla, E. Jiménez, F. Romero-Sarria, J.A. Odriozola
Poster

Influence of surface dynamics on the catalytic properties of PtCu Model catalyst for PROX reaction
R. Castillo, V. Pérez-Dieste, C. Escudero, F. Romero-Sarria, M. Datur, M.A.Centeno, J.A. Odriozola
Poster

ImagineNano2018

13 – 15 marzo [Bilbao, España]

Exploring the photo-catalytic properties of Nb2O5 nanoparticles synthesized by different procedures
J.A. Navío; F.J.Sánchez-Fernández; C. Jaramillo-Páez; M.C. Hidalgo
Poster

6th World Congress and Expo on Nanotechnology and Materials | NANOTECHNOLOGY 2018

16 – 18 abril [Valencia, España]

Environmental Applications of Nanosized Zinc Oxide (ZnO) for Water purification
J.A. Navío

25th International Conference on Chemical Reaction Engineering “Engineering the Chemical Transformation by Bridging Science and Technology” | ISCRE25

20 – 23 mayo [Florencia, Italia]

Micromonoliths coated with Pt/Al_2O_3 catalyst for the simultaneous combustion of H_2, CO and CH_4: Effect of the catalytic layer thickness and thermal conductivity
O.H. Laguna, O. Sanz, M.A.Centeno, M. Montes, J.A. Odriozola
Comunicación oral

Intensification of Catalytic Processes with Structured Catalysts and Reactors
Oihane Sanz, Luis M. Gandía, José Antonio Odriozola, Mario Montes
Poster

10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications | SPEA10
4 – 8 junio [Almeria, España]

Hydrogen Photo-production from Methanol: in-situ Analysis of the Active Phase in Mono- and Bimetallic Cu-Ni co-catalysts
M.J. Muñoz-Batista, D. Motta Meira, G. Colón, A. Kubacka, M. Fernández-García
Poster

Influence of Electrolyte Addition on TiO_2 Phase Composition: Superior Photocatalytic Performace of Brookite-Anatase Biphasic TiO_2 vs. Pure Phases
M.A. Lara, M.J. Sayagués, J.A Navío, M.C. Hidalgo
Poster

Coupling of WO_3 with anataseTiO_2 sample with high {001} facet exposition: effect on the photocatalytic properties
M.A. Lara, C.A. Jaramillo-Páez, J.A. Navío, M.C. Hidalgo
Poster

BixTiyOz-Fe Multiphase Systems with High Photocatalytic Performance in the Visible
P. Zambrano, J.A Navío, M.C. Hidalgo
Poster

A Zn-rich/($ZnWO_4$) material synthesized by a facile procedure. Characterization and Evaluation of its photocatalytic properties
C.A. Jaramillo-Páez, J.A. Navío, P. Sánchez-Cid, M.C. Hidalgo
Poster

3rd Fundamentals and Applications of Cerium Dioxide in Catalysis
25 – 27 junio [Barcelona, España]

Enhancing the performance of the Fischer-Tropsch reaction by adding a Pt/CeO_2 catalyst: WGS or CO hydrogenation? An operando DRIFTS-MS study at moderated pressures
L.F. Bobadilla, A. Egaña, R. Castillo, F. Romero-Sarria, O. Sanz, M. Montes, J.A. Odriozola
Comunicación oral

8th International Symposium on Carbon for Catalysis | CarboCat–VIII

26 – 29 junio [Oporto, Portugal]

Au/C catalysts for 2,5-furandicarboxylic acid production
C. Megías-Sayago, J.L. Santos, A. Lolli, S. Ivanova, S. Albonetti, M.A. Centeno, F. Cavani, J.A. Odriozola
Comunicación oral

Hydrodeoxygenation of vanillin over carbon supported noble metal catalysts
J.L. Santos, P. Mäki-Arvela, M. A. Centeno, D. Yu. Murzin
Comunicación oral

Kinetics of catalytic coke gasification by air and by CO_2
M.A.N.D.A. Lemos, S.A.C. Carabineiro, M.A. Centeno, L.F. Bobadilla, F. Lemos, L.S. Lobo
Poster

Functionalized metallurgical coke as catalysts supports of the direct coal liquefaction
D.A. Rico, Y.Y. Agámez, E.R Romero, M.A. Centeno, J.A. Odriozola, J.J. Díaz
Poster

Carbon 2018, the world Conference on Carbon

1 – 6 julio [Madrid, España]

Ruthenium Supported on various carbon materials for sugar hydrogenation
J.L. Santos, A. Aho, D. Yu. Murzin, M.A. Centeno, J.A. Odriozola
Comunicación oral

5-HMF production from fructose over functionalized carbon materials
Charf Eddine Bounoukta, Jose Luis Santos Muñoz, Fatima Ammari, Nuria Rendón, Anna Penkova, Svetlana Ivanova, Miguel Ángel Centeno, José Antonio Odriozola
Poster

12th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts" | PREPA12

8 – 12 julio [Louvain-La-Neuve, Bélgica]

Effect of preparation method of supported Ru nanoparticles in CO_2 methanation: influence of the residual species
S. Navarro, A. Szego, L.F. Bobadilla, O.H. Laguna, F. Romero-Sarria, M.A.Centeno, J.A. Odriozola
Poster

Noble metal nanoparticles inmobilization on carbonaceous materials: influence of synthesis parameters on the metallic size
J.L. Santos, J.C. Navarro, C. Megías-Sayago, S. Ivanova, A. Monzón, M.A.Centeno
Poster

4th International Congress on Waster, Waste and Energy Management | WaterWaste18

18 – 20 julio [Madrid, España]

Zinc Oxide (ZnO) for Water purification
J.A. Navío, C. Jaramillo-Páez, P. Sánchez-Cid, M.C. Hidalgo
Poster

Photocatalytic properties of coupled system TiO_2-WO_3 versus its parent oxides
J.A. Navío, C. Jaramillo-Páez, P. Sánchez-Cid, M.C. Hidalgo
Poster

XXVI Congreso Iberoamericano de Catálisis | CICAT2018

9 – 14 septiembre [Coimbra, Portugal]

XAS study: entendiendo los catalizadores Pt-Cu para la reacción de oxidación preferencial de CO (PROX)
R. Castillo, S. Ivanova, F. Romero-Sarria, M.A. Centeno, M. Daturi, J.A. Odriozola
Comunicación oral

Reactor de Rh en microcanales para la obtención de gas de síntesis via reformado de biogás
Victoria Garcilaso, Miguel A. Centeno, Jose A. Odriozola
Comunicación oral

Producción de Hidrógeno a partir de ácido fórmico sobre catalizadores paladio-carbón biomásico
J.L. Santos, F. Cazaña, A. Monzón, M.A. Centeno, J.A. Odriozola
Comunicación oral

Intercambio isotópico de 18º2 y C18O2 sobre catalizadores Pt/$CePO_4$: implicaciones mecanísticas en las reacciones de WGS/R-WGS
S. Navarro-Jaén, N. Bion, M.A. Centeno, O.H. Laguna, J.A. Odriozola
Comunicación oral

Catalizadores híbridos bifuncionales para la reaccion de deshidratación de glucosa/fructosa a HMF
C. Megías-Sayago, S. Ivanova, M.A. Centeno, J.A. Odriozola
Comunicación oral

SBA-15 modificada con fósforo como soporte catalítico para reacciones de interés energético
J. C. Navarro, L.M. Martínez T, M.A. Centeno, J.A. Odriozola
Poster

Influencia del método de preparación en la interacción Ni-Mg-Al: efecto en la reacción de reformado de metano con vapor de agua
Lola Azancot, Luis F. Bobadilla, José M. Córdoba, Miguel A. Centeno, José A. Odriozola
Poster

Influencia del agua en la reacción de Fischer-Tropsch: estudio operando a presiones moderadas
Luis F. Bobadilla, Elena Jiménez Barrera, Francisca Romero-Sarria, José A. Odriozola
Poster

Estudio operando DRIFT/MS de la separación CH_4/CO_2 sobre materiales SAPO-34: efecto de la relación Si/Al/P
Marta Romero, Juan C. Navarro, Luis F. Bobadilla, Svetlana Ivanova, María I. Domínguez, Francisca Romero-Sarria, José A. Odriozola
Poster

Carbón activo funcionalizado para la reacción de deshidratación de fructosa en 5-hidroximetilfurfural (5-HMF) en ausencia de disolventes orgánicos
Charf Eddine Bounoukta, Fatima Ammari, Nuria Rendon, Svetlana Ivanova, Miguel Angel Centeno, José Antonio Odriozola
Poster

The IV Energy & Materials Research Conference | EMR2018 Conference

4 – 5 octubre [Málaga, España]

Development of TiO_2/SiO_2 films on borosilicate glass for photo-catalytic applications in gas phase
J.A. Navío, Juan M. Marin, Fidel Granda, Laila Galeano, Luis A. Rios, Gloria Restrepo
Poster

11th International Vanadium Symposium

5 – 8 noviembre [Montevideo, Uruguay]

Kinetics of catalytic coke gasification by air and by CO_2
M.A.N.D.A. Lemos, S.A.C. Carabineiro, M.A. Centeno, L.F. Bobadilla, F. Lemos, L.S. Lobo
Comunicación oral

International Congress: "Materials applied to the environment"

5 – 7 diciembre [Agadir, Marruecos]

Synthesis of ZnP/BiP catalyst with enhanced UV light photocatalytic activity
Y. Naciri, A. Chennah, A. Bouddoch, B. Bakiz, A. Taoufyq, C. Jaramillo-Páez, J. A. Navío, M. Ezahri, S.Villain, F. Guinneton, A. Benlhachemi
Comunicación oral

Photocatalytic Removal of Sulfadiazine using ZnP/BiP Composite Prepared by Coprecipitation Method
Y. Naciri, A. Chennah, A. Bouddoch, B. Bakiz, A. Taoufyq, C. Jaramillo-Páez, J. A. Navío, M. Ezahri, S.Villain, F. Guinneton, A. Benlhachemi
Poster

CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESSES AND MEETINGS

PARTICIPACIÓN EN LA ORGANIZACIÓN DE CONGRESOS Y REUNIONES / PARTICIPATION IN ORGANISING AND MEETINGS

III Encuentro de Jóvenes Investigadores de la SECAT
25 – 27 junio [Valencia, España]
José Antonio Odriozola [Miembro del Comité Científico)
Miguel Angel Centeno [Miembro del Comité Científico)

COMUNICACIONES / COMMUNICATIONS

III Encuentro Jóvenes Investigadores SECAT 2018
25 – 27 junio [Valencia, España]

Screening de catalizadores para la valorización de CO_2 mediante la reacción de Sabatier
J.C. Navarro, M. A. Centeno, O.H. Laguna, J. A. Odriozola
Poster

Effect of metal-support interaction in the catalytic performance of Ni-based catalysts
L. Azancot, L.F. Bobadilla, J.M. Córdoba, M. A. Centeno, J.A. Odriozola
Poster

FORMACION / TRAINING

TESIS DOCTORALES/ DOCTOR DEGREE THESIS

Título:	**Utilización de la Espectroscopía Infrarroja para el Estudio de Catalizadores Heterogéneos**
Autor:	Elena María Jiménez Barrera
Directores:	Francisca Romero Sarria y José Antonio Odriozola Gordón

Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla
Fecha: 9 de febrero de 2018

Título: **Desarrollo de Sistemas Catalíticos Mesoporosos Nanoestructurados para la Producción de Hidrógeno y la Síntesis Directa de Agua Oxigenada**
Autor: Alberto Rodríguez Gómez
Directores: Alfonso Caballero Martínez y Rosa María Pereñíguez Rodríguez
Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla
Fecha: 16 de marzo de 2018

Título: **Desarrollo de materiales foto-funcionales para aplicaciones medioambientales**
Autor: César Augusto Jaramillo Páez
Directores: José Antonio Navío Santos y María del Carmen Hidalgo López
Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla
Fecha: 7 de septiembre de 2018

Título: **Aprovechamiento de gas no convencional en procesos GTL**
Autor: Victoria Garcilaso de la Vega González
Directores: José Antonio Odriozola Gordón y Miguel Angel Centeno Gallego
Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla
Fecha: 22 de octubre de 2018

Título: **Estudio de catalizadores basados en platino para la reacción de PROX: influencia de los depósitos de carbono**
Autor: Rafael Castillo Barrera
Directores: José Antonio Odriozola Gordón y Marco Daturi
Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla y Universidad de Caen (Francia)
Fecha: 19 de diciembre de 2018

Formación de Graduados / Master Degree Thesis

Título: **Catalizadores metal noble/carbón para aplicaciones medioambientales**
Autor: Hugo Rodríguez Molina

Directores: Miguel Angel Centeno Gallego, María Isabel Domínguez Leal
Grado: Trabajo Fin de Grado
Centro: Universidad de Sevilla
Año Académico: 2018-2019 (21 septiembre 2018)

Título: **Metales en medicina: aplicaciones biomédicas del cobre**
Autor: Omar Azougagh
Directores: Svetlana Lyubomirova Ivanova
Grado: Trabajo Fin de Grado
Centro: Universidad de Sevilla
Año Académico: 2018-2019 (25 septiembre 2018)

Título: **Aplicación de métodos “single molecule” para estudiar in vitro metaloproteinas en células**
Autor: Pep Mir Darder
Directores: Luis F. Bobadilla
Grado: Trabajo Fin de Grado
Centro: Universidad de Sevilla
Año Académico: 2018-2019 (diciembre 2018)

Título: **Explorando las propiedades foto-catalíticas del Nb2O5 sintetizado por diferentes procedimientos químicos**
Autor: Francisco Javier Sánchez Fernández
Directores: José Antonio Navío Santos y Mª Carmen Hidalgo López
Grado: Trabajo Fin de Grado
Centro: Universidad de Sevilla
Año Académico: 2017-2018 (diciembre 2018)

Título: **Acoplamiento de Ag_2CO_3 a un fotocatalizador de ZnO optimizado: ventajas frente a desventajas**
Autor: Pablo M. Sánchez-Cid Bueno
Directores: José Antonio Navío Santos y Mª Carmen Hidalgo López
Grado: Trabajo Fin de Grado
Centro: Universidad de Sevilla
Año Académico: 2018-2019 (septiembre 2018)

Estancias y Visitas de Personal del ICMS en otros Centros
Personnel of the ICMS in Other Laboratories

Laboratorio de Catálisis y Espectroquímica CNRS-Universidad de Caen
Ciaen, Francia **Rafael Castillo Barrero** 1/09/2018 al 31/10/2018

Synchrotron ALBA –CIRCLE (NAP-XPS)
Barcelona, España **José Antonio Odriozola Gordón** 1/03/2018 al 04/03/2018

	Rafael Castillo Barrero	1/03/2018 al 04/03/2018
	José Luis Santos Muñoz	1/03/2018 al 04/03/2018
	Juan Carlos Navarro de Miguel	1/03/2018 al 04/03/2018
Instituto Universitario de Investigación en Nanociencia de Aragón (INA)		
Zaragoza, España	**José Luis Santos Muñoz**	15/10/2018 al 28/10/2018

Estancias y Visitas de Investigadores en el ICMS

Personnel of the Other Laboratories in the ICMS

Universidad Nacional de Bogotá		
Bogotá, Colombia	**Jahaziel David Amaya Bayona**	18/12/2017 al 10/02/2018
Universidad Pontificia Bolivariana		
Medellin, Colombia	**Manuel Alejandro Domínguez Ortiz**	22/01/2018 al 16/04/2018
Université Setif1		
Setif, Argelia	**Meriem Chebout**	08/01/2018 al 09/04/2018
	Charaf Eddine Bounoukta	03/01/2018 al 03/07/2018
	Charaf Eddine Bounoukta	11/10/2018 al 30/08/2018
Ecole Nationale Superiere de Chimie de Lille		
Lille, Francia	**Damien Derlique**	29/03/2018 al 30/08/2018
Institut textile et Chimie de Lyon (ITECH)		
Lyon, Francia	**Manale Benchiboun**	15/06/2018 al 31/07/2018
Universitá Degli Studi di Salerno		
Salerno, Italia	**Luigi Panzone**	24/09/2018 al 10/02/2019
Universidad de Surrey		
Surrey, Reino Unido	**Tomás Ramírez Reina**	07/11/2018 al 15/11/2018
Centre des Études Doctorales IBN ZOHR (CEDOC)/Université IBN ZOHR		
Agadir, Marruecos	**Naciri Yassine**	15/01/2018 al 15/04/2018
Universidad Juárez Autónoma de Tabasco		
Villahermosa, México	**Yareli Bolaina Lorenzo**	01/09/2018 al 30/11/2018

EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Molino de bolas de movimiento planetario PM100 de RETSCH
- Espectrofotómetro Infrarrojos: Thermo-Nicolet Nexus FT-IR; Thermo-Nicolet 380 FT-IR
- Accesorio DRIFTS, celdas de alta y baja temperatura
- Sistema de vacío cuarzo/vidrio para adsorción de moléculas sonda seguido por FT-IR
- Espectrómetro de masas: Balzers Thermostar
- Sistema TPR-TPO (con posibilidad de realizar pulsos) seguido de espectrómetro de masas (Balzers) y detector de conductividad térmica. PID Eng&Tech.
- Equipos comerciales de actividad catalítica Microactivity Reference PID Eng&Tech (4)
- Microscopio metalográfico: Leica DMIRM
- Rotavapor: Heidolph Hei-VAP Value
- Equipo de ultra-alto vacío para espectroscopía XPS y Auger equipado con cañón de argón para realizar devastado iónico.
- Estufas: P-Selecta; P-Selecta digiheat
- Ph-metros: Crison pH burette 24; Crison phMeter Basic 20; Crison micropH2000.
- Cromatógrafos (2): Agilent Technologies 7890 A GC System; Agilent Technologies 6890 N Network GC System.
- Micro-cromatógragos, microGC (2): Micro Gas Cromatograph CP-4900 Varian (2)
- HPLC: Varian 356-LC, Solvent Delivery Module Varian ProStar.
- Horno de soldadura: Microtest Máquina de ensayos EM2/200/FR
- Baño de ultrasonidos: P-Selecta Ultrasons Medi-II
- Horno Energon
- Horno para tratamiento de aceros a alta temperatura equipado con medidores de flujo e inyector de agua.
- Planta Piloto de Integración de reacciones catalíticas Reference PID Eng&Tech
- Espectrómetro Uv-Vis (Varian Cary 100, con esfera integradora para
- muestras sólidas)
- Analizador de Carbón Orgánico (TOC-V CHP Shimadzu 5000ª)
- Cromatógrafo (HPLC Agilent Technologies 1200)
- Espectrómetro IR (Varian 660-IR FTIR Spectrometer)
- Dip-Coater con cámara de temperatura (SS-00 AB Table Dry Oven MTI
- Corporation)
- Espectrofotómetro FTIR con celdas DRIFTS y ATR.
- Sistema de análisis TPR/TPO con detector TCD y espectrómetro de masas.
- 6 reactores catalíticos de gases con detección por cromatografía de gases y espectrometría de masas.
- 2 reactores catalíticos de líquidos que permiten el seguimiento de hasta 8 reacciones de forma simultánea con control de temperatura y flujo de gases.
- 4 reactores catalíticos de líquidos de alta presión y temperatura con agitación interna y control de flujo de gases.
- Reactores fotocatalíticos con lámparas de Xe y Hg.
- Espectrofotómetros FTIR con accesorios DRIFTS, ATR y sistema de vacío en cuarzo/vidrio para adsorción de moléculas sonda

- Espectrómetros de masas
- Sistemas TPR-TPO (con posibilidad de realizar pulsos) seguido de espectrómetro de masas y detector de conductividad térmica.
- Microscopio metalográfico
- Rotavapor
- Estufas
- Ph-metros
- Cromatógrafos de Gases
- Micro-cromatógragos, microGC
- Cromatografos HPLC
- Horno de soldadura: Microtest Máquina de ensayos EM2/200/FR
- Baño de ultrasonidos
- Hornos
- Horno para tratamiento de aceros a alta temperatura equipado con medidores de flujo e inyector de agua.
- Planta Piloto de Integración de reacciones catalíticas Reference PID Eng&Tech
- Espectrómetro Uv-Vis, con esfera integradora para muestras sólidas)
- Analizador de Carbón Orgánico
- Dip-Coater con cámara de temperatura
- Reactores catalíticos de gases con detección por cromatografía de gases y espectrometría de masas.
- Reactores catalíticos de líquidos que permiten el seguimiento de hasta 8 reacciones de forma simultánea con control de temperatura y flujo de gases.
- Reactores catalíticos de líquidos de alta presión y temperatura con agitación interna y control de flujo de gases.
- Reactores fotocatalíticos con lámparas de Xe y Hg.

INGENIERÍA DE CERÁMICOS PARA AMBIENTES EXTREMOS

ENGINEERED CERAMICS FOR EXTREME ENVIRONMENTS

GRUPO DE INVESTIGACIÓN

Materiales de Diseño para la Energía y Medioambiente

Designed Materials for the Energy and Environment [642007]

PERSONAL / PERSONNEL

Catedráticos

- Dr. Miguel Angel Castro Arroyo
- Dr. Manuel Jiménez Melendo
- Dra. Pilar Malet Maenner
- Dr. Julián Martínez Fernández
- Dr. Antonio Ramírez de Arellano-López

Científicos Titulares

- Dr. José Jesús Benítez Jiménez
- Dra. María Dolores Alba Carranza

Profesores Titulares

- Dr. Alfonso Bravo León
- Dra. Caroline M. Clauss Klamp
- Dr. Joaquin Ramírez Rico

Becarios Predoctorales

- Ldo. Rafael Cabezas Rodríguez
- Lda. María del Pilar Orihuela Espina
- Ldo. Francisco J. Osuna Barroso

Personal Contratado

- Dra. Esperanza Pavón González

Proyectos de Investigación / Research Projects

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
Ministerio de Economía y Competitividad

Nuevo concepto de caldera de biomasa basada en materiales biocerámicos y combustión porosa para operación eficiente con residuos

Bioceramic Materials for New Biomass Domestic Bolier Concept based on Porous Combustion for a Wide Biomass/Residues Feedstock

Código/Code:	MAT2016-76526-R
Periodo/Period:	30-12-2016 / 29-12-2019
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	60.500 €
Investigador responsable/Research head:	Joaquin Ramírez Rico /Ricado Chacartegui
Componentes/Research group:	Manuel Jiménez Melendo, Julián Martínez Fernández

RESUMEN / ABSTRACT

En la Unión Europea se generan anualmente más de cinco toneladas de residuos por personas, siendo aproximadamente el 60% de esta cantidad materia orgánica. La tecnología de las calderas de biomasa actuales no permiten el uso de estos residuos funcionando con altos valores de eficiencia, bajas emisiones y alta fiabilidadad de operación, siendo especialmente relevante en calderas de pequeño tamaño.

El principal objetivo de este proyecto es desarrollar un nuevo concepto de tecnología para calderas de biomasa doméstica capaz de operar con gran variedad de mezclas de biomasas y residuos agrícolas. Para ello se aprovecharán las sinergias de la integración de investigadores del: i) Grupo Maquinas y Motores Térmicos, GMTS, especialistas en combustión, calderas y máquinas térmicas ii) Grupo Materiales Biomiméticos y Multifuncionales, MBM, especialistas en la obtención de cerámicos porosos bioderivados, así como en caracterización físico-química y microestructural. El proyecto se completa con la colaboración de empresas en la evaluación de la tecnología y su aplicabilidad industrial En la Unión Europea se generan anualmente más de cinco toneladas de residuos por personas, siendo aproximadamente el 60% de esta cantidad materia orgánica. La tecnología de las calderas de biomasa actuales no permiten el uso de estos residuos funcionando con altos valores de eficiencia, bajas emisiones y alta fiabilidadad de operación, siendo especialmente relevante en calderas de pequeño tamaño.

El principal objetivo de este proyecto es desarrollar un nuevo concepto de tecnología para calderas de biomasa doméstica capaz de operar con gran variedad de mezclas de biomasas y residuos agrícolas. Para ello se aprovecharán las sinergias de la integración de investigadores del: i) Grupo Maquinas y Motores Térmicos, GMTS, especialistas en combustión, calderas y máquinas térmicas ii) Grupo Materiales Biomiméticos y Multifuncionales, MBM, especialistas en la obtención de cerámicos porosos bioderivados, así como en caracterización físico-química y microestructural. El proyecto se completa con la colaboración de empresas en la evaluación de la tecnología y su aplicabilidad industrial

El proyecto se basa en la innovadora integración de material biocerámico microporoso en las cámaras de combustión de calderas de biomasa de modo que actúen con diferentes funciones: combustor microporoso, filtro de partículas y recuperador de calor. Estas funcionalidades pueden ser simultáneas, en función de la región del flujo en que se encuentren y el rango de temperaturas de esa región. Este material biocerámico es desarrollado a partir de precursores vegetales para obtener elementos de Carburo de Silicio (SiC). Para ello se usan materiales locales sin tratar, produciendo elementos hechos a medida con propiedades microestructurales adecuadas para trabajar con altas temperaturas. Así, productos con geometrias complejas pueden ser obtenidos con relativamente bajo coste comparados con otros materiales con características macánicas y químicas similares. La integración de componentes basados en estos materiales posibilita nuevos diseños de calderas de biomasa con un alto control de la combustión, las temperaturas y la emisión de partículas. El nuevo diseño evita la sinterización y fusión de las cenizas, actuando en la formación y evolución de contaminantes, inhibiendo los mecanismos de producción de dioxinas y activando la completa oxidación del monóxido de carbono (CO) y soots. El nuevo concepto permitirá la operación con una importante varieda de mezclas biomasa/ residuos agrícolas con bajas emisiones aun cuando el combustible pesente un alto contenido de cenizas, resolviendo el principal reto para el desarrollo del uso residuos agrícolas en calderas de biomasa (especialmente las de menor tamaño). El desarrollo de esta tecnología permitirá ampliar los recursos de la Unión Europea para calefacción de uso doméstico. En la actualidad este uso supone un 30% del consumo energético total en la misma. La propuesta incluye el estudio de los procesos básicos de combustión, flujos, fabricación a medida de las matrices de materiales biocerámicos, así como estudio y desarrollo de prototipos de componentes y del sistema final. Estos serán estudiados a nivel de ensayos de laboratorio con residuos agrícolas, forestales y de la industria olivarera.

EU generates more than five tons of waste per person every year and about 60 % is organic waste. Current biomass domestic boiler technology does not allow the use of these residues with high efficiency, ultra-low emissions and high reliability operation. The main objective of this proposal is the development of a new concept of biomass domestic boiler technology able to combine these characteristics for operation with multiple biomass/residues blends. It is based on the integration of novel bioceramic porous materials matrices in combustion chamber and gases pathflow with functions as microporous combustors, particles filters and heat accumulators. These functions are simultaneous depending on the region of the boiler. Matrices of bioceramic materials are developed from wood precursors to obtain SiC elements through a process patented by the University of Seville. It uses local raw material, and produces parts with tailor made microstructure/properties, adequate for high temperature and reactive operation. Products with complex geometries can be obtained at relatively low cost compared with other materials of similar chemical and mechanical properties. The integration of components based on these materials allows new designs of biomass boilers with high control of combustion, temperature and particle emission. It avoids ash sintering and melting, acting on the formation and evolution mechanisms of ash and dioxins and activating the complete oxidation of CO and soots. The new concept allows the operation to a wider biomass/residues feedstock with low emissions and low maintenance even with fuels with high ash content, produced from many residues, solving main challenges for their extended use and increasing the European fuel resources for domestic heating. Domestic heating in Europe consumes 30% of the total energy. The proposal includes prototypes development, fuel supply characteristics and preparation (geometry, compactness, composition, etc.) and combustion products management. Biomass/residues blends from agriculture, forestry, olive oil industry among others will be tested both in laboratory.

Tratamiento sostenible de residuos industriales: Materiales adsorbentes de diseño y bionanocomposites en la inmovilization de metales pesados y productos de fision Susteinable industrial waste treatment: designed adsorbent materials and bionanocomposites for inmobilizing heavy metals and fision products

Código/Code:	MAT2015-63929-R
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	60.500 €
Investigador responsable/Research head:	Maria Dolores Alba Carranza
Componentes/Research group:	Miguel Angel Castro Arroyo, Ana Carmen Perdigón Aller, María del Mar Orta Cuevas

RESUMEN / ABSTRACT

El Proyecto de investigación que se presenta aborda la exigencia tecnológica y medioambiental de desarrollar metodologías avanzadas para la eliminación de agentes contaminantes. El interés y los esfuerzos encaminados al desarrollo de nuevas tecnologías orientadas a tratamientos más eficientes en la inmovilización y revalorización de los residuos peligrosos es creciente en los planes de I+D+i. El objetivo central del proyecto se basa en el diseño de una estrategia de funcionalización de silicatos laminares de alta carga expansibles y en la síntesis de bionanocomposites a partir de ellos para conseguir una actividad eficaz respecto de la inmovilización de residuos tóxicos y peligrosos, catiónicos y aniónicos. Este objetivo es un cambio cualitativo en el trabajo que se viene desarrollando en el diseño de sistemas modelos adsorbentes con aplicaciones medioambientales de clara repercusión en la mejora de la calidad de vida de la población y conservación del medioambiente, ya que la funcionalización de diseño de los silicatos sintéticos permitirá la adsorción de un amplio abanico de adsorbentes en estado de oxidación aniónico-catiónico. La finalidad y objetivos del proyecto se centran en la Focus Area WASTE de H2020 y esta Focus Area se desarrolla dentro del reto 2 y 5 de H2020 y dentro del Reto 5 y 3 de los Planes Estatales de Investigación.

El proyecto ha despertado el interés de diversas empresas observadoras, EPOs, (ENRESA y la Agencia de la Energía y para la Sostenibilidad del Ayuntamiento de Sevilla) impulsando la colaboración público-privada. Por tanto, la investigación desarrollada auna los principios básicos de la estrategia estatal de Ciencia y Tecnología: Poner la I+D+I al servicio de la ciudadanía, del bienestar social y de un desarrollo sostenible, hacer de la I+D+I un factor de mejora de la competitividad empresarial (transferencia de los resultados al sector privado, ver interes de los

EPOs) y reconocer y promover la I+D como un elemento esencial para la generación de nuevos conocimientos de excelencia.

La viabilidad de la propuesta se garantiza porque el equipo de investigación, EI, por un lado, ha desarrollado con éxito la síntesis de silicatos laminares hidratables de alta carga, a través de un método novedoso que permite ajustar la carga deseada para el material, y, por otro, ha conseguido exitosamente su organofuncionalización (patente ES2362597B1). Además, ha desarrollado la metodología necesaria para el correcto progreso de este proyecto, en estrecha colaboración con otros Grupos de investigación internacionales de reconocido prestigio (e.g. CNRS-Universidad de Lille, Universidad de Cambridge...). Además el EI ha demostrado que potencia la agrupación de las capacidades y competencias científico-técnicas esenciales para abordar esta propuesta de marcado caracter transversal.

The focus of the project addresses the requirement of advanced environmental technology methodologies for removing pollutants. Recently, the interest and efforts to develop new technologies for more efficient treatments for the immobilization and the revaluation of hazardous waste are increasing in R & D plans. The overall object of the project is based on the design of a strategy of functionalization of highly charged swelling phyllosilicates and their later transformation on bionanocomposite for the effective retention and immobilization of hazardous waste, both cationic and anionic. This object represents a qualitative change in the work that is being nowdays developed in the field of model adsorbents systems with environmental applications that will improve the quality life of the population and the environmental conservation, because the designed functionalization of the synthetic silicates will allow the adsorption of a wide range of adsorbents in different oxidation states, cationic or anionic. The objectives are conformed to the Focus Area WASTE of the H2020 program and it is developed on the 2nd and 5th challenge of the H2020 program and on the 5th and 3rd challenge of the national research program.

The project has attracted interest from various observers companies, EPOs, (ENRESA and the Water and Local Energy Agency and Sustainability of the City of Seville), the public-private collaboration being promoted. Therefore, the research combines the basic principles of the National Strategy of Science and Technology: Putting the R&D&I at the service of citizens, social welfare and sustainable development, making the R&D&I a factor of improving business competitiveness (transfer of results to the private sector, see interest of EPOs) and recognize and promote R&D&I as an essential element for the generation of new excellence knowledge.

The viability of the proposal is ensured, first, because the research team, RT, has accomplished the synthesis of hydratable high charged phyllosilicates, with a novel and original method that allows setting the material desired charge, and, later, has successfully achieved their organofunctionalization (patent ES 2 362 597 B1). Second, the RT has developed the required methodology for the development of this project in closed scientific collaboration with other well recognized international groups (i.e. CNRS-University of Lille, University of Cambridge...). The RT enhances the clustering of their capabilities and scientific-technical skills which are essential to address this proposal with a remarkable transverse character.

Estudio de la inmovilización de metales pesados por micas de alta carga sintéticas organofuncionalizadas: pruebas a escala de laboratorio / Inmobilization of heavy metals by synthetic high-charged organomicas: Test at laboratory scale

Código/Code: P12-FQM-567
Periodo/Period: 16-05-2014 / 16-02-2019
Organismo Financiador/Financial source: Junta de Andalucía
Importe total/Total amount: 174.455 €
Investigador responsable/Research head: María Dolores Alba Carranza

RESUMEN / ABSTRACT

El tema central del proyecto aborda la exigencia tecnológica mediambiental de desarrollar metodologías avanzadas para la eliminación de agentes contaminantes. El interés y los esfuerzos encaminados al desarrollo de nuevas tecnologías orientadas a tratamientos más eficientes en la inmovilización y revalorización de los residuos peligrosos es crecientes en los planes de I + D + i de los últimos años. Es en este escenario donde debe encuadrarse el presente proyecto y en concreto en el marco de la gestión de cationes de metales pesados, tema de elevado interés social en la presente década.

Desde la segunda mitad del siglo XX la Humanidad se ha enfrentado a un enorme desarrollo científico y tecnológico que es el responsable de un incremento de la contaminación mediambiental. Como ejemplo podemos mencionar dos problemas que en la actualidad son motivos de preocupación y actuación de la Junta de Andalucía: contaminación de los litorales andaluces y las aguas residuales urbanas. Por tanto, estamos ante un problema complejo en el que los agentes contaminantes son variados, las fuentes de procedencia son diversas y las vías o rutas seguidas por los distintos contaminantes, frecuentemente, escapan al control necesario para evitar efectos indeseados sobre el entorno natural y urbano. Es por ello, que se demanda una investigación a nivel básico y aplicado de los mecanismos necesarios para la inmovilización de dichos cationes nocivos.

Los objetivos y alcance de este proyecto se basan en los avances llevados a cabos por otros grupos de investigación de la gestión de estos tipos de contaminantes y en los últimos resultados de la investigación llevada a cabo por el equipo de investigación que han permitido el diseño de silicatos laminares expansibles de alta carga con especiales propiedades como precursores para la retención de residuos nocivos. Por tanto, se propone en este proyecto la organofuncionalización de dichas micas sintéticas con grupos tioles o con cationes de alquilamonio de longitud de cadena variable y la evaluación de su capacidad de adsorción y retención irreversible de metales pesados.

The focus of the project addresses the environmental technological requirement to develop advanced methods for removing pollutants. The interest and efforts to develop new technologies aimed at more efficient treatment in detention and revaluation of hazardous waste is increasing in R & D plans. It is in this scenario where this project should be framed and in

particular in the framework of the management of heavy metal cations, issue of high public interest in this decade.

Since the second half of the twentieth century, humanity has faced a huge scientific and technological development that is responsible for increased environmental pollution. As an example, we can mention two problems that are currently of concern and action of the Andalusian: Andalusian coastal pollution and urban wastewater. Therefore, this is a complex problem that pollutants sources are varied of origin and routes followed by various pollutants are diverse and, frequently, it is beyond the control necessary to avoid urban undesirable effects on the natural environment and. Therefore, a basic level research is demaned to implement the necessary mechanisms for the immobilization of such harmful cations.

The objectives and scope of this project are based on advances made by other research groups in the management of these types of contaminants and the latest research conducted by the research team that allowed design expandable high-charged layered silicates with special properties as precursors for the retention of harmful residues. Therefore, it is proposed in this project the organofunzionalization of such synthetic micas with thiol groups or alkylammonium cations of varying chain length and evaluation of its adsorption capacity and irreversible retention of heavy metals.

Otros Proyectos / Other Projects

Bases genéticas de la composición y propiedades biofísicas de la cutícula del fruto del tomate. Aprovechamiento de la variabilidad natural

Código/Code:	AGL2015-65246-R
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	187.550 €
Investigador responsable/Research head:	Rafael Fernández Muñoz (IHSM)
Componentes/Research group:	José Jesús Benítez, Fernando Gallardo Alba (UMA), Antonio Heredia Bayona (IHSM)

ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

Plant cuticle under global change: Biophysical implications

Heredia-Guerrero, JA; Guzman-Puyol, S; Benitez, JJ; Athanassiou, A; Heredia, A; Dominguez, E
Global Change Biology, **24** (2018) 2749-2751
Julio, 2018 | **DOI:** 10.1111/gcb.14276

Climatic stressors due to global change induce important modifications to the chemical composition of plant cuticles and their biophysical properties.
In particular, plant cuticles can become heavier, stiffer and more inert, improving plant protection.
The climatic stressors that modify the chemical composition of plant tissues have been recently reviewed by Suseela and Tharayil (2018). In particular, the authors stated that the response of plants to global change effects (viz. increasing temperatures and frequent drought periods) can induce important modifications in plant cuticles such as an increase of the main cuticle components (cutin and polysaccharides), a preponderance of cutan, heavier wax loads, and changes in the chemical composition of waxes, mainly the accumulation of longer aliphatic compounds. In this letter, we would like to emphasize the biophysical consequences that this new scenario involves and how it would affect plant performance.

Iron-Catalyzed Graphitic Carbon Materials from Biomass Resources as Anodes for Lithium-Ion Batteries

Gomez-Martin, A; Martinez-Fernandez, J; Ruttert, M; Heckmann, A; Winter, M; Placke, T; Ramirez-Rico, J
Chemsuschem, **11** (2018) 2776-2787
Agosto, 2018 | **DOI:** 10.1002/cssc.201800831

Graphitized carbon materials from biomass resources were successfully synthesized with an iron catalyst, and their electrochemical performance as anode materials for lithium-ion batteries (LIBs) was investigated. Peak pyrolysis temperatures between 850 and 2000 degrees C were covered to study the effect of crystallinity and microstructural parameters on the anodic behavior, with a focus on the first-cycle Coulombic efficiency, reversible specific capacity, and rate performance. In terms of capacity, results at the highest temperatures are comparable to those of commercially used synthetic graphite derived from a petroleum coke precursor at higher temperatures, and up to twice as much as that of uncatalyzed biomass-derived carbons. The opportunity to graphitize low-cost biomass resources at moderate temperatures through this one-step environmentally friendly process, and the positive effects on the specific capacity, make it interesting to develop more sustainable graphite-based anodes for LIBs.

Sustainable Fabrication of Plant Cuticle-Like Packaging Films from Tomato Pomace Agro-Waste, Beeswax, and Alginate

Tedeschi, G; Benitez, JJ; Ceseracciu, L; Dastmalchi, K; Itin, B; Stark, RE; Heredia, A; Athanassiou, A; Heredia-Guerrero, JA
ACS Sustainable Chemistry & Engineering, **6** (2018) 14955-14966

Noviembre, 2018 | **DOI:** 10.1021/acssuschemeng.8b03450

Plant cuticles have been used as models to produce hydrophobic films composed of sodium alginate, the fatty acid fraction of tomato pomace agrowaste, and beeswax. The fabrication process consisted of the blending of components in green solvents (water and ethanol) and a subsequent thermal treatment (150 degrees C, 8 h) to polymerize unsaturated and polyhydroxylated fatty acids from tomato pomace. When sodium alginate and tomato pomace fatty acids were blended, free-standing films were obtained. These films were characterized to evaluate their morphological (SEM), chemical (solid-state NMR, ATR-FTIR), mechanical (tensile tests), thermal (TGA), and hydrodynamic (water contact angle, uptake, and permeability) properties. A comparison between nonpolymerized and polymerized samples was carried out, revealing that the thermal treatment represents a sustainable route to create structured, composite networks of both components. Finally, beeswax was added to the blend with the same amounts of sodium alginate and tomato pomace fatty acids. The presence of the wax improved the hydrophobicity and the mechanical and water barrier properties as well as decreased the water uptake. These results indicate that polymerized plant cuticle-like films have valuable potential for packaging applications.

A comprehensive and in-depth analysis of the synthesis of advanced adsorbent materials

Osuna, FJ; Cota, A; Pavon, E; Alba, MD
Journal of Cleaner Production, **194** (2018) 665-672
Septiembre, 2018 | **DOI:** 10.1016/j.jclepro.2018.05.179

Na-Mica-4, a synthetic fluorophlogopite, is an attractive adsorbent. However, the synthesis at large scale demands an economically prized, feasible scalable and sustainable synthesis method, which requires a deep knowledge of the influence of each synthesis step. A set of Na-Mica-4 were synthesized by methods that had one synthesis parameter as variable. The purity, crystallinity and heteroatoms distribution were analysed thorough X-ray diffraction and nuclear magnetic resonance. The results shed a light on the main factors for the design of the final product and indicated that an environmental friendship synthesis could be possible.

Performance improvement in olive stone's combustion from a previous carbonization transformation

Gomez-Martin, A; Chacartegui, R; Ramirez-Rico, J; Martinez-Fernandez, J
Fuel, **228** (2018) 254-262
Septiembre, 2018 | **DOI:** 10.1016/j.fuel.2018.04.127

Under the framework of circular economy, agricultural wastes are an interesting carbon-based feedstock for thermal energy and power generation. Their use could extend the availability of biomass-based fuel and, at the same time, would reduce negative environmental effects. However, depending on the residues' characteristics, their direct combustion in boilers presents some challenges which could be overcome with a carbonization pretreatment. In this paper, the main mechanisms of thermochemical transformation of an abundant agricultural waste, olive stone, into biochar products via slow carbonization are analyzed, with emphasis on the effect of peak carbonization temperature. Thermogravimetric and differential scanning calorimetry analysis are used to evaluate the performance of the resulting biochars compared to raw olive stone in combustion processes and to assess the correlation between the peak carbonization temperature and compositional and fuel properties. Results show that with a prior treatment up to an optimum temperature of 800 degrees C the energy density is increased up to three times compared to the raw material. These findings suggest that carbonization of olive stones reduces the barriers to their direct use in current biomass boiler technology.

Experimental measurement of the filtration efficiency and pressure drop of wall-flow diesel particulate filters (DPF) made of biomorphic Silicon Carbide using laboratory generated particles

Orihuela, MP; Gomez-Martin, A; Miceli, P; Becerra, JA; Chacartegui, R; Fino, D
Applied Thermal Engieering, **131** (2018) 41-53
Febrero, 2018 | **DOI:** 10.1016/j.applthermaleng.2017.11.149

Biomorphic Silicon Carbide (bioSiC) has been recently introduced in the scope of porous ceramic substrates for hot gas filtration applications, where it has demonstrated to have good thermal and mechanical properties, and a high potential to meet the requirements for current Diesel Particulate Filters (DPF). In this experimental study, a small wall-flow bioSiC diesel filter was characterized using a soot generator, the particle size distribution of which being similar to the one generated by a diesel engine. The bioSiC samples were manufactured from Medium Density Fiberboard (MDF) following a general manufacturing procedure for bioSiC ceramics, but paying special attention in the mechanizing stage to the geometry and optimal design of the honeycomb structure required for diesel engine applications. The samples had a cell density of 57.59 cell/cm(2) (371.6 cpsi), a square cross section of 9.2 x 9.2 mm, and a length of 31 mm. To generate the particle laden stream and perform the filtration tests, a synthetic Soot Generator (SG) was used. Tests were performed under controlled and reproducible conditions, with a fixed gas flow rate of 5 LPM and a soot mass flow rate of 4 mg/h. The filtration efficiency was determined with the aid of a Scanning Mobility Particle Sizer (SMPS) from the measurements of the particle concentration upstream and downstream the filter samples. During the soot loading process, the pressure drop was also monitored. The results show that, in the initial stage (clean filter), bioSiC wall-flow DPFs may have a filtration efficiency between 0.7 and 0.85 and a pressure drop of around 2 kPa for a normalized wall velocity of 0.01 m/s at ambient temperature. The filtration performance of wall-flow bioSiC particle filters showed in this work can help us to better understand their real potential for automotive applications.

Heteroatom framework distribution and layer charge of sodium Taeniolite

Perdigon, AC; Pesquera, C; Cota, A; Osuna, FJ; Pavon, E; Alba, MD
Applied Clay Science, **158** (2018) 246-251
Junio, 2018 | **DOI:** 10.1016/j.clay.2018.03.036

The most advanced applications of clays depend crucially on their hydration state and swelling is probably the most important feature of expandable 2:1 layered silicate. Sodium Taeniolite, Na-TAE, a swelling trioctahedral fluormica, has been synthesized and studied using thermogravimetric analysis, X-ray diffraction, scanning electron microscopy and infrared and solid state NMR spectroscopies. The results indicated the formation of a swelling 2:1 phyllosilicate with actual layer charge lower than the nominal one. Herein, a new heteroatom distribution and more accurate composition could be deduced.

Valorization of Tomato Processing by-Products: Fatty Acid Extraction and Production of Bio-Based Materials

Benitez, JJ; Castillo, PM; del Rio, JC; Leon-Camacho, M; Dominguez, E; Heredia, A; Guzman-Puyol, S; Athanassiou, A; Heredia-Guerrero, JA
Materials, **11** (2018) art. 2211
Noviembre, 2018 | **DOI:** 10.3390/ma11112211

A method consisting of the alkaline hydrolysis of tomato pomace by-products has been optimized to obtain a mixture of unsaturated and polyhydroxylated fatty acids as well as a non-hydrolysable secondary residue. Reaction rates and the activation energy of the hydrolysis were calculated to reduce costs associated with chemicals and energy consumption. Lipid and non-hydrolysable fractions were chemically (infrared (IR) spectroscopy, gas chromatography/mass spectrometry (GC-MS)) and thermally (differential scanning calorimetry (DSC), thermogravimetric analysis (TGA)) characterized. In addition, the fatty acid mixture was used to produce cutin-based polyesters. Freestanding films were prepared by non-catalyzed melt-polycondensation and characterized by Attenuated Total Reflected-Fourier Transform Infrared (ATR-FTIR) spectroscopy, solid-state nuclear magnetic resonance (NMR), DSC, TGA, Water Contact Angles (WCA), and tensile tests. These bio-based polymers were hydrophobic, insoluble, infusible, and thermally stable, their physical properties being tunable by controlling the presence of unsaturated fatty acids and oxygen in the reaction. The participation of an oxidative crosslinking side reaction is proposed to be responsible for such modifications.

Packing Defects in Fatty Amine Self-Assembled Monolayers on Mica as Revealed from AFM Techniques

Benitez, JJ; Heredia-Guerrero, JA; San-Miguel, MA; Galloway, HC
Journal of Physical Chemistry B, **122** (2018) 493-499
Enero, 2018 | **DOI:** 10.1021/acs.jpcb.7b03603

Self-assembled monolayers of n-octadecylamine (ODA-SAMs) on mica have been prepared and studied by contact and jumping mode atomic force microscopy (AFM). Adhesion and friction data show that the compactness of the monolayers spontaneously increases as they are allowed to ripen. Molecular packing can also be induced by the controlled mechanical perturbation exerted by the probe when getting into and out of contact intermittently. Under these conditions, defects and vacancies aggregate giving rise to detectable pinholes uniformly distributed in AFM images. Created pinhole density was found to decrease with ripening time, thus confirming the proposed spontaneous self-healing mechanism. Pinhole density is also suggested as a parameter characterizing the packing degree of ODA-SAMs, and it has been related to their tribological properties. Additionally, molecular dynamics simulations were used to corroborate the compatibility between the packing degree and the observed topography of ODA-SAMs on mica.

Cesium adsorption isotherm on swelling high-charged micas from aqueous solutions: Effect of temperature

Osuna, FJ; Cota, A; Pavon, E; Pazos, MC; Alba, MD
American Mineralogist, **103** (2018) 623-628
Abril, 2018 | **DOI:** 10.2138/am-2018-6203

The potential use of a new family of synthetic swelling micas for cesium immobilization from aqueous solution was evaluated and the structural modifications after adsorption were analyzed. The results have revealed that they are good cesium adsorbents compared to natural clays and as the layer charge increases, the adsorption capacity and affinity increase. The cesium ions are adsorbed through a cation exchange mechanism, but an inner sphere complex with the basal O atoms of the tetrahedral sheet is favored. These findings imply that is possible to design minerals with improved environmental applications.

Behavior of High-Strength Polypropylene Fiber-Reinforced Self-Compacting Concrete Exposed to High Temperatures

Rios, JD; Cifuentes, H; Leiva, C; Garcia, C; Alba, MD
Journal of Materials in Civil Engineering, **30** (2018) 04018271
Noviembre, 2018 | **DOI:** 10.1061/(ASCE)MT.1943-5533.0002491

In this study we analyzed the use of high-performance structural concrete reinforced with polypropylene fibers in applications requiring long exposure times to high temperatures, such as thermal energy storage systems. We analyzed the behavior of the concrete at different temperatures (hot tests: 100 degrees C, 300 degrees C, 500 degrees C and 700 degrees C), cooled-down states (cold tests) and exposure times (6, 24, and 48h). We also experimentally determined the thermogravimetric analysis, fracture behavior, compressive strength, Young's modulus, and tensile strength of concrete. Subsequently, we performed a comprehensive analysis of the thermal and mechanical behavior of high-performance concrete under different thermal conditions. We applied longer exposure times to broaden the available results on the behavior of high-performance fiber-reinforced concrete when subjected to high temperatures. Results show that, once thermal and moisture equilibriums are reached, exposure time does not have any influence on mechanical properties. They also provide useful information about the influence of high temperatures on the different parameters of fiber-reinforced concrete and its application for thermal energy storage structures.

Environmentally friendly monolithic highly-porous biocarbons as binder-free supercapacitor electrodes

Orlova, TS; Shpeizman, VV; Glebova, NV; Nechitailov, AA; Spitsyn, AA; Ponomarev, DA; Gutierrez-Pardo, A; Ramirez-Rico, J
Reviews on Advanced Materials Science, **55** (2018) 50-60
Noviembre, 2018

A simple, low-cost and environmentally friendly method has been used to obtain highly porous biomorphic carbon monoliths with a good combination of interconnected macro-, meso- and microporosity, and good electrical conductivity and mechanical strength, making these biocarbon materials interesting for electrochemical applications as binder-free electrodes. Highly porous monolithic biocarbons were obtained from beech wood precursors through pyrolysis and subsequent surface modification in a steam heated to 970 degrees C with different activation times. The obtained biocarbons demonstrated good electrical conductivity and mechanical strength. They were studied as electrodes for supercapacitors in half cell experiments, demonstrating maximum gravimetric capacitance of 200 F g(-1) in a basic media at scan rate 1 mV s(-1). Galvanostatic charge-discharge experiments showed maximum capacitance of 185 F g(-1) at current density of 0.15 A g(-1) and similar to 100 F g(-1) at current density of 0.75 A g(-1). It has been shown that in addition to the developed porous surface, the micropores with diameters exceeding 1 nm play a key role for the enhanced electrochemical capacity. Long-cycling experiments demonstrated excellent stability of the monolithic biocarbon electrodes with no reduction of the initial capacitance values after 600 cycles in voltammetry.

Comparison of solvent extraction and extraction chromatography resin techniques for uranium isotopic characterization in high-level radioactive waste and barrier materials

Hurtado-Bermudez, S; Villa-Alfageme, M; Mas, JL; Alba, MD
Applied Radiation and Isotopes, **137** (2018) 177-183
Julio, 2018 | **DOI:** 10.1016/j.apradiso.2018.04.008

The development of Deep Geological Repositories (DGP) to the storage of high-level radioactive waste (HLRW) is mainly focused in systems of multiple barriers based on the use of clays, and particularly bentonites, as natural and engineered barriers in nuclear waste isolation due to their remarkable properties.
Due to the fact that uranium is the major component of HLRW, it is required to go in depth in the analysis of the chemistry of the reaction of this element within bentonites. The determination of uranium under the conditions of HLRW, including the analysis of silicate matrices before and after the uranium-bentonite reaction, was investigated. The performances of a state-of-the-art and widespread radiochemical method based on chromatographic UTEVA resins, and a well-known and traditional method based on solvent extraction with tri-n-butyl phosphate (TBP), for the analysis of uranium and thorium isotopes in solid matrices with high concentrations of uranium were analysed in detail.
In the development of this comparison, both radiochemical approaches have an overall excellent performance in order to analyse uranium concentration in HLRW samples. However, due to the high uranium concentration in the samples, the chromatographic resin is not able to avoid completely the uranium contamination in the thorium fraction.

CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

COMUNICACIONES / COMMUNICATIONS

55th Annual Meeting The Clay Minerals Society

11 – 14 junio [Illinois, Estados Unidos]

Al/Fe Pillared from synthetic high charged Na-2-mica
J.R. Chaparro; C. Pazos; L.D. Ruiz; E. Pavón; M.D. Alba; A. Cota; F.J. Osuna
Comunicación oral

33° Congreso Latinoamericano de Química | 33-CLAQ

9 – 12 octubre [La Habana, Cuba]

Síntesis sostenibles de materiales adsorbentes de diseño para gestiones medioambientales
María D. Alba;Cota A.;Osuna F.J.;Pavón E.
Conferencia invitada

Uso conjunto del sistema precursor silicato-hidróxido-carbonato, una nueva perspectiva en la obtención de minerales de arcilla
Ch.F Varela Olivera; M.C. Pazos; M.D. Alba
Comunicación oral

Funcionalización superficial de adsorbentes de diseño para la gestión medioambiental
F.J. Osuna; A. Cota; E. Pavón; M.D. Alba
Poster

Cinética y termodinámica de adsorción de antimicrobianos por zeolitas naturales y sintéticas: influencia de las propiedades texturales y estructurales
R. Ibis Meneau Hernández; K. Borrego; M.L. Garrido; R. Ruiz; T. Farías; M.D. Alba
Poster

EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Horno tubular hasta 1200º C
- Horno tubular en atmósfera controlada hasta 1700º C
- Horno de Cámara hasta 1650º C
- Horno de Cámara hasta 1200 ºC
- Estufa hasta 400º C
- Estufa hasta 200º C
- Caja de guantes
- Reactores hidrotermales
- Línea de vacío
- 3 microscopios AFM.
- Microscopio STM en aire.
- Calorímetro diferencial de barrido (DSC).
- Analizador mecánico dinámico (DMA).
- Máquina de ensayos mecánicos por tracción.
- Analizador de ángulo de contacto.
- Balanza Langmuir-Blodgett (LB).
- Spin coater.

MECANOQUÍMICA Y REACTIVIDAD DE MATERIALES
MECHANOCHEMISTRY AND REACTIVITY OF MATERIALS

GRUPOS DE INVESTIGACIÓN

Materiales Avanzados
Advanced Materials [642010]

Propiedades Mecánicas de Sólidos
Mechanical Properties of Solids [642016]

Reactividad de Sólidos
Reactivity of Solids [642008]

PERSONAL / PERSONNEL

Catedráticos

Dr. Diego Gómez García

Investigadores Científicos

Dr. Luis Allan Pérez Maqueda
Dra. Concepción Real Pérez
Dr. Pedro José Sánchez Soto

Científicos Titulares

Dra. María Jesús Diánez Millán
Dr. Francisco José Gotor Martínez
Dra. Rosalía Poyato Galán
Dra. María Jesús Sayagués de Vega

Profesores Titulares

Dra. María Dolores Alcalá González
Dra. María Regla Ayala Espinar

Investigadores Contratados

Dr. José Manuel Córdoba Gallego
Dr. Antonio Perejón Pazo
Dr. Pedro E. Sánchez Jiménez
Dra. Beatriz Sarrión Aceytuno

Proyectos de Investigación / Research Projects

Integración del proceso Ca-looping en centrales de energía solar concentrada para el almacenamiento termo-químico de energía Integration of the Ca-looping process in concentrated solar power plants for thermochemical energy storage

Código/Code:	CTQ2017-83602-C2-1-R
Periodo/Period:	01-01-2018 / 31-12-2021
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	145.200 €
Investigador responsable/Research head:	Luis A. Pérez Maqueda, Pedro Enrique Sánchez Jiménez
Componentes/Research group:	María Jesús Diánez Millán

RESUMEN / ABSTRACT

El proyecto solicitado se enmarca dentro del reto general de encontrar nuevas tecnologías de almacenamiento de energía baratas y no contaminantes que permitan superar una de las limitaciones mayores de las fuentes renovables que es la intermitencia en la generación de electricidad. En particular, en este proyecto se propone realizar una integración de la tecnología de Ca-looping en una planta termosolar de concentración. La tecnología de Ca-looping, originariamente propuesta para procesos de captura de CO2, se basa en procesos de carbonatación-descarbonatación (o calcinación) de óxido de calcio-carbonato cálcico repetidos de forma cíclica. Nuestro grupo de investigación ha trabajado durante varios años en esta tecnología, con el objeto de comprender los mecanismos de desactivación conforme se incrementa el número de ciclos. Así, hemos estudiado los mecanismos cinéticos de estos procesos y los cambios microestructurales que tienen lugar a medida que se ciclan los compuestos. En un proyecto coordinado que concluye a finales de año (SOLARTEQH, Retos 2014) hemos realizado ya una propuesta de integración de Ca-Looping para almacenamiento de energía solar. Este proyecto ha dado lugar a una propuesta H2020 (SOCRATCES) aprobada y que comenzará a comienzos del año próximo. En el proyecto CALSOLAR que ahora presentamos se pretende avanzar más en esta idea de integración para incrementar los valores de proyecto eficiencia termoeléctrica. El subproyecto 1 realizará las tareas de coordinación de todo el proyecto. Además, en el subproyecto 1 se realizará la selección, preparación y caracterización de los compuestos a utilizar en el proyecto. En este sentido, se trabajará con empresas mineras que nos facilitarán distintas materias primas (principalmente calizas y dolomitas) con diverso grado de pureza y cristalinidad. Se prepararán compuestos con sílicas nanoestructuradas obtenidas a partir de cascarilla de arroz (suministradas por arroceras del valle del Guadalquivir). Se investigarán compuestos preparados a partir de escorias de acerías (suministrados por dos empresas del sector afincadas en Andalucía) que son ricos en calcio para su aplicación en ciclos de almacenamiento termoquímico. En el subproyecto, se diseñará y construirá un equipo termogravimétrico que permita realizar experimentos en las condiciones realistas de los ciclos de almacenamiento térmico. Así el equipo permitirá trabajar en condiciones de presión absoluta controlada de CO2 y en vapor sobrecalentado. En dicho instrumento se realizarán los ciclos de almacenamiento y se estudiarán las condiciones óptimas de dichos ciclos. Se investigarán los mecanismos cinéticos de carbonatación y descarbonatación y se estudiarán los cambios microestructurales durante el ciclado. En el equipo de investigación está compuesto por personal con gran experiencia en las tareas propuestas y se cuenta con la participación de investigadores extranjeros con gran experiencia en reacciones sólido-gas y en caracterización microestructural por microscopía de alta resolución. Además, participa una investigadora de la empresa Abengoa con extensa experiencia en almacenamiento termoquímico en plantas solares. Se trabajará en este subproyecto de forma totalmente coordinada con los investigadores del subproyecto 2 con idea de establecer conjuntamente las condiciones de proceso óptimas. Finalmente, los resultados obtenidos del proyecto podrán demostrase en la planta piloto que se construye en el marco el proyecto H2020 SOCRATCES

The proposal deals with the general social challenge of finding new cheap and environmentally friendly energy storage technologies to overcome the intermittency of energy generation from renewable sources. Particularly, in this project we propose integrating Ca-looping technology within a thermosolar concentration plant. Ca-Looping technology was originally proposed for CO2 capture and it is based on cycled carbonation-calcination of calcium oxide-calcium carbonate. Our research group has been working on this technology for several years with the objective of understanding the deactivation mechanisms as the number of cycles increases. Thus, we have studied the kinetic mechanisms of these processes and the microstructural changes that takes place during cycling. In a coordinated project that is about to finish this year (SOLARTEQH, Retos 2014) where we already proposed the integration of Ca-Looping for thermosolar energy storage. This project was the basis of a H2020 proposal (SOCRATCES) that has been recently approved and that will start by the beginning of 2018. The project CALSOLAR is a step forward in the integration to increase the efficiency of the plant. Subproject 1 will coordinate the new project. Moreover, subproject 1 will select, prepare and characterize all compounds investigated in the project. We will work with mining companies that will provide the raw materials (mainly limestone and dolomite) with different purities and crystallinity. Composite materials with nanostructured silica obtained from rice husk (provided by rice mills from the Guadalquivir area) will be prepared. Compounds obtained from steel slags (supplied by nearby steel mills) rich in calcium will be prepared. Within subproject 1, a new thermogravimetric instrument to perform thermal storage cycles under realistic conditions will be designed and constructed in our laboratories. This instrument should work under different controlled CO2 pressures and under superheated steam. The kinetic mechanisms of carbonation and decarbonation and the microstructural changes will be investigated during cycling. The working team is experienced in the tasks of the project while some additional external scientists will participate. Thus, two foreign professors with solid backgrounds in solid-gas reactions and high resolution TEM are collaborating with us. Moreover, an industrial scientist from Abengoa with a very broad experience in thermal storage and thermosolar power plants is also included in the team. Both subprojects will work in a coordinated way with the aim of setting the optimum conditions for the final application. Finaly, the results of the project will be directly applied to the pilot plant constructed within the H2020 SOCRATCES project.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Almacenamiento TErmoQuímico Híbrido de energía SOLAR concentrada SOLARTEQH Hybrid thermochemical storage of concentrated solar energy SOLARTEQH

Código/Code:	CTQ2014-52763-C2-1-R
Periodo/Period:	01-01-2015 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	82.280 €
Investigador responsable/Research head:	Luis Allan Pérez Maqueda
Componentes/Research group:	María Jesús Diánez Millán, José Manuel Criado Luque

RESUMEN / ABSTRACT

Actualmente existen proyectos dentro de los prgramas Sunshot (USA) y FP7 (UE) en los que se analiza la viabilidad de lechos fluidizados de sólidos granulados para el almacenamiento químico de energía solar concentrada. Uno de los materiales considerados es la caliza natural ($CaCO_3$), abundante y barata. Usando una mezcla CO_2/aire en porcentajes relativos adecuados a las temperaturas de trabajo (600ºC-900ºC) se descarbonataría el $CaCO_3$ mediante reacción endotérmica en períodos de elevada irradiación o se carbonataría el CaO liberando calor cuando la temperatura descendiese por debajo de un cierto valor. Mediante la variación del %CO_2 en el gas de fluidización se provocarían las reacciones de descarbonatación-carbonatación según se desee reducir o aumentar la temperatura del lecho en función de la intensidad de radiación solar y de la demanda. Este control ayudaría a paliar el efecto de la variabilidad de la intensidad de radiación solar sobre la transferencia de calor al ciclo de vapor para la producción de corriente eléctrica. Además de tratarse de un almacenamiento de energía sin pérdidas, la densidad energética del $CaCO_3$ (~1 $MWhr/m^3$) es mayor que la de las sales fundidas actualmente empleadas en plantas comerciales (0.25-0.40 $MWhr/m^3$), siendo además la caliza un material no corrosivo, no degradable y que permitiría operar a mayores temperaturas y aumentar así la eficiencia de conversión termoeléctrica. No obstante, la fluidización de la caliza es altamente heterogénea, formándose canales de gas y agregados no fluidizables en el lecho que reducirían en gran medida la transferencia térmica, la eficacia de contacto sólido/gas y por tanto el grado de conversión. Por otra parte, se han puesto en marcha plantas piloto basadas en almacenamiento térmico en lechos fluidizados de sólidos granulados inertes de alta capacidad calorífica como la arena o el carburo de silicio que presentan un estado de fluidización uniforme con alta transferencia térmica. Estos sistemas poseen inevitables pérdidas térmicas y son necesarios grandes volúmenes para garantizar el suministro de calor al ciclo de vapor en períodos de baja radiación. Nuestro proyecto se basa en complementar de manera sinérgica las ventajas del almacenamiento térmico en lechos fluidizados de sólidos inertes con el químico mediante lechos fluidizados de mezclas de sólidos inertes fluidizables con otros basados en CaO (arena y caliza naturales por ejemplo). En nuestro trabajo evaluaremos la transferencia y almacenamiento de energía solar concentrada de estos sistemas híbridos. El plan de trabajo contemplará acotar las condiciones óptimas de concentración de CO_2 en el gas de fluidización y proporción de arena/caliza en función de la temperatura para las que la eficacia de

almacenamiento se viera optimizada. Estudiaremos las propiedades físicas y químicas de mezclas de arena/caliza y los parámetros físicos que favorezcan la transferencia y almacenamiento de calor en función de la intensidad de la radiación solar. Así mismo se explorarán métodos de estabilización térmica del CaO con el objeto de incrementar la reversibilidad de carbonatación/calcinación en condiciones prácticas. De manera paralela se desarrollará un modelo termodinámico que incluya aquellos procesos que afectan a la eficiencia energética del mismo y sirva para establecer parámetros óptimos de operación con el objetivo final de transferencia al sector tecnológico para lo que se contará con el apoyo de Abengoa Solar.

There are current projects within the Sunshot (USA) initiative and UE FP7 program in which the feasibility of fluidized beds for permanent chemical storage of concentrated solar energy is analyzed. One of the materials considered is the cheap and abundantly available natural limestone ($CaCO_3$). Using a CO_2/air mixture in suitable relative proportions according to the operating temperatures (600-900ºC), $CaCO_3$ would be decarbonated by endothermic reaction in periods of high irradiation or the CaO would be carbonated releasing heat when the temperature falls below a certain value. By varying the %CO_2 in the fluidization gas, either decarbonation or carbonation would be provoked as desired to reduce or increase the bed temperature based on the intensity of solar radiation and electricity demand. This control would help to alleviate the effect of the variability of sunlight intensity. Besides of the permanent storage of energy, the energy density of $CaCO_3$ (about 1 MWhr/m^3) is greater than that of molten salts currently used in commercial plants (0.25-0.40 MWhr /m^3). Furthermore, natural limestone is non-corrosive material, not degradable and would allow operation at higher temperatures thus increasing the thermoelectric conversion efficiency. However, the fluidization of limestone is typically very heterogeneous, being characterized by the formation of gas channels and large unfluidizable aggregates in the bed which greatly reduce the effectiveness of solid/gas contact and thus the heat transfer efficiency of the reaction. On the other hand, other projects have leaded to the development of successful small-scale pilot plants based on the thermal storage in fluidized beds of inert solids with high heat capacity such as fine silica sand or silicon carbide with good fluidization properties and thus characterized by a high heat transfer. However, these systems present unavoidable heat losses and large volumes are needed to ensure a supply of heat to the power cycle in periods of low solar irradiation. Our project is based on synergistically combine the heat storage in fluidized beds of fluidizable inert solids (such as sand) with the permanent chemical storage of CaO precursors (such as natural limestone) by the use of fluidized beds of mixtures of both granular materials. Experimental measurements will allow characterizing the behavior of the sand/natural limestone mixtures for the transfer and storage of concentrated solar energy. The working plan shall limit the optimum concentration of CO_2 in the fluidizing gas and proportion of sand/limestone as a function of temperature for optimizing the energy storage efficiency. The physic-chemical properties of mixtures of sand/limestone that favor heat transfer and storage according to the intensity of solar radiation will be delimited. Also thermal and chemical stabilization methods will be explored in order to increase the reversibility of the carbonation/calcination reaction under practical conditions. In parallel, a thermodynamic modeling work will be carried out that includes processes that affect the energy efficiency and serve as a starting point to establish optimum operating parameters with the ultimate goal of transferring the knowledge to the technology sector. For this final purpose the project has the support of Abengoa Solar.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Desarrollo de cermets con aleaciones de alta entropía de mezcla como fase ligante para aplicaciones de mecanizado Development of cermets with high entropy alloys as binder phase for machining applications

Código/Code:	MAT2014-52407-R
Periodo/Period:	01-01-2015 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	90.750 €
Investigador responsable/Research head:	Francisco José Gotor Martínez
Componentes/Research group:	José Manuel Córdoba Gallego, María Dolores Alcalá González, Pedro José Sánchez Soto, Concepción Real Pérez, María Jesús Sayagués de Vega

RESUMEN / ABSTRACT

El mecanizado es parte esencial de los procesos de fabricación empleados en muchos sectores industriales y posee una importante implicación económica, al representar una proporción significativa del coste total de fabricación. El éxito del mecanizado depende de múltiples factores, entre los que destaca la herramienta de corte utilizada. El mecanizado de alta velocidad y de los materiales denominados difíciles de mecanizar, como las superaleaciones empleadas en la fabricación de motores a reacción, imponen unas condiciones extremas de trabajo caracterizadas por altas temperaturas, presiones y tensiones, que pueden provocar el fallo prematuro en servicio de la herramienta de corte. Además, el deterioro de la herramienta, debido a un excesivo desgaste y deformación, hace que resulte difícil mantener las tolerancias y la integridad de la superficie mecanizada, lo que compromete seriamente las propiedades de fatiga de la pieza y, por tanto, su aplicabilidad y vida útil. La importante implicación económica de este tipo de mecanizados hace que la industria europea se haya marcado como objetivo primordial mejorar la productividad de estos procesos e incrementar su precisión y calidad, promoviendo la búsqueda de nuevos materiales para herramienta que se adapten mejor a estos nuevos requerimientos.

De los materiales para herramienta que se emplean en la actualidad, los cermets son los que mejor se adaptarían a las exigencias de estos mecanizados, ya que poseen una alta resistencia al desgaste, una estabilidad química elevada y una resistencia mecánica que se mantiene a alta temperatura. Pero, sería necesario mejorar ostensiblemente la tenacidad de fractura y la tolerancia al daño hasta valores próximos a los que presentan los carburos cementados. Durante los últimos años se ha producido un continuado proceso de optimización de los cermets, modificando principalmente la microestructura y la composición química de las fases cerámicas empleadas. En el proyecto MAT2011-22981 demostramos que los cermets denominados de solución sólida completa, caracterizados por poseer una única fase cerámica homogénea formada por un carbonitruro complejo, permiten alcanzar una buena combinación de dureza y tenacidad y una alta resistencia a la oxidación.

En el presente proyecto, que puede considerarse como complementario al MAT2011-22981, se pretende mejorar aún más las propiedades de los cermets, pero actuando en este caso sobre la fase ligante, que es en última instancia la principal causante de la cohesión y la tenacidad del material. Las aleaciones de alta entropía de mezcla se postulan como candidatas idóneas para sustituir a las fases ligantes actuales, ya que presentan una alta resistencia, una buena ductilidad y un excelente comportamiento mecánico a elevadas temperaturas. El objetivo general del presente proyecto se centra en el desarrollo de cermets de solución sólida completa con una fase metálica ligante formada por aleaciones de alta entropía de mezcla. Los materiales que se desarrollarán poseerán una microestructura sencilla, similar a la que presentan los actuales carburos cementados, pero con una elevada complejidad composicional, ya que ambas fases constituyentes (cerámica y metálica) serán soluciones sólidas con un número importante de componentes, al menos cinco. Con estos nuevos cermets, se pretenden mantener las propiedades óptimas que presentan actualmente y mejorar aquellas que limitan su uso potencial en los mecanizados más exigentes.

Machining is an essential part of the manufacturing processes in many industries and has significant economic implications, as it represents an important proportion of the total manufacturing cost. The success of machining depends on many factors, among which the correct choice of the cutting tool. High-speed machining and difficult-to-cut materials, such as superalloys employed in the fabrication of aircraft engines, impose extreme working conditions to cutting-tools, which are characterized by high temperatures, pressures and tensions that can lead to the premature failure in service. Furthermore, the deterioration of the cutting-tool due to an excessive wear and deformation makes it difficult to maintain the tolerances and the surface integrity of the workpiece, severely compromising the fatigue properties and, therefore, its applicability and lifetime. The European industry has as a main objective to improve the productivity, accuracy and quality of these highly-demanding machining processes, stimulating the search for new cutting-tool materials that are better suited to these new requirements.

Cermets have properties, such as high wear resistance, high chemical stability and good mechanical strength at high temperature, well-adapted to the requirements of these machining processes. But for a realistic application, it is necessary to significantly increase the fracture toughness and damage tolerance to values close to those of cemented carbides. In the last few years, there has been an ongoing process of cermets optimization, mainly by modifying the microstructure and chemical composition of the ceramic phase. In a previous project (MAT2011-22981), we have shown that the so-called complete solid solution cermets, characterized by single phase ceramic particles consisting of a complex carbonitride, allow achieving a good combination of hardness and fracture toughness.

In this new project, which can be considered as complementary to MAT2011-22981, we propose to further improve the properties of cermets, also acting on the binder phase as it is ultimately responsible for the cohesion and toughness of the material. High entropy alloys (HEAs), which are composed of at least five major metal elements in equal or near equal atomic percent (as opposed to traditional alloy systems that are typically based on only one or two major elements), can be postulated as suitable to replace current binder phase in cermets. These alloys often exhibit superior properties than conventional alloys, including high strength and ductility at high temperature and good wear and corrosion resistances. The main goal of this project focuses on the development of complete solid solution cermets with HEAs as the binder phase. The cermets to be developed will have a simple microstructure; similar to cemented carbides, but high compositional complexity, since the two constituent phases (ceramic and binder) will be complex solid solutions with a high number of components (at least five). With these new cermets, we try to maintain their current optimal properties, while improving those limiting their potential use in the most demanding machining processes.

Cerámicas nanoestructuradas a base de carburo de boro y nitruro de titanio para aplicaciones estructurales Boron carbide and titanium nitride-based nanostructured ceramics for structural applications

Código/Code:	MAT2015-71411-R
Periodo/Period:	01-01-2016 / 31-12-2019
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	157.300 €
Investigador responsable/Research head:	Diego Gómez García / Arturo Domínguez Rodríguez
Componentes/Research group:	Francisco L. Cumbreras Hernández, Felipe Gutíerrez Mora, Ana Morales Rodríguez

RESUMEN / ABSTRACT

El proyecto tiene como misión la fabricación de forma controlada científicamente de nanocerámicos de carburo de boro y de nitruro de titanio mediante la técnica de chispa de plasma. Se estudiarán las propiedades mecánicas de ambos cerámicos a temperatura ambiente (dureza y tenacidad), así como su plasticidad a alta temperatura (resistencia a la fluencia, deformación a velocidad constante).

Se pretende estudiar la influencia de la microestructura en la respuesta mecánica, así como dilucidar los mecanismos que controlan la plasticidad (particularmente la interacción de dislocaciones con maclas). Los resultados se modelarán analíticamente o mediante simulación a escala mesoscópica (vía modelos de campos de fases).

Boron carbide and titanium nitride are among the most promising ceramic materials nowadays. In the first case, this is due to the outstandng mechanical properties (it is the third hardest material in nature) and its high resistance to chemical attack. In the case of Titanium nitride, its remarkable optical properties and electrical conductivity makes this a potential material for electronic devices. In both cases, sintering is a challenging issue due to the low diffusitivity. In this project, sintering of these materials by spark plasma sintering will be studied and the conditions for nanostructuration will be determined. Preliminary results show that average grain sizes as low as 100 nm can be achieved. In a second stage, plasticity will be studied. A previous model developed by the authors show that twinning is a key ingredient as a driving force of plasticity of boron carbide. The case of titanium nitride is mostly exciting because the stacking fault energy is the lowest ever known and it can make twinnin very favoured. The comparison between these two systems can be a clue about the basic mechanism for hardening in these ceramic materials.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Procesado y caracterización microestructural, mecánica y eléctrica de compuestos cerámica-grafeno

Processing and microstructural, mechanical and electrical characterization of ceramic-graphene composites

Código/Code:	MAT2015-67889-P
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	89.177 €
Investigador responsable/Research head:	Angela Gallardo López (UEI). Rosalía Poyato Galán
Componentes/Research group:	Antonio Muñoz Bernabé, Felipe Gutiérrez Mora, Ana Morales Rodríguez

RESUMEN / ABSTRACT

En la actualidad se plantean interesantes expectativas sobre los compuestos cerámica/grafeno, propuestos para aplicaciones en catálisis, almacenamiento y conversión de energía, protección del medio ambiente y biotecnología. Pero aún se requieren importantes esfuerzos para dar respuesta a cuestiones abiertas. Hay que incidir en aspectos como la resistencia a la cizalla de las intercaras cerámica-grafeno -esencial para asegurar la transferencia de carga efectiva sobre las láminas de grafeno-, la distribución homogénea del grafeno en la matriz cerámica y la relación de tamaños entre matriz y refuerzo, para maximizar el aumento de tenacidad y de conductividad eléctrica, así como también explorar sus propiedades mecánicas a alta temperatura.

En este proyecto se plantea un estudio sistemático de compuestos de matrices cerámicas con grafeno, desde la fabricación hasta la caracterización microestructural, mecánica y eléctrica, con el objetivo de mejorar la comprensión de los mecanismos que controlan estas propiedades al incorporar nanoestructuras de grafeno a una matriz cerámica. Se procesarán compuestos de dos matrices cerámicas diferentes, de alúmina y de circona tetragonal dopada con óxido de itrio (3YTZP), con grafeno mediante técnicas coloidales, prestando especial atención a la dispersión del grafeno en la matriz cerámica, aspecto no exento de dificultades y que es clave para conseguir la mejora de las propiedades. La sinterización se realizará en un horno de descarga de plasma (SPS, spark plasma sintering) de última generación, optimizando las condiciones para conseguir compuestos densos y de tamaño de grano nanométrico. Para el análisis microestructural se utilizarán técnicas como la difracción de rayos X, la espectroscopía Raman, y la microscopía electrónica de barrido y transmisión. Con ellas se evaluarán las fases cristalográficas presentes, el tamaño de grano, la distribución de las nanoestructuras de grafeno, etc.

Desde el punto de vista del diseño de materiales avanzados, es fundamental investigar la relación entre microestructura y propiedades mecánicas y eléctricas. Las propiedades

mecánicas a temperatura ambiente (dureza, tenacidad a la fractura y resistencia a flexión) se abordarán mediante indentación y ensayos de flexión, a escalas macro y microscópica. A alta temperatura, se estudiará la deformación plástica de los compuestos cerámica-grafeno mediante ensayos de fluencia en atmósferas controladas. También se estudiará el comportamiento tribológico de los compuestos y se evaluará su conductividad eléctrica, una de las propiedades más interesantes ya que se modifica de forma notoria como resultado de la incorporación del grafeno a estos sistemas cerámicos. La respuesta eléctrica se analizará en un amplio rango de temperaturas, bien mediante espectroscopía de impedancia compleja, bien mediante medidas de conductividad en corriente continua en el caso de los compuestos menos resistivos.

Nowadays, interesting prospects are proposed for ceramic-graphene composites, in application fields such as catalysis, energy storage and conversion, environment protection and biotechnology. A great effort is still required to answer open questions. Issues such as shear resistance of the ceramic-graphene interface essential to obtain an effective load transfer to the graphene sheets-, distribution of graphene in the ceramic matrix -to maximize the reinforcement mechanisms and electrical conductivity- and the high temperature mechanical properties in these composites need special attention.

A systematic study of ceramic matrix graphene composites, including processing and microstructural, mechanical and electrical characterization is proposed in this project, with the aim of improving the comprehension of mechanisms controlling these properties when adding graphene nanostructures to a ceramic matrix.

Both alumina and yttria tetragonal zirconia (3YTZP) graphene composites will be processed by means of colloidal techniques. Special attention will be devoted to the dispersion of graphene in the ceramic matrix which is not a straightforward aspect, but is key to improve mechanical and functional properties. Sintering will be carried out by spark plasma sintering, SPS. Conditions will be optimized in order to obtain fully dense composites with nanometric grain size. Microstructural analysis will be performed by X ray diffraction, Raman spectroscopy, scanning and transmission electronmicroscopy (SEM and TEM). The present crystallographic phases, grain size and distribution of graphene nanostructures will be evaluated.

In order to design advanced materials, it is necessary to study the relationship between microstructure and mechanical or electrical properties. Room temperature mechanical properties (hardness, fracture toughness and flexural resistance) will be characterized by indentation and bending tests at macro and microscopic scales. At high temperature, the plastic behavior of these ceramic-graphene composites will be assessed by creep tests under controlled atmosphere. Tribological behavior of the composites will also be studied to evaluate their resistance to wear. The electrical response will be assessed in a wide range of temperatures by means of complex impedance spectroscopy or by direct current conductivity measurements in the composites with lower resistivity. This is a most interesting property since it can be strongly increased when incorporating graphene to these ceramic systems.

Preparación por molienda reactiva de nanocomposites de interés tecnológico
Preparation of technically interesting nanocomposites by mechanochemistry

Código/Code:	P11-TEP-7858 (Proyecto de Excelencia)
Periodo/Period:	16-05-2013 / 31-03-2018
Organismo Financiador/Financial source:	Junta de Andalucía
Importe total/Total amount:	198.739 €
Investigador responsable/Research head:	Luis A. Pérez Maqueda
Componentes/Research group:	José Manuel Criado Luque, María Jesús Diánez Millán, José Luís Pérez Rodríguez, Juan Poyato Ferrera, Pedro Enrique Sánchez Jiménez, Antonio Perejón Pazo

RESUMEN / ABSTRACT

Los materiales compuestos nanométricos o nanocomposites presentan un gran interés tecnológico y académico. Estos materiales están constituidos por dos o más fases diferentes con un grado de interacción nanométrico pues una de las fases presenta al menos una dimensión menor de 100 nm. Ello les confiere unas propiedades que no se pueden conseguir con composites o materiales convencionales. En el presente proyecto se propone el uso de la molienda reactiva para obtener nanocomposites de diversa naturaleza. Esta estrategia es sostenible desde el punto de vista medioambiental a la vez que sencilla de aplicar y escalar. Para este propósito se pretende desarrollar, con la imprescindible colaboración de la empresa andaluza de ingeniería mecánica MC2, un molino planetario de alta energía con características específicas y únicas con respecto a los equipos actualmente disponibles en el mercado. Dicha empresa llevará a cabo además un estudio de las fuerzas que operan sobre la muestra en función de las variables operacionales del molino, lo que contribuirá a una mjor comprensión del mecanismo de las reacciones mecanoquímicas. Se llevará a cabo la síntesis por molienda reactiva de dos tipos de nanocomposites: a) nanocomposites de cobre reforzado tanto con inclusiones cerámicas como por precipitación a partir de aleaciones en base de cobre preparadas por aleado mecánico y b) nanocomposites tanto de zirconia parcialmente estabilizada (PSZ) como de zirconia totalmente estabilizada (TSZ) reforzada con alúmina. En este último caso, se propone para la sinterización de los polvos cerámicos, preparados por molienda reactiva, un método novedoso que implica calentar la muestra a la vez que se somete a un campo eléctrico. Con este procedimiento se espera una reducción drástica de la temperatura requerida para la compactación total de la zirconia. El estudio de la cinética de sinterización bajo los efectos de un campo eléctrico se llevará a cabo mediante un equipo a desarrollar en el proyecto a partir de un dilatómetro que se modificará de modo que permita seguir la evolución de la dimensión de la muestra en función de la temperatura estando ésta sometida a un campo eléctrico.

Nanocomposites are of the most academic and technical interest. Those materials consist of two or more different phases being the dimension of one of the phases smaller than 100 nm. Thus, those materials have outstanding properties as compared with conventional ones. In this project, mechanochemistry is proposed for the preparation of different

nanocomposites. This preparation procedure is sustainable from the environmental point of view and easy to scale-up. In the frame of the project, a unique high energy planetary ball mill will be developed in collaboration with the MC2 enterprise. Moreover, a study of the forces as a function of the milling conditions will be performed in order to get a better understanding of the processes involved in the mechanochemical reactions. Two types of nanocomposites will be prepared: a) copper reinforced nanocomposites and b) partially and totally stabilized zirconia. In the latter case, powders will be sintered using a kind of field assisted sintering procedure. It is expected a reduction in the sintering temperature of the zirconia. The kinetics of the sintering process with and without electric field will be performed within the project using an new dilameter that will be constructed for this purpose.

ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

Phase-pure $BiFeO_3$ produced by reaction flash-sintering of Bi_2O_3 and Fe_2O_3

Gil-Gonzalez, E; Perejon, A; Sanchez-Jimenez, PE; Sayagues, MJ; Raj, R; Perez-Maqueda, LA
Journal of Materials Chemistry A, **6** (2018) 5356-5366
Abril, 2018 | **DOI:** 10.1039/c7ta09239c

Mixed powders of Bi_2O_3 and Fe_2O_3 are shown to yield single-phase, dense nanostructured polycrystals of $BiFeO_3$ in reaction flash sintering experiments, carried out by applying a field of 50 V cm(-1) and with the current limit set to 35 mA mm(-2). The furnace was heated at a constant rate with the reaction sintering taking place abruptly upon reaching 625 degrees C. Remarkably, an intermediate bismuth-rich phase of the oxide that forms just before reaching the flash temperature transforms, and at the same time sinters, into singlephase BiFeO3 within a few seconds after the onset of the flash. The BiFeO3 so produced is electrically insulating, a property that is critical to its applications. This one-step synthesis of single-phase polycrystals of complex oxides from their basic constituents, by reaction flash sintering, is a significant development in the processing of complex oxides, which are normally difficult to sinter by conventional methods.

Low-cost Ca-based composites synthesized by biotemplate method for thermochemical energy storage of concentrated solar power

Benitez-Guerrero, M; Valverde, JM; Perejon, A; Sanchez-Jimenez, PE; Perez-Maqueda, LA
Applied Energy, **210** (2018) 108-116
Enero, 2018 | **DOI:** 10.1016/j.apenergy.2017.10.109

An ever more environmentally conscious society demands the use of green, sustainable and high-efficiency renewable energy resources. However, large-scale energy storage remains a challenge for a deep penetration of power produced from renewables into the grid. The Calcium-Looping (CaL) process, based on the reversible carbonation/calcination of CaO, is a promising technology for thermochemical energy storage (TCES) in Concentrated Solar Power (CSP) plants. Natural limestone to be used as CaO precursor is cheap, non-toxic and abundant. Nevertheless, recent works have shown that carbonation of CaO derived limestone at optimum conditions for

TCES is limited by pore-plugging, which leads to severe deactivation for large enough particles to be employed in practice. In our work, we have synthesized inexpensive CaO/SiO2 composites by means of a biotemplate method using rice husk as support. The morphological and compositional features of the biomorphic materials synthesized help improve the CaO multicycle activity under optimum CSP storage conditions and for particles sufficiently large to be managed in practical processes.

Calcium-Looping performance of mechanically modified Al_2O_3-CaO composites for energy storage and CO_2 capture

Benitez-Guerrero, M; Valverde, JM; Sanchez-Jimenez, PE; Perejon, A; Perez-Maqueda, LA
Chemical Engineering Journal, **334** (2018) 2343-2355
Febrero, 2018 | **DOI:** 10.1016/j.cej.2017.11.183

This work reports the Calcium-Looping (CaL) multicycle performance under energy storage and CO_2 capture conditions of different Al-composites prepared by milling mixtures of nanoalumina and natural limestone powders. The micro-and nanostructure of the composites have been analyzed by X-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy as affected by the type of CaL conditions employed, either for energy storage in Concentrated Solar Power (CSP) plants or for post-combustion CO_2 capture. Two types of calcium aluminates are formed under these diverse CaL conditions. A calcium aluminate with ratio Ca/Al < 1 ($Ca_4Al_6O_{13}$) is formed under CaL-CSP conditions, which helps stabilize the CaO microstructure and mitigate pore-plugging. On the other hand, a crystalline phase $Ca_3Al_2O_6$ is formed (Ca/Al > 1) under CaL-CO_2 capture conditions presumably due to the higher calcination temperature, which withdraws from the sorbent a relatively higher amount of active Ca. Moreover, the addition of nano-alumina, and the consequent generation of calcium aluminate, affects in a diverse way the microstructure and morphology of the CaO particles as depending on the CaL application, which critically modifies the performance of the composites.

Effect of milling mechanism on the CO_2 capture performance of limestone in the Calcium Looping process

Benitez-Guerrero, M; Valverde, JM; Perejon, A; Sanchez-Jimenez, PE; Perez-Maqueda, LA
Chemical Engineering Journal, **346** (2018) 549-556
Agosto, 2018 | **DOI:** 10.1016/j.cej.2018.03.146

This work analyzes the relevant influence of milling on the CO_2 capture performance of CaO derived from natural limestone. Diverse types of milling mechanisms produce contrasting effects on the microstructure of the CaO formed after calcination of the milled limestone samples, which affects crucially the kinetics of carbonation at conditions for CO_2 capture. The capture capacity of CaO derived from limestone samples milled using either shear or impact based mills is impaired compared to as-received limestone. After calcination of the milled samples, the resulting CaO porosity is increased while crystallinity is enhanced, which hinders carbonation. Conversely, if the material is simultaneously subjected to intense impact and shear stresses, CaO porosity is promoted whereas CaO cristanillity is reduced, which enhances carbonation in both the reaction and solid-state diffusion controlled regimes.

Pressure Effect on the Multicycle Activity of Natural Carbonates and a Ca/Zr Composite for Energy Storage of Concentrated Solar Power

Sarrion, B; Sanchez-Jimenez, PE; Perejon, A; Perez-Maqueda, LA; Valverde, JM

ACS Sustainable Chemistry & Engineering, **6** (2018) 7849-7858
Junio, 2018 | **DOI:** 10.1021/acssuschemeng.8b00981

This work is focused on the use of the Calcium-Looping process (CaL) in Concentrated Solar Power (CSP) plants for Thermochemical Energy Storage (TCES). Cheap, abundant and nontoxic natural carbonate minerals, such as limestone and dolomite, can be employed in this application to store energy through the cyclic calcination/carbonation of $CaCO_3$. In a recent work, a closed CO_2 cycle has been proposed for an efficient CaL-CSP integration in which the CO_2 in excess effluent from the carbonator is used to generate electricity by means of a gas turbine. Process simulations show that the thermoelectric efficiency is enhanced as the carbonator pressure and temperature are increased provided that the multicycle CaO conversion is not affected. On the other hand, the use of just one reactor for both calcination and carbonation has been suggested to reduce capital cost. However, the experimental results shown in the present work indicate that sintering is notably enhanced as the pressure in the reactor is increased. Such an adverse effect is mitigated for a $ZrO_2/CaCO_3$ composite with a low Zr content as compared to natural carbonates. These results are relevant to process simulations for better assessing the global efficiency of the CaL-CSP integration.

Carbonation of Limestone Derived CaO for Thermochemical Energy Storage: From Kinetics to Process Integration in Concentrating Solar Plants

Ortiz, C; Valverde, JM; Chacartegui, R; Perez-Maqueda, LA

ACS Sustainable Chemistry & Engineering, **6** (2018) 6404-6417
Mayo, 2018 | **DOI:** 10.1021/acssuschemeng.8b00199

Thermochemical energy storage (TCES) is considered as a promising technology to accomplish high energy storage efficiency in concentrating solar power (CSP) plants. Among the various possibilities, the calcium-looping (CaL) process, based on the reversible calcination–carbonation of $CaCO_3$ stands as a main candidate due to the high energy density achievable and the extremely low price, nontoxicity, and wide availability of natural CaO precursors such as limestone. The CaL process is already widely studied for CO_2 capture in fossil fuel power plants or to enhance H_2 production from methane reforming. Either one of these applications requires particular reaction conditions to which the sorbent performance (reaction kinetics and multicycle conversion) is extremely sensitive. Therefore, specific models based on the conditions of any particular application are needed. To get a grip on the optimum conditions for the carbonation of limestone derived CaO in the CaL-CSP integration, in the present work is pursued a multidisciplinary approach that combines theoretical modeling on reaction kinetics, lab-scale experimental tests at relevant CaL conditions for TCES, process modeling, and simulations. A new analytic equation to estimate the carbonation reaction rate as a function of CO_2 partial pressure and temperature is proposed and validated with experimental data. Using the kinetics analysis, a carbonator model is proposed to assess the average carbonation degree of the solids. After that, the carbonator model is incorporated into an overall process integration scheme to address the optimum operation conditions from thermodynamic and kinetics considerations.

Results from process simulations show that the highest efficiencies for the CaL-CSP integration are achieved at carbonator absolute pressures of ~3.5–4 bar, which leads to an overall plant efficiency (net electric power to net solar thermal power) around 41% when carbonation is carried out at 950 °C under pure CO_2.

On the determination of thermal degradation effects and detection techniques for thermoplastic composites obtained by automatic lamination

Martin, MI; Rodriguez-Lence, F; Guemes, A; Fernandez-Lopez, A; Perez-Maqueda, LA; Perejon, A

Composites part A-Applied science and manufacturing, **111** (2018) 23-32
Agosto, 2018 | **DOI:** 10.1016/j.compositesa.2018.05.006

Automatic lay-up and in-situ consolidation with thermoplastic composite materials is a technology under research for its expected use in the profitable manufacturing of structural aeronautical parts. This study is devoted to analysing the possible effects of thermal degradation produced by this manufacturing technique.

Rheological measurements showed that there is negligible degradation in PEEK for the temperatures reached during the process. Thermogravimetric analysis under linear heating and constant rate conditions show that thermal degradation is a complex process with a number of overlapping steps. A general kinetic equation that describes the degradation of the material with temperature has been proposed and validated. Attenuated total reflectance Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy confirmed that there is no remarkable degradation. The use of a combination of in-situ and ex-situ experimental techniques, including kinetic modelling, not only provides reliable information about degradation but also allows setting optimal processing conditions.

Molten carbonate salts for advanced solar thermal energy power plants: Cover gas effect on fluid thermal stability

Fereres, S; Prieto, C; Gimenez-Gavarrell, P; Rodriguez, A; Sanchez-Jimenez, PE; Perez-Maqueda, LA

Solar Energy Materials and Solar Cells, **188** (2018) 119-126
Diciembre, 2018 | **DOI:** 10.1016/j.solmat.2018.08.028

The eutectic mixture Li_2CO_3-Na_2CO_3-K_2CO_3 is investigated as a high temperature heat transfer fluid and storage medium alternative for molten salt solar thermal power plants. This salt has an operating temperature range of 400–700 °C, enabling the use of higher temperature/efficiency power cycles. However, this carbonate mixture is known to thermally decompose in air. This study evaluates the thermal stability of the salt mixture under different cover gases: air, nitrogen, carbon dioxide, and an 80/20 carbon dioxide/air mixture. Initial characterization is performed through thermogravimetric analysis (TGA), followed by larger scale testing in a custom-made reactor to simulate conditions closer to its practical use. The results show improved thermal stability with a CO_2 atmosphere. The decomposition kinetics under different cover gases are estimated from TGA data. However, larger-scale, longer duration experiments show much slower decomposition rates compared to the classical TGA approach. These findings indicate that the main contribution to mass loss in TGA is due to vaporization rather than thermal decomposition. Thus, a proper evaluation of the molten salt´s thermal stability can only be obtained from reactor experiments where vaporization is inhibited. Very long induction periods (of the order of days) are observed, suggesting that the kinetic decomposition mechanism is a nucleation and growth type. Other considerations for future plants incorporating these high temperature salts are discussed.

Development of a novel TiNbTa material potentially suitable for bone replacement implants

Chicardi, E; Gutierrez-Gonzalez, CF; Sayagues, MJ; Garcia-Garrido, C

Materials & Design, **145** (2018) 88-96
Mayo, 2018 | **DOI:** 10.1016/j.matdes.2018.02.042

A novel (beta + gamma)-TiNbTa alloy has been developed by a combined low energy mechanical alloying (LEMA) and pulsed electric current sintering process (PECS). Microstructurally, this material presents interesting characteristics, such as a submicrometric range of particle size, a body-centered phase (beta-TiNbTa) and, mainly, a novel face-centered cubic Ti-based alloy (gamma-TiNbTa) not previously reported. Related to mechanical performance, the novel (beta + gamma)-TiNbTa shows a lower E (49 +/- 3 GPa) and an outstanding yield strength (sigma(y) 1860 MPa). This combination of original microstructure and properties makes to the (beta + gamma)-TiNbTa a novel material potentially suitable as biomaterial to fabricate bone replacement implants, avoiding the undesirable and detrimental stressshielding problem and even the usual damage on the mechanical strength of Ti-based foams biomaterials.

Role of calcium looping conditions on the performance of natural and synthetic Ca-based materials for energy storage

Sarrion, B; Perejon, A; Sanchez-Jimenez, PE; Perez-Maqueda, LA; Valverde, JM

Journal of CO2 utilization, **28** (2018) 374-384
Diciembre, 2018 | **DOI:** 10.1016/j.jcou.2018.10.018

In this work, the multicycle activity of natural CaO precursors (limestone and dolomite) and Ca-based composites ($Ca_3A_{l2}O_6/CaCO_3$ and ZrO2/$CaCO_3$ mixtures) has been studied for Thermochemical Energy Storage (TCES) in Concentrated Solar Power (CSP) plants by means of the Calcium-Looping process (CaL), using two integration schemes proposed elsewhere that differ in the calcination stages. Under CSP-He conditions, calcination for CaO regeneration is performed under pure He at low temperatures (725 degrees C) while under CPS-CO_2 conditions calcination is carried out under pure CO_2 at high temperatures (950 degrees C). The latter avoids the use of selective membranes to separate He from CO_2 even though it requires the use of more expensive materials for solar receptors. Carbonation/calcination conditions drastically affect the multicycle CO_2 uptake of the materials tested. Effective multicycle conversion is higher in CSP-He tests due to the mild conditions employed for calcination, which mitigates CaO sintering. On the other hand, the harsh calcination conditions used in CSP-CO_2 tests enhance sintering of CaO derived from limestone and the $Ca_3Al_2O_6/CaCO_3$ composite due to the low Tammann temperature of $Ca_3Al_2O_6$. CaO sintering is hindered by the presence of inert oxides with high Tammann temperatures, such as ZrO_2 in the ZrO2/$CaCO_3$ composite and MgO in dolomite. Dolomite derived CaO shows high effective conversion values along the carbonation/calcination cycles when tested under both types of conditions, as compared to limestone and the composites, which suggests that the integration scheme based on CSP-CO_2 conditions would be a feasible alternative to CSP-He if natural dolomite were used as CaO precursor.

Synergy achieved in silver-TiO_2 nanocomposites for the inhibition of biofouling on limestone

Becerra, J; Zaderenko, AP; Sayagues, MJ; Ortiz, R; Ortiz, P
Building and Environment, **141** (2018) 80-90
Agosto, 2018 | **DOI:** 10.1016/j.buildenv.2018.05.020

Biodeterioration of stone monuments is estimated to be as high as 20-30% of the total degradation suffered by Cultural Heritage constructions. With regard to this problem, bactericidal treatments are mainly based on cleaning. These processes, while effective in the short term, require frequent reapplications increasing potential damages to the monument. Silver nanoparticles offer many advantages over traditionally employed products, such as their prolonged biocide efficacy and their low toxicity to humans and environment. The aim of this study was to evaluate the applicability and effectiveness of seven nanocomposite treatments based on titanium dioxide and/or silver nanoparticles to prevent biodeterioration of limestone monuments. These nanocomposites were characterized by UV Visible spectrophotometry, Dynamic Light Scattering and Electron Microscopy. To assess their bactericidal activity, accelerated weathering tests were performed on limestones from the quarry of Utrera, a source widely employed in such iconic monuments as the Cathedral of Seville (Spain). Furthermore, the samples of biopatina employed in our assays stemmed from the fa ades of historical buildings from Seville. Our results show that silver and titanium dioxide nanocomposites stabilized by citrate achieve a high biocide effect while maintaining color alterations at a low level.

Influence of the Mn content on the TiNbxMn alloys with a novel fcc structure

Chicardi, E; Aguilar, C; Sayagues, MJ; Garcia-Garrido, C
Journal of Alloys and Compounds, **746** (2018) 601-610
Mayo, 2018 | **DOI:** 10.1016/j.jallcom.2018.02.306

This work studies the structural evolution of TiNbxMn alloys (x: 0-12 wt%) synthetized by mechanical alloying in a planetary ball mill with different milling times between 1 h and 120 h. The specimens were characterized by X-ray diffraction patterns, scanning and transmission electron microscopies and Energy-dispersive X-ray spectroscopy. It was observed an evolution of the alloys developed from the raw Ti, Nb and Mn elements to bcc-TiNbxMn alloys and, finally, novel fcc-TiNbxMn alloys, with Fm3m space group symmetry, not previously observed. The presence of Mn promotes other interesting effects: a) the decreasing of the crystallite and the particle sizes, reaching values close to 4 nm and 400 nm, respectively, b) the partial amorphization of the fcc-TiNbxMn alloys due to the combined effect of the Mechanical Alloying and the difference of Mn atomic size in comparison with Ti and Nb and c) the presence of Mn that decreases the Fe amount (from milling media) in the as-milled powders.

Optimizing the homogenization technique for graphene nanoplatelet/yttria tetragonal zirconia composites: Influence on the microstructure and the electrical conductivity

Lopez-Pernia, C; Munoz-Ferreiro, C; Gonzalez-Orellana, C; Morales-Rodriguez, A; Gallardo-Lopez, A; Poyato, R
Journal of Alloys and Compounds, **767** (2018) 994-1002
Octubre, 2018 | **DOI:** 10.1016/j.jallcom.2018.07.199

3 mol% yttria tetragonal zirconia polycrystalline (3YTZP) ceramic composite powders with 10 vol% nominal content of graphene nanoplatelets (GNPs) were prepared using four different homogenization routines: dispersion of the powder mixture by ultrasonication in isopropyl alcohol, homogenization in a high-energy planetary ball mill in wet or dry conditions after ultrasonication, and milling of the powders in a high-energy planetary ball mill in dry conditions. A significant effect of the homogenization routine on the powders particle size distribution was revealed by laser granulometry and Raman spectroscopy. Highly densified composites were obtained after spark plasma sintering (SPS) and remarkable differences on the GNP size, shape and distribution throughout the ceramic matrix and also in the electrical conductivity were observed in the four different composites. The composite with the best performance in terms of electrical conductivity was the one prepared after planetary ball milling of the powders in dry conditions as a consequence of the reduced dimensions of the GNPs and their excellent distribution throughout the ceramic matrix.

Nanostructured vanadium carbonitride prepared by combustion synthesis during mechanical milling

Jalaly, M; Gotor, FJ; Sayagues, MJ
Journal of Alloys and Compounds, **763** (2018) 18-24
Septiembre, 2018 | **DOI:** 10.1016/j.jallcom.2018.05.352

Vanadium carbonitride (VCN) nanoparticles were synthesized by a mechanically induced magnesiothermic combustion in a $Mg/V_2O_5/C_3H_6N_6$ system. Initial materials ignited after a short milling time of 6 min. Various characterizations such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HRTEM) and elemental mapping confirmed that the product of the combustion was a mixed carbonitride. In this process, magnesium reduces vanadium oxide to generate elemental V and a great amount of heat. Melamine decomposes due to the temperature rise, and its decomposed species form the carbonitride compound. The chemical composition of the synthesized product was estimated to be $VC_{0.26}N_{0.36}$.

Effects of milling time, sintering temperature, Al content on the chemical nature, microhardness and microstructure of mechanochemically synthesized FeCoNiCrMn high entropy alloy

Alcala, MD; Real, C; Fombella, I; Trigo, I; Cordoba, JM
Journal of Alloys and Compounds, **749** (2018) 834-843
Junio, 2018 | **DOI:** 10.1016/j.jallcom.2018.03.358

FeCoNiCrMn(Al)-based powdered high entropy alloys were synthesized by a short time mechanical alloying process in a high energy planetary ball milling from mixtures of elemental powders, and subsequently sintered by a pressureless procedure. The composition and microstructure of the HEA phases before and after the sintering process were studied by X-ray diffraction, energy dispersive X-ray analysis (EDX) and scanning electron microscopy. The microhardness and tensile strength values for Fe1,8Co1,8Ni1,8Cr1,8Mn1,8Al1,0 HEA sintered at 1400 degrees C sample were 3,7 GPa and 1011 MPa, respectively. Statistical Fisher-Pearson coefficient of skewness and kurtosis were played to determine the optimum synthesis milling time. The use of NaCl as additive led on to a reduction of the as-milled grain size. After sintering, SEM study confirmed a segregation of the initial HEA phase directly related to the melting temperature of the elements. Three melting temperature groups were described (Cr, FeCoNi and Mn) and they agree with the observation in the elemental mapping study. The presence of Al favored the segregation of Cr.

Scalable synthesis of potential solar cell absorber Cu_2SnS_3 (CTS) from nanoprecursors

Hegedus, M; Balaz, M; Tesinsky, M; Sayagues, MJ; Siffalovic, P; Krulakova, M; Kanuchova, M; Briancin, J; Fabian, M; Balaz, P
Journal of Alloys and Compounds, **768** (2018) 1006-1015
Noviembre, 2018 | **DOI:** 10.1016/j.jallcom.2018.07.284

The present paper demonstrates an easy and scalable mechanochemical synthesis of ternary sulfide Cu_2SnS_3 (CTS) as a promising solar cell absorber. For the synthesis, pre-milled nanoparticles of CuS and SnS were used. The pure CTS phase was readily obtained after 60 min of milling in a laboratory planetary ball mill and 240 min in an industrial eccentric vibration industrial mill, respectively. The reaction progress of laboratory scale synthesis was studied by the quantitative Rietveld analysis. The reaction speed reaches its maximum at 4.6 min and the reaction is completed at approximately 60 min, according to the fitted data. The products of the syntheses were further characterized by X-ray powder diffractometry, Raman spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy and UV-Vis spectroscopy. The results revealed formation of near-stoichiometric CTS nanoparticles with tetragonal I-42m symmetry. An average crystallites size of approximately 10-15 nm was determined for CTS phase. The SEM images support quintessential polydisperse character of the powders obtained by ball-milling approach. The materials seem to be suitable for photovoltaic applications with the band-gap energies of approximately 1.16-1.19 eV.

Fabrication and characterization of WC-HEA cemented carbide based on the CoCrFeNiMn high entropy alloy

Velo, IL; Gotor, FJ; Alcala, MD; Real, C; Cordoba, JM
Journal of Alloys and Compounds, **746** (2018) 1-8
Mayo, 2018 | **DOI:** 10.1016/j.jallcom.2018.02.292

A high entropy alloy (HEA, CoCrFeNiMn) synthesized by mechanical alloying was used as the binder for the densification of WC by a pressureless high temperature procedure. Three different WC were used by modifying its microstructure with a high energy ball milling treatment. The alloy content in the HEA-WC mixture was varied from 10 to 30% vol. The microstructure and properties of the sintered composites were studied by X-ray diffraction, scanning electron microscopy and microindentation.

Mechanosynthesis of Sr1-xLaxTiO$_3$ anodes for SOFCs: Structure and electrical conductivity

Sayagues, MJ; Gotor, J; Pueyo, M; Poyato, R; Garcia-Garcia, FJ
Journal of Alloys and Compounds, **763** (2018) 679-686
Septiembre, 2018 | **DOI:** 10.1016/j.jallcom.2018.05.243

Sr$_{1-x}$LaxTiO$_3$ (SLT; 0 <= x <= 0.5) powder samples were synthesised at room temperature by a mechanochemical method from SrO, La2O3 and TiO2 mixtures in 90 min. The obtained SLT samples as potential anode materials in solid oxide fuel cells (SOFCs) were investigated. The microstructure, electrical conductivity and chemical compatibility with yttria-stabilised zirconia (YSZ) were studied. The powder samples had a nanometric character after milling. After a subsequently heating at 900 degrees C, the particle size slightly increased, but still remained nanometric. At this high temperature, a good chemical compatibility with YSZ was found. The x = 0.2 sample gave the best electrical conductivity values, i.e. 0.23 W cm(-2). These features make such as-obtained samples good candidates to be used as anodes in SOFCs.

Crystallization Kinetics of Nanocrystalline Materials by Combined X-ray Diffraction and Differential Scanning Calorimetry Experiments

Gil-Gonzalez, E; Perejon, A; Sanchez-Jimenez, PE; Medina-Carrasco, S; Kupcik, J; Subrt, J; Criado, JM; Perez-Maqueda, LA
Crystal Growth & Design, **18** (2018) 3107-3116
Mayo, 2018 | **DOI:** 10.1021/acs.cgd.8b00241

Crystallization is one key aspect in the resulting properties of nanocrystalline functional materials, and much effort has been devoted to understanding the physical mechanisms involved in these processes as a function of temperature. The main problems associated with crystallization kinetic studies come from the limitations of the employed techniques, and the obtained results may vary significantly depending on the choice of the measurement method. In this work, a complete description of the thermal crystallization event of nanocrystalline BiFeO3 has been performed by combining the information obtained from three different experimental techniques: in situ high-temperature X-ray diffraction, transmission electron microscopy, and differential scanning calorimetry. Interestingly, the kinetic analysis of the X-ray diffraction and differential scanning calorimetry data yields almost identical results, although the physical properties measured by both techniques are different. This allows the unambiguous determination of the kinetic parameters. The importance of a proper definition of the conversion degree, which is limited by the employed measurement technique, is also highlighted.

Is an alumina-whisker-reinforced alumina composite the most efficient choice for an oxidation-resistant high-temperature ceramic?

Tamura, Y; Moshtaghioun, BM; Zapata-Solvas, E; Gomez-Garcia, D; Dominguez-Rodriguez, A; Cerecedo-Fernandez, C; Valcarcel-Juarez, V
Journal of the European Ceramic Society, **38** (2018) 1812-1818
Abril, 2018 | **DOI:** 10.1016/j.jeurceramsoc.2017.10.006

The search of a competitive ceramic material for structural applications demands several requisites: a simple microstructure with easy reproducibility, good intrinsic mechanical properties and most of all, an optimal oxidation resistance. This later point is a challenging point for most ultrahigh refractory materials.

In this work an alumina (Al_2O_3) whisker-reinforced Al_2O_3 composite prepared by spark plasma sintering (SPS) is studied. It will be shown that, although the microstructure is quite similar to that of pure monolithic one, there is a notorious enhancement of the high-temperature deformation resistance, reaching up to one order of magnitude over the pure Al_2O_3 specimen. On the other hand, the activation energy of these composites increases notably. The results are explained in terms of an original model. A comparison with reported data shows that such composite is as efficient as a SiC-whisker-reinforced Al_2O_3 composite, with the advantage of its oxidation resistance and much less fabrication cost.

Spark plasma sintering of titanium nitride in nitrogen: Does it affect the sinterability and the mechanical properties?

Moshtaghioun, BM; Gomez-Garcia, D; Dominguez-Rodriguez, A
Journal of the European Ceramic Society, **38** (2018) 1190-1196
Abril, 2018 | **DOI:** 10.1016/j.jeurceramsoc.2017.12.029

Titanium nitride ceramics have an intrinsic interest due to its optical and structural applications. However, the conditions for sintering of dense pieces are not still clarified. This research work is focused on the spark plasma sintering (SPS) of near-fully dense fine-grained TiN. The main goal is giving a response to a longstanding debate: can the external atmosphere favor sintering? Different sintering atmospheres, either vacuum or a nitrogen flow, have been used during SPS heating to this purpose. X ray diffraction analysis has showed the presence of TiN as the main phase with traces of Ti_4O_7 in optimal SPS conditions (1600 °C, one minute dwell time). Our results show that the use of a nitrogen flow while heating can improve sinterability very slightly, but mechanical properties are essentially unaltered within the experimental uncertainty. The hardness reaches values as high as 20GPa whereas fracture toughness can be evaluated around 4 MPam1/2.

Exotic grain growth law in twinned boron carbide under electric fields

Moshtaghioun, BM; Gomez-Garcia, D; Rodriguez, AD
Journal of the European Ceramic Society, **38** (2018) 4590-4596
Noviembre, 2018 | **DOI:** 10.1016/j.jeurceramsoc.2018.06.029

Grain growth is a ubiquitous phenomenon in all materials, and it affects both structural and functional properties. Despite its intrinsic importance, a full comprehension of grain growth

from a fundamental point of view-i.e., from the nanoscale to the macroscale-is still a pending issue. In practical terms, our knowledge relies on the classical kinetic laws reported sixty years ago.
This paper reports the violation of such classical laws in boron carbide ceramics consolidated by spark plasma sintering. The conjunction of high temperature gradients with large compressive stress when a pulse electric current passes through the ceramic powders gives rise to an intense twinning-detwinning formation. These forming steps at the grain boundaries change the grain mobility drastically. Therefore, a new 'exotic' law for grain-growth kinetics is found and validated at different temperatures and dwell times.

High temperature creep of 20 vol%. SiC-HfB_2 UHTCs up to 2000 degrees C and the effect of La_2O_3 addition

Zapata-Solvas, E; Gomez-Garcia, D; Dominguez-Rodriguez, A; Lee, WE
Journal of the European Ceramic Society, **38** (2018) 47-56
Enero, 2018 | **DOI:** 10.1016/j.jeurceramsoc.2017.08.028

High temperature compressive creep of SiC-HfB2 UHTCs up to 2000 °C has been studied. Microstructural analysis after deformation reveals formation of new phases in the Hf-B-Si and Hf-B-Si-C systems, which are responsible for the poor creep resistance. RE oxide additions have a negative effect reducing the creep resistance of SiC-HfB2 UHTCs. A simplistic analysis for the required creep resistance is described, indicating that only SiC-HfB2 UHTCs could withstand re-entry conditions for 5 min in a single use. However, RE oxide addition to SiC-HfB2UHTCs does not provide the required creep resistance for them to be candidate materials for hypersonic applications.

Graphene or carbon nanofiber-reinforced zirconia composites: Are they really worthwhile for structural applications?

Cano-Crespo, R; Moshtaghioun, BM; Gomez-Garcia, D; Moreno, R; Dominguez-Rodriguez, A
Journal of the European Ceramic Society, **38** (2018) 3994-4002
Septiembre, 2018 | **DOI:** 10.1016/j.jeurceramsoc.2018.04.045

The use of allotropic phases of carbon (i.e. nanotubes, graphene or carbon nanofibers) as second phases to design ceramic composites is a hot topic at present. Researchers try to provide a remarkable improvement of the parent ceramic assuming that some of the outstanding mechanical properties of these phases migrate to the resultant composite. This reasonable idea has been questioned severely in the case of nanotubes addition but there is not any analysis for the other two phases cited previously. To elucidate this question, zirconia was selected as a model ceramic. This paper reports the mechanical properties of zirconia composites reinforced either with graphene or carbon nanofibers, with special emphasis on the high-temperature plasticity.

High-temperature compressive creep of novel fine-grained orthorhombic ZrO_2 ceramics stabilized with 12 mol% Ta doping

Sponchia, G; Moshtaghioun, BM; Riello, P; Benedetti, A; Gomez-Garcia, D; Dominguez-Rodriguez, A; Ortiz, AL

Journal of the European Ceramic Society, **38** (2018) 2445-2448

Mayo, 2018 | **DOI:** 10.1016/j.jeurceramsoc.2017.12.055

A novel fine-grained orthorhombic ZrO_2 ceramic stabilized with 12 mol% Ta doping was fabricated by spark plasma sintering from home-made powders, and its high-temperature mechanical properties evaluated for the first time by compressive creep tests in both Ar and air. It was found that the high-temperature plasticity of the ceramic deformed in Ar, under which the Ta-doped orthorhombic ZrO_2 is a black suboxide with abundant oxygen vacancies in its crystal structure, is controlled by grain boundary sliding (stress exponent similar to 2, and activation energy similar to 780-800 kJ/mol). However, the high-temperature plasticity of the ceramic deformed in air, under which the Ta-doped orthorhombic ZrO_2 is a white oxide due to the elimination in situ of oxygen vacancies, is controlled by recovery creep (stress exponent 3, and activation energy similar to 750 kJ/mol). It was also observed that black Ta-doped orthorhombic ZrO_2 is more creep resistant than its white counterpart with the same grain size, and that the former deforms as the more conventional Y_2O_3-stabilized ZrO_2 does.

Combined kinetic analysis of multistep processes of thermal decomposition of polydimethylsiloxane silicone

Garcia-Garrido, C; Perez-Maqueda, LA; Criado, JM; Sanchez-Jimenez, PE

Polymer, **153** (2018) 558-564

Septiembre, 2018 | **DOI:** 10.1016/j.polymer.2018.08.045

In this work, we studied the thermal decomposition of a widely employed silicone elastomer, polydimethylsiloxane, in an inert atmosphere. This silicone elastomer has several applications due to its high thermal stability such as MEMS (microelectromechanical systems) precursors, microfluidic components, adhesives, lubricants, and precursors for non-porous ceramics. Therefore, a reliable description of the thermal decomposition kinetics is important to prevent or control the decomposition in such applications. While the decomposition has been amply reported as a complex process, most kinetic studies published on this system use simplified methods that avoid the fact that the entire process cannot be described by a single kinetic triplet. Here, we have studied the decomposition process by first separating the overall reaction into its three constituent steps which were subsequently analysed independently. The deconvolution was carried out using Fraser-Suzuki function that is capable of fitting an asymmetric peak fitting function. The resulting kinetic parameters proved to be able to reconstruct the original experimental curves but are also capable of producing accurate predictions of curves recorded at heating schedules different from those employed to record the experimental data used in the kinetic analysis. Finally, it was found that the rate limiting step of all stages is the diffusion of the gases released during the polymer decomposition through the transforming polymeric matrix.

Synthesis and characterization of SiC/Si_3N_4 composites from rice husks

Real, C; Cordoba, JM; Alcala, MD
Ceramics International, **44** (2018) 14645-14651
Agosto, 2018 | **DOI:** 10.1016/j.ceramint.2018.05.090

$SiC-Si_3N_4$ composites have been obtained by carbothermal reduction of rice husk under a nitrogen-argon atmosphere at 1450 degrees C, which is a lower temperature than those used by other authors. On the other hand, tailoring the argon/nitrogen ratio led to the obtained of $SiC-Si_3N_4$ composites across the whole range of compositions. Phosphoric acid treatment permited the synthesis of the composite without a pyrolysis step. The final products were characterized by X-ray diffractometry, IR spectroscopy and scanning electron microscopy.

The role of carbon nanotubes on the stability of tetragonal zirconia polycrystals

Morales-Rodriguez, A; Poyato, R; Gutierrez-Mora, F; Munoz, A; Gallardo-Lopez, A
Ceramics International, **44** (2018) 17716-17723
Octubre, 2018 | **DOI:** 10.1016/j.ceramint.2018.06.238

The effect of single walled carbon nanotubes (SWNT) at zirconia grain boundaries on the stability of a tetragonal zirconia polycrystalline matrix has been explored in as-sintered composites and after low temperature hydro thermal degradation (LTD) experiments. For this purpose, highly-dense 3 mol% Y_2O_3-doped tetragonal zirconia polycrystalline (3YTZP) ceramics and SWNT/3YTZP composites were prepared by spark plasma sintering (SPS). Quantitative X-ray diffraction analysis and microstructural observations point out that an increasing amount of well-dispersed SWNT bundles surrounding zirconia grains decreases the metastable tetragonal phase retention in the ceramic matrix after sintering. In contrast, the tetragonal ceramic grains in composites with SWNTs are less sensitive to the presence of water, i.e. to undergo a martensitic transformation under LTD conditions, than monolithic 3YTZP ceramics. The SWNT incorporation diminishes micro-cracking due to tetragonal to monoclinic ZrO_2 phase transformation in the composites.

Corrigendum to “Dense graphene nanoplatelet/yttria tetragonal zirconia composites: Processing, hardness and electrical conductivity” [Ceram. Int. 43 (2017) 11743–11752]

Gallardo-Lopez, A; Marquez-Abril, I; Morales-Rodriguez, A; Munoz, A; Poyato, R
Ceramics International, **44** (2018) 1225-1225
Enero, 2018 | **DOI:** 10.1016/j.ceramint.2017.10.015 (Correction)

Grain-boundary diffusion coefficient in alpha-Al_2O_3 from spark plasma sintering tests: Evidence of collective motion of charge disconnections

Tamura, Y; Zapata-Solvas, E; Moshtaghioun, BM; Gomez-Garcia, D; Dominguez-Rodriguez, A
Ceramics International, **44** (2018) 19044-19048
Octubre, 2018 | **DOI:** 10.1016/j.ceramint.2018.07.073

The sintering of fine-grained a-alumina by spark plasma sintering (SPS) was performed to study grain growth under SPS conditions. Grain growth is found to be extensive at relative densities above 95%. A grain growth versus dwell time analysis during SPS allows for the determination of the grain-boundary diffusion coefficient. This study shows that the remarkable enhancement of grain-boundary diffusion derived from a previous analysis could be a consequence of the presence of the recently discovered “disconnections” at the grain boundaries of alpha-alumina. Their presence, together with their electric charge and the external electric field at the boundaries, are the key ingredients for a violation of the typical grain growth kinetic law. When they are introduced appropriately, an updated value of the grain-boundary diffusion coefficient is achieved. A comparison with other values reported previously in the literature through other techniques and a critical analysis are also carried out.

Effects of additives on the synthesis of TiC_xN_{1-x} by a solid-gas mechanically induced self-sustaining reaction

Chicardi, E; Gotor, FJ; Alcala, MD; Cordoba, JM
Ceramics International, **44** (2018) 7605-7610
Mayo, 2018 | **DOI:** 10.1016/j.ceramint.2018.01.179

The synthesis of TiC_xN_{1-x} from Ti/C mixtures in a N-2 atmosphere performed in a high-energy planetary mill was used as example to study the influence of the use of additives in mechanically induced self-sustaining reaction (MSR) processes. In particular, the effect of the addition of TiN, TiC, Si_3N_4 and SiC was analyzed. The self-sustaining reaction was extinguished when additive contents of 50, 40, 40 and 30 wt% for TiN, TiC, Si_3N_4 and SiC, respectively, were employed. These additives cannot be regarded as real inert since they served as an extra solid source for nitrogen and carbon, modifying the final stoichiometry of the TiC_xN_{1-x} phase. The adiabatic temperature (T-ad) determined for the mixtures with no MSR effect was well above the empirical limit value of 1800 K adopted as criterion for the occurrence of the self-propagating high-temperature synthesis (SHS) process. The ignition time (t(ig)) of the MSR process was practically invariant for low additive contents (approximately 50 min) and tended to increase up to maximum values of 85-95 min for the larger additive contents.

Electrical conduction mechanisms in graphene nanoplatelet/yttria tetragonal zirconia composites

Poyato, R; Osuna, J; Morales-Rodriguez, A; Gallardo-Lopez, A
Ceramics International, **44** (2018) 14610-14616
Agosto, 2018 | **DOI:** 10.1016/j.ceramint.2018.05.082

Yttria tetragonal zirconia polycrystalline (3YTZP) ceramic composites with 5, 10 and 20 vol% graphene nano-platelets (GNPs) were prepared by spark plasma sintering (SPS) and their electrical conductivity as a function of temperature was characterized. The composites exhibit anisotropic microstructures so the electrical conductivity studies were carried out in two directions: perpendicular (sigma(perpendicular to)) and parallel (sigma(parallel to)) to the SPS pressing axis. The composites with 5 and 10 GNP vol% showed high electrical anisotropy, whereas the composite with 20 GNP vol % exhibited nearly isotropic electrical behavior. sigma(perpendicular to) shows metallic-type behavior in the composites with 10 and 20 vol%

GNP revealing that charge transport takes place through defect-free GNPs. For the composite with 5 vol % GNP the observed semiconductor-type behavior was explained by a two dimensional variable range hopping mechanism. sigma(parallel to)shows metallic-type conductivity in the composite with 20 GNP vol% and positive d sigma(parallel to)/dT slope in the composites with 5 and 10 GNP vol%.

Investigation of use of coal fly ash in eco-friendly construction materials: fired clay bricks and silica-calcareous non fired bricks

Eliche-Quesada, D; Sandalio-Perez, JA; Martinez-Martinez, S; Perez-Villarejo, L; Sanchez-Soto, PJ
Ceramics International, **44** (2018) 4400-4412
Marzo, 2018 | **DOI:** 10.1016/j.ceramint.2017.12.039

The use of coal fly ash (CFA) as raw material for the manufacture of two construction materials, fired clay bricks and silica-calcareous non-fired bricks, was investigated. Fired clay bricks were manufactured using a commercial clay and different waste ratios (0-50 wt%), moulded at 10 MPa and fired at 1000 degrees C (4 h). Silica-calcareous non fired bricks were prepared using two wastes as raw material: CFA and “geosilex”(G), a hidrated lime residue which comes entirely from acetylene industry waste. Different proportions CFA (80-30 wt%) G (20-70 wt%) were investigated. Raw materials were moulded at 10 MPa and cured in water at room temperature during 28 days. The results indicated that the incorporation of up to 20 wt% of CFA produced fired clay bricks with physical and mechanical properties similar to control bricks without waste. However, additions of a higher amount (30-50 wt%) of residue resulted in a more pronounced decrease in mechanical properties (between 25-50%) due to an increase in open porosity. The technological characterization of the silica-calcareous non fired bricks showed a reduction in the values of bulk density and water absorption when the coal fly ash content decreases. Silica-calcareous non-fired bricks containing between 40 and 60 wt% of CFA had the highest values of compressive strength in the range 46-43 MPa. These silica-calcareous non-fired bricks, 60CFA-40 G, 50CFA-50 G and 40CFA-60 G, presented the optimum amount of pozzolanic materials (SiO_2 and Al_2O_3) in the coal fly ash and calcium hydroxide in the geosilex to give rise to the formation of calcium silicate hydrates and calcium aluminate hydrates, the phases responsible for the mechanical resistance increase of the construction materials. Therefore, CFA-clay fired bricks and silica-calcareous CFA-Geosilex non-fired bricks presented optimal technological properties that attain the quality standards.

Synthesis of vaterite $CaCO_3$ as submicron and nanosized particles using inorganic precursors and sucrose in aqueous medium

Perez-Villarejo, L; Takabait, F; Mahtout, L; Carrasco-Hurtado, B; Eliche-Quesada, D; Sanchez-Soto, PJ
Ceramics International, **44** (2018) 5291-5296
Abril, 2018 | **DOI:** 10.1016/j.ceramint.2017.12.142

It is reported the synthesis of $CaCO_3$ vaterite as stable nanoparticles and submicron-sized by a simple and relatively rapid procedure. XRD, SEM and FTIR techniques have been used to characterize the precipitated products. The synthesis is based on chemical precipitation of inorganic salt precursors, calcium nitrate tetra hydrate and sodium bicarbonate, and using the disaccharide sucrose as an additive in aqueous medium. The role of the disaccharide sucrose is to control the vaterite precipitation after nucleation and growth. It has been found that an increase in sugar concentration promotes the crystal precipitation of vaterite with spherulitic morphology, as revealed by SEM, and changed the surface of the precipitated particles. There is a significant difference between $CaCO_3$ precipitation in the absence and presence of sucrose. Addition of 0% of sucrose leads to 83% of calcite as identified by XRD methods. In contrast, addition of 67% of sucrose in aqueous medium produces 100% vaterite. The present results may be useful to provide a quick, simple, inexpensive and novel method for the controlled synthesis of new advanced biomaterials based on vaterite particles without hazardous chemicals and inert atmosphere, with great possibilities for industrial scale production.

A new combustion route for synthesis of TaB_2 nanoparticles

Jalaly, M; Gotor, FJ
Ceramics International, **44** (2018) 1142-1146
Enero, 2018 | **DOI:** 10.1016/j.ceramint.2017.10.074

Tantalum diboride (TaB_2) nanoparticles were synthesized through a mechanically induced self-sustaining reaction (MSR). In this method, the ternary system of $Mg/Ta_2O_5/B$ was employed in which, magnesium was used as a reducing agent for reduction of tantalum oxides in a combustive regime. The processing route of TaB_2 by the solid-state combustion was very short-term and the product purification was extremely easy and rapid. The synthesis mechanism was studied and revealed that magnesiothermic reduction of tantalum oxide is the initiator of the total reaction, while borothermic reduction of the oxide may occur in parallel.

Isosymmetric structural phase transition of the orthorhombic lanthanum gallate structure as a function of temperature determined by Rietveld analysis

Tang, Y. Q.; Lopez-Cartes, C.; Aviles, M. A.; Cordoba, J. M.
Crystengcomm, **20** (2018) 5562-5569
Octubre, 2018 | **DOI:** 10.1039/c8ce00726h

High energy planetary ball milling has been used to synthesize pseudo-cubic highly-pure $LaGaO_3$ in one hour from its oxide components in an air atmosphere. Calcination at different temperatures led to the crystallization of lanthanum gallate in an orthorhombic structure with its local lanthanum coordination number environment changing from 12 to 7 when the temperature was increased. This change was attributed to the thermal expansion of the Ga-O bonds that varied non-monotonically inducing GaO6 tilting. Rietveld analysis, Raman spectroscopy, and transmission electron microscopy were used to elucidate the $LaGaO_3$ structures at different temperatures.

Mechanochemical synthesis, structural, magnetic, optical and electrooptical properties of $CuFeS_2$ nanoparticles

Dutkova, E; Bujnakova, Z; Kovac, J; Skorvanek, I; Sayagues, MJ; Zorkovska, A; Kovac, J; Balaz, P
Advanced Powder Technology, **29** (2018) 1820-1826
Agosto, 2018 | **DOI:** 10.1016/j.apt.2018.04.018

The rapid mechanochemical synthesis of nanocrystalline $CuFeS_2$ particles prepared by high-energy milling for 60 min in a planetary mill from copper, iron and sulphur elements is reported. The $CuFeS_2$ nanoparticles crystallize in tetragonal structure with mean crystallite size of about 38 ± 1 nm determined by XRD analysis. HRTEM study also revealed the presence of nanocrystals with the size of 5–30 nm with the tendency to form agglomerates. The Raman spectrum confirms the chalcopyrite structure. Low temperature magnetic data for $CuFeS_2$ support the coexistence of antiferromagnetic and paramagnetic spin structure. Moreover, the hysteresis loops taken at temperatures from 5 K to 300 K revealed a presence of very small amount of ferromagnetic phase, which seems to be associated with the non-consumed elemental Fe in as-prepared nanoparticles. The optical band gap of $CuFeS_2$nanoparticles has been detected to be 1.05 eV, larger than band gap of the bulk material. The wider gap possibly resulted from the nano-size effect. Photoresponses of $CuFeS_2$ nanoparticles were confirmed by I-V measurements under dark and light illumination. It was demonstrated that mechanochemical synthesis can be successfully employed in the one step preparation of nanocrystalline $CuFeS_2$ with good structural, magnetic, optical and electrooptical properties.

Surface modification of Ti-6Al-4V alloys manufactured by selective laser melting: Microstructural and tribo-mechanical characterization

Torres, Y; Sarria, P; Gotor, FJ; Gutierrez, E; Peon, E; Beltran, AM; Gonzalez, JE
Surface & Coatings Technology, **348** (2018) 31-40
Agosto, 2018 | **DOI:** 10.1016/j.surfcoat.2018.05.015

Medical grade of both titanium (Ti) and Ti6A14V alloy are recognized as the metallic biomaterials with the better outcomes for clinical repair of bone tissue thanks to their suitable mechanical properties and corrosion resistance. However, those Ti advantages are not enough to avoid failure risks of bone implants; between 5 and 10% of Ti implants fail due to a deficient osseointegration, within 5 years of post-implantation. Most of these failures indicate the necessity of getting a better biomechanical-biofunctional balance. Microstructural and tribo-mechanical characterizations were performed on Ti6A14V samples obtained by selective laser melting and subjected to different surface treatments (thermal stress relief, acid etching, chemical treatment and thermochemical treatment). Scanning electron microscopy and X-ray diffraction were used for detailed characterization of the elemental composition, phase analysis and surface morphology. Micro-hardness and scratch tests were employed to evaluate the tribo-mechanical properties, which were improved after consecutive surface treatments. Protuberances with spherical morphology, as a remainder of the original powder, were present on the surface. The resulting modified surfaces were constituted by rutile (major phase) and anatase (minor phase). Submicro-nano-topographies were obtained after the chemical and thermochemical treatments.

Vitrification and derived glass-ceramics from mining wastes containing vermiculite and lithium aluminium phosphate

Rincon, JM; Callejas, P; Sanchez-Soto, PJ; Jordan, MM
Materials Letters, **227** (2018) 86-89
Septiembre, 2018 | **DOI:** 10.1016/j.matlet.2018.05.001

The waste vitrification of abandoned open sky vermiculite deposits has been considered by combining with a natural phosphate mineral residue. Several batches haven been designed from the composition system: Li_2O-MgO-Al_2O_3-P_2O_5-SiO_2 including some Fe_2O_3 and Fluoride. The resulting glasses are transparent and smooth green coloured, giving rise after TTT treatments to several opal, opaque glass-ceramics with iridescent surface. Full characterization has been carried out by XRD and electron microscopy with EDS, as well as by XPS spectroscopies, concluding that the main crystalline phases formed were alpha-cordierite and beta-spodumene. The surface of these glass-ceramics from vermiculiteamblygonite is enriched in Fe_2O_3. Compared to the parent glasses, the final glass-ceramics exhibited and improvement in fracture toughness.

The effect of vitreous phase on mullite and mullite-based ceramic composites from kaolin wastes as by-products of mining, sericite clays and kaolinite

Sanchez-Soto, PJ; Eliche-Quesada, D; Martinez-Martinez, S; Garzon-Garzon, E; Perez-Villarejo, L; Rincon, JM

Materials Letters, **223** (2018) 154-158

Julio, 2018 | **DOI:** 10.1016/j.matlet.2018.04.037

Mullite precursors were prepared using kaolin waste, sericite clay containing kaolinite and industrial kaolin with addition of alumina in a wet medium to synthesize mullite (72 wt% Al2O3 and 28 wt% SiO2). Uniaxial pressed bars of the powdered mullite precursors were fired in the range 1400-1600 degrees C with soaking times 30-120 min. The resultant materials were studied by XRD and SEM-EDX. Bulk densities, apparent porosities and flexural strengths in four points were determined in the fired bars at 1500, 1550 and 1600 degrees C. It was concluded that the thermal behaviour of these mullite precursors was influenced by the presence of impurities in the raw materials. These impurities originate a liquid phase forming a glassy phase which produces a progressive and enhanced densification of the mullite materials by reaction sintering at 1500-1600 degrees C. The technical properties were also influenced by the relative proportion of vitreous phase. The microstructure of characteristic mullite crystals was revealed by SEM. It was emphasized the use of kaolin waste by-products of mining and sericite clays as valuable raw materials for mullite preparation.

Biomass fly ash and aluminium industry slags-based geopolymers

Perez-Villarejo, L; Bonet-Martinez, E; Eliche-Quesada, D; Sanchez-Soto, PJ; Rincon-Lopez, JM; Castro-Galiano, E

Materials Letters, **229** (2018) 6-12

Octubre, 2018 | **DOI:** 10.1016/j.matlet.2018.06.100

Geopolymers are a new class of non-Portland cements produced using an alumino-silicate material and an activating solution, which is mainly composed of sodium or potassium and waterglass to be subsequently cured at relatively low temperatures. Those can be formulated by adding natural minerals, waste and/or industrial by-products. The study investigates the microstructural properties of geopolymers synthesized from metakaolin (MK) and the admixture of fly ash (FBA) and aluminium industry slags (AIS) at different ages of curing. Five different geopolymer compositions were prepared and characterized by XRD, ATR-FTIR and SEM/EDS. The study revealed that geopolymeric gels are identified, which show mainly glassy microstructures, in agreement with the X-ray amorphous diffraction patterns, broad FTIR features and confirmed by SEM/EDS, with promising results prior to an industrial scale.

Manufacture of sustainable clay ceramic composite with composition SiO_2-Al_2O_3-CaO-K_2O materials valuing biomass ash from olive pomace

Bonet-Martinez, E; Perez-Villarejo, L; Eliche-Quesada, D; Sanchez-Soto, PJ; Carrasco-Hurtado, B; Castro-Galiano, E
Materials Letters, **229** (2018) 21-25
Octubre, 2018 | **DOI:** 10.1016/j.matlet.2018.06.105

Fly ash is a biomass combustion by-product produced by dragging ash from the base of the furnace. Disposing of ash is a growing economic and environmental burden. Based on physical and chemical properties, fly ash could be used in the manufacture of construction materials. This paper investigates the influence of biomass fly ash from olive pomace as additive to manufacture of clay ceramic composite materials. Fired clay brick at 950 degrees C were prepared containing between 0 and 25 wt% fly ash. Final products are studied by water absorption, bulk density, loss of ignition, linear shrinkage, compressive strength and physisorption N-2. The results reveal that the porosity of the materials increases with the level of fly ash replacement (10% up to 25 wt%) resulting in to increased water absorption and decreased compressive strength. Fired clay brick developed in this study can be used for construction materials based on criteria of the current regulations.

Self-propagating mechanosynthesis of HfB_2 nanoparticles by a magnesiothermic reaction

Jalaly, M; Gotor, FJ; Sayagues, MJ
Journal of the American Ceramic Society, **101** (2018) 1412-1419
Abril, 2018 | **DOI:** 10.1111/jace.15297

A mechanically induced self-sustaining reaction (MSR) was used to synthesize hafnium diboride nanoparticles. Along this route, magnesium was selected as a robust reducing agent for co-reduction in boron and hafnium oxides in a combustive manner. Combustion occurred after a short milling period of 12 minutes. The hafnium diboride nanoparticles had a polygonal faceted morphology and were 50-250 nm in diameter. The assessment of the processing mechanism revealed that the initial combustive reduction in B_2O_3 to elemental B by Mg was the major step for progressing the overall reaction. After that, HfO_2 can be reduced to elemental Hf, followed by the synthesis of HfB_2 phase.

Self-propagating mechanosynthesis of HfB_2 nanoparticles by a magnesiothermic reaction

Jalaly, M; Gotor, FJ; Sayagues, MJ
Journal of the American Ceramic Society, **101** (2018) 1412-1419
Abril, 2018 | **DOI:** 10.1111/jace.15297

A mechanically induced self-sustaining reaction (MSR) was used to synthesize hafnium diboride nanoparticles. Along this route, magnesium was selected as a robust reducing agent for co-reduction in boron and hafnium oxides in a combustive manner. Combustion occurred after a short milling period of 12 minutes. The hafnium diboride nanoparticles had a polygonal faceted morphology and were 50-250 nm in diameter. The assessment of the processing mechanism revealed that the initial combustive reduction in B_2O_3 to elemental B by Mg was the major step for progressing the overall reaction. After that, HfO_2 can be reduced to elemental Hf, followed by the synthesis of HfB_2 phase.

An approach to the heating dynamics of residues from greenhouse-crop plant biomass originated by tomatoes (Solanum lycopersicum, L.)

Garzon, E; Morales, L; Ortiz-Rodriguez, IM; Sanchez-Soto, PJ
Environmental Science and Pollution Research, **25** (2018) 25880-25887
Septiembre, 2018 | **DOI:** 10.1007/s11356-018-2577-y

The most representative of greenhouse-crop plant biomass residues of tomatoes (Solanum lycopersicum L.) were selected for this study by using X-ray fluorescence spectrometry (XRF) and X-ray powder diffraction (XRD). The heating dynamics in air in the 600-1150 degrees C range of these residues for the production of renewable energy and the resultant ashes have been investigated. A total of 11 elements were determined by XRF in the biomass ashes and some minor elements. The content of alkaline elements and chlorides decreased as increasing heating temperature and disappeared at 1150 degrees C. Alkaline salts, NaCl and KCl, were volatilized by heating since 800 degrees C. The total contents of S and P in the biomass ashes were associated to $CaSO_4$, and a complex phosphate identified by XRD. $CaCO_3$ present at 600 degrees C was decomposed to CaO with disappearance at 1000 degrees C. By heating, new silicates were formed by solid-state reactions in the biomass residue. The minor elements have been found in a relative proportion lower than 0.9wt.% and they characterized the obtained ashes, with potential use as micronutrients.

Development of a novel fcc structure for an amorphous-nanocrystalline Ti-33Nb-4Mn (at.%) ternary alloy

Chicardi, E; Garcia-Garrido, C; Sayagues, MJ; Torres, Y; Amigo, V; Aguilar, C
Materials Characterization, **135** (2018) 46-56
Enero, 2018 | **DOI:** 10.1016/j.matchar.2017.11.021

In this work, a novel amorphous-nanocrystalline titanium-niobium-manganese solid solution ternary alloy with a Ti-33Nb-4Mn (at.%) nominal composition was developed by a High-Energy Mechanical Alloying. Nb and Mn were added to the elemental Ti as a beta-phase (bcc) stabilizer and an amorphization promoter, respectively. The system evolved from the elemental Ti, Nb and Mn raw materials to a body centred cubic (bcc) TiNbMn alloy and, finally, to the formation of an original and stable face centred cubic (fcc) nanocrystalline TiNbMn alloy, not reported until now, at short milling time (20 h). This alloy remains invariant until 120 h. In turn, the partial amorphization of the system occurs and increases until at intermediate milling time (80 h). The production of both original fcc and the amorphous TiNbMn alloy may be beneficial for reducing the Young's modulus and improving the mechanical strength pursued for the Ti alloy. The optimal milling time respect to the amorphization, nanocrystalline size and Fe mount from milling media was 60 h and 80 h (TiNbMn60h and TiNbMn80h), with > 50 wt% of an amorphous phase and a crystalline domain size of approximately 5 nm.

Core-rim structure formation in TiC-Ni based cermets fabricated by a combined thermal explosion/hot-pressing process

Lemboub, S; Boudebane, S; Gotor, FJ; Haouli, S; Mezrag, S; Bouhedja, S; Hesser, G; Chadli, H; Chouchane, T

International Journal of Refractory Metals & Hard Materials, **70** (2018) 84-92

Enero, 2018 | **DOI:** 10.1016/j.ijrmhm.2017.09.014

TiC-Ni-based cermets were obtained by thermal explosion from different elemental mixtures (Ti, C, Ni and X, where X = Cr, Mo or W) and subsequently densified by hot-pressing under a cyclic load. The whole process was performed in a single stage in the same experimental device according to the following thermal and pressure procedure: a heating rate ramp up to 1573 K without applying any load followed by an isothermal dwelling under a compressive cyclic load of 32 MPa. The thermal explosion synthesis occurred during the heating ramp at a temperature close to 1273 K that was practically independent of the starting nominal composition. The influence of different refractory elements on the chemical composition and microstructure of cermets was studied. SEM characterization showed that only with Mo and W, the cermets developed the characteristic core-rim structure. A high densification was achieved, but decreased when the refractory elements were added. Nevertheless, in these cases higher hardness values were obtained.

Influence of temperature on the biaxial strength of cemented carbides with different microstructures

Chicardi, E; Bermejo, R; Gotor, FJ; Llanes, L; Torres, Y

International Journal of Refractory Metals & Hard Materials, **71** (2018) 82-91

Febrero, 2018 | **DOI:** 10.1016/j.ijrmhm.2017.11.003

The effect of the temperature on the mechanical strength of WC-Co cemented carbides with different microstructures (grain size and binder content) was evaluated. Biaxial flexural tests were performed on three cemented carbide grades at 600 °C using the ball-on-three-balls (B3B) method. Results were interpreted by Weibull statistics and compared to biaxial strength results at room temperature. A detailed fractographic analysis, supported by Linear Elastic Fracture Mechanics, was performed to differentiate the nature and size of critical defects and the mechanism responsible for the fracture. A significant decrease in the mechanical strength (around 30%) was observed at 600 °C for all grades of cemented carbides. This fact was ascribed to the change in the critical flaw population from sub-surface (at room temperature) to surface defects, associated with the selective oxidation of Co. Additionally, an estimation of the fracture toughness at 600 °C was attempted for the three cemented carbides, based upon the B3B strength results, the corresponding number of the tested specimens fragments and the macroscopic area of the B3B fracture surfaces. The fracture toughness was not affected by the temperature, at least up to 600 °C. In addition, the good agreement with the Single Edge Notch

Beam toughness data suggests the possibility of employing this approach for fracture toughness evaluation of brittle materials under different testing conditions.

Spanish and Portuguese Gilding Threads: Characterization Using Microscopic Techniques

Perez-Rodriguez, JL; Albardonedo, A; Robador, MD; Duran, A
Microscopy and Microanalysis, **24** (2018) 574-590
Octubre, 2018 | **DOI:** 10.1017/S1431927618015167

Gilding threads collected from Spanish and Portuguese palaces and from the embroideries and adornments of sculptures of the Virgin and Christ that form part of Sevillian Holy Week were analyzed and compared (20 artifacts were evaluated). The study covered a broad time period with examples from the 13th to 14th centuries, 18th to 20th centuries, and also including modern embroideries. A combination of scanning electron microscopy and energy-dispersive X-ray spectroscopy was used. The knowledge of the layered structures of the threads has provided very valuable information regarding the manufacturing techniques. The different metal threads found in the embroidery studied consisted of gold, silver, copper, and alloys of these metals and aluminium. The fabrication procedures often differed in the different workshops and changed with time. In the modern embroideries, a decrease of precious metal concentration was detected. The threads were wound around a core of silk threads.

Effect of Basicity on the Hydrolysis of the Bi(III) Aqua Ion in Solution: An Ab Initio Molecular Dynamics Study

Ayala, R; Martinez, JM; Pappalardo, RR; Refson, K; Marcos, ES
Journal of Physical Chemistry A, **122** (2018) 1905-1915
Febrero, 2018 | **DOI:** 10.1021/acs.jpca.7b12402

Hydrolysis of the Bi(III) aqua ion under a range of solution conditions has been studied by means of ab initio molecular dynamics simulations. While the Bi(III) aqua ion is stable in pure water, there is an increasing degree of hydrolysis with the number of hydroxide anions in the medium. This is accompanied by a monotonic decrease of the total coordination number to an asymptotic value of similar to 6, reached under extreme basicity conditions. Comparison of the simulated Bi(III) hydrolyzed species with the experimental species distribution at different degrees of basicity suggests that, at the PBE/DFT level of theory here employed, liquid water shows an overly acidic character. Predictions of theoretical EXAFS and XANES spectra were generated from the AIMD trajectories for different Bi hydrolyzed species, [Bi(HO)(m)(H_2O)(n)](3-m+), m = 0-3 and n = 7-2. Comparison with available experimental spectra is presented. Spectral features joined to the degree of hydrolysis and hydration are analyzed.

Thermal behaviour of sericite clays as precursors of mullite materials

Gonzalez-Miranda, FD; Garzon, E; Reca, J; Perez-Villarejo, L; Martinez-Martinez, S; Sanchez-Soto, PJ
Journal of Thermal Analysis and Calorimetry, **132** (2018) 967-977

Mayo, 2018 | **DOI:** 10.1007/s10973-018-7046-9

Thermal analysis of some sericite clays, from several deposits in Spain, which are not exploited at this time, has been studied. The samples have been previously characterized by mineralogical and chemical analysis. Sericite clays have interesting properties, with implications in ceramics and advanced materials, in particular concerning the formation of mullite by heating. According to this investigation by differential thermal and thermogravimetric analysis (DTA-TG), the sericite clay samples can be classified as: Group (I), sericite-kaolinite clays, with high or medium sericite content, characterized by an endothermic DTA peak of dehydroxylation of kaolinite with mass loss, which overlapped with dehydroxylation of sericite, and Group (II), sericite-kaolinite-pyrophyllite clays, with broader endothermic DTA peaks, in which kaolinite is dehydroxylated first and later sericite and pyrophyllite with the main mass loss, appearing the peaks overlapped. X-ray diffraction analysis of the heated sericite clay samples evidenced the decomposition of dehydroxylated sericite and its disappearance at 1050 A degrees C, with formation of mullite, the progressive disappearance of quartz and the formation of amorphous glassy phase. The vitrification temperature is similar to 1250 A degrees C in all these samples, with slight variations in the temperatures of maximum apparent density (2.41-2.52 g mL(-1)) in the range 1200-1300 A degrees C. The fine-grained sericite content and the presence of some mineralogical components contribute to the formation of mullite and the increase in the glassy phase by heating. Mullite is the only crystalline phase detected at 1400 A degrees C with good crystallinity. SEM revealed the dense network of rod-shaped and elongated needle-like mullite crystals in the thermally treated samples. These characteristics are advantageous when sericite clays are applied as ceramic raw materials.

Study of the thermal decomposition of historical metal threads

Perez-Rodriguez, JL; Perez-Maqueda, R; Franquelo, ML; Duran, A
Journal of Thermal Analysis and Calorimetry, **134** (2018) 15-22
Octubre, 2018 | **DOI:** 10.1007/s10973-017-6924-x

In this work, it is reported that thermal analysis techniques such as differential thermal analysis and thermogravimetric analysis are very useful for evaluating metals threads and fibres used in the manufacture of historical artifacts. Thermal analysis has been used to characterize the silk, cotton and linen employed as supports and the copper, silver and aluminium as the metallic components in the studied threads. Other organic compounds, mainly added for the conservation of the threads, have also been characterized.

The dizinc bond as a ligand: A computational study of elongated dizinc bonds

Ayala, R; Carmona, E; Galindo, A
Inorganic Chimica Acta, **470** (2018) 197-205
Enero, 2018 | **DOI:** 10.1016/j.ica.2017.06.008

Following the synthesis of [Zn-2(eta(2)-C5Me5)(2)] (in short [Zn2Cp*(2)]) many complexes of the directly bonded Zn-Zn unit were prepared and characterized, leading to the recognition of an isolobal analogy between the Zn-Zn bond and the molecule of dihydrogen. Prompted by these results, we have investigated eta(2)-eta(2)-coordination of [Zn2Cp2] and [Zn2Ph2] (Cp = C5H5, Ph = C6H5) to several selected transition metal fragments and report herein the results of a QTAIM study of complexes [(ZnR)(2)Fe(CO)(4)], [(eta(2)-Zn2R2)M(CO)(5)]] and [(eta(2)-Zn2R2)Pd(PR'(3))(2)] (for R = Cp, Ph; M = Cr, Mo, W; and R' = F, H, Me). A decrease of rho(BCP), Delta(2) rho(BCP) and delocalization indexes delta(Zn, Zn), relative to corresponding values in the parent molecules of [Zn2Cp2] and [Zn2Ph2], accompanied dizinc coordination. In most cases the computed d(Zn, Zn) parameters were indicative of significant electron density sharing between the two Zn atoms. Nevertheless, the interaction with [Fe(CO)(4)] resulted in oxidative cleavage of the coordinated Zn-Zn bond, due to high pi backdonation to the sigma* Zn-2 MO as deduced from the delta(M, O-CO) index. The Zn-Zn bond critical points identified in our study are discussed. The computed Zn-Zn contacts concentrate in the range 2.44-2.58 angstrom, and we propose that this interval corresponds to elongated dizinc bonds.

Mechanically induced combustion synthesis of niobium carbonitride nanoparticles

Jalaly, M; Gotor, FJ; Sayagues, MJ
Journal of Solid State Chemistry, **267** (2018) 106-112
Noviembre, 2018 | **DOI:** 10.1016/j.jssc.2018.08.027

Niobium carbonitride [Nb(C,N)] nanoparticles were synthesized by a combustive mechanochemical reaction in the Mg/Nb2O5/C3H6N6 system. High-energy ball milling was used to promote a mechanically induced self-sustaining reaction (MSR). Combustion occurred after a very short milling period of 5 min. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) analyses revealed that the nature of the product is an intermixed carbonitride material. The formation mechanism of Nb(C,N) resulted from the magnesiothermic reduction of niobium oxide to generate elemental Nb, which then reacted with the species generated from the melamine decomposition.

Obituary Note: Prof. Jose Manuel Criado

Perez-Maqueda, L; Koga, N; Malek, J
Thermochimica Acta, **663** (2018) A1
Mayo, 2018 | **DOI:** 10.1016/j.tca.2018.05.004

The late Prof. Jose Manuel Criado (1944.6.13–2018.2.27)

It is with the profoundest regret that we must report the passing of Prof. José Manuel Criado on February 27, 2018 at the age of 73. We express our most sincere condolences to his family, colleagues and friends.

Prof. Criado was born in Sevilla, Spain, on June 13th, 1944. He studied chemistry at the University of Seville and recieved his PhD from the same university under the supervision of Prof. Francisco González García and Prof. José María Trillo. He held a position as assistant professor at the Department of Inorganic Chemistry of the University of Seville from 1968 until 1972. Then, he joined the Consejo Superior de Investigaciones Científicas (CSIC) or National Research Council of Spain. In this institution he was junior researcher, senior researcher and, from 1986, full professor. Moreover, he has been visiting professor in a number of international institutions such as Stanford University (USA), CNRS Thermodynamics and Microcalorimetry Center in Marseille (France), University of Salford (UK), Macaulay Research Institute (UK), Institute of Inorganic Chemistry (Czech Republic), University of Chile (Chile). He had long-lasting collaborations with scientists from all over the world and visited labs in many countries. For many years, he used to spend some weeks abroad in the frame of collaboration projects with a number of international research groups, of special importance where his projects with the Czech Republic or Chile that lasted for over 20 years. He also served as an editorial board member of Thermochimica Acta for a long time and contributed largely to the further development of our academic field.

First research works of Prof. Criado were done within the field of heterogeneous catalysis, but very soon, he got interested in reactivity of solids and thermal analysis. Thus, most of his scientific career has been devoted to the study of kinetics of solid-state processes and mechanochemisty. He published about 240 papers in international journals. In the field of kinetics of solid-state processes, he made significant contributions, such as showing the limitations of using single linear heating rate experiments for extracting kinetic parameters, the proposal of master curves for discerning the kinetic model followed by the process or the combined analysis of experimental data obtained under different heating schedules. Moreover, after learning about the sample controlled thermal analysis (SCTA) method directly from Prof. Rouquerol in Marseille (France) and Profs. Paulik brothers in Budapest (Hungary), he constructed several of these instruments and extended the use of SCTA to the kinetic analysis of heterogeneous reactions, highlighting its advantages over conventional heating. Additionally, he used the kinetic control of solid-state processes by SCTA for the preparation of a number of functional and structural materials with controlled microstructures and properties. In the field of mechanochemistry, he made substantial contributions to the preparation of materials by gas–solid reaction using high energy planetary ball mills specially modified by him to work under controlled gas atmosphere.

Probably, the main contribution of Prof. Criado as a scientist has been as teacher and mentor for many of us. Despite of spending most of his scientific career in a research center rather than in a university, his laboratories were always full of students, postdocs and visitors from all over the world. He devoted a great effort to motivate and stimulate young people to pursue a career in science. His enthusiasm for science was sincere, as he loved science and research. Thus, he worked until the very last days and, even, when he could not go to the institute because he did not feel well, he worked in a small lab at home. He was very generous and always shared his knowledge with others. Thus, he expended long hours teaching about kinetics, making the complex equations easy to understand. Only those with a deep knowledge have this ability! It is not rare that many of his former students, postdocs and coworkers have permanent positions as professors and scientist in a number of international institutions. Another significant feature of Prof. Criado was his hospitality. He and his wife Maria Jesús Dianez, who joined his research group few years ago, has always his home doors open to any coworker or visitor.

We will all miss him not only as a scientist with a deep knowledge but as a friend we loved so much.

Synthesis, characterization and combined kinetic analysis of thermal decomposition of hydrotalcite ($Mg_6Al_2(OH)(_{16})CO_3$ center dot $4H(_2)O$)

Yahyaoui, R; Jimenez, PES; Maqueda, LAP; Nahdi, K; Luque, JMC
Thermochimica Acta, **667** (2018) 177-184
Septiembre, 2018 | **DOI:** 10.1016/j.tca.2018.07.025

Here, a kinetic study of the thermal decomposition of synthesized hydrotalcite, Mg-6 Al-2 $CO_3(OH)(16)$center dot H_2O, has been carried out using thermogravimetric experiments in air atmosphere. It is shown that the thermal decomposition occurs in two well differentiated stages. The first one is a single-step dehydration process that comprises the release of four water molecules. On the other hand, the second stage is complex and corresponds to both dehydroxylation and decarbonation processes which occur simultaneously. The kinetic parameters describing all processes were calculated by means of a combined approach comprising isoconversional, model-fitting and deconvolution methods. It was concluded that dehydroxilation and decarbonization cannot be separated by TG experiments and the two stages contributing to the complex process do not apparently match the expected stoichiometry of the process. Therefore, it is proposed that such stages mark a change on the reaction mechanism due to the structural collapse of the laminar double hydroxide.

Gildings from Andalusia: Materials used in different types of artworks along centuries

Perez-Rodriguez, JL; Robador, MD; Albardonedo, A; Duran, A
Journal of Cultural Heritage, **31** (2018) 112-121
Mayo, 2018 | **DOI:** 10.1016/j.culher.2017.11.009

The majority of the studied artworks were altarpieces, sculptures and/or wood-based works from different periods. Non-traditional gilding techniques have been first described in this paper, such as those that employ materials as oil in the gilding on bole, glue and bole with lead white in mordant gilding, vermilion in the preparation layers; and brass gilding or those with aluminium, lead chromate, mica or corla trying to imitate the golden hue in restoration or repaint processes. For the determination of the composition of the different gilded layers, spectroscopic techniques, such as FTIR and micro-Raman, and SEM-EDX elemental chemical analyses were successfully used.

Degradation of a LDPE film applied as a greenhouse cover design material: the effect of ageing and mechanical modelling

Garzon, Eduardo; Ortiz Rodriguez, Isabel Maria; Castillo, Jose; Sanchez-Soto, Pedro José
Revista de la Construcción, **17** (2018) 457-464
Diciembre, 2018 | **DOI:** 10.7764/RDLC.17.3.457 DEC 2018

In this work, we studied the mechanical performance of an LDPE film (0.22 mm in thickness) used as a material in the design of greenhouse covers. We investigated the effects of ageing at different periods of its service life and applying chemical substance treatments used as pesticides on greenhouse crops and after breakage using mechanical traction. Numerical simulations were performed using the finite element method. For this purpose, one section of the complete geometry of the greenhouse cover and different load conditions (1-5 kPa) were considered for the modelling. The performance of the polymer was assumed to be linearly elastic to simplify the governing equations. The study demonstrated that the LDPE film used was no longer effective as a greenhouse cover film due to the degradation of its mechanical properties. It was shown that the general performance of this film was in the plastic zone and its performance was non-linear. The results deduced from the present study are of interest because they show the material failure process of greenhouse covers in relation to the degradation process.

ARTICULOS PUBLICADOS EN REVISTAS (NO SCI) / PAPERS IN NON-SCI JOURNALS

Mesoporous silica by solution-combustion synthesis followed by Etching
F. Salehtash, M. Jalaly, H.B.M. Emrooz, F.J. Gotor, M.J. Sayagués
International Journal of Self-Propagating High-Temperature Synthesis, **27**[4] (2018) 221-227

Spark plasma sintered zirconia ceramic composites with graphene-based nanostructures
Gallardo-López, A.; López-Pernía, C.; Muñoz-Ferreiro, C.; González-Orellana, C.; Morales-Rodríguez, A.; Poyato, R.
Ceramics, **1** (2018) 153-154

Las vidrieras de la Catedral de Burgos (Reseña Bibliográfica)
P.J. Sánchez-Soto
Revista LLULL, **41** (2018) 223-260

LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS

Influence of Bauxite Ore on Chemical and Mineralogical Composition Variability of Red Mud
L. Pérez-Villarejo; D. Eliche-Quesada; B. Carrasco-Hurtado; P.J. Sánchez-Soto; S. Martínez-Martínez; G.N. Angelopoulos
Red Mud. Production, Composition and Impact, ed. Kay Richard, Nova Science Publishers Inc., New York, págs. 109-122

CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

PARTICIPACIÓN EN LA ORGANIZACIÓN DE CONGRESOS Y REUNIONES / PARTICIPATION IN ORGANISING AND MEETINGS

I Jornada de Jóvenes Investigadores de Cerámica y Vidrio en Sevilla

28 marzo [Sevilla, España]
Rosalía Poyato Galán [Miembro del Comité Organizador Local)

COMUNICACIONES / COMMUNICATIONS

VII Congreso Internacional de Biomateriales

12 – 16 marzo [La Habana, Cuba]

Effect of heat treatment on apatite coatings deposited on titanium surface modified by precalcification treatments
A.M. Beltrán, Y. Martín, J.E. González, I. Montealegre, E. Peón, E. González, F.J. Gotor, Y. Torres
Poster

42nd International Conference and Exposition on Advanced Ceramics and Composites

21 – 26 enero [Florida, Estados Unidos]

Young modulus and electrical conductivity of GNP/3YTZP composites prepared by PLS
C. Lopez Pernia; R. Poyato; A. Gallardo López; A. Morales Rodríguez
Comunicación oral

Effect of ball milling on microstructure of pressureless sintered GNP/3YTZP composite
C. Lopez-Pernia; A. Morales-Rodriguez; A. Gallardo-Lopez; R. Poyato
Poster

4th International Conference and Expo on Ceramics and Composite Materials

14 – 15 mayo [Roma, Italia]

Effect of the homogenization treatment on the microstructure and the electrical conductivity of 3YTZP/graphene nanoplatelet composites
C. Lopez-Pernia; C. Muñoz-Ferreiro; C. González-Orellana; A. Morales-Rodriguez; A. Gallardo-Lopez; R. Poyato
Comunicación oral

Role of sintering method on graphene/3YTZP composites
C. López-Pernía; R. Poyato; A. Morales-Rodríguez; A. Gallardo-López
Comunicación oral

XV Congreso Nacional de Materiales and I Iberian Meeting on Materials Science

4 – 7 junio [Salamanca, España]

Surface treatment of apatite coatings deposited on titanium for bio-medical applications
A.M. Beltrán, Y. Martín-Santana, J. González-Ruiz, P. Trueba, I. Montealegre-Meléndez, F.J. Gotor, J.A. Rodríguez-Ortiz, Y. Torres
Poster

Mechanical alloying of FeCoNiCrMn high entropy alloy: Effects of process control agents (PCA) on particle size
A.G. de la Obra, C. Real, E. Chicardi, F.J. Gotor
Poster

Effect of carbon content on the microstructure and mechanical properties of mechanochemically synthesized WC-HEA hard metals
L. Gómez-Millán, M.D. Alcalá, F.J. Gotor, C. Real, M.A. Avilés, J.M. Córdoba
Poster

XV Congreso Nacional de Materiales/ I Iberian Meeting on Material Science

4 – 6 julio [Salamanca, España]

Mechanosynthesis of titanate and aluminate perovskite based photocatalysts
Yunqing Tang, M. C. Hidalgo, M.A. Avilés, J.M. Córdoba
Conferencia Invitada

CIMTEC 2018

4 – 8 junio [Perugia, Italia]

Creep behaviour of alumina reinforced composites sintered by Spark Plasma Sintering
R. Cano-Crespo; B. Malmal-Moshtaghioun; D. Gómez-García; R. Moreno; A. Domínguez-Rodríguez
Comunicación oral

16th European Inter-Regional Conference on Ceramics | CIEC16

9 – 11 septiembre [Turin, Italia]

Key findings in the processing of ceramic composites based on zirconia and graphene platelets
A. Gallardo-López; C. López-Pernía; C. Muñoz-Ferreiro; C. González-Orellana; A. Morales-Rodríguez; R. Poyato
Comunicación oral

Study of the influence of graphene nanoplatelets on the hydrothermal degradation of zirconia in 3-YTZP/GNP composites
C. González-Orellana; A. Morales-Rodríguez; R. Poyato; A. Gallardo-López
Poster

Incorporating two-dimensional nanostructures as a second phase to a zirconia matrix
C. Muñoz-Ferreiro; R. Poyato; A. Morales-Rodríguez; Á. Gallardo-López
Poster

V Congreso Hispano-Luso de Cerámica y Vidrio, LVI Congreso de la Sociedad Española de Cerámica y Vidrio y II Reunión Bienal de la Sociedad Española de Cerámica y Vidrio

8 – 10 octubre [Barcelona, España]

In-situ reduced graphene oxide-zirconia composites consolidated by SPS
C. López-Pernía, R. Poyato, A. Morales-Rodríguez, A. Gallardo-López
Comunicación oral

Different powder homogenization techniques for obtaining 3YTZP/graphene nanoplatelet composites
R. Poyato, C. López-Pernía, C. Muñoz-Ferreiro, C. González-Orellana, A. Morales-Rodríguez, A. Gallardo-López
Comunicación oral

Fluencia a altas temperaturas de composites de alúmina y de composites de zircona reforzados con óxido de grafeno y con nanofibras de carbono sinterizados por SPS
R. Cano-Crespo; B. Malmal-Moshtaghioun; R. Moreno; D. Gómez-García; A. Domínguez-Rodríguez
Comunicación oral

Influence of the preferential graphene nanoplatelets alignment within the ceramic matrix on the scratch behavior
F. Gutiérrez-Mora, A. Gallardo-López, C. Muñoz-Ferreiro, A. Morales-Rodríguez, A. Muñoz, J.C. Sánchez-López, R. Poyato
Comunicación oral

Fabrication of 3D materials from graphene nano-platelets
Á. Gallardo-López, A. Morales-Rodríguez, R. Poyato
Poster

Sludge from marble cutting and treatment as raw material for sustainable eco-friendly cement
S. Martínez-Martínez; L. Pérez-Villarejo; P.J. Sánchez-Soto; A. Christogerou; D. Kanallepoulou; M. Kamitsou; G.N. Angelopoulos
Poster

Dureza y tenacidad a la fractura de composites de zirconа reforzados con nanofibras de carbono y con óxido de grafeno sinterizados por SPS
R. Cano-Crespo; B. Malmal-Moshtaghioun; R. Moreno; D. Gómez-García; A. Domínguez-Rodríguez
Poster

33º Congreso Latinoamericano de Química, X Congreso de Ciencias, Tecnología e Innovación Química

9 – 12 octubre [La Habana, Cuba]

Efecto del régimen de grabado ácido sobre las características superficiales de la aleación Ti6Al4V obtenida mediante fusión selectiva láser
J. Negrín-González, E. Peon, P. Sarria, A. López, A.M. Beltrán, F.J. Gotor, Y. Torres
Comunicación oral

CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESSES AND MEETINGS

COMUNICACIONES / COMMUNICATIONS

Congreso Nacional de Medio Ambiente | CONAMA 2018

28 – 29 noviembre [Madrid, España]

Desarrollo preliminar y estudio térmico de diferentes tipos de clínker de eco-cemento sostenible con el medio ambiente utilizando residuos industriales y piedra caliza con alto porcentaje en óxido de magnesio en su composición
S. Martínez-Martínez; L. Pérez-Villarejo; D. Eliche-Quesada; P.J. Sánchez-Soto; A. Christogerou; D. Kanellopoulou; M. Kamitsou; G.N. Angelopoulos
Comunicación oral

FORMACION / TRAINING

TESIS DOCTORALES/ DOCTOR DEGREE THESIS

Título:	**Sistemas de almacenamiento termoquímico para energía solar concentrada**
Autor:	Beatriz Sarrión Aceytuno

Directores: Luis Allan Pérez Maqueda y José Manuel Valverde Millán (US)
Calificación: Sobresaliente “Cum Laude”
Centro: Universidad de Sevilla
Fecha: 9 de noviembre de 2019

FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

Título: **Propagación de fisuras en compuestos 3YTZP con nanoplaquetas de grafeno preparados con diferentes rutas de procesado**
Autor: Javier Castillo Seoane
Directores: Rosalía Poyato Galán, Angela Gallardo López, Ana Morales Rodríguez
Grado: Trabajo Fin de Grado
Año Académico: 2017-2018 (junio 2018)

Título: **Fabricación de materiales de herramientas laminados del tipo cermet/WC-Co**
Autor: Eduardo Rodríguez Macarro
Directores: Francisco José Gotor Martínez
Grado: Trabajo Fin de Grado
Año Académico: 2017-2018 (29 junio 2018)

Título: **Diseño, fabricación y caracterización de laminados de tipo WC-Co/WC-Co**
Autor: Elena Fernández Carmona
Directores: Francisco José Gotor Martínez
Grado: Trabajo Fin de Grado
Año Académico: 2017-2018 (10 julio 2018)

Título: **Procesado, microestructura y propagación de fisuras en compuestos de 3YTZP con nanoestructuras bidimensionales**
Autor: Carmen Muñoz Ferreiro
Director: Rosalía Poyato Galán
Grado: Trabajo Fin de Master
Año Académico: 2017-2018 (10 septiembre 2018)

DOCENCIA / TEACHING

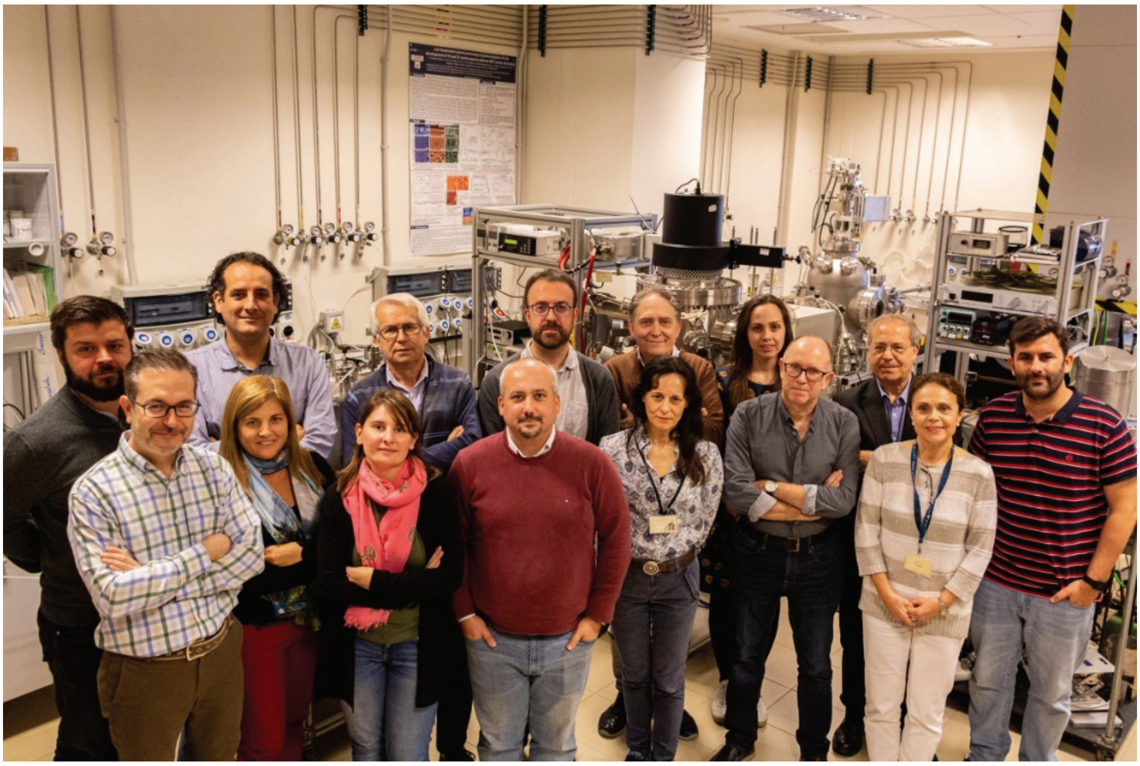
Máster en Biotecnología Sanitaria

Caracterización de materiales nanoestructurados
María Jesús Sayagués de Vega
Lugar: Universidad Pablo de Olavide

EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Microdurómetro FM700 Future-Tech
- Máquina de ensayo universal AGS-J, Shimadzu
- 3 Termobalanzas CI Electronics
- 2 molinos planetarios PULVERISETTE 7 (Fritsch)
- 1 molino planetario PULVERISETTE 7 Premium Line (Fritsch)
- 1 molino planetario PULVERISETTE 4 (Fritsch)
- 1 molino planetario PM100 (Retsch)
- 1 molino vibratorio MM301 (Retsch)
- 1 molino vibratorio SPEX 8000
- 1 molino centrífugo PULVERISETTE (Fritsch)
- 1 molino de atrición O1HD (Union Process)
- Horno horizontal alta temperatura 1800ºC AGNI
- Horno horizontal alta temperatura 1600ºC Carbolite
- Horno horizontal 1200ºC Carbolite
- Microcortadora metalográfica manual EVOLUTION (REMET)
- Microcortadora metalográfica MICROMET (REMET)
- Prensa automática metalográfica IPA30 (REMET)
- Pulidora automática LS2 (REMET)
- Analizador Termomecánico TMA 1000 (Linseis)
- Calorímetro diferencial de barrido DSC (TA instruments Q200)
- Horno horizontal 1150ºC Hobersal
- Impedancímetro Agilent 4294ª
- Multímetro Keysight B2901A
- Equipo de Hot-Press TERMOLAB

MATERIALES FUNCIONALES NANOESTRUCTURADOS
NANOSTRUCTURED FUNCTIONAL MATERIALS



GRUPOS DE INVESTIGACIÓN

Materiales Nanoestructurados y Microestructura
Nanostructured Materials and Microstructure [642015]
http://nanomatmicro.icmse.csic.

Materiales para Bioingeniería y Regeneración Tisular
Materials for Bioengineering and Tissue Regeneration [642014]

Nanotecnología en Superficies y Plasma
Nanotechnologies on Surfaces and Plasma [642012]
http://sincaf.icms.us-csic.es/

Tribología y Protección de Superficies
Tribology and Protection of Surfaces [861494]

PERSONAL / PERSONNEL

Profesores de Investigación

Dr. Juan Pedro Espinós Manzorro
Dra. Asunción Fernández Camacho
Dr. Agustín Rodríguez González-Elipe

Catedráticos

Dr. José Cotrino Bautista

Investigadores Científicos

Dr. Angel Barranco Quero
Dr. Juan Carlos Sánchez López
Dr. Francisco Yubero Valencia

Científicos Titulares

Dra. Ana Isabel Borrás Martos
Dra. María Aránzazu Díaz Cuenca
Dr. Alberto Palmero Acebedo
Dra. T. Cristina Rojas Ruiz

Investigadores Contratados

Dr. Rafael Álvarez Molina
Dra. Vanda C. Fortio Godinho
Dr. Jorge Gil Rostra
Dra. Ana María Gómez Ramírez
Dra. M. Carmen López Santos
Dr. Juan Ramón Sánchez Valencia

Becarios Predoctorales

Ldo. Aurelio García Valenzuela
Ldo. José Manuel Obrero Pérez

Personal Contratado

Ldo. Dirk Hufschmidt
Ing. Tec. M. Rocío García Gil

PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

Superficies super-hielofóbicas para prevenir la formación de hielo en aeroplanos Super-IcePhobic surfaces to prevent ice formation on aircraft

Código/Code:	H2020-TRANSPORT/0149
Periodo/Period:	01-02-2016 / 31-01-2019
Organismo Financiador/Financial source:	Unión Europea
Importe total/Total amount:	86.579,04 €
Investigador responsable/Research head:	Agustín R. González-Elipe

RESUMEN / ABSTRACT

La acumulación de hielo representa un grave problema para los aviones, ya que la presencia incluso de una capa apenas visible puede limitar seriamente la funcionalidad de las alas, las hélices, los parabrisas, las antenas, las rejillas de ventilación, las tomas de aire y las cubiertas. El Proyecto PHOBIC2ICE tiene como objetivo desarrollar tecnologías y herramientas de simulación predictiva para evitar o mitigar este fenómeno.

El proyecto PHOBIC2ICE, mediante la aplicación de un enfoque innovador de simulación y modelado, permitirá el diseño y fabricación de superficies hielofóbicas con funcionalidades mejoradas. Se desarrollarán varios tipos de recubrimientos poliméricos, metálicos e híbridos usando diferentes métodos de deposición. Se prepararán superficies tratadas con láser y anodizadas. En consecuencia, el proyecto se centra en la recopilación de conocimientos fundamentales sobre los fenómenos asociados con los problemas de repulsión de hielo. Este conocimiento dará una mejor comprensión del proceso de acreción de hielo en diferentes superficies modificadas y recubiertas. La infraestructura de investigación certificada (túnel de viento de hielo) y las pruebas de vuelo previstas ayudarán a desarrollar soluciones integrales para abordar la cuestión de la formación de hielo y elevarán el nivel de innovación del Proyecto.

La solución propuesta será respetuosa con el medio ambiente, contribuirá a la reducción del consumo de energía y ayudará a eliminar la necesidad de procedimientos frecuentes de deshielo sobre suelo. Esto contribuirá a la reducción del coste, la contaminación y el retraso de vuelo.

The accretion of ice represents a severe problem for aircraft, as the presence of even a scarcely visible layer can severely limit the function of wings, propellers, windshields, antennas, vents, intakes and cowlings. The PHOBIC2ICE Project aims at developing technologies and predictive simulation tools for avoiding or mitigating this phenomenon.

The PHOBIC2ICE project, by applying an innovative approach to simulation and modelling, will enable the design and fabrication of icephobic surfaces with improved functionalities. Several types of polymeric, metallic and hybrid coatings using different deposition methods will be developed. Laser treated and anodized surfaces will be prepared. Consequently, the Project focuses on collecting fundamental knowledge of phenomena associated with icephobicity issues. This knowledge will give better understanding of the ice accretion process on different coatings and modified surfaces. Certified research infrastructure (ice wind tunnel) and flight tests planned will aid in developing comprehensive solutions to address ice formation issue and will raise the Project's innovation level.

The proposed solution will be environment-friendly, will contribute to the reduction of energy consumption, and will help eliminate the need for frequent on-ground de-icing procedures. This in turn will contribute to the reduction of cost, pollution and flight delay.

Unión Europea
Fondo Europeo de Desarrollo Regional
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
"Una manera de hacer Europa"

Arquitecturas de multicapas nanostructuradas para el desarrollo de dispositivos optofluídicos sensores y procesos de funcionalización superficial avanzada (NANOFLOW)

Nanostructured multilayered architectures for the development of optofluidic responsive devices, smart labers, and advanced Surface functionalization (NANOFLOW)

Código/Code:	MAT2016-79866-R
Periodo/Period:	31-12-2016 / 31-12- 2019
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	332.750 €
Investigador responsable/Research head:	Angel Barranco Quero / Francisco Yubero Valencia
Componentes/Research group:	Ana Isabel Borrás Martos, Juan Pedro Espinós Manzorro, Fabián Frutos Rayego (US), Germán de la Fuente Leis (ICTP), Fernando Lahoz Zamarro (IPNA), Ricardo Molina Mansilla (IQAC), Alberto Palmero Acebedo, Victor Joaquin Rico Gavira, Agustín R. González-Elipe

RESUMEN / ABSTRACT

NANOFlow es un projecto multidisciplinar que persigue el desarrollo de nuevos dispositivos optofluídicos mediante la integración de materiales nanostructurados multifuncionales. El proyecto está sólidamente fundamentado en la experiencia de los componentes del grupo de investigación en campos como la síntesis de películas multifuncionales, procesos avanzados de modificación de superficies y en el desarrollo de dispositivos fotónicos multicapa. El objetivo principal de este proyecto de investigación es combinar e integrar los distintos métodos avanzados de síntesis y procesado disponibles en la fabricación de dispositivos optofluídicos singulares que sean capaces de responder a la presencia de líquidos mediante un cambio físico. La combinación de este tipo de procesos de integración junto con el desarrollo de nuevos métodos de de detección fotónica, el uso de microplasmas de gran área como fuentes de luz y de sustratos flexibles que incorporan elementos sensores definen un conjunto muy rico de posibilidades de desarrollo de aplicaciones prácticas que se explorarán en el proyecto. Además, en el proyecto también se llevarán a cabo estudios de simulación de crecimiento de películas delgadas que, en combinación con estudios

de diagnosis, permitirán ajustar los procesos de crecimiento para conseguir la funcionalidades requeridas. De esta forma, el proyecto NANOFlow intenta cubrir toda la cadena tecnológica que va desde el desarrollo de nuevos materiales hasta la aplicación final incluyendo estudios de caracterización, rutas sintéticas flexibles, búsqueda de procesos alternativos de bajo costo y alto rendimiento (por ejemplo métodos de fabricación empleando plasmas a presión atmosférica), integración de dispostivos y test de éstos en condiciones reales.

Las actividades de desarrollo planteadas en NANOFlow culminan en el desarrollo de tres tipos de dispositivos innovadores como son: las etiquetas inteligentes con actividad sensora y posibilidad de usarse como sistemas de trazabilidad y anticopia (por ejemplo integrados en el empaquetado de productos alimentarios), un dispositivos optofluídico multisensor versátil y un sistema de limpieza optofluídico fotocatalítico que integra una microplasma emisor de luz, interruptores ópticos de luz UV y visible actuados por líquidos y una superficie fotocatalítica nanoestructurada. Los tres dispositivos funcionan sobre la base de una actuación o respuesta optofluídica y están diseñados para poder usarse de forma directa en sistemas de detección, manipulación y monitorización de líquidos.

Las actividades de investigación en los distintos paquetes de trabajo del proyecto y los dispositivos finales se han propuesto para responder al Reto nº 2 de la convocatoria referida a “Seguridad y calidad alimentaria”. Además, algunas de las actividades del proyecto, por ejemplo el tercer dispositivo, están también relacionados con el Reto nº 3 “Energía Segura, eficiente y limpia”. Es interesante indicar que las actividades propuestas en NANOFlow son de particular relevancia en el contexto geográfico de Andalucía donde la agricultura, la producción de alimentos y la energía son tres de los más relevantes sectores estratégicos.

NANOFlow is a multidisciplinary Project that aims the development of novel optofluidics sensing devices integrating advanced multifunctional nanostructured materials. The project is solidly grounded in the research group experience in the synthesis of nanoestructured functional thin films, advance surface treatments and development of planar photonic structures The main objective of the project is to combine and integrate the available synthetic and processing methodologies in the fabrication of optofluidic components capable of modifying their physical behavior when they are exposed to liquids. The integration of these optofluidic components together with accessory technologies based on new principles of photonic detection, large surface area microplasmas discharge as light sources or flexible substrates for the fabrication of sensing tags define an ambitious landscape of applications that will be explored in the project. Besides, the modeling of thin film growth in combination with advanced deposition diagnosis methodologies will be combined to adjust the thin film deposition processes to the desired functionalities.Therefore, NANOFlow aims to cover all the scientific-technological chain from the materials development to the final applications including advanced characterization, flexible synthetic routes, alternative low-cost and high throughput process (e.g. atmospheric plasma synthesis), device integration and testing of devices in real conditions.

The NANOFlow research activities will culminate in the development of three innovative devices, namely smart labels for sensing, traceability and anticounterfeiting applications (e.g. smart labels incorporated in food-packaging), a versatile optofluidic multisensing device and an optofluidic photocatalytic cleaning system that will integrate a large area microplasma source, liquid actuated UV/Visible optical switches and a photocatalytic nanostructured surface. All of these devices will operate under the basis of an optofluidic actuation and/or response and are designed to present clear potentialities for direct application in liquid sensing, manipulation and monitoring.

The NANOFlow research activities in the different work-packages and, particularly, the final devices are intended to have a direct impact in the Theme 2 (Seguridad and Calidad Alimentaria) of the "RETOS" defined in the call covering this project proposal.. Besides, some of the activities proposed, in particular the third device are also connected with the Theme 3 (Energía segura eficiente y limpia) of the call. It is very interesting to stress that these activities are of particular relevance in the geographical context of Andalucia where Agriculture, Food production and Energy are three of the most relevant strategic sectors.

Recubrimientos para aplicaciones en energía y alta temperatura High temperatura energy application coatings

Código/Code:	MAT2015-65539-P
Periodo/Period:	01-01-2016 / 31-12-2019
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	83.006 €
Investigador responsable/Research head:	Juan Carlos Sánchez López
Componentes/Research group:	Teresa Cristina Rojas Ruiz, Maria Belinda Sigüenza Carballo, Iñigo Braceras Izaguirre, Marta Brizuela Parra

RESUMEN / ABSTRACT

La protección de las superficies frente a la temperatura, los fenómenos de oxidación o el desgaste ha logrado un progreso substancial mediante el desarrollo de nuevos materiales y recubrimientos con propiedades mejoradas tales como dureza extrema, baja fricción y tasas de desgaste, elevada resistencia ante la temperatura y la oxidación. Estas mejoras suponen un enorme ahorro de energía y reducción de costes debido a la vida media de los componentes mecánicos sin necesidad de sustitución, así como, a una reducción del impacto medioambiental. Este campo de investigación tiene una profunda repercusión en una gran variedad de sectores industriales (energía, herramientas de mecanizado, automoción, aeronáutico, metalurgia, etc.). El reto para la mayoría de estos procesos de funcionalización superficial residen en un control estricto de la micro y nanoestructura de la superficie y de las intercaras que hagan posible la aparición de nuevas propiedades y aplicaciones que la nanotecnología ofrece.

En este proyecto, se prepararán recubrimientos nanoestructurados para la protección de componentes sometidos a altas temperaturas y ambientes agresivos buscando un comportamiento mejorado. Este objetivo será abordado para tres diferentes aplicaciones que contribuirían a procesos energéticos más eficientes, energías renovables y soluciones para disminuir el impacto medioambiental. Basándonos en el sistema Cr-Al-N, se depositarán diferentes recubrimientos mediante la técnica de pulverización catódica reactiva cambiando la

composición química (contenido en metal, incorporación de dopantes tales como Y o Si); microestructura; distribución de fases; arquitectura (multicapa/nanocomposite) o estructuras más complejas (tándem, multicapa en gradiente) sobre los sustratos apropiados dependiendo de la aplicación prevista: a) resistencia a la oxidación a alta temperatura (hasta 1000ºC) para herramientas; b) absorbedores solares selectivos estables térmicamente a medias (300-500ºC) y alta temperatura (>600ºC); resistencia a la corrosión para componentes en turbinas de vapor supercríticos (650ºC/100% vapor).

La investigación sobre los mecanismos de oxidación, transformaciones de fases, modificaciones estructurales, etc. serán objeto de un estudio detallado sobre los sustratos definidos para lograr un conocimiento fundamental sobre los procesos de degradación y los efectos protectores. El establecimiento de correlaciones entre las propiedades iniciales y el comportamiento funcional permitirá una mejor comprensión de los mecanismos de protección y por ende, una optimización de tales sistemas en forma de recubrimientos nanoestructurados para las aplicaciones previstas.

The protection of surfaces from thermal, wear and oxidation phenomena has reached a substantial progress by developing new materials and coatings with improved properties as extreme hardness, low friction and wear rates, increased thermal and oxidation resistance. These improvements suppose a huge energy-saving and cost reduction due to the increased life-time of mechanical components without needs of replacement as well as a reduction in the environmental impact. This field of research has a deep impact in a large variety of industrial sectors (energy, machining tools, automotive, aeronautic, metallurgy, etc.). The challenge for most of these surface functionalization procedures is to get a strict control of the micro and nanostructure of the surface and interfaces that make possible the advent of new properties and applications that nanotechnology concept offers.

In this project, tailored nanostructured coatings for protection of components submitted to high temperature and aggressive environments are prepared seeking for an improved performance. This goal will be explored for three different applications that would contribute to an energy efficiency, renewable energies and solutions to decrease environmental impact. Based on the Cr-Al-N system, different coatings will be prepared by reactive magnetron sputtering technology changing chemical composition (metal content, incorporation of dopants like Y or Si); microstructure; phase distribution; architecture (multilayer/ nanocomposite) or more complex structures (tandem, multilayer gradient) on appropriated substrates depending on the foreseen application: a) oxidation resistance at high temperature (up to 1000ºC) for tool components; b) thermal stable solar selective absorber coating for mid (300-500ºC) and high temperature (>600ºC); c) corrosion resistant coating for supercritical turbine components (650ºC and 100% steam atmosphere).

The investigation of the oxidation mechanisms, phase transformations, structural modifications, etc. will be object of a careful study directly over the defined substrates for these applications to get fundamental knowledge on the degradation phenomena and protective effects. The establishment of the relationships between the initial properties and observed functional performance will enable the better understanding of the protection mechanisms and the optimization of such nanostructured coating systems for the selected application.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Desarrollo de catalizadores soportados sobre estructuras porosas para aplicaciones de generación y combustión catalítica de hidrógeno en el contexto de energías renovables

Development of supported catalysts on porous structrures for hydrogen generation and catalytic combustión applications in the framework of renewable energies

Código/Code:	CTQ2015-65918-R
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	177.870 €
Investigador responsable/Research head:	Asunción Fernández Camacho
Componentes/Research group:	Mª Carmen Jiménez de Haro, Vanda Godinho, Gisela Arzac, Dirk Hufschmidt, Rocio García

RESUMEN / ABSTRACT

El agotamiento de combustibles fósiles a corto y medio plazo y los cambios climáticos producidos por el efecto invernadero son algunas de las principales consecuencias del uso extendido de estos combustibles. En este escenario el hidrógeno como vector de transporte y almacenamiento de energía es un candidato muy atractivo en el contexto de un mayor uso de las energías renovables y limpias. En consecuencia se plantean actualmente retos importantes para el desarrollo de tecnologías adecuadas, tanto en la producción de hidrógeno libre de CO2, como en su transporte y almacenamiento seguro, y en su combustión eficiente para producir calor ó electricidad en una pila de combustible. Sobre la base de los proyectos previos del grupo en el estudio de hidruros complejos para almacenamiento de hidrógeno y en el desarrollo de catalizadores y procesos integrados de generación y uso del hidrógeno en aplicaciones portátiles; se abordarán en este proyecto nuevas investigaciones para desarrollar catalizadores novedosos soportados sobre estructuras porosas: membranas y espumas de materiales poliméricos, metálicos y cerámicos de alto interés actual. Los catalizadores se desarrollarán y estudiarán en reacciones seleccionadas de generación y combustión de acuerdo a las siguientes líneas de actuación:

1) Desarrollo de materiales novedosos con alto valor añadido del conjunto soporte-catalizador. Por un lado los soportes porosos basados en membranas de PTFE, espumas metálicas de Ni y espumas cerámicas de SiC. El objetivo es desarrollar los nuevos catalizadores sobre soportes de interés como membranas separadoras, electrolitos, electrodos ó combustores de hidrógeno. Los nuevos catalizadores persiguen la reducción del uso de metales nobles (i.e. bimetálicos Pt-Cu, Ni-Fe) y el desarrollo de nuevos materiales metal-metaloide (carburos, boruros, etc.). Se usarán métodos químicos de impregnación, y muy especialmente

la tecnología de deposición de películas delgadas, pulverizacón catódica, que hemos aplicado recientemente con éxito a la fabricación de catalizadores de Co. La metodología abre un campo de investigación de gran interés al permitirnos el control de la microestructura y/o la composición (i.e. Co, Co-B, Co-C) de los catalizadores a demanda.

2) La caracterización microestructural y química de los nuevos materiales y catalizadores desarrollados en el proyecto. Se trata típicamente de materiales con una microestructura y nanoestructura controlada en donde las modernas técnicas nanoscopicas van a jugar un papel fundamental en la fabricación a medida de estos.

3) Estudio de actividad en tres ensayos catalíticos: i) la generación hidrolítica de hidrógeno, ii) la descomposición fotocatalítica del agua y iii) la combustión catalítica del hidrógeno. Todas ellas reacciones de alto interés en el contexto del uso del hidrógeno como vector de transporte y almacenamiento de energías renovables.—Sobre la base de los resultados obtenidos en estas líneas de actuación, el proyecto se ha diseñado para alcanzar un conocimiento fundamental y un diseño racional en la nanoescala de catalizadores soportados en sustratos porosos. Las relaciones composición-estructura-propiedades se investigarán usando los ensayos catalíticos y fotocatalíticos acoplados a la microscopía electrónica de alta resolución analítica y otras técnicas espectroscópicas.

The depletion of fossil fuels (in a short and long term) and the global warming derived from greenhouse effect are consequences of the extensive use of these fuels. In this context, hydrogen appears as an attractive, clean and abundant energy carrier in the context of a wider use of clean and removable energies. For the implementation of the "hydrogen economy" many technological challenges regarding hydrogen production (free from CO2), transport, storage (in a safe manner) and combustion (to produce heat or electricity) should be met first. New research will be conducted in this project on the basis of our previous results regarding the study of complex hydrides for hydrogen storage and the development of catalysts and processes for hydrogen generation and use in portable applications. In particular, new catalysts will be developed on porous structures such as polymeric, metallic and ceramic membranes and/or foams with high actual interest. Catalysts will we developed and studied for hydrogen generation and combustion reactions according to the following research lines:

1) Development of new materials (catalysts and supports) with a high added value of the complete system catalyst + support. Porous Ni and SiC foams together with PTFE membranes will be selected as supports for the studies. The main objective is to design new catalysts on technologically interesting supports such as separating membranes, electrolytes, electrodes and/or hydrogen combustors. These new catalysts will be developed following the objective of reducing the amount of noble metals by combining or replacing with another non-noble metals (e.g. Pt-Cu and Ni-Fe) and/or with metalloids (e.g carbides, borides, etc). Wet impregnation methods will be used and special emphasis will be put on the use of the PVD methodology (magnetron sputtering) recently employed in our laboratory for the fabrication of Co thin films with very good results. The latter methodology opens a highly interesting research field because permits to tune microstructure and composition (i.e. Co, Co-B, Co-C) on demand.

2) Characterization of the prepared materials from a microstructural and chemical point of view. Modern nanoscopies will play a key role in the characterization, comprehension and further improvement of these highly nanostructured catalysts.

3) Catalytic studies on the prepared materials will be carried out in three catalytic tests: i) the hydrogen generation through hydrolysis reactions, ii) the photocatalytic water splitting, and iii) the catalytic hydrogen combustion. These reactions are of high interest in the context of the hydrogen economy.—The interaction of these three research lines as proposed in this project will permit to achieve basic knowledge on the rational design of nanocatalysts supported on porous materials. Structure-composition-activity relationships will be established through catalytic and photo-catalytic studies in combination with characterization techniques based on high resolution analytical TEM and additional spectroscopic techniques.

OTROS PROYECTOS / OTHER PROJECTS

Red de Terapia Cellular (TERCEL)

Código/Code:	RD16/0011/0022
Periodo/Period:	01-01-2016 / 31-12-2020
Organismo Financiador/Financial source:	Instituto de Salud Carlos III
Importe total/Total amount:	182.286,50 €
Investigador responsable/Research head:	José Becerra Ratia (UMA)
Componentes/Research group:	Daniel Amat Trujillo (CIBER-BBN), Maria Aránzazu Díaz Cuenca, Leonor Santos Ruiz (CIBER-BBN)

Implantes personalizados de titanio poroso bioingenierizados para cirugía constructiva maxilofacial. Pruebas de concepto y ensayo preclinico

Código/Code:	BIO2015-66266-R
Periodo/Period:	01-01-2016 / 31-12-2018
Organismo Financiador/Financial source:	Ministerio Economia y Competitividad
Importe total/Total amount:	133.100 €
Investigador responsable/Research head:	José Becerra Ratia (UMA)
Componentes/Research group:	Maria Aránzazu Díaz Cuenca, Leonor Santos Ruiz (CIBER-BBN)

Desarrollo de capas finas y nanoestructuradas porosas mediante técnicas de evaporación y plasmas para el desarrollo de materiales y sistemas de detección avanzados

Código/Code:	201560E055
Periodo/Period:	01-07-2015 / 30-06-2019
Organismo Financiador/Financial source:	CSIC (Intramural)
Importe total/Total amount:	229.723 €
Investigador responsable/Research head:	Agustín R. González-Elipe

Sostenibilidad de las líneas estratégicas Materiales Nanoestructurados y Microestructura (NANOMAT)

Código/Code: 201760E002
Periodo/Period: 01-01-2017 / 31-12-2019
Organismo Financiador/Financial source: CSIC (Intramural)
Importe total/Total amount: 325.481 €
Investigador responsable/Research head: Asunción Fernández Camacho

Funcionalización superficial de materiales para aplicaciones avanzadas

Código/Code: 201560E055
Periodo/Period: 01-07-2015 / 30-06-2019
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 51.500 €
Investigador responsable/Research head: Agustín R. González-Elipe

Preparación de dispositivos microfluídicos magnetoópticos basados en películas delgadas magnéticos porosas

Código/Code: COOPB20349
Periodo/Period: 01-01-2018 / 31-12-2019
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad (Programa CSIC de Cooperación Científica para el desarrollo I-COOP+)
Importe total/Total amount: 19.900 €
Investigador responsable/Research head: Francisco Yubero Valencia

NanoDispositivos 3D (NanoD3D): Nanohilos y nanoárboles para la nueva generación de nanodispositivos autoalimentados

Código/Code: EUIN2017-89059
Periodo/Period: 01-01-2018 / 31-12-2019
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 10.000 €
Investigador responsable/Research head: Ana Isabel Borras Martos

Sensores optofluídicos y electroquímicos 1D preparados mediante técnicas de PVD a ángulo rasante

Código/Code: 201860E050
Periodo/Period: 01-06-2018 / 31-05-2021
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 208.029 €
Investigador responsable/Research head: Agustín R. González-Elipe

CONVENIOS Y CONTRATOS / CONTRACTS AND AGREEMENTS

Conjunto de análisis de componentes de dispositivos espaciales y elementos relacionados con su fabricación

Periodo/Period: 14-09-2018 / 31-10-2018
Organismo Financiador/Financial source: ALTER TECHNOLOGY TÜV NORD S.A.U.
Importe total/Total amount: 7.139 €
Investigador responsable/Research head: Ana Isabel Borras Martos

Procesos de activación de cintas poliméricas metalizadas para condensadores

Periodo/Period: 01-11-2017 / 30-04-2018
Organismo Financiador/Financial source: EPCOS ELECTRONIC COMPONENTS, S.A.
Importe total/Total amount: 43.560 €
Investigador responsable/Research head: José Cotrino Bautista

Monitorización en tiempo real de múltiples propiedades de fluidos mediante transductores fotónicos y electromagnéticos (REMO)

Periodo/Period: 01-09-2015 / 30-09-2018
Organismo Financiador/Financial source: Universidad Carlos III, Indra Sistemas S.A., Universidad Politécnica de Madrid, Repsol S.A.
Importe total (ICMS)/Total amount (ICMS): 220.000 €
Investigador responsable (ICMS)/Research head (ICMS): Agustín R. González-Elipe
Componentes/Research group: Francisco Yubero Valencia, Jorge Gil Rostra, Victor Rico Gavira, Juan Pedro Espinós Manzorro, Angel Barranco Quero, Ana Isabel Borrás Martos

Caracterización superficial de membranas de ósmosis inversa

Periodo/Period: 06-04-2018 / 01-04-2020
Organismo Financiador/Financial source: ACCIONA AGUA, S.A.U.
Importe total/Total amount: 11.371 €
Investigador responsable/Research head: Juan Pedro Espinós Manzorro

Desarrollo de Capas PVD

Periodo/Period: 08-05-2017 / 07-05-2019
Organismo Financiador/Financial source: FLUBETECH, S.L.
Importe total/Total amount: 7.260 €
Investigador responsable/Research head: Juan Carlos Sánchez López

Research on tribological systems. Functional coatings and their characterization

Periodo/Period: 23-10-2014 / 31-12-2018
Organismo Financiador/Financial source: Robert Bosch Gmbh
Importe total/Total amount: 24.490 €
Investigador responsable/Research head: Juan Carlos Sánchez López
Componentes/Research group: Santiago Domínguez Meister

Caracterización microstructural y química de materiales para avisadores sonoros

Periodo/Period: 19-01-2010 / 31-12-2018
Organismo Financiador/Financial source: CLARTON HORN
Importe total/Total amount: 41.491 €
Investigador responsable/Research head: Asunción Fernández Camacho
Componentes/Research group: Vanda Fortio Godinho

Cooperación Internacional y Otros International Cooperation and Others

Nano-Phenomena and Functionality of Modern Carbon-Based Tribo-Coatings

Periodo/Period: 1-06-2015 / 30-06-2018
Código/Code: CARBTRIB
Entidad Financiadora/Financial source: Leverhulme Trust (UK)
Investigador responsable/Research head: Feodor Borodich
Participantes/Participants: Juan Carlos Sánchez López

Universidad Nacional de Ciencia y Tecnología de Rusia (National University of Science and Technology «MISiS») y la Agencia Estatal Consejo Superior de Investigaciones Científicas (CSIC) a través del Instituto de Ciencia de Materiales de Sevilla (ICMS)

Periodo/ Period: 02-12-2016 / 01-02-2019
Código/Code: C-ES-2016-101
Referencia VATC: 20171119
Investigador responsable/Research head: Juan Carlos Sánchez López

EXPERIMENTOS EN GRANDES INSTALACIONES / LARGE FACILITY EXPERIMENTS

Sincrotrón BESSY II / BESSY II Synchrotron

Influence of surface dynamics on the catalytic properties of a PtCu model catalyst for PrOx reaction

Código/Code:	181-06759 ST/R Magnetic domains behaviour in a concentric spin valve nanowire
Periodo/Period:	26-03-2018 / 29-03-2018
Organismo Financiador/Financial source:	BESSY II Synchrotron
Instalación Científica:	1.1-P: UE49_PGM SPEEM
Investigador principal/Research head:	Víctor López-Flores
Investigadores/Researchers:	J.R. Sánchez-Valencia, A. Borrás

PATENTES / PATENTS

Sensor, apparatus and method for determining a concentration of a solute in a solution

Inventores: Francisco Yubero Valencia, Angel Barranco Quero, Agustín Rodríguez González-Elipe, Manuel Oliva Ramírez
Tipo de Patente: Internacional
Número de Solicitud: PCT/ES2016/070764
Fecha Solicitud: 26 de abril de 2018
Entidad Titular: Consejo Superior de Investigaciones Científicas, Universidad Politécnica de Madrid y Universidad de Zaragoza

Procedimiento de obtención de un material sólido con agregados gaseosos mediante pulverización catódica por magnetrón en condiciones estáticas o cuasiestáticas para reducir el consumo de gas

Inventores: Dirk Hufschmidt, Vanda Fortio Godinho, M. Carmen Jiménez de Haro, M. Asunción Fernández Camacho
Tipo de Patente: Nacional
Número de Solicitud: 201831107
Fecha Solicitud: 15 de noviembre de 2018
Entidad Titular: Consejo Superior de Investigaciones Científicas

ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

Nanoporous Pt-based catalysts prepared by chemical dealloying of magnetron-sputtered Pt-Cu thin films for the catalytic combustion of hydrogen

Giarratano, F; Arzac, GM; Godinho, V; Hufschmidt, D; de Haro, MCJ; Montes, O; Fernandez, A
Applied Catalysis B: Environmental, **235** (2018) 168-176
Noviembre, 2018 | **DOI:** 10.1016/j.apcatb.2018.04.064

In this work, we prepared SiC-supported Pt-Cu thin films by magnetron sputtering for use as catalysts for the combustion of hydrogen under oxidizing conditions. We tested the catalysts as prepared and after chemical dealloying. A methodology is presented to fabricate catalytic thin films of a desired composition with tailored magnetron targets with lower Pt consumption. The deposition gas was changed to prepare columnar (Ar-deposited) and closed-porous (He-deposited) films to study the effect of the microstructure on the activity. The effect of composition was also studied for the columnar samples. The as-prepared Pt-Cu thin films showed significant activity only at temperatures higher than 100 °C. Dealloying permitted an increase in the activity to achieve near room-temperature activity. The dealloyed closed-porous He-deposited sample was the most active, being able to convert as much as 13.15 LH2·min−1 gPt−1 at 70 °C (Ea = 1 kJ mol−1). This sample was preferentially dealloyed on the surface, yielding an almost pure Pt shell (96% at. Pt) and a Cu-depleted interior (71% at. Pt). This compositional inhomogeneity enabled the sample to achieve enhanced activity compared to the Ar-deposited columnar sample (with similar initial composition, but uniformly dealloyed), probably due to the compressive surface lattice strain. The dealloyed closed-porous He-deposited sample was shown to be durable over five cycles.

Self-Assembly of the Nonplanar Fe(III) Phthalocyanine Small-Molecule: Unraveling the Impact on the Magnetic Properties of Organic Nanowires

Filippin, AN; Lopez-Flores, V; Rojas, TC; Saghi, Z; Rico, VJ; Sanchez-Valencia, JR; Espinos, JP; Zitolo, A; Viret, M; Midgley, PA; Barranco, A; Borras, A
Chemistry of Materials, **30** (2018) 879-887
Febrero, 2018 | **DOI:** 10.1021/acs.chemmater.7b04515

In this article we show for the first time the formation of magnetic supported organic nanowires (ONWs) driven by self-assembly of a nonplanar Fe(III) phthalocyanine chloride (FePcCl) molecule. The ONWs grow by a crystallization mechanism on roughness-tailored substrates. The growth methodology consists of a vapor deposition under low vacuum and mild temperature conditions. The structure, microstructure, and chemical composition of the FePcCl NWs are thoroughly elucidated and compared with those of Fe(II) phthalocyanine NWs by a consistent and complementary combination of advanced electron microscopies and X-ray spectroscopies. In a further step, we vertically align the NWs by conformal deposition of a SiO_2 shell. Such orientation is critical to analyze the magnetic properties of the FePcCl and FePc supported NWs. A ferromagnetic behavior below 30 K with an easy axis perpendicular to the phthalocyanine plane was observed in the two cases with the FePcCl nanowires presenting a wider hysteresis.

These results open the path to the fabrication of nanostructured one-dimensional small-molecule spintronic devices.

Enhancing Moisture and Water Resistance in Perovskite Solar Cells by Encapsulation with Ultrathin Plasma Polymers

Idigoras, J; Aparicio, FJ; Contreras-Bemal, L; Ramos-Terron, S; Alcaire, M; Sanchez-Valencia, JR; Borras, A; Barranco, A; Anta, JA

ACS Applied Materials & Interfaces, **10** (2018) 11587-11594

Abril, 2018 | **DOI:** 10.1021/acsami.7b17824

A compromise between high power conversion efficiency and long-term stability of hybrid organic inorganic metal halide perovskite solar cells is necessary for their outdoor photovoltaic application and commercialization. Herein, a method to improve the stability of perovskite solar cells under water and moisture exposure consisting of the encapsulation of the cell with an ultrathin plasma polymer is reported. The deposition of the polymer is carried out at room temperature by the remote plasma vacuum deposition of adamantane powder. This encapsulation method does not affect the photovoltaic performance of the tested devices and is virtually compatible with any device configuration independent of the chemical composition. After 30 days under ambient conditions with a relative humidity (RH) in the range of 35-60%, the absorbance of encapsulated perovskite films remains practically unaltered. The deterioration in the photovoltaic performance of the corresponding encapsulated devices also becomes significantly delayed with respect to devices without encapsulation when vented continuously with very humid air (RH > 85%). More impressively, when encapsulated solar devices were immersed in liquid water, the photovoltaic performance was not affected at least within the first 60 s. In fact, it has been possible to measure the power conversion efficiency of encapsulated devices under operation in water. The proposed method opens up a new promising strategy to develop stable photovoltaic and photocatalytic perovskite devices.

In situ monitoring of the phenomenon of electrochemical promotion of catalysis

Espinos, JP; Rico, VJ; Gonzalez-Cobos, J; Sanchez-Valencia, JR; Perez-Dieste, V; Escudero, C; de Lucas-Consuegra, A; Gonzalez-Elipe, AR

Journal of Catalysis, **358** (2018) 27-34

Febrero, 2018 | **DOI:** 10.1016/j.jcat.2017.11.027

In this work we investigate by in-situ near-ambient pressure photoemission (NAPP) spectroscopy the phenomenon of Electrochemical Promotion of Catalysis (EPOC). We studied the reduction and diffusion kinetics of alkaline ions in a solid electrolyte cell formed by a nickel electrode supported on K+-beta-alumina electrolyte. Experiments in ultra-high vacuum and in the presence of steam showed that the amount of potassium atoms supplied to the surface is probably affected by nickel electronic modifications induced by adsorbed OH- groups. It was also deduced that part of the segregated potassium would be adsorbed at inner interfaces where it would be inaccessible to the photoelectron analyzer. A migration mechanism of the promoter is proposed consisting in: (i) the electrochemical reduction of the alkali ions (potassium) at the Ni/solid electrolyte/gas interface; (ii) the spillover of potassium atoms onto the Ni gas-exposed surface; and (iii) the diffusion of potassium atoms to Ni inner grain boundary interfaces.

Dye Giant Absorption and Light Confinement Effects in Porous Bragg Microcavities

Oliva-Ramirez, M; Gil-Rostra, J; Simonsen, AC; Yubero, F; Gonzalez-Elipe, AR
ACS Photonics, **5** (2018) 984-991
Marzo, 2018 | **DOI:** 10.1021/acsphotonics.7b01283

This work presents a simple experimental procedure to probe light confinement effects in photonic structures. Two types of porous 1D Bragg microcavities with two resonant peaks in the reflection gap were prepared by physical vapor deposition at oblique angle configurations and then infiltrated with dye solutions of increasing concentrations. The unusual position shift and intensity drop of the transmitted resonant peak observed when it was scanned through the dye absorption band have been accounted for by the effect of the light trapped at their optical defect layer. An experimentally observed giant absorption of the dye molecules and a strong anomalous dispersion in the refractive index of the solution are claimed as the reasons for the observed variations in the Bragg microcavity resonant feature. Determining the giant absorption of infiltrated dye solutions is proposed as a general and simple methodology to experimentally assess light trapping effects in porous photonic structures.

Copper-containing mesoporous bioactive glass promotes angiogenesis in an in vivo zebrafish model

Romero-Sanchez, LB; Mari-Beffa, M; Carrillo, P; Medina, MA; Diaz-Cuenca, A
Acta Biomateriala, **68** (2018) 272-285
Marzo, 2018 | **DOI:** 10.1016/j.actbio.2017.12.032

The osteogenic and angiogenic responses of organisms to the ionic products of degradation of bioactive glasses (BGs) are being intensively investigated. The promotion of angiogenesis by copper (Cu) has been known for more than three decades. This element can be incorporated to delivery carriers, such as BGs, and the materials used in biological assays. In this work, Cu-containing mesoporous bioactive glass (MBG) in the SiO2-CaO-P2O5compositional system was prepared incorporating 5% mol Cu (MBG-5Cu) by replacement of the corresponding amount of Ca. The biological effects of the ionic products of MBG biodegradation were evaluated on a well-known endothelial cell line, the bovine aorta endothelial cells (BAEC), as well as in an in vivo zebrafish (Danio rerio) embryo assay. The results suggest that ionic products of both MBG (Cu free) and MBG-5Cu materials promote angiogenesis. In vitro cell cultures show that the ionic dissolution products of these materials are not toxic and promote BAEC viability and migration. In addition, the in vivo assay indicates that both exposition and microinjection of zebrafish embryos with Cu free MBG material increase vessel number and thickness of the subintestinal venous plexus (SIVP), whereas assays using MBG-5Cu enhance this effect.

Robust polarization active nanostructured 1D Bragg Microcavities as optofluidic label-free refractive index sensor

Oliva-Ramirez, M; Gil-Rostra, J; Yubero, F; Gonzalez-Elipe, AR
Sensors and Actuators B-Chemical, **256** (2018) 590-599

Marzo, 2018 | **DOI:** 10.1016/j.snb.2017.10.060

In this work we report the use of polarization active porous 1D Bragg microcavities (BM) prepared by physical vapor deposition at oblique angles for the optofluidic analysis of liquid solutions. These photonic structures consist of a series of stacked highly porous layers of two materials with different refractive indices and high birefringence. Their operational principle implies filling the pores with the analyzed liquid while monitoring with linearly polarized light the associated changes in optical response as a function of the solution refractive index. The response of both polarization active and inactive BMs as optofluidic sensors for the determination of glucose concentration in water solutions has been systematically compared. Different methods of detection, including monitoring the BM wave retarder behavior, are critically compared for both low and high glucose concentrations. Data are taken in transmission and reflection modes and different options explored to prove the incorporation of these nanostructured transducers into microfluidic systems and/or onto the tip of an optical fiber. This analysis has proven the advantages of the polarization active transducer sensors for the optofluidic analysis of liquids and their robustness even in the presence of light source instabilities or misalignments of the optical system used for detection.

Tribological properties of TiC/a-C:H nanocomposite coatings prepared via HiPIMS

Sanchez-Lopez, JC; Dominguez-Meister, S; Rojas, TC; Colasuonno, M; Bazzan, M; Patelli, A

Applied Surface Science, **440** (2018) 458-466
Mayo, 2018 | **DOI:** 10.1016/j.apsusc.2018.01.135

High power impulse magnetron sputtering (HiPIMS) technology has been employed to prepare TiC/a-C:H nanocomposite coatings from a titanium target in acetylene (C2H2) reactive atmospheres. Gas fluxes were varied from 1.3 to 4.4 sccm to obtain C/Ti ratios from 2 to 15 as measured by electron probe microanalysis (EPMA). X-ray diffraction and transmission electron microscopy demonstrate the presence of TiC nanocrystals embedded in an amorphous carbon-based matrix. The hardness properties decrease from 17 to 10 GPa as the carbon content increases. The tribological properties were measured using a pinon-disk tribometer in ambient air (RH = 30-40%) at 10 cm/s with 5 N of applied load against 6-mm 100Cr6 balls. The friction coefficient and the film wear rates are gradually improved from 0.3 and 7 x 10(-6) mm(3)/N m to 0.15 and 2 x 10(-7) mm(3)/N m, respectively, by increasing the C2H2 flux. To understand the tribological processes appearing at the interface and to elucidate the wear mechanism, microstructural and chemical investigations of the coatings were performed before and after the friction test. EPMA, X-ray photoelectron and electron energy-loss spectroscopies were employed to obtain an estimation of the fraction of the a-C:H phase, which can be correlated with the tribological behavior. Examination of the friction counterfaces (ball and track) by Raman microanalysis reveals an increased ordering of the amorphous carbon phase concomitant with friction reduction. The tribological results were compared with similar TiC/a-C(:H) composites prepared by the conventional direct current process.

Electrophoretic deposition of mixed copper oxide/GO as cathode and N-doped GO as anode for electrochemical energy storage

Jafari, EA; Moradi, M; Hajati, S; Kiani, MA; Espinos, JP
Electrochimica Acta, **268** (2018) 392-402
Abril, 2018 | **DOI:** 10.1016/j.electacta.2018.02.122

In this work, energy storage properties of mixed copper oxide wrapped by reduced graphene oxide and nitrogen-doped reduced graphene oxide were investigated. First, co-electrophoretic deposition technique was used to coat GO@CuO on nickel foam; followed by electrochemical phase transformation to rGO@CuxO. Electron spectroscopy analyses (XPS, REELS and UPS) confirm the phase transformation and electrochemical reduction. Then, an electrophoretic deposition was carried out for coating nitrogen-doped graphene oxide on nickel foam coupled to its electrochemical reduction to the NrGO. The cathode and anode performances were studied by galvanostatic charge-discharge, cyclic voltammetry and impedance spectroscopy. The rGO@CuxO and NrGO exhibit a favorable specific capacity of 267.2 and 332.6 C g(-1) at 2 A g(-1), respectively. High electrochemical activity and elimination of polymer binders with a maximum potential of 1.6 V are among the advantages of rGO@CuxO//NrGO electrochemical charge storage device. Furthermore, fabricated device provided a maximum specific power and specific energy of 11917.24 W kg(-1) and 14.15 Wh kg(-1), respectively, with 86% capacity retention after 2000 cycles.

Nanostructural Analysis of Porous Oblique Angle Deposited (OAD) Multilayer Systems by Grazing-Incidence Small-Angle X-Ray Scattering

Oliva-Ramirez, M; Lopez-Santos, C; Yubero, F; Gonzalez-Elipe, AR
Advanced Optical Materials, **5** (2018) 1800530
Septiembre, 2018 | **DOI:** 10.1002/admi.201800530

This work reports a thorough characterization analysis of various porous thin film multilayers by means of grazing-incidence small-angle X-ray scattering (GISAXS). Alternated TiO_2/SiO_2 nanocolumnar layers deposited at oblique angles are fabricated in slanted, chiral, and zig-zag configurations by rotating azimuthally the substrate from one layer to the next. Multilayer systems formed by the stacking of 3 and 15 alternant thin films of these two oxides are morphologically characterized by scanning electron microscopy (SEM) and structurally by GISAXS. This technique has provided a means to determine various vertical and lateral correlation lengths and to assess the anisotropic electron density distribution along the structural elements existing in the multilayers. This information can be systematically used to account for the actual arrangement of nanostructural elements in multilayer systems.

The Role of Surface Recombination on the Performance of Perovskite Solar Cells: Effect of Morphology and Crystalline Phase of TiO_2 Contact

Idigoras, J; Contreras-Bernal, L; Cave, JM; Courtier, NE; Barranco, A; Borras, A; Sanchez-Valencia, JR; Anta, JA; Walker, AB
Advanced Materials Interfaces, **5** (2018) art. 1801076
Noviembre, 2018 | **DOI:** 10.1002/admi.201801076

Herein, the preparation of 1D TiO_2 nanocolumnar films grown by plasma-enhanced chemical vapor deposition is reported as the electron selective layer (ESL) for perovskite solar devices. The impact of the ESL architecture (1D and 3D morphologies) and the nanocrystalline phase (anatase and amorphous) is analyzed. For anatase structures, similar power conversion efficiencies are achieved using an ESL either the 1D nanocolumns or the classical 3D nanoparticle film. However, lower power conversion efficiencies and different optoelectronic properties are found for perovskite devices based on amorphous 1D films. The use of amorphous TiO_2 as electron selective contact produces a bump in the reverse scan of the current-voltage curve as well as an additional electronic signal, detected by impedance spectroscopy measurements. The dependence of this additional signal on the optical excitation wavelength used in the IS experiments suggests that it stems from an interfacial process. Calculations using a drift-diffusion model which explicitly considers the selective contacts reproduces qualitatively the main features observed experimentally. These results demonstrate that for a solar cell in which the contact is working properly the open-circuit photovoltage is mainly determined by bulk recombination, whereas the introduction of a “bad contact” shifts the balance to surface recombination.

Sensing and biosensing with screen printed electrodes modified with nanostructured nickel oxide thin films prepared by magnetron sputtering at oblique angles Salazar, P; Garcia-Garcia, FJ; Gonzalez-Elipe, AR
Electrochemistry Communications, **94** (2018) 5-8
Septiembre, 2018 | **DOI:** 10.1016/j.elecom.2018.07.020

This work reports about the sensing and biosensing applications of a novel screen printed electrode (SPE) modified by nanostructured nickel oxide thin films obtained by reactive magnetron sputtering under an oblique angle configuration. Using these films as electrodes we demonstrate their ability to detect hydrogen peroxide under neutral pH conditions. Furthermore, as a proof-of-concept, NiO-modified SPEs have been developed and their cholesterol biosensing properties determined by cyclic voltammetry and chronoamperometry.

Nanostructured hybrid device mimicking bone extracellular matrix as local and sustained antibiotic delivery system

Borrego-Gonzalez, S; Romero-Sanchez, LB; Blazquez, J; Diaz-Cuenca, A
Microporous and Mesoporous Materials, **256** (2018) 165-176
Enero, 2018 | **DOI:** 10.1016/j.micromeso.2017.08.010

A fluidic permeable and stable in wet media, MBG-NfGel, device consisting of a mesoporous ceramic embodied in a nanofibrillar biodegradable polymer has been processed using appropriate thermally induced phase separation (TIPS) processing variables of 5.4% (wt/v) gelatin in 50/50 water/ethanol (v/v) ratio. The device comprises high surface area mesoporous bioactive glass (MBG) microparticles within a fibrous matrix of 170 nm average diameter nanofibers gelatin, forming a meshwork of 0.2-1.6 mu m range voids. Gentamicin sulphate (GS) antibiotic high loading capacity and sustained release ability, as well as in vitro bioactivity and osteoprogenitor cells biocompatibility supports long-term antibacterial and bone growth stimulation properties. Antibiotic local delivery functionality in vitro of this device has been analysed and discussed in relation to other systems previously reported. The presented device properties as well as its industrial scalability potential, in terms of process reliability and absence of toxic chemical agents, low raw material biopolymer cost and immunogenicity, are other important advantages. These advantages rank MBG-NfGel device as a potential candidate to further development for application as local antibiotic device in bone surgery and therapy.

Microstructural engineering and use of efficient poison resistant Au-doped Ni-GDC ultrathin anodes in methane-fed solid oxide fuel cells

Garcia-Garcia, FJ; Yubero, F; Gonzalez-Elipe, AR; Lambert, RM
International Journal of Refractory Metals & Hard Materials, **43** (2018) 885-893
Enero, 2018 | **DOI:** 10.1016/j.ijhydene.2017.11.020

Ultrathin porous solid oxide fuel cell (SOFC) anodes consisting of nickel-gadolinia-dopedceria (Ni-GDC) cermets with a unique porous micro-columnar architecture with intimate contact between the GDC and the Ni phases were made by magnetron sputtering at an oblique deposition angle and characterised in detail by a variety of methods prior to use in hydrogen or methane-fuelled SOFCs. These Ni-GDC anodes exhibited excellent transport properties, were robust under thermal cycling and resistant to delamination from the underlying yttria-stabilised zirconia electrolyte. Similarly prepared Au-doped Ni-GDC anodes exhibited the same morphology, porosity and durability. The gold associated exclusively with the Ni component in which it was present as a surface alloy. Strikingly, whatever their treatment, a substantial amount of Ce3+ persisted in the anodes, even after operation at 800 degrees C under fuel cell conditions. With hydrogen as fuel, the un-doped and Au doped Ni-GDC anodes exhibited identical electrochemical performances, comparable to that of much thicker commercial state-of-the-art Ni-GDC anodes. However, under steam reforming conditions with CH4/H(2)0 mixtures the behaviour of the Au-doped Ni-GDC anodes were far superior, exhibiting retention of good power density and dramatically improved resistance to deactivation by carbon deposition. Thus two distinct beneficial effects contributed to overall performance: persistence of Ce3+ in the working anodes could induce a strong metal-support interaction with Ni that enhanced the catalytic oxidation of methane, while formation of a Ni Au surface alloy that inhibited carbonisation and poisoning of the active nickel surface.

Strong activation effect on a ru-co-c thin film catalyst for the hydrolysis of sodium borohydride

Arzac, GM; Paladini, M; Godinho, V; Beltran, AM; de Haro, MCJ; Fernandez, A
Scientific Reports, **8** (2018) art. 9755
Junio, 2018 | **DOI:** 10.1038/s41598-018-28032-6

In this work, we prepared a series of Ni foam supported Ru-Co, Ru-Co-B and Ru-Co-C catalysts in the form of columnar thin films by magnetron sputtering for the hydrolysis of sodium borohydride. We studied the activity and durability upon cycling. We found a strong activation effect for the Ru-Co-C sample which was the highest ever reported. This catalyst reached in the second cycle an activity 5 times higher than the initial (maximum activity 9310 ml.min(-1).g(CoRu)(-1) at 25 degrees C). Catalytic studies and characterization of the fresh and used samples permitted to attribute the strong activation effect to the following factors: (i) small column width and amorphous character (ii) the presence of Ru and (iii) dry state before each cycle. The presence of boron in the initial composition is detrimental to the durability. Our studies point out to the idea that after the first cycle the activity is controlled by surface Ru, which is the most active of the two metals. Apart from the activation effect, we found that catalysts deactivated in further cycles. We ascribed this effect to the loss of cobalt in the form of hydroxides, showing that deactivation was controlled by the chemistry of Co, the major surface metal component of the alloy. Alloying with Ru is beneficial for the activity but not for the durability, and this should be improved.

Influence of irrigation conditions in the germination of plasma treated Nasturtium seeds

Molina, R; Lopez-Santos, C; Gomez-Ramirez, A; Vilchez, A; Espinos, JP; Gonzalez-Elipe, AR
Scientific Reports, **8** (2018) art. 16442
Noviembre, 2018 | **DOI:** 10.1038/s41598-018-34801-0

Plasma treatments had emerged as a useful technique to improve seed germination. In this work we investigate the influence of different irrigation conditions and plasma treatments on the germination of nasturtium seeds. During plasma treatment, seeds experience a progressive weight loss as a function of treatment time that has been associated to water release, a process that is more pronounced after longer plasma treatment times. Seeds treated for short times (<30 s) are able to germinate more efficiently than untreated specimen under hydric stress (drought conditions), while plasma treatments for longer times (up to 300 s) impaired germination independently on irrigation conditions. Characterization analysis of plasma treated seeds by FTIR-ATR, SEM/EDX and XPS showed that plasma treatment affected the chemical state of pericarp while, simultaneously, induced a considerable increase in the seeds water uptake capacity. The decrease in germination efficiency found after plasma treatment for long times, or for short times under optimum irrigation conditions, has been attributed to that the excess of water accumulated in the pericarp hampers the diffusion up to the embryo of other agents like oxygen which are deemed essential for germination.

Engineering of III-Nitride Semiconductors on Low Temperature Co-fired Ceramics

Manuel, JM; Jimenez, JJ; Morales, FM; Lacroix, B; Santos, AJ; Garcia, R; Blanco, E; Dominguez, M; Ramirez, M; Beltran, AM; Alexandrov, D; Tot, J; Dubreuil, R; Videkov, V; Andreev, S; Tzaneva, B; Bartsch, H; Breiling, J; Pezoldt, J; Fischer, M; Muller, J
Scientific Reports, **8** (2018) art. 6879
Mayo, 2018 | **DOI:** 10.1038/s41598-018-25416-6

This work presents results in the field of advanced substrate solutions in order to achieve high crystalline quality group-III nitrides based heterostructures for high frequency and power devices or for sensor applications. With that objective, Low Temperature Co-fired Ceramics has been used, as a non-crystalline substrate. Structures like these have never been developed before, and for economic reasons will represent a groundbreaking material in these fields of Electronic. In this sense, the report presents the characterization through various techniques of three series of specimens where GaN was deposited on this ceramic composite, using different buffer layers, and a singular metal-organic chemical vapor deposition related technique for low temperature deposition. Other single crystalline ceramic-based templates were also utilized as substrate materials, for comparison purposes.

Growth of nanocolumnar porous TiO_2 thin films by magnetron sputtering using particle collimators

Garcia-Valenzuela, A; Alvarez, R; Rico, V; Cotrino, J; Gonzalez-Elipe, AR; Palmero, A
Surface & Coatings Technology, **343** (2018) 172-177
Junio, 2018 | **DOI:** 10.1016/j.surfcoat.2017.09.039

The selective incorporation of deposition species with preferential directionality is analyzed during the growth of TiO_2 thin films by magnetron sputtering. Using wisely-designed collimators, tilted nanocolumnar morphologies are grown in a ballistic deposition regime, i.e. when most deposition species arrive at the film surface along well-defined preferential directions, and also in a thermalized deposition regime, when these species follow an isotropic momentum distribution in the plasma gas. The obtained results suggest that the use of particle collimators may promote the growth of porous thin films even in the classical magnetron sputtering configuration, when the target and the substrate are parallel. General insights are given on this approach and, as a proof of concept, its principles applied for the synthesis of nanostructured films in a laboratory-size reactor.

High-temperature oxidation of CrAlYN coatings: Implications of the presence of Y and type of steel

Rojas, TC; Dominguez-Meister, S; Brizuela, M; Sanchez-Lopez, JC
Surface & Coatings Technology, **354** (2018) 203-213
Octubre, 2018 | **DOI:** 10.1016/j.surfcoat.2018.09.020

Nanolayered CrAlN and CrAlYN/CrAlN (average contents of Al approximate to 25 at.% and Y approximate to 1.6 at. %) coatings are deposited on M2 and 316 steel substrates and heated to 1000 degrees C in air for 2 h to study their oxidation mechanism, the thermal stability and the reactive element (RE) effect of yttrium. CrAlN on M2 develops a Cr_2O_3/Al_2O_3 passivation layer that preserves in high degree the fcc-CrAlN structure however iron ions leave the substrate and travel to the surface along the column boundaries. The CrAlYN/CrAlN coatings deposited on steels are not stable at 1000 degrees C, and the initial fcc-CrAlN phase is partially transformed to hcp-Al(O)N and Cr-Fe phases (M2) and Cr2N and Al_2O_3 (316). The addition of Y changes the predominant scale growth direction. Inward oxygen diffusion becomes dominant but a reduction of the oxide scale thickness as compared to CrAlN is not observed. The advanced microstructural analysis made by transmission electron microscopy combined with electron energy loss spectroscopy determined that yttrium migrates mainly to the oxide scale (forming mixed oxides with substrate elements - V and Mo, either as dispersed particles or segregated at the grain boundaries) in M2, and to the oxide interface and column boundaries (forming Al-Y oxides and YN, respectively) in 316 steel. The benefits of addition of Y in improving the oxidation resistance are discussed comparatively with literature data. The RE effect of yttrium is thus observed to be dependent on the substrate, film architecture and composition.

Adhesion enhancement of DLC hard coatings by HiPIMS metal ion etching pretreatment

Santiago, JA; Fernandez-Martinez, I; Wennberg, A; Molina-Aldareguia, JM; Castillo-Rodriguez, M; Rojas, TC; Sanchez-Lopez, JC; Gonzalez, MU; Garcia-Martin, JM; Li, H; Bellido-Gonzalez, V; Monclus, MA; Gonzalez-Arrabal, R

Surface & Coatings Technology, **349** (2018) 787-796
Septiembre, 2018 | **DOI:** 10.1016/j.surfcoat.2018.04.090

Poor adhesion is a recurrent problem for the wider use of diamond-like carbon (DLC) coatings in industrial applications. In this work, we investigate the effectiveness of high-power impulse magnetron sputtering (HiPIMS) metal ion etching to improve the adhesion of DLC coatings on high speed steel substrates. The influence of HiPIMS pretreatment parameters, the metal ion selection for the process and the addition of bonding layers on the adhesion properties were studied. Daimler-Benz and nanoscratch test methods were used to evaluate the adhesion. The elemental composition, morphology and microstructure of the samples were evaluated by EELS, SEM, AFM and HRTEM. In general, samples pretreated with HiPIMS metal ion etching withstand larger critical loads than those pretreated by conventional Ar + glow discharge and bonding layers. The pretreatment is proven to be very effective at removing surface contaminants and providing a gradual interface. The selection of Cr over Ti contributes to a significant improvement on the adhesion due to the reduction of the oxygen level at the interface thus ensuring an optimal coating-substrate contact and a more compliant structure, which prevents the delamination failure.

In Vitro Comparative Study of Oxygen Plasma Treated Poly(Lactic-Co-Glycolic) (PLGA) Membranes and Supported Nanostructured Oxides for Guided Bone Regeneration Processes

Torres-Lagares, D; Castellanos-Cosano, L; Serrera-Figallo, MA; Lopez-Santos, C; Barranco, A; Rodriguez-Gonzalez-Elipe, A; Gutierrez-Perez, JL

Materials, **11** (2018) art. 752
Mayo, 2018 | **DOI:** 10.3390/ma11050752

(1) Background: The use of physical barriers to prevent the invasion of gingival and connective tissue cells into bone cavities during the healing process is called guided bone regeneration. The objective of this in-vitro study was to compare the growth of human osteoblasts on Poly(Lactic-co-Glycolic) (PLGA) membranes modified with oxygen plasma and Hydroxyapatite (HA), silicon dioxide (SiO2), and titanium dioxide (TiO2) composite nanoparticles, respectively. (2) Methods: All the membranes received a common treatment with oxygen plasma and were subsequently treated with HA nanostructured coatings (n = 10), SiO2 (n = 10) and TiO2 (n = 10), respectively and a PLGA control membrane (n = 10). The assays were performed using the human osteoblast line MG-63 acquired from the Center for Scientific Instrumentation (CIC) from the University of Granada. The cell adhesion and the viability of the osteoblasts were analyzed by means of light-field microphotographs of each condition with the inverted microscope Axio Observer A1 (Carl Zeiss). For the determination of the mitochondrial energy balance, the MitoProbe ™ JC-1 Assay Kit was employed. For the determination of cell growth and the morphology of adherent osteoblasts, two techniques were employed: staining with phalloidin-TRITC and staining with

DAPI. (3) Results: The modified membranes that show osteoblasts with a morphology more similar to the control osteoblasts follow the order: PLGA/PO2/HA > PLGA/PO2/SiO2 > PLGA/PO2/TiO2 > PLGA ($p < 0.05$). When analysing the cell viability, a higher percentage of viable cells bound to the membranes was observed as follows: PLGA/PO2/SiO2 > PLGA/PO2/HA > PLGA/PO2/TiO2 > PLGA ($p < 0.05$), with a better energy balance of the cells adhered to the membranes PLGA/PO2/HA and PLGA/PO2/SiO2. (4) Conclusion: The membrane in which osteoblasts show characteristics more similar to the control osteoblasts is the PLGA/PO2/HA, followed by the PLGA/PO2/SiO2.

Colorimetric energy sensitive scintillator detectors based on luminescent multilayer designs

Ferrer, FJ; Gil-Rostra, J; Gonzalez-Elipe, AR; Yubero, F
Sensors and Actuators A-Physical, **272** (2018) 217-222
Abril, 2018 | **DOI:** 10.1016/j.sna.2018.01.062

In this work we present a new concept for energy sensitive radiation-beam scintillator detectors based on a luminescent multilayer design, where each layer within the stack consists of a rare-earth-doped highly transparent oxide. For a given type of particle beam (i.e., protons, a particles, etc.), its penetration depth, and therefore its energy loss at a particular buried layer, depends on its initial kinetic energy. Relying on this principle and since the intensity of the luminescent response of each layer and substrate should be proportional to the energy deposited by the radiation beam, we prove that a characteristic energy dependent color emission is obtained depending on both the phosphors integrated in the luminescent stack and on the primary energy and type of particle beam. Phosphor doping, emission efficiency, layer thickness, and multilayer structure design are key parameters to achieve a broad gamut in colorimetric response. The developed scintillators are designed to operate in a transmission geometry (light detection from the opposite side of the incident radiation) which is well suited for high energy particle detection in fields such as oncotherapy, space radiation, or of fusion studies. The principles of the method are illustrated with a case example typical of ion beam accelerators devoted to materials analysis. It is obtained that the kinetic energy of protons/alpha particle beams can be distinguished and evaluated with a sensitivity of 0.06/0.25 chromaticity units per MeV in the 0.7-2.0 MeV range.

Nickel/Copper Bilayer-modified Screen Printed Electrode for Glucose Determination in Flow Injection Analysis

Salazar, P.; Rico, V.; Gonzalez-Elipe, Agustin R.
Electroanalysis, **30** (2018) 187-193
Enero, 2018 | **DOI:** 10.1002/elan.201700592

This work reports about the performance of a Ni/Cu-modified screen printed electrodes (SPE/Ni/Cu), prepared by physical vapor deposition (PVD) in an oblique angle configuration (OAD), for non-enzymatic glucose sensing applications. SPE/Ni/Cu electrodes showed an excellent reversibility and a catalytic behavior for detection of glucose that were controlled by the diffusion of reactants up to the active sites at the electrode surface. The study with a flow injection analysis (FIA) setup of the main experimental variables affecting the detection process has shown that the developed electrode system had an excellent glucose sensitivity of 1.04AM(-1)cm(-2) (R-2:0.999), a linear response up to 1mM, a limit of detection of 0.33M and a time of analysis of ca. 30s per sample. The selectivity of the sensor was checked against various interferences, including ascorbic acid, uric acid, acetaminophen and other sugars, in all cases with excellent results. The feasibility of using this sensor for practical applications was successfully confirmed by determining the glucose concentration in different commercial beverages.

Biodegradabiliy of spherical mesoporous silica particles (MCM-41) in simulated body fluid (SBF)

Boccardi, E; Philippart, A; Beltran, AM; Schmidt, J; Liverani, L; Peukert, W; Boccaccini, AR
American Mineralogist, **103** (2018) 350-354
Marzo, 2018 | **DOI:** 10.2138/am-2018-6281

Mesoporous silica particles of type MCM-41 (Mobile Composition of Matter No. 41), exhibiting highly ordered mesoporosity (pores with diameter between 2 and 50 nm) and surface roughness, are developed and used as a functional coating on bioactive glass-based scaffolds for bone tissue engineering. The degradability and the mesostructure stability of these novel MCM-41 particles were evaluated. The particles are immersed in simulated body fluid (SBF) for up to 28 days at 37 degrees C, and the variation of the ordered porosity, surface characteristics, and chemical composition of the particles are assessed by SEM-EDX, HRTEM, FTIR, ICP-OES, and pH measurements. The results indicate that the MCM-41 particles are affected by immersion in SBF only during the first few days; however, the surface and the mesopore structure of the particles do not change further with increasing time in SBF. The pore channel diameter increased slightly, confirming the stability of the developed material. The release of dissolved Si-species, which reached a maximum of 260 mg SiO_2 per gram of material, could play a key role in gene activation of osteoblast cells and in inducing new bone matrix formation.

Microemulsion Assisted Sol-Gel Method as Approach to Load a Model Anticancer Drug inside Silica Nanoparticles for Controlled Release Applications

Jaramillo, N; Paucar, C; Fernandez, A; Negrete, CG; Garcia, C
Collid and Interface Science Communications, **24** (2018) 13-17
Mayo, 2018 | **DOI:** 10.1016/j.colcom.2018.03.002

Silica nanoparticles are attractive carriers due to their improved safety and effectiveness in drug delivery. Silica nanoparticles were synthesized by using microemulsion assisted sol-gel method, and a model anticancer drug 5-fluorouracil (5-FU) was added to the silica precursor before hydrolysis and condensation reactions start. The obtained materials were characterized by Transmission Electron Microscopy (TEM) and Fourier Transform Infrared Spectroscopy (FTIR). Drug encapsulation within silica nanoparticles causes an increase in particle size. However, particle morphology is not affected. The drug release profile was obtained through high performance liquid chromatography (HPLC). The encapsulation approach showed to be effective for sustaining a continuous and increasing release during testing time (98 h). Further studies were performed to evaluate the cytotoxic effects of silica nanoparticles with loaded 5-FU on

Chinese hamster ovary cells (CHO-K1). Materials are non-cytotoxic for all concentration tested (5-200 mu g/mL).

The nanostructure of porous cobalt coatings deposited by magnetron sputtering in helium atmosphere

Lacroix, B; Godinho, V; Fernandez, A

Micron, **108** (2018) 49-54

Mayo, 2018 | **DOI:** 10.1016/j.micron.2018.02.004

In this work, (scanning) transmission electron microscopy has been used to study the nanostructure of porous cobalt coatings obtained by magnetron sputtering using helium as process gas. This nanostructure consists of closed pores of different nanometric size (about 4-20 nm) that are distributed all over a nanocrystalline Co matrix and filled with the deposition gas. Spatially resolved electron energy-loss spectroscopy analysis was applied to measure and map, with high lateral resolution, the relevant physical properties (density, pressure and He-K edge shift) of helium trapped inside these individual nanopores, in order to provide new insights about the growth mechanism involved in such systems. In particular, a coefficient of proportionality, C = 0.039 eV nm(3), between the blue shift of the He K-edge and the He density has been found. In addition, very high He densities (10-100 at./nm(3)) and pressures in the gigapascal range (0.05-5.0 GPa) have been measured. The linear dependence of these parameters as a function of the inverse radii obeying to the Laplace-Young law for most of the pores suggests that their formation during the coating's growth takes place in regime of elastic deformation of the Co matrix.

Quantitative analysis of Yb 4d photoelectron spectrum of metallic Yb

Pauly, N; Yubero, F; Tougaard, S

Surface & Coatings Technology, **50** (2018) 1168-1173

Noviembre, 2018 | **DOI:** 10.1002/sia.6402

The measured Yb 4d(3/2) intensity is larger than the Yb 4d(5/2) in X-ray photoelectron (XPS) emission of metallic Yb, which is unexpected. The shape and intensity of photoelectron peaks are strongly affected by extrinsic excitations due to electron transport out of the surface (including bulk and surface effects) and to intrinsic excitations due to the sudden creation of the static core hole. To quantitatively extract from experimental XPS the primary excitation spectrum (ie, the initial excitation process) of the considered transition, these effects must be included within the theoretical description. The combined effect of both extrinsic and intrinsic excitations can be described by an effective energy-differential inelastic electron scattering cross section for XPS evaluated by a dielectric response model with the dielectric function as only input. Then, using this cross section, a direct evaluation of the primary excitation spectrum is performed by standard peak shape analysis for thick homogeneous samples. We use this approach in the present paper to determine the Yb 4d photoemission spectrum for metallic Yb. We show that the unexpected larger intensity of Yb 4d(3/2) compared to 4d(5/2) can be fully accounted for by our model and that the total spectrum consists of a sum of symmetric primary excitation peaks.

LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS

Descargas eléctricas en gases: plasmas
Cotrino, J.; Albellá, J.M.
"Capas delgadas y modificación superficial de materiales", (2018) Ed. José M. Albella, Biblioteca de Ciencias, Editorial Consejo Superior de Investigaciones Científicas, págs. 69-103
ISBN: 978-84-00-10438-2

Mecanismos de nucleación y crecimiento de capas delgadas
Palmero, A.; Albella, J.M.
"Capas delgadas y modificación superficial de materiales", (2018) Ed. José M. Albella, Biblioteca de Ciencias, Editorial Consejo Superior de Investigaciones Científicas, págs. 105-135
ISBN: 978-84-00-10438-2

Caracterización morfológica de superficies y capas delgadas
Alvarez, R.; Palmero, A.; González-Elipe, A.R.
"Capas delgadas y modificación superficial de materiales", (2018) Ed. José M. Albella, Biblioteca de Ciencias, Editorial Consejo Superior de Investigaciones Científicas, págs. 369-398
ISBN: 978-84-00-10438-2

Técnicas de microscopía electrónica (SEM, TEM)
Landa-Cánovas, A.R.; Rojas Ruiz, T.C.
"Capas delgadas y modificación superficial de materiales", (2018) Ed. José M. Albella, Biblioteca de Ciencias, Editorial Consejo Superior de Investigaciones Científicas, págs. 579-608
ISBN: 978-84-00-10438-2

Caracterización mecánica y tribológica de recubrimientos
Sánchez-López, J.C.; Albella, J.M.
"Capas delgadas y modificación superficial de materiales", (2018) Ed. José M. Albella, Biblioteca de Ciencias, Editorial Consejo Superior de Investigaciones Científicas, págs. 611-640
ISBN: 978-84-00-10438-2

Caracterización mecánica y tribológica de los recubrimientos
Sánchez-López, J.C.; Albella, J.M.
"Capas delgadas y modificación superficial de materiales", (2018) Ed. José M. Albella, Biblioteca de Ciencias, Editorial Consejo Superior de Investigaciones Científicas, págs. 643-672
ISBN: 978-84-00-10438-2

CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

COMUNICACIONES / COMMUNICATIONS

12th International Symposium Hydrogen & Energy
11 – 16 febrero [Ginebra, Suiza]

Formic acid as H2 carrier: Study of liquid vs. gas phase decomposition reaction on supported Pd heterogeneous catalysts
G.M. Arzac; D. Hufschmidt; J. Lopez-Viejobueno; A. Fernández
Poster

ImagineNano2018
13 – 15 marzo [Bilbao, España]

Photonic applications of nanocolumnar Au films obtained by glancing angle deposition with magnetron sputtering
M.U. González; A. Vitrey; R. Alvarez; A. Palmero; P. Díaz-Núñez; A. Rivera; O. Peña-Rodríguez; J.M. García-Martín
Comunicación oral

European Hydrogen Energy Conference 2018 | EHEC2018
14 – 16 marzo [Málaga, España]

Activation effect on a Co-Ru-C thin film catalyst for the hydrolysis of sodium borohydride
G.M. Arzac; M. Paladini; V. Godinho; A.M. Beltran; M.C. Jiménez de Haro; A. Agar Monclova; A. Fernández
Comunicación oral

European Conference on Nanofilms 2018 | ECNF2018
20 – 22 marzo [Cranfield, Gran Bretaña]

Structure-based design an d applications of closed porous coatings fabricated by magnetron sputtering
V. Godinho; A. Fernández
Conferencia Invitada

3rd CARBTRIB Workshop on "Nano-Phenomena and Functionality of Modern Carbon-based Tribo-Coatings"

4 – 5 abril [Viena, Austria]

Tribological behaviour of vertically aligned carbon nanotubes embedded in epoxy resin
J.C. Sánchez-López, Clemens Schaber, Stanislav Gorb
Comunicación oral

Frictional Contact of TiC/a-C(:H) Coatings
I.G. Goryacheva, E.V. Torskaya, J.C. Sánchez-López
Comunicación oral

First International Conference on Optics, Photonics and Laser (OPAL)

9 – 11 mayo [Barcelona, España]

Rare-earth doped optical fibers in a fabry-Perot microcavity for sensor applications
F lahoz;I R Martin;K Soler-Carracedo;J M Caceres;J Gil-Rostra;F Yubero;A R Gonzalez-Elipe
Comunicación oral

4th International Conference on Industrial Engineering |ICIE-2018

15 – 18 mayo [Sochi, Rusia]

Fracture of TiC/a-C(:H) Coatings in Friction Contact
E. Torskaya;A. Mezrin;J.C. Sánchez-López
Comunicación oral

Study of TiC/a-C(:H) Coatings Before and After Friction by Nanoindentation
E. Torskaya; T. Muravyeva; J.C. Sánchez-López
Comunicación oral

E-MRS 2018 Spring Meeting

18-22 junio [Estrasburgo, Francia]

Multifunctional organic thin films and supported nanostructures by plasma assisted vacuum deposition for the development of photonic and optoelectronic devices and components
F. Aparicio; M. Alcaire; A. Mora; J. R. Sánchez-Valencia, A. Borrás, A. Barranco.
Poster

Plasma Assited deposition of superhydrophobic and antifreezing nanofabrics.
M. Alcaire; M. C. López-Santos; F. Aparicio; J. R. Sánchez-Valencia; A. Barranco; A. Borrás.
Comunicación oral

The 9th Vacuum and Surface Science Conference of Asia and Australia | VASSCAA-9

13 – 16 agosto [Sidney, Australia]

Near Future Challenges and Recent Highlights
F. Yubero
Conferencia Invitada

Dye Giant Absorption and Light Confinement Effects in Porous Bragg Microcavities
F. Yubero; J. Gil-Rostra; A.R. González-Elipe; M. Oliva-Ramirez
Comunicación oral

The 15th International Conference on Near-Field Optics, Nanophotonics & Related Techniques

26 – 31 agosto [Troyes, Francia]

Black gold coatings fabricated by glancing angle deposition with sputtering
M.U. González; R. Alvarez; A. Palmero; J.M. García-Martín
Poster

16th International Conference on Plasma Surface Engineering

17 – 21 septiembre [Garmisch-Partenkirchen, Alemania]

Thermal stability and tribomechanical properties of hard Cr-doped DLC coatings deposited by HIPIMS
J.A. Santiago; I. Fernández; A. Wennberg; T. Polcar; T. Vitu; J. Molina; C. Rojas; J.C. Sánchez-López; R. González Arrabal; M. Monclus
Comunicación oral

Magnetron Sputtering Depositions at Oblique Angles on Seeded Substrates for the Development of sub-Micron Structural and Chemical Patterns
A. Palmero; A. Garcia-Valenzuela; R. Alvarez; B. Lacroix; V. Rico; R. Gago; L. Vazquez; J. Solis; A. R. Gonzalez-Elipe; J. Cotrino
Comunicación oral

Insights into the high temperature oxidation resistance of cathodic arc evaporated nitride coatings with different layer architectures
S. Mato; G. Alcalá Penades; I. Ciarsolo; J. Barriga; J. Pérez Trujillo; J.C. Sánchez López
Comunicación oral

Plasma processing of metal-porphyrins and phthalocyanines for the fabrication of low dimensional metal nanostructured layers
A.N. Filippin; M. Macías Montero; M. Alcaire; A. Barranco, J. R. Sánchez-Valencia; A. Borrás et al.
Comunicación Oral

Synthesis and applications of 1D and 3D supported nanostructures developed by plasma assisted vacuum deposition methods
N. Filippin; M. Alcaire; M. Macias; J. Idigoras; F. Aparicio; V. Lopez-Flores; C. Lopez-Santos; A. Barranco; A. Borras
Comunicación oral

Post-annealing structural rearrangement of M/CuOx (M=Ag, Au) nanocomposite thin films showing Localized Surface Plasmon Resonance
D. Martínez-Martinez; M. Proença; J. Borges; M.S. Rodrigues; J.C.Sanchez-Lopez; F. Vaz
Poster

On the reactive-element effect of Y in the oxidation of CrAlYN films
J.C. Sanchez-Lopez; T. Cristina Rojas; S. Domínguez-Meister; M. Brizuela
Poster

One-dimensional nanoelectrodes fabricated by plasma-assisted techniques
J.R. Sánchez Valencia; V. Lopez-Flores; R. Alvarez; F. Garcia-Garcia; F.J. Aparicio; J. Gil-Rostra; T. C. Rojas; A. Palmero; A. Barranco; A. Borras
Poster

Comparative microstructure, chemical composition, optical and tribo-mechanical properties of CrAlN coatings deposited by HiPIMS and DC magnetron sputtering
S. Domínguez-Meister; I. Braceras; M. Brizuela; T.C. Rojas; J.C. Sánchez-López
Poster

Structural and optical characterization of $Cr_{1-x}Al_x(O)N$ films prepared by HiPIMS
T.C. Rojas; A. Caro; G. Lozano; J.C. Sánchez-López
Poster

Optimized design of cathodic arc evaporated nitride multilayer regarding their high-temperature oxidation resistance and mechanical behaviour
G.Alcalá Penadés, S. Mato, J. Barriga, F.J. Pérez, J.C. Sánchez-López
Poster

2018 European Nuclear Physics Conference
2 – 7 septiembre [Bolonia, Italia]

Test of a 3He target to be used for transfer reactions in inverse kinematics
A. Fernández; V. Godinho; D. Hufschmidt
Comunicación oral

Xth International Workshop on Microwave Discharges: Fundamentals and Applications,
3 – 21 septiembre [Zvenigorod, Russia]

Metal oxide nanotubes prepared by Microwave-Plasma Enhanced Chemical Vapour Deposition for advanced applications
J.R. Sanchez-Valencia, A. Borras et al.
Conferencia Invitada

Science and Applications of Thin Films, Conference & Exhibition | SATF 2018

17 – 21 septiembre [Izmir, Turquia]

Metal films by Laser Ablation Backwriting on Glass
L.A. Angurel; R. Molina; V. Rico; F. Yubero; A.R. González-Elipe; D. Muñoz-Rojas; C.M. de la Huerta; V.H. Nguyen; G.F. de la Fuente
Conferencia Invitada

Materials Science and Engineering

26 – 28 septiembre [Darmstadt, Alemania]

Black gold coatings fabricated using glancing angle deposition with substrate rotation by sputtering
J.M. Garcia-Martin; M.U. González;R. Alvarez; A. Palmero
Comunicación oral

International Conference on Photonics Research | INTER-PHOTONICS 2018

8 – 12 octubre [Antalya, Turquia]

Fluorecent optical microresonators for optofluidic sensor applications
F. Lahoz; I.R. Martin; K. Soler-Carracedo; J. Gil-Rostra; F. Yubero; A.R. Gonzalez-Elipe
Conferencia Invitada

Optical sensing in biological tissue based on resonant microcavities
S. Soler-Carracedo; F. Lahoz; I.R. Martin; V. Mesa-Infante; T. Gonzalez-Hernandez; G. Cuesto; A. Acebes; J. Gil-Rostra; F. Yubero; A.R. González-Elipe
Comunicación oral

V Congreso Hispano-Luso de Cerámica y Vidrio, LVI Congreso de la Sociedad Española de Cerámica y Vidrio y II Reunión Bienal de la Sociedad Española de Cerámica y Vidrio

8 – 10 octubre [Barcelona, España]

Influence of the preferential graphene nanoplatelets alignment within the ceramic matrix on the scratch behavior
F. Gutiérrez-Mora, A. Gallardo-López, C. Muñoz-Ferreiro, A. Morales-Rodríguez, A. Muñoz, J.C. Sánchez-López, R. Poyato
Comunicación oral

12th Annual Conference CIBER-BBN 2018
12 – 13 noviembre [Valladolid, España]

Osteoprogenitor cell Performance of a Synthetic Collagen Sponge
S. Borrego-González; G.A. Rico-Llanos; R. Visser; A. Díaz-Cuenca; J. Becerra
Poster

Reactive Magnetron Sputtering 2018
6 – 7 diciembre [Bélgica]

Magnetron Sputtering Deposition of Porous Thin Films at Oblique Geometries: Fundamentals and Applications
A. Palmero
Conferencia Invitada

CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESS AND MEETINGS

COMUNICACIONES / COMMUNICATIONS

II Workshop Español de Protonterapia
15 – 16 marzo [Sevilla, España]

Energy-Sensitive Ion-and Cathode-Luminescent Radiation-Beam Monitors Based on Multilayer Thin-Film Designs
F.J. Ferrer; J. Gil Rostra; A.R. González-Elipe; F. Yubero
Poster

XV Congreso Nacional de Materiales. I Iberian Meeting on Materials Science
4 – 6 julio [Salamanca, España]

Nano-structuring of ITO via self-organization upon high repletion rate femtosecond-laser irradiation for anisotropic conductivity applications
D. Puerto; M.C. Lopez Santos; C. Florian; J. Siegel; J. Gil Rostra; A.R. Gonzalez-Elipe; J. Solis
Comunicación oral

48º Reunión Anual SEPES

11 – 13 octubre [Valladolid, España]

Revisión de la Importancia de los Métodos de Análisis de Fluorescencia en Odontología Restauradora Estética
T.J. Martins; F.A. Martins; J.J. Segura-Egea; A. Díaz-Cuenca
Poster

39º Congreso Nacional de la Asociación Española de Endodoncia

1 – 3 noviembre [Málaga, España]

Respuesta Bioactiva In Vitro del Nuevo Cemento Biocerámico Endodóncico MTA HPRepair: Implicaciones en la Terapia Pulpar Vital
M.C. Jiménez-Sánchez; A. Díaz-Cuenca; J.J. Segura-Egea
Poster

Parámetros Físico-Químicos y Proceso de Hidratación de los Cementos Bioactivos ProRootMTA White, NeoMTA Plus y MTA HPRepair
M.C. Jiménez-Sánchez; A. Díaz-Cuenca; J.J. Segura-Egea
Poster

X CPAN DAYS

29 – 13 octubre [Salamanca, España]

Caracterización por técnicas IBA de blancos de reacciones nucleares
F.J. Ferrer; B. Fernandez-Martinez; J. Praena; J.P. Fernandez-Garcia; V. Godinho; P. Torres; A. Fernandez-Camacho; J. Gomez-Camacho
Comunicación oral

12th Annual Conference CIBER-BBN 2018

12 – 13 noviembre [Valladolid, España]

Osteoprogenitor cell Performance of a Synthetic Collagen Sponge
S. Borrego-González; G.A. Rico-Llanos; R. Visser; A. Díaz-Cuenca; J. Becerra
Poster

FORMACION / TRAINING

TESIS DOCTORALES/ DOCTOR DEGREE THESIS

Título: **Plasmas de descarga de barrera dieléctrica con empaquetamiento ferroeléctrico a presión atmosférica aplicados a la producción de hidrógeno, amoniaco y a la descontaminación de aire**
Autor: Antonio Méndez Montoro de Damas
Directores: Ana María Gómez Ramírez, José Cotrino Bautista y Agustín R. González-Elipe
Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla
Fecha: 9 de marzo de 2018

Título: **Desarrollo y estudio de nuevo materiales catalíticos preparados por pulverización catódica para la generación de hidrógeno mediante reacción de hidrólisis del borohidruro de sodio**
Autor: Mariana Paladini San Martin
Directora: Gisela Arzac Di Tomaso, Vanda Cristina Fortio Godinho y Asunción Fernández Camacho
Calificación: Sobresaliente "Cum Laude"
Centro: Universidad de Sevilla
Fecha: 14 de septiembre de 2018

FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

Título: **Simulación del crecimiento de películas delgadas mediante técnicas de MONTE CARLO**
Autor: Jesús López Arenal
Directores: Alberto Palmero Acebedo
Grado: Trabajo Fin de Master
Año Académico: 2017-2018 (4 octubre 2018)

DOCENCIA / TEACHING

5th Intensive School on Conservation Science: Ceramic Materials

Layers' microsctructure: influence and utility control for specific applications
Agustín R. González-Elipe
Lugar: Toledo, España

Máster Oficial y Doctorado en Biotecnología Avanzada

Nanotecnología
María Aránzazu Díaz Cuenca
Lugar: Universidad Internacional de Andalucía. Universidad de Málaga

EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Sistema de Magnetron Sputttering para la preparación de láminas delgadas
- Potenciostato y sistema electroquímico
- Sistema de medida de ángulos de contacto (advancing and receding)
- Equipo de crecimiento en vacío de nanofibras y otros materiales nanoestructurados
- Microscopio de efecto túnel (STM)
- Sistema de desorción térmica programada
- Espectrómetro de Fotoemisión (XPS)
- Analizador de potencial Z, tamaño de partícula y pesos moleculares (Malvern, ZS90)
- Bomba híbrida de vacío resistente a químicos VACUUBRAND RC-6
- Software y sondas para monitorización para equipo de liofilización CHRIST EPSILON 2-4 LSC
- Liofilizador de altas prestaciones Epsilon 2-4 (CHRIST)
- Estufa de desecación de 90 litros (RAYPA)
- Cámara Incubadora Opaq + Orbital Maxi (OVAN)
- pH & Ion-metro GLP 22+ (CRISON A)
- Malvern, Modelo Zetasizer Nano: para determinar mediante "Dynamic light scattering" la distribución de tamaños de partícula de sistemas coloidales en suspensión (disolvente acuoso u orgánico) en los rangos 1-3000 nanómetros.
  Este equipo también es adecuado para la evaluación del potencial "Z" de sistemas coloidales en suspensión (disolvente acuoso u orgánico) mediante medidas de Movilidad Electroforética.
- Colorímetro Dr. Lange: para la medida de parámetros de color (x, y, Y/L*a*b*, etc.) de superficies y polvos
- Ellipsómetro espectroscópico Woolan VB-400 con rango de frecuencias entre 300 y 1700 nm. Medida de índices de refracción y coeficiente de extención de capas delgadas y superficies.

- Espectrómetro visible-UV CARY-100. Medidas de coeficiente de absorción con luz normal y polarizada.
- Fluorímetro espectroscópico (HORYBA Jobin Yvon Fluorolog) con accesorio para la determinación de tiempos de vida. Microscopio de fluorescencia (HORYBA Jobin Yvon sigle photon controller: FluoroHub).
- Medidor de ángulos de contacto líquidos. Medidas ángulos de avance y retroceso, así como de energías de adhesión de líquidos sobre superficies (Dataphysics Contact Angle System SCA 20).
- Medida de cuatro puntos de conductividad eléctrica en superficies y láminas delgadas (Fuente de corriente Keithley 617 y voltímetro Keithley 2400).
- Medidas eléctricas en capas delgadas en función de la temperatura y la atmósfera
- Microscopio de Fuerzas atómicas (AFM) para la caracterización de superficies (Cervantes de Nanotec).
- Microscopio de efecto túnel (STM) con posibilidad de trabajar desde nitrógeno líquido hasta 600 ºC (VT-STM de Omicrom).
- Técnicas de caracterización de plasmas: sonda de Langmuir (Plasma Consult single and double sound), espectroscopía de emisión óptica (Avantes 200-900 nm resolución 1 nm) y espectrometría de masas (Hyden=
- Espectrómetro FT-IR con celda DRIFT (Pelkin elmer Spectrum One)
- Sistema de medida de porosidades en capas delgadas.
- Sistema de desorción térmica programada dotado con espectroscopía Auger (VG-8047).
- Espectrómetro de XPS (espectrómetro VSW) con sistema REELS de alta resolución (Kimball Physics EGPS-1022B) y fuente de átomos incorporada (Oxford Scientific Osprey plasma Source).

<u>Laboratorio de síntesis y catálisis</u>

Material básico de laboratorio químico: PHmetro, agitadores, calefactores, estufa de secado a vacío, centrífuga.

Reactores y material de vidrio convencional para síntesis de nanopartículas y catalizadores por via química.

Rotavapor, sistemas de filtrado.

Cámara seca MBRAUN.

Dos campanas extractoras.

Reactores catalíticos de lecho fijo para catálisis heterogenea solido-gas.

Reactores catalíticos para catálisis heterogenea sólido-líquido.

Sistemas controladores de flujo másico (gases y líquidos evaporados), bombas peristálticas para líquidos.

Tres cromatógrafos de gases, columnas y detectors FID y TCD.

Buretas automáticas para medición de gases.

<u>Cámaras de deposición de recubrimientos y películas delgadas y tratamientos con plasma.</u>

Sistema de tratamiento con plasmas Diener.

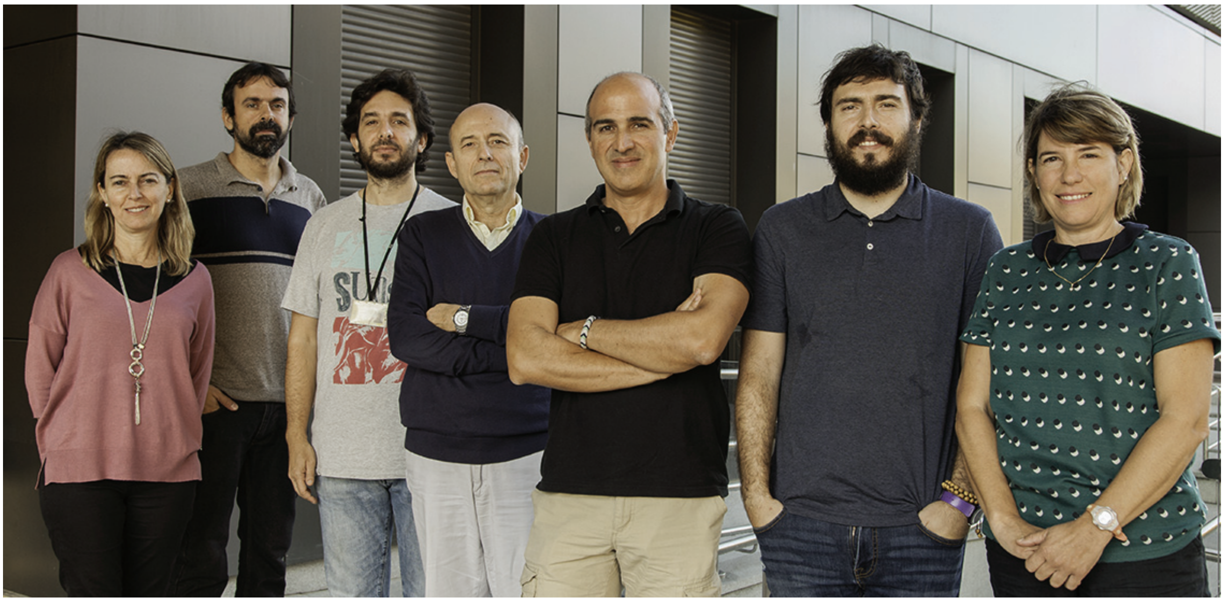
Tres cámaras de deposición por la técnica de pulverización catódica (magnetrón sputtering). Con una dotación total de 7 cabezas magnetrón, 2 fuentes DC, 2 fuentes RF y 1 fuente pulsada, portamuestras girables, calentables y "biased".
Una cámara de deposición por la técnica de pulverización catódica con fuente HIPIMS.

Equipamiento para microscopía electrónica
Sistema de preparación de muestras en película delgada TXP de Leica.
Pulidora, trípode y microscopio óptico.
TEM de 300kV Tecnai F30 dotado de modo STEM, detector HAADF, analizador EDX Oxford Max80 y filtro de energías GIF Quantum.

Propiedades mecánicas de superficies y recubrimientos
Tribómetro CSM (movimiento lineal y rotativo) para evaluación de coeficientes de fricción y desgaste.
Tribómetro de alta temperatura (hasta 800ºC) –Microtest
Calotest para medida de espesores y evaluación del desgaste.
Equipo de rayado (Scratch-test) hasta 200N (Tribotechnic).
Perfilómetro-rugosímetro (Mahr) de tipo táctil y resolución vertical nanométrica.

Propiedades eléctricas de materiales
Sistema de medida de espectroscopía de impedancia compleja, formado por un impedancímetro Agilent modelo 4294ª, un horno Hobersal ST115020, y una celda de medida hermética para la realización de medidas en atmósfera.

MATERIALES ÓPTICOS
OPTICAL MATERIALS



GRUPOS DE INVESTIGACIÓN

Materiales Coloidales
Colloidal Materials [642011]
http://colmat.icmse.csic.es

Materiales Ópticos Multifuncionales
Multifunctional Optical Materials [642013]
http://mom.icmse.csic.es

PERSONAL / PERSONNEL

Profesores de Investigación

Dr. Hernán R. Míguez García
Dr. Manuel Ocaña Jurado

Científicos Titulares

Dra. Ana Isabel Becerro Nieto
Dr. Mauricio E. Calvo Roggiani
Dr. Gabriel Lozano Barbero
Dra. Nuria O. Núñez Álvarez

Doctores Distinguidos

Dr. Juan F. Galisteo López

Investigadores Contratados

Dra. Laura Calio

Becarios Predoctorales

Lda. Victoria Esteso Carrizo
Ldo. Daniel González Mancebo
Ldo. José María Miranda Muñoz
Ldo. Andrea Rubino

Personal Contratado

Ldo. Miguel Anaya Martín (hasta agosto)
Lda. Elena Cabello Olmo
Lda. Lucía T. Castillo Flores
Lda. M. Carmen Gutiérrez Lázaro
Ldo. Mariano Laguna Moreno

PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

Materiales ópticos basados en nanofósforos para la próxima generación de dispositivos emisores de luz Nanophosphor-based photonic materials for next generation light-emitting devices NANOPHOM

Código/Code: H2020-ERC-STG/0259
Periodo/Period: 1-04-2017 / 31-03-2022
Organismo Financiador/Financial source: European Commission STARTING GRANT
Importe total/Total amount: 1.499.739 €
Investigador responsable/Research head: Gabriel S. Lozano Barbero

RESUMEN / ABSTRACT

El desarrollo de fuentes de luz eficientes y respetuosas con el medio ambiente constituye una parte esencial de la estrategia mundial para reducir el consumo mundial de electricidad. Los diodos emisores de luz (LED de sus siglas en inglés) emergen como la alternativa a la iluminación convencional, debido a su alta eficiencia de conversión de energía, larga vida útil, conmutación rápida, robustez y tamaño compacto. Sin embargo, su implementación en la industria electrónica de consumo se ve obstaculizada por el control limitado sobre el brillo, la calidad del color y la direccionalidad de la emisión de LED que proporcionan los elementos ópticos convencionales cuyo funcionamiento se basa en la óptica geométrica.

Este proyecto explora nuevas formas de controlar las propiedades de emisión de nanomateriales luminiscentes, superando los límites impuestos por la óptica convencional, mediante el uso de arquitecturas nanofotónicas. El desarrollo de materiales ópticos fiables y escalables basados en nanofósforos permitirá un control espectral y angular fino sobre la emisión de luz, abordando las deficiencias que los LED actuales presentan. El nuevo diseño óptico de estos dispositivos estará basado en la integración de multicapas ópticas, texturas superficiales, y nano dispersores de composición, tamaño y forma controlados, para obtener materiales que posean propiedades ópticas que faciliten un control preciso de la radiación visible.

Nanophom permitirá mejorar nuestra comprensión sobre fenómenos fundamentales como la formación de modos fotónicos en medios ópticos complejos a los que se puede acoplar la luz, así como avanzar en el desarrollo de dispositivos de iluminación de estado sólido de alta eficiencia.

Energy-efficient and environmentally friendly light sources are an essential part of the global strategy to reduce the worldwide electricity consumption. Light-emitting diodes (LEDs) emerge as a key alternative to conventional lighting, due to their high power-conversion efficiency, long lifetime, fast switching, robustness, and compact size. Nonetheless, their implementation in the consumer electronic industry is hampered by the limited control over brightness, colour quality and directionality of LED emission that conventional optical elements relying on geometrical optics provide.

This project exploits new ways of controlling the emission characteristics of nanophosphors, surpassing the limits imposed by conventional optics, through the use of nanophotonic concepts. The development of reliable and scalable nanophosphor-based photonic materials will allow ultimate spectral and angular control over the light emission properties, addressing the critical shortcomings of current LEDs. The new optical design of these devices will be based on multilayers, surface textures and nano-scatterers of controlled composition, size and shape, to attain large-area materials possessing photonic properties that will enable a precise management of the visible radiation.

Nanophom will significantly advance our comprehension of fundamental phenomena like the formation of photonic modes in complex optical media to which light can couple, as well as advancing the state of the art of high-efficiency solid-state lighting devices.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Materiales ópticos avanzados para dispositivos optoelectrónicos más eficientes Advanced optical materials for more efficient optoelectronic devices

Código/Code:	MAT2017-88584-R
Periodo/Period:	01-01-2018 / 31-12-2020
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	181.500 €
Investigador responsable/Research head:	Hernán Míguez García
Componentes/Research group:	Juan F. Galisteo López, Mauricio E. Calvo Roggiani, Gabriel S. Lozano Barbero

RESUMEN / ABSTRACT

El proyecto MODO busca optimizar el diseño óptico de dispositivos optoelectrónicos, ya sean fotovoltáicos o emisores de luz, con el objetivo de aumentar su eficiencia o dotarles de nueva funcionalidad. La hipótesis en la que se basa este proyecto es que este objetivo principal puede lograrse mediante la integración de materiales ópticos que permitan controlar la interacción radiación-materia en las láminas absorbentes u ópticamente activas del dispositivo. La estrategia propuesta consiste en realizar, secuencialmente, el diseño, preparación, caracterización e integración en prototipos de estructuras fotónicas de diverso tipo (cristales fotónicos, partículas metálicas, medios ópticos desordenados, superficies corrugadas), empleando principalmente técnicas de procesado en solución escalables y compatibles con las usualmente empleadas para la fabricación de los dispositivos objeto de estudio.

La tecnología optoelectrónica basada en perovskitas ha despertado en los últimos años un interés extraordinario debido a las altas eficiencias de conversión de energía lumínica en eléctrica, superiores al 20%, que se han alcanzado en un tiempo relativamente corto comparado con la evolución de otras tecnologías fotovoltáicas. Por otro lado, presentan elevados

rendimientos cuánticos de fotoemisión en el verde y el rojo, lo que también las convierte en candidadatas a recubrimientos emisores de luz. Sin embargo, estas expectativas se ven parcialmente ensombrecidas debido a los problemas de estabilidad y potencial impacto ambiental que estas perovskitas presentan. Es uno de los objetivos prioritarios de este proyecto proponer soluciones a estos problemas concretos a través de diseños ópticos que permitan reducir tanto la cantidad de material empleado como la exposición de la lámina activa a ambientes que induzcan su degradación. Se presente ahondar en la compresión de los fenómenos que intervienen en la degradación fotoinducida de estos materials en entornos de distinto tipo, lo que nos permitirá proponer soluciones concretas para desarrollar láminas de perovskita más estables y eficientes. Por otra parte, el proyecto MODO explorará la mejora de una nueva tecnología fotovoltáica, propuesta muy recientemente, basada en nanocristales semiconductores de AgBiS2, de muy bajo impacto ambiental pero con una absorción óptica aún muy inferior al resto de celdas emergentes.

Simultáneamente, se aplicarán a dispositivos emisores de luz, basados en nanocristales semiconductores y compuestos orgánicos foto- y electroluminiscentes, conceptos orientados a la amplificación direccional de la luminiscencia en rangos espectrales seleccionados a través del control de la densidad local de estados fotónicos. Se explorará la posibilidad de controlar la dinámica de decaimiento de estodos excitados a escala macroscópica y la de observar de emisión láser. En todos los casos, el rendimiento energético de los dispositivos objeto de estudio no ha sido optimizado anteriormente desde el punto de vista del diseño óptico.

La propuesta se enmarca dentro del Reto Social denominado “Energía segura, eficiente y limpia” y tiene como objetivo desarrollar tecnología fotónica empleando herramientas de la nanotecnología y del campo de materiales avanzados, todas ellas identificadas como Tecnologías Facilitadoras Esenciales en el programa de H2020 e incluídas en la Estrategia Española de Ciencia y Tecnología.

The MODO project is focused on the optimization of the optical design of optoelectronic devices, be they photovoltaic or light emitting ones, with the aim of increasing their efficiency or endow them with new functionalities. The hypothesis on which it is based is that this goal can be reached by means of the integration of optical materials that allow controlling the radiation-matter interaction in the absorbing or optically active layers of the device. The strategy herein proposed is based on the sequential realization of design, preparation, characterization and integration of devices of diverse photonic structures (photonic crystals, metallic particles, disordered optical media, corrugated surfaces) employing mainly solution processing techniques fully compatible with those used to fabricate the targeted devices. Optoelectronic technology based on perovskites has attracted a great deal of interest in the last years as a result of the high solar to electric power conversion efficiency, above 20%, that have been reached in a relatively short time compared to other photovoltaic technologies. At the same time, they present high photoemission quantum yields in the green and the red, which make them also good candidates as color converter layers for LEDs. However, these expectations are partially threatened by both the stability problems and potentially toxic environmental effects they present. It is one of the main goals of this project to propose solutions to specific drawbacks present in the optoelectronic technology based on hybrid perovskites through the implementation of optical designs that gives rise to a reduction of both the amount of material employed as well as the exposure to environments that typically degrade them. We seek to deepen our understanding of phenomena that give rise to the photoinduced degradation of these materials when exposed to diverse environments, which will allow us to propose specific solutions to develop more stable and efficient perovskite layers. Simultaneously, concepts based on the strict control over the local density of photon states and oriented to the directional amplification of luminescence at selected spectral ranges will be applied to light emitting devices based on semiconductor nanocrystals as well as to photo- and electro-luminescent organic compounds. Full control over the excited state decay dynamics over large areas and observation of laser emission will also be sought after. In all cases, the energy efficiency of the targeted devices has not been optimized before from the point of view of the optical design.

The proposal is included in the framework of the Societal Challenge called "Secure, clean and efficient energy" and aims to develop photonic technology using nanotechnology tools and in the advanced materials field, all identified as Key Enabling Technologies KETs in the Spanish Strategy on Science and Technology, aligned with the European Program H2020.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Verificación de la existencia de fuerzas de Casimir repulsivas en la macroescala en láminas delgadas suspendidas y autosoportadas

Verification of the existence of macroscale repulsive Casimir forces in suspended self-standing films

Código/Code:	FIS2017-91018-EXP
Periodo/Period:	01-11-2018 / 31-10-2020
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Importe total/Total amount:	36.300 €
Investigador responsable/Research head:	Hernán Míguez García

RESUMEN / ABSTRACT

El proyecto VERSUS tiene como objetivo principal realizar la primera observación de fuerzas de Casimir-Lifshitz repulsivas en sistemas macroscópicos plano-paralelos. Para esto se centraá en el diseño, fabricación y caracterización de materiales ópticos que permitan controlar la intensidad y naturaleza de la fuerza de Casimir-Lifshitz, de forma que puedan observarse y caracterizarse fenómenos de levitación debido al balance de ésta y la fuerza gravitatoria. Esta propuesta, readicalmente novedosa, hace uso de técnicas de espectroscoìa óptica (basadas en interferencia óptica entre los haces parcialmente reflejados y transmitido en las intercaras del sistema plano-paralelo) para caracterizar la distancia de equilibrio a la que el sistema levita sobre un sustrato. Para ello, se parte de diseños de materiales cuyas propiedades ópticas y densidades son tales que sumergidas en distintos fluidos leviten sobre ciertos sustratos como resultado del balance de esas fuerzas, como recientemente ha sido demostrado de forma teórica por el equipo solicitante. Nuestro grupo ha demostrado teóricamente que existen combinaciones de materiales que fabricados en forma de láminas delgadas (< 1 micra) pueden levitar a distancias del orden de las pocas decenas o centenas de nanómetros sobre un sustrato adecuado. En particular, láminas de tefón, poliestireno y sílice inmersas en glicerol levitan sobre una oblea de silicio, siendo las distancias de equilibrio controlables y sintonizables a través del grosor de las láminas delgadas y la temperatura del sistema. Las láminas delgadas autosoportadas deben ser compactas, mecánicamente estables, de superficies planas, grosor controlado y químicamente afines al fluido en el que están sumergidas. La observación macroscópicas de fuerzas repulsivas de Casimir-Lifshitz, nunca reportada anteriormente, mediante medidas de espectroscopía óptica constituiria un logro sin precedentes en el campo del estudio de las interacciones fundamentales de la materia.

The ultimate goal of the VERSUS project is the first observation of repulsive Casimir-Lifshitz forces in macroscopic plane-parallel systems. To this end, it will focus on the design, fabrication, and characterization of optical materials that allow controlling the intensity and nature of the Casimir-Lifshitz force, so that levation phenomena can be observed and characterized due to the balance between the latter and gravity force. This radically new approcah makes use of optical spectroscopic techniques (based on optical interferometry between the partially reflected and transmitted light at the interfaces of the plane-parallel system) for characterizing the equilibrium distance at which the system levitates over a substrate. According to very recent results attained by the applicant group, it is possible to find materials whose optical constants and densities are such that when they are immersed in a fluid they can levitate over a substrate as a result of the aforementioned force balance. Our group has recently demonstrated theoretically that there is a number of materials that prepared in this films (<1 micrometer) can levitate several tens or hundreds of nanometers over a carefully selected substrate. Specifically, thin layers made of teflon, polystyrene or silicon dioxide immersed in glycorel are expected to levitate over a silicon wafer, being possible to tune the equilibrium distances at which such layers will be suspended through their thicknesses and temperature of the system. The devised selft-standing thin films (in single layers or multilayer arrangements) must be compact, mechanically stable, of smooth surfaces, of controlled thickness, and chemically compatible with the fluid in which they are immersed. The macroscopic observation of repulsive Casimir-Lifshitz forces, never reported before, through optical spectroscopic measurements would constitute an unprecedented milestone in the field of fundamental matter interactions.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Adquisición de un equipo de medida de espectroscopía ultrarrápida de estados transitorios para el servicio de espectroscopías del ICMS.

Código/Code:	EQC2018-004413-P
Periodo/Period:	01-01-2018 / 31-12-2020
Organismo Financiador/Financial source:	Ministerio de Ciencia e Innovación
Importe total/Total amount:	441.843,34 €
Investigador responsable/Research head:	Hernán Míguez García

RESUMEN / ABSTRACT

La técnica que pretende implementarse, la espectroscopía ultrarrápida de absorción de estados transitorios, es actualmente una de las más potentes para estudiar los procesos de excitación de materiales y compuestos empleados en numerosos campos tales como energía

fotovoltaica, iluminación, fotosíntesis o catálisis, lo que explica la diversidad temática de los grupos que apoyan esta propuesta. Pese a su sofisticación, es una técnica ya imprescindible para la mayor parte de grupos de relevancia internacional en los ámbitos mencionados. Andalucía, aunque cuenta con grupos de gran reconocimiento en esos campos, no dispone de un laboratorio de referencia en este tipo de caracterización que dé servicio a la comunidad científica relacionada, lo que supone una clara desventaja competitiva con respecto a otros países. La adquisición de este equipo a través del Servicio General de Espectroscopías del ICMS, permitirá solucionar esta desventaja. El ICMS, a través de su Unidad Estructural de Materiales Ópticos, cuenta con personal permanente recientemente incorporado al centro altamente cualificado y con experiencia en este tipo de caracterización, adquirida en estancias postdoctorales en centros nacionales y extranjeros de gran prestigio.

Ultrafast absorption spectroscopy of transient states is nowadays one of the most powerful ones to analyze excitation processes in materials and compounds used in numerous fields such as photovoltaics, lighting, photosynthesis or catalysis, which explains the great diversity of groups supporting this application. In spite of its sophistication, it is already an irreplaceable technique for most groups of international relevance in these fields. Andalucía, although it counts with renowned groups in these areas, does not have an open laboratory that can provide support to the related scientific community, which implies a competitive disadvantage with respect to other countries. The acquisition of this equipment through the General Spectroscopy Service of the ICMS will help to solve this situation. The ICMS, through its Department of Optical Materials, counts with recently incorporated permanent scientific staff skilled and trained in this type of characterization, attained during postdoctoral stays in national and international centers of great prestige.

OTROS PROYECTOS / OTHER PROJECTS

Nanopartículas basadas en matrices inorgánicas de tierras raras para aplicaciones biotecnolóticas

Código/Code:	201560E056
Periodo/Period:	01-06-2015 / 01-05-2019
Organismo Financiador/Financial source:	CSIC (Intramural)
Importe total/Total amount:	75.789 €
Investigador responsable/Research head:	Ana Isabel Becerro Nieto

Materiales ópticos avanzados para dispositivos optoelectrónicos más eficientes

Código/Code:	PIC2016FR1
Periodo/ Period:	01-01-2017 / 31-12-2019
Organismo Financiador/Financial source:	CSIC (PIC)
Importe total/Total amount:	10.000,00 €
Investigador responsable/Research head:	Ana Isabel Becerro Nieto

Fotofísica de perovskitas híbridas de metal-haluro

Código/Code:	201860I068
Periodo/ Period:	22/11/2018 / 21/11/2019
Organismo Financiador/Financial source:	CSIC
Importe total/Total amount:	5.000,00 €
Investigador responsable/Research head:	Juan F. Galisteo López

Arquitecturas fotonicas para fuentes de luz mas versatiles

Código/Code:	201860I067
Periodo/ Period:	22/11/2018 / 21/11/2019
Organismo Financiador/Financial source:	CSIC
Importe total/Total amount:	5.000,00 €
Investigador responsable/Research head:	Gabriel S. Lozano Barbero

Convenios y Contratos / Contracts and Agreements

Evaluación de la aplicabilidad de diversas estructuras inorgánicas como matriz huésped en el desarrollo de pigmentos inorgánicos (PAINTINK)

Periodo/Period:	01-03-2018 / 15-04-2019
Organismo Financiador/Financial source:	AL-FARBEN, S.A.
Importe total/Total amount:	82.764 €
Investigador responsable/Research head:	Manuel Ocaña Jurado
Componentes/Research group:	Nuria Núñez Alvarez, Ana Isabel Becerro Nieto

SPIRE: Solar Power Integrated Renewable Energy System (FEDER INTERCONNECTA)

Periodo/Period:	24-11-2016 / 31-12-2018
Organismo Financiador/Financial source:	GHENOVA INGENIERIA S.L.U.
Importe total/Total amount:	302.500 €
Investigador responsable/Research head:	Hernán Míguez García
Componentes/Research group:	Gabriel S. Lozano Barbero, Mauricio Calvo Roggiani, Juan F. Galisteo López, Alberto Jiménez Solano

PATENTES / PATENTS

Efficient transparent white light emitting layered phosphor structure of tunable shade, process for obtaining said structure and uses

Inventores: Dongling Geng, Hernán R. Míguez García, Gabriel S. Lozano Barbero
Tipo de Patente: Nacional
Número de Solicitud: 18382592
Fecha Solicitud: 3 de marzo de 2018
Entidad Titular: Consejo Superior de Investigaciones Científicas

ABX3 compounds with perovskite crystalline structure infiltrated within a porous metal oxide film

Inventores: Andrea Rubino, Mauricio E. Calvo Roggiani, Hernán R. Míguez García, Juan F. Galisteo López
Tipo de Patente: Nacional
Número de Solicitud: 18382341
Fecha Solicitud: 18 de mayo de 2018
Entidad Titular: Consejo Superior de Investigaciones Científicas y Universidad de Sevilla

ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

High voltage vacuum-deposited CH3NH3PbI3–CH3NH3PbI3 tandem solar cells

Avila, J; Momblona, C; Boix, P; Sessolo, M; Anaya, M; Lozano, G; Vandewal, K; Miguez, H; Bolink, HJ
Energy & Environmental Science, **11** (2018) 3292-3297
Noviembre, 2018 | **DOI:** 10.1039/c8ee01936c

The recent success of perovskite solar cells is based on two solid pillars: the rapid progress of their power conversion efficiency and their flexibility in terms of optoelectrical properties and processing methods. That versatility makes these devices ideal candidates for multi-junction photovoltaics. We report an optically optimized double junction CH3NH3PbI3-CH3NH3PbI3 tandem solar cell where the matched short-circuit current is maximized while parasitic absorption is minimized. The use of an additive vacuum-deposition protocol allows us to reproduce calculated stack designs, which comprise several charge selective materials that ensure appropriate band alignment and charge recombination. This rationalized configuration yields an unprecedented open circuit voltage of 2.30 V. Furthermore, this tandem solar cell features efficiencies larger than 18%, higher than those of the individual sub-cells. Low photo-current values allow reducing the losses associated to the series resistance of transparent contacts, which opens the door to the realization of efficient large area modules.

Photonic structuring improves the colour purity of rare-earth nanophosphors

Geng, DL; Cabello-Olmo, E; Lozano, G; Miguez, H
Materials Horizons, **5** (2018) 661-667
Julio, 2018 | **DOI:** 10.1039/c8mh00123e

Nanophosphor integration in an optical cavity allows unprecedented control over both the chromaticity and the directionality of the emitted light, without modifying the chemical composition of the emitters or compromising their efficiency. Our approach opens a route towards the development of nanoscale photonics based solid state lighting.

Highly Efficient and Environmentally Stable Flexible Color Converters Based on Confined $CH_3NH_3PbBr_3$ Nanocrystals

Rubino, A; Anaya, M; Galisteo-Lopez, JF; Rojas, TC; Calvo, ME; Miguez, H
ACS Applied Materials & Interfaces, **10** (2018) 38334-38340
Noviembre, 2018 | **DOI:** 10.1021/acsami.8b11706

In this work, we demonstrate a synthetic route to attain methylammonium lead bromide (CH3NH3PbBr3) perovskite nanocrystals (nc-MAPbBr(3), 1.5 nm < size < 3 nm) and provide them with functionality as highly efficient flexible, transparent, environmentally stable, and adaptable color converting films. We use nanoparticle metal oxide (MOx) thin films as porous scaffolds of controlled nanopores size distribution to synthesize nc-MAPbBr(3) through the infiltration of perovskite liquid precursors. We find that the control over the reaction volume imposed by the nanoporous scaffold gives rise to a strict control of the nanocrystal size, which allows us to observe well-defined quantum confinement effects on the photo-emission, being the luminescence maximum tunable with precision between lambda = 530 nm (green) and lambda = 490 nm (blue). This hybrid nc-MAPbBr(3)/MOx structure presents high mechanical stability and permits subsequent infiltration with an elastomer to achieve a self-standing flexible film, which not only maintains the photo-emission efficiency of the nc-MAPbBr(3) unaltered but also prevents their environmental degradation. Applications as adaptable color-converting layers for light-emitting devices are envisaged and demonstrated.

The Role of Metal Halide Perovskites in Next-Generation Lighting Devices

Lozano, G.
Journal of Physical Chemistry Letters, **9** (2018) 3987-3997
Julio, 2018 | **DOI:** 10.1021/acs.jpclett.8b01417

The development of smart illumination sources represents a central challenge for current technology. In this context, the quest for novel materials that enable efficient light generation is essential. Metal halide compounds with perovskite crystalline structure (ABX(3)) have gained tremendous interest in the last five years since they come as easy-to-prepare high performance semiconductors. Perovskite absorbers are driving the power-conversion-efficiencies of thin film photovoltaics to unprecedented values. Nowadays, mixed-cation, mixed-halide lead perovskite solar cells reach efficiencies consistently over 20% and promise to get close to 30% in multijunction devices when combined with silicon cells at no surcharge. Nonetheless, perovskites' fame extends further since extensive research on these novel semiconductors has also revealed their brightest side. Soon after their irruption in the photovoltaic scenario, demonstration of efficient color tunable-with high color purity-perovskite emitters has opened new avenues for light generation applications that are timely to discuss herein.

Origin of Light-Induced Photophysical Effects in Organic Metal Halide Perovskites in the Presence of Oxygen

Anaya, M; Galisteo-Lopez, JF; Calvo, ME; Espinos, JP; Miguez, H
Journal of Physical Chemistry Letters, **9** (2018) 3891-3896
Julio, 2018 | **DOI:** 10.1021/acs.jpclett.8b01830

Herein we present a combined study of the evolution of both the photoluminescence (PL) and the surface chemical structure of organic metal halide perovskites as the environmental oxygen pressure rises from ultrahigh vacuum up to a few thousandths of an atmosphere. Analyzing the changes occurring at the semiconductor surface upon photoexcitation under a controlled oxygen atmosphere in an X-ray photoelectron spectroscopy (XPS) chamber, we can rationalize the rich variety of photophysical phenomena observed and provide a plausible explanation for light-induced ion migration, one of the most conspicuous and debated concomitant effects detected during photoexcitation. We find direct evidence of the formation of a superficial layer of negatively charged oxygen species capable of repelling the halide anions away from the surface and toward the bulk. The reported PL transient dynamics, the partial recovery of the initial state when photoexcitation stops, and the eventual degradation after intense exposure times can thus be rationalized.

Absorption and Emission of Light in Optoelectronic Nanomaterials: The Role of the Local Optical Environment

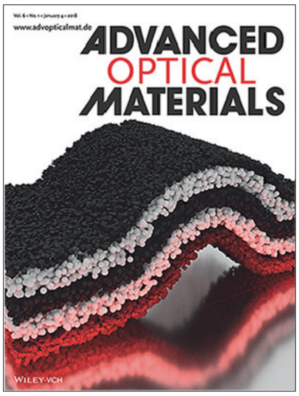
Jimenez-Solano, Alberto; Galisteo-Lopez, Juan F.; Miguez, Hernan
Journal of Physical Chemistry Letters, **9** (2018) 2077-2084
Abril, 2018 | **DOI:** 10.1021/acs.jpclett.8b00848

Tailoring the interaction of electromagnetic radiation with matter is central to the development of optoelectronic devices. This becomes particularly relevant for a new generation of devices offering the possibility of solution processing with competitive efficiencies as well as new functionalities. These devices, containing novel materials such as inorganic colloidal quantum dots or hybrid organic-inorganic lead halide perovskites, commonly demand thin (tens of nanometers) active layers in order to perform optimally and thus maximizing the way electromagnetic radiation interacts with these layers is essential. In this Perspective, we discuss the relevance of tailoring the optical environment of the active layer in an optoelectronic device and illustrate it with two real-world systems comprising photovoltaic cells and light emitting devices.

Unexpected Optical Blue Shift in Large Colloidal Quantum Dots by Anionic Migration and Exchange

Acebron, M; Galisteo-Lopez, JF; Lopez, C; Herrera, FC; Mizrahi, M; Requejo, FG; Palomares, FJ; Juarez, BH
Journal of Physical Chemistry Letters, **9** (2018) 3124-3130
Junio, 2018 | **DOI:** 10.1021/acs.jpclett.8b00741

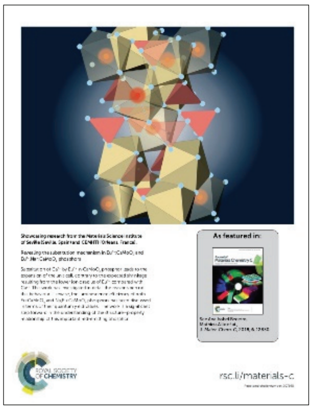
Compositional changes taking place during the synthesis of alloyed CdSeZnS nanocrystals (NCs) allow shifting of the optical features to higher energy as the NCs grow. Under certain synthetic conditions, the effect of those changes on the surface/interface chemistry competes with and dominates over the conventional quantum confinement effect in growing NCs. These changes, identified by means of complementary advanced spectroscopic techniques such as XPS (X-ray photoelectron spectroscopy) and XAS (X-ray absorption spectroscopy), are understood in the frame of an ion migration and exchange mechanism taking place during the synthesis. Control over the synthetic routes during NC growth represents an alternative tool to tune the optical properties of colloidal quantum dots, broadening the versatility of the wet chemical methods.



Flexible and Adaptable Light-Emitting Coatings for Arbitrary Metal Surfaces based on Optical Tamm Mode Coupling

Jiménez-Solano, A.; Galisteo-López, J.; Míguez, H.
Advanced Optical Materials, **6** (2018) 1700560
Enero, 2018 | **DOI:** 10.1002/adom.201700560

This study demonstrates a design that maximizes the power radiated into free space from a monolayer of nanoemitters embedded in a flexible distributed Bragg reflector conformably attached to a metal surface. This is achieved by positioning the light source at the precise depth within the multilayer for which optical Tamm states provide enhanced quantum yield and outcoupling efficiency, which are combined to optimize the luminous power radiated by the surface of the ensemble. This approach, based on the adhesion of flexible multilayer stacks onto metal surfaces with an arbitrary curvature, is versatile and permits the realization of spectrally narrow monodirectional or self-focusing light-emitting surfaces.



Revealing the substitution mechanism in Eu^{3+}:CaMoO$_4$ and Eu^{3+},Na^{+}:CaMoO$_4$ phosphors

Becerro, AI; Allix, M; Laguna, M; Gonzalez-Mancebo, D; Genevois, C; Caballero, A; Lozano, G; Nunez, NO; Ocana, M
Journal of Materials Chemistry C, **6** (2018) 47
Diciembre, 2018 | **DOI:** 10.1039/c8tc04595j

Eu^{3+}-Doped calcium molybdate is an excellent phosphor for lighting and display devices due to the very intense pure red emission after UV excitation. It has been reported in the literature that the CaMoO$_4$ unit cell volume expands after Eu^{3+} doping, in spite of the smaller Eu^{3+} ionic radius compared with Ca^{2+}. Likewise, several studies found that the emission intensity of the phosphor could be improved by codoping with alkaline ions like Li^+, Na^+ or K^+. None of these studies correlated the apparent volume expansion and luminescence enhancement with the crystal structural details. This paper analyses the aliovalent substitution mechanism and crystal structure of Eu^{3+}:$CaMoO_4$ and Eu^{3+},Na^+:$CaMoO_4$ phosphors using complementary techniques like Raman spectroscopy, EXAFS and SPD. We found that the substitution mechanism was different for both systems, with Ca site vacancies forming in the Eu^{3+}:$CaMoO_4$ phosphors and leading to Ca1-3xEu2xxMoO$_4$ compositions, while the Eu^{3+},Na^+:$CaMoO_4$ phosphors formed Ca1-2xEuxNaxMoO4. SPD showed that the cell volume expansion observed with increasing Eu^{3+} content is related to the increase of the Mo-O bond distance due to the higher electronegativity of Eu^{3+} compared with Ca^{2+}. Finally, it was shown that the luminescence properties, i.e. lifetime values and quantum yields (the latter reported here for the first time), do not depend on the presence of monovalent ions in the crystal structure but, exclusively, on the Eu^{3+} content of the phosphor. The integral and detailed analysis of the materials presented in this paper, ranging from crystal structure to luminescent properties including elemental composition, allows a full picture of the structure-property relationships that had never been addressed before for $CaMoO_4$-based phopshors.

Room temperature synthesis of water-dispersible Ln($^{3+}$):CeF_3 (Ln = Nd, Tb) nanoparticles with different morphology as bimodal probes for fluorescence and CT imaging

Gonzalez-Mancebo, D; Becerro, AI; Rojas, TC; Olivencia, A; Corral, A; Balcerzyk, M; Cantelar, E; Cusso, F; Ocana, M

Journal of Colloid and Interface Science, **520** (2018) 134-144

Junio, 2018 | **DOI:** 10.1016/j.jcis.2018.03.007

The singular properties of lanthanide-based inorganic nanoparticles (NPs) has raised the attention of the scientific community in biotechnological applications. In particular, those systems with two or more functionalities are especially interesting. In this work, an effective and commercially attractive procedure has been developed that renders uniform, water-dispersible Ln($^{3+}$):CeF_3 (Ln = Tb, Nd) NPs with different shapes and size. The method consists of the homogeneous precipitation, in a mixture of polyol and water, of cations and anions using precursors that allow the controlled release of the latter. The advantages of the reported method are related to the absence of surfactants, dispersing agents or corrosive precursors as well as to the room temperature of the process. The obtained Tb:CeF_3 NPs produce an intense emission after excitation through the Ce-Tb energy transfer band located in the UV spectral region, thus being potentially useful as phosphors for in-vitro imaging purposes. On the other hand, the synthesized Nd:CeF_3 NPs are good candidates for in-vivo imaging because their excitation and emission wavelengths lie in the biological windows. Finally, the excellent X-ray attenuation efficacy of the Nd:CeF($_3$)NPs is shown, which confers double functionality to this material as both luminescence bioprobe and contrast agent for X-ray computed-tomography.

Improving the Bulk Emission Properties of $CH_3NH_3PbBr_3$ by Modifying the Halide-Related Defect Structure

Tiede, David O.; Calvo, Mauricio E.; Galisteo-Lopez, Juan F.; Miguez, Hernan

Journal of Physical Chemistry C, **122** (2018) 27250-27255

Diciembre, 2018 | **DOI:** 10.1021/acs.jpcc.8b09315 DEC 6 2018

The peculiar defect chemistry of hybrid organic–inorganic lead halide perovskites is believed to be partially responsible for the outstanding performance of this solution-processed material in optoelectronic devices. While most effort has been put on the management of halide defects (the ones presenting the highest mobility) for $CH_3NH_3PbI_3$, its bromide counterpart has not been so widely studied. Although the former is the material of choice for photovoltaics, the latter is present in most light-emitting applications. Here, we report how the exposure of $CH_3NH_3PbBr_3$ single crystals to a bromine atmosphere strongly affects its emission properties. Such improvement takes place in the absence of apparent signs of degradation and remains for tens of hours. We propose an explanation based on the defect structure for this material where bromine-related defects can act as deep or shallow traps. These results are of relevance for a material expected to be present in a new generation of solution-processed light-emitting devices.

Synthesis and optical properties of environmentally benign and highly uniform $NaCe(MoO_4)(2)$ based yellow nanopigments

Laguna, M; Nuñez, NO; Fernandez, M; Ocaña, M
Journal of Alloys and Compounds, **739** (2018) 542-548
Marzo, 2018 | **DOI:** 1 10.1016/j.jallcom.2017.12.158

A method for the synthesis of uniform and aggregation free $NaCeMoO_4$ based nanospheroids with tunable size is reported. The procedure is based on a precipitation reaction at 120 degrees C for 20 h from solutions containing Na_2MoO_4, sodium citrate and $Ce(NO_3)(3)$ and different amounts of $Y(NO_3)(3)$ or $Gd(NO_3)(3)$. The role played by the later compounds on the formation of the particles and their morphological and structural characteristics is analyzed through the analysis of the mechanism of particle formation. The chromaticity coordinates of the obtained samples are also evaluated showing that the here reported nanoparticles constitute an ecofriendly alternative to more toxic commercial yellow pigments. The synthesized nanoparticles are also free of aggregation in water suspensions and might be suitable for injet-printing technologies.

Structural, optical and X-ray attenuation properties of Tb^{3+}: $Ba_xCe_{1-x}F_{3-x}$ (x=0.18-0.48) nanospheres synthesized in polyol medium

Gonzalez-Mancebo, D; Becerro, AI; Genevois, C; Allix, M; Corral, A; Parrado-Gallego, A; Ocana, M
Dalton Transactions, **47** (2018) 8382-8391
Julio, 2018 | **DOI:** 10.1039/c8dt01202d

Uniform $Ba_{0.18}Ce_{0.82}F_{2.82}$ nanospheres have been obtained after aging a solution of barium and cerium nitrates and sodium tetrafluoroborate in a mixture of ethylene glycol and water at 120 degrees C for 20 hours. The diameter of the spheres could be tailored from 65 nm to 80 nm by varying the $NaBF_4$ concentration while maintaining their colloidal stability in aqueous suspension. Increasing the aging temperature led to a phase transformation from hexagonal to cubic symmetry and to a concomitant increase of the Ba/Ce ratio, which reached a value close to the nominal one (50/50) at 240 degrees C. The same method was successful in obtaining Tb^{3+}-doped nanospheres with homogeneous cation distribution and the same morphological features as the undoped material. An intense green emission was observed after the excitation of the Tb^{3+}-doped samples through the Ce^{3+}-Tb^{3+} energy transfer (ET) band. The ET efficiency increased with increasing Tb content, the maximum emission being observed for the 10% Tb-doped nanospheres. Aqueous suspensions of the latter sample showed excellent X-ray attenuation values that were superior to those of an iodine-based clinically approved contrast agent. Their fluorescence and X-ray attenuation properties make this material a potential dual bioprobe for luminescence bioimaging and X-ray computed tomography.

Absorption enhancement in methylammonium lead iodide perovskite solar cells with embedded arrays of dielectric particles

Jimenez-Solano, A; Carretero-Palacios, S; Miguez, H

Optics Express, **26** (2018) A865-A878
Septiembre, 2018 | **DOI:** 10.1364/OE.26.00A865

In the field of hybrid organic-inorganic perovskite based photovoltaics, there is a growing interest in the exploration of novel and smarter ways to improve the cells light harvesting efficiency at targeted wavelength ranges within the minimum volume possible, as well as in the development of colored and/or semitransparent devices that could pave the way both to their architectonic integration and to their use in the flowering field of tandem solar cells. The work herein presented targets these different goals by means of the theoretical optimization of the optical design of standard opaque and semitransparent perovskite solar cells. In order to do so, we focus on the effect of harmless, compatible and commercially available dielectric inclusions within the absorbing material, methylammonium lead iodide (MAPI). Following a gradual and systematic process of analysis, we are capable of identifying the appearance of collective and hybrid (both localized and ex tended) photonic resonances which allow to significantly improve light harvesting and thus the overall efficiency of the standard device by above 10% with respect to the reference value while keeping the semiconductor film thickness to a minimum. We believe our results will be particularly relevant in the promising field of perovskite solar cell based tandem photovoltaic devices, which has posed new challenges to the solar energy community in order to maximize the performance of semitransparent cells, but also for applications focusing on architectonic integration.

LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS

Teodora Stoyanova Lyubenova · Juan Carda · Manuel Ocaña

Nuevos pigmentos cerámicos más respetuosos con el medio ambiente

Una propuesta de innovación tecnológica en la industria cerámica

Nuevos pigmentos cerámicos más respetuosos con el medio ambiente
Teodora Sloyanova Lyubenova, Juan B. Carda y Manuel Ocaña Jurado
Editorial Académica Española / OmniScriptum GmbH & Co. KG
Número de Páginas: 132
ISBN: 978-620-2-14754-5
Grupo Opticos (cambiar de sitio)

Una propuesta de innovación tecnológica en la industria cerámica. Este volumen recoge los avances en el desarrollo de pigmentos cerámicos con coloraciones rojizas que tanto se le han resistido a la industria cerámica, debido a su inestabilidad térmica, toxicidad o elevado coste. Los materiales se han desarrollado mediante vías alternativas a los métodos convencionales de obtención de pigmentos para lograr así reducir costes económicos y energéticos, disminuir la contaminación y dotar el producto final con mayor valor añadido. Este libro combina investigación científica y desarrollo tecnológico y puede ser de utilidad para investigadores y profesionales en el campo de los materiales cerámicos que deseen promover la innovación con el fin de aprovechar nuevas oportunidades

CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

Research Workshop Fundamental Processes in Perovskite and Thin Film Solar Cells 2017
2 – 3 octubre [Sevilla, España]
Hernán Míguez García [Miembro del Comité Organizador)

COMUNICACIONES / COMMUNICATIONS

KIT – LNM – MPI for Solid State Research
16 – 20 julio [Stuggart, Alemania]

Photonic materials for energy-saving applications
Gabriel Lozano
Conferencia invitada

Seminario Internacional: Plastics are Future
24 - 25 abril [Valencia, España]

Nuevas fronteras en materiales fotónicos: un concepto original en protección de rayos UV
M. Calvo
Conferencia invitada

10th International Conference on Hybrid and Organic Photovoltaics | HOPV18

28 – 31 mayo [Alicante, España]

Absorption and emission of light in optoelectronic nanomaterials: the role of the local optical environment
J.F. Galisteo-López, A. Jiménez-Solano, H. Míguez
Comunicación oral

ABX3 perovskite nanocrystals template in porous matrices
M. Calvo, A. Rubino, M. Anaya, J.F. Galisteo, H. Míguez
Comunicación oral

Origin of light induced ion migration on organic metal halide perovskites in the presence of oxygen
H. Míguez
Comunicación oral

Materials Science Engineering | MSE2018

26 – 28 septiembre [Darmstadt, Alemania]

Porous photonic nanostructures prepared by wet deposition methods
M. Calvo
Conferencia invitada

Photonic tuning of the emission color of rare-earth nanophosphors by integration
D. Geng
Comunicación oral

MRS Fall Meeting & Exhibit

25 – 30 noviembre [Massachusetts, Estados Unidos]

Mie Glasses: Optically disordered materials for optoelectronics applications
G. Lozano
Conferencia Invitada

Workshop “Correlated Disorder, Hyperuniformity and Local Self-Uniformity: From Biomimetics to Photonic Integrated Circuits”

25 – 30 noviembre [University of Surrey, Guildford, United Kingdom]

Mie Glasses: Optically disordered materials for optoelectronics applications
G. Lozano
Conferencia Invitada

2nd World Chemistry Conference and Exhibition (WCCE)

9 – 11 julio [Valencia, España]

Micro emulsion mediated synthesis and properties of uniform Eu:CaWO4 Nano phosphors for optical and CT imaging
M. Ocaña; M. Laguna; N.O. Nuñez; A. Corral; A. Parrado-Gallego; M. Balcerzyk; D. Gonzalez-Mancebo; A.I. Becerro
Conferencia Invitada

3rd International Conference on Polyol Mediated Synthesis (PMS)

25 – 27 junio [Madrid, España]

Uniform Ln^{3+}:CeF_3 (Ln= Nd; Tb) nanoparticles synthesized in polyol media as bimodal bioprobes for fluorescence and CT bio-imaging
A.I. Becerro; D. Gonzalez-Mancebo; T.C. Rojas; A. Corral; M. Balcerzyk; E. Cantelar; F. Cusso; M. Ocaña
Conferencia Invitada

16th International Conference on Plasma Surface Engineering

17 – 21 septiembre [Garmisch-Partenkirchen, Alemania]

Stuctural and optical characterization of Cr1-xAlx(O)N films prepared by HiPIMS
T.C. Rojas; A. Caro; G. Lozano; J.C. Sánchez-López
Poster

NanMed 2018

23 – 25 octubre [Venecia, Italia]

High intensity emitting Eu3+,Bi3+:LaF3 nanoparticles for luminescence bioimaging and X-ray computed tomography
A.I. Becerro; D. González Mancebo; A. Corral; M. Balzercyk; M. Ocaña
Poster

CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESS AND MEETINGS

COMUNICACIONES / COMMUNICATIONS

Congreso de Estudiantes de Física COEFIS XI
15-16 marzo [Santa Cruz de Tenerife, España]

Nanomateriales ópticoa para dispositivos optoelectrónicos
Hernán Míguez
Charla invitada

Workshop: Materiales y Tecnicas Opticas Avanzadas
1 agosto [Buenos Aires, Argentina]

Relevancia del entorno óptico local para la optimización del rendimiento de dispositivos optoelectrónicos
H. Miguez
Conferencia Invitada

Spanish Conference on Nanophotonics | CEN2018
3 – 5 octubre [San Sebastian, España]

Optimizing the emission from light sources in nanoporous photonic crystals
J.F. Galisteo-Lopez
Comunicación oral

Optical disorder for enhanced colour conversion and efficient bifacial dye-sensitized solar cells. The Mie glass: fabrication and characterization
José M. Miranda-Muñoz
Póster

X CPAN DAYS
29 – 13 octubre [Salamanca, España]

Nanopartículas de lantánidos para imagen multimodal. Biodistribución en ratón por MicroPET y NanoCT
L. Fernández-Maza; A. Corral; A.I. Becerro; D. González-Mancebo; A. Parrado; M. Balcerzyk; M. Ocaña
Comunicación oral

FORMACION / TRAINING

TESIS DOCTORALES/ DOCTOR DEGREE THESIS

Título: **Optical design of perovskite materials and solar cells**
Autor: Miguel Anaya Martín
Directores: Mauricio Calvo Roggiani y Hernán Míguez García
Calificación: Sobresaliente “Cum Laude”
Centro: Universidad de Sevilla
Fecha: 17 de mayo de 2018

FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

Título: **Estudios fotofísicos de láminas de perovskita**
Autor: David Otto Tiede
Directores: Juan F. Galisteo López, H. Míguez García
Grado: Trabajo Fin de Grado
Año Académico: 2017-2018 (11 junio 2018)

Título: **Modelización de dispositivos fotovoltáicos**
Autor: Juan Carlos Jurado Quero
Directores: Sol Carretero Palacios, H. Míguez García
Grado: Trabajo Fin de Grado
Año Académico: 2017-2018 (11 junio 2018)

Título: **Modelización de medios ópticos desordenados débilmente dispersores**
Autor: Rafael Garzón Cubero
Directores: Sol Carretero Palacios, H. Míguez García
Grado: Trabajo Fin de Master
Año Académico: 2017-2018 (29 junio 2018)

Título: **Desarrollo de medios ópticos desordenados con aplicaciones para dispositivos optoelectrónicos**
Autor: Borja Ortín Vinader
Directores: Gabriel Lozano Barbero, Hernán Míguez García
Grado: Trabajo Fin de Grado
Año Académico: 2017-2018 (11 julio 2018)

Título:	**Síntesis, caracterización y funcionalización de nanopartículas luminiscentes basadas en $LuVO_4$**
Autor:	José María Gordón Pidal
Directores:	Manuel Ocaña Jurado, Nuria Nuñez Alvarez
Grado:	Trabajo Fin de Master
Año Académico:	2017-2018 (21 septiembre 2018)

DOCENCIA / TEACHING

Doble Máster en Profesorado de Enseñanza Secundaria Obligatoria y Bachillerato, Formación Profesional y Enseñanza de Idiomas y Física Avanzada

Modelos de Sistemas Físicos

Gabriel Lozano Barbero

Lugar: Universidad de Córdoba

PREMIOS Y RECONOCIMIENTOS / PRIZES AND ACKNOWLEDGEMENTS

Jiménez Solano, Premio NANOMATMOL a la mejor tesis doctoral 2017

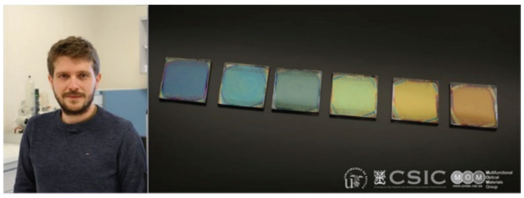
El trabajo de Alberto Jiménez Solano ha sido reconocido con el segundo accésit del premio a la mejor tesis doctoral presentada en 2017, concedido por el Grupo especializado de Nanociencia y materiales moleculares (NanoMatMol) de la Real Sociedad Española de Química (RSEQ) y de la Real Sociedad Española de Física (RSEF).

Alberto Jiménez Solano realizó sus estudios de doctorado en el Instituto de Ciencia de Materiales de Sevilla, adscrito al cicCartuja, bajo la supervisión del Prof. Hernán Míguez y el Dr. Juan F. Galisteo.

La defensa de su tesis se celebró el 23 de junio de 2017. Titulada, Diseño de la absorción y emisión ópticas de nanomateriales en entornos fotónicos controlados, versa sobre el control de las propiedades ópticas de nanomateriales mediante su integración en estructuras fotónicas.

Estos estudios abren una nueva vía para la realización de dispositivos de iluminación con propiedades bajo demanda, así como para nuevas estructuras en el campo de la energía solar.

La entrega del premio se realizará en 2019 en Zaragoza durante la celebración de la XXXVII Bienal de la RSEF.



Miguel Anaya Martín. Premio GEFES 2018. Mejor tesis experimental.

Miguel Anaya llevó a cabo su tesis doctoral “Optical Design of Perovskite Materials and Solar Cells”. bajo la supervisión del Prof. Hernán Míguez y el Dr. Mauricio Calvo en el Grupo de Materiales Ópticos Multifuncionales del Instituto de Ciencia de Materiales de Sevilla (CSIC-US). Actualmente se encuentra haciendo una estancia postdoctoral asociado al **Cavendish Laboratory de la Universidad de Cambridge y al Darwin College como Junior Research Fellow**.

Las perovskitas ABX3 de metal haluro son una familia de semiconductores con excelentes propiedades para su uso en dispositivos optoelectrónicos emergentes. La tesis de Miguel se enfocó en el estudio de las propiedades ópticas de estos materiales con el objetivo de conferirles nuevas cualidades y diseñar celdas solares con un desempeño mejorado. Esta investigación reúne una serie de resultados seminales en el campo que van desde la proposición del primer modelo óptico aplicado a dispositivos fotovoltaicos basados en perovskitas hasta el entendimiento del efecto de la atmósfera en la fotofísica de estos semiconductores. Fruto de ello, se demuestra la primera estructura fotónica integrable en celdas solares de perovskita para otorgarles color a la carta y un novedoso método para obtener nanocristales de perovskita mostrando efectos de confinamiento cuántico. Estos resultados, por tanto, han supuesto un avance tanto a nivel fundamental como a nivel tecnológico.

ESTANCIAS Y VISITAS DE PERSONAL DEL ICMS EN OTROS CENTROS
PERSONNEL OF THE ICMS IN OTHER LABORATORIES

Fondazione Istituto italiano di Tecnologia		
Milan, Italia	**Andrea Rubino**	2 semanas
Instituto de Nanosistemas. Universidad de San Martín.		
Buenos Aires, Argentina	**Hernán Míguez García**	3 meses
Imperial College London		
Londres, Reino Unido	**José María Miranda Muñoz**	3 meses
Purdue School of Science. Indiana University–Purdue University Indianapolis (IUPUI)		
Indianapolis, EE.UU.	**Victoria Esteso Carrizo**	3 meses

ESTANCIAS Y VISITAS DE INVESTIGADORES EN EL ICMS
PERSONNEL OF THE OTHER LABORATORIES IN THE ICMS

Universidad de Alejandría.

Alejandría, Egipto.	**Enas Moustafa Mohamed Abdelghafar**	5 meses

Laboratory of Supramolecular Biomaterials and Chemistry. Université de Strasbourg

Strasbourg, Francia	**Brian Nicholas Di Marco**	2 semanas

Universidad de Kioto, Japón

Kioto, Japón	**Kazuki Noguch**	1 mes
	Taisuke Atsumi	1 mes
	Shunsuke Murai	1 mes

College of William and Mary. Williamsburg, VA (USA),

Virginia, Estado Unidos	**Aaron Isaac Bayles**	10 meses

EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Potenciostato y sistema electroquímico
- Analizador de potencial Z, tamaño de partícula y pesos moleculares (Malvern, ZS90)
- Liofilizador de altas prestaciones Epsilon 2-4 (CHRIST)
- Estufa de desecación de 90 litros (RAYPA)
- Cámara Incubadora Opaq + Orbital Maxi (OVAN)
- pH & Ion-metro GLP 22+ (CRISON A)
- Espectrómetro visible-UV CARY-100. Medidas de coeficiente de absorción con luz normal y polarizada.
- Fluorímetro espectroscópico (HORYBA Jobin Yvon Fluorolog) con accesorio para la determinación de tiempos de vida. Microscopio de fluorescencia (HORYBA Jobin Yvon sigle photon controller: FluoroHub).
- Sistema de medida de porosidades en capas delgadas.
- Vis-NIR FTIR espectrofotómetro Bruker GmbH Fuente de excitación continua normal y angular. Specular Reflectance Attached Microscope.
- Tunable Supercontinuum White Laser Source. Fianium LTD 4W total output 400nm – 2400nm range Acousto-Optic Tunable Filter
- Perfilómetro mecánico DektakXT en su versión automática (platina XY motorizada y giro de 360º motorizado) y que incluye soporte de muestras cerámico para muestras flexibles.
- Fluorímetro Edinburgh FLS1000 con accesorios (esfera integradora y criostato).

UNIDAD EXTERNA DE INVESTIGACIÓN: FÍSICA DE MATERIALES

EXTERNAL UNIT: PHYSICS OF MATERIALS

PERSONAL / PERSONNEL

Catedrático

Dr. Alejandro Conde Amiano
Dra. Clara F. Conde Amiano
Dr. Alberto Criado Vega
Dr. Arturo Domínguez Rodríguez
Dr. Luis Esquivias Fedriani
Dr. Victorino Franco García
Dr. Antonio Muñoz Bernabé

Profesor Titular

Dr. Javier S. Blázquez Gámez
Dra. Josefa María Borrego Moro
Dra. María Dolores Estrada de Oya
Dra. M. del Carmen Gallardo Cruz
Dra. Ángela Gallardo López
Dr. Felipe Gutiérrez Mora
Dr. José María Martín Olalla
Dra. Ana Morales Rodríguez
Dr. Francisco Javier Romero Landa

Investigador Contratado

Dr. Jhon J. Ipus Bados
Dr. Victor Morales Flórez

Becario Predoctoral

Ldo. Luis M. Moreno Ramírez
Lda. Cristina López Pernía
Ldo. Alejandro F. Manchón Gordón

Proyectos de Investigación / Research Projects

Modelado y Control de la Histéresis en Materiales Magnetocalóricos para Refrigeración y Conversión de Energía

Código/Code:	MAT2016-77265-R
Periodo/Period:	30-12-2016 / 29-12-2019
Organismo Financiador/Financial source:	Ministerio de Economía y Competitividad
Investigador responsable/Research head:	Victorino Franco García / Javier Sebastián Blázquez Gámez
Componentes/Research group:	Josefa María Borrego Moro, Alejandro Conde Amiano, Clara Francisca Conde Amiano, Jhon J. Ipus Bados

Materiales Magnéticos y Eficiencia Energética: Caracterización y Modelado Magnetic Materials and Energy Efficiency: Characterization and Models

Código/Code:	MAT2013-45165-P
Periodo/Period:	01-01-2014 / 31-12-2017
Organismo Financiador/Financial source:	Ministerio de Ciencia e Innovación
Importe total/Total amount:	118.530,61 €
Investigador responsable/Research head:	Alejandro Conde Amiano / Victorino Franco García
Componentes/Research group:	Clara F. Conde Amiano, Josefa María Borrego Moro, Javier S. Blázquez Gámez , Jhon J. Ipus Bados, Laszlo F. Kish

RESUMEN / ABSTRACT

Se estudiarán materiales magnéticos con aplicacabilidad en sistemas para un uso eficiente de la energía, centrando nuestra atención, fundamentalmente, en dos aspectos interrelacionados: la refrigeración magnética y los materiales compuestos para la recuperación de energía. En lo referente al efecto magnetocalórico, se estudiarán materiales con una transición de fase de primer orden, en los que el control de la microestructura, la composición y campos externos como la presión o el campo eléctrico pueden alterar la respuesta termomagnética. Se abordará la problemática actual de dos familias de materiales magnetocalóricos con alto interés tecnológico: los compuestos del tipo LaFeSi y las aleaciones Heusler. Los primeros, especialmente los compuestos hidrogenados, son altamente prometedores para aplicaciones industriales, pero sufren una migración del hidrógeno que da

lugar a una disminución del pico de respuesta magnetocalórica que se desdobla en dos picos menores. El control de la microestructura y la modificación de la composición debe dar lugar a una mejora en la estabilidad de las propiedades. Las aleaciones Heusler, a pesar de contar con una elevada respuesta magnetocalórica, presentan dificultades para su aplicación tecnológica, debido a la significativa irreversibilidad de la transición microestructural. Esfuerzos combinados de modificación de la composición y modelado de la transición de fase deben permitirnos minimizar esta histéresis térmica y mejorar la aplicabilidad de las aleaciones Heusler. El estudio experimental de materiales magnetocalóricos requiere de técnicas apropiadas para la caracterización de la variación de entropía magnética y de la variación de temperatura adiabática. La primera puede obtenerse mediante medidas indirectas de imanación, pero los protocolos de medida para materiales con una transición de fase de primer orden existentes en la actualidad implican procedimientos costosos en tiempo (y, consecuentemente, de alto coste económico). La modelización de las transiciones de fase nos permitirá diseñar algoritmos de medida más eficientes. Por otra parte, la caracterización de la respuesta dinámica de los materiales magnetocalóricos sólo puede hacerse mediante la medida directa de la variación de temperatura adiabática, existiendo un número muy limitado de dispositivos comerciales que permitan realizar estas medidas de manera fiable, especialmente para muestras de reducida masa. Realizaremos estudios para desarrollar y optimizar un equipo de medida directa de la variación de temperatura adiabática para el estudio de la respuesta dinámica de los materiales, lo que tendrá implicaciones directas en el análisis de la viabilidad de emplear estos materiales en dispositivos refrigeradores. En especial, se estudiará la posibilidad de realizar medidas con excitación AC para la detección de pequeñas respuestas. El tercer bloque de estudio de este proyecto se centra en el análisis de otros efectos cruzados en materiales con transiciones de fase magnéticas o magnetoestructurales. Mediante el desarrollo de materiales multiferroicos artificiales, preparados por procedimientos combinados de aleado mecánico y “spin coating”, estudiaremos la viabilidad de la recuperación de energía por medios termomagnéticos.

In this project, we will study magnetic materials with applicability in systems for energy efficiency. Our interest will be focused in two interrelated topics: magnetic refrigeration and composite materials for energy harvesting. Concerning magnetocaloric effect, we will study materials with a first order phase transition, which thermomagnetic response can be controlled through tailoring microstructure and composition. Other external excitations, such as pressure and electric field, can also affect the thermomagnetic response. We will focus on some of the currently open problems of two families of magnetocaloric materials with high technological interest: LaFeSi-type compounds and Heusler alloys. In hydrogenated compounds of the former family, despite their promising industrial applicability, hydrogen migrates yielding a reduction of the peak of the magnetocaloric response, which splits in two smaller peaks. The control of the microstructure and the compositional tailoring should lead to an enhancement of the stability of the properties. Heusler alloys, despite their high magnetocaloric response, show a strong irreversibility at the microstructural transition, which hinders their technological application. Tailoring the composition along with modelling of the phase transition should allow us to minimize the detrimental thermal hysteresis and to enhance the applicability of Heusler alloys. The experimental study of magnetocaloric materials requires appropriate techniques for the characterization of the isothermal magnetic entropy change and the adiabatic temperature change. Although the former can be obtained from indirect measurements of magnetization, the measurement protocols for materials with a first order phase transition used nowadays demand long time measurements (and, consequently, have a high economical cost). Modeling of the phase transitions will allow us to design more efficient measurement algorithms. On the other hand, the characterization of the dynamic response of the magnetocaloric materials can only be performed by direct measurements of the adiabatic temperature change. However, there is a reduced number of commercial devices supplying reliable measurements of this magnitude, especially for samples with a low mass. We will carry out studies for developing and optimizing a setup for the characterization of the dynamic response of materials. This will have direct implications in the analysis of the viability to use these materials in refrigerators. Particularly, we will study the viability to perform AC measurements to detect weak reponses. Finally, the analysis of cross-effects in materials with magnetic or magnetostructural transitions will be undertaken. Especially, we will study the viability for thermomagnetic energy harvesting through the development of artificial multiferroic materials prepared by combined mechanical alloying and spin coating techniques.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Procesado y caracterización microestructural, mecánica y eléctrica de compuestos cerámica-grafeno Processing and microstructural, mechanical and electrical characterization of ceramic-graphene composites

Código/Code:	MAT2015-67889-P
Periodo/Period:	01-01-2016 / 31-9-2019
Organismo Financiador/Financial source:	Ministerio de Ciencia e Innovación
Importe total/Total amount:	89.177,00€
Investigador responsable/Research head:	Ángela Gallardo López / Rosalía Poyato Galán
Componentes/Research group:	Antonio Muñoz Bernabé, Ana Morales Rodríguez, Felipe Gutiérrez Mora.

RESUMEN / ABSTRACT

En la actualidad se plantean interesantes expectativas sobre los compuestos cerámica-grafeno, propuestos para aplicaciones en catálisis, almacenamiento y conversión de energía, protección del medio ambiente y biotecnología. Pero aún se requieren importantes esfuerzos para dar respuesta a cuestiones abiertas. Hay que incidir en aspectos como la resistencia a la cizalla de las intercaras cerámica-grafeno -esencial para asegurar la transferencia de carga efectiva sobre las láminas de grafeno-, la distribución homogénea del grafeno en la matriz cerámica y la relación de tamaños entre matriz y refuerzo, para maximizar el aumento de tenacidad y de conductividad eléctrica, así como también explorar sus propiedades mecánicas a alta temperatura.

En este proyecto se plantea un estudio sistemático de compuestos de matrices cerámicas con grafeno, desde la fabricación hasta la caracterización microestructural, mecánica y eléctrica, con el objetivo de mejorar la comprensión de los mecanismos que controlan estas propiedades al incorporar nanoestructuras de grafeno a una matriz cerámica. Se procesarán compuestos de dos matrices cerámicas diferentes, de alúmina y de circona tetragonal dopada con óxido de itrio

(3YTZP), con grafeno mediante técnicas coloidales, prestando especial atención a la dispersión del grafeno en la matriz cerámica, aspecto no exento de dificultades y que es clave para conseguir la mejora de las propiedades. La sinterización se realizará en un horno de descarga de plasma (SPS, spark plasma sintering) de última generación, optimizando las condiciones para conseguir compuestos densos y de tamaño de grano nanométrico. Para el análisis microestructural se utilizarán técnicas como la difracción de rayos X, la espectroscopía Raman, y la microscopía electrónica de barrido y transmisión. Con ellas se evaluarán las fases cristalográficas presentes, el tamaño de grano, la distribución de las nanoestructuras de grafeno, etc.

Desde el punto de vista del diseño de materiales avanzados, es fundamental investigar la relación entre microestructura y propiedades mecánicas y eléctricas. Las propiedades mecánicas a temperatura ambiente (dureza, tenacidad a la fractura y resistencia a flexión) se abordarán mediante indentación y ensayos de flexión, a escalas macro y microscópica. A alta temperatura, se estudiará la deformación plástica de los compuestos cerámica-grafeno mediante ensayos de fluencia en atmósferas controladas. También se estudiará el comportamiento tribológico de los compuestos y se evaluará su conductividad eléctrica, una de las propiedades más interesantes ya que se modifica de forma notoria como resultado de la incorporación del grafeno a estos sistemas cerámicos. La respuesta eléctrica se analizará en un amplio rango de temperaturas, bien mediante espectroscopía de impedancia compleja, bien mediante medidas de conductividad en corriente continua en el caso de los compuestos menos resistivos.

Nowadays, interesting prospects are proposed for ceramic-graphene composites, in application fields such as catalysis, energy storage and conversion, environment protection and biotechnology. A great effort is still required to answer open questions. Issues such as shear resistance of the ceramic-graphene interface –essential to obtain an effective load transfer to the graphene sheets-, distribution of graphene in the ceramic matrix -to maximize the reinforcement mechanisms and electrical conductivity- and the high temperature mechanical properties in these composites need special attention.

A systematic study of ceramic matrix graphene composites, including processing and microstructural, mechanical and electrical characterization is proposed in this project, with the aim of improving the comprehension of mechanisms controlling these properties when adding graphene nanostructures to a ceramic matrix. Both alumina and yttria tetragonal zirconia (3YTZP) graphene composites will be processed by means of colloidal techniques. Special attention will be devoted to the dispersion of graphene in the ceramic matrix which is not a straightforward aspect, but is key to improve mechanical and functional properties. Sintering will be carried out by spark plasma sintering, SPS. Conditions will be optimized in order to obtain fully dense composites with nanometric grain size. Microstructural analysis will be performed by X ray diffraction, Raman spectroscopy, scanning and transmission electron microscopy (SEM and TEM). The present crystallographic phases, grain size and distribution of graphene nanostructures will be evaluated.

In order to design advanced materials, it is necessary to study the relationship between microstructure and mechanical or electrical properties. Room temperature mechanical properties (hardness, fracture toughness and flexural resistance) will be characterized by indentation and bending tests at macro and microscopic scales. At high temperature, the plastic behavior of these ceramic-graphene composites will be assessed by creep tests under controlled atmosphere. Tribological behavior of the composites will also be studied to evaluate their resistance to wear. The electrical response will be assessed in a wide range of temperatures by means of complex impedance spectroscopy or by direct current conductivity measurements in the composites with lower resistivity. This is a most interesting property since it can be strongly increased when incorporating graphene to these ceramic systems.

Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"
JUNTA DE ANDALUCIA

Procesado, caracterización y propiedades mecánicas de cerámicos nanoestructurados reforzados con nanotubos de carbono

Código/Code: P12-FQM-1079 (Proyecto de Excelencia)
Periodo/Period: 30-01-2014 / 16-02-2019
Organismo Financiador/Financial source: Junta de Andalucía
Investigador responsable/Research head: Arturo Domínguez Rodríguez
Componentes/Research group: Luis María Esquivias Fedriani, Angela Gallardo López, Diego Gómez García, Felipe Gutiérrez Mora, Victor Morales Flórez, Ana Morales Rodríguez, Rodrígo Moreno Botella, Antonio Muñoz Bernabé, Rosalía Poyato Galán, Eugenio Zapata Solvas

ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

Magnetocaloric effect: From materials research to refrigeration devices
V. Franco, J.S. Blazquez, J.J. Ipus, J.Y. Law, L.M. Moreno-Ramírez, A. Conde
Progress in Materials Science, **93** (2018) 112-232
DOI: 10.1016/j.pmatsci.2017.10.005

The magnetocaloric effect and its most straightforward application, magnetic refrigeration, are topics of current interest due to the potential improvement of energy efficiency of cooling and temperature control systems, in combination with other environmental benefits associated to a technology that does not rely on the compression/expansion of harmful gases. This review presents the fundamentals of the effect, the techniques for its measurement with consideration of possible artifacts found in the characterization of the samples, a comprehensive and comparative analysis of different magnetocaloric materials, as well as possible routes to improve their performance. An overview of the different magnetocaloric prototypes found in literature as well as alternative applications of the magnetocaloric effect for fundamental studies of phase transitions are also included.

A quantitative criterion for determining the order of magnetic phase transitions using the magnetocaloric effect
J.Y. Law, V. Franco, L.M. Moreno-Ramírez, A. Conde, D.Y. Karpenkov, I. Radulov, K.P. Skokov, O. Gutfleisch
Nature Communications, **9** (2018) 2680
DOI: 10.1038/s41467-018-05111-w

The ideal magnetocaloric material would lay at the borderline of a first-order and a second-order phase transition. Hence, it is crucial to unambiguously determine the order of phase transitions for both applied magnetocaloric research as well as the characterization of other phase change materials. Although Ehrenfest provided a conceptually simple definition of the order of a phase transition, the known techniques for its determination based on magnetic measurements either provide erroneous results for specific cases or require extensive data analysis that depends on subjective appreciations of qualitative features of the data. Here we report a quantitative fingerprint of first-order thermomagnetic phase transitions: the exponent n from field dependence of magnetic entropy change presents a maximum of $n > 2$ only for first-order thermomagnetic phase transitions. This model-independent parameter allows evaluating the order of phase transition without any subjective interpretations, as we show for different types of materials and for the Bean-Rodbell model.

The role of Ni in modifying the order of the phase transition of La(Fe,Ni,Si)(13)
L.M. Moreno-Ramírez, C. Romero-Muniz, J.Y. Law, V. Franco, A. Conde, I.A. Radulov, F. Maccari, K.P. Skokov, O. Gutfleisch
Acta Materialia, **160** (2018) 137-146
DOI: 10.1016/j.actamat.2018.08.054

In this work, we study the effect of Ni substitution on the magnetocaloric properties of La(Fe,Si)(13) compounds. Sample quality has been optimized by a combination of induction melting and suction casting techniques, which allowed to shorten the annealing time by an order of magnitude and expand the existing range of LaFe11.6-xNixSi1.4 phase with cubic NaZn13-type structure up to x = 0.4. According to our Density Functional Theory calculations, Ni addition does not significantly alter the crystal structure (finding that Ni atoms occupy preferably 96i positions) as well as the total magnetic moment; both predictions are in agreement with experimental results. With increasing of Ni concentration, the transition temperature increases and the order of the phase transition changes from first to second-order type. In addition, we show that the magnetic field dependence of magnetocaloric effect enables a clear analysis of the order of phase transition even for compositions near the critical point, surpassing the accuracy of conventionally used techniques for determining the order of magnetic phase transitions (e.g. Banerjee's criterion).

Correction of the shape effect on magnetic entropy change in ball milled Fe70Zr30 alloys
A.F. Manchon-Gordon, J.J. Ipus, L.M. Moreno-Ramírez, J.S. Blázquez, C.F. Conde, V. Franco, A. Conde
Journal of Alloys and Compounds, **765** (2018) 437-443
DOI: 10.1016/j.jallcom.2018.06.176

The field dependence of the magnetic entropy change (Delta S-M) after mechanical alloying of Fe70Zr30 composition starting from high purity powders is studied. Samples with different shapes and different crystalline fraction X were analyzed. Although the results show that the proposed correction of the demagnetizing field has not a significant effect on Delta S-M(T) curves (similar to 5% underestimation), it is necessary in order to properly analyze the field dependence of this magnitude (vertical bar Delta S-M vertical bar = aH(n)). This correction allows recovering the theoretically predicted field dependence as well as a deeper analysis on multiphase systems. In fact, the biphasic character of the studied system changes the value of the field exponent : it decreases below two above Curie temperature (T-C), and it increases at T-C. We show that, assuming a non-interacting phase model, it is possible to obtain the value of the exponent for the main phase from the intercept of n vs X/Delta S-M .

Optimizing the homogenization technique for graphene nanoplatelet/yttria tetragonal zirconia composites: Influence on the microstructure and the electrical conductivity
C. López-Pernía, C. Muñoz-Ferreiro, C. González-Orellana, A. Morales-Rodríguez, Á. Gallardo-López, R. Poyato
Journal of Alloys and Compounds, **767** (2018) 994-1002
DOI: 10.1016/j.jallcom.2018.07.199

3 mol% yttria tetragonal zirconia polycrystalline (3YTZP) ceramic composite powders with 10 vol% nominal content of graphene nanoplatelets (GNPs) were prepared using four different homogenization routines: dispersion of the powder mixture by ultrasonication in isopropyl alcohol, homogenization in a high-energy planetary ball mill in wet or dry conditions after ultrasonication, and milling of the powders in a high-energy planetary ball mill in dry conditions. A significant effect of the homogenization routine on the powders particle size distribution was revealed by laser granulometry and Raman spectroscopy. Highly densified composites were obtained after spark plasma sintering (SPS) and remarkable differences on the GNP size, shape and distribution throughout the ceramic matrix and also in the electrical conductivity were observed in the four different composites. The composite with the best performance in terms of electrical conductivity was the one prepared after planetary ball milling of the powders in dry conditions as a consequence of the reduced dimensions of the GNPs and their excellent distribution throughout the ceramic matrix.

Creep study on alumina and alumina/SWCNT nanocomposites
M. Castillo-Rodríguez, A. Muñoz, A. Domínguez-Rodríguez
Journal of the European Ceramic Society, **38** (2018) 5497-5502
DOI: 10.1016/j.jeurceramsoc.2018.08.013

Alumina and alumina/SWCNT nanocomposites have been sintered by spark plasma sintering, obtaining relative densities higher than 99%. Microstuctural characterization revealed a grain microstructure in the submicron range, where alumina/SWCNT nanocomposites exhibited a good CNTs dispersion thought the ceramic matrix. Creep experiments performed in both materials showed a similar mechanical behavior, where the addition of CNTs seems to have a negligible effect on the strain rate, in contrast to results reported by other authors, Grain boundary sliding accommodated by lattice diffusion has been identified as the high temperature deformation mechanisms in both samples, alumina and alumina/SWCNT nanocomposites. We have discussed about the role of CNTs influence on the plasticity of these composites.

Graphene or carbon nanofiber-reinforced zirconia composites: Are they really worthwhile for structural applications?

R. Cano-Crespo, B.M. Moshtaghioun, D. Gómez-García, R. Moreno, A. Domínguez-Rodríguez
Journal of the European Ceramic Society, **38** (2018) 3994-4002
DOI: 10.1016/j.jeurceramsoc.2018.04.045

The use of allotropic phases of carbon (i.e. nanotubes, graphene or carbon nanofibers) as second phases to design ceramic composites is a hot topic at present. Researchers try to provide a remarkable improvement of the parent ceramic assuming that some of the outstanding mechanical properties of these phases migrate to the resultant composite. This reasonable idea has been questioned severely in the case of nanotubes addition but there is not any analysis for the other two phases cited previously. To elucidate this question, zirconia was selected as a model ceramic. This paper reports the mechanical properties of zirconia composites reinforced either with graphene or carbon nanofibers, with special emphasis on the high-temperature plasticity.

High-temperature compressive creep of novel fine-grained orthorhombic ZrO2 ceramics stabilized with 12 mol% Ta doping

G. Sponchia, B.M. Moshtaghioun, P. Riello, A. Benedetti, D. Gómez-García, A. Domínguez-Rodríguez, A.L. Ortiz
Journal of the European Ceramic Society, **38** (2018) 2445-2448
DOI: 10.1016/j.jeurceramsoc.2017.12.055

A novel fine-grained orthorhombic ZrO2 ceramic stabilized with 12 mol% Ta doping was fabricated by spark plasma sintering from home-made powders, and its high-temperature mechanical properties evaluated for the first time by compressive creep tests in both Ar and air. It was found that the high-temperature plasticity of the ceramic deformed in Ar, under which the Ta-doped orthorhombic ZrO2 is a black suboxide with abundant oxygen vacancies in its crystal structure, is controlled by grain boundary sliding (stress exponent similar to 2, and activation energy similar to 780-800 kJ/mol). However, the high-temperature plasticity of the ceramic deformed in air, under which the Ta-doped orthorhombic ZrO2 is a white oxide due to the elimination in situ of oxygen vacancies, is controlled by recovery creep (stress exponent 3, and activation energy similar to 750 kJ/mol). It was also observed that black Ta-doped orthorhombic ZrO2 is more creep resistant than its white counterpart with the same grain size, and that the former deforms as the more conventional Y2O3-stabilized ZrO2 does.

Spark plasma sintering of titanium nitride in nitrogen: Does it affect the sinterability and the mechanical properties?

B.M. Moshtaghioun, D. Gómez-García, A. Domínguez-Rodríguez
Journal of the European Ceramic Society, **38** (2018) 1190-1196

DOI: 10.1016/j.jeurceramsoc.2017.12.029

Titanium nitride ceramics have an intrinsic interest due to its optical and structural applications. However, the conditions for sintering of dense pieces are not still clarified. This research work is focused on the spark plasma sintering (SPS) of near-fully dense fine-grained TiN. The main goal is giving a response to a longstanding debate: can the external atmosphere favor sintering? Different sintering atmospheres, either vacuum or a nitrogen flow, have been used during SPS heating to this purpose. X ray diffraction analysis has showed the presence of TiN as the main phase with traces of Ti4O7 in optimal SPS conditions (1600 degrees C, one minute dwell time). Our results show that the use of a nitrogen flow while heating can improve sinterability very slightly, but mechanical properties are essentially unaltered within the experimental uncertainty. The hardness reaches values as high as 20GPa whereas fracture toughness can be evaluated around 4 MPam(1/2).

Is an alumina-whisker-reinforced alumina composite the most efficient choice for an oxidation-resistant high-temperature ceramic?

Y. Tamura, B.M. Moshtaghioun, E. Zapata-Solvas, D. Gómez-García, A. Domínguez-Rodríguez, C. Cerecedo-Fernández, V. Valcarcel-Juarez

Journal of the European Ceramic Society, **38** (2018) 1812-1818

DOI: 10.1016/j.jeurceramsoc.2017.10.006

The search of a competitive ceramic material for structural applications demands several requisites: a simple microstructure with easy reproducibility, good intrinsic mechanical properties and most of all, an optimal oxidation resistance. This later point is a challenging point for most ultrahigh refractory materials.

In this work an alumina (Al_2O_3) whisker-reinforced Al_2O_3 composite prepared by spark plasma sintering (SPS) is studied. It will be shown that, although the microstructure is quite similar to that of pure monolithic one, there is a notorious enhancement of the high-temperature deformation resistance, reaching up to one order of magnitude over the pure Al_2O_3 specimen. On the other hand, the activation energy of these composites increases notably. The results are explained in terms of an original model. A comparison with reported data shows that such composite is as efficient as a SiC-whisker-reinforced Al_2O_3 composite, with the advantage of its oxidation resistance and much less fabrication cost.

High temperature creep of 20 vol%. SiC-HfB2 UHTCs up to 2000 degrees C and the effect of La2O3 addition

E. Zapata-Solvas, D. Gómez García, A. Domínguez Rodríguez, WE Lee

Journal of the European Ceramic Society, **38** (2018) 47-56

DOI: 10.1016/j.jeurceramsoc.2017.08.028

High temperature compressive creep of SiC-HfB2 UHTCs up to 2000 degrees C has been studied. Microstructural analysis after deformation reveals formation of new phases in the Hf-B-Si and Hf-B-Si-C systems, which are responsible for the poor creep resistance. RE oxide additions have a negative effect reducing the creep resistance of SiC-HfB2 UHTCs. A simplistic analysis for the required creep resistance is described, indicating that only SiC-HfB2 UHTCs could withstand re-entry conditions for 5 min in a single use. However, RE oxide addition to SiC-HfB2 UHTCs does not provide the required creep resistance for them to be candidate materials for hypersonic applications.

The role of carbon nanotubes on the stability of tetragonal zirconia polycrystals
A. Morales-Rodriguez, R. Poyato, F. Gutierrez-Mora, A. Munoz, A. Gallardo-López
Ceramics International, **44** (15) (2018) 17716-17723
DOI: 10.1016/j.ceramint.2018.06.238

The effect of single walled carbon nanotubes (SWNT) at zirconia grain boundaries on the stability of a tetragonal zirconia polycrystalline matrix has been explored in as–sintered composites and after low–temperature hydrothermal degradation (LTD) experiments. For this purpose, highly–dense 3 mol% Y2O3–doped tetragonal zirconia polycrystalline (3YTZP) ceramics and SWNT/3YTZP composites were prepared by spark plasma sintering (SPS). Quantitative X–ray diffraction analysis and microstructural observations point out that an increasing amount of well–dispersed SWNT bundles surrounding zirconia grains decreases the metastable tetragonal phase retention in the ceramic matrix after sintering. In contrast, the tetragonal ceramic grains in composites with SWNTs are less sensitive to the presence of water, i.e. to undergo a martensitic transformation under LTD conditions, than monolithic 3YTZP ceramics. The SWNT incorporation diminishes micro–cracking due to tetragonal to monoclinic ZrO2 phase transformation in the composites.

Electrical conduction mechanisms in graphene nanoplatelet/yttria tetragonal zirconia composites
R. Poyato, J. Osuna, A. Morales-Rodríguez, Á. Gallardo-López
Ceramics International, **44** (12) (2018) 14610-14616
DOI: 10.1016/j.ceramint.2018.05.082

Yttria tetragonal zirconia polycrystalline (3YTZP) ceramic composites with 5, 10 and 20 vol% graphene nanoplatelets (GNPs) were prepared by spark plasma sintering (SPS) and their electrical conductivity as a function of temperature was characterized. The composites exhibit anisotropic microstructures so the electrical conductivity studies were carried out in two directions: perpendicular (σ⊥) and parallel (σ||) to the SPS pressing axis. The composites with 5 and 10 GNP vol% showed high electrical anisotropy, whereas the composite with 20 GNP vol% exhibited nearly isotropic electrical behavior. σ⊥ shows metallic-type behavior in the composites with 10 and 20 vol% GNP revealing that charge transport takes place through defect-free GNPs. For the composite with 5 vol% GNP the observed semiconductor-type behavior was explained by a two dimensional variable range hopping mechanism. σ|| shows metallic-type conductivity in the composite with 20 GNP vol% and positive dσ||/dT slope in the composites with 5 and 10 GNP vol%.

Grain-boundary diffusion coefficient in alpha-Al_2O_3 from spark plasma sintering tests: Evidence of collective motion of charge disconnections
Y. Tamura, E. Zapata-Solvas, B.M. Moshtaghioun, D. Gómez-García, A. Domínguez Rodríguez
Ceramics International, **44** (2018) 19044-19048

DOI: 10.1016/j.ceramint.2018.07.073

The sintering of fine-grained a-alumina by spark plasma sintering (SPS) was performed to study grain growth under SPS conditions. Grain growth is found to be extensive at relative densities above 95%. A grain growth versus dwell time analysis during SPS allows for the determination of the grain-boundary diffusion coefficient. This study shows that the remarkable enhancement of grain-boundary diffusion derived from a previous analysis could be a consequence of the presence of the recently discovered "disconnections" at the grain boundaries of alpha-alumina. Their presence, together with their electric charge and the external electric field at the boundaries, are the key ingredients for a violation of the typical grain growth kinetic law. When they are introduced appropriately, an updated value of the grain-boundary diffusion coefficient is achieved. A comparison with other values reported previously in the literature through other techniques and a critical analysis are also carried out.

Corrigendum to "Dense graphene nanoplatelet/yttria tetragonal zirconia composites: Processing, hardness and electrical conductivity"[Ceram. Int. 43 (2017) 11743–11752]
A. Gallardo-López, I. Márquez-Abril, A. Morales-Rodríguez, A. Muñoz, R. Poyato
Ceramics International **44** (1), 1225

Influence of the starting temperature of calorimetric measurements on the accuracy of determined magnetocaloric effect
L.M. Moreno-Ramírez, V. Franco, A. Conde, H.N. Bez, Y. Mudryk, V.K. Pecharsky
Journal of Magnetism and Magnetic Materials, **457** (2018) 64-69
DOI: 10.1016/j.jmmm.2018.02.083

Availability of a restricted heat capacity data range has a clear influence on the accuracy of calculated magnetocaloric effect, as confirmed by both numerical simulations and experimental measurements. Simulations using the Bean-Rodbell model show that, in general, the approximated magnetocaloric effect curves calculated using a linear extrapolation of the data starting from a selected temperature point down to zero kelvin deviate in a non-monotonic way from those correctly calculated by fully integrating the data from near zero temperatures. However, we discovered that a particular temperature range exists where the approximated magnetocaloric calculation provides the same result as the fully integrated one. These specific truncated intervals exist for both first and second order phase transitions and are the same for the adiabatic temperature change and magnetic entropy change curves. The effect of this truncated integration in real samples was confirmed using heat capacity data of Gd metal and Gd5WSi2Ge2 compound measured from near zero temperatures.

Evolution of Fe environments and phase composition during mechanical amorphization of Fe70Zr30 and Fe70Nb30 alloys
A.F. Manchon-Gordon, J.J. Ipus, J.S. Blazquez, C.F. Conde, A. Conde
Journal of Non-Crystalline Solids, **494** (2018) 78-85
DOI: 10.1016/j.jnoncrysol.2018.04.061

Amorphous Fe-Zr and Fe-Nb alloys with 70 at.% Fe have been prepared by ball milling a mixture of elemental powders. The combination of Mossbauer spectroscopy, X-ray diffraction, scanning electron microscopy and differential scanning calorimetry techniques supplies detailed information about the composition as well as microstructural parameters of remaining crystalline and amorphous phases developed during milling. Detailed analysis of the Fe environments allows us to distinguish Fe atoms in paramagnetic sites between those incorporated to crystalline Zr or Nb rich phases and those Fe atoms in amorphous phase.

On the Use of JMAK Theory to Describe Mechanical Amorphization: A Comparison between Experiments, Numerical Solutions and Simulations

J.S. Blazquez, A.F. Manchon-Gordon, J.J. Ipus, C.F. Conde, A. Conde
Metals, **8** (2018) 450
DOI: 10.3390/met8060450

The kinetics of amorphization during ball milling is generally analyzed using two different approaches: the classical Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory and Delogu and Cocco's model for which a region deterministically transforms after it reaches a certain number of collisions. The application of JMAK analysis to the latter model predicts Avrami exponents to be higher than the experimental ones (typically close to one). We develop simulations based on the probabilistic character of the nucleation phenomenon and concave growth of the amorphous phase in the core of a nanocrystal. The predictions of our simulations are in good agreement with the low Avrami exponents and with the size evolution of the remaining crystallites found experimentally. From these values, the parameters involved in the simulated model (growth rate and probability of nucleation) can be estimated.

Controlling of magnetocaloric effect in Gd2O3@SiO2 nanocomposites by substrate dimensionality and particles' concentration

A. Zelenakova, P. Hrubovcak, O. Kapusta, A. Berkutova, V. Zelenak, V. Franco
AIP Advances, **8** (2018) 048105
DOI: 10.1063/1.4993974

The magnetocaloric effect (MCE) of hybrid nanostructures consisting of fine gadolinium oxide (Gd2O3) nanoparticles with diameter 7 nm and 12 nm loaded into the pores of the periodically ordered mesoporous silica with hexagonal (SBA-15) or cubic (SBA-16) symmetry were investigated. The concentration effect of the added nanoparticles (NPs) and the effect of the silica matrix dimensionality on the structural properties, magnetization M(H), magnetic entropy change Delta S-M, and parameters A(T) and B(T) derived from Arrott plots were studied in four samples. Examined nanocomposites exhibited reasonable high values of magnetic entropy change Delta S-M varying from 29 J/kgK established for Gd2O3@SBA-15 up to 64 J/kgK observed in Gd2O3@SBA-16 at maximal field change 5 T at low temperatures. This suggests that studied nanocomposites, where diamagnetic silica matrices serve as nanoreactors for growth of Gd2O3 nanoparticles and their symmetry strongly affect magnetic properties of whole composites, could be feasible for cryomagnetic refrigeration applications.

Preface to Special Topic: 23rd Soft Magnetic Materials Conference, 10-13 September 2017, Sevilla, Spain
V. Franco, A. Conde
AIP Advances, **8** (2018) 047001
DOI: 10.1063/1.5022053

La0. 59Li0. 24TiO3 ceramics obtained by spark plasma sintering: electric behavior analysis
J.S. Pereira, F. Guerrero, Y. Romaguera-Barcelay, J. Anglada-Rivera, JCC Sales Jr, RS Silva, Y Zulueta, R Poyato, A Gallardo, A Almeida, J Agostinho Moreira, Y Leyet
Materials Research Express **6** (1), (2018) 015504
DOI: 10.1088/2053-1591/aae496

This work describes the electric study of Lithium lanthanum titanate (La0.59Li0.24TiO3) ceramics performed by Complex Impedance Spectroscopy. The nanoparticle powders have been synthesized through high energy ball milling and sintered via Spark Plasma Sintering technique. The experimental impedance data have been analyzed using the equivalent circuit model, the Extended Jonscher universal law and the derivative method. From these models, we have determined the dielectric response as well as the grain and grain boundary conductivity. The samples show ionic conductivity values between 10−5 to 10−4 S cm−1 in the studied temperature range, and activation energy values 0.24 eV and 0.48 eV for grain and grain boundary, respectively. These results confirm the Li+ ions mobility through the crystalline structure of the material.

ARTICULOS PUBLICADOS EN REVISTAS (NO SCI) / PAPERS IN NON-SCI JOURNALS

Spark Plasma Sintered Zirconia Ceramic Composites with Graphene-Based Nanostructures
Á. Gallardo-López, C. López-Pernía, C. Muñoz-Ferreiro, C. González-Orellana, A. Morales-Rodríguez, R. Poyato
Ceramics, **1 (1)** (2018) 153-164
DOI: 10.3390/ceramics1010014

The addition of graphene-based nanostructures (GBNs) can improve the inherent fragility of ceramics and provide them with improved electrical and thermal conductivities. However, both the starting material (ceramic matrix and GBNs) and the processing/sintering approach are crucial for the final composite microstructure and properties. This work focuses on the influence of the content and dimensions of the GBN filler (10 and 20 vol%; 3 and~ 150 layers), the powder-processing conditions (dry versus wet), and the homogenization method (ultrasound sonication versus high-energy planetary ball milling) on GBN/tetragonal zirconia (3YTZP) composites. The microstructure and electrical properties of the spark plasma sintered (SPS) composites were quantified and analyzed. The highest microstructural homogeneity with an isotropic microstructure was achieved by composites prepared with thicker GBNs milled in dry conditions. A high content (20 vol%) of few-layered graphene as a filler maximizes the electrical conductivity of the composites, although it hinders their densification.

CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

COMUNICACIONES / COMMUNICATIONS

42nd International Conference and Exposition on Advanced Ceramics and Composites
21 – 26 enero [Florida, Estados Unidos]

Young modulus and electrical conductivity of GNP/3YTZP composites prepared by PLS
C. Lopez Pernia; R. Poyato; A. Gallardo López; A. Morales Rodríguez
Comunicación oral

Effect of ball milling on microstructure of pressureless sintered GNP/3YTZP composite
C. Lopez-Pernia; A. Morales-Rodriguez; A. Gallardo-Lopez; R. Poyato
Poster

4th International Conference and Expo on Ceramics and Composite Materials
14 – 15 mayo [Roma, Italia]

Effect of the homogenization treatment on the microstructure and the electrical conductivity of 3YTZP/graphene nanoplatelet composites
C. Lopez-Pernia; C. Muñoz-Ferreiro; C. González-Orellana; A. Morales-Rodriguez; A. Gallardo-Lopez; R. Poyato
Comunicación oral

Role of sintering method on graphene/3YTZP composites
C. López-Pernía; R. Poyato; A. Morales-Rodríguez; A. Gallardo-López
Comunicación oral

16th European Inter-Regional Conference on Ceramics | CIEC16
9 – 11 septiembre [Turin, Italia]

Key findings in the processing of ceramic composites based on zirconia and graphene platelets
A. Gallardo-López; C. López-Pernía; C. Muñoz-Ferreiro; C. González-Orellana; A. Morales-Rodríguez; R. Poyato
Comunicación oral

Study of the influence of graphene nanoplatelets on the hydrothermal degradation of zirconia in 3-YTZP/GNP composites
C. González-Orellana; A. Morales-Rodríguez; R. Poyato; A. Gallardo-López

Poster

Incorporating two-dimensional nanostructures as a second phase to a zirconia matrix
C. Muñoz-Ferreiro; R. Poyato; A. Morales-Rodríguez; Á. Gallardo-López
Poster

V Congreso Hispano-Luso de Cerámica y Vidrio, LVI Congreso de la Sociedad Española de Cerámica y Vidrio y II Reunión Bienal de la Sociedad Española de Cerámica y Vidrio

8 – 10 octubre [Barcelona, España]

In-situ reduced graphene oxide-zirconia composites consolidated by SPS
C. López-Pernía, R. Poyato, A. Morales-Rodríguez, A. Gallardo-López
Comunicación oral

Influence of the preferential graphene nanoplatelets alignment within the ceramic matrix on the scratch behavior
F. Gutiérrez-Mora, A. Gallardo-López, C. Muñoz-Ferreiro, A. Morales-Rodríguez, A. Muñoz, J.C. Sánchez-López, R. Poyato
Comunicación oral

Different powder homogenization techniques for obtaining 3YTZP/graphene nanoplatelet composites
R. Poyato, C. López-Pernía, C. Muñoz-Ferreiro, C. González-Orellana, A. Morales-Rodríguez, A. Gallardo-López
Comunicación oral

Fluencia a altas temperaturas de composites de alúmina y de composites de zircona reforzados con óxido de grafeno y con nanofibras de carbono sinterizados por SPS
R. Cano-Crespo; B. Malmal-Moshtaghioun; R. Moreno; D. Gómez-García; A. Domínguez-Rodríguez
Comunicación oral

Fabrication of 3D materials from graphene nano-platelets
Á. Gallardo-López, A. Morales-Rodríguez, R. Poyato
Poster

DOCENCIA / TEACHING

Máster Profesorado de ESO y Bachillerato, FP

Complementos de formación disciplinar en Física y Química
Dr. Javier S. Blázquez
Lugar: Universidad de Sevilla

EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Calorímetro de barrido diferencial (Perkin-Elmer DSC7)
- Criostato para espectrómetro Móssbauer
- Balanza termogravimétrica (Perkin-Elmer TGA-7)
- Espectrómetro Mössbauer (Wissel MB-500) con horno y criostato.
- Coercímetro (desarrollado en el laboratorio)
- Magnetómetro de muestra vibrante (LakeShore 7000) con horno y criostato.
- Equipo de medida directa de temperatura adiabática (Advanced Magnetic Technologies).
- Molino Planetario (Fritszch Pulverisette Vario 4)
- Equipo de solidificación por enfriamiento ultrarrápido (melt spinning, Bühler)
- Equipo de fusión por arco (MAM1, Bühler)
- Calorímetro de conducción, resolución en la medida del flujo de calor mejor que 0,1 W, fluctuaciones en temperatura del orden de 10-6 K, velocidad de barrido menor de 0,01K/h, rango 80-320K, es posible aplicar tensión uniaxial hasta 30 kg/cm2 y campo eléctrico hasta 800V/cm
- Calorímetro de conducción, rango 80-400K, campo eléctricos 2000V/cm
- Medida de constante dieléctrica, en los mismos calorímetros,
- Medida de ciclo de histéresis en Ferroeléctricos.
- Analizador de Impedancia

SERVICIOS GENERALES
GENERAL SERVICES

SERVICIO DE ESPECTROSCOPIAS / SPECTROSCOPY SERVICE

El Servicio de Espectroscopias incluye las Unidades de Espectroscopía Raman, Espectroscopía Infrarroja y Espectroscopía Ultravioleta-Visible. Este servicio está dedicado a la determinación de la estructura molecular de los compuestos químicos y la caracterización de materiales.

This Service consists of four different spectroscopies: Raman Spectroscopy, Infrared Spectroscopy and Ultraviolet-Visible Spectroscopy. It is devoted to the determination of molecular structure of chemical compounds and materials.

ESPECTROSCOPÍA MICRO-RAMAN / MICRO-RAMAN SPECTROSCOPY

La espectroscopía Raman se basa en un proceso fotónico en el que la radiación incidente es dispersada por la muestra, produciéndose transiciones de tipo vibracional y rotacional. En general, el espectro Raman se interpreta como un espectro vibracional que ofrece información muy similar al espectro de infrarrojo, aunque las vibraciones que se ven reflejadas en el espectro Raman no son siempre las mismas que en aquél. Para que un modo vibracional sea activo en espectroscopía Raman es necesario que se produzcan cambios en la polarizabilidad de los enlaces químicos o la molécula considerada, lo que conlleva la producción de momentos dipolares inducidos. Su campo de aplicación es muy extenso: semiconductores, compuestos del carbono (grafito, diamante, nanotubos, fibras…), catalizadores, pigmentos, etc.

Raman spectroscopy is based on a photonic process in which the incident radiation is dispersed by the sample. This latter is perturbed leading to vibrational and rotational transitions. In general, the Raman spectrum is interpreted like a vibrational one, providing information very similar to the infrared spectroscopy, although the Raman active vibrations are not always the same as those excited with infrared radiation. A Raman vibration mode is active if there is a change of polarizability of the chemical bonds or the considered molecule, which in turn results in the generation of induced dipolar momentam. Its application fields are very broad: semiconductors, carbon compounds (graphite, diamond, nanotubes, fibers…), catalysts, pigments, etc.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- LabRAM Horiba Jobin Yvon dotado de un microscopio confocal y 3 longitudes de excitación (785 cm^{-1} rojo, 532 cm^{-1} verde, y 325 cm^{-1} UV)
  LabRAM Horiba Jobin Yvon equipped with a confocal microscope and 3 excitation lasers (785 cm^{-1} red, 532 cm^{-1} green, and 325 cm^{-1} UV)

Responsables Científicos/ Scientific Responsibles: Dr. Juan Carlos Sánchez López, Dr. Hernán Míguez García y Dr. Miguel Angel Centeno Gallego
Personal Técnico/ Technical Assistant: Dr. Miguel Angel Avilés Escaño

ESPECTROSCOPÍA INFRARROJA / INFRARED SPECTROSCOPIES

La espectroscopía de Infrarrojos (FT-IR) se basa en la absorción de radiación infrarroja por parte de los materiales. Esta absorción supone un cambio en la energía vibracional de los enlaces, siempre que se produzca un cambio en la polarización de dicho enlace. El resultado obtenido es un espectro en el que se representa la radiación absorbida o transmitida en función del número de onda de la radiación, lo cual permite identificar el enlace correspondiente.
El equipo en el ICMS cubre un rango de número de ondas que va desde 5000 a 250 cm-1 (óptica de CsI) y se puede trabajar con purga o en vacío. Se halla equipado con accesorios para trabajar en los modos de Reflectancia Difusa (DRIFT), Reflectancia Total Atenuada (ATR) y Reflexión Especular. Dispone de un microscopio de Infrarrojos que tiene una resolución lateral de 10 µm.

Infrared spectroscopy (FT-IR) is based on the selective absorption of the infrared radiation by the materials. This absorption means a change in the vibrational energy of the chemical bonds, whenever it occurs a change in the polarization. The result is a spectrum showing the absorbed or transmitted radiation as a function of the wavenumber of the radiation, which can be assigned to the corresponding chemical bound.
The equipment at the ICMS works in a wavenumber range from 5000 to 250 cm^{-1} (CsI optic), and can operate with a gas purge or in vacuum. It is equipped with several accessories to do Diffuse Reflectance (DRIFT), Attenuated Total Reflectance (ATR) or Specular Reflectance. It has got an Infrared Microscope with a lateral resolution of 10 µm.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- JASCO FT/IR-6200 IRT-5000
  JASCO FT/IR-6200 IRT-5000

Responsables Científicos/ Scientific Responsibles: Dr. Juan Carlos Sánchez López, Dr. Hernán Míguez García y Dr. Miguel Angel Centeno Gallego
Personal Técnico/ Technical Assistant: Dr. Miguel Angel Avilés Escaño

ESPECTROSCOPÍA ÓPTICA EN EL RANGO VIOLETA, VISIBLE E INFRARROJO CERCANO / ULTRAVIOLET-VISIBLE SPECTROSCOPIES

La técnica de espectroscopía en el rango ultravioleta, visible e infrarrojo cercano (UV-Vis-NIR) nos permite conocer como materiales de distinta morfología (principalmente polvos, láminas y partículas o moléculas en suspensión) reflejan y transmiten la luz incidente en el rango comprendido entre 190 nm y 3000 nm. De esta forma, es posible extraer información sobre su eficiencia como filtros ópticos, ya sean especulares o difusores, y/o sobre la luz absorbida por ellos, lo que indirectamente nos permite estimar su gap electrónico (en el caso de dieléctricos), las transiciones electrónicas que tienen lugar (en el caso de moléculas o sistemas dopados con átomos de otra especie), o las resonancias plasmónicas (en el caso de metales).

The Ultraviolet-Visible Spectroscopy (UV-Vis) reports on the existing energy differences between the more external occupied electronic levels and the nearer unoccupied ones.
There are equipments in the laboratory, which work in the wavelength range of 190 nm to 900 nm. It can operate in the Transmission mode or in Diffuse Reflectance Modes.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- SHIMADZU UV-2101 PC
  SHIMADZU UV-2101 PC
- Cary 5000 + UMA (Universal Measurement Accesory)
  Cary 5000 + UMA (Universal Measurement Accesory)
- Cary 300
  Cary 300

Responsables Científicos/ Scientific Responsibles: Dr. Juan Carlos Sánchez López, Dr. Hernán Míguez García y Dr. Miguel Angel Centeno Gallego
Personal Técnico/ Technical Assistant: Dr. Miguel Angel Avilés Escaño

SERVICIO DE ANÁLISIS TEXTURAL Y TÉRMICO / TEXTURAL AND THERMAL ANALYSIS SERVICE

Este servicio incluye las siguientes Unidades: Análisis Térmico, Fisi-quimisorción, Análisis de Tamaño de Partícula y Potencial Z. Está dedicado a la determinación de la textura, estructura y comportamiento térmico de los materiales.

This Service includes the following units: Thermal Analysis, Physisorption and Chemisorption, Particle Size and Z-potential determination. It is devoted to the characterization of texture, microstructure and thermal behavior of advanced materials.

FISI-QUIMISORCIÓN / PHYSISORPTION-CHEMISORPTION

Este servicio constituye una herramienta básica para la caracterización microestructural de sólidos pulverulentos de distinta naturaleza, en cuanto a porosidad, superficie específica y superficie químicamente activa.

En el servicio se dispone de un analizador de adsorción de gases (Micromeritics, ASAP 2020) que proporciona isotermas de adsorción y desorción, a partir de los cuales se obtienen de ellas la superficie específica y distribución del tamaño de poro y de microporo de estos materiales, incorporando también los accesorios necesarios para medidas de quimisorción.

This service constitutes a basic tool for the microstructural characterization of powdered solids of different natures, regarding to their porosity, specific surface area and chemically active surface.

This service is composed by a phyisisorption analyser (Micromeritics, ASAP 2020) which provides the complete adsorption/desorption isotherms, from which the specific surface area, pore and micropore size distribution and concentration of reactive sites are obtained. The instrument is also equipped for carrying out chemisorption of different reactive molecules, as O_2, H_2, CO, etc.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Analizador científico de fisisorción ASAP2010 (Micromeritics)
  Physisorption analyser ASAP 2010 (Micromeritics)
- Analizador de quimisorción ASAP2010 (Micromeritics)
  Chemisorption analyser ASAP 2010 (Micromeritics)
- Analizador de fisisorción multimuestra TRISTAR II (Micromeritics)
  Multisample physisorption analyser TRISTAR II (Micromeritics)
- Analizador de fisisorción multimuestra TRISTAR II-Kr (Micromeritics)
  Multisample physisorption analyser TRISTAR II-Kr (Micromeritics)

Responsables Científicos/ Scientific Responsibles: Dr. Gerado Colón Ibáñez y Dr. Miguel Angel Centeno Gallego
Personal Técnico/ Technical Assistant: Dª Cristina Gallardo López

ANÁLISIS TÉRMICO / THERMAL ANALYSIS

Las técnicas de análisis térmico permiten estudiar aquellos cambios físicos o químicos que ocurren en los sólidos en función de la temperatura y que conlleven modificaciones en su masa o intercambios de calor con su entorno.
En el servicio se pueden realizar experimentos desde temperatura ambiente hasta 1500ºC, tanto en atmósfera inerte (N_2) como reactiva (aire, O_2,…).
Se dispone de dos técnicas: Análisis Termogravimétrico (TG) y Análisis Térmico Diferencial (ATD).

Thermal analysis techniques allow to studying physical or chemical changes occurring in solid in samples as a function of the temperature. Those changes should involve either a mass change or a heat flow.
The experiments can be performed in the range from room temperature to 1500ºC, both under inert (N_2), or reactive (air, O_2,…) atmospheres.
Two different techniques are available: Thermogravimetry (TG) and Differential Thermal Analysis (DTA)

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Equipo de análisis térmico simultáneo TG/ATD/CDB TA Instruments Q600
  TA Instruments Q600 Simultaneous TG/DTA/DSC instrument
- Equipo termogravimétrico TG, TA Instruments Q5000
  Thermogravimetric instrument TG, TA Instruments Q5000

Responsable Científico/ Scientific Responsible: Dr. Luis A. Pérez Maqueda
Personal Técnico/ Technical Assistant: Dª Cristina Gallardo López

TAMAÑO DE PARTÍCULAS Y POTENCIAL Z / PARTICLE SIZE AND Z POTENTIAL ANALYSIS

Se dispone de las técnicas de Dispersión Dinámica de Luz y de Difracción Láser (LD), que permiten determinar la distribución de tamaños de partícula de sistemas coloidales en suspensión (disolvente acuoso u orgánico) en los rangos que van de 3 a 3000 nanómetros (DLS) o de 0.05 a 900 micras (LD).

Así mismo, se dispone de la técnica de Análisis de Movilidad Electroforética para la evaluación del potencial "Z" de sistemas coloidales en suspensión (disolvente acuoso u orgánico).

Dynamic light scattering (DLS) and Laser diffraction (LD) are available for the determination of particle size distributions of colloidal systems (dispersed in aqueous or organic dispersions solutions) in the range 3-3000 nanometers (DLS) and 0.05-900 microns (LD).

Electrophoretic mobility measurements can be also performed for the evaluation of Z potential in colloidal systems (aqueous or organic dispersions).

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Malvern modelo Zetamaster (DLS) y MalvernSizer (LD)
  Malvern model Zetamaster (DLS) and MalvernSizer (LD)

Responsable Científico/ Scientific Responsible: Dr. Manuel Ocaña Jurado
Personal Técnico/ Technical Assistant: Dª Cristina Gallardo López

SERVICIO DE MICROSCOPÍA ELECTRÓNICA / ELECTRON MICROSCOPY SERVICE

El servicio está dedicado a la caracterización química y estructural de muestras sólidas mediante técnicas de microscopía electrónica. Las técnicas de caracterización disponibles en el servicio son la Microscopía Electrónica de Transmisión (TEM) y la Microscopía Electrónica de Barrido (SEM), con el equipamiento anexo de preparación de muestras para TEM y SEM.

This Service is devoted to the chemical and structural characterization of solid samples by means of electron microscopies. The characterization techniques available at ICMS are Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM), with additional equipment for TEM and SEM sample preparation.

MICROSCOPÍA ELECTRÓNICA DE BARRIDO / SCANNING ELECTRON MICROSCOPY

La microscopía electrónica de barrido proporciona información microestructural, morfológica y de composición química en escala microscópica. Se puede aplicar a todo tipo de materiales y problemáticas de estudio en ciencia de materiales: cerámicas, plásticos, metales, minerales, catalizadores, muestras de patrimonio histórico, capas finas, recubrimientos, interfases, nanopartículas, etc. El equipo SEM es un microscopio de emisión de campo de cátodo frío que permite realizar imágenes de la morfología y textura superficial de las muestras con una resolución de 1 nm a 15kV. También permite trabajar a bajo voltaje en muestras sin metalizar y en modo transmisión (STEM-in-SEM) en muestras electrón-transparentes. Acoplado al detector de rayos-X (EDX) permite análisis elementales y mapas composicionales.

The scanning electron microscopy provides information about the microstructure, morphology and chemical composition at the microscopic scale of solid samples. It can be applied to all type of materials including ceramics, polymers, metals, minerals, catalysts, samples from cultural heritage, thin films, coatings, interfaces, nanoparticles, etc. The SEM microscope is a field emission cold cathode equipment which enables images of the surface morphology and texture of samples with a resolution of 1 nm at 15kV. It also allows working at low voltages with non-metalized samples and in transmission mode for electron-transparent samples (STEM-in-SEM). Coupled to the X-ray detector (EDX) enables compositional analysis and elemental mapping.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Microscopio SEM, modelo Hitachi S4800 SEM-FEG: cañón de emisión de campo de cátodo frío y voltaje de 0.5-30 kV, resolución de 1 nm a 15kV. Dotado de analizador EDX Bruker-X Flash-4010 con una resolución de 133 eV (en la línea MnKα) y detector con portamuestras para trabajar en modo transmisión (STEM-in-SEM).
  Hitachi S4800 SEM-FEG microscope: cold cathode field emission gun with voltage from 0.5 to 30 kV, resolution of 1nm at 15 kV. Equipped with a Bruker-X Flash-4010 EDX

detector with a resolution of 133 eV (at the MnKα line), and a detector with sample holder to work in transmission mode (STEM-in- SEM).

- Equipamiento adicional en el "laboratorio de preparación de muestras para microscopía electrónica" (ver sección abajo)
  Additional equipment in the "electron microscopy samples preparation laboratory" (see the section below)

Responsable Científico/ Scientific Responsible: Dra. Asunción Fernández Camacho
Personal Técnico/ Technical Assistant: Dra. M. Carmen Jiménez de Haro

MICROSCOPÍA ELECTRÓNICA DE TRANSMISIÓN / TRANSMISSION ELECTRON MICROSCOPY

La microscopía electrónica de transmisión es una técnica ampliamente utilizada para la caracterización estructural y química de materiales a escala microscópica y nanoscópica, proporcionando imágenes bidimensionales de la textura de la muestra, forma y tamaño de grano y/o de partícula, grado de homogeneidad a escala microscópica, grado de cristalinidad de la muestra, identificación de fases cristalinas, e imágenes de alta resolución que identifican dominios cristalinos. El equipo está dotado de un analizador EDX para el análisis composicional. Puede aplicarse a todo tipo de materiales y campos de estudio en ciencia y tecnología de materiales trabajando sobre muestras electrón-transparentes preparadas en su caso ad-hoc para este fin. El servicio realiza microscopía en modo transmisión: Imágenes en campo claro y campo oscuro, difracción de electrones de área selecta y microscopía electrónica de alta resolución así como análisis elemental de area selecta. No se dispone de modo STEM.

The transmission electron microscopy is a widely used technique for the microstructural and chemical characterization at micro and nanoscales, providing two-dimensional images of the sample texture and shape as well as grain and/or particle size, degree of homogeneity at the microscopic scale, degree of crystallinity of the sample, identification of crystalline phases, and high resolution images to identify the crystalline domains. The microscope is equipped with an EDX analyzer for compositional analysis. It can be applied to all type of materials and research topics in materials science and technology working with electron-transparent samples prepared ad-hoc for this end. The service performs transmission electron microscopy: Imaging in bright and dark field, selected area electron diffraction and high resolution electron microscopy, as well as elemental analysis of selected areas. It does not provide STEM mode.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Microscopio Philips CM20 (200kV) con una resolución estructural de 0.14 nm entre líneas y 0.23 nm entre puntos, portamuestras de uno y dos giros y de calentamiento. Acoplados al equipo se dispone de un sistema de análisis por Energías Dispersivas de Rayos X (EDX X-Max 80T, Oxford Instruments) y una cámara CCD (Gatan) para registro de imágenes.

Philips CM200 microscope (200kV) with a structural resolution of 0.14 nm between lines and 0.23 nm between points. Sample holders with one and two angles and heating. It is equipped with a X-ray Energy Dispersive Analyzer (EDX X-Max 80T, Oxford Instruments) and a CCD GATAN camera for image acquisitions.

- Equipamiento adicional en el “laboratorio de preparación de muestras para microscopía electrónica” (ver sección abajo)
  Additional equipment in the “electron microscopy samples preparation laboratory” (see the section below)

Responsable Científico/ Scientific Responsible: Dra. Asunción Fernández Camacho
Personal Técnico/ Technical Assistant: Dª Olga Montes Amorín (cicCartuja) y Dª María Inmaculada Roja Cejudo

LABORATORIO DE PREPARACIÓN DE MUESTRAS PARA MICROSCOPÍA ELECTRÓNICA / ELECTRON MICROSCOPY SAMPLES PREPARATION LABORATORY

El laboratorio de preparación de muestras para TEM y SEM dispone de metalizador de oro, evaporador de carbón, metalizador de Cr y carbón, cortadora de disco, pulidora, “disc-grinder”, cortadora ultrasónica, pulidora cóncava (dimple) y adelgazador iónico (Fischione 1010).

The laboratory for TEM and SEM samples preparation has a gold coater, a carbon evaporator, a metallization system for Cr and carbon, a diamond wheel cutter, a grinder with disc-grinder device, an ultrasonic cutter, a concave polishing (dimple) and ion thinning (Fischione 1010).

Responsable Científico/ Scientific Responsible: Dra. Asunción Fernández Camacho
Personal Técnico/ Technical Assistants: Dª María Inmaculada Roja Cejudo, Dª Olga Montes Amorín (CicCartuja) y Dra. M. Carmen Jiménez de Haro

SERVICIO DE DIFRACCIÓN DE RAYOS X
X-RAY DIFFRACTION LABORATORY SERVICE

La difracción de rayos-X permite la identificación cualitativa y cuantitativa de sustancias cristalinas y su caracterización microestructural y textural.

El servicio dispone en la actualidad de cuatro difractómetros independientes, configurados específicamente para abordar el análisis de muestras policristalinas de muy distinta naturaleza, en lo referente a su composición, estabilidad química, cristalinidad, etc.

Asimismo, con alguno de ellos se pueden llevar a cabo, además de los análisis rutinarios (θ-2θ), otros varios mas avanzados, como pueden ser:

- Seguir las transformaciones de fase "in situ" provocadas por calentamientos en atmósfera inerte (vacio, Ar) o reactiva (H2, O2,..).
- Caracterizar materiales en la nanoescala (1-100 nm) mediante el estudio de la dispersión de rayos-X a ángulos bajos (SAXS).
- Determinar el grosor, densidad y rugosidad de películas delgadas, mediante Reflectometría de rayos-X.
- Obtener la estructura cristalina de materiales inestables a la atmósfera o muy transparentes a los rayos-X, mediante el empleo de capilares.

X-ray diffraction allows the qualitative and quantitative identification of crystalline substances and their microstructural and textural characterization.
At present, four independent diffractometers are available in this service, specifically configured to analyze the composition, chemical stability, crystallinity and many other properties in polycrystalline samples of a varied nature. Besides ordinary analyses (θ-2θ), part of the equipment can perform some advanced studies as:

- Direct monitoring of transformations undergone in materials under heating, such as phase changes, under inert o reactive atmosphere.
- To characterize materials at the nanoscale (1-100 nm) through X-ray scattering at low angles, using the SAXS technique.
- To measure some physical parameters of layers such as density, thickness and surface roughness with the reflectometry setup.
- To obtain the diffraction patterns of samples either sensitive to the atmosphere or highly transparent to X-rays (organic compounds) employing the capillary configuration.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Difractómetro Panalytical X'PERT PRO con cargador automático de muestras
  Diffractometer PANALYTICAL X'PERT PRO with automatic sample charger
- Difractómetro PHILIPS X'PERT PRO con cámara de alta temperatura (1200 ºC) ANTON PAAR HTK 1200
  Diffractometer PHILIPS X'PERT PRO with high temperature chamber (1200ºC) ANTON PAAR HTK 1200
- Difractómetro Panalytical X'PERT PRO (reflectometría, SAXS, ángulo rasante y capilares)
  Diffractometer PANALYTICAL X'PERT PRO (reflectometry, SAXS, low angle scattering and capillary)
- Difractómetro de polvo SIEMENS D5000 DUAL (reflexión y transmisión)
  Diffractometer SIEMENS D5000 DUAL (reflection and transmission)

Responsable Científico/ Scientific Responsible: Dra. Concepción Real Pérez
Personal Técnico/Technical Assistant: D. José María Martínez Blanes

SERVICIO DE ANÁLISIS DE SUPERFICIE/ SURFACE ANALYSIS SERVICE

El Servicio de Análisis de superficie consta de un espectrómetro de Espectroscopía de Fotoelectrones de Rayos X (XPS). Este servicio está dedicado al análisis químico y electrónico de superficies sólidas. También permiten conocer la composición en profundidad (desde la superficie hacia el interior) de los sólidos.

The surface analysis service consists of an X-ray Photoelectron Spectrometer (XPS). This service is devoted to the electronic and chemical analysis of solid surfaces. It also provides information about the compositional depth profile of solids (from their surface toward their bulk).

ESPECTROSCOPÍA DE FOTOEMISIÓN DE ELECTRONES / X-RAY PHOTOELECTRON SPECTROSCOPY

Las “Espectroscopías de Fotoelectrones” (XPS/ESCA y AES) son unas poderosas técnicas de análisis cuantitativo no destructivo, sensibles exclusivamente a las primeras capas de la superficie de los sólidos (20-30 Å), lo que permite obtener información sobre las propiedades químicas, físicas y electrónicas de las mismas.
El interés técnico de esta información es enorme en campos tales como corrosión, catálisis, tratamientos de superficies, fenómenos de flotación y adherencia, segregación de fases, etc.
La característica más importante de la Espectroscopía de Fotoelectrones (XPS/ESCA) es que permitir diferenciar distintos estados de oxidación y/o situaciones del entorno (coordinación) de los átomos en las muestras sólidas analizadas. El límite de detección es del 0.5% para cada especie química.
El servicio dispone actualmente de dos instrumentos independientes.

Typically, “photoelectron spectroscopies” are a powerful set of non-destructive analysis techniques, exclusively sensitive to the more superficial few atomic layers (20-30 Å), allowing to obtain valuable information about their chemical, physical and electronic properties.
The technical interest of the resulting information is huge in fields such as catalysis, corrosion, surface treatments,, floating and adhesion phenomena, or segregation processes, among others. The most remarkable characteristic of X-Ray Photoelectron Spectroscopy (XPS/ESCA) is that it allows to discriminate, for a given element, between different oxidation states or chemical surroundings (coordination).

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

Espectrómetro de Fotoelectrones VG ESCALAB 210, compuesto de:
Photoelectron Spectrometer VG ESCALAB 210, consisting on:

- Cámara de análisis, analizador hemiesférico multicanal VG ESCALAB 210, manipulador de cuatro ejes, y fuentes de excitación de rayos X (dual, AlKα y MgKα, acromático), de

luz ultravioleta y de haces de electrones, lo que permite realizar análisis superficiales mediante técnicas de XPS, UPS y REELS, así como estudios angulares.
Analysis Chamber, equipped with a hemispheric multichannel analyser VG ESCALAB 210, a four axis manipulator, a dual X-ray source (achromatic AlKα, Mg Kα), a UV lamp, and a electron gun, allowing to perform surface analysis by XPS, UPS and REELS, including angular resolved studies.

- Dos Precámaras de tratamientos, con vacío residual de 10^{-8} y 10^{-9} mbar respectivamente, en las que es posible someter a las muestras a tratamientos diversos como: calentamientos a alta temperatura (T<800ºC) bajo atmósfera controlada, desbastado iónico con gases inertes o reactivos, exposición a plasmas, iluminación con laser, deposición de metales, óxidos y compuestos sencillos, exfoliación in situ, etc.
  Two prechambers for different treatments, with ultimate vacuum levels of 10-8 and 10-9 mbar respectively, where samples can be subjected to diverse treatments and transferred to the analysis chamber without exposure to the atmosphere. The possible treatments include heating at high temperature (< 800C) under controlled atmosphere, ion sputtering with inert or reactive gases, exposure to plasma, laser treatments, deposition of metals, oxides or simple compounds, exfoliation, etc.

Espectrómetro de Fotoelectrones SPECS, compuesto de:
Photoelectron Spectrometer SPECS, consisting on:

- Cámara de análisis, dotada de analizador hemiesférico multicanal PHOIBOS 100, manipulador de tres ejes, y fuentes de excitación de rayos X (dual, Alkα y MgKα).
  Analysis Chamber, equipped with a hemispheric multichannel analyser PHOIBOS 100, three axis manipulator and dual X-ray source (achromatic Al Kα, Mg Kα).
- Precámara de tratamiento de alta Presión y alta Temperatura (HPHT Cell). En esta Cámara es posible someter a las muestras a tratamientos térmicos en presencia de gases hasta una presión de 20 atm y 800 ºC, tanto en estático como en dinámico (simultáneamente).
  Pre-chamber for High Pressure/High Temperature treatments (HPHT Cell).Samples can be subjected to treatments in the presence of gases up to 20 bar and 800ºC (simultaneously). These treatments can be performed either under static or flowing gas conditions. After treatments, samples can be transferred to the analysis chamber without exposure to the atmosphere.
- Una cámara de inserción rápida dotada de sistema de aparcamiento/ desgasificado, que permite evacuar las muestras a temperatura reducida (T < 150ºC). También es posible la realización de tratamientos de desbatado iónico o la incorporación de otros sistemas (iluminación con luz Uv-Vis, evaporación de metales, u otros compuestos, etc.)
  A Fast entry chamber, equipped with a parking and degassing system, allowing the samples to be evacuated at moderate temperature (T < 150ºC). It is also possible to sputter the samples under an accelerated ion beam (0.5- 5.0 kV) using inert or reactive gases. Incorporation of some other equipment (Visible light illumination, metal evaporators) is also contemplated.

Responsables Científicos/ Scientific Responsibles: Dr. Juan Pedro Espinós Manzorro y Dr. Juan Pedro Holgado Vázquez

SERVICIO DE MECANIZADO/ MECHANIZED WORKSHOP

Se trata de un servicio horizontal fundamental para el Instituto y unidades externas adscritas al mismo. Ya que permite mejorar, modificar y adecuar el material y equipamiento científico a las necesidades de cada investigador y/o investigación en curso. Incluso llegando a su fabricación partiendo de una necesidad concreta. Ofreciendo asesoramiento técnico, diseño y fabricación de todos los elementos anteriormente descritos.
Además brinda la posibilidad de realizar pequeñas reparaciones y parte del mantenimiento general del equipamiento científico y de laboratorio.

This is a service essential for the Institute and external drives attached to the same. Because it allows you to improve, modify and adapt the material and scientific equipment to the needs of each researcher and/or research in progress. Even going to the extent of their manufacture on the basis of a specific need. Offering technical advice, design and manufacture of all elements described above.

INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

El servicio cuenta con herramientas manuales y herramientas eléctricas para la conformación de materiales muy diversos. Contando con la posibilidad unión de diversos materiales mediante los procesos de soldeo que se pueden realizar en el servicio:

The service account with hand tools and power tools for the formation of very diverse materials. With the possibility union of various materials by welding processes that can be performed in the service:

- Soldadura fuerte con diferentes aportes
  Brazing with different contributions
- Soldadura por arco eléctrico
  Electric arc welding
- Soldadura TIG sobre aceros
  TIG welding on steel

Para los procesos de mecanizado por arranque de viruta se cuenta con las siguientes máquinas-herramientas:

For the processes of machining by chip is has the following machine-tools:

- Centro de mecanizado,HAAS TM 1P
  HAAS machining center,TM 1P
- Taladro vertical, ERLO TSAR32
  Vertical drill, ERLO TSAR32
- Torno paralelo convencional PINACHO SC200
  Conventional lathe PINACHO SC200

- Torno paralelo semiautomático PINACHO SMART TURN180
  Semi-automatic lathePINACHO SMART TURN180

Responsable/ Responsible: Dra. Ana Isabel Becerro Nieto
Personal Técnico: D. Juan Carlos Sánchez Martín y D. Manuel Perea Domínguez

ACTIVIDADES DIVULGATIVAS Y FORMATIVAS

OUTREACH AND TEACHING ACTIVITIES

DOCENCIA / TEACHING

CURSOS DE POSTGRADO / POSTGRADUATE COURSES

MÉTODOS FÍSICOS DE ANÁLISIS DE CAPAS FINAS Y SUPERFICIES DE SÓLIDOS

Curso de Postgrado del CSIC
Programa 2018

Métodos Físicos de Análisis de Capas Finas y Superficies de Sólidos

Sevilla, del 25 al 29 de Junio de 2018

Este curso de postgrado pretende familiarizar a los asistentes con algunos de los métodos físicos de análisis más utilizados en la actualidad para la caracterización de capas finas y superficies. El curso, de una semana de duración, constará de clases teóricas y sesiones prácticas. Será impartido por profesores de la Universidad de Sevilla e investigadores del CSIC, en las instalaciones y con el equipamiento científico disponible en el Instituto de Ciencia de Materiales de Sevilla y el Centro Nacional de Aceleradores.

Está dirigido a científicos e ingenieros especializados en temas de análisis, diagnóstico e investigación en materiales y superficies. También se considera especialmente adecuado para alumnos de tercer ciclo de ingenierías de materiales.

Temáticas

Espectroscopias de Fotoemisión (XPS, UPS)
Microscopias Electrónicas de Transmisión y Barrido (TEM y SEM)
Espectroscopias Electrónicas (EDX, PEELS, EFTEM)
Difracción de Rayos X
Retrodispersión de Iones (RBS)
Microscopias de Aproximación de puntas (AFM, STM)
Utilización de Plasmas
Espectroscopias Ópticas y Vibracionales (UV-vis, Elipsometría, Fluorescencia, Raman, Infrarrojo)
Análisis Tribológico y Mecánico

Director:
Dr. Juan Pedro Espinós Manzorro
Instituto de Ciencia de Materiales de Sevilla. CSIC-Universidad Sevilla

Organizado por el Instituto de Ciencia de Materiales de Sevilla
Directores: Dr. Juan Pedro Espinós
Fecha de Celebración: 25 al 29 de junio de 2018
Horas lectivas: 25 de teoría + 15 de prácticas
Dirigido a: Grado de Doctor, Estudiante de Doctorado o Especialista de Empresa

Este curso de postgrado pretende familiarizar a los asistentes con algunos de los métodos físicos de análisis más utilizados en la actualidad para la caracterización, de materiales en general, y de capas finas y superficies en particular. El curso, de carácter intensivo y una semana de duración, consta de clases teóricas y sesiones prácticas. Estas últimas, desarrolladas con grupos de reducidos de alumnos, se realizarán con el equipamiento científico disponible en el Instituto de Ciencia de Materiales de Sevilla, el Centro Nacional de Aceleradores y el Servicio de Espectroscopía de Fotoelectrones de la Universidad de Sevilla.
El contenido y enfoque de los temas y otras actividades del curso son eminentemente prácticos, estando dirigido a científicos e ingenieros especializados en temas de análisis, diagnóstico, investigación en superficies, etc. También se considera especialmente adecuado para alumnos de tercer ciclo relacionados con la temática tratada.

Teoría**:**
Interacción de Fotones, Electrones e Iones con la Materia Condesada. Métodos Físicos de Análisis de Capas Finas y Superficies de Sólidos | Dr. Asunción Fernández Camacho
Espectroscopía de Fotoemisión de Rayos X: Composición Superficial | Dr. Juan Pedro Espinós
Espectroscopía de Fotoemisión de Rayos X: Estado Químico en la Superficie de Sólidos | Dr. Agustín R. González-Elipe
Pérdida de Energía de Electrones en Superficies: Perfiles de Composición y Caracterización Óptica en el EUV | Dr. Francisco Yubero Valencia
Caracterización Óptica y Vibracional: UV-visible, Elipsometría y Color | Dr. Francisco Yubero Valencia
Microscopía Electrónica de Efecto Túnel | Dr. Juan Ramón Sánchez Valencia
Plasmas en la Tecnología de Películas Delgadas | Dr. José Cotrino Bautista
Microscopía Electrónica de Transmisión: Fundamentos y Aplicaciones Generales | Dra. Asunción Fernández Camacho

Microscopía Electrónica de Barrido| Dra. María del Carmen Jiménez de Haro

Espectroscopías Electrónicas: X-EDS y EELS Imágenes Filtradas en Energía (EFTEM) | Dra. Cristina Rojas Ruiz

Nanomanipulación, Procesado y Análisis de Propiedades en el Microscopio Electrónico | Dra. Ana Borrás Martos

Análisis Tribológico y Mecánico de Capas Delgadas | Dr. Juan Carlos Sánchez López

La difracción y Reflectometría de Rayos X de Películas Delgadas | Dr. José María Martínez Blanes

Microscopías de Fuerzas Atómicas | Dra. Carmen López Santos

Caracterización Óptica y Vibracional: Fluorescencia, Infrarrojo y Raman | Dr. Angel Barranco Quero

La absorción de Rayos X de Películas Delgadas | Dr. Juan Pedro Holgado Vázquez

Retrodispersión Rutherford: Perfiles de Composición | Dr. Francisco Javier Ferrer (CNA)

Prácticas:

a. Microscopías Electrónicas de Transmisión y Barrido | Dra. Cristina Rojas Ruiz | Dra. Carmen Jiménez de Haro | Lda. Olga Montes

b. Espectroscopía de Fotoemisión, XPS | Dr. Juan Pedro Holgado | Dra. Florencia Vattier

c. Difracción de Rayos X | Dr. José M. Martínez Blanes

d. Retrodispersión Rutherford | Dr. Javier García

e. Microscopía de Fuerzas Atómicas | Dr. Carmen López Santos | Dr. Juan Ramón Sánchez Valencia

f. Espectroscopía de Fotoemisión, UPS | Dr. Juan Pedro Espinós

g. Absorción de Rayos X, EXAFS y XANES | Dr. Juan Pedro Holgado

MÁSTER / MASTER

MÁSTER EN CIENCIA Y TECNOLOGÍA DE NUEVOS MATERIALES

Organizado por la Universidad de Sevilla

Coordinador: Dr. Joaquín Ramírez Rico

Fecha de Celebración: Curso Académico 2017-18

Créditos necesarios: 60

Dirigido a: Licenciados en Química, Física, así como, los Titulados en Ingeniería afines (Ingenieros Químicos, de Materiales, etc.)

Especialidades: Materiales para la Energía y el Medio Ambiente. Ingeniería de Superficies, Materiales Estructurales y Funcionales.

Mención de Calidad

Química del Estado Sólido (Créditos: 5) | Dra. Pilar Malet Maenner

Fisica del Estado Sólido (Créditos: 5) | Dra. Angela Gallardo López | Dra. Josefa Borrego | Dr. Manuel Jiménez Melendo
Técnicas de Caracterización de Materiales (Créditos: 8) | Dr. Julián Martínez Fernández | Dr. Juan M. Montes Martos (US)
Síntesis de Materiales y Nanoestructuras (Créditos: 7) | Dra. María Dolores Alcalá | Dra. Svetlana Ivanova | Dr. Francisco J. Gotor Martínez
Catalizadores para la Energía y el Medio Ambiente (Créditos: 5) | Dr. José Antonio Odriozola Gordón
Materiales con Funcionalidad Superficial (Créditos: 5) | Dra. Rosa María Pereñiguez Rodríguez | Dra. Leidy Marcela Martínez Tejada
Recuperación y Transformación de Materiales (Créditos: 5) | Dra. Svetlana Ivanova | Dr. Leidy Marcela Martínez Tejada
Corrosión y Recubrimientos Protectores (Créditos: X) | Dr. Leidy Marcela Martínez Tejada
Procesado de Materiales Estructurales (Créditos: 5) | Dr. Alfonso Bravo León | Dr. José Antonio Rodríguez Ortíz
Comportamiento Mecánico (Créditos: 5) | Dr. Arturo Domínguez Rodríguez | Dr. Diego Gómez García
Comportamiento Magnético (Créditos: 5) Dr. Javier S. Blázquez Gámez | Dr. Victorino Franco García
Comportamiento Térmico, Dieléctrico y Óptico de Materiales (Créditos: 5) Dr. Francisco Javier Romero Landa | Dra. Carmen Gallardo Cruz
Propiedades Térmicas, Dieléctricas y Ópticas (Créditos: X) | Dr. Hernán Míguez García | Dr. Gabriel Lozano Barbero
Computación en Ciencia de Materiales (Créditos: 5) | Dra. Regla Ayala Espinar | Dr. Antonio Córdoba Zurita (US) | Dr. Felipe Gutiérrez Mora

MÁSTER INTERUNIVERSITARIO "LÁSER, PLASMA Y TECNOLOGÍA DE SUPERFICIES"

Máster Interuniversitario
Plasma, Láser y Tecnologías de Superficie

Nanotecnologías Innovadoras para Ingeniería Avanzada

- Curso de máster oficial de un año.
- Clases teóricas y prácticas *on-line*.
- Colaboración de empresas de alta tecnología.
- Válido para programa de doctorado.
- Ayudas de movilidad para dos semanas de prácticas en los laboratorios participantes.
- Clases impartidas por expertos reconocidos internacionalmente.

- Nanociencia
- Nanotecnología
- Tecnología de Vacío
- Láseres
- Ingeniería de Materiales
- Tecnología de Plasmas
- Simulación por Ordenador
- Tecnologías Avanzadas

Estudiantes Objetivo
Graduado en Física
Graduado en Química
Graduado en Ingeniería
Profesionales de la Industria

Más información en http://www.uco.es/plasma_laser_superficie

Organizado por:

Organizado por la Universidad de Córdoba, Universidad Politécnica de Madrid, Instituto de Ciencia de Materiales de Sevilla y el Instituto de Ciencia de Materiales de Madrid
Coordinador: Dr. Joaquín Ramírez Rico
Fecha de Celebración: Curso Académico 2017-18
Créditos necesarios: 60
Dirigido a: Licenciados en Química, Física, así como, los Titulados en Ingeniería afines (Ingenieros Químicos, de Materiales, etc.)
Especialidades: Materiales para la Energía y el Medio Ambiente. Ingeniería de Superficies, Materiales Estructurales y Funcionales.
Mención de Calidad
Coordinador: Dr. Joaquín Ramírez Rico
Fecha de Celebración: Curso Académico 2017-18
Créditos necesarios: 60
Dirigido a: Licenciados en Química, Física, así como, los Titulados en Ingeniería afines (Ingenieros Químicos, de Materiales, etc.)

Especialidades: Materiales para la Energía y el Medio Ambiente. Ingeniería de Superficies, Materiales Estructurales y Funcionales.

Mención de Calidad

Máster "Láser, Plasma y Tecnología de Superficies"

Interaccion de partículas y radiación con la materia. Láseres
Asunción Fernández Camacho
Técnicas de caracterización de superficies y láminas delgadas
T. Cristina Rojas Ruiz, Agustín R. González-Elipe, Victor Joaquín Rico Gavira, María del Carmen López Santos
Tecnología de lámina delgada
Ana Isabel Borrás Martos, Agustín R. González-Elipe, Victor Joaquín Rico Gavira, María del Carmen López Santos
Nanotecnología de superficies y sus aplicaciones
Angel Barranco Quero, Francisco Javier Aparicio Rebollo, Juan Ramón Sánchez Valencia, Victor López Flores
Funcionalización de superficies para aplicaciones mecánicas, protectoras y de bioactividad controladas
Juan Carlos Sánchez-López, María Carmen López Santos, Francisco Yubero Valencia
Nuevos materiales para dispositivos
Victor López Flores, Ana Isabel Borrás Martos
Materiales e Ingeniería de Superficies
Ana Isabel Becerro Nieto
Plasmas y Tecnología de superficies
Alberto Palmero

Lugar: Universidad de Córdoba, Universidad Politécnica de Madrid, Instituto de Ciencia de Materiales de Madrid

Asimismo, el personal del ICMS ha impartido cursos regulares de primer y segundo ciclos de las correspondientes Licenciaturas y/o Grados en Química, Física y Farmacia e Ingeniería de Materiales y Biología en la Universidad de Sevilla.

CONFERENCIAS INVITADAS IMPARTIDAS POR PERSONAL DEL ICMS
INVITED CONFERENCES BY PERSONNEL OF THE ICMS

18 de abril | **Conferencia inaugural: Dióxido de carbon y agua juntos para un futuro energético sostenible**
Asunción Fernández Camacho
Lugar: VI Feria de la Ciencia de Jerez

2 de mayo | **Líneas de Investigación en Materiales Ópticos en el ICMS**
Hernán Míguez
Lugar: 2º Taller de Física del Estado Sólido. Universidad de Sevilla

2 de mayo | **Diseño de estructuras fotónicas: control de la emisión de nanósforos integrados en resonadores ópticos**
Elena Cabello Olmo
Lugar: 2º Taller de Física del Estado Sólido. Universidad de Sevilla

7 de mayo | **La Carrera Investigadora**
Gabriel Lozano
Lugar: Conferencias del Departamento de Fisica. Universidad de Córdoba

7 de mayo | **Materiales que alumbran**
Gabriel Lozano
Lugar: Conferencias del Departamento de Fisica. Universidad de Córdoba

10 de mayo | **Webinar: New insights into optical materials for optoelectronic applications**
Gabriel Lozano
Webinar: Materials Today. Connecting the materials community

16 de mayo | **Materiales ópticos para dispositivos opto-electrónicos más versátile y eficientes**
Hernán Míguez
Lugar: Sesión Científica organizada por la Sección de Ciencias Físicas y Química de la Real Academia de Ciencias, RSEF y la RSEQ

5 de julio | **Nanomateriales ópticos para dispositivos optoelectrónicos**
Hernán Míguez
Lugar: Ciclo de Seminarios de la Gcia. Investigación y Aplicaciones CAC-CNEA 2018

15 de agosto | **Del Laboratorio a la Empresa: Recorridos desde la Ciencia Básica hasta la Aplicación Tecnológica**
Hernán Míguez
Lugar: Universidad Nacional de San Martín, Argentina

24 de octubre | **Caracterización de capas nanoestructuradas funcionales preparadas por HiPIMS**
Juan Carlos Sánchez López
Lugar: IQS-Instituto Químico de Sarriá, Barcelona, España

15 de noviembre | **Synthesis and applications of 1D and 3D supported nanostructures developed by plasma assisted vacuum deposition methods**
Ana Isabel Borrás
Lugar: MRI-Seminar Queen Mary University of London. School of Engineering and Materials Science (Reino Unido)

4 de diciembre | **Synthesis and applications of supported 1D and 3D nanomaterials**
Ana Isabel Borrás
Lugar: Faculty of Mathematics and Physics. Department of Macromolecular Physics. University of Prague

CONFERENCIAS Y SEMINARIOS IMPARTIDOS EN EL ICMS
CONFERENCES AND SEMINAR IN THE ICMS

25 de abril | **Levitación de nanopartículas en alto vacío mediante trampas ópticas y de iones**
Dr. Raúl A. Rica Alarcón
Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada

La levitación de nanopartículas en alto vacío ha emergido como un sistema singular que permite explorar distintas fronteras de la física, en particular en física estadística y la aplicabilidad de la mecánica cuántica en la mesoescala [1-4]. En este seminario, daré una introducción a la rica fenomenología observada en este tipo de sistemas, y describiré nuestros progresos en la implementación de distintos tipos de levitación, tales como la levitación óptica y mediante el uso de trampas de iones. Primero presentaré algunos resultados que demuestran un control muy preciso sobre la dinámica no lineal de una nanopartícula atrapada ópticamente, así como de la dinámica estocástica bi-estable que presenta el sistema [5]; a continuación introduciré el uso de trampas de iones como alternativa a las ópticas, permitiendo el atrapamiento estable de nanopartículas con grados internos de libertad tales como nanodiamantes con defectos nitrógeno-vacante [6,7]. Finalmente, veremos cómo es posible controlar la carga de la nanopartícula creando un plasma cerca de la trampa, y discutiremos algunas de las posibilidades que ofrece esta nueva configuración.

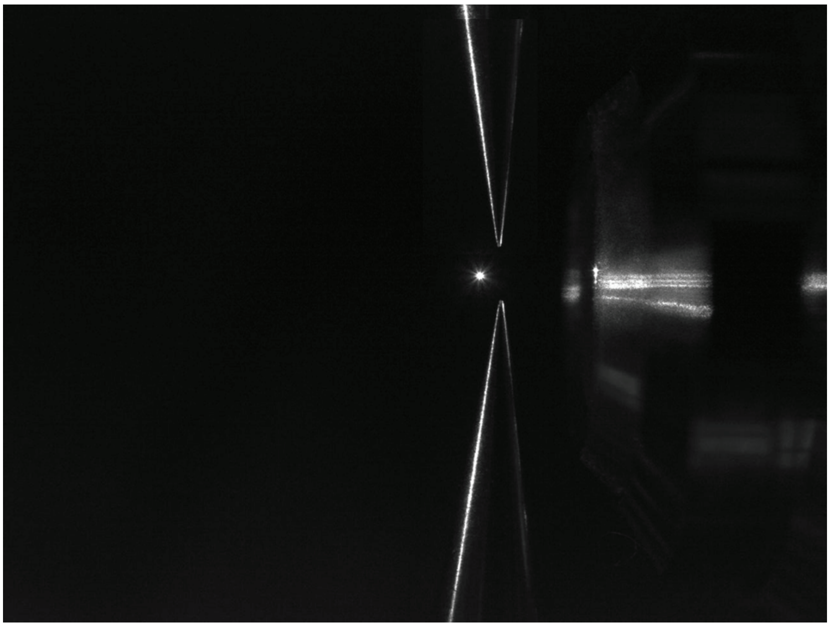


Fig.1 Imagen de una única nanopartícula atrapada mediante una trampa de Paul y situada en el foco de un haz láser focalizado mediante un objetivo.
La visualización es posible gracias al scattering emitido por la partícula tras su interacción con el haz.

[1] J. Gieseler et al. Phys. Rev. Lett. 109, 103603 (2012)
[2] J. Gieseler et al. Nature Nano. 9, 358-364 (2014)
[3] V. Jain et al. Phys. Rev. Lett. 116, 243601 (2016)
[4] N. Kiesel et al. PNAS 110, 14180-14185 (2013)
[5] F. Ricci et al. Nature Comms. 8, 15141 (2017)
[6] I. Alda et al. Appl. Phys. Lett. 109, 163105 (2016)
[7] G.P. Conangla et al. preprint arXiv:1803.05527 (2018)

Ciclo de Conferencias / ICMS Invited Lectures

18 de enero | **Nanostructures – Preparation and Applications**
Dr. B. Rauschenbach
Leibniz-Institut für Oberflächmodifizierung

Nanostructures with a three dimensional tailored shapes are promising candidates for a variety of applications. Sputter technology, oblique angle deposition and glancing angle deposition are sophisticated methods to create nanostructures with custom-made structure geometries. Selected results of these three methods to prepare nano- and micro-structures are presented. (1.) Low-energy ion beam sputtering, i.e. the removal of atoms from a surface due to the impact of energetic ions or atoms, is an inherent part of numerous surface processing techniques. Two prominent examples are the spontaneous formation of well-ordered ripple or dot pattern and the realization of experimental conditions where surface relaxation dominates and smooth surfaces are emerging. Both special cases are of high interest for many potential applications in nanotechnology. (2.) Combining ion sputter deposition or electron beam evaporation and oblique angle deposition represents an elegant and powerful technique to sculpture manifold surface morphologies on the nanometer scale. Besides different examples of films prepared by oblique deposition a model describing the growth of nanostructures for the full angle of incidence range (0° - 90°) is proposed. Predictions of this model for tilt angles and porosities are shown and compared to an off-lattice computer simulation as well as to deposited films of different materials. (3.) A constant or periodically interrupted substrate rotation during deposition is used to tailor structures like chevrons, posts, circular and quadratic spirals or zig-zags. The growth of these nanostructures on nonpatterned substrates, regularly arranged Si nanostructures and the growth conditions are discussed. Regular arrays of nanostructures are grown on several substrates by patterning with Au dots using selfassembled mono- and double layers of polystyrene nano-spheres as evaporation mask or electron beam lithography. Finally, examples are given for the applications of sculptured thin films in the field of chemical and biosensors.

16 de febrero | **Plasma catalysis for CO_2 conversion: A better understanding of the underlying mechanisms**

Dra. A. Bogaerts

Research group PLASMANT, University of Antwerp, Department of Chemistry, Belgium

Plasma catalysis is gaining increasing interest for CO_2 conversion. To improve this application in terms of conversion, energy efficiency and product formation, a good insight in the underlying mechanisms is desirable. We try to obtain this by computer modelling and experiments.

Experimentally, we study two types of plasma reactors, i.e., dielectric barrier discharges (DBDs) in which we insert packing materials to investigate plasma catalysis, as well as a gliding arc (GA) discharge. In this talk, I will show some results for both, illustrating the superior energy efficiency of a GA reactor. In addition, we also simulate the plasma chemistry as well as the optimum reactor design, in the three types of plasma reactors most commonly used for CO_2 conversion, i.e., DBDs, GA discharges and microwave (MW) plasmas. For the plasma reactor design, we use 2D or 3D computational fluid dynamics modelling. For the plasma chemistry, we make use of zero-dimensional chemical kinetics modeling, which solves continuity equations for the various plasma species, based on production and loss terms, as defined by the chemical reactions. Typically, up to 100 different species are considered, which react among each other in up to 1000 different chemical reactions.

When studying the plasma chemistry in pure CO_2, we focus especially on the the role of vibrationally excited CO_2 levels, which are the key species for enhanced energy efficiency of the CO2 conversion. Our model reveals the relative importance of various processes, responsible for the CO_2 conversion, and this is linked to the energy efficiency in the various types of plasma reactors.

We have also studied the plasma chemistry in CO_2/CH_4 and in CO_2/H_2O mixtures, to produce value-added chemicals. The main products formed are a mixture of H_2 and CO, or syngas, with a tuneable H_2/CO ratio depending on the gas mixing ratio. The production of oxygenated compounds, such as methanol, formaldehyde, etc, is very limited, showing the need for combining with a catalyst. A detailed chemical kinetics analysis allows to elucidate the different pathways leading to the observed results, and to propose solutions on how to further improve the formation of value-added products.

Likewise, we also studied the plasma chemistry in a CO_2/N_2 mixture, to investigate the effect of this important impurity in effluent gases on the CO_2 conversion, energy efficiency and product formation. Several harmful compounds, i.e., N_2O and NO_x compounds, are produced in the range of several 100 ppm. The reaction pathways for the formation of these compounds are again explained based on a kinetic analysis, which allows proposing solutions on how to prevent the formation of these harmful compounds.

Finally, we also study plasma-catalyst interactions, by experiments, atomic scale simulations (density functional theory), as well as fluid and particle-in-cell – Monte Carlo simulations. The latter is used to investigate whether plasma can be formed inside catalyst pores.

15 de marzo | **Nanostructured N-doped Carbon and Carbon nitride materials: Enzyme-like Heterogeneous Catalysts?**

Dr. M. Antonietti

Max Planck Institute of Colloids and Interfaces, Research Campus Golm, D-14424 Potsdam, Alemania

Carbon nanoparticles and nanostructures which are doped with the element nitrogen (“N-doped”) have special properties, among them high oxidation resistance and high electronic conductivity. These carbon materials can be made by thermal condensation

Of special monomers, among them for instance nucleobases
About 10 years ago, it was found that such carbons are very powerful electrocatalysts, even when metal-free, an can catalyse a number of "world reactions", such as the reduction of oxygen or the conversion of soda water into formic acid. In addition, the materials are also very favourable supports for metallic nanocatalysts, which is attributed to a bulk heterojunction effect.
When going to even high nitrogen contents, Carbon nitrides or polyheptazinimides are obtained, and the resulting semiconductors can promote artificial photosynthesis, including water splitting and CO2 conversion. I will present a number of completely new chemical reactions only possible with such colloids which indicate how such clusters could have contributed to the existence of chemical diversity, potentially also on a prebiotic earth-like planet.

References:

1) Polymeric Graphitic Carbon Nitride as a Heterogeneous Organocatalyst: From Photochemistry to Multipurpose Catalysis to Sustainable Chemistry; Wang, Yong; Wang, Xinchen; Antonietti, Markus ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 51 68-89 (2012)
2) Efficient Metal-Free Oxygen Reduction in Alkaline Medium on High-Surface-Area Mesoporous Nitrogen-Doped Carbons Made from Ionic Liquids and Nucleobases: Yang, Wen; Fellinger, Tim-Patrick; Antonietti, Markus, JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 133 206-209 (2011)

13 de abril | **Halide Perovskites for Photovoltaic and Light-Emission Applications**
Dr. S. Stranks
Cavendish Laboratory, Cambridge

Metal halide perovskites are exotic hybrid crystalline materials developed out of curiosity. Unexpectedly, solar cells and light-emitting diodes (LEDs) incorporating these perovskites are rapidly emerging as serious contenders to rival the leading technologies. Photovoltaic power conversion efficiencies have jumped from 3% to over 22% in just seven years of academic research, and we are witnessing a similarly astonishing pace in LEDs. Here, I will give an overview of some of our key photophysical findings to advance understanding of the optoelectronic behaviour of the perovskite materials and operation of the state-of-the-art devices. I will cover topics including charge carrier diffusion and recombination, as well as ion migration and its potential impact on device performance. I will identify avenues towards eliminating losses by focusing on the relationships between micro- and nano-scale optoelectronic, chemical and structural properties of these materials as neat films and in operating devices. Understanding these properties is key to further development of the field and to bringing the perovskite technology to commercialisation.

26 de abril | **Stretching the wave: the quest for long-wavelength phosphors for displays, lighting and medical imaging**
Dr. D. Poelman
Ghent University, Bélgica

Most of today's high efficiency white LEDs are based on a blue-emitting LED chip, combined with one or more phosphor materials. In order to achieve the high colour quality necessary for home lighting, new phosphors should be developed having suitable emission in the red part of the

spectrum, thus decreasing the CCT (correlated colour temperature) and increasing the CRI (colour rendering index) of the white light. We will discuss the requirements for this class of materials for both displays and lighting: they have to combine a sufficiently long dominant wavelength with a minimal fraction of the emission beyond 650 nm, where the eye sensitivity is low. Materials include both Eu-doped and Mn-doped compounds. Using Eu, the challenge is to stretch the emission to a sufficiently long wavelength, while using Mn, efforts are needed to tune the emission to a sufficiently short wavelength.
For some applications, such as in vivo medical imaging, even longer wavelengths are needed, typically in the range between 650 and 950 nm, in the so-called first tissue transparency window. We will evaluate the possible use of Cr3+ or Mn4+ as dopants for this application. In addition, we will try to turn these phosphors into persistent luminescent emitters, showing emission up to hours after the excitation has ended. Such long afterglow materials open op exciting possibilities for medical imaging, avoiding many of the drawbacks of commonly used imaging methods.

24 de mayo | **Solid state chemistry of oxides: some properties and applications**
Dr. A. West
University of Sheffield, Reino Unido

The talk will focus on the common occurrence of a variable metal-oxygen ratio in many inorganic oxides and its consequences for a diverse range of electrical properties and applications. Comparisons will be made between the occurrence of non–stoichiometry in many oxides and the exact stoichiometry of molecular compounds. In some cases, oxygen in oxides is more than just an inert O2- packing ion in a crystal structure, but can take part in redox processes similar to transition metal cations. Topics covered in the talk should include: lithium battery cathodes, black rutile, p-n transitions in oxide ceramics and memristive switching phenomena, to illustrate the underlying physical processes responsible for the diverse range of properties.

18 de octubre | **Electric Field Manipulation of Matter via Synchrotron Radiation**
Prof. T. Tskalakos
Rutgers University

Flash Sintering (FS), a relatively new method, densifies ceramic powders, in seconds, at very low temperatures. A non-equilibrium rise in current, under applied electric field, is used to densify matter. EDXRD Temperature Calibration utilizes white energy dispersive x-ray diffraction (EDXRD) from a synchrotron source to track the lattice expansion of the ceramic during FS. In this presentation, studies on the following materials will be discussed: ZnO, TiO2, CeO2 and BiFeO3 oxides and B4C , TiB2 ZrB2 and BN nonoxides. This In-Situ investigation analysis of mechanisms at the onset of FS, the cause of enhanced sintering kinetics during FS and applied temperatures for each theory will be presented. New ways of performing FS experiments on ZnO by ramping the current linearly and by AC power supply, microstructural inhomogeneity, grain growth, and other physical properties will be also shown. FS of BiFeO3 is a homogeneous process at exceptionally low temperatures (350 ºC < Tc) will be described as well as the excellent dielectric properties that are discovered.

18 de octubre | **Electric Field Manipulation of Matter via Synchrotron Radiation**
Prof. T. Tskalakos
Rutgers University

Flash Sintering (FS), a relatively new method, densifies ceramic powders, in seconds, at very low temperatures. A non-equilibrium rise in current, under applied electric field, is used to densify matter. EDXRD Temperature Calibration utilizes white energy dispersive x-ray diffraction (EDXRD) from a synchrotron source to track the lattice expansion of the ceramic during FS. In this presentation, studies on the following materials will be discussed: ZnO, TiO2, CeO2 and BiFeO3 oxides and B4C , TiB2 ZrB2 and BN nonoxides. This In-Situ investigation analysis of mechanisms at the onset of FS, the cause of enhanced sintering kinetics during FS and applied temperatures for each theory will be presented. New ways of performing FS experiments on ZnO by ramping the current linearly and by AC power supply, microstructural inhomogeneity, grain growth, and other physical properties will be also shown. FS of BiFeO3 is a homogeneous process at exceptionally low temperatures (350 ºC < Tc) will be described as well as the excellent dielectric properties that are discovered.

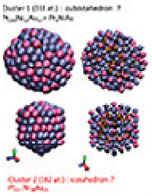
8 de noviembre | **Plasma sputtering synthesis of nanocatalyst for fuel cells: Experiments and molecular dynamics simulations**
Dr. P. Brault
CNRS-Université d’Orléans

Hydrogen powered fuel cells are expected be a relevant solution for green and sustainable energy delivery. Major breakthroughs remain to be achieved. One of them is to lower the noble metal content used as catalysts in the fuel cell electrodes for electrochemical conversion of H2 and O2 from air into electricity, heat and water.

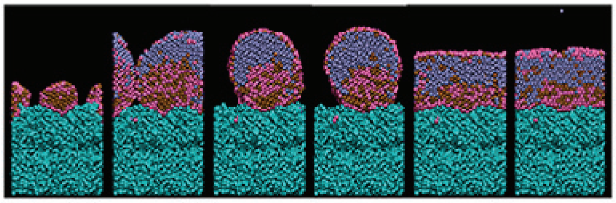
Plasma sputtering deposition of supported nanocatalysts has been demonstrated to improve electrode efficiency of low temperature proton exchange membrane fuel cells. Indeed, sputtering can act as an atom source with a controlled energy distribution, which, in turn, enables to control the nanocatalyst growth on the porous carbon electrode with a controlled in-depth profile. This allow to drastically reduce the noble metal content up to a factor 100. Another way is to alloy the noble metal catalyst (here Pt) with a common metal (Fe, Ni, Mo, …) and also with gold. The latter being not a catalyst but is expected to prevent nanocatalyst sintering during fuel cell operation. Very recently, direct growth of Pt alloy nanocatalyst in the plasma phase have been carried out using gas condensation source leading to well defined and narrow nanocluster size distributions.

As the nanoparticle growth by sputtering methods is atomic by nature, simulations at the molecular level are expected to be relevant for understanding basic mechanisms of this deposition method. Indeed, molecular dynamics (MD) as being able to exactly calculating the trajectory of atomic systems is a suitable method for addressing this topic, especially in the context of plasma sputtering. Very recently, it has been shown that MD simulations allowed confirming and predicting the morphology and structure of Pt nanocatalysts as well as for PtxPdyAuz and PtxNiyAuz. Direct growth in the plasma phase mimicking the gas condensation source is also studied. Initial conditions of MD simulations are selected for matching experimental chemical and physical methods. Radial distribution functions and X-Ray

Diffraction pattern are systematically computed for enabling direct comparison with experiments.



Pt_3NiAu free nanocatalysts grown in argon



$PdAu@Pt_2$ core-shell nanocatalyst grown on model porous carbon. evolution against increasing deposition time (from right to left)

13 de diciembre | **Hybrid Nanoparticles for Therapy and Diagnosis**
Dr. Jesús Martínez de la Fuente
Instituto de Ciencia de Materiales de Aragón-CSIC/Universidad de Zaragoza

In the last decades, inorganic nanoparticles have been steadily gaining more attention from scientists from a wide variety of fields such as material science, engineering, physics or chemistry. The very different properties compared to that of the respective bulk, and thus intriguing characteristics of materials in the nanometre scale, have driven nanoscience to be the centre of many basic and applied research topics. Moreover, a wide variety of recently developed methodologies for their surface functionalization provide these materials with very specific properties such as drug delivery and circulating cancer biomarkers detection. In this talk we describe the synthesis and functionalization of magnetic and gold nanoparticles as therapeutic and diagnosis tools against cancer:

-Pseudo-spherical gold nanoparticles derivatized with with fluorescent dyes, cell penetrating peptides and small interfering RNA (siRNA) complementary to the proto-oncogene myc have been tested using a hierarchical approach including three biological systems of increasing complexity: in vitro cultured human cells, in vivo invertebrate (freshwater polyp, Hydra) and in vivo vertebrate (mouse) model. Selection of the most active functionalities was assisted step by step through functional testing adopting this hierarchical strategy. Merging these chemical and biological approaches lead to a siRNA/RGD gold nanoparticle capable of targeting tumor cells in lung cancer xenograft mouse model, resulting in successful and significant c-myc oncogene downregulation followed by tumor growth inhibition and prolonged survival of the animals.

-Gold nanoprisms (NPRs) have been functionalized with PEG, glucose, cell penetrating peptides, antibodies and/or fluorescent dyes, aiming to enhance NPRs stability, cellular uptake and imaging capabilities, respectively. Cellular uptake and impact was assayed by a multiparametric investigation on the impact of surface modified NPRs on mice and human primary and transform cell lines. Under NIR illumination, these nanoprobes can cause apoptosis. Moreover, these nanoparticles have also been used for optoacoustic imaging, as well as for tumoral marker detection using a novel type of thermal ELISA nanobiosensor using a thermosensitive support.

-Magnetic nanoparticles functionalized with DNA molecules and further hybridizing with different length fluorophore-modified DNA have allowed the accurate determination of temperature spatial mapping induced by the application of an alternating magnetic field. Due to the design of these DNAs, different denaturalization temperatures (melting temperature, Tm) could be achieved. The quantification of the denaturalized DNA, and by interpolation onto a Boltzmann fitting model, it has been possible to calculate the local temperature increments at different distances, corresponding to the length of each modified DNA, from the surface of the nanoparticles. The local increments achieved were up to 15ºC, and the rigidity conferred by the double strand DNA allowed to evaluate the temperature at distances up to 5.6 nm from the nanoparticle surface.

ICMS - sci - talks

23 de enero | **Photonic tuning of the emission of nanophosphor films**
Dr. Gabriel Lozano

6 de febrero | **Cobalt carbide identified as catalytic site for the dehydrogenation of ethanol to acetaldehyde**
Dr. Alfonso Caballero

20 de febrero | **Low temperature plasma processing of platinum porphyrins for the development of metal nanostructured layers**
Dr. Juan Ramón Sánchez-Valencia

13 de marzo | **Outstanding visible photocatalytic activity of a new mixed bismuth titanate material**
Dra. Carmen Hidalgo

10 de abril | **Improving the pollutant removal efficiency of packed-bed plasma reactors incorporating ferroelectric components**
Dr. José Cotrino

8 de mayo | **Multifunctional Eu-doped NaGd(MoO4)2 nanoparticles functionalized with poly (L-lysine) for optical and MRI imaging**
Dr. Manuel Ocaña

22 de mayo | **Performance of biomorphic Silicon Carbide as particulate filter in diesel boilers**
Dr. Joaquín Ramírez Rico

5 de junio | **The role of cobalt hydroxide in deactivation of thin film Co-based catalysts for sodium borohydride hydrolysis**
Dra. Gisela Arzac

19 de junio | **Tailoring the emission from nanometric light sources via Tamm modes in flexible coatings**

Dr. Juan Galisteo

18 de septiembre | **In situ monitoring of the phenomenon of Electrochemical Promotion of Catalysis**
Dr. Juan Pedro Espinós

9 de octubre | **Origin of light induced instability of organic-inorganic perovskites in the presence of oxygen**
Dr. Hernán Míguez

25 de octubre | **Isosymmetric structural phase transition of the orthorhombic lanthanum gallate structure as a function of temperature determined by Rietveld analysis**
Dr. José Manuel Córdoba

6 de noviembre | **Characterization and Validation of a-Si Magnetron-Sputtered Thin Films as Solid He Targets with High Stability for Nuclear Reactions**
Dra. Vanda Godinho

20 de noviembre | **Structural control in porous/compact multilayer systems grown by magnetron sputtering**
Dr. Rafael Álvarez Molina

12 de diciembre | **Exotic grain growth in boron carbide polycrystals under electric fields**
Dr. Diego Gómez

DIVULGACIÓN / DISSEMINATION

FERIA DE LA CIENCIA / FAIR OF SCIENCE

La XVI Feria de la Ciencia de Sevilla (del 10 al 12 de mayo de 2018, Palacio de Congreso y Exposiciones de Sevilla, FIBES) constituye un punto de encuentro donde se desarrollaron actividades de divulgación de la Ciencia y la Tecnología, realizando demostraciones y experimentos para facilitar la comprensión de contenidos científicos. El Instituto de Ciencia de Materiales de Sevilla presentó la actividad: “Catálisis para un mundo mejor y más sostenible”.
Coordinadora: Dra. T. Cristina Rojas Ruiz
Unidad “Catálisis para el medioambiente y la energía”
Investigador Responsable: Dr. Juan Pedro Holgado
Monitores: Alvaro Caro Martínez, Francisco Javier Osuna Barroso, Rosa María Pereñiguez Rodríguez, Cristina López Pernía, María del Carmen Hidalgo López, Francisco Rodríguez Peligro, Florencia Vattier Lagarrigue, Daniel González Mancebo, José Manuel Obrero Pérez, Nuria Ofelia Núñez Alvarez, Angeles María López Martín, Victor Joaquín Rico Gavira, Gerardo Colón Ibañez, César A. Jaramillo Páez, Nuria García Moncada

The Fair of Science (10 to 12 May 2018, in Seville) constituted a meeting point where many activities for spreading of science and technology were carried out. Demonstrations and experiments where presented to facilitate the understanding of scientific aspects. The Materials Science Institute of Seville presented the activity: “Catálisis para un mundo mejor y más sostenible”
Coordinator: Dra. T. Cristina Rojas Ruiz
Research Unit: Catalysis and Environmental Energy
Scientific Responsible: Dr. Juan Pedro Holgado
Monitors: Alvaro Caro Martínez, Francisco Javier Osuna Barroso, Rosa María Pereñiguez Rodríguez, Cristina López Pernía, María del Carmen Hidalgo López, Francisco Rodríguez Peligro, Florencia Vattier Lagarrigue, Daniel González Mancebo, José Manuel Obrero Pérez, Nuria Ofelia Núñez Alvarez, Angeles María López Martín, Victor Joaquín Rico Gavira, Gerardo Colón Ibañez, César A. Jaramillo Páez, Nuria García Moncada

SEMANA DE LA CIENCIA Y LA TECNOLOGÍA / SCIENCE AND TECHNOLOGY WEEK

Este evento de carácter europeo está diseñado para demostrar cómo la ciencia y la tecnología nos afectan y cómo éstas pueden ser utilizadas para mejorar nuestras vidas y el mundo que nos rodea.

Coordinadora: Dra. T. Cristina Rojas Ruiz

Café con Ciencia

El café con ciencia es una actividad que acerca de forma original y atractiva la ciencia y sus protagonistas. Esta actividad de divulgación genera un punto de contacto entre profesionales de la ciencia y alumnos de secundaria, promoviendo la reflexión sobre diversos asuntos en un entorno cercano y participativo.

En esta edición se compartirán desayuno con estudiantes de bachillerato para dialogar sobre temas concretos de sus estudios y sobre sus respectivas trayectorias profesionales. Esta actividad cumple el triple objetivo de comunicar la ciencia a través de sus propios protagonistas, promover la cultura científica y fomentar vocaciones investigadoras.

Las mesas de encuentro tienen una hora de duración, y se desarrollan con grupos reducidos de quince alumnos.

Mesa. Juan Ramón Sánchez Valencia. Tema “Nanomateriales mucho más que miniaturización”

Cuenta la ciencia

Cuenta la ciencia es una actividad que pretende acercar y fomentar la cultura científica a los ciudadanos de distintas edades de pueblos y barrios de la provincia de Sevilla, que por su localización pueden presentar más dificultades de acceso a la oferta de actividades de divulgación científica. También se pretende despertar la vocación científica en los niños y jóvenes, así como transmitir la importancia y el papel del profesional científico en el desarrollo de la sociedad del bienestar. Para conseguir estos objetivos, investigadores del Instituto se desplazaron hacia los centros culturales para realizar las siguientes actividades.

Centro Cultural Biblioteca de Montequinto

Charla
Materiales Fotónicos: nanotecnologías para el control de la luz,
Dr. Mauricio Calvo

Taller de ciencia
Dirigido a niños de primaria, en donde se realizaron experimentos sencillos de química sobre materiales para el medio Ambiente y la Energía.
Dr. Juan Pedro Holgado

Desayunos–Científicos
Nanomateriales: mucho más que miniaturización
Dr. Juan Ramon Sánchez
¿Podemos tener cerámicas a la carta manipulando el nanomundo?
Dra. Rosalía Poyato

Biblioteca de San Jerónimo

Taller de ciencia
Diamante, grafito y grafeno ¿son familia? donde niños de primaria aprendieron a construir las estructuras químicas del diamante, grafito y grafeno y se les explicó las características y aplicaciones de estos materiales.
Dra. Rosalía Poyato Galán

Desayuno –Científico
Reduciendo el desgaste con Nanomateriales: divide y vencerás
Dr. Juan Carlos Sánchez-López

Charla–Coloquio
Energía Nuclear.
Dra. Mª Dolores Alba Carranza

Durante la semana de la ciencia se expusieron en la Biblioteca de Montequinto posters con los trabajos de investigación que se realizan en las distintas Unidades del ICMS.

PARTICIPACION EN LA NOCHE EUROPEA / EUROPEAN RESEARCHERS' NIGHT

Dos Investigadores del Instituto han participado en la European Researchers' Night, una iniciativa promovida por la Comisión Europea en el marco del programa Horizonte 2020. El evento se celebró el 28 de septiembre de forma simultánea en trescientos cincuenta ciudades europeas.

En Sevilla han unido esfuerzos el Consejo Superior de Investigaciones Científicas (CSIC), la Universidad de Sevilla (US), la Universidad Pablo de Olavide (UPO) y el Ayuntamiento de Sevilla para ofrecer un programa conjunto compuesto por talleres, microencuentros y espectáculos diseñados para buscar un acercamiento distendido entre la ciudadanía y la comunidad científica, mediante la diversión y el lenguaje divulgativo.

Este singular formato ofrece una oportunidad a los ciudadanos de acercarse a los investigadores y vencer algunos tópicos sobre la profesión científica. Y a los investigadores ofrece una oportunidad de salir de sus laboratorios y demostrar que no viven ajenos a la realidad exterior.

LA NOCHE EUROPEA
DE L@S INVESTIGADOR@S
MUJERES Y HOMBRES QUE HACEN CIENCIA PARA TI

Dr. **Juan Galisteo López.** Controlando la luz en la nanoescala

Dra. **Rosalía Poyato Galan** taller titulado" Diamante, grafito y grafeno…¿son familia?"

PARTICIPACION EN EL DÍA INTERNACIONAL DE LA MUJER Y LA NIÑA EN LA CIENCIA/ INTERNATIONAL WOMEN AND GIRL'S DAY IN SCIENCE

Actividades enmarcadas dentro de la iniciativa de la plataforma 11F, para conmemorar el Día Internacional de la mujer y la niña en la ciencia, con el objetivo de hacer visible el trabajo de las científicas y de fomentar la vocación investigadora en las niñas.

Talleres

5 febrero:	"Mujer + Científica + Grafeno = ¿por qué no?" Taller impartido a alumnos de 4º de ESO y 1º de Bachillerato. Dra. Rosalía Poyato Galán. Escuelas Salesianas Mª Auxiliadora (Sevilla).
8 febrero:	"Pequeños Científicos". Taller impartido a alumnos de 1º a 4º de Primaria. Dra. Rosalía Poyato Galán. Escuelas Salesianas Mª Auxiliadora (Sevilla).
14 febrero:	"Diamante, grafito y grafeno…¿son familia?". Dra. Rosalía Poyato Galán. Taller impartido a alumnos de 5º y 6º de Primaria. CEIP Marie Curie (Sevilla).
15 febrero:	"Mujer + Científica + Grafeno = ¿por qué no?". Dra. Rosalía Poyato Galán. Taller impartido a alumnos de 4º de ESO. IES Margarita Salas (Sevilla).

Mesa Redonda

12 febrero:	"Físicas en Sevilla: pasado, presente y futuro". Ponente: Dra. Rosalía Poyato Galán. Facultad de Física (Universidad de Sevilla).

Café con Ciencia

13 febrero:	"Viaja al nanomundo de la mano de una mujer científica". Dra. Rosalía Poyato Galán.

Charlas

15 febrero:	"Experiencia de científicas". Alumnos de 4 ESO. CP Nuestra señora del Águila de Alcala de Guadaira. Dra. Gisela M. Arzac Di Tomaso.

15 febrero: "Mujeres y Ciencia". Alumnos de primaria. CP Ana María Matute de Dos Hermanas. Dr. Juan Pedro Holgado Vázquez.

CHARLA-COLOQUIO en la Biblioteca de Montequinto, bajo el título 'Mujeres, Sabias y Científicas. Invisibles y olvidadas' impartida por Dña. Adela Muñoz Páez.

Organizado por el Instituto de Ciencia de Materiales de Sevilla

Presentación: Dra. T. Cristina Rojas Ruiz y el Dr. Juan Pedro Holgado

13 de Febrero

VISITAS GUIADAS / GUIDED VISITS

Durante 2018, Grupos de Estudiantes de Centros Educativos han visitado las Instalaciones del ICMS.

Coordinación: Dr. T. Cristina Rojas Ruiz

Participantes: Dra. M. Carmen Jiménez de Haro, Dr. Victor J. Rico Gavira, Jose Manuel Obrero Pérez, Jose María Miranda, Victoria Esteso, Mariano Laguna Moreno, Daniel Gonzalez Mancebo, Dr. Gerardo Colon, Dra. Ana Isabel Becerro, Dra. Teresa Cristina Rojas, Nieto

25 enero – IES Martinez Montañes

22 febrero – IES El Majuelo

15 marzo – Colegio Entreolivos

9 abril - Colegio BVM Irlandesas Ntra. Sra. De Loreto

26 abril – IES Itálica

14 noviembre – Escuelas Francesas

16 noviembre – IES Gustavo Adolfo Becquer

18 diciembre – Colegio Sagrada Familia

OTRAS ACTIVIDADES / OTHER ACTIVITIES

Jornadas de las Artes y las Ciencias. Escuelas Francesas

29 enero [Sevilla, España]

Nanotecnología
Hernán Míguez
Charla invitada

Jornadas Universidad-Empresa. Oportunidades de Colaboración Universidad-Empresa ante el nuevo Programa de investigación e Innovación Horizon Europe

11-12 diciembre [Sevilla, España]

Nanotecnologías y materiales avanzados
Hernán Míguez
Charla invitada