ICMS

# Instituto de Ciencia de Materiales de Sevilla

# Memoria de Actividades
# Annual Report

Consejo
Superior de
Investigaciones
Científicas

Universidad
de Sevilla

Junta de
Andalucía

2014

Consejo Superior de Investigaciones Científicas
Universidad de Sevilla
Junta de Andalucía

# INSTITUTO DE CIENCIA DE MATERIALES DE SEVILLA

## Memoria de Actividades
## Annual Report
## 2014

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EDITA
**Instituto de Ciencia de Materiales de Sevilla (ICMS)**
Centro Mixto entre el Consejo Superior de Investigaciones
Científicas y la Universidad de Sevilla
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DISEÑO Y MAQUETACIÓN
José Carlos Rivero Cabello

COMISIÓN MEMORIA-ICMS
Gerardo Colón Ibáñez - Francisco José Gotor Martínez - Hernán R. Míguez García

# INDICE

# TABLE OF CONTENTS

# El ICMS en 2014
# ICMS in 2014

# Presentación Presentation

A través de esta Memoria 2014, el Instituto de Ciencia de Materiales de Sevilla (ICMS) pretende comunicar lo mejor de las actividades científicas realizadas a lo largo del periodo.

El ICMS es un Centro Mixto del Consejo Superior de Investigaciones Científicas (CSIC) y la Universidad de Sevilla (US), cofinanciado asimismo por la Junta de Andalucía. Está incluido en el Área de Ciencia y Tecnología de Materiales, una de las 8 en las que el CSIC estructura sus actividades científicas. Desde su creación en 1986, está integrado por personal científico de la Universidad de Sevilla y el CSIC, cuenta en la actualidad con 134 personas, 45 de las cuales son científicos permanentes.

De acuerdo con la estructura establecida en el vigente Plan Estratégico 2014-2017, nuestro centro se organiza en torno a 5 líneas de investigación, las que enraizando en disciplinas de la Química y Física del Estado Sólido y de la Ingeniería de Materiales, pretenden abarcar los aspectos más modernos y novedosos de la Ciencia de Materiales actual. Nuestro empeño fundamental para los años venideros sigue siendo el desarrollo de trabajos de investigación que definan "el estado del arte" de la disciplina, y que a su vez sirva de apoyo al desarrollo de un nuevo sistema económico en el que la base científica y tecnológica pase a ser un pilar fundamental de la misma. Por tanto, uno de nuestros más importantes objetivos es realizar una actividad de I+D fuertemente vinculada al entorno socio-económico, local, autonómico e internacional.

A pesar de las actuales limitaciones en la financiación, incorporación de nuevo personal y de disponibilidad de espacio que venimos padeciendo, en este último caso tanto para la ubicación de personal científico y técnico como para la instalación de equipamiento científico, la promoción de la actividad científica, la instalación del equipamiento científico más innovador y la incorporación de jóvenes científicos seguirá siendo nuestro gran objetivo diario.

Through this Activity Report 2014, the Institute of Materials Science of Seville (ICMS) is trying to communicate the best of its scientific activities for the period.

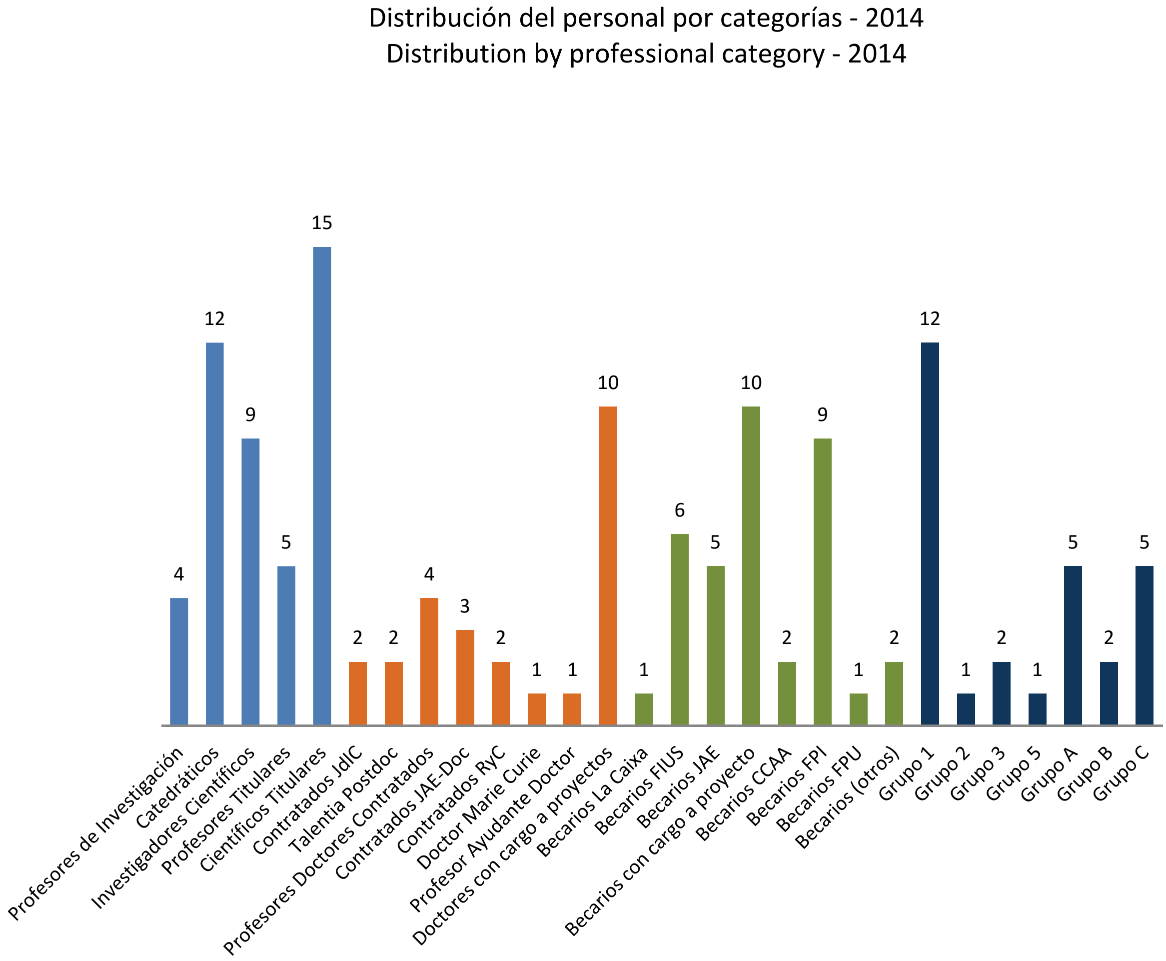
The ICMS is a joint Center of the Spanish Research Council (CSIC) and the University of Seville (US), also funded by the Junta de Andalucia. It is included in the "Field of Science and Technology of Materials", one of the eight within the scientific framework of the CSIC. It was founded in 1986, and integrated by scientific staff of the University of Seville and the CSIC, including today more than 134 people, 45 of which are permanent scientific staff.

The current Strategic Plan 2014-2017 organizes our Center in 5 lines of research, which related with disciplines of solid state chemistry and physic, as well as materials engineering subjects, are intended to cover the most modern and innovative aspects of the current material science. Our basic commitment for years to come is to support, as far as possible, the development of a new economic system, in which the scientific and technological basis should become a fundamental pillar of the same. Therefore, development of a R+D activity according to the State of the Art, is the top priority, if not the only, of our research centre. In spite of the financial, personnel and space limitations we are suffering today, both for the location of scientific and technical staff and for the installation of scientific equipment, the promotion of the scientific activity, the installation of the most innovative scientific equipment and the incorporation of young scientist staff will remain our great daily goal.

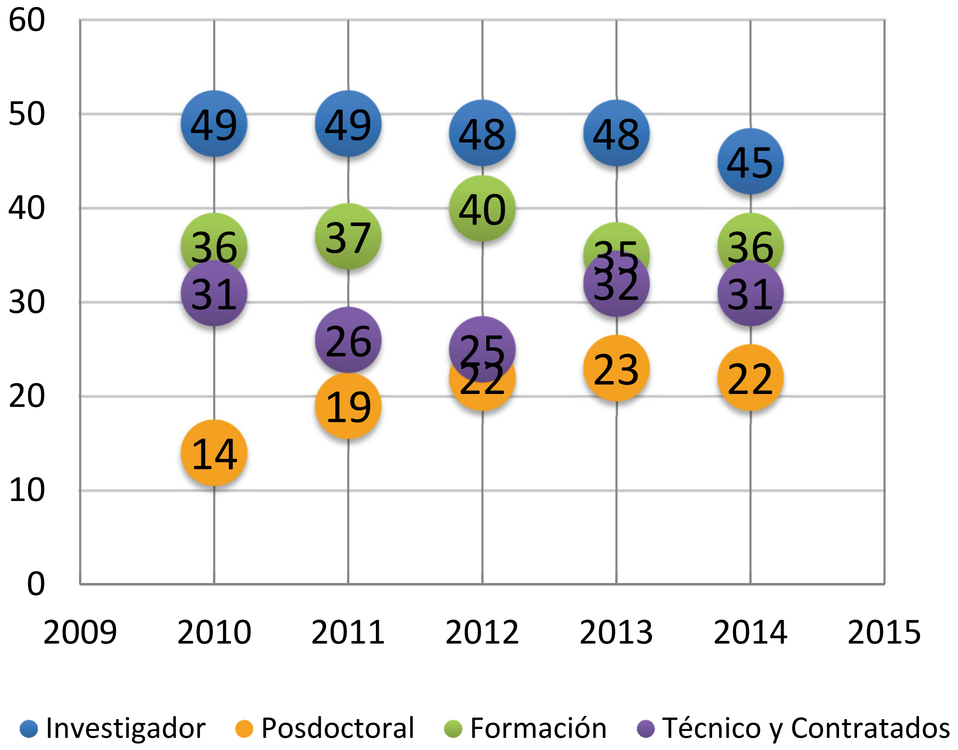
Dr. **Alfonso Caballero Martínez**
Director del Instituto de Ciencia de Materiales de Sevilla

# Datos Estadísticos del ICMS
## Statistical Data of ICMS

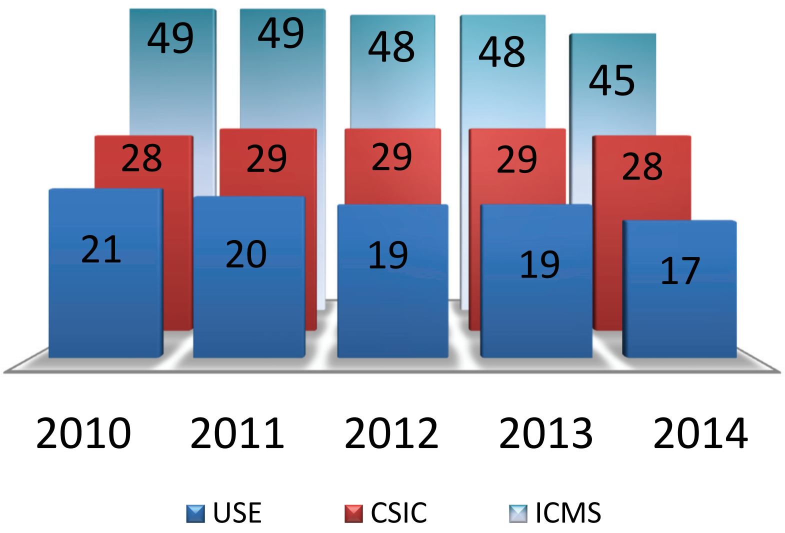
## RECURSOS HUMANOS / HUMAN RESOURCES


Distribución del personal por categorías - 2014
Distribution by professional category - 2014

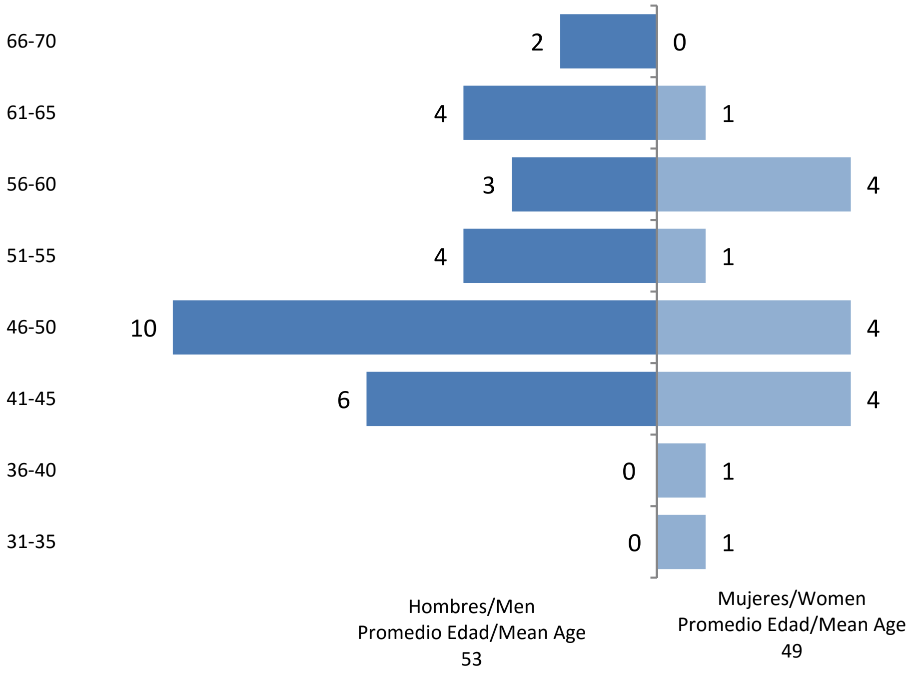
Evolución 2010-2014 del personal
Evolution of Staff



Evolución 2010-2014 del personal investigador
Evolution of Research Staff



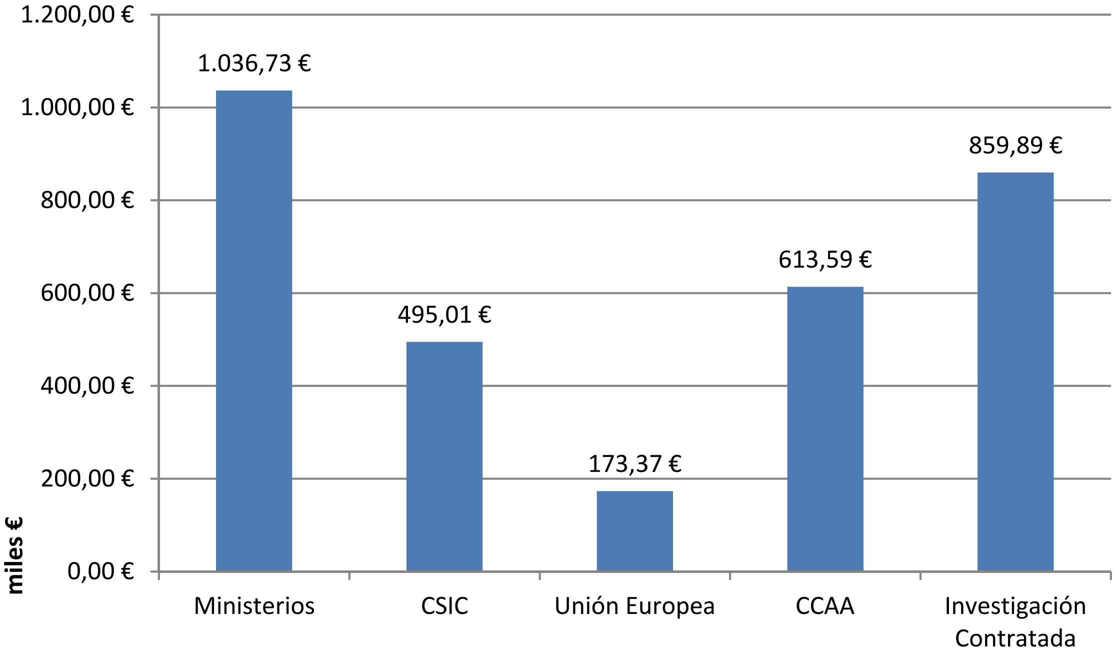
Distribución del personal Investigador (sexo y edad)
Distribution by Scientific staff (gender and age)



## FINANCIACIÓN / FUNDING

Evolución 2010-2014 de la Financiación conseguida por año
Evolution of the funding of the ICMS

Financiación del ICMS por Organismo Financiador
Funding of ICMS classified by source



## 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<br>JOURNAL | ARTÍCULOS<br>PAPERS | FACTOR DE IMPACTO<br>IMPACT FACTOR (*) |
|---|---|---|
| ENERGY & ENVIRONMENTAL SCIENCE | 1 | 20,523 |
| ACS CATALYSIS | 2 | 9,312 |
| NEW PHYTOLOGIST | 1 | 7,672 |
| APPLIED CATALYSIS B-ENVIRONMENTAL | 10 | 7,435 |
| NANOSCALE | 2 | 7,394 |
| JOURNAL OF CATALYSIS | 1 | 6,921 |
| CHEMICAL COMMUNICATIONS | 1 | 6,834 |
| ACS APPLIED MATERIALS & INTERFACES | 2 | 6,723 |
| CRITICAL REVIEWS IN SOLID STATE AND MATERIALS SCIENCES | 1 | 6,450 |
| JOURNAL OF POWER SOURCES | 1 | 6,217 |
| CARBON | 1 | 6,196 |
| APPLIED ENERGY | 4 | 5,613 |
| CATALYSIS SCIENCE & TECHNOLOGY | 1 | 5,426 |
| SOLAR ENERGY MATERIALS AND SOLAR CELLS | 1 | 5,337 |
| ENVIRONMENTAL SCIENCE & TECHNOLOGY | 1 | 5,330 |
| CRYSTAL GROWTH & DESIGN | 1 | 4,891 |
| JOURNAL OF PHYSICAL CHEMISTRY C | 6 | 4,772 |
| JOURNAL OF MATERIALS CHEMISTRY C | 2 | 4,696 |
| CHEMCATCHEM | 1 | 4,556 |
| JOURNAL OF HAZARDOUS MATERIALS | 1 | 4,529 |
| PHYSICAL CHEMISTRY CHEMICAL PHYSICS | 2 | 4,493 |
| TISSUE ENGINEERING PART A | 1 | 4,448 |
| CORROSION SCIENCE | 2 | 4,197 |
| DALTON TRANSACTIONS | 2 | 4,197 |
| ADVANCED OPTICAL MATERIALS | 1 | 4,062 |
| CRYSTENGCOMM | 1 | 4,034 |
| FRONTIERS IN PLANT SCIENCE | 1 | 3,948 |
| APPLIED CATALYSIS A-GENERAL | 1 | 3,942 |
| CATALYSIS TODAY | 1 | 3,893 |

| REVISTA<br>JOURNAL | ARTÍCULOS<br>PAPERS | FACTOR DE IMPACTO<br>IMPACT FACTOR (*) |
|---|---|---|
| RSC ADVANCES | 5 | 3,840 |
| NANOTECHNOLOGY | 1 | 3,821 |
| JOURNAL OF MOLECULAR CATALYSIS A-CHEMICAL | 1 | 3,615 |
| FUEL | 3 | 3,520 |
| MATERIALS & DESIGN | 3 | 3,501 |
| MICROPOROUS AND MESOPOROUS MATERIALS | 2 | 3,453 |
| CHEMPHYSCHEM | 3 | 3,419 |
| JOURNAL OF BIOMEDICAL MATERIALS RESEARCH PART A | 1 | 3,369 |
| INTERNATIONAL JOURNAL OF HYDROGEN ENERGY | 1 | 3,313 |
| JOURNAL OF PHYSICAL CHEMISTRY B | 1 | 3,302 |
| JOURNAL OF THE ELECTROCHEMICAL SOCIETY | 1 | 3,266 |
| POLYMER DEGRADATION AND STABILITY | 2 | 3,163 |
| JOURNAL OF ALLOYS AND COMPOUNDS | 4 | 2,999 |
| JOURNAL OF THE EUROPEAN CERAMIC SOCIETY | 4 | 2,947 |
| EUROPEAN JOURNAL OF INORGANIC CHEMISTRY | 1 | 2,942 |
| ENERGY & FUELS | 1 | 2,790 |
| APPLIED SURFACE SCIENCE | 2 | 2,711 |
| MATERIALS | 1 | 2,651 |
| JOURNAL OF QUANTITATIVE SPECTROSCOPY & RADIATIVE TRANSFER | 1 | 2,645 |
| APPLIED CLAY SCIENCE | 2 | 2,467 |
| PLASMA PROCESSES AND POLYMERS | 3 | 2,453 |
| JOURNAL OF MATERIALS SCIENCE | 3 | 2,371 |
| SPECTROCHIMICA ACTA PART A-MOLECULAR AND BIOMOLECULAR SPECTROSCOPY | 1 | 2,353 |
| POWDER TECHNOLOGY | 1 | 2,349 |
| JOURNAL OF VACUUM SCIENCE & TECHNOLOGY A | 1 | 2,322 |
| CONSTRUCTION AND BUILDING MATERIALS | 1 | 2,296 |
| MATERIALS RESEARCH BULLETIN | 1 | 2,288 |
| APPLIED GEOCHEMISTRY | 1 | 2,268 |
| MATERIALS CHEMISTRY AND PHYSICS | 1 | 2,259 |
| POLYMER TESTING | 1 | 2,240 |
| THERMOCHIMICA ACTA | 1 | 2,184 |
| EPL | 1 | 2,095 |
| SURFACE & COATINGS TECHNOLOGY | 1 | 1,998 |
| MICRON | 1 | 1,998 |

| REVISTA JOURNAL | ARTÍCULOS PAPERS | FACTOR DE IMPACTO IMPACT FACTOR (*) |
|---|---|---|
| AMERICAN MINERALOGIST | 1 | 1,964 |
| MATERIALS SCIENCE IN SEMICONDUCTOR PROCESSING | 1 | 1,955 |
| SURFACE SCIENCE | 2 | 1,925 |
| MICROSCOPY AND MICROANALYSIS | 2 | 1,877 |
| THIN SOLID FILMS | 2 | 1,759 |
| JOURNAL OF MOLECULAR MODELING | 1 | 1,736 |
| MATERIALS AND MANUFACTURING PROCESSES | 1 | 1,629 |
| BIOMED RESEARCH INTERNATIONAL | 1 | 1,579 |
| JOURNAL OF VACUUM SCIENCE & TECHNOLOGY B | 1 | 1,464 |
| ARCHAEOMETRY | 1 | 1,519 |
| WASTE MANAGEMENT & RESEARCH | 1 | 1,297 |
| SURFACE AND INTERFACE ANALYSIS | 3 | 1,245 |
| REACTION KINETICS MECHANISMS AND CATALYSIS | 1 | 1,170 |
| OXIDATION OF METALS | 1 | 1,140 |
| NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH SECTION B-BEAM INTERACTIONS WITH MATERIALS AND ATOMS | 1 | 1,124 |
| MICROSCOPY | 1 | 0,900 |
| SPECTROSCOPY LETTERS | 1 | 0,852 |
| PHYSICS OF THE SOLID STATE | 2 | 0,821 |
| ACTA PHYSICA POLONICA A | 1 | 0,530 |
| MINERALS | 1 | 0,100 |
| ADVANCED MATERIALS INTERFACES | 1 | - |
| **Total** | **138** | **3,835** |

(*) Factor de Impacto correspondiente al año 2014
Journal Citation Reports of 2014

# COMPOSICIÓN Y ESTRUCTURA

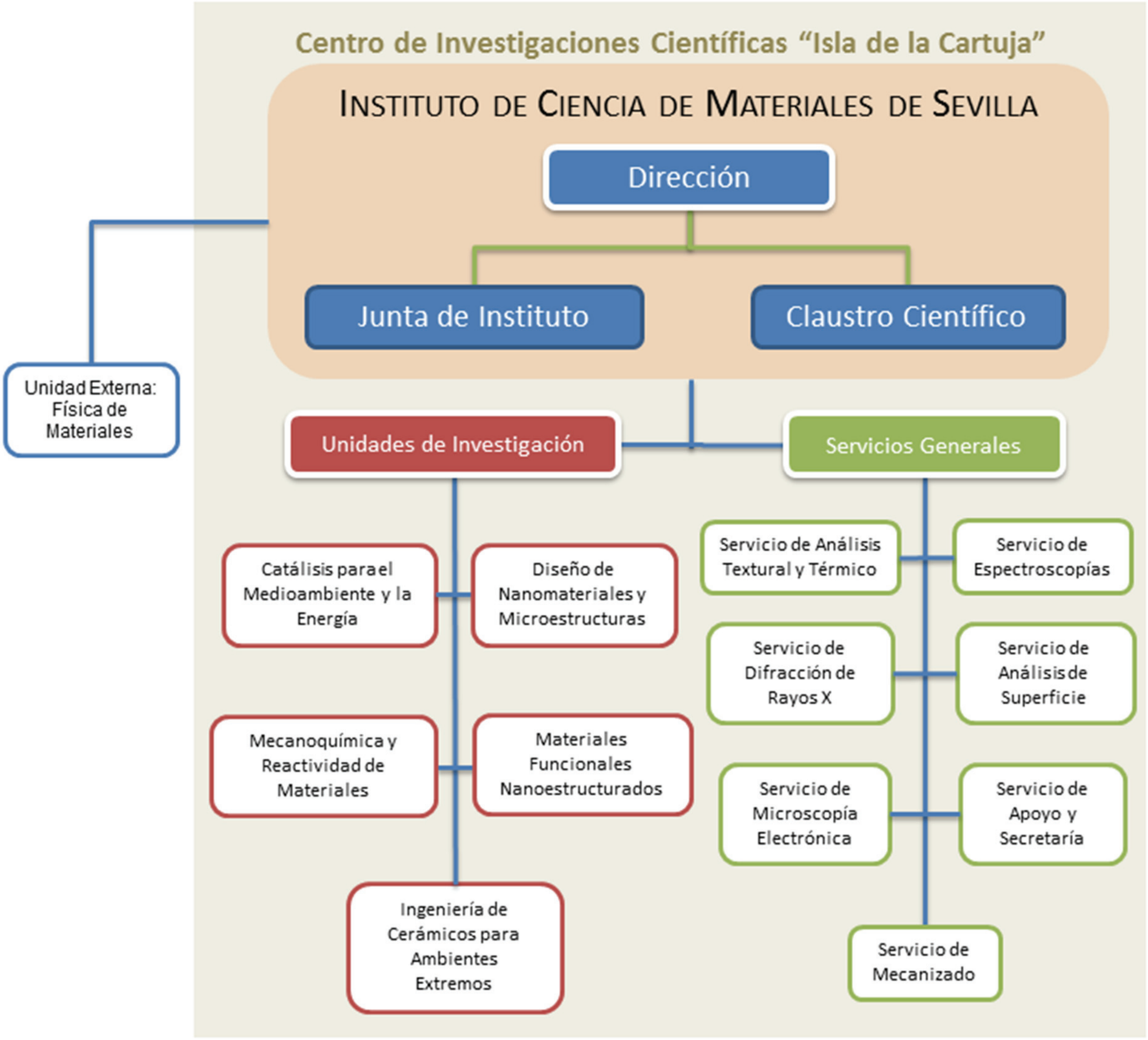
## STRUCTURE AND ORGANISATION

## 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 (desde 10 abril) |
| | D. Juan Pedro Espinós Manzorro |

## JUNTA DE INSTITUTO / INSTITUTE BOARD

| | |
|---|---|
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| Vicedirector / Vicedirector: | D. **Ana Isabel Becerro Nieto** |

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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

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Becerro Nieto, Ana Isabel
Borrás Martos, Ana Isabel
Bravo León, Alfonso
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Clauss Klamp, Caroline
Conde Amiano, Clara F.
Cotrino Bautista, José
Díaz Cuenca, María Aranzazu
Domínguez Rodríguez, Arturo
Espinós Manzorro, Juan Pedro
Estrada de Oya, María Dolores
Fortio Godinho, Vanda C.
Franco García, Victorino
García García, Francisco J.
Gil Rostra, Jorge
Gómez Ramírez, Ana María
Hidalgo López, M. Carmen
Ivanova, Svetlana
Jiménez Melendo, Manuel
Li, Yuelong
Laguna Espitia, Oscar Hernando
Lozano Barbero, Gabriel
Malet Maenner, Pilar
Martínez Tejada, Leidy Marcela
Muñoz Bernabé, Antonio
Núñez Alvarez, Nuria
Odriozola Gordón, José Antonio
Palmero Acebedo, Alberto
Pereñíguez Rodríguez, Rosa
Poyato Ferrera, Juan
Ramírez de Arellano-López, Antonio
Real Pérez, Concepción
R. González-Elipe, Agustín
Romero Sarria, Francisca
Sánchez Jiménez, Pedro E.
Sánchez Soto, Pedro José
Salazar Carballo, Pedro A.
Ternero Fernández, Fátima A.
Zapata Solvas, Eugenio
Alcalá González, María Dolores
Aparicio Rebollo, Francisco J.
Avilés Escaño, Miguel Angel
Barranco Quero, Angel
Benítez Jiménez, José Jesús
Borrego Moro, Josefa
Calvo Roggiani, Mauricio
Castillo Rodríguez, Miguel
Centeno Gallego, Miguel Angel
Colón Ibáñez, Gerardo
Córdoba Gallego, José Manuel
Diánez Millán, María Jesús
Domínguez Leal, María Isabel
Escudero Belmonte, Alberto
Esquivias Fedriani, Luis M.
Fernández Camacho, Asunción
Galisteo López, Juan Francisco
Gallardo Cruz, Carmen
García Navarro, Ana
Gómez García, Diego
Gotor Martínez, Francisco José
Holgado Vázquez, Juan Pedro
Jiménez de Haro, M. Carmen
Justo Erbez, Angel
Lacroix, Bertrand
López Santos, María del Carmen
Macías Azaña, Manuel
Martínez Fernández, Julián
Míguez García, Hernán
Navío Santos, José Antonio
Ocaña Jurado, Manuel
Orta Cuevas, M. Mar
Penkova, Anna Dimitrova
Pérez Maqueda, Luis Allan
Poyato Galán, Rosalía
Ramírez Rico, Joaquín
Rico Gavira, J. Victor
Rojas Ruiz, Cristina
Ruiz Conde, Antonio
Sánchez López, Juan Carlos
Sánchez Valencia, Juan Ramón
Sayagués De Vega, M. Jesús
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**

Dr. Manuel Macías Azaña
Dra. Francisca Romero Sarria

**Investigadores Contratados**

Dra. María Isabel Domínguez Leal
Dra. Svetlana Lyuvimirova Ivanova
Dra. Anna Dimitrova Penkova
Dra. Fátima Ternero Fernández
Dr. Oscar Hernando Laguna Espitia
Dra. Leidy Marcela Martínez Tejada
Dra. Rosa Pereñíguez Rodríguez

**Becarios Predoctorales**

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Lda. Victoria G. de la Vega-González
Ldo. Victor M. González de la Cruz
Ldo. Sergio Alberto Obregón Alfaro
Ldo. Tomás Ramírez Reina
Ldo. José Luis Santos Muñoz
Lda. Nuria García Moncada
Lda. Miriam González Castaño
Lda. Cristina Megías Sayago
Lda. Sandra Palma del Valle
Ldo. Alberto Rodríguez Gómez

## 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

**Investigadores Contratados**

Dra. M. Mar Orta Cuevas
Dr. Joaquin Ramírez Rico

**Becarios Predoctorales**

Ldo. Antonio A. Gutiérrez Pardo
Ldo. Fredy A. Huaman Mamani
Ldo. Francisco J. Osuna Barroso
Lda. M. Carmen Vera García

**Personal Contratado**

Dr. Antonio Perejón Pazo

# MECANOQUÍMICA Y REACTIVIDAD DE MATERIALES
# MECHANOCHEMISTRY AND REACTIVITY OF MATERIALS

## PERSONAL / PERSONNEL

**Catedráticos**

Dr. Juan Poyato Ferrera

**Investigadores Científicos**

Dr. Angel Justo Erbez
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. María Jesús Sayagués de Vega

**Profesores Titulares**

Dra. María Dolores Alcalá González

**Profesor Vinculado "Ad Honorem"**

Dr. José Manuel Criado Luque
Dr. José Luis Pérez Rodríguez

**Investigadores Contratados**

Dra. María Regla Ayala Espinar
Dr. José Manuel Córdoba Gallego
Dr. Pedro E. Sánchez Jiménez

**Becarios Predoctorales**

Lda. Cristina García Garrido
Lda. Eva Gil González

**Personal Contratado**

Lda. M. Rocío Rodríguez Laguna

## MATERIALES FUNCIONALES NANOESTRUCTURADOS NANOSTRUCTURED FUNCTIONAL MATERIALS

### PERSONAL / PERSONNEL

**Profesor de Investigación**

Dr. Juan Pedro Espinós Manzorro
Dr. Manuel Ocaña Jurado
Dr. Agustín Rodríguez González-Elipe

**Catedráticos**

Dr. José Cotrino Bautista

**Investigadores Científicos**

Dr. Hernán R. Míguez García
Dr. Francisco Yubero Valencia

**Científicos Titulares**

Dr. Angel Barranco Quero
Dra. Ana Isabel Becerro Nieto
Dra. Ana Isabel Borrás Martos
Dra. María Aránzazu Díaz Cuenca
Dra. Nuria O. Núñez Álvarez
Dr. Alberto Palmero Acebedo

**Profesor Visitante**

Dr. Richard M. Lambert

**Investigadores Contratados**

Dr. Rafael Álvarez Molina
Dr. Francisco J. Aparicio Rebollo
Dr. Mauricio E. Calvo Roggiani
Dra. Sol Carretero Palacios
Dr. Alberto Escudero Belmonte
Dr. Juan F. Galisteo López
Dr. Francisco J. García García
Dra. Ana María Gómez Ramírez
Dr. Yuelong Li
Dr. Gabriel Lozano Barbero
Dra. M. Carmen López Santos
Dr. Pedro A. Salazar Carballo
Dr. Juan Ramón Sánchez Valencia

**Becarios Predoctorales**

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Ldo. Miguel Anaya Martín
Lda. Sara Borrego González
Ldo. Gabriel Castillo Dali
Ldo. Pedro Castillero Durán
Ldo. José Raúl Castro Smirnov
Lda. Victoria Esteso Carrizo
Ldo. Alejandro N. Filippin Emilio
Ldo. Alberto Jiménez Solano
Ldo. Mariano Laguna Moreno
Ldo. Manuel Oliva Ramírez
Ldo. Noe Orozco Corrales
Ldo. Julián Parra Barranco
Lda. Liliam Beatriz Romero Sánchez

**Personal Contratado**

Dra. Ana García Navarro
Dr. Jorge Gil Rostra
Lda. M. Carmen Gutiérrez Lázaro
Ldo. Antonio Méndez Montoro de Damas

# DISEÑO DE NANOMATERIALES Y MICROESTRUCTURAS
# TAILORED NANOMATERIALS AND MICROSTRUCTURE

## PERSONAL / PERSONNEL

**Profesores de Investigación**

Dra. Asunción Fernández Camacho

**Catedráticos**

Dr. Luis M. Esquivias Fedriani
Dr. Diego Gómez García

**Investigadores Científicos**

Dr. Juan Carlos Sánchez López

**Científicos Titulares**

Dra. Rosalía Poyato Galán
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# RESEARCH UNITS

# CATÁLISIS PARA EL MEDIOAMBIENTE Y LA ENERGÍA

# CATALYSIS FOR ENVIRONNMENT AND ENERGY

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## PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

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### Aprovechamiento de gas no convencional: Reactores de microcanales en GTL Valorization of Non-conventional gas: microchannel reactors in GTL

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|---|---|
| Código/Code: | ENE2012-37431-C03-01 |
| Periodo/Period: | 01-01-2013 / 31-12-2015 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 234.000 € |
| Investigador responsable/Research head: | José Antonio Odriozola Gordón |
| Componentes/Research group: | Svetlana Ivanova, Anna Dimitrova Penkova, Tomás Ramírez Reina, Sandra Palma del Valle, Ara Muñoz Murillo, María Isabel Domínguez Leal, Francisca Romero Sarria |

RESUMEN / ABSTRACT

Existen en la actualidad fuentes de gas que podríamos agrupar bajo el calificativo de no-convencional que incluyen el que se encuentra confinado en formaciones geológicas de baja permeabilidad, el gas asociado al crudo, los pequeños yacimientos en lugares remotos, el biogas producido en la digestión anaerobia de residuos y los denominados product gas generados en la gasificación de biomasa y en la combustión de alquitran. La composición de todas estas fuentes de gas es similar estando constituidas por una mezcla de metano y dióxido de carbono con cantidades inferiores de otros gases permanentes. La concentración de CO2 puede llegar a ser de hasta el 40% en volumen como ocurre con el gas asociado de algunos campos off-shore y el biogas producido por fermentación de residuos agrícolas. La valorización de este gas mediante el proceso GTL (Gas to Liquid) es una alternativa cuando su localización remota o distante de los gaseoductos no permite ser agregado a las fuentes convencionales o no puede ser consumido in situ, ya que los combustibles líquidos son más fáciles de almacenar y transportar y tienen aplicación directa en el transporte.

La tecnología GTL convencional no es aplicable ya que su viabilidad económica exige instalaciones y suministros a una escala elevadísima. Por ello, se está desarrollando esa misma tecnología en reactores de microcanales de pared catalítica que consiguen incrementar de forma notable el rendimiento de las unidades de producción de gas de síntesis y síntesis de Fischer-Tropsch (SFT), al poder trabajar con elevadas velocidades espaciales, mejorando el control de la temperatura y con ello de la selectividad y la seguridad del proceso; además, la naturaleza modular basada en la replicación de unidades simplifica de forma considerable el escalado del proceso, adaptándose bien a unidades de producción de gas no convencional que, por lo general, no son grandes.

En el presente proyecto se pretende desarrollar la tecnología de microcanales para el proceso GTL utilizando mezclas metano-dióxido de carbono para simular las fuentes de gas no convencional. Los estudios que hemos venido realizando sobre reactores de microcanales de-

berán ampliarse a condiciones de presión y temperatura más drásticas, lo que debe permitir validar y mejorar la selección de materiales para la construcción y las técnicas de unión.

La aplicación de esta tecnología requiere el desarrollo de nuevos catalizadores activos, selectivos y estables que se adapten a los procesos GTL en reactores de microcanales. Se diseñarán catalizadores para el reformado al vapor, el reformado seco y la oxidación parcial de metano para la producción de gas de síntesis, así como catalizadores SFT. Se construirán reactores de microcanales para el ensayo de dichos catalizadores, se obtendrán las ecuaciones cinéticas de los catalizadores seleccionados y se modelarán y simularán los reactores construidos.

Apart from the large reserves, natural gas is present in a wide variety of sources that can be grouped as non-conventional gas, including non-conventional natural gas confined in low-permeability geological deposits, associated gas, biogas produced by anaerobic digestion of residues and product gas a result of biomass and tar gasification. Most of them are, in general, far from marketplaces and transport infrastructures, present in small or medium fields that does not allow large-scale GTL plants and, as in the associated gas in oil fields contribute to increase GHG. These gases have a similar composition, they mainly contain methane and carbon dioxide, the later may reach 40% by volume as in some off-shore oild fields and biogas produced by digestion of crop residues. Recent trends in the use of syngas are dominated by the conversion of inexpensive remote natural gas into liquid fuels (“gas to liquids” or GTL) forecasts the use of non-conventional gas in compact syngas units for GTL processes resulting in liquid fuels of easier storage and transportation having direct aplication for transport.

GTL technology developed for microchannel reactors notably increases the production yield of syngas and Fischer-Tropsch synthesis (FTS) units on running the reaction under high space velocities and improving temperature control, therefore enhancing selectivity and process safety. Modularity, which is based on unit replication, simplifies the scaling-up and allows an easier adjust to small and medium size production units.

In this Project, we aim at developing microchannel technologies for GTL using CH4-CO2 mixtures that simulate non-conventional gas resources. Our previous studies on microchannel reactor technology will be put forward to adapt to the elevated temperatures and pressures required for the GTL process. This will allow validation of the bonding techniques as well as improve materials selection to fit these drastic requirements.

New catalysts adapted to the GTL process in microchannels will be developed for steam and dry reforming of methane as well as for the partial oxidation of methane and the FTS. These catalysts must be active, selective and stable under reaction conditions and will be tested in powder, in structured form (micromonoliths) and in microchannels units. For them kinetic equations will be developed and the built microchannel reactor will be modeled and simulated.

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# Desarrollo de nuevos procesos industriales basados en sistemas catalíticos para la obtención sostenible de ingredientes base en fragancias y aromas Development of new industrial processes based on catalytic systems for Sustainable production of base compounds of fragrances and aromas

Código/Code: IPT-2011-1553-420000
Periodo/Period: 04-05-2011 / 31-12-2014
Organismo Financiador/Financial source: Programa INNPACTO. Ministerio de Economía y Competitividad
Importe total/Total amount: 183.423 €
Investigador responsable/Research head: Juan Pedro Holgado Vázquez
Componentes/Research group: Alfonso Caballero Martínez, Víctor Manuel González de la Cruz, Rosa Pereñíguez Rodríguez, Gerardo Colón Ibáñez

## RESUMEN / ABSTRACT

En la actualidad, los procesos industriales utilizados para la transformación de muchos compuestos utilizados en el campo de las fragancias y los aromas ofrecen bajos rendimientos y generan una enorme cantidad de residuos peligrosos, que requieren varias etapas de segregación y tratamiento de los mismos durante el proceso. La mayor parte de estos procesos se basan en reacciones de oxidación/reducción de compuestos estequiometricos, o están basados en sistemas de catálisis homogénea, los cuales presentan inconvenientes asociados con la corrosión, la recuperación del catalizador de la mezcla de reacción y su regeneración para su posible reutilización. En este contexto "eco-amigable", existe un interés creciente para el uso de oxidantes menos contaminantes, tales como el peróxido de hidrógeno o el oxígeno molecular, y la integración de dichos oxidantes en sistemas de catálisis heterogénea. Obviamente uno de los mayores retos que presentan las reacciones basadas en sistemas catalíticos es lograr el máximo rendimiento (producto de conversión por selectividad) con objeto de reducir el consumo de reactivos (materias primas), y minimizar los procesos de separación y eliminación de subproductos no deseados fruto de la ineficacia del proceso. En este tipo de reacciones (con compuestos principalmente orgánicos, muchos de origen natural), no es, en general, difícil obtener una alta conversión, pero dado que estos compuestos presentan multiples funcionalidades y/o puntos susceptibles de ser oxidados, el reto se centra en la obtención de una alta selectividad, generalmente incluso a nivel enantiomérico.

En el marco del proyecto, se han seleccionado procesos de interés en la industria cosmética y alimentaria, con objeto de conseguir el desarrollo a escala industrial de procesos basados en sistemas de catálisis heterogénea para la obtención de compuestos intermedios de gran valor añadido en el mercado de los perfumes y aromas, como son, entre otros, el proceso de obtención de la l-carvona a partir de la oxidación catalítica del d-limoneno.

Nowadays, most of the industrial processes used for transformations of many compounds used in the field of fragrances and aromas have low yields, and generate a lot of environmentally noxious products, being necessary to accomplish several stages of segregation and treatment during the process of production of these chemicals. Most of these processes are done by reduction or oxidation reactions using stoichiometric compounds, or are based in homogeneous catalysis, that present associated hitches associated with corrosion, recovery of the catalysts from reaction media and its regeneration for its possible recycle. In this "environmentally friendly" context, there is a growing interest in the use of oxidants less contaminants, such as molecular oxygen or hydrogen peroxide, and the integration of these oxidants into heterogeneous catalysis processes. Obviously, one of the big challenges for catalytic systems is to maximize the yield (conversion times selectivity), in order to reduce the consumption of reactants (raw material), and minimize the separation and elimination of undesired sub-products obtained as consequence of process inefficacy. In these type of reactions (with mainly organic products, many from natural sources), it is not, as a general rule, difficult to obtain a high conversion, but as the starting materials present many functionalities and/or points susceptible to be oxidized, the main challenge is to obtain a (very) high selectivity, in many cases even at enantiomer level.

In this project, we have selected processes and reactions with a direct interest in the food and cosmetic industry, with the scope to develop processes, at industrial scale, based on heterogeneous catalysts to obtain compounds with high added value in the aromas and fragrances fields, such as the production of l-carvone from catalytic oxidation of d-limonene.

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## 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 / 31-12-2017
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).

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## **Desarrollo de sistemas catalíticos nanoestructurados preparados mediante sol-gel y de deposición fotoquímica para aplicaciones energéticas y medioambientales (NanoFotoCat)** Development of nanostructured catalyticsystems prepared by sol-gel and fotoassisted deposition (PAD) methods for energy and environmental applications

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|---|---|
| Código/Code: | ENE2011-24412 |
| Periodo/Period: | 01-01-2012 / 31-12-2014 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 102.850 € |
| Investigador responsable/Research head: | Alfonso Caballero Martínez |
| Componentes/Research group: | Gerardo Colón Ibáñez, Juan Pedro Holgado Vázquez, Sergio Obregón Alfaro, Rosa María Pereñíguez Rodríguez, Fátima Ternero Fdez. |

RESUMEN / ABSTRACT

En el presente proyecto se plantea el desarrollo de una serie de catalizadores nanoestructurados basados en metales de transición tales como Ni, Cu, Au o Pd, y depositados en soportes activos ($TiO_2$, $CeO_2$, $WO_3$, $Fe_2O_3$ y soportesmesoporosos como SBA-15 dopado con titania y ceria). Se utilizarán métodos de preparación convencionales (impregnación, deposición-precipitación, etc.), junto con procedimientos de síntesis de desarrollo más reciente, como métodos sol-gel y, muy especialmente, el denominado Fotodeposición Asistida Fotoquímicamente (Photochemical Assisted Deposition, PAD). De esta forma, esperamos controlar de manera rigurosa a la escala nanométrica tanto el tamaño de la partícula metálica y/o bimetálica, como la interacción metal-soporte. En el caso concreto del método PAD, uno de los objetivos principales del proyecto es el estudio y la optimización de las variables del proceso de deposición de manera que, además de controlar el tamaño de la partícula metálica desde diámetros en torno a 15nm hasta sistemas atómicamente dispersos sobre soportes activos como ceria o titania, nos permita diseñar la distribución de los metales en la partícula metálica, haciendo uso de procesos controlados de fotodeposición consecutivos y/o simultáneos de los metales. Esta metodología debe permitir la obtención de distribuciones metálicas de tipo core-shell o aleadas, lo que como es conocido, puede llegar a afectar de manera fundamental a las prestaciones catalíticas. Estas prestaciones serán comprobadas en diferentes reacciones de interés energético y/o medioambiental, tanto en fase gas como en fase líquida. Así, los sistemas basados en niquel y oro se utilizarán en las reacciones de reformado húmedo y seco de metano (Steam and Dry Methane Reforming, SRM/DRM) y la oxidación selectiva de CO (Preferential Oxidation of CO, PROX), respectivamente. Los sistemas mono y bimetálicos basados en paladio y paladio-oro serán utilizados para la optimización de la reacción de síntesis directa de agua oxigenada a partir de hidrógeno y oxígeno, realizada en fase líquida a alta presión. La

correlación entre el estado físico-químico y la reactividad de los sistemas catalíticos nos permitirá aclarar aspectos fundamentales de los mecanismos de las reacciones heterogéneas propuestas.

In the present project we propose the development of a series of nanostructured catalysts based on transition metals such as Ni, Cu, Au or Pd deposited in active supports ($TiO_2$, $CeO_2$, $WO_3$, $Fe_2O_3$ and mesoporous supportslike SBA-15 doped with titania and ceria). Conventional methods of preparation will be used (impregnation, deposition-precipitation, etc.), along with procedures of synthesis of more recent development, like sol-gel and, very specially, the denominated Photochemical Assisted Deposition (PAD). In this way, we expect to control at the nanometric scale the size of the metallic and/or bimetallic particle, along with the interaction between the metal and support surface. In the case of the PAD method, one of the primary targets of the project is the study and optimization of the different parameters affecting the deposition process. So that, besides the control of the metallic particle size from diameters around 15nm to atomic dispersed systems on active supports like ceria or titania, it would allow us to design the distribution of metals in bimetallic particles, making use of consecutive and/or simultaneous controlled processes of fotodeposition of metals. Using this methodology, we will try to obtain metallic distributions of different kinds: core-shell, alloys, etc., which as it is well-known, can strongly affect the catalytic performances. These benefits will be verified in different catalytic reactions of energetic and/or environmental interest, both in gas and liquid phase. Thus, the systems based on nickel and gold will be used in the steam and dry reforming reactions of methane and the selective oxidation of CO (Preferential Oxidation of CO, PROX), respectively. The bimetallic catalytic systems based on palladium and palladium-gold will be used for the optimization of the reaction of direct synthesis of hydrogen peroxide from hydrogen and oxygen, made in liquid phase at high pressure. The correlation between the physical-chemistry state and the reactivity of the catalytic systems will allow us to clarify fundamental aspects of the mechanisms of the proposed heterogeneous reactions.

JUNTA DE ANDALUCIA

## Nuevos fotocatalizadores basados en compuestos de $Bi^{3+}$ altamente fotoactivos en el visible New $Bi^{3+}$ based photocatalysts highly active in the visible

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|---|---|
| Código/Code: | P09-FQM-4570 (Proyecto de Excelencia) |
| Periodo/Period: | 11-03-2011 / 31-03- 2015 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 82.000 € |
| Investigador responsable/Research head: | Gerardo Colón Ibáñez |
| Componentes/Research group: | Carmen Hidalgo López, J. Antonio Navío Santos, Manuel Macías Azaña, Sebastián Murcia |

### RESUMEN / ABSTRACT

El objetivo principal de este proyecto es el desarrollo de una nueva generación de materiales nanoestructurados alternativos al $TiO_2$ que presenten una alta fotoactividad en la región del visible y que puedan ser utilizados de forma competitiva y eficiente en procesos de tratamiento de efluentes líquidos y gaseosos mediante el aprovechamiento de la luz solar. El presente proyecto pretende desarrollar nuevos sistemas de nanocatalizadores heterogéneos basados en $Bi^{3+}$ ($Bi_2WO_4$, $Bi_2MoO_6$, $BiVO_4$, $Bi_3O_4Cl$, $CaBi_2O_4$, $PbBi_2Nb_2O_9$,…) que presenten unas propiedades optoelectrónicas adecuadas para el aprovechamiento de la energía solar en el rango del visible (Fotocatálisis Solar) y que al mismo tiempo exhiban unas propiedades fisicoquímicas mejoradas que optimicen el proceso fotocatalítico desde el punto de vista de difusión y transferencia de portadores de carga fotogenerados.

The main objective of this project is the development of a new generation of nanostructured materials alternative to $TiO_2$ with high photoactivity in the visible region that could be efficiently used in liquid or gaseous effluent treatment. The present project intent to develop new heterogeneous nanocatalytic systems based on $Bi^{3+}$ ($Bi_2WO_4$, $Bi_2MoO_6$, $BiVO_4$, $Bi_3O_4Cl$, $CaBi_2O_4$, $PbBi_2Nb_2O_9$,…) exhibiting appropriated optoelectronic properties for the solar light use in the visible range (Solar Photocatalysis). Moreover, from the point of view of the photoinduced charge carriers diffusion and transfer, the improved physicochemical properties would optimize the photocatalytic process.

## Aprovechamiento $CO_2$ para la obtención de gas de síntesis en catalizadores $CO_2$ Utilization for synthesis gas obtaining: Use of structured catalysts

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|---|---|
| Código/Code: | P11-TEP-8196 (Proyecto de Excelencia) |
| Periodo/Period: | 01-02-2013 / 01-02- 2016 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 137.425 € |
| Investigador responsable/Research head: | Miguel Angel Centeno Gallego |
| Componentes/Research group: | Svetlana Ivanova, Maria Isabel Domínguez Leal, José Antonio Odriozola Gordón, Tomás Ramírez Reina, Francisca Romero Sarria |

RESUMEN / ABSTRACT

Hoy en día no existen dudas acerca de que la concentración de gases de efecto invernadero, en particular la de $CO_2$, está aumentando de manera considerable en la atmósfera terrestre. Para evitar este aumento continuado se debe aumentar la eficiencia en la producción de energía, disminuir la intensidad del uso de las fuentes fósiles y, finalmente, potenciar la captura y secuestro del $CO_2$. Todo esto debe conseguirse manteniendo el crecimiento económico y la calidad de vida. En consecuencia, si tenemos en cuenta el desarrollo de las naciones menos industrializadas y el intensivo consumo energético necesario para aumentar su nivel de vida, la captura y secuestro de $CO_2$ parece la alternativa más favorable.

En el presente proyecto se propone la utilización del $CO_2$ como materia prima para el reformado de gas natural como paso previo a la obtención de combustibles líquidos sintéticos. Usando tecnologías convencionales, esta propuesta sólo es económicamente viable asociada a grandes reservas de gas natural. Sin embargo, la tecnología de microcanales permite abordar la síntesis de combustibles sintéticos de forma discontinua y con capacidad de producción flexible de modo económicamente viable. Para ello, es necesario el diseño, caracterización y ensayo de catalizadores activos, selectivos y estables en la reacción de reformado de metano con vapor y $CO_2$:

$$CO_2 + 3CH_4 + 2H_2O \rightarrow 4CO + 8H_2$$

La selección de estos catalizadores culminará con la estructuración de los mismos utilizando soportes metálicos con microcanales paralelos (micromonolitos) a fin de establecer las condiciones necesarias para, en un futuro, la construcción de reactores de microcanales.

Nowadays, the concentration of greenhouse gases, GHG, in the atmosphere, specifically $CO_2$, is continuously increasing. In order to avoid or minimize such increment, three different strategies must be applied: i) the improvement of the efficiency on the energy production systems, ii) the lower utilisation of fossil fuels and iii) the implementation of processes of $CO_2$ capture and sequestration. Since the economic growth and the life quality must be maintained, particularly in the less developed countries, the last item is the most favourable approximation for a sustainable development.

In the present Project, the utilisation of $CO_2$ as raw material for natural gas reforming is proposed as preliminary step in the production of synthetic liquid fuels.By using conventional technologies, this proposal is economically viable only exploiting natural gas reserves. However, microchanel technology allows the discontinuous production of the synthetic fuels, with a high and flexible production in an economic way. Our project is focussed in the design, characterization and testing of active, selective and stable catalysts in the steam-dry reforming of methane, SDRM:

$$CO_2 + 3CH_4 + 2H_2O \rightarrow 4CO + 8H_2$$

The final step of the project is the structuration of the selected catalysts in metallic micromonoliths with parallel channels as an intermediate step for their future implementation on microchannel reactors.

## CONVENIOS Y CONTRATOS / CONTRACTS AND AGREEMENTS

### Protocol for XPS analysis of different samples form Group of Inorganic Chemistry and Catalysis

| | |
|---|---|
| Código/Code: | 20132331 |
| Periodo/Period: | 22-03-2013 / 22-05-2015 |
| Organismo Financiador/Financial source: | University Utrecht |
| Importe total/Total amount: | 3.000 € |

Investigador responsable/Research head: Juan Pedro Holgado Vázquez

## Experimentos en Grandes Instalaciones / Large Facility Experiments

### Sincrotrón ALBA / ALBA Synchrotron

**Impact of Ce-Zn Sinergism on the catalytic behavior of Au/CeO2-ZnO for pure $H_2$ production**

Código/Code: 2013110762
Periodo/Period: 23-09-2014 / 29-09-2014
Organismo Financiador/Financial source: Sincrotrón ALBA
Instalación Científica: ALBA línea BL22-CL/ESS. Cerdanyola del Vallés, Barcelona (España)
Investigador principal/Research head: Víctor López Flores
Investigadores/Researchers: Leidy Marcela Martínez, Svetlana Ivanova, Miriam González Castaño

### Sincrotrón SOLEIL / SOLEIL Synchrotron

**Impact of Ce-Zn Sinergism on the catalytic behavior of Au/CeO2-ZnO for pure $H_2$ production**

Código/Code: 20140594
Periodo/Period: 30-09-2014 / 5-10-2014
Organismo Financiador/Financial source: Sincrotrón ALBA
Instalación Científica: SOLEI L-Línea SAMBA (GIF-sur-YVETTE (Francia)
Investigador principal/Research head: Víctor López Flores
Investigadores/Researchers: Leidy Marcela Martínez, Svetlana Ivanova, Miriam González Castaño

## Patentes / Patents

**Catalizadores de oro soportado en CuO/ZnO/$Al_2O_3$ con estructura hidrotalcitas y uso del mismo para la reacción de desplazamiento del gas del agua**

Inventores: Tomás Ramírez Reina, Svetlana Lyubomirova Ivanova, Miguel Angel Centeno Gallego, José Antonio Odriozola Gordón, José Luis Santos Muñoz
Tipo de Patente: Nacional
Solicitud número: 201400683
Fecha Solicitud: 6 Agosto 2014
Entidad/es Titular/es: Universidad de Sevilla y CSIC

## 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 a través del Instituto de Ciencia de Materiales de Sevilla.

El responsable de esta Unidad Asociada, por parte de la Universidad de Las Palomas de Gran Canaria, fue el Prof. Dr. Jesús Pérez Peña, hasta el 9 de julio de 2014 fecha en que el Presidente del CSIC resuelve aprobar la continuidad de dicha asociación a través del Instituto de Ciencia de Materiales de Sevilla, con el Prof. Dr. José Antonio Navío Santos, Catedrático de la Universidad de Sevilla y el Prof. Dr. Óscar Manuel González Díaz, Profesor Titular de la Universidad de Las Palmas de Gran Canaria, éste último como nuevo responsable de la Unidad Asociada.

Las líneas principales de actuación son:
- “Fotocatálisis en procesos ambientales”
- “Espectro-electroquímica aplicada al medio ambiente”
- “Materiales para tratamientos de aguas residuales”

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

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.

## ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

### Active Site Considerations on the Photocatalytic H-2 Evolution Performance of Cu-Doped $TiO_2$ Obtained by Different Doping Methods

Valero, JM; Obregon, S; Colon, G
*ACS Catalysis*, **4** (2014) 3320-3329
October, 2014 | **DOI:** 10.1021/cs500865y

A photocatalytic $H_2$ evolution reaction was performed over copper doped $TiO_2$. The influence of sulfate pretreatment over fresh $TiO_2$ support and the Cu doping method has been evaluated. Wide structural and surface characterization of catalysts was carried out in order to establish a correlation between the effect of sulfuric acid treatment and the further Cu-$TiO_2$ photocatalytic properties. Notably a different copper dispersion and oxidation state is obtained by different metal decoration methods. From the structural and surface analysis of the catalysts we have stated that the occurrence of highly disperse and reducible $Cu^{2+}$ species is directly related to the photocatalytic activity for the $H_2$ production reaction. Highly active materials have been obtained from a chemical reduction method leading to 18 $mmol \cdot h^{-1} \cdot g^{-1}$ for 3 mol % copper loading.

### Correlation study between photo-degradation and surface adsorption properties of phenol and methyl orange on $TiO_2$ Vs platinum-supported $TiO_2$

Murcia, JJ; Hidalgo, MC; Navio, JA; Arana, J; Dona-Rodriguez, JM
*Applied Catalysis B: Environmental*, **150-151** (2014) 107-115
May, 2014 | **DOI:** 10.1016/j.apcatb.2013.12.010

Adsorption of phenol and methyl orange on the surface of $TiO_2$ and Pt–$TiO_2$ photocatalysts was investigated by FT-IR spectroscopy. It was found that platinum plays an important role in the adsorption properties of the studied substrates on $TiO_2$. Platinum deposits modified the phenol-photocatalyst interaction providing new adsorption sites on $TiO_2$ surface. On Pt–$TiO_2$ photocatalysts, phenol mainly interacts via formation of adsorbed phenolates species. It was also found that the adsorption of methyl orange on titania and Pt–$TiO_2$ photocatalysts occurs via interaction of the azo group with surface $Ti^{4+}$. Pt photodeposition significantly increases the $TiO_2$ photoreactivity in phenol and methyl orange photo-degradation; however, this increase depends on the properties of the Pt deposits. Moreover, it was observed that platinum content is the main factor determining the substrate-photocatalyst interaction and therefore the Pt–$TiO_2$ photocatalytic performance.

### Could an efficient WGS catalyst be useful in the CO-PrOx reaction?

Reina, TR; Papadopoulou, E; Palma, S; Ivanova, S; Centeno, MA; Ioannides, T; Odriozola, JA

*Applied Catalysis B: Environmental*, **150-151** (2014) 554-563
May, 2014 | **DOI:** 10.1016/j.apcatb.2014.01.001

This work presents an evaluation of a high performance series of water gas shift (WGS) catalysts in the preferential CO oxidation reaction (PrOx) in order to examine the applicability of the same catalyst for both processes as a first step for coupling both reactions in a single process. Gold based catalysts are applied in an extensive study of the CO-PrOx reaction parameters, such as λ, WHSV, CO concentration and $[H_2O]/[CO_2]$ ratio in order to obtain the best activity/selectivity balance. CO and $H_2$ oxidation reactions were treated separately in order to establish the degree of $CO/H_2$ oxidation competition. Additionally the catalysts behavior in the CO-PrOx parallel reactions such a WGS and RWGS have been also carried out to analyze their effect on product composition.

### Effect of gold on a $NiLaO_3$ perovskite catalyst for methane steam reforming

Palma, S; Bobadilla, LF; Corrales, A; Ivanova, S; Romero-Sarria, F; Centeno, MA; Odriozola, JA
*Applied Catalysis B: Environmental*, **144** (2014) 846-854
January, 2014 | **DOI:** 10.1016/j.apcatb.2013.07.055

The effect of gold addition to a supported Ni SRM catalyst has been studied in this work in order to determine the influence of gold on both the amount and type of carbon species formed during the reaction. The structure of the support, a mixed La–Al perovskite, determines the catalyst reducibility and Ni particle size. Gold addition affects the metal particle size increasing metal dispersion on increasing the gold content. Therefore, although gold blocks step Ni sites, the more active sites for Csingle bondH activation, and increases electron density on nickel, the higher dispersion results in an apparently higher activity upon gold addition. Moreover, gold addition increases the catalyst stability by decreasing the rate of growth of carbon nanotubes.

### Excellent photocatalytic activity of $Yb^{3+}$, $Er^{3+}$ co-doped $BiVO_4$ photocatalyst

Obregon, S.; Colon, G.
Applied Catalysis B: Environmental, **152-153** (2014) 328-334
June, 2014 | **DOI:** 10.1016/j.apcatb.2014.01.054

Ytterbium-Erbium co-doped $BiVO_4$ have been synthesized by means of a surfactant free hydrothermal method having good photoactivities under sun-like excitation for the degradation of Methylene Blue and $O_2$ evolution reactions. From the structural and morphological characterization it has been stated that the presence of $Yb^{3+}$ and $Er^{3+}$ induces the stabilization of the tetragonal phase probably due to its substitutional incorporation in the $BiVO_4$ lattice. The occurrence of the $Yb^{3+}$,$Er^{3+}$ co-doped monoclinic-tetragonal $BiVO_4$ heterostructure induces the higher photocatalytic activities. The best photocatalytic performance was attained for the sample with 1:4 $Er^{3+}$:$Yb^{3+}$ ratio. The observed NIR photoactivity clearly denotes the occurrence of an up-conversion mechanism involved in the overall photocatalytic process.

### Heterostructured $Er^{3+}$ doped $BiVO_4$ with exceptional photocatalytic performance by cooperative electronic and luminescence sensitization mechanism

Obregon, S; Colon, G
*Applied Catalysis B: Environmental*, **158-159** (2014) 242-249
October, 2014 | **DOI:** 10.1016/j.apcatb.2014.04.029

Er-$BiVO_4$ has been synthesized by means of mw-assisted hydrothermal method having good photoactivity under sun-like excitation. It is stated that the precursor addition sequence plays a critical role which determine the further structural feature of $BiVO_4$. From the structural and morphological characterization, it can be demonstrated that the presence of $Er^{3+}$ would induce the stabilization of the tetragonal phase probably due to the formation of tetragonal-$ErVO_4$ seeds previous to $BiVO_4$ formation. The best photocatalytic performance is attained for the sample with 0.75 at% $Er^{3+}$ content. At this dopant loading a mixture of tetragonal and monoclinic phase (70% tetragonal) is obtained. The dramatic increase in the photocatalytic activity for 0.75 at% Er-$BiVO_4$ is related to the occurrence of such heterostructure. For this system, the MB degradation rate constant appears drastically higher as bare m-$BiVO_4$. Furthermore, activities of photocatalysts for visible-light-driven $O_2$ evolution have been evaluated, demonstrating that the photocatalytic activity of this Er-doped system ($O_2$ evolution rate, 1014 µmol $g^{-1}$ $h^{-1}$) is 20 times as that of undoped m-$BiVO_4$ ($O_2$ evolution rate, 54 µmol $g^{-1}$ $h^{-1}$). From the obtained results, the cooperative conjunction of electronic and luminescence mechanism involved in the reaction is proposed to be the origin of the enhanced photocatalytic efficiencies of such systems.

### Improved $H_2$ production of Pt-$TiO_2$/g-$C_3N_4$-MnOx composites by an efficient handling of photogenerated charge pairs

Obregon, S; Colon, G
*Applied Catalysis B: Environmental*, **144** (2014) 775-782
January, 2014 | **DOI:** 10.1016/j.apcatb.2013.07.034

Pt-$TiO_2$/g-$C_3N_4$-MnOx hybrid structures are synthesized by means of a simple impregnation method of Pt-$TiO_2$ and g-$C_3N_4$-MnOx. From the wide structural and surface characterization we have stated that $TiO_2$/g-$C_3N_4$ composites are formed by an effective covering of g-$C_3N_4$ by $TiO_2$. The modification of composite by Pt and/or MnOx leads to improved photoactivities for phenol degradation reaction. Moreover, enhanced photoactivities have been obtained for composites systems for $H_2$ evolution reaction. The notably photocatalytic performance obtained was related with the efficient separation of charge pairs in this hybrid heterostructure.

### In situ XAS study of an improved natural phosphate catalyst for hydrogen production by reforming of methane

Abba, MO; Gonzalez-DelaCruz, VM; Colon, G; Sebti, S; Caballero, A
*Applied Catalysis B: Environmental*, **150-151** (2014) 459-465
May, 2014 | DOI: 10.1016/j.apcatb.2013.12.031

Some nickel catalysts supported on natural phosphate (NP) have been tested for the dry methane reforming reaction. Although the original impregnated 15%Ni/NP catalyst has no activity at all, the modification of the support by mechano-chemical and/or acid treatment strongly improved the catalytic performance, yielding a series of very active and stable catalysts. The chemical and physical characterization by X-ray diffraction (XRD), temperature programmed reduction (TPR), in situ X-ray absorption spectroscopy (XAS) and other techniques have shown that these treatments mainly modify the interaction between the nickel phase and the support surface. The nickel ions occupy calcium position in the surface of the phosphate phase, which stabilizes and improves the dispersion of nickel species. The final reduced catalysts present a much better dispersed metallic phase interacting with the NP surface, which has been identified as responsible for the observed outstanding catalytic performances.

### Production of hydrogen by water photo-splitting over commercial and synthesised Au/$TiO_2$ catalysts

Mendez, JAO; Lopez, CR; Melian, EP; Diaz, OG; Rodriguez, JMD; Hevia, DF; Macias, M

*Applied Catalysis B: Environmental*, **147** (2014) 439-452
April, 2014 | **DOI:** 10.1016/j.apcatb.2013.09.029

$H_2$ production from methanol/water photo-splitting was compared using various commercial photocatalysts (Evonik P25 (P25), Hombikat UV-100 (HB) and Kronos vlp7000 (KR)) and others synthesised with a sol–gel-hydrothermal (HT) process and a sol–gel method followed by calcination (SG400 and SG750). All photocatalysts had been surface modified with Au at different concentrations, from 0.2 to 6.0 wt.%, using the photodeposition method. A complete characterisation study of the different photocatalysts was performed (BET, XRD, TEM, SEM-EDX, FTIR, UV–vis Reflectance Diffuse Spectra and aggregate size). The experiments were conducted for 3.5 h using 1 g $L^{-1}$ of photocatalyst with methanol (25 vol.%) as sacrificial agent. In addition to $H_2$ generation, production of the main intermediates, formaldehyde and formic acid, and of $CO_2$ was also evaluated. The commercial photocatalyst KR at 0.8 wt.% Au had the highest $H_2$ production of all the photocatalysts studied with 1542.9 μmol $h^{-1}$. Of the photocatalysts synthesised by our group, SG750 at Au loading of 2.0 wt.% gave the highest $H_2$ production of 723.1 μmol $h^{-1}$. The SG750 photocatalyst at Au loading of 2.0 wt.% also had the highest $H_2$ production yield per unit of surface area at 45.5 μmol g $h^{-1}$ $m^{-2}$.

### Pt vs. Au in water-gas shift reaction

Castano, MG; Reina, TR; Ivanova, S; Centeno, MA; Odriozola, JA

*Journal of Catalysis*, **314** (2014) 1-9
May, 2014 | **DOI:** 10.1016/j.jcat.2014.03.014

This work presents a comparison of the gold- and platinum-based catalysts behavior in the water–gas shift (WGS) reaction. The influence of the support, e.g., its composition and electronic properties, studied in detail by means of UV–Vis spectroscopy, of the metal nature and dispersion and of the stream composition has been evaluated. The catalytic performance of the samples is directly correlated with the electronic properties modification as a function of metal and/or support. Both metals present high activity in the selected reaction although in a different operation temperature window.

### Effect of the type of acid used in the synthesis of titania–silica mixed oxides on their photocatalytic properties

Llano, B; Hidalgo, MC; Rios, LA; Navio, JA
*Applied Catalysis B: Environmental*, **150-151** (2014) 389-395
May, 2014 | DOI: 10.1016/j.apcatb.2013.12.039

$TiO_2$–$SiO_2$ mixed oxides were synthesized by the sol–gel technique using three different acids, i.e., acetic, sulfuric, or chlorhydric acid. Their photocatalytic behavior was evaluated on the phenol oxidation in liquid phase and correlated with the characterization results. It was found that the kind of acid used during the preparation strongly influences the phase composition and stability of the $TiO_2$ phases incorporated in the silica structure as well as the photocatalytic activity. In all cases, silica introduced a dispersive effect that stabilized the $TiO_2$ crystalline phases upon calcination at 700 °C. $SO_4^{2-}$ and $CH_3COO-$ ions stabilized the anatase phase at high calcination temperatures (700 °C) leading to samples with the highest photoactivities. Cl− ions induced the formation of traces of rutile and brookite resulting in a lower photoactivity. The highest photoactivity was achieved with the catalyst synthesized with acetic acid and calcined at 700 °C (TS1-700-ace). The photocatalytic performance of this material was even better than that obtained with the commercial catalyst Degussa P-25.

### Improved O-2 evolution from a water splitting reaction over $Er^{3+}$ and $Y^{3+}$ co-doped tetragonal $BiVO_4$

Obregon, S; Colon, G
*Catalysis Science & Technology*, **4** (2014) 2042-2050
July, 2014 | **DOI:** 10.1039/C4CY00050A

Erbium–yttrium co-doped $BiVO_4$ with a tetragonal structure is synthesized by means of a surfactant free hydrothermal method. The studied photocatalyst shows good photoactivity under sun-like excitation for the degradation of methylene blue (MB) and for $O_2$ evolution. From structural and morphological characterization, it has been stated that the presence of lanthanides induces the stabilization of the tetragonal phase. This is probably due to the substitutional occupation that occurs in the $BiVO_4$ lattice. The photocatalytic performance under visible-NIR radiation clearly evidences the occurrence of an up-conversion process involved in the overall photo-electronic mechanism. The tetragonal phase $Er_{0.0075}$,$Y_{0.03}$–$Bi_{0.9625}VO_4$ system gives the highest $O_2$ evolution rate (425 µmol $g^{-1}$ $h^{-1}$) under sun-like excitation, being 8 times higher than that attained for m-$BiVO_4$ (53 µmol $g^{-1}$ $h^{-1}$).

### Bifunctional, Monodisperse $BiPO_4$-Based Nanostars: Photocatalytic Activity and Luminescent Applications

Becerro, AI; Criado, J; Gontard, LC; Obregon, S; Fernandez, A; Colon, G; Ocana, M
*Crystal Growth & Design*, **14** (2014) 3319-3326
July, 2014 | **DOI:** 10.1021/cg500208h

Monodisperse, monoclinic $BiPO_4$ nanostars have been synthesized by a homogeneous precipitation reaction at 120 °C through controlled release of $Bi^{3+}$ cations from a Bi–citrate chelate, in a mixture of glycerol and ethylene glycol, using $H_3PO_4$ as the phosphate source. The set of experimental conditions necessary to obtain uniform nanoparticles is very restrictive, as the change in either the polyol ratio or the reactant concentrations led to ill-defined and/or aggregated particles. The morphology of the particles consists of a starlike, hierarchical structure formed by the ordered arrangement of nanorod bundles. Transmission electron tomography has revealed that the nanostars are not spherical but flattened particles. Likewise, Fourier transform infrared spectroscopy and thermogravimetry have shown that the synthesized nanostars are functionalized with citrate groups. The mechanism of formation of the nanostars has been analyzed to explain their morphological features. The as-synthesized $BiPO_4$ nanostars exhibit an efficient photocatalytic performance for the degradation of Rhodamine B. Finally, it has been demonstrated that the stars can be $Eu^{3+}$-doped up to 2 mol % without any change in the particle morphology or symmetry, and the doped samples show emission in the orange-red region of the visible spectrum after ultraviolet excitation. These experimental observations make this material a suitable phosphor for biotechnological applications.

## Viability of $Au/CeO_2$-$ZnO/Al_2O_3$ Catalysts for Pure Hydrogen Production by the Water-Gas Shift Reaction

Reina, TR; Ivanova, S; Delgado, JJ; Ivanov, I; Idakiev, V; Tabakova, T; Centeno, MA; Odriozola, JA
*ChemCatChem*, 6 (2014) 1401-1409
May, 2014 | **DOI:** 10.1002/cctc.201300992

The production of $H_2$ pure enough for use in fuel cells requires the development of very efficient catalysts for the water–gas shift reaction. Herein, a series of gold catalysts supported on ZnO-promoted $CeO_2$–$Al_2O_3$ are presented as interesting systems for the purification of $H_2$ streams through the water–gas shift reaction. The addition of ZnO remarkably promotes the activity of an $Au/CeO_2/Al_2O_3$ catalyst. This increase in activity is mainly associated with the enhanced oxygen storage capacity exhibited for the Zn-containing solids. High activity and good stability and resistance towards start-up–shut-down situations was found, which makes these catalysts a promising alternative for CO clean-up applications.

## A study of the optical properties of metal-doped polyoxotitanium cages and the relationship to metal-doped titania

Lv, YK; Cheng, J; Matthews, PD; Holgado, JP; Willkomm, J; Leskes, M; Steiner, A; Fenske, D; King, TC; Wood, PT; Gan, LH; Lambert, RM; Wright, DS
*Dalton Transactions*, **43** (2014) 8679-8689
June, 2014 | **DOI:** 10.1039/C4DT00555D

To what extent the presence of transition metal ions can affect the optical properties of structurally well-defined, metal-doped polyoxotitanium (POT) cages is a key question in respect to how closely these species model technologically important metal-doped $TiO_2$. This also has direct implications to the potential applications of these organically-soluble inorganic cages as photocatalytic redox systems in chemical transformations. Measurement of the band gaps of the series of closely related polyoxotitanium cages $[MnTi_{14}(OEt)_{28}O_{14}(OH)_2]$ (1), $[FeTi_{14}(OEt)_{28}O_{14}(OH)_2]$ (2) and $[GaTi_{14}(OEt)_{28}O_{15}(OH)]$ (3), containing interstitial Mn(II), Fe(II) and Ga(III) dopant ions, shows that transition metal doping alone does not lower the band gaps below that of $TiO_2$ or the corresponding metal-doped $TiO_2$. Instead, the band gaps of these cages are within the range of values found previously for transition metal-doped $TiO_2$ nanoparticles. The low band gaps previously reported for 1 and for a recently reported related Mn-doped POT cage appear to be the result of low band gap impurities (most likely amorphous Mn-doped $TiO_2$).

### Exalted photocatalytic activity of tetragonal $BiVO_4$ by $Er^{3+}$ doping through a luminescence cooperative mechanism

Obregon, S; Lee, SW; Colon, G
*Dalton Transactions*, **43** (2014) 311-316
January, 2014 | **DOI:** 10.1039/C3DT51923F

Er-doped $BiVO_4$ are synthesized by means of a surfactant free microwave assisted hydrothermal method having good photoactivities under sun-like excitation for the degradation of methylene blue. From the structural and morphological characterization, it has been stated that the presence of $Er^{3+}$ induces a slight stabilization of the tetragonal phase, probably due to its incorporation in the $BiVO_4$ lattice. The best photocatalytic performances were attained for the samples with $Er^{3+}$ content higher than 3 at%. The occurrence of the $Er^{3+}$ doped tetragonal $BiVO_4$ clearly induces higher photocatalytic activities. The existence of a luminescence process has been related with the enhanced photoactivity observed.

### Metallic structured catalysts: Influence of the substrate on the catalytic activity

Dominguez, MI; Perez, A; Centeno, MA; Odriozola, JA
*Applied Catalysis A-General*, **478** (2014) 45-57
May, 2014 | **DOI:** 10.1016/j.apcata.2014.03.028

In order to study the influence of the metallic substrate on the catalytic activity of structured micromonolithic catalysts, a $CuOx/CeO_2$ catalyst was deposited on different oxidized or enameled metallic micromonoliths and tested in the PROX reaction under ideal and realistic conditions. The obtained results show as both activity and selectivity depend on the nature of the alloy and the nature of the interphase between the metal substrate and the catalyst layer. In oxidized micromonoliths, diffusion of Cr and Fe has been observed. For enameled micromonoliths, together with that diffusion, the interaction of the glass-ceramic interphase with the reactive gas streams resulted in the partial hydrolysis of this layer leading to diffusion toward the catalyst surface of the hydrolysis products, namely Na, Ca and Si cations. In some cases, the alteration of the surface composition favors the spreading of the copper active phase. As a result, it must be concluded that the metallic substrates are not spectators, at least in the PROX reaction, playing a fundamental role in the performances of the catalytic devices.

### Heterogeneous selective oxidation of fatty alcohols: Oxidation of 1-tetradecanol as a model substrate

Corberan, VC; Gomez-Aviles, A; Martinez-Gonzalez, S; Ivanova, S; Dominguez, MI; Gonzalez-Perez, ME

*Catalysis Today*, **238** (2014) 49-53

December, 2014 | DOI: 10.1016/j.cattod.2014.03.033

Selective oxidation of fatty alcohols, i.e., linear long-chain alkanols, has been scarcely investigated to date, despite its potential application in high value chemical's production. We report for the first time the liquid phase heterogeneous oxidation of 1-tetradecanol, used as a model molecule for fatty alcohols, according to green chemistry principles by using a Au/$CeO_2$-$Al_2O_3$ catalyst and O-2 as oxidant at normal pressure. High selectivity to tetradecanal (ca. 80%) or to tetradecanoic acid (60-70%) are reached at medium conversion (up to 38%), depending on the reaction conditions used. Comparison with similar tests of 1-octanol oxidation shows that the increase of the carbon chain length decreases the alcohol conversion and the formation of ester, probably due to a greater steric effect.

### A ternary $Er^{3+}$-$BiVO_4$/$TiO_2$ complex heterostructure with excellent photocatalytic performance

Obregon, S; Colon, G

*RSC Advances*, **4** (2014) 20765-20771

January, 2014 | **DOI:** 10.1039/C3RA46603E

Ternary erbium doped $BiVO_4$/$TiO_2$ complexes are synthesized by means of a simple impregnation method with good photoactivities under sun-like excitation for the degradation of phenol. From the structural and morphological characterization it has been stated that the presence of $Er^{3+}$ induces a slight stabilization of the tetragonal phase probably due to its incorporation in the $BiVO_4$ lattice. Therefore a ternary heterostructured material has been obtained. The best photocatalytic performance was attained for the samples with 1 wt% of $Er^{3+}$-doped $BiVO_4$ content with respect to $TiO_2$. The occurrence of a complex structural mixture with the adequate band position leads to effective charge pair separation which induces higher photocatalytic activities.

### Surface Oxygen Vacancies in Gold Based Catalysts for CO Oxidation

Romero-Sarria, F; Plata, JJ; Laguna, OH; Marquez, AM; Centeno, MA; Sanz, JF; Odriozola, JA

*RSC Advances*, **4** (2014) 13145-13152

April, 2014 | **DOI:** 10.1039/c3ra46662k

Experimental catalytic activity measurements, Diffuse Reflectance Infrared Fourier Spectroscopy, and Density Functional Theory calculations are used to investigate the role and dynamics of surface oxygen vacancies in the CO oxidation with $O_2$ catalyzed by Au nanoparticles supported on a Y-doped $TiO_2$ catalyst. Catalytic activity measurements show that the CO conversion is improved in a second cycle of reaction if the reactive flow is composed by CO and $O_2$ (and inert) while if water is present in the flow, the catalyst shows a similar behaviour in two successive cycles. DRIFTS-MS studies indicate the occurrence of two simultaneous phenomena during the first cycle in dry conditions: the surface is dehydroxylated and a band at 2194 cm$^{-1}$ increases (proportionally to the number of surface oxygen vacancies). Theoretical calculations were conducted in order to explain these observations. On one hand, the calculations show that there is a competition between gold nanoparticles and OH to occupy the surface oxygen vacancies and that the adsorption energy of gold on these sites increases as the surface is being dehydroxylated. On another hand, these results evidence that a strong electronic transfer from the surface to the $O_2$ molecule is produced after its adsorption on the Au/$TiO_2$ perimeter interface (activation step), leaving the gold particle in a high oxidation state. This explains the appearance of a band at a wavenumber unusually high for the CO adsorbed on oxidized gold particles (2194 cm$^{-1}$) when $O_2$ is present in the reactive flow. These simultaneous phenomena indicate that a gold redispersion on the surface occurs under reactive flow in dry conditions generating small gold particles very actives at low temperature. This fact is notably favoured by the presence of surface oxygen vacancies that improve the surface dynamics. The obtained results suggest that the reaction mechanism proceeds through the formation of a peroxo-like complex formed after the electronic transfer from the surface to the gas molecule.

### Gold supported on CuOx/$CeO_2$ catalyst for the purification of hydrogen by the CO preferential oxidation reaction (PROX)

Laguna, OH; Hernandez, WY; Arzamendi, G; Gandia, LM; Centeno, MA; Odriozola, JA
*Fuel*, **134** (2014) 9-20
February, 2014 | **DOI:** 10.1016/j.jqsrt.2013.10.007

We design a fully stable numerical solution of the Maxwell's equations with the transfer matrix method (TMM) to understand the interaction between an electromagnetic field and a finite, one-dimensional, non-periodic structure. Such an exact solution can be tailored from a conventional solution by choosing an adequate transformation between its reference systems, which induces a mapping between its associated TMMs. The paper demonstrates theoretically the numerical stability of the TMM for the exact solution within the framework of Maxwell's equations, but the same formalism can efficiently be applied to resolve other classical or quantum linear wave-propagation interaction in one, two, and three dimensions. This is because the formalism is exclusively built up for an in depth analysis of the TMM's symmetries.

### Influence of the acid–base properties over NiSn/MgO–$Al_2O_3$ catalysts in the hydrogen production from glycerol steam reforming

Bobadilla, LF; Penkova, A; Romero-Sarria, F; Centeno, MA; Odriozola, JA
*International Journal of Hydrogen Energy*, **39** (2014) 5704-5712
April, 2014 | **DOI:** 10.1016/j.ijhydene.2014.01.136

In this work we have investigated the hydrogen production from glycerol steam reforming. The effect of the acid-base properties was evaluated using four catalysts based in an alloy Ni-Sn as active phase supported over (Upsilon)-Al2O3 with different content in MgO, varying between 0 and 30 wt.% The incorporation of MgO results in the formation of $MgAl_2O_4$ spinel, which modifies the acid-base properties of the catalyst. Addition of MgO favored the glycerol conversion into gas, and the catalyst loaded with 10 wt.% MgO exhibited better catalytic performance and higher stability. A blank test with quartz was performed indicating that pyrolysis of glycerol takes place in the quartz.

### Understanding the Role of the Cosolvent in the Zeolite Template Function of Imidazolium-Based Ionic Liquid

Ayala, R; Ivanova, S; Blanes, JMM; Romero-Sarria, F; Odriozola, JA
*Journal of Physical Chemistry B*, **118** (2014) 3650–3660
April, 2014 | **DOI:** 10.1021/jp410260g

In this work, a study for understanding the role played by [ClBmim], [$BF_4$Bmim], [$PF_6$Bmim], and [$CH_3SO_3$Bmim] ionic liquids (ILs) in the synthesis of zeolites is presented. The use of [ClBmim] and [$CH_3SO_3$Bmim] ILs, as reported earlier [ Chem. Eur. J. 2013, 19, 2122] led to the formation of MFI or BEA type zeolites. Contrary, [$BF_4$Bmim] and [$PF_6$Bmim] ILs did not succeed in organizing the Si–Al network into a zeolite structure. To try to explain these results, a series of quantum mechanical calculations considering monomers ([XBmim]) and dimers ($[XBmim]_2$) by themselves and plus cosolvent (water or ethanol) were carried out, where X ≡ Cl–, $BF_4$–, $PF_6$–, or $CH_3SO_3$–. Our attention was focused on the similarities and differences among the two types of cosolvents and the relation between the structure and the multiple factors defining the interactions among the ILs and the cosolvent. Although a specific pattern based on local structures explaining the different behavior of these ILs as a zeolite structuring template was not found, the calculated interaction energies involving the Cl– and $CH_3SO_3$– anions were very close and larger than those for $BF_4$– and $PF_6$– species. These differences in energy can be used as an argument to describe their different behavior as structure directing agents. Moreover, the topology of the cosolvent is also an ingredient to take into account for a proper understanding of the results.

### Spinodal decomposition and precipitation in Cu–Cr nanocomposite

Sheibani, S; Heshmati-Manesh, S; Ataie, A; Caballero, A; Criado, JM
*Journal of Alloys and Compounds*, **587** (2014) 670-676
February, 2014 | **DOI:** 10.1016/j.jallcom.2013.11.019

In this study, spinodal decomposition and precipitation mechanism of mechanically alloyed supersaturated Cu–3wt.%Cr and Cu–5wt.%Cr solid solutions was investigated under nonisothermal aging. Decomposition mechanism and kinetics were studied using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. Also, the microstructure was characterized by transmission electron microscopy (TEM). Effect of $Al_2O_3$ reinforcement on the aging kinetics was also evaluated. It was found that Cu–3wt.%Cr and Cu–5wt.%Cr solid solutions undergo spinodal decomposition at initial stages of ageing. However, decomposition mechanism was changed to nucleation and growth by the aging progress. The aging kinetics for the Cu–Cr/$Al_2O_3$ composition appeared to be slightly faster than that for Cu–Cr, since the ageing activation energy is decreased in presence of $Al_2O_3$ nano-particles. This behavior is probably due to the higher dislocation density and other structural defects previously produced during ball milling. A detailed comparison of the DSC results with those obtained by TEM, showing good consistency, has been presented. The average size of Cr-rich precipitates was about 10 nm in the copper matrix.

## Pyridine adsorption on NiSn/MgO-$Al_2O_3$: An FTIR spectroscopic study of surface acidity

Penkova, A; Bobadilla, LF; Romero-Sarria, F; Centeno, MA; Odriozola, JA
*Applied Surface Science*, **317** (2014) 241-251
October, 2014 | **DOI:** 10.1016/j.apsusc.2014.08.093

The acid-base properties of MgO-$Al_2O_3$ supports and NiSn/MgO-$Al_2O_3$ catalysts were evaluated by IR spectroscopy using pyridine as a probe molecule. The results indicate that only Lewis acid sites were detected on the surface of the supports as well as on the catalysts. Nevertheless, Bronsted acid sites were not detected. In the support without MgO three kinds of coordinatively unsaturated acid sites were detected: $Al^{3+}$ cations occupying octahedral, tetrahedral and tetrahedral with cationic vacancy in the neighbourhood. The last sites appear as the strongest. Moreover, they are able to activate the pyridine molecules leading to the formation of an intermediate ce-pyridone complex. When MgO or NiO were added to the alumina, the number and strength of the Lewis acid sites decreased and significant changes were observed in the tetrahedral sites with adjoining cation vacancies. The incorporation of the $Mg^{2+}$ cations into the alumina's structure takes place on the vacant tetrahedral positions, forming spinel $MgAl_2O_4$. As a result, the fraction of tetrahedral sites with adjoining cationic vacancy diminished and the intermediate ce-pyridone complex in the support with the highest MgO loading was hardly detected. The addition of $Ni^{2+}$ cations leads to the filling of the free octahedral positions, resulting in the formation of a $NiAl_2O_4$ spinel structure and the thermal stability of the ce-pyridone species decreases. In the catalysts, the progressive reduction of the number and strength of the Lewis acid sites is due to a competitive formation of the two types of $MgAl_2O_4$ and $NiAl_2O_4$ spinels. In the catalyst NiSn/30MgO-$Al_2O_3$ no cationic vacancies were detected and the surface reaction with ce-pyridone formation did not occur.

## Phase assembly and electrical conductivity of spark plasma sintered $CeO_2$-$ZrO_2$ ceramics

Poyato, R; Cruz, SA; Cumbrera, FL; Moreno, B; Chinarro, E; Odriozola, JA
*Journal of Materials Science*, **49** (2014) 6353-6362
June, 2014 | **DOI:** 10.1007/s10853-014-8361-6

$Ce_x Zr_{1-x} O_2$ (x = 0.10, 0.16 and 0.33) nanocrystalline powders were obtained by a two-step synthesis technique and sintered by spark plasma sintering (SPS). As consequence of the reduction of $Ce^{4+}$ to $Ce^{3+}$ species by carbon in the graphite environment in SPS, phase assemblies including tetragonal, monoclinic and pyrochlore phases were generated in the ceramics during the sintering process. The electrical conductivity was highly dependent on phase assembly and atmosphere ($N_2$, $H_2$ and $O_2$). A significant decrease in the activation energy was noticed in the ceramics with high pyrochlore content when measuring the conductivity in $H_2$ atmosphere, consequence of the strong reduction promoted in these ceramics during the measurement. Equal conduction behavior with similar activation energy was observed in all the ceramics when measuring in $O_2$ atmosphere.

### Promoting effect of Ce and Mg cations in Ni/Al catalysts prepared from hydrotalcites for the dry reforming of methane

Djebarri, B; Gonzalez-Delacruz, VM; Halliche, D; Bachari, K; Saadi, A; Caballero, A; Holgado, JP; Cherifi, O
*Reaction Kinetics, Mechanisms and Catalysis*, 111 (2014) 259-275
February, 2014 | **DOI:** 10.1007/s11144-013-0646-2

Several catalytic systems containing Ni/Mg/Al/Ce were synthesized from nitrates of $Ni^{2+}$, $Mg^{2+}$, $Al^{3+}$ and $Ce^{3+}$ cations with $M^{2+}/M^{3+} = 2$ ratios by means of the carbonate co-precipitation method and subsequent calcination at 800 A degrees C. Atomic absorption spectroscopy, X-ray diffraction (XRD), FT-IR spectroscopy, BET, temperature programmed reduction and scanning electron microscopy were used in order to describe the structural, morphological and surface characteristics of the solids completely. The effect of substitution/incorporation of Al by Ce and/or Mg on NiAl sample was studied. XRD analyses confirm that on Al-containing samples (NiAl, NiMgAl), the formation of the precursors layered double hydroxide structure. On the other hand, on cerium containing samples (NiCe, NiMgCe), poorly resolved diffractograms were observed what can be explained by the large radius of cerium. The catalysts were evaluated in the reaction of $CO_2$ reforming of methane at 750 A degrees C. NiCe and NiMgAl catalysts exhibit higher activity and a H-2/CO ratio of almost 1. NiAl and NiMgCe samples showed lower conversions and a $CH_4/CO_2$ ratio < 1, indicating the occurrence of reverse water gas shift reaction.

## LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS

### Twenty years of golden future in the Water Gas Shift reaction

T.R. Reina, M. González, S. Palma, S. Ivanova, J.A. Odriozola
En: *Heterogeneous Gold Catalysts and Catalysis,* capitulo 5, paginas: 111-139, 1ª Edicion 2014. Royal Society of Chemistry. RSC Catalysis Book Series Nº18. Zhen Ma, Sheng Dai (editores)
ISBN: 978-1-84973-917-7

### Role of oxygen vacancies in gold oxidation catalysis

O.H. Laguna, M.I. Domínguez, F. Romero-Sarria, J.A. Odriozola, M.A. Centeno
En: *Heterogeneous Gold Catalysts and Catalysis,* capitulo 13, paginas: 489-511, 1ª Edicion 2014. Royal Society of Chemistry. RSC Catalysis Book Series Nº18. Zhen Ma, Sheng Dai (editores)
ISBN: 978-1-84973-917-7

### Hybrid Organic-Inorganic Materials Based on Polyoxometalates and Ionic Liquids and Their Application in Catalysis

S. Ivanova
ISRN Chemical Engineering, vol 2014, 2014, Article ID 963792, 13 paginas

An overview of the recent advances in the field of polyoxometalate, ionic liquid hybrids, is proposed with a special attention paid to their application in catalysis, more precisely biphasic and heterogeneous catalysis. Both components of the hybrids are separately outlined pointing to their useful properties and potential for catalysis, followed by the description of the hybrids preparation and synergy between components in a large range of organic transformations. And finally a vision on the future developments is proposed.

## CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

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

**XXIV Congreso Iberoamericano de Catálisis CICAT2014**
15 – 19 septiembre [Medellín, Colombia]

Miguel Angel Centeno Gallego [Miembro del Comité Científico)

### COMUNICACIONES / COMMUNICATIONS

**European Hydrogen Energy Conference – EHEC2014**
12 – 14 marzo [Sevilla, España]

**Microreactors technology for hydrogen production and purification**
S. Palma; O.H. Laguna; A. Perez; S. Ivanova; F. Romero-Sarria; M.A. Centeno; J.A. Odriozola
Comunicación oral

**ANQUE-ICCE-BIOTEC 2014 Congresses on Chemistry, Chemical Engineering and Biotechnology**
1 – 4 julio [Madrid, España]

**Hydrothermal synthesis of Metastable Bi20TiO32 Phase with High Visible-Light Photocatalytic activity**
P. Zambrano, J.A. Navío, M.C. Hidalgo
Comunicación oral

**One Pot Feasible Synthesis of Exposed (001) Facets Nanolaminar TiO2 with high Photocatalytic Activity**
M.A. Lara, J.A. Navío, M.C. Hidalgo
Póster

## The 11th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts"

6 – 10 julio [Louvain-la-Neuve, Bélgica]

**Enamelling of metallic microchannels reactors**
B. Álvarez-Baladrón; M.I. Domínguez; A. Pérez; L.M. Martínez; M.A. Centeno; J.A. Odriozola
Póster

## Fundamentals and applications of cerium dioxide in catalysis

11 – 14 julio [Udine, Italia]

**Boosting the activity of Au/$CeO_2$/$Al_2O_3$ catalysts for the WGS reaction**
T.R. Reina; S. Ivanova; M.A. Centeno; J.A. Odriozola
Póster

## International symposium on advanced ceramic materials and sustainability

15 – 16 septiembre [Jaén, España]

**Microchannel reactors for fuel process**
M.I. Domínguez
Conferencia invitada

## XXIV Congreso Iberoamericano de Catálisis CICAT2014

15 – 19 septiembre [Medellín, Colombia]

**Reactores de microcanales para aplicaciones energéticas**
J.A. Odriozola

**CONFERENCIA PLENARIA**
En esta conferencia se analizaron los diferentes aspectos que deben considerarse para el diseño de reactores de microcanales, incluyendo el diseño de los catalizadores, para las reacciones catalíticas de interés en las tecnologías basadas en el uso de hidrógeno, concretamente en las reacciones de reformado, desplazamiento del gas de agua (WGS), oxidación selectiva de CO en presencia de $H_2$ (CO-PROX) y metanación selectiva de CO.

**Papel de las vacantes de oxígeno en reacciones de oxidación**
M.A. Centeno
Conferencia Invitada

**Catalizadores Ru-Ni: La Importancia en el modo de adición de los metales**
A. Alvarez; M.A. Centeno; J.A. Odriozola
Comunicación oral

**Estudio por espectroscopía Raman in-situ del catalizador Ru/$TiO_2$ en la reacción de metanación selectiva de CO**
L.M. Martínez T.; A. Muñoz; M.A. Centeno; J.A. Odriozola
Comunicación oral

**Diseño de catalizadores Au/CeO2-CuO/$Al_2O_3$ para la producción y limpieza de hidrógeno vía WGS**
T.R. Reina; S. Ivanova; M.A. Centeno; J.A. Odriozola
Comunicación oral

**Influencia del espesor de la capa catalítica y la presencia del buffer en monolitos Pt (2%)/CeAl en WGS**
M. González-Castaño; M.I. Domínguez; L.M. Martínez T.; S. Ivanova; M.A. Centeno; J.A. Odriozola
Comunicación oral

**Modelado de microrreactores con diferente espesor de capa catalítica para la reacción CO-PROX**
O.H. Laguna; G. Arzamendi; L.M. Gandía; M.A. Centeno; J.A. Odriozola
Comunicación oral

**Catalizadores Au/$TiO_2$, Au/$Y_2O_3$ y Au/$TiO_2$-$Y_2O_3$ para las reacciones de oxidación de CO (TOX) y desplazamiento de gas de agua (WGS)**
O.H. Laguna; A. Álvarez M; F. Romero-Sarria; J.A. Odriozola
Póster

**Catalizadores Pt/$Al_2O_3$ y Cu-Pt/$Al_2O_3$ en la reacción de CO-PROX: Modificación de los sitios superficiales**
S. Palma del Valle; F. Romero-Sarria; Ph. Bazin; L. Oliviero; J.A. Odriozola
Póster

**Hidroxiapatitos con wolframio como nuevos catalizadores de oxidación de compuestos aromáticos**
V.I. Parvulescu; B. Cojocaru; M. Tudorache; M.I. Domínguez; M.A. Centeno; J.A. Odriozola
Póster

**Oxidación Catalítica de CO sobre óxidos provenientes de hidrotalcitas promovidas con tierras raras, mediante intercambio con quelatos**
A. Pérez; O.H. Laguna; M.A. Centeno; J.A. Odriozola; R. Molina; S. Moreno
Póster

**Reacción de desplazamiento del gas del agua utilizando catalizadores peletizados de Cu-Ni soportados en carbón activado**
O.Arbeláez; T.R. Reina; S. Ivanova; F. Bustamante; M.A. Centeno; A. Luz Villa; L.M. Martínez T.
Póster

**Síntesis de biodiésel mediante reacciones simultáneas de esterificación y transesterificación con catalizadores basados en óxido de molibdeno**
A. Navajas, I. Reyero, E. Jiménez-Barrera, F. Romero-Sarria, L. Gandía
Póster

### 3rd General Meeting. Reducible Oxide Chemistry, Structure and Functions
12 – 14 noviembre [Barcelona, España]

**Electronic properties of dispersed copper oxide entities interacting with ceria: near-ambient XPS analysis of the reduction under CO**
M. Monte; D. Costa; J. C. Conesa; G. Munuera; A. Martínez-Arias
Comunicación oral

### 2014 AIChE Annual Meeting
16 – 21 noviembre [Atlanta, Estados Unidos de América]

**Structuring Pd/ZnO catalysts for methanol steam reforming**
M. Montes; I. Velasco; O. Sanz; J.A. Odriozola; L.M. Gandía
Conferencia invitada

**Effect of methanol concentration on the performance of CuOx/$CeO_2$ catalysts for CoProx**
J.A. Odriozola; S. Palma; O.H. Laguna; F. Romero-Sarria; M.A. Centeno; M. Montes
Comunicación oral

**Unrevealing the mechanism of the WGS reaction over Au/$CeO_2$-FeOx/$Al_2O_3$ catalysts**
J.A. Odriozola; T. Ramírez-Reina; M. González-Castaño; S. Ivanova; M.A. Centeno
Comunicación oral

**Influence of the preparation method in Ru-Ni catalysts for dry reforming of methane**
J.A. Odriozola; A. Álvarez; A.C. Roger; M.A. Centeno
Comunicación oral

## CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESSES AND MEETINGS

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

### I Encuentro de Jóvenes Investigadores de la SECAT
22 – 24 junio [Málaga, España]

José Antonio Odriozola Gordón [Miembro del  Comité Científico)
Miguel Angel Centeno Gallego [Miembro del  Comité Científico)

## COMUNICACIONES / COMMUNICATIONS

### I Encuentro de Jóvenes Investigadores de la SECAT

22 – 24 junio [Málaga, España]

**Influencia del espesor de la capa catalítica y la presencia del buffer en monolitos Pt(2%)/CeAl en WGS**
M. González-Castaño; M.I. Domínguez; L.M. Martínez; S. Ivanova; M.A. Centeno; J.A. Odriozola
Comunicación oral

**Simulación mediante ASPEN PLUS de la modificación de la composición $CH_4/CO_2/H_2O$ para el reformado de Biogás**
V. Garcilaso de la Vega; A. Álvarez; O.H. Laguna; M.A. Centeno; J.A. Odriozola
Póster

**Estudio de la actividad catalítica a través de la adsorción de CO sobre catalizadores $Pt\text{-}Al_2O_3$ y $Cu/Pt\text{-}Al_2O_3$**
E.M. Jiménez-Barrera, F. Romero-Sarria
Póster

### Eighth National Conference on Chemistry. Chemistry for Sustainable Development

26 – 27 junio [Sofia, Bulgaria]

**Copper-based layered double hydroxides as catalysts for water gas shift reaction**
I. Ivanov; T.R. Reina; S. Ivanova; T. Tabakova; M.A. Centeno; J.A. Odriozola; V. Idakiev
Póster

### XXIII Reunión de la Sociedad Española de Arcillas

10 – 12 septiembre [Toledo, España]

**Nanoarquitecturas arcilla-anatasa: produccion fotocatalítica de hidrógeno**
J. Pérez-Carvajal; P. Aranda; S. Obregón; G. Colón; E. Ruiz-Hitzky
Comunicación oral

## 🟩 FORMACION / TRAINING

## TESIS DOCTORALES/ DOCTOR DEGREE THESIS

| | |
|---|---|
| **Título:** | **Producción de hidrógeno a partir de metanol: diseño, síntesis y caracterización de un catalizador de PROX** |

**Autor:** Sandra Palma del Valle
**Directores:** Francisca Romero-Sarria, José Antonio Odriozola Gordón
**Calificación:** Sobresaliente “Cum Laude”
**Centro:** Universidad de Sevilla

**Título:** **Estudio de la actividad catalítica y de la interacción metal-soporte en sistemas de níquel soportados en $ZrO_2$ y $CeO_2$, activos en las reacciones de reformado de metano**
**Autor:** Victor Manuel González de la Cruz
**Directores:** Alfonso Caballero Martínez, Juan Pedro Holgado Vázquez
**Calificación:** Sobresaliente “Cum Laude”
**Centro:** Universidad de Sevilla

**Título:** **Diseño y caracterización de catalizadores basados en oro para la reacción de wáter gas shift**
**Autor:** Tomás Ramírez Reina
**Directores:** José Antonio Odriozola Gordón, Svetlana Ivanova
**Calificación:** Sobresaliente “Cum Laude”
**Centro:** Universidad de Sevilla

**Título:** **Catalizadores de $Ru/TiO_2$ para la metanación selectiva de CO**
**Autor:** Ara Muñoz Murillo
**Directores:** José Antonio Odriozola Gordón, Miguel Angel Centeno Gallego
**Calificación:** Sobresaliente “Cum Laude”
**Centro:** Universidad de Sevilla

## FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

**Título:** **Catalizadores Pt/Na/C para la reacción de Water Gas shift**
**Autor:** José Luis Santos Muñoz
**Directores:** Miguel Angel Centeno Gallego, José Antonio Odriozola Gordón
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Estudio del dopado electroquímico de electrodos nanoestructurados de WO3**
**Autor:** Augusto Márquez Maqueda
**Directores:** Svetlana Ivanova, Juan Antonio Montalvo, Thomas Berger
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Materiales híbridos basados en polioxometalatos y líquidos iónicos para su aplicación en reacciones de catálisis heterogénea**
**Autor:** Cristina Megías Sayago
**Directores:** José Antonio Odriozola, Svetlana Ivanova, Francisca Romero Sarria
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Valorización de residuos de biomasa: preparación de carbones amorfos**
**Autor:** Rafael Castillo Barrero
**Directores:** José Antonio Odriozola, Paloma Álvarez Mateos
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Preparación de nanopartículas "core-shell" como soporte de marcadores biológicos**
**Autor:** Alba Gallego Ripoll
**Directores:** María Isabel Domínguez Leal, Svetlana Ivanova
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Preparación de sólidos microporosos para la activación de $CO_2$**
**Autor:** Elizabeth Domínguez García
**Directores:** María Isabel Domínguez Leal, Francisca Romero Sarria
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Propiedades optoelectrónicas de nanopartículas de sulfuro de plata**
**Autor:** Javier Amaya Suárez
**Directores:** José Antonio Odriozola, Javier Fernández Sanz
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (27 junio 2014)

**Título:** **Síntesis y caracterización de materiales biocompatibles tipo hidrotalcita**
**Autor:** Zaineb Debbagh
**Directores:** María Isabel Domínguez Leal, Regla Ayala Espinar
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (19 septiembre 2014)

**Título:** **Hidroxiapatitos como sustitutos óseos**
**Autor:** María de la Luz Bravo-Ferrer Moreno
**Directores:** Svetlana Lyubomirova Ivanova, María Isabel Domínguez Leal
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (19 septiembre 2014)

**Título:** **Síntesis de materiales híbridos como sensores de ácidos grasos procedentes del metabolismo de la insulina**
**Autor:** Alba María Fernández Sotillo
**Directores:** Svetlana Lyubomirova Ivanova y María Isabel Domínguez Leal
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (24 septiembre 2014)

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

| | | |
|---|---|---|
| **Departamento de Química Aplicada. Facultad de Ciencias Químicas de San Sebastián. Universidad del Pais Vasco** | | |
| San Sebastián, España | **José Antonio Odriozola Gordón** | 5 dias |
| | **Oscar Hernando Laguna** | 5 dias |
| **Universidad de Antioquia** | | |
| Medellin, Colombia | **Marcela Martínez Tejada** | 5 dias |
| **Synchrotron ALBA** | | |
| Barcelona, España | **Svetlana Ivanova** | 1 semana |
| | **Miriam González Castaño** | 1 semana |
| | **Marcela Martínez Tejada** | 1 semana |
| **Synchrotron SOLEIL** | | |
| Paris, Francia | **Svetlana Ivanova** | 1 semana |
| | **Miriam González Castaño** | 1 semana |
| | **Marcela Martínez Tejada** | 1 semana |

## Estancias y Visitas de Investigadores en el ICMS
## Personnel of the Other Laboratories in the ICMS

| | | |
|---|---|---|
| **Pontificia Universidad Javeriana** | | |
| Bogotá, Colombia | **Mario Rodrigo Rubio Haaslet** | 12 dias |

| | | |
|---|---|---|
| **Université Setif1**<br>Sefit, Argelia | **Derradji Chebli** | 12 dias |
| | **Abdallah Bouguettoucha** | 12 dias |
| | **Meriem Chebout** | 12 dias |
| | **Fatima Ammari** | 4 semanas |
| **Departamento de Ingeniería Química. Facultad de Ingeniería, UDEA**<br>Medellin, Colombia | **Oscar Felipe Arbelaez Pérez** | 1 mes |
| **Universidad de Tolima**<br>Bogotá, Colombia | **Cesar Augusto Jaramillo Pérez** | 1 mes |
| **Universidad Nacional**<br>Bogotá, Colombia | **Yazmin Yaneth Agámez Pertuz** | 6 semanas |
| | **Diego Arcelio Rico Sierra** | 2 meses |
| **ENSICAEN. L'Ecole Nationales Supérieure D'Ingenieurs de Caen**<br>Caen, Francia | **Estelle Le Saché** | 3 meses |
| | **Joachim Rambaud** | 3 meses |

## 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

## 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

**Investigadores Contratados**

Dra. M. Mar Orta Cuevas
Dr. Joaquin Ramírez Rico

**Becarios Predoctorales**

Ldo. Antonio A. Gutiérrez Pardo
Ldo. Fredy A. Huaman Mamani
Ldo. Francisco J. Osuna Barroso
Lda. M. Carmen Vera García

**Personal Contratado**

Dr. Antonio Perejón Pazo

## PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

### Filtros Bio-Cerámicos para Partículas en Motores Diesel / Bio-ceramics for diesel engine particulate filters

Código/Code: MAT2013-41233-R (Programa Retos)
Periodo/Period: 01-01-2014 / 31-12-2016
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 163.265,30 €
Investigador responsable/Research head: Julián Martínez Fernández /Ricado Chacartegui
Componentes/Research group: José Antonio Becerra Villanueva, Alfonso Bravo León, Manuel Jiménez Melendo, Antonio Ramírez de Arellano López, Joaquín Ramirez Rico, Francisco Varela Feria

RESUMEN / ABSTRACT

La importancia del control de las emisiones de partículas en motores diésel es fundamental dados el volumen global de los mismos y el impacto medioambiental y económico asociado. Los sistemas de control de partículas basados en modificaciones del proceso de combustión en el motor no son suficientes para alcanzar las exigencias normativas actuales, y menos las futuras, y por tanto necesariamente hay que emplear sistemas de postratamiento como los filtros. Existe un amplio margen de mejora de los mismos tanto en fiabilidad, control de la degradación de prestaciones, durabilidad, operación multicombustible y reducción de costes.

En el presente proyecto se abordará el desarrollo y fabricación de un filtro de partículas regenerativo en motores diésel que mejore las especificaciones de los sistemas actuales, basado en una nueva generación de materiales cerámicos bioderivados, y que integre sistemas para la combustión de partículas. Para ello se aprovecharán las sinergias integrando investigadores del: i) Grupo Maquinas y Motores Térmicos, GMTS, especialistas en motores de combustión interna 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.

Se trabajará en las siguientes líneas:

- Determinación de rutas de procesado para el desarrollo de elementos filtrantes con propiedades físico-químicas idóneas, en base a los conocimientos previos en materiales bioderivados y nuevas tecnologías relativas al uso de geles de $SiO_2$.
- Determinación de catalizadores idóneos y sistemas para su deposición.
- Fabricación de los elementos filtrantes constituidos de soporte poroso más catalizador.
- Caracterización exhaustiva de las propiedades microstructurales y físico-químicas de interés para la aplicación.
- Desarrollo de sistemas de activación para la regeneración del filtro.

- Diseño y fabricación de los filtros con geometría idónea y dimensiones prototipo.
- Diseño de la unidad piloto y estudio de la integración y operación sobre el motor de referencia.
- Diseño final del filtro para su instalación industrial.

Estudios previos desarrollados por MBM en estos materiales bioderivados han demostrado su potencialidad como elementos filtrantes de gas a altas temperaturas en plantas de gasificación de carbón, lo que avala el éxito de este proyecto, que abordará las mejoras necesarias para desarrollar la tecnología en las condiciones de combustión de los motores diésel, bajo condiciones dinámicas en vehículos y filtros regenerativos.

Una reducción de contaminantes en las emisiones de los motores diésel tendría un gran impacto medioambiental, para la salud y económico, debido a los cerca de 100 millones de vehículos diésel circulando en Europa y una industria vinculada con más de 2 millones de empleos directos y tendencia creciente en el mercado. Este proyecto aborda el Reto Social 3 del Horizonte 2020, Energía segura, limpia y eficiente. Además el uso de materiales biocerámicos permite la sustitución de los elementos metálicos empleados en la actualidad, por lo que también se alinea con el Reto Social 5 del Horizonte 2020 en la búsqueda de alternativas a las materias primas esenciales en aplicaciones ya existentes reduciendo la dependencia de importaciones y sostenibilidad de las aplicaciones.

The importance of controlling particulate emissions from diesel engines is essential given its volume and the associated environmental and economic impact. Control systems based on modifications of the combustion process in the engine are not sufficient to meet the requirements of current regulations, less future ones, and therefore it must necessarily be employed post treatment systems such as filters. There is considerable scope for improving them both in reliability, degradation of control performance, durability, multifuel operation and cost reduction.

This project will assess the development and manufacturing of regenerative particulate filter for diesel engines to improve the current system specifications, based on a new generation of ceramic bio-derivated materials, with integrated systems for particle combustion. This objectives will be achieved integrating researchers synergies from: i ) Thermal Engines and Machines Group, GMTS , specialists in internal combustion engines ii ) Multifunctional Biomimetic Materials Group, MBM, specialists in obtaining bio-derivated porous ceramic as well as physical, chemical and microstructural characterization. In addition, the project is completed with the collaboration of companies in assessing technology and its industrial applicability.

The following research lines will be addressed:

- Determination of processing routes that enable the development of filter elements with suitable physical, and chemical properties, based on prior knowledge in bio-derivated materials and new technologies regarding the use of $SiO_2$ gels.
- Identification of suitable catalysts and systems for its deposition.
- Manufacture of the filter elements consisting of porous support and catalyst.
- Thorough characterization of the physical, chemical and microstructural properties of interest for the application.
- Development of activation systems for the filter regeneration.

- Design and manufacturing of the filters with suitable geometry and prototype dimensions.
- Pilot unit design and study of the integration and operation of engine.
- Final design of the filter for industrial facility.

Previous studies developed by MBM in these bio-derivated materials have demonstrated their potential as gas filter elements at high temperatures in coal gasification plants, which supports the likelihood of success of this project, which will address the improvements needed to develop the technology in the combustion conditions of diesel engines, under dynamic conditions in vehicles and regenerative filters.

A reduction of pollutant emissions from diesel engines would have a great environmental impact, health and economic development, with about 100 million diesel vehicles circulating in Europe and a related industry with over 2 million direct jobs and growing trend in market. This project addresses the Social Challenge 3 Horizon 2020, Secure, clean and efficient energy. In addition, using bioceramics allows replacement of metal components used today, which also aligns with the Social Challenge 5 of the Horizon 2020 in search of alternatives to essential raw materials in existing applications by reducing dependence on imports and sustainability of applications.

JUNTA DE ANDALUCIA

## Obtención de bioplásticos tipo polihidroxialcanoato (PHA) de cadena larga a partir de desechos de epidermis de frutos comerciales / The obtention of fatty polyhydroxyalcanoate (PHA) bioplastics from peels residues of commercial fruits

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| Código/Code: | P11-TEP-7418 (Proyecto de Excelencia) |
| Periodo/Period: | 16-05-2013 / 15-05-2015 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 174.455 € |
| Investigador responsable/Research head: | José Jesús Benítez Jiménez |
| Componentes/Research group: | Antonio Heredia Bayona, Miguel Angel San Miguel Barrera, Jaime Oviedo López, J. Alejandro Heredia Guerrero, Santiago Domínguez Meister, Daniel Aguilera Puerto, Francisco Javier Navas Martos, José Manuel de la Torre Ramírez |

### RESUMEN / ABSTRACT

El presente proyecto de investigación tiene por objeto el estudio de la viabilidad de la implementación de un proceso a escala planta piloto que permita obtener un material bioplástico a partir de una materia prima asequible y de bajo coste como son los desechos de pieles (epidermis) de frutos. La oportunidad de la propuesta parte de proponer un nuevo tipo de material polimérico completamente inocuo, biodegradable y ecológico como sustituto de plásticos tradicionales obtenidos a partir del petróleo que conllevan un serio problema medioambiental, tanto en su producción industrial como en su posterior desecho. Por otro lado, el concepto de sostenibilidad medioambiental se extiende no sólo a la biodegradabilidad del produc-

to final y al bajo impacto del proceso de producción propuesto, también a su obtención a partir de un recurso vegetal que no se retrae de la cadena alimenticia animal y humana, como es el caso de los bioplásticos qu<e se vienen fabricando actualmente a partir de maíz o patata. Por otro lado, y en nuestro ámbito territorial andaluz, la materia prima es especialmente accesible dado el volumen de la actividad agroalimentaria. En este mismo sentido, el nuevo bioplástico podría paliar un importante problema de eliminación de residuos plásticos en explotaciones agrarias ya que se concibe como plenamente compostable y, por tanto, capaz de generar biomasa asimilable por la siguiente generación de plantas. El producto propuesto viene, además, a completar la gama de polihidroxialcanoatos (PHA) a los miembros de la serie obtenidos a partir de polihidroxiácidos de cadena larga. Las propiedades singulares de esta nueva familia puede ser un buen complemento de los ya conocidos y podría dar lugar a aplicaciones novedosas y de mayor valor añadido.

The main objective of this project is to evaluate the feasibility of scaling up a procedure to obtain fatty polyhydroxyalcanoate (PHA) bioplastics from a low-cost and abundant source like peels residues of commercial fruits. The strength of the proposal relies on the introduction of a new non-toxic and fully biodegradable polymeric material as a substitute for environmental-hostile petroleum-based plastics. The overall sustainability is extended to the use of a low-impact synthetic route and to the processing of a plant residue rather than crops intended for human or cattle feeding. The project is considered of additional interest in regions with an agricultural based economy like Andalusia and with an important environmental impact arising from the greenhouse activity. The proposal also covers the study of new and more specific applications of such bio-based fatty polyhydroxyalcanoates.

JUNTA DE ANDALUCIA

## **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**

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| Código/Code: | P12-FQM-567 |
| Periodo/Period: | 16-05-2014 / 15-05-2018 |
| 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.

JUNTA DE ANDALUCIA

## Bioener: Aplicación de tecnologías biomiméticas a sistemas energéticos

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| Código/Code: | P09-TEP-5152 (Proyecto de Excelencia) |
| Periodo/Period: | 02-02-2009 / 03-02-2014 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 311.167,68 € |
| Investigador responsable/Research head: | Julián Martínez Fernández |
| Componentes/Research group: | Antonio R. De Arellano-López, Alfonso Bravo León, Manuel Jiménez Melendo, F.M. Varela Feria, Joaquín Ramírez Rico, Antonio Gutiérrez Pardo |

RESUMEN / ABSTRACT

Los avances tecnológicos han permitido diversificar y optimizar la producción de energía, lo que ha conducido al mismo tiempo, a desarrollar nuevas vías de almacenamiento de la misma. En particular, a medida que se diversifican los métodos de producción energética, es necesario desarrollar nuevos materiales para almacenamiento de energía, para su uso en dispositivos de consumo y transporte.  Esto es especialmente importante para países que, como España, llevan años aumentando la presencia de las renovables en su carta de tecnologías de producción eléctrica y son actualmente líderes mundiales del sector.  El Plan de Fomento de las Energías Renovables 2000-2010 tiene como objetivo para este año generar hasta el 30% de las necesidades de consumo energético nacionales a partir de energías renovables, mientras que en algunas comunidades autónomas la cuota de renovables supone ya más del 75% del consumo anual. La progresiva penetración de las renovables debe ir necesariamente acompañada del desarrollo de nuevas tecnologías de distribución y almacenamiento energético, teniendo en cuenta que la potencia suministrada por las renovables es intermitente y variable, al depender las condiciones meteorológicas.

Otra estrategia a corto plazo para reducir la dependencia de los combustibles fósiles es la mejora de la eficiencia los sistemas de generación de energía convencionales mediante el aumento de las temperaturas de operación, por ejemplo en turbinas de combustión de gas. El desarrollo de nuevos materiales para aplicaciones de alta temperatura ha ido tradicionalmente ligado a la demanda de mayores eficiencias. De entre ellos, los materiales cerámicos se postulan como candidatos para aplicaciones en entornos químicamente agresivos a temperaturas superiores a los 1000ºC. Carburos y nitruros en particular, con su elevado punto de fusión y excelentes propiedades termomecánicas, están siendo extensamente estudiados en la actualidad para este tipo de aplicaciones. Los cerámicos porosos también son de gran interés en aplicaciones energéticas, como intercambiadores de calor o sistemas de filtrado de gas de síntesis, entre otros.

De las líneas de investigación en nuevos materiales para almacenamiento energético, el desarrollo de nuevos sistemas de almacenamiento electroquímico tendrá un gran impacto a corto plazo, especialmente en el consumidor final: el desarrollo de baterías y condensadores electroquímicos de alta capacidad es clave para la viabilidad de tecnologías que, como los vehículos eléctricos, deberán implantarse en un corto plazo para reducir nuestra dependencia de los combustibles fósiles. Es por esta razón que los materiales para almacenamiento electro-

químico han recibido gran atención de la comunidad científica y constituyen uno de los grandes retos tecnológicos actuales.

El carburo de silicio biomórfico (bioSiC) es un material cerámico obtenido por infiltración reactiva de preformas de carbono obtenidas mediante pirólisis de precursores vegetales. El precursor, generalmente madera, se mecaniza en bruto y se carboniza mediante un proceso de pirólisis en atmósfera controlada a alta temperatura, obteniéndose un material de carbono macroporoso (bioC) cuya microestructura es similar a la del precursor vegetal. Este precursor se mecaniza hasta una forma cercana al producto final y se infiltra reactivamente con silicio líquido o gaseoso para obtener un material de SiC/Si que presenta unas excelentes propiedades termomecánicas, con una microestructura que mimetiza la microestructura de la madera original. Es posible seleccionar las propiedades del material resultante mediante la elección adecuada del precursor. El silicio residual puede eliminarse para obtener un material de SiC macroporoso. Es posible, por último, reinfiltrar el bioSiC poroso con otros materiales, por ejemplo metales para obtener cermets bioSiC/Al o bioSiC/Cu.

La posibilidad de producir materiales de carbono macroporosos con nanoporosidad controlada es interesante para su uso en aplicaciones electroquímicas, puesto que es posible infiltrar o recubrir los macroporos con una fase secundaria que proporcione funcionalidad adicional, por ejemplo en pilas de litio con arquitectura tridimensional o en supercondensadores oxido/carbono. En este sentido, el desarrollo de nuevos carbonos con porosidad y/o estructura controlada puede abrir una puerta hacia nuevas arquitecturas y diseños de dispositivo capaces de almacenar mayores densidades de energía.

La mayoría de materiales nanoporosos de carbono utilizados en la actualidad se obtienen mediante la activación de carbones obtenidos por pirólisis de precursores orgánicos sintéticos, aunque en los últimos años el carbono obtenido a partir de carburos ha sido objeto de gran interés. Es posible, mediante el tratamiento a alta temperatura de carburos metálicos en una atmósfera clorada, obtener carbonos nanoporosos de alta pureza que resultan idóneos para aplicaciones electroquímicas. En este sentido ya se ha demostrado la posibilidad de obtener carbono nanoporoso a partir de carburos obtenidos por infiltración reactiva de precursores vegetales.

El objetivo de este proyecto es doble: por un lado, se estudiará en detalle el procedimiento de obtención de materiales de carbono a partir de precursores vegetales, prestando atención a la posibilidad de introducir distintos gases (CO2, vapor de agua) durante el proceso de pirólisis para obtener carbones activos con nanoporosidad para su uso en sistemas de almacenamiento electroquímico. Se estudiará además el efecto de la temperatura de pirólisis en el grado de cristalinidad, nanoporosidad, tamaño de cristal y estructura del carbono resultante, y se explorará la posibilidad de promover la cristalización del carbono mediante el uso de distintos catalizadores. Se caracterizará la microestructura de los materiales resultantes, así como sus propiedades físicas y termo-mecánicas.

Technological advances have made possible to diversify and optimize energy production, which in turn has motivated the development of new ways to store energy. In particular, as production methods diversify, it is necessary to develop new materials for energy storage, both large scale and in consumer devices and transportation. This is especially important in the context of higher penetration of renewable energies, which often depend on climatological conditions and require ways to store excess energy at production peaks, so it can be used when production decreases.

In parallel to this strategy and to reduce the share of fossil fuels in the overall energy production, it is necessary to increase the efficiency of conventional power generation systems, for example by increasing material's life and operating temperatures, for example in gas turbine systems, among others. The development of materials for high temperature applications, especially ceramics, has been traditionally linked to the search for increased efficiency of power generation systems. Ceramic materials, due to their high melting point, good creep resistance and resistance to corrosion, are seen as candidates for application in chemically aggressive environments at temperatures over 1000 ºC. Carbides and nitrides in particular are being studied extensively for this kind of applications. Porous ceramics are also of great interest in energy applications, such as heat exchangers or syngas filtration systems, among others.

Among active research lines in the development of new materials for energy storage, electrochemical storage is expected to have the largest impact in the end consumer, as the design of high capacity batteries and electrochemical capacitors is key for the viability of technologies such as plug-in electric cars. For this reason, research into new materials for electrochemical storage has become a strong focal point among the scientific community and constitutes one to the great technological challenges of today.

Biomorphic silicon carbide (bioSiC) is a ceramic material obtained by reactive infiltration of carbon performs derived by pyrolysis of natural precursors. The precursor, usually wood, is rough-machined and then converted to carbon by pyrolysis in a controlled atmosphere at high temperatures. The result is a macroporous carbon material (bioC) with a microstructure that closely resembles that of the original precursor. This carbon template is then machined to near net shape and is melt reacted with silicon either in liquid or vapor phase to obtain a SiC composite with some residual Si that shows excellent thermomechanical properties and a microstructure that closely mimics that of the original wood precursor. Tailoring the material's properties is possible by adequate selection of the precursor, which determines the microstructure and thus the properties of the bioSiC. It is also possible to remove the remaining silicon through chemical etching to obtain a macroporous SiC material which can then be reinfiltrated to create novel composites and cermets, such as bioSiC/Al or bioSiC/Cu.

The prospect of producing macroporous carbon materials with controlled nanoporosity is interesting for electrochemical applications, as it would be possible to infiltrate or coat macropores with a second phase the provides additional function, for instance in three dimensional lithium batteries or carbon/oxide supercapacitors. In this way, the development of new carbon materials with controlled structure and porosity could open the door to novel architectures and designs for devices able to store larger amounts of energy.

Most nanoporous carbon materials used nowadays are obtained through activation of carbons made from pyrolysis of synthetic precursors, although in the last years carbide-derived carbons have been the subject of great interest. It is possible to obtain high-purity nanoporous carbon through high temperature chlorination of metallic carbides, which rank among the best carbon materials for electrochemical applications. In this direction, is has already been shown that carbides obtained from natural precursors, such as bioSiC are viable precursors to carbide-derived carbons.

This proposal's aim is two-fold: on one side, the bioC processing will be studied in detail, paying special attention to precursor selection and to the possibility of introducing different atmospheres during the pyrolysis process, such as CO2 or water vapor, that promote nanoporosity in the material. The effect of processing parameter in the degree of crystallinity, nanoporosity, crystallite size and structure of the resulting carbon material will be assessed. The possibility of promoting carbon graphitization through the use of different catalysis in the pyrolysis process will be studied. The resulting carbon's microstructure and physical properties will be studied and correlated to the processing parameters.

On the other side, the effect of the aforementioned treatments on the bioSiC material will be studied, and the possibility of obtaining novel cermets in-situ, such as bioSiC/Al, bioSiC/Ti, through melt infiltration, will be assessed. In a last step, the possibility of obtained carbon materials with enhanced structure from the ceramic carbides will be explored.

## Convenios y Contratos / Contracts and Agreements

### Materiales Vítreos Cementantes de Alta Eficiencia y Bajo Impacto Ambiental (MAVIT)

Periodo/Period: 01-01-2012 / 31-12-2014
Organismo Financiador/Financial source: Refractarios ALFRAN, S.A.
importe total/Total amount: 181.500 €
Investigador responsable/Research head: Joaquín Ramírez Rico
Componentes/Research group: Julián Martínez Fernandez, María del Carmen Vera García, M. Dolores Alba Carranza

### Waste to Biofuel-encargo 2

Periodo/Period: 21-02-2014 / 18-03-2014
Organismo Financiador/Financial source: Abengoa research, S.L.
importe total/Total amount: 55.083,72 €
Investigador responsable/Research head: María del Mar Orta Cueva
Componentes/Research group: M. Dolores Alba Carranza, Miguel Ángel Castro

### Waste to Biofuel-encargo 3

Periodo/Period: 22-05-2014 / 30-05-2014
Organismo Financiador/Financial source: Abengoa research, S.L.
importe total/Total amount: 36.017,17 €
Investigador responsable/Research head: María del Mar Orta Cueva
Componentes/Research group: M. Dolores Alba Carranza, Miguel Ángel Castro

### Realización de medidas de Resonancia Magnética Nuclear a 4 muestras en un RMN de 700 MHz solicitado por Abengoa Research S.L. en el marco "Waste to Biofuel"

Periodo/Period: 21-11-2014 / 31-12-2014
Organismo Financiador/Financial source: Abengoa research, S.L.
importe total/Total amount: 1.528,64 €
Investigador responsable/Research head: María del Mar Orta Cueva
Componentes/Research group: M. Dolores Alba Carranza, Miguel Ángel Castro

### Caracterización de las propiedades físico-químicas de materiales sólidos del proyecto waste to biofuel (W2B)

| | |
|---|---|
| Periodo/Period: | 12-12-2014 / 30-12-2014 |
| Organismo Financiador/Financial source: | Abengoa research, S.L. |
| importe total/Total amount: | 16.652,75 € |
| Investigador responsable/Research head: | María del Mar Orta Cueva |
| Componentes/Research group: | M. Dolores Alba Carranza**,** Miguel Ángel Castro |

## ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

### Biomechanical properties of the tomato (Solanum lycopersicum) fruit cuticle during development are modulated by changes in the relative amounts of its components

Espana, L; Heredia-Guerrero, JA; Segado, P; Benitez, JJ; Heredia, A; Dominguez, E
*New Phytologist*, **202 (3)** (2014) 790-802
May, 2014 | **DOI:** 10.1111/nph.12727

- In this study, growth-dependent changes in the mechanical properties of the tomato (Solanum lycopersicum) cuticle during fruit development were investigated in two cultivars with different patterns of cuticle growth and accumulation.

- The mechanical properties were determined in uniaxial tensile tests using strips of isolated cuticles. Changes in the functional groups of the cuticle chemical components were analysed by attenuated total reflectance–Fourier transform infrared (ATR-FTIR).

- The early stages of fruit growth are characterized by an elastic cuticle, and viscoelastic behaviour only appeared at the beginning of cell enlargement. Changes in the cutin: polysaccharide ratio during development affected the strength required to achieve viscoelastic deformation. The increase in stiffness and decrease in extensibility during ripening, related to flavonoid accumulation, were accompanied by an increase in cutin depolymerization as a result of a reduction in the overall number of ester bonds.

- Quantitative changes in cuticle components influence the elastic/viscoelastic behaviour of the cuticle. The cutin:polysaccharide ratio modulates the stress required to permanently deform the cuticle and allow cell enlargement. Flavonoids stiffen the elastic phase and reduce permanent viscoelastic deformation. Ripening is accompanied by a chemical cleavage of cutin ester bonds. An infrared (IR) band related to phenolic accumulation can be used to monitor changes in the cutin esterification index.

### Direct evidence of Lowenstein's rule violation in swelling high-charge micas

Pavon, E; Osuna, FJ; Alba, MD; Delevoye, L
*Chemical Communications*, **53** (2014) 6984-6986
July, 2014 | **DOI:** 10.1039/C4CC01632G

The structure of high-charged micas, Na-n-micas (n = 2 and 4), a family of synthetic silicates with a wide range of applications, was investigated through the use of 17O solid-state NMR at natural abundance in order to preserve quantitative spectral information. The use of a very high-field and highly sensitive probehead, together with 17O NMR literature data allowed for the detection of an isolated signal at 26 ppm, assigned partially to AlOAl, as evidence of the violation of Lowenstein's rule for Na-4-mica.

### Ceramic Barrier Layers for Flexible Thin Film Solar Cells on Metallic Substrates: A Laboratory Scale Study for Process Optimization and Barrier Layer Properties

Delgado-Sanchez, JM; Guilera, N; Francesch, L; Alba, MD; Lopez, L; Sanchez, E
*ACS Applied Materials & Interfaces*, **6** (2014) 18543-18549
November, 2014 | **DOI:** 10.1021/am504923z

Flexible thin film solar cells are an alternative to both utility-scale and building integrated photovoltaic installations. The fabrication of these devices over electrically conducting low-cost foils requires the deposition of dielectric barrier layers to flatten the substrate surface, provide electrical isolation between the substrate and the device, and avoid the diffusion of metal impurities during the relatively high temperatures required to deposit the rest of the solar cell device layers. The typical roughness of low-cost stainless-steel foils is in the hundred-nanometer range, which is comparable or larger than the thin film layers comprising the device and this may result in electrical shunts that decrease solar cell performance. This manuscript assesses the properties of different single-layer and bilayer structures containing ceramics inks formulations based on $Al_2O_3$, AlN, or $Si_3N_4$ nanoparticles and deposited over stainless-steel foils using a rotogravure printing process. The best control of the substrate roughness was achieved for bilayers of $Al_2O_3$ or AlN with mixed particle size, which reduced the roughness and prevented the diffusion of metals impurities but AlN bilayers exhibited as well the best electrical insulation properties.

### Interaction of Hydrated Cations with Mica-n (n = 2, 3 and 4) Surface

Pavon, E; Castro, MA; Cota, A; Osuna, FJ; Pazos, MC; Alba, MD
*Journal of Physical Chemistry C*, **118** (2014) 2115-2121
January, 2014 | **DOI:** 10.1021/jp4110695

High charged swelling micas, with layer charge between 2 and 4, have been found to readily swell with water, and complete cation exchange (CEC) can be achieved. Because of their high CEC, applications like radioactive cation fixation or removal of heavy metal cations from wastewater were proposed. Their applicability can be controlled by the location of the interlayer cation in a confined space with a high electric field. In synthetic brittle micas, the interlayer cation has a low water coordination number; therefore, their coordination sphere would be completed by the basal oxygen of the tetrahedral layer as inner-sphere complexes (ISC). However, no direct evidence of these complexes formation in brittle micas has been reported yet. In this contribution, we mainly focus on the understanding the mechanisms that provoke the formation of ISC in high charge swelling micas, Mica-n. A whole series of cations (X) were used to explore the influence of the charge and size of the interlayer cation. Three brittle swelling micas, Mica-n (n = 4, 3 and 2), were selected in order to analyze the influence of the layer charge in the formation of ISC. The contribution of the ISC has been analyzed thorough the evolution of the 060 reflection and the changes in the short-range order of the tetrahedral cations will be followed $^{29}$Si and $^{27}$Al MAS NMR. The results showed that ISC was favored in X-Mica-4 and that provoked a high distortion angle between the Si–Al tetrahedra. When the content of aluminum decreases, the electrostatic forces between the layers are relaxed, and the hydrated cations did not interact so strongly with the tetrahedral sheet, having the opportunity to complete their hydration sphere.

### New Bio-Ceramization Processes Applied to Vegetable Hierarchical Structures for Bone Regeneration: An Experimental Model in Sheep

Filardo, G; Kon, E; Tampieri, A; Cabezas-Rodriguez, R; Di Martino, A; Fini, M; Giavaresi, G; Lelli, M; Martinez-Fernandez, J; Martini, L; Ramirez-Rico, J; Salamanna, F; Sandri, M; Sprio, S; Marcacci, M

*Tissue Engineering Part A*, **20** (2014) 763-773
February, 2014 | **DOI:** 10.1089/ten.tea.2013.0108

Bone loss is still a major problem in orthopedics. The purpose of this experimental study is to evaluate the safety and regenerative potential of a new scaffold based on a bio-ceramization process for bone regeneration in long diaphyseal defects in a sheep model. The scaffold was obtained by transformation of wood pieces into porous biomorphic silicon carbide (BioSiC®). The process enabled the maintenance of the original wood microstructure, thus exhibiting hierarchically organized porosity and high mechanical strength. To improve cell adhesion and osseointegration, the external surface of the hollow cylinder was made more bioactive by electrodeposition of a uniform layer of collagen fibers that were mineralized with biomimetic hydroxyapatite, whereas the internal part was filled with a bio-hybrid HA/collagen composite. The final scaffold was then implanted in the metatarsus of 15 crossbred (Merinos-Sarda) adult sheep, divided into 3 groups: scaffold alone, scaffold with platelet-rich plasma (PRP) augmentation, and scaffold with bone marrow stromal cells (BMSCs) added during implantation. Radiological analysis was performed at 4, 8, 12 weeks, and 4 months, when animals were sacrificed for the final radiological, histological, and histomorphometric evaluation. In all tested treatments, these analyses highlighted the presence of newly formed bone at the bone scaffolds' interface. Although a lack of substantial effect of PRP was demonstrated, the scaffold+BMSC augmentation showed the highest value of bone-to-implant contact and new bone growth inside the scaffold. The findings of this study suggest the potential of bio-ceramization processes applied to vegetable hierarchical structures for the production of wood-derived bone scaffolds, and document a suitable augmentation procedure in enhancing bone regeneration, particularly when combined with BMSCs.

### Infrared and Raman spectroscopic features of plant cuticles: a review

Heredia-Guerrero, JA; Benitez, JJ; Dominguez, E; Bayer, IS; Cingolani, R; Athanassiou, A; Heredia, A

*Frontiers in Plant Science*, **25** (2014)
June, 2014 | **DOI:** 10.3389/fpls.2014.00305

The cuticle is one of the most important plant barriers. It is an external and continuous lipid membrane that covers the surface of epidermal cells and whose main function is to prevent the massive loss of water. The spectroscopic characterization of the plant cuticle and its components (cutin, cutan, waxes, polysaccharides and phenolics) by infrared and Raman spectroscopies has provided significant advances in the knowledge of the functional groups present in the cuticular matrix and on their structural role, interaction and macromolecular arrangement. Additionally, these spectroscopies have been used in the study of cuticle interaction with exogenous molecules, degradation, distribution of components within the cuticle matrix, changes during growth and development and characterization of fossil plants.

### Enhanced activity of clays and its crucial role for the activity in ethylene polymerization

Camejo-Abreu, C; Tabernero, V; Alba, MD; Cuenca, T; Terreros, P
*Journal of Molecular Catalysis A-Chemical*, **393** (2014) 96-104
November, 2014 | **DOI:** 10.1016/j.molcata.2014.05.030

This paper presents a study of the effects of different treatments on the polymerization activity of modified clays as cocatalysts. To achieve this goal, an intercalating cation was introduced into two smectites and these clays were then modified with trimethyl aluminium. The results for ethylene polymerization, when a zirconocene complex was used as catalyst, and the structure analysis, allow us to obtain interesting deductions about the generation mode of the active species. All active materials employed as support activators presented aluminium in a pentahedral environment together with acidic hydrogen atoms. These two features were detected only after TMA treatment and they seem to be crucial elements in active cocatalyst generation. Moreover, a material without structural aluminium displayed the best activity pointing to the new aluminium species generated in the solid matrix as the determining factor for the activity. We proposed a synergic effect between Lewis acid aluminium centres and acidic Bronsted protons that generate the SiOHAl groups that activate the zirconium compound.

### A new route of synthesis of Na-Mica-4 from sodalite

Naranjo, M; Castro, MA; Cota, A; Pavon, E; Pazos, MC; Alba, MD
*Microporous and Mesoporous Materials*, **188** (2014) 176-180
March, 2014 | **DOI:** 10.1016/j.micromeso.2013.12.004

Synthesis of Na-Mica-4 has been achieved by a “mix and calcine” method using sodalite and magnesium fluoride as the only precursors. Previous research found sodalite as a key intermediate reaction product in the formation of Na-Mica-4 when the NaCl melt method was employed. Similarities in structure, chemical composition and cation distribution in products using the proposed method and the NaCl melt method are described and suggest that Na-Mica-4 is a very stable product. The use of sodalite as precursor provokes microporous formation in the final mica. The absence of excess Na leads to a lower particle size and to the presence of less impurity in the calcined product. Different sodalites could be used in the synthesis of different Na-Mica-4 with presumably different physicochemical properties.

## Influence of the synthesis parameter on the interlayer and framework structure of lamellar octadecyltrimethylammonium kanemite

Corredor, JI; Cota, A; Pavon, E; Osuna, FJ; Alba, MD
*Applied Clay Science*, **95** (2014) 9-17
June, 2014 | **DOI:** 10.1016/j.clay.2014.02.030

Inorganic–organic nanostructures, used as host materials for selective adsorption of functional molecules and as mesostructured material precursors, can be constructed by the interlayer modification of inorganic layered materials with surfactants. The formation mechanism is mainly determined by the surfactant assemblies in the 2D limited space. In this paper, a detailed structural analysis of the lamellar mesophases prepared from kanemite, a lamellar silicate, and octadecyltrimethylammonium (ODTMA) under various conditions was reported. The adsorbed amount of ODTMA and the long and short range structural orders were explored by TGA, XRD, IR/FT and MAS NMR spectroscopies. The results revealed that ODTMA molecules were efficiently intercalated in the interlayer space of kanemite and, in all synthesis conditions, an ordered lamellar structure was obtained. The ODTMA adsorption in kanemite caused changes not only in the interlayer space but also in the silicate framework, where five-member rings were formed. The characteristics of the final products were influenced by the synthesis conditions, although the separation mode, filtration or centrifugation, was not relevant. Therefore, the adsorption conditions of ODTMA in kanemite will contribute to the design of novel layered materials with potential environmental and technological use.

## Quantification and comparison of the reaction properties of FEBEX and MX-80 clays with saponite: Europium immobilisers under subcritical conditions

Villa-Alfageme, M; Hurtado, S; Castro, MA; El Mrabet, S; Orta, MM; Pazos, MC; Alba, MD
*Applied Clay Science*, **101** (2014) 10-15
November, 2014 | **DOI:** 10.1016/j.clay.2014.08.012

The evaluation of the retention mechanisms in FEBEX and MX-80 bentonites, selected as reference materials to construct engineered barriers, carries major implications in the safe storage of immobilisation capacity through a recently discovered chemical retention mechanism and the structural analysis of the reaction products. Hydrothermal treatments were accomplished with immobilisation capacity through a recently discovered chemical retention mechanism and the structural analysis of the reaction products. Hydrothermal treatments were accomplished with $Eu(NO_3)_3$ (151Eu and 153Eu, with 52.2% 153Eu) and spiked with radioactive 152Eu for the quantification of the reactions. Results were compared with saponite as the reference smectite. The strong dependence of the reaction parameters with temperature and time was quantified and the reaction velocity was evaluated. The velocity follows these trends: 240 days are needed for the total retention of europium for temperatures over 200 °C; below 150 °C, significantly longer reaction times, on the order of three years, are required to complete the reaction. Clays do not influence velocity rates, but the retention capacity of bentonites remains lower than for saponite. At 300 °C, the milliequivalents retained by the three clays are consistently over CEC. The structural analyses reveal not only adsorption of europium but also the presence of $Eu(OH)_3$ precipitation and $Eu_2SiO_3$ confirming the existence of a chemical reaction.

### Characterization of porous graphitic monoliths from pyrolyzed wood

Gutierrez-Pardo, A; Ramirez-Rico, J; de Arellano-Lopez, AR; Martinez-Fernandez, J
*Journal of Materials Science*, **49** (2014) 7688-7696
November, 2014 | **DOI:** 0.1007/s10853-014-8477-8

Porous graphitic carbons were obtained from wood precursors using Ni as a graphitization catalyst during pyrolysis. The structure of the resulting material retains that of the original wood precursors with highly aligned, hierarchical porosity. Thermal characterization was performed by means of thermogravimetry and differential scanning calorimetry, and the onset temperature for graphitization was determined to be similar to 900 A degrees C. Structural and microstructural characterization was performed by means of electron microscopy, electron and x-ray diffraction, and Raman spectroscopy. The effect of maximum pyrolysis temperature on the degree of graphitization was assessed. No significant temperature effect was detected by means of Raman scattering in the range of 1000-1400 A degrees C, but at temperatures over the melting point of the catalyst, the formation of graphite grains with long-range order was detected.

### Competitive effect of the metallic canister and clay barrier on the sorption of $Eu^{3+}$ under subcritical conditions

El Mrabet, S; Castro, MA; Hurtado, S; Orta, MM; Pazos, MC; Villa-Alfageme, M; Alba, MD
*Applied Geochemistry*, **40** (2014) 25-31
January, 2014 | **DOI:** j.apgeochem.2013.10.014

An in depth knowledge and understanding of high activity radionuclide (HLRW) immobilization processes on the materials composing the engineered barrier (clay and metallic canister) is required to ensure the safety and the long-term performance of radioactive waste disposal procedures. Therefore, the aim of this study was to understand the mechanisms involved in the retention of $Eu^{3+}$ by two components of the multibarrier system, the bentonite barrier and the canister. As such, a comparative study of the interaction of trivalent $Eu^{3+}$, used to simulate trivalent actinides, with both bentonite and a metallic canister has been undertaken in this work. To this end, we designed a minireactor into which the bentonite was introduced and compacted. The minireactor-bentonite system was then submitted to a hydrothermal reaction with a $7.9 \times 10^{-2}$ M solution of $Eu^{3+}$ at 300 °C for 4.5 days. SEM and XRD results revealed that both bentonite and the container were involved in the immobilization of europium by the formation of insoluble europium silicate phases. The presence of europium silicate adsorbed on the surface of the metallic canister indicates the competitive effect of both components of the engineered barrier (bentonite and metallic canister) in HLRW immobilization. These results suggested that the canister could play a role in the HLRW immobilization even during its corrosion process.

### Effect of clays and metal containers in retaining $Sm^{3+}$ and $ZrO^{2+}$ and the process of reversibility

El Mrabet, S; Castro, MA; Hurtado, S; Orta, MM; Pazos, MC; Villa-Alfageme, M; Alba, MD
*American Mineralogist*, **99 (4)** (2014) 696-703
April, 2014 | **DOI:** 10.2138/am.2014.4665

Knowledge and understanding about radionuclides retention processes on the materials composing the engineered barrier (clay mineral and metallic container waste) are required to ensure the safety and the long-term performance of radioactive waste disposal. Therefore, the present study focuses on the competitiveness of clay and the metallic container in the process of adsorption/desorption of the radionuclides simulators of $Am^{3+}$ and $UO^{22+}$. For this purpose, a comparative study of the interaction of samarium (chosen as chemical analog for trivalent americium) and zirconyl (as simulator of uranyl and tetravalent actinides) with both FEBEX bentonite and metallic container, under subcritical conditions, was carried out. The results revealed that the AISI-316L steel container, chemical composition detailed in Table 1, immobilized the high-radioactive waste (HRW), even during the corrosion process. The $ZrO^{2+}$ was irreversibly adsorbed on the minireactor surface. In the case of samarium SEM/EDX analysis revealed the formation of an insoluble phase of samarium silicate on the container surface. There was no evidence of samarium diffusion through the metallic container. Samarium remained adsorbed by the container also after desorption experiment with water. Therefore, steel canister is actively involved in the HRW immobilization.

### Biomimetic polymers of plant cutin: an approach from molecular modeling

San-Miguel, MA; Oviedo, J; Heredia-Guerrero, JA; Heredia, A; Benitez, JJ
*Journal of Molecular Modeling*, **20** (2014) 2329
July, 2014 | **DOI:** 10.1007/s00894-014-2329-y

Biomimetics of materials is based on adopting and reproducing a model in nature with a well-defined functionality optimized through evolution. An example is barrier polymers that protect living tissues from the environment. The protecting layer of fruits, leaves, and non-lignified stems is the plant cuticle. The cuticle is a complex system in which the cutin is the main component. Cutin is a biopolyester made of polyhydroxylated carboxylic acids of 16 and 18 carbon atoms. The biosynthesis of cutin in plants is not well understood yet, but a direct chemical route involving the self-assembly of either molecules or molecular aggregates has been proposed. In this work, we present a combined study using experimental and simulation techniques on self-assembled layers of monomers selectively functionalized with hydroxyl groups. Our results demonstrate that the number and position of the hydroxyl groups are critical for the interaction between single molecules and the further rearrangement. Also, the presence of lateral hydroxyl groups reinforces lateral interactions and favors the bi-dimensional growth (2D), while terminal hydroxyl groups facilitate the formation of a second layer caused by head–tail interactions. The balance of 2D/3D growth is fundamental for the plant to create a protecting layer both large enough in 2D and thick enough in 3D.

### Effect of carbonization temperature on the microplasticity of wood-derived bio-carbon

Shpeizman, VV; Orlova, TS; Kardashev, BK; Smirnov, BI; Gutierrez-Pardo, A; Ramirez-Rico, J
*Physics of the Solid State*, **56** (2014) 538-545
March, 2014 | **DOI:** 10.1134/S1063783414030305

The uniaxial compression strength under stepped loading and the 325-nm-stepped deformation rate of biocarbon samples obtained by carbonization of beech wood at different temperatures in the 600–1600°C range have been measured using high-precision interferometry. It has been shown that the strength depends on the content of nanocrystalline phase in biocarbon. The magnitude of deformation jumps at micro- and nanometer levels and their variation with a change in the structure of the material and loading time have been determined. For micro- and nanometer-scale jumps, standard deviations of the differences between the experimentally measured deformation rate at loading steps and its magnitude at the smoothed fitting curve have been calculated, and the correlation of the error with the deformation prior to destruction has been shown. The results obtained have been compared with the previously published data on measurements of the elastic properties and internal friction of these materials.

### Thermal conductivity at the amorphous-nanocrystalline phase transition in beech wood biocarbon

Parfen'eva, LS; Orlova, TS; Smirnov, BI; Smirnov, IA; Misiorek, H; Jezowski, A; Ramirez-Rico, J
*Physica of the Solid State*, **56** (2014) 1071-1080
May, 2014 | **DOI:** 10.1134/S1063783414050229

High-porosity samples of beech wood biocarbon (BE-C) were prepared by pyrolysis at carbonization temperatures T carb = 650, 1300, and 1600°C, and their resistivity ρ and thermal conductivity κ were studied in the 5–300 and 80–300 K temperature intervals. The experimental results obtained were evaluated by invoking X-ray diffraction data and information on the temperature dependences ρ(T) and κ(T) for BE-C samples prepared at T carb = 800, 1000, and 2400°C, which were collected by the authors earlier. An analysis of the κ(T carb) behavior led to the conclusion that the samples under study undergo an amorphous-nanocrystalline phase transition in the interval 800°C < T carb < 1000°C. Evaluation of the electronic component of the thermal conductivity revealed that the Lorentz number of the sample prepared at T carb = 2400°C exceeds by far the classical Sommerfeld value, which is characteristic of metals and highly degenerate semiconductors.

## ■ LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS

### Libro Blanco de Prácticas tuteladas en el Grado en Farmacia

María del Mar Arroyo Jiménez;Guadalupe Beitia Berrotarán;Gema Blázquez Abellán;Fernando Caro Cano;María Falcón Romero;Ana Mª Fernández Olleros;Jesús Gastelut San Felipe;Rafael Giménez Martínez;Francisco González López;Mª Candelas Guinea López;Mª Candelas Guinea López;... Mª del Mar Orta Cuevas
Editorial CERSA – Compañía Española de Reprografía y Servicios, S.A., (España)
ISBN: Libro Blanco de Prácticas tuteladas en el Grado en Farmacia

**Nuevos Plásticos Biodegradables Inspirados en la Cutina Vegetal.**
J.A. Heredia-Guerrero, E. Domínguez, A. Heredia y J.J. Benítez.
Alimentaria. Investigación, Tecnología y Seguridad. Especial Monográfico "Tecnologías para el Packaging", pp. 50-53, marzo (2014).

**High-Temperature Mechanical Behavior of Hard Ceramics**
J. Ramírez Rico y J. Martínez-Fernández
En: *Comprehensive Hard Materials, Vol. 2*, L. Llanes y V. Sarin
Elsevier, 2014

## ■ CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

### COMUNICACIONES / COMMUNICATIONS

**V Congreso Internacional de Educación Superior en Ciencias Farmacéuticas EDUSFARM 2014**
25 – 28 junio [Sevilla, España]

**Desarrollo de una rúbrica como sistema de evaluación de competencias de la asignatura "Química Analítica Aplicada" de grado en Farmacia**
Mª Teresa Morales Millán; Inmaculada Romero del Río; Dolores Hernanz Vila; Mª Ángeles Herrador Morillo; Mª Teresa Montaña González; Guillermina Galán Alfonso; Mª José Navas Sánchez; Ana Mª Jiménez Moreno; Mª del Mar Orta Cuevas; Diego L García González; Julia Martín Bueno; AgustÍn García Asuero
Póster

**Versatilidad de los Trabajos Fin de Grado vinculados a la asignatura Prácticas Tuteladas**
Mª del Mar Orta Cuevas; Jose Manuel Vega Pérez; Ángeles Jos Gallego; Jesús Sanchez Bursón
Póster

## ■ CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESS AND MEETINGS

### COMUNICACIONES / COMMUNICATIONS

**XIII Congreso Nacional de Materiales**
18 – 20 junio [Barcelona, España]

**Microstructure of sintered SiC-fiber bonded ceramics brazed to metallic systems using Ag-Cu-Ti alloys**

M. Carmen Vera García; Stefano Rizzo; Valentina Casalegno; Milena; Salvo; Joaquín Ramírez-Rico; Julián Martínez-Fernández; Mrityunjay Singh
Póster

**VI Jornadas de I+D en gestión de residuos radiactivos**
11-13 Junio 2014 (Cuenca, España)

**Retención de actínidos y productos de fisión en arcillas y micas**
M.D. Alba
Conferencia invitada

## FORMACION / TRAINING

## FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

| | |
|---|---|
| **Título:** | **Evaluación de la capacidad de adsorción de silicatos laminares diseñados para la barrera de ingeniería de los almacenes de residuos radiactivos** |
| **Autor:** | Francisco Javier Osuna Barroso |
| **Directores:** | María Dolores Alba Carranza |
| **Grado:** | Trabajo Fin de Master |
| **Año Académico:** | 2013-2014 (27 junio 2014) |

## DOCENCIA / TEACHING

**Resonancia Magnética Nuclear en Estado Sólido**
**Silicatos de Elementos de Tierras Raras**
Dra. M. Dolores Alba Carranza
**Lugar:** Curso de Postgrado del CSIC. Instituto de Cerámica y Vidrio

## ESTANCIAS Y VISITAS DE PERSONAL DEL ICMS EN OTROS CENTROS
## PERSONNEL OF THE ICMS IN OTHER LABORATORIES

Dr. Joaquín Ramírez Rico. Visiting Scholar en el departamento Applied Physics and Applied Mathematics, Columbia University, New York, USA. Desarrollo de técnicas in-situ de análisis de tensiones mecánicas en materiales férreos. Supervisor: Ismail C. Noyan.

## ESTANCIAS Y VISITAS DE INVESTIGADORES EN EL ICMS
## PERSONNEL OF THE OTHER LABORATORIES IN THE ICMS

Sante Durastante, Ingeniero Industrial por la Universidad Dell´Aquila (Italia). Alumno del programa Leonardo da Vinci Mobility auspiciado por la Comunidad Europea. Inicio: 12/05/2014 – final: 26/10/2014

## 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

## PERSONAL / PERSONNEL

**Catedráticos**

Dr. Juan Poyato Ferrera

**Investigadores Científicos**

Dr. Angel Justo Erbez
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. María Jesús Sayagués de Vega

**Profesores Titulares**

Dra. María Dolores Alcalá González

**Profesor Vinculado "Ad Honorem"**

Dr. José Manuel Criado Luque
Dr. José Luis Pérez Rodríguez

**Investigadores Contratados**

Dra. María Regla Ayala Espinar
Dr. José Manuel Córdoba Gallego
Dr. Pedro E. Sánchez Jiménez

**Becarios Predoctorales**

Lda. Cristina García Garrido
Lda. Eva Gil González

**Personal Contratado**

Lda. M. Rocío Rodríguez Laguna

## PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

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

### Diseño por procedimientos mecanoquímicos de materiales estructurales para aplicaciones tecnológicas de alta temperatura
### Mechanochemical design of structural materials for high-temperature technological applications

Código/Code: MAT2011-22981
Periodo/Period: 01-01-2012 / 31-12-2014
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 80.000 €
Investigador responsable/Research head: Francisco J. Gotor Martínez
Componentes/Research group: M. Jesús Sayagués de Vega, Concepción Real Pérez, M. Dolores Alcalá González, Pedro José Sánchez Soto, José Manuel Córdoba Gallego, Ernesto Chicardi Augusto

RESUMEN / ABSTRACT

Los carburos, nitruros y boruros de los metales de transición son componentes esenciales de un gran número de materiales compuestos empleados para fines estructurales y de protección a altas temperaturas. Esto es debido a una excelente combinación de propiedades físicas y químicas que les confiere una buena resistencia mecánica, al desgaste, a la oxidación y a la corrosión. Los materiales basados en estos compuestos refractarios se vienen diseñando con un importante carácter multifásico, condicionado por la alta multifuncionalidad que se les exige y por la imposibilidad de alcanzar las propiedades requeridas a partir de un único compuesto.

Durante el procesado de estos materiales es frecuente observar importantes gradientes de composición e interacciones entre las distintas fases constitutivas que dificultan alcanzar las propiedades deseadas. En el presente proyecto, pretendemos abordar un nuevo diseño para este tipo de materiales consistente en incorporar la mayor parte de sus componentes esenciales como soluciones sólidas complejas. Esto permitirá reducir el número final de fases en el material y obtener con mayor garantía de éxito las propiedades preestablecidas para las diversas aplicaciones tecnológicas. Para ello, planteamos una nueva ruta de síntesis basada en el proceso mecanoquímico denominado reacción de auto-propagación inducida mecánicamente (MSR), ya que nuestro grupo ha demostrado que este método permite obtener de manera sencilla soluciones sólidas pertenecientes a los sistemas MT-B-C-N con un elevado control de la estequiometría. El objetivo principal del presente proyecto consiste en incorporar el método MSR a la metodología empleada para el desarrollo de materiales constituidos por soluciones sólidas que puedan ser utilizados en aplicaciones de alta temperatura. Se pretende caracterizar adecuadamente las propiedades de los materiales obtenidos y compararlas con aquellos fabricados con la metodología hasta ahora empleada.

Carbides, nitrides and borides of transition metals are essential components of a large number of composite materials used for structural and protective applications at high temperature because they show an excellent combination of physical and chemical properties, which confers good mechanical strength, and wear, oxidation and corrosion resistances. The materials based on these refractory compounds are designed by employing multiphasic systems, due to the high multi-functionality that are required and the inability to achieve the intended properties from a single phase material.

During the processing of these materials is common to observe important compositional gradients and interactions between the different constituent phases that hinder achieving the desired properties. In this project, we intend to undertake a new design for this type of material of incorporating most of its key components such as complex solid solutions. This will reduce the final number of phases in the material and obtain greater assurance of success with the preset properties for technological applications. To this end, we propose a new synthesis route based on the mechanochemical process called as mechanically-induced self-sustaining reaction (MSR). Our research group has shown that this method allows obtaining solid solutions belonging to M-B-C-N systems with a high control of the stoichiometry. The main objective of this project is to incorporate the method MSR to the methodology used for the development of materials consisting of solid solutions that can be used in high temperature applications. It is intended to adequately characterize the properties of the developed materials and to compare them with those made using the methods so far employed.

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## Procesado de cerámicas avanzadas a partir de precursores poliméricos (PDC) por métodos de control inteligente de la temperatura Processing of advanced ceramics from polymeric precursors by smart temperature methods

| | |
|---|---|
| Código/Code: | CQT2011-27626 |
| Periodo/Period: | 01-01-2012 / 31-12-2014 |
| Organismo Financiador/Financial source: | Ministerio de Ciencia e Innovación |
| Importe total/Total amount: | 66.550 € |
| Investigador responsable/Research head: | Luis A. Pérez Maqueda |
| Componentes/Research group: | Maria Jesús Diánez, José Manuel Criado, Pedro E. Sánchez Jiménez, Antonio Perejón Pazo |

### RESUMEN / ABSTRACT

Los materiales cerámicos preparados a partir de precursores poliméricos, más conocidos por las siglas PDC (polymer derived ceramics), constituyen un tema de gran interés actual. Estos materiales se preparan a partir de un polímero, que se somete a un proceso de curado previo a su descomposición térmica a temperaturas relativamente suaves si se comparan con las requeridas en un procesado cerámico convencional a partir de precursores en polvo. Este método presenta la ventaja de conducir directamente al producto final consolidado sin requerir el complejo proceso de compactación requerida por los métodos convencionales de proce-

sado cerámico. Es por lo tanto un método "near-net shape". Estos materiales presentan propiedades eléctricas, termomecánicas y de resistencia a la oxidación muy interesantes que le confieren un amplio potencial de aplicaciones que abarcan desde la nanotecnología a la aeronáutica. Sin embargo, una limitación importante en la síntesis de estos materiales radica en la dificultad de controlar la velocidad de descomposición térmica de la pieza precerámica polimérica de modo que no se produzcan defectos, tales como fracturas, que hacen inservible el material. En este proyecto se propone el uso de los métodos de control inteligente de temperatura para el procesado de estos precursores poliméricos precerámicos. En estudios previos hemos puesto de manifiesto las ventajas de esta metodología para controlar la estructura y microestructrura de productos preparados a partir de transformaciones térmicas de precursores y para estudios cinéticos de reacciones en estado sólido. Así mediante el uso de los métodos de control inteligente de temperatura pretendemos obtener PDC libres de defectos, estudiar la influencia de las condiciones de la preparación en la nanoestructura de los productos y ahondar en el conocimiento de los procesos de conversión polímero-cerámica, con especial hincapié en el estudio de las cinéticas de los procesos involucrados. Los productos obtenidos se caracterizarán en cuanto a su nanoestructura y propiedades, en particular el coeficiente piezoeléctrico, la capacidad de inserción de litio y la resistencia a la oxidación.

Ceramic materials prepared from polymer precursors, known as polymer-derived ceramics (PDC) are a subject of the most interest. These materials are prepared from a polymer that is first cured and then ceramified, usually by thermal treatment at relatively low temperature if compared with those needed in conventional ceramic processing from ceramic powders. Thus, the final product is directly obtained in a near-net shape process. These materials have very interesting electrical, thermomecanical and oxidation resistance properties. Thus, a number of applications from nanotechnology to aeronautics have been proposed. Nevertheless, a significant limitation of the use of these materials is is related with the ceramification process of the preceramic piece. During this thermal conversion, some defects, such as cracks, appear in the pieces. In this project, we propose the use of smart temperature controlled methods for the processing of the preceramic polymeric precursors. In previous studies, we have shown the advantages of this methodology for controlling the structure and microstructure of the products prepared by thermal transformation of precursors. In addition, this methodology is also useful for kinetic studies of solid state reactions. In the present project, we expect to obtain defect free PDC materials and to study the influence of the preparation conditions on the nanostructure of the products and get new insights in polymer to ceramic conversion process, paying special attention to the study of the kinetics of the involved processes. The so-obtained products will be characterized in terms of their nanostructure and properties, in particular piezoresistivity, lithium insertion capacity and oxidation resistance.

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

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|---|---|
| Código/Code: | P11-TEP-7858 (Proyecto de Excelencia) |
| Periodo/Period: | 16-05-2013 / 15-05-2017 |
| 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 Diánes 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.

JUNTA DE ANDALUCIA

## Síntesis y caracterización de materiales cerámicos no oxídicos obtenidos por descomposición de precursores poliméricos

## Synthesis and characterization of non oxide ceramic obtained by the thermal decomposition of polymeric precursors

Código/Code: TEP-1900
Periodo/Period: 16-05-2014 / 15-05-2016
Organismo Financiador/Financial source: Junta de Andalucía
Importe total/Total amount: 11.760 €
Investigador responsable/Research head: Pedro E. Sánchez Jiménez
Componentes/Research group: Antonio Perejón Pazo, Cristina García Garrido

RESUMEN / ABSTRACT

En los últimos años se ha incrementado sustancialmente el interés por las cerámicas derivadas de polímeros debido al amplísimo abanico de potenciales propiedades que presentan. Este tipo de cerámicas son más conocidas por las siglas PDC (polymer derived ceramics). Estos materiales se obtienen como producto de la descomposición térmica de un precursor polimérico, que deja como residuo una cerámica, habitualmente de naturaleza no oxídica, de tipo SiC, Si3N4, BN, etc. Las PDCs presentan una serie de propiedades termomecánicas y eléctricas de gran interés, así como una elevada resistencia a la temperatura y a la oxidación que los hacen muy adecuados para aplicaciones en condiciones extremas. Así, se han propuesto numerosas aplicaciones que abarcan desde la nanotecnología a la aeronáutica. Una importante ventaja es que dichas propiedades dependen en gran medida de las características químicas del precursor polimérico de partida así como del procedimiento de conversión en cerámica. Por tanto, es posible dirigir las propiedades de la cerámica final seleccionando cuidadosamente el precursor y las condiciones experimentales de ceramización. Además, las temperaturas necesarias para obtener materiales cerámicas por esta vía son relativamente suaves si se comparan con las necesarias mediante procesado cerámico convencional por consolidación de polvos cerámicos. Sin embargo, estos materiales presentan una limitación para ciertas aplicaciones debido a que durante la transformación en cerámica se producen defectos o fracturas que pueden llegar a hacer inservible el material. A pesar de su importancia, existen pocos estudios sistemáticos en los que se haya abordado la influencia de las condiciones de preparación en las propiedades finales de las cerámicas. En concreto, se planea utilizar los métodos de control inteligente de temperatura para el procesado de estos precursores poliméricos precerámicos. Esta metodología permite controlar con gran precisión las condiciones experimentales y ha demostrado ser muy útil para de controlar la estructura y microestructrura de productos preparados a partir de transformaciones térmicas de precursores. Así mediante el uso de los métodos de control inteligente de temperatura pretendemos obtener PDC libres de defectos, estudiar la influencia de las condiciones de la preparación en la nanoestructura de los productos y ahondar en el conocimiento de los procesos de conversión polímero-cerámica. Los productos obtenidos se caracterizarán en cuanto a su nanoestructura y propiedades, en particular la piezoresistividad, porosidad, capacidad de inserción de litio y la resistencia a la oxidación.

There has been a substantial interest during the last years in polymer derived ceramics due to the wide array of interesting properties they exhibit. This type of ceramic, best known by the acronym PDCs, are obtained by the thermal decomposition of a polymeric precursor and are mainly non oxidic, such as SiC, Si3N4, BN, etc. PDCs exhibit a wide array of thermomechanical and electrical properties of great interest, as well as a high thermal and oxidation resistance which make them promising candidates for working under extreme environmental conditions. Thus, several potential applications ranging from nanotechnology to aeronautics have been proposed. A big advantage of these materials is that their properties depend on both the chemical properties of the original polymeric precursor and the processing conditions. Therefore, by carefully selecting the precursor and the experimental degradation conditions it would be possible to tailor the properties of the final ceramic. Moreover, the temperatures needed to prepare these ceramics are much milder than those required by means of conventional ceramic processing or powder consolidation techniques. However, there is an important disadvantage that has severely limited their usability in that cracks are formed during the transformation into a ceramic so that the final pieces might be rendered unusable. Despite the important of processing, there are few systematic studies assessing the influence of ceramification conditions on the final properties. In this proposal, we plan to use smart temperature controlled methods to study the synthesis of different types of PDC. This methodology allows for great precision in the control of experimental conditions such as temperature and gas pressure and has been previously proved useful to help control the microstructure of materials synthesized by thermal transformations from precursors. Thus, we plan to use this methodology to synthesise defect-free PDCs and to study the influence of experimental conditions on the nanostructure and properties of the final ceramic material. At the same time, the information provided by the systematic study will help to better comprehend the underlying physics of the as yet poorly understood polymer-ceramic transformation. The prepared powders will be characterised in terms of nanostructure and properties such of piezoresistivity, porosity, lithium insertion capability and oxidation resistance.

## Nanogeneradores ferroeléctricos basados en polímeros para aplicaciones en generación de energía y sensores Ferroelectric polymer-based piezoelectric nanogenerators for energy harvesting and sensor applications

| | |
|---|---|
| Periodo/Period: | 01-10-2014 / 30-09-2016 |
| Organismo Financiador/Financial source: | Junta de Andalucía /Unión Europea |
| Importe total/Total amount: | 152.498 € |
| Investigador responsable/Research head: | Pedro E. Sánchez Jiménez |

RESUMEN / ABSTRACT

La generación de energía a partir de fuentes ambientales ha generado un enorme interés pues ofrece una slución energética para aplicaciones de bajo consumo tales como sensores inalámbricos, dispositivos portátiles, implantes biomédicos o dispositivos de monitorización estructural o medioambiental. Por ejemplo, se considera que el número de dispositivos de uso diario conectados a internet se estima 50.000 millones para el año 2020. La mayoría de estos dispositivos (“internet of things”) son de un tamaño muy reducido o se encuentran integrados en otros equipos mayores. La manera más sostenible de proporcionar energía a estos dispositivos es la autogeneración, de tal manera que no sea necesario recargarlos durante toda su vida útil. En este sentido, la generación de energía a partir de vibraciones ambientales es particularmente atractiva pues es una fuente de disponibilidad casi ilimitada y extraordinariamente barata al producirse por fuentes tales como las partes móviles de equipos, fluidos o incluso personas. Los generadores piezoeléctricos de escala nanométrica, también conocidos como nanogeneradores, son capaces de convertir vibraciones a pequeña escala en energía eléctrica, y por tanto son candidatos para reemplazar baterías que requieran una recarga constante, las cuales no se redimensionan con facilidad a muy pequeño tamaño La generación de energía mediante nanogeneradores piezoeléctricos es una tecnología emergente y esta propuesta se basa en la preparación de materials novedosos polímero-cerámica con propiedades piezoeléctricas que puedan utilizarse para diseñar dispositivos baratos, medioambientalmente limpios y que se puedan integrar fácilmente como nanogeneradores en dispositivos electrónicos.

Harvesting energy from ambient sources in our environment has generated tremendous interest as it offers a fundamental energy solution for small-power applications including, but not limited to, ubiquitous wireless sensor nodes, portable, flexible and wearable electronics, biomedical implants and structural/environmental monitoring devices. As an example, consider that the number of smart devices linking everyday objects via the internet is estimated to grow to 50 billion by the year 2020. Most of these “Internet of Things” devices will be extraordinarily small and in many cases embedded, and will wirelessly provide useful data that will make our lives easier, better and more energy-efficient. The only sustainable way to power them is using ambient energy harvesting that lasts through the lifetime of the product, and hence the need for commercially viable small scale energy harvesters that can operate in any environment. In this context, energy harvesting from ambient vibrations is particularly attractive, as these are ubiquitously available and easily accessible, originating from ever-present

sources such as the moving parts of devices and machines, fluid flow and even body movements. Nanoscale piezoelectric energy harvesters, also known as nanogenerators2, are capable of converting small-scale vibrations into electrical energy, thus offering a means of superseding batteries that require constant replacing/recharging, and that do not scale easily with size. Nanogenerators can thus pave the way for the realization of the next generation of self-powered electronic devices, with profound implications in disciplines as far-reaching as biomedicine, robotics, smart environmental monitoring and resource management, to name a few. Nano-piezoelectric energy harvesting is an emerging technology and this proposal is designed to tackle the challenge of developing novel materials with enhanced piezoelectric properties that are cheap, environment-friendly, bio-compatible and easily integrated as nanogenerators into electronic devices.

## Convenios y Contratos / Contracts and Agreements

### Composol-Desarrollo de nuevos componentes para la tecnología solar cilindro parabólico para muy altas temperaturas

| | |
|---|---|
| Código/Code: | 20124462 |
| Periodo/Period: | 25-11-2011 / 24-02-2015 |
| Organismo Financiador/Financial source: | Proyectos e Implantación de Tuberias, SA |
| Importe total/Total amount: | 319.440 € |
| Investigador responsable/Research head: | Luis A. Pérez Maqueda |
| Componentes/Research group: | Pedro E. Sánchez Jiménez, M. Jesús Diánez Millán, José Manuel Criado Luque, Enrique Jiménez Roca, M. Carmen Jiménez de Haro |

### Desarrollo de un receptor cerámico de alta temperatura y presión para sistemas solares híbridos (“CERSOL”)

| | |
|---|---|
| Código/Code: | 20135212 |
| Periodo/Period: | 26-04-2013 / 31-12-2014 |
| Organismo Financiador/Financial source: | Abengoa Solar New Technologies, S.A. |
| Importe total/Total amount: | 278.300 € |
| Investigador responsable/Research head: | Luis A. Pérez Maqueda |
| Componentes/Research group: | Pedro E. Sánchez Jiménez, M. Jesús Diánez Millán, José Manuel Criado Luque, Antonio Perejón Pazo, Cristina García Garrido, M. Rocio Rodríguez Laguna |

### Nuevo concepto de planta de torre con fluidos a muy alta temperatura y mayores rendimientos de ciclo respecto a los actuales

| | |
|---|---|
| Código/Code: | 20135581 |
| Periodo/Period: | 09-04-2013 / 31-12-2014 |
| Organismo Financiador/Financial source: | Abengoa Research, S.L. |
| Importe total/Total amount: | 42.350 € |

| | |
|---|---|
| Investigador responsable/Research head: | Luis A. Pérez Maqueda |
| Componentes/Research group: | Pedro E. Sánchez Jiménez, M. Jesús Diánez Millán, José Manuel Criado Luque, Cristina García Garrido, M. Rocio Rodríguez Laguna |

## PATENTES / PATENTS

### Procedimiento post-sintesis de modificación de la superficie de nanopartículas superparamagnéticas de óxidos de hierro

Inventores: María Jesús Sayagués de Vega
Tipo de Patente: Nacional
Número de Solicitud: 201430524
Fecha Solicitud: 9 Septiembre 2014
Entidad/es Titular/es: CSIC y Universidad Pablo de Olavide

## MODELO DE UTILIDAD

### Procedimiento para la evaluación del potencial de rehabilitación del Patrimonio Arquitectónico popular mediante una herramienta informática

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## ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

### Chemical and electrical properties of LSM cathodes prepared by mechanosynthesis

Moriche, R.; Marrero-López, D.; Gotor, F.J.; Sayagués, M.J.
*Journal of Power Sources*, **252** (2014) 43-50
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Mechanosynthesis of La1−xSrxMnO3 (x = 0, 0.25, 0.5, 0.75 and 1) was carried out at room temperature from stoichiometric mixtures of $La_2O_3$, $Mn_2O_3$ and SrO, obtaining monophasic powders with the perovskite structure. Physical properties of these materials and their chemical compatibility with the electrolyte yttria stabilized zirconia (YSZ), which depend strongly on the La/Sr ratio, were evaluated to corroborate availability to be implemented as cathode material in solid oxide fuel cells (SOFCs). Electrical conductivity values in air ranged between 100 and 400 S $cm^{-1}$ in the temperature range of 25–850 °C. Samples presented low reactivity with YSZ in the working temperature range (600–1000 °C) maintaining the grain size small enough to preserve the catalytic activity for oxygen reduction.

### Calcium-looping for post-combustion $CO_2$ capture. On the adverse effect of sorbent regeneration under $CO_2$

Valverde, JM; Sanchez-Jimenez, PE; Perez-Maqueda, LA
*Applied Energy*, **126** (2014) 161-171
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The multicyclic carbonation/calcination (c/c) of CaO solid particles at high temperature is at the basis of the recently emerged Calcium-looping (CaL) technology, which has been shown to be potentially suitable for achieving high and sustainable post-combustion $CO_2$ capture efficiency. Despite the success of pilot plant projects at the MWth scale, a matter of concern for scaling-up the CaL technology to a commercial level (to the GWth scale) is that the CaO carbonation reactivity can be recovered only partially when the sorbent is regenerated by calcination at high temperatures (around 950 °C) as required by the $CO_2$ high concentration in the calciner. In order to reactivate the sorbent, a novel CaL concept has been proposed wherein a recarbonator reactor operated at high temperature/high $CO_2$ concentration leads to further carbonation of the solids before entering into the calciner for regeneration. Multicyclic thermogravimetric analysis (TGA) tests demonstrate the feasibility of recarbonation to reactivate the sorbent regenerated at high calcination temperatures yet at unrealistically low $CO_2$ partial pressure mainly because of technical limitations concerning low heating/cooling rates. We report results from multicyclic c/c and carbonation/recarbonation/calcination (c/r/c) TGA tests at high heating/coling rates and in which the sorbent is regenerated in a dry atmosphere at high $CO_2$ partial pressure. It is shown that at these conditions there is a drastic drop of CaO conversion to a very small residual value in just a few cycles. Moreover, the introduction of a recarbonation stage has actually an adverse effect. Arguably, $CaCO_3$ decomposition in a $CO_2$ rich atmosphere is ruled by $CO_2$ dynamic adsorption/desorption in reactive CaO (1 1 1) surfaces as suggested by theoretical studies, which would preclude the growth of the regenerated CaO crystal structure along these reactive surfaces, and this effect would be intensified by recarbonation. Nevertheless, the presence of $H_2O$ in the calciner, which is also adsorbed/desorbed dynamically in CaO reactive planes, would shield $CO_2$ adsorption/desorption thus mitigating the deeply detrimental effect of $CO_2$ on the carbonation reactivity of the regenerated CaO structure. Oxy-combustion, which produces a significant amount of $H_2O$, is currently used in pilot-scale plants to raise the temperature in the calciner. Auxiliary techniques are being explored to help heating the partially carbonated solids since oxyxombustion represents an important penalty to the CaL technology. Our study suggests that steam injection would be necessary in a dry calciner environment to avoid a sharp loss of CaO conversion if the sorbent is regenerated at high $CO_2$ partial pressure.

### Nanosilica supported CaO: A regenerable and mechanically hard $CO_2$ sorbent at Ca-looping conditions

Sanchez-Jimenez, PE; Perez-Maqueda, LA; Valverde, JM
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This work presents a $CO_2$ sorbent that may be synthesized from low-cost and widely available materials following a simple method basically consisting of impregnation of a nanostructured silica support with a saturated solution of calcium nitrate. In a first impregnation stage, the use of a stoichiometric $CaO/SiO_2$ ratio serves to produce a calcium silicate matrix after calcination. This calcium silicate matrix acts as a thermally stable and mechanically hard support for CaO deposited on it by further impregnation. The CaO-impregnated sorbent exhibits a stable CaO conversion at Ca-looping conditions whose value depends on the CaO wt% deposited on the calcium silicate matrix, which can be increased by successive reimpregnations. A 10 wt% CaO impregnated sorbent reaches a stable conversion above 0.6 whereas the stable conversion of a 30 wt% CaO impregnated sorbent is around 0.3, which is much larger than the residual conversion of CaO derived from natural limestone (between 0.07 and 0.08). Moreover, particle size distribution measurements of samples predispersed in a liquid and subjected to high energy ultrasonic waves indicate that the CaO-impregnated sorbent has a relatively high mechanical strength as compared to limestone derived CaO.

### Role of precalcination and regeneration conditions on postcombustion $CO_2$ capture in the Ca-looping technology

Valverde, JM; Sanchez-Jimenez, PE; Perez-Maqueda, LA

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The Ca-looping (CaL) technology is already recognized as a potentially viable method to capture $CO_2$ from postcombustion gas in coal fired power plants. In this process, $CO_2$ is chemisorbed by CaO solid particles derived from precalcination of cheap and widely available natural limestone. The partially carbonated solids are regenerated by calcination under high $CO_2$ concentration. Novel CaL concepts are proposed to further improve the efficiency of the technology such as the introduction of a recarbonation reactor in between the carbonation and calcination stages to mitigate the progressive deactivation of the regenerated CaO. Process simulations aimed at retrieving optimum design parameters and operating conditions to scale-up the technology yield results critically dependent on the multicyclic sorbent performance. Nevertheless, technical limitations usually preclude lab-scale tests from mimicking realistic CaL conditions necessarily involving high $CO_2$ concentration for sorbent regeneration and quick transitions between carbonation and calcination. In this work, a lab-scale experimental analysis is reported on the CaO multicyclic conversion at CaL conditions closely resembling those to be expected in practice. The results presented evidence a relevant role of precalcination conditions. Precalcination in air leads to a strongly adverse effect on the activity of the sorbent regenerated under high $CO_2$ concentration, which is further hindered if a recarbonation stage is introduced. On the other hand, sorbent deactivation is mitigated if precalcination is carried out at conditions similar to those used for sorbent regeneration. In this case, recarbonation helps lessening the loss of multicyclic conversion, which is further enhanced by the synergistic combination with heat pretreatment. Moreover, the present study shows that the kinetics of carbonation is strongly dependent on precalcination and regeneration conditions. The diffusion controlled carbonation phase and recarbonation are intensified if the sorbent is precalcined and regenerated under high $CO_2$ concentration whereas the reaction controlled carbonation phase is notably hampered.

### Relevant Influence of Limestone Crystallinity on $CO_2$ Capture in The Ca-Looping Technology at Realistic Calcination Conditions

Valverde, JM; Sanchez-Jimenez, PE; Perez-Maqueda, LA
*Environmental Science & Technology*, **48** (2014) 9882-9889
August, 2014 | **DOI:** 10.1021/es5014505

We analyze the role of limestone crystallinity on its $CO_2$ capture performance when subjected to carbonation/calcination cycles at conditions mimicking the Ca-looping (CaL) technology for postcombustion $CO_2$ capture. The behavior of raw and pretreated limestones (milled and thermally annealed) is investigated by means of thermogravimetric analysis (TGA) tests under realistic sorbent regeneration conditions, which necessarily involve high $CO_2$ partial pressure in the calciner and quick heating rates. The pretreatments applied lead to contrasting effects on the solid crystal structure and, therefore, on its resistance to solid-state diffusion. Our results show that decarbonation at high $CO_2$ partial pressure is notably promoted by decreasing solid crystallinity. CaO regeneration is fully achieved under high $CO_2$ partial pressure at 900 °C in short residence times for the milled limestone whereas complete regeneration for raw limestone requires a minimum calcination temperature of about 950 °C. Such a reduction of the calcination temperature and the consequent mitigation of multicyclic capture capacity decay would serve to enhance the efficiency of the CaL technology. On the other hand, the results of our study suggest that the use of highly crystalline limestones would be detrimental since excessively high calcination temperatures should be required to attain full decarbonation at realistic conditions.

### The Mitigation Effect of Synthetic Polymers on Initiation Reactivity of CL-20: Physical Models and Chemical Pathways of Thermolysis

Yan, QL; Zeman, S; Jimenez, PES; Zhang, TL; Perez-Maqueda, LA; Elbeih, A
*Journal of Physical Chemistry C*, **118** (2014) 22881-22895
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In this paper, the thermal decomposition physical models of different CL-20 polymorph crystals and their polymer bonded explosives (PBXs) bonded by polymeric matrices using polyisobutylene (PIB), acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), Viton A, and Fluorel binders are obtained and used to predict the temperature profiles of constant rate decomposition. The physical models are further supported by the detailed decomposition pathways simulated by a reactive molecular dynamics (ReaxFF-lg) code. It has been shown that both ε-CL-20 and α-CL-20 decompose in the form of γ-CL-20, resulting in close activation energy (169 kJ $mol^{-1}$) and physical model (first-order autoaccelerated model, AC1). Fluoropolymers could change the decomposition mechanism of ε-CL-20 from the "first-order autocatalytic" model to a "three-dimensional nucleation and growth" model (A3), while the polymer matrices of Formex P1, Semtex, and C4 could change ε-CL-20 decomposition from a single-step process to a multistep one with different activation energies and physical models. Compared to fluoropolymers, PIB, SBR and NBR may make ε-CL-20 undergo more complete N–NO2 scission before collapse of the cage structure. This is likely the main reason why those polymer bases could greatly mitigate the decomposition process of ε-CL-20 from a single step

to a multistep, resulting in lower impact sensitivity, whereas fluoropolymers have only a little effect on that. For ε-CL-20 and its PBXs, the impact sensitivity depends not only on the heat built-up period of their decomposition, but also on the probability of hotspot generation (defects in solid crystals and interfaces) especially when it decomposes in a solid state.

### Thermal Stability of Multiferroic $BiFeO_3$: Kinetic Nature of the beta-gamma Transition and Peritectic Decomposition

Perejon, A; Sanchez-Jimenez, PE; Criado, JM; Perez-Maqueda, LA
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The thermal stability of $BiFeO_3$ prepared by mechanosynthesis and sintered at 850 °C has been studied by DSC as a function of the atmosphere and temperature. It has been found that neither the phase transitions nor the thermal stability of $BiFeO_3$ is affected by the atmosphere in which the heating process is performed. The material is unstable above the α–β transition (TC) and slowly decomposes to produce $Bi_2O_3$ and $Bi_2Fe_4O_9$. The kinetics of this slow process has been studied by performing heating–cooling DSC cycles, concluding it follows an Avrami–Erofeev nucleation and growth kinetic model. The β–γ transition and the peritectic decomposition of $BiFeO_3$ overlap and are kinetically controlled. The kinetics of this complex process has been studied for the first time employing a new kinetic analysis procedure implying the deconvolution and subsequent analysis of the individual contributing stages. Thus, it has been demonstrated that the decomposition of $BiFeO_3$ is accelerated when the sample is heated above the β–γ transition and both processes also follow Avrami–Erofeev kinetic models.

### Single phase, electrically insulating, multiferroic La-substituted $BiFeO_3$ prepared by mechanosynthesis

Perejon, A; Sanchez-Jimenez, PE; Perez-Maqueda, LA; Criado, JM; de Paz, JR; Saez-Puche, R; Maso, N; West, AR
*Journal of Materials Chemistry C*, **2** (2014) 8398-8411
October, 2014 | **DOI:** 10.1039/C4TC01426J

Single phase, electrically insulating samples of $Bi_{1-x}La_xFeO_3$ solid solutions have been prepared by mechanosynthesis over the whole compositional range for the first time. Lanthanum substitution influenced the kinetics of the mechanochemical reaction and crystallite size of the products. For $0 \leq x \leq 0.15$, an increase in the La content produced a significant decrease in the weight-normalized cumulative kinetic energy required to obtain the final product and an increase in the resulting crystallite size. Larger La contents did not affect either the reactivity or the crystallite size. The effect of x on the structure has been identified. Samples in the ranges $x \leq 0.15$ and $x \geq 0.45$ gave single phase solid solutions with R3c and Pnma space groups, respectively, while for the intermediate range, a non-centrosymetric Pn21a(00γ)s00 super structure was obtained. For $0 \leq x \leq 0.30$, differential scanning calorimetry showed two endothermic effects corresponding to the Néel temperature (TN, antiferromagnetic–paramagnetic transition) and the Curie temperature (TC, ferroelectric–paraelectric transition), demonstrating their multiferroic character. Compositions with a larger La content only showedTN. Dilatometric and permittivity measurements confirmed the results obtained by DSC for the ferroelectric–paraelectric transition. The composition dependence of TN and TC showed that, at low x, TN < TC, but a cross-over, or isoferroic transition occurred at x [[similar]] 0.28, when TN = TC = 386 °C. Ceramics with 0 ≤ x ≤ 0.15 were highly insulating at room temperature with a resistivity, extrapolated from the Arrhenius plots, of [[similar]] 7 × 1016 to 8 × 1014 Ω cm and an activation energy [[similar]] 1.14–1.20 eV. Magnetization of the samples improved with La substitution.

### The effect of polymer matrices on the thermal hazard properties of RDX-based PBXs by using model-free and combined kinetic analysis

Yan, QL; Zeman, S; Jimenez, PES; Zhao, FQ; Perez-Maqueda, LA; Malek, J
*Journal of Hazardous Materials*, **271** (2014) 185-195
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In this paper, the decomposition reaction models and thermal hazard properties of 1,3,5-trinitro-1,3,5-triazinane (RDX) and its PBXs bonded by Formex P1, Semtex 1A, C4, Viton A and Fluorel polymer matrices have been investigated based on isoconversional and combined kinetic analysis methods. The established kinetic triplets are used to predict the constant decomposition rate temperature profiles, the critical radius for thermal explosion and isothermal behavior at a temperature of 82 C. It has been found that the effect of the polymer matrices on the decomposition mechanism of RDX is significant resulting in very different reaction models. The Formex P1, Semtex and C4 could make decomposition process of RDX follow a phase boundary controlled reaction mechanism, whereas the Viton A and Fluorel make its reaction model shifts to a two dimensional Avrami-Erofeev nucleation and growth model. According to isothermal simulations, the threshold cook-off time until loss of functionality at 82 degrees C for RDX-C4 and RDX-FM is less than 500 days, while it is more than 700 days for the others. Unlike simulated isothermal curves, when considering the charge properties and heat of decomposition, RDX-FM and RDX-C4 are better than RDX-SE in storage safety at arbitrary surrounding temperature.

### Enhanced oxidation resistance of Ti(C,N)-based cermets containing Ta

Chicardi, E; Gotor, FJ; Cordoba, JM
*Corrosion Science*, **84** (2014) 11-20
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(TixTa1−x)(C0.5N0.5)–Co-based cermets with various Ta contents (x = 0, 0.01, 0.05, 0.1 and 0.2) were oxidized at 900 °C for 48 h in static air. A parabolic rate law, which is indicative of the formation of a protective oxide layer, was observed for all samples. The multi-layered oxide scale and the internal oxidation region that formed as the oxidation progressed toward the interior of the cermet specimens were characterized using XRD, SEM and EDS. The enhanced oxidation resistance achieved in cermets composed by a hard component with stoichiometry Ti0.95Ta0.05C0.5N0.5 may satisfy the optimal requirements for many applications in the field of cutting tools.

### High and stable $CO_2$ capture capacity of natural limestone at Ca-looping conditions by heat pretreatment and recarbonation synergy

Valverde, JM; Sanchez-Jimenez, PE; Perez-Maqueda, LA
*Fuel*, **123** (2014) 79-85
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The Ca-looping (CaL) process, based on the multicyclic carbonation/calcination of limestone derived CaO, has emerged recently as a potentially economically advantageous technology to achieve sustainable postcombustion and precombustion $CO_2$ capture efficiencies. Yet, a drawback that hinders the efficiency of the CaL process is the drastic drop of limestone capture capacity as the number of carbonation/calcination cycles is increased. Precalcination of limestone at high temperatures for a prolonged period of time has been proposed as a potential technique to reactivate the sorbent, which is however precluded by regeneration temperatures above 850 degrees C and low $CO_2$ concentrations in the carbonator to be found in the practical situation. Under these conditions, heat pretreatment leads to a stable yet very small CaO conversion. On the other hand, the introduction of a recarbonation stage between the ordinary carbonation and calcination stages has been shown to decelerate the rate of sorbent activity decay even though this favorable effect is not noticeable up to a number of above 10-15 cycles. The present manuscript demonstrates that the synergetic action of heat pretreatment and recarbonation yields a high and stable value for the multicyclic conversion of limestone derived CaO. It is foreseen that recarbonation of heat pretreated limestone would lead to a reduction of process costs especially in the case of precombustion applications. Even though sorbent purging will always be needed because of ash accumulation and sul-phation in postcombustion $CO_2$ capture applications, the stable and high multicyclic CaO conversion achieved by the combination of these techniques would make it necessary to a lesser extent.

### Multicyclic conversion of limestone at Ca-looping conditions: The role of solid-sate diffusion controlled carbonation

Sanchez-Jimenez, PE; Valverde, JM; Perez-Maqueda, LA
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Limestone derived CaO conversion when subjected to multiple carbonation/calcination cycles is a subject of interest currently fueled by several industrial applications of the so-called Ca-looping (CaL) technology. The multicyclic CaO conversion at Ca-looping conditions exhibits two main features as demonstrated by thermogravimetric analysis (TGA). On one hand, carbonation occurs by two well differentiated phases: a first kinetically-driven fast phase and a subsequent much slower solid-state diffusion controlled phase. On the other, carbonation in the fast phase usually shows a drastic decay with the cycle number along the first carbonation/calcination cycles. This trend can be reversed by means of heat pretreatment, which induces a marked loss of fast conversion in the first carbonation but enhances diffusion of $CO_2$ in the solid. Upon decarbonation the regenerated CaO skeleton displays an increased conversion in the fast carbonation phase of the next cycle, a phenomenon which has been referred to as reactivation. Nonetheless, sorbent reactivation is hampered by looping carbonation/calcination conditions as those to be likely found in practice such as carbonation stages characterized by low $CO_2$ concentrations and short duration and calcination stages at high temperatures in a $CO_2$ enriched atmosphere, which causes a sintering and loss of activity of the regenerated CaO skeleton. We analyze in this work sorbent reactivation as affected by heat pretreatment and carbonation/calcination conditions. Aimed at shedding light on the role played by these conditions on reactivation we look separately at the multicyclic evolution of conversion in the kinetic and diffusive phases. Generally, the evolution of multicyclic conversion after the first cycle can be described by a balance between the surface area gain due to diffusive carbonation and the surface area loss as caused by sintering in the calcination stage. A significant gain of relative surface area after the first cycle, which is favored by harshening the heat pretreatment conditions, leads however to a marked decay of it during subsequent cycles, which precludes reactivation for an extended interval of cycles. On the other hand, sorbent grinding, if performed before heat pretreatment, leads to a less marked but more sustainable reactivation along the cycles. A novel observation reported in our work is that pretreatment of limestone in a $CO_2$ atmosphere leads upon a subsequent quick decarbonation to a CaO skeleton with extraordinarily enhanced reactivity in the kinetically-driven carbonation phase and with a high resistance to solid-state diffusion, which can be attributed to annealing of the crystal structure as reported by independent studies.

### Analysis on the mechanical strength of WC-Co cemented carbides under uni-axial and biaxial bending

Torres, Y; Bermejo, R; Gotor, FJ; Chicardi, E; Llanes, L
*Materials & Design*, **55** (2014) 851-856
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The mechanical strength of three WC-Co grades was determined and compared under uniaxial and biaxial bending. Uniaxial four-point bending was conducted on bar-shaped specimens; biaxial testing was performed on discs using the ball-on-three-balls (B3B) method. Strength results were analysed within the frame of the Weibull theory. Differences in characteristic strength between uniaxial and biaxial bending were explained as an effect of the effective surface tested in each case. A higher Weibull modulus was obtained in one grade, independent of the testing method, which was related to its higher fracture toughness. The use and validity of the B3B biaxial test to determine the strength distribution of cemented carbides is discussed.

### Effect of tantalum content on the microstructure and mechanical behavior of cermets based on (TixTa1−x)(C0.5N0.5) solid solutions

Chicardi, E; Torres, Y; Cordoba, JM; Hvizdos, P; Gotor, FJ
*Materials & Design*, **53** (2014) 435-444
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Titanium–tantalum carbonitride, (Ti, Ta)(C, N), based cermets with different Ti and Ta contents were prepared using a mechanically induced self-sustaining reaction and then densified using a pressureless sintering process. Complete microstructural and mechanical characterizations were performed on the materials, which revealed that the size of the carbonitride ceramic particle was significantly reduced when the Ta content was increased. The flexural strength and fracture toughness were measured using the ball on three balls test and the indentation microfracture test, respectively. The strength profile was analyzed under the framework of Weibull theory. The change in the mechanical properties as a function of the Ta content was correlated with the normalized microstructural parameters, such as the binder mean free path. The decrease in toughness and flexural strength was attributed to the presence of intermetallic compounds in the binder phase, which was also corroborated by the nanoindentation tests.

### Processing and characterisation of cermet/hardmetal laminates with strong interfaces

Gotor, FJ; Bermejo, R; Cordoba, JM; Chicardi, E; Medri, V; Fabbriche, DD; Torres, Y
*Materials & Design*, **58** (2014) 226-233
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Cemented carbides and cermets are potential materials for high speed machining tools. However, cemented carbides are not chemically stable at high temperature and cermets present poor fracture toughness. Novel cermet/hardmetal multilayer systems show a huge potential for this intended application. It would be possible to achieve the right balance of the required thermomechanical properties using cermet as temperature protective outer layers and hardmetal as reinforcement layers. In this work, preliminary results on the microstructural and mechanical characterisation of a multilayer TiCxN1−x–Co/WC–Co composite densified by hot pressing are presented, with special attention to the properties of the interface. Microstructural observations revealed the existence of strong bonding interfaces between cermet and hardmetal layers due to chemical interaction during the sintering process. As a consequence, owing to the different coefficient of thermal expansion between cermet and hardmetal, a tensile and compressive biaxial residual stress of σres,Cermet ≈ +260 ± 50 MPa and σres,WC–Co ≈ −350 ± 70 MPa was estimated in the corresponding layers. Microindentation cracks introduced in the cermet layers (the less toughness material) and propagated transversely to the layers were arrested at the interface, showing the combined effect of toughness and compressive stresses on crack shielding.

### Characterization of thermally stable gamma alumina fibres biomimicking sisal

Benitez-Guerrero, M; Perez-Maqueda, LA; Sanchez-Jimenez, PE; Pascual-Cosp, J
*Microporous and Mesoporous Materials*, **185** (2014) 167-178
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Mesoporous gamma alumina fibres of high surface area, stable up to 1000 °C, were synthesized by bioreplica technique using sisal fibres as templates. Alumina formation during pyrolysis and calcination of fibres infiltrated with aluminium chloride solution has been studied, paying special attention to the interaction between the precursor and sisal fibres, using several experimental techniques such as ATR-FTIR, coupled TG-FTIR and thermo-XRD analysis. The morphology and microstructure of the resulting alumina fibres were characterized using SEM and TEM. The crystallographic analysis of the alumina sample performed by electron and X-ray diffraction suggests that fibres are constituted by η and γ-$Al_2O_3$ crystallites, whose chemical structure was confirmed by ATR-FTIR and $Al^{27}$-MAS-NMR.

The specific surface area and porosity of ceramic fibres were determined by $N_2$ and $CO_2$ adsorption–desorption measurements. Resulting alumina fibres retain high specific surface areas of 200 and 150 $m^2/g$ even after calcination at 1000 °C for 15 h in dry air and for 4 h in wet air, respectively.

### Understanding the Role of the Cosolvent in the Zeolite Template Function of Imidazolium-Based Ionic Liquid

Ayala, R; Ivanova, S; Blanes, JMM; Romero-Sarria, F; Odriozola, JA
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April, 2014 | **DOI:** 10.1021/jp410260g

In this work, a study for understanding the role played by [ClBmim], [$BF_4$Bmim], [$PF_6$Bmim], and [$CH_3SO_3$Bmim] ionic liquids (ILs) in the synthesis of zeolites is presented. The use of [ClBmim] and [$CH_3SO_3$Bmim] ILs, as reported earlier [ Chem. Eur. J. 2013, 19, 2122] led to the formation of MFI or BEA type zeolites. Contrary, [BF4Bmim] and [PF6Bmim] ILs did not succeed in organizing the Si–Al network into a zeolite structure. To try to explain these results, a series of quantum mechanical calculations considering monomers ([XBmim]) and dimers ($[XBmim]_2$) by themselves and plus cosolvent (water or ethanol) were carried out, where $X \equiv Cl^-$, $BF_4^-$, $PF_6^-$, or $CH_3SO_3^-$. Our attention was focused on the similarities and differences among the two types of cosolvents and the relation between the structure and the multiple factors defining the interactions among the ILs and the cosolvent. Although a specific pattern based on local structures explaining the different behavior of these ILs as a zeolite structuring template was not found, the calculated interaction energies involving the $Cl^-$ and $CH_3SO_3^-$ anions were very close and larger than those for $BF_4^-$ and $PF_6^-$ species. These differences in energy can be used as an argument to describe their different behavior as structure directing agents. Moreover, the topology of the cosolvent is also an ingredient to take into account for a proper understanding of the results.

### Enhanced general analytical equation for the kinetics of the thermal degradation of poly(lactic acid)/montmorillonite nanocomposites driven by random scission

Carrasco, F; Perez-Maqueda, LA; Santana, OO; Maspoch, ML
*Polymer Degradation and Stability*, **101** (2014) 52-59
March, 2014 | **DOI:** 10.1016/j.polymdegradstab.2014.01.014

An enhanced general analytical equation has been developed in order to evaluate the kinetic parameters of the thermal degradation of nanocomposites, composed of poly(lactic acid) (PLA) and organo-modified montmorillonite (OMMT) nanoparticles. This improvement has consisted of replacing the n-order conversion function by a modified form of the Sestak–Berggren equation f(α) = c (1 − α)nαm that led to a better adjustment of experimental data and also adequately represented the conventional mechanisms for solid-state processes. The kinetic parameters so obtained have been compared to those determined by conventional differential and isoconversional methods. Given that the thermal degradation of PLA has been argued to be caused by random chain scission reactions of ester groups, the conversion function f(α) = L (L − 1)x(1 − x)L−1, corresponding to a random scission mechanism, has been tested. Once optimized the kinetic model, the thermal degradation kinetics of nanocomposites (0.5 and 2.5% of OMMT) was compared to that of the polymer matrix. Moreover, the thermal stability of nanocomposites was tested and compared to that of the polymer matrix.

### Improvement of the thermal stability of branched poly(lactic acid) obtained by reactive extrusion

Carrasco, F; Cailloux, J; Sanchez-Jimenez, PE; Maspoch, ML
*Polymer Degradation and Stability*, **104** (2014) 40-49
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One-step reactive extrusion-calendering process (REX-calendering) has been used in order to obtain sheets of 1 mm from poly(lactic acid) modified with a styrene-acrylic multifunctional oligomeric agent. In a preliminary internal mixer study, torque versus time has been monitored in order to ascertain chain extender ratios and reaction time. Once all the parameters were optimized, reactive extrusion experiments have been performed. An enhanced general analytical equation has been developed in order to evaluate the kinetic parameters of the thermal degradation of PLA sheets manufactured by reactive extrusion. This improvement has consisted of replacing the n-order conversion function by a modified form of the Sestak–Berggren equation $f(\alpha) = c\ (1 - \alpha)n\alpha m$ that led to a better adjustment of experimental data and also adequately represented the conventional mechanisms for solid-state processes. The kinetic parameters so obtained have been compared to those determined by conventional differential methods and n-order reaction kinetics. Given that the thermal degradation of PLA has been argued to be caused by random chain scission reactions of ester groups, the conversion function $f(\alpha) = 2\ (\alpha 1/2 - \alpha)$, corresponding to a random scission mechanism for L = 2 (as well as other functions for L values up to 8), has been tested. Once optimized the kinetic model, the thermal degradation kinetics of sheets obtained by REX-calendering process was compared to that of conventional sheets and polymer matrix.

### An investigation on the formation mechanism of nano $ZrB_2$ powder by a magnesiothermic reaction

Jalaly, M; Bafghi, MS; Tamizifar, M; Gotor, FJ
*Journal of Alloys and Compounds*, **588** (2014) 36-41
March, 2013 | **DOI:** 10.1016/j.jallcom.2013.11.050

Nanocrystalline zirconium diboride ($ZrB_2$) powder was produced by mechanochemistry from the magnesiothermic reduction in the $Mg/ZrO_2/B_2O_3$ system. The use of high-energy milling conditions was essential to induce a mechanically induced self-sustaining reaction (MSR) and significantly reduce the milling time required for complete conversion. Under these conditions, it was found that the ignition time for $ZrB_2$ formation was only about a few minutes. In this study, the mechanism for the formation of $ZrB_2$ in this system was determined by studying the relevant sub-reactions, the effect of stoichiometry, and the thermal behavior of the system.

### Spinodal decomposition and precipitation in Cu–Cr nanocomposite

Sheibani, S; Heshmati-Manesh, S; Ataie, A; Caballero, A; Criado, JM

*Journal of Alloys and Compounds*, **587** (2014) 670-676
February, 2014 | DOI: 10.1016/j.jallcom.2013.11.019

In this study, spinodal decomposition and precipitation mechanism of mechanically alloyed supersaturated Cu–3wt.%Cr and Cu–5wt.%Cr solid solutions was investigated under nonisothermal aging. Decomposition mechanism and kinetics were studied using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. Also, the microstructure was characterized by transmission electron microscopy (TEM). Effect of $Al_2O_3$ reinforcement on the aging kinetics was also evaluated. It was found that Cu–3wt.%Cr and Cu–5wt.%Cr solid solutions undergo spinodal decomposition at initial stages of ageing. However, decomposition mechanism was changed to nucleation and growth by the aging progress. The aging kinetics for the Cu–Cr/$Al_2O_3$ composition appeared to be slightly faster than that for Cu–Cr, since the ageing activation energy is decreased in presence of $Al_2O_3$ nano-particles. This behavior is probably due to the higher dislocation density and other structural defects previously produced during ball milling. A detailed comparison of the DSC results with those obtained by TEM, showing good consistency, has been presented. The average size of Cr-rich precipitates was about 10 nm in the copper matrix.

### The role of boron oxide and carbon amounts in the mechanosynthesis of $ZrB_2$–SiC–ZrC nanocomposite via a self-sustaining reaction in the zircon/magnesium/boron oxide/graphite system

Jalaly, M; Bafghi, MS; Tamizifar, M; Gotor, FJ
*Journal of Alloys and Compounds*, **598** (2014) 113-119
June, 2014 | **DOI:** 10.1016/j.jallcom.2014.02.033

Herein, $ZrSiO_4/B_2O_3$/Mg/C system was used to synthesize a $ZrB_2$-based composite by means of a high energy ball milling process. A mechanically induced self-sustaining reaction was achieved in this system. A nanocomposite powder of $ZrB_2$–SiC–ZrC was prepared with an ignition time of approximately 6 min of milling. The role of the stoichiometric amounts of $B_2O_3$ and carbon was investigated to clarify the governing mechanism for the formation of the product.

### Effect of Heat Pretreatment/Recarbonation in the Ca-Looping Process at Realistic Calcination Conditions

Valverde, JM; Sanchez-Jimenez, PE; Perez-Maqueda, LA
*Energy & Fuels*, **27** (2014) 4062-4067
June, 2014 | **DOI:** 10.1021/ef5007325

Even though an increasing number of pilot-scale plants are demonstrating the potential efficiency of the Ca-looping technology to capture $CO_2$ at a commercial level, a still standing matter of concern is the loss of carbonation reactivity of the regenerated CaO by calcination, which is expected to be particularly marked at realistic conditions necessarily implying a high $CO_2$ partial pressure in the calciner. In this work, we address the effect of previously reported strategies for sorbent reactivation, namely heat pretreatment and the introduction of a recarbonation stage before regeneration. Both techniques, either combined or separately, are shown to favor the carbonation reactivity, albeit CaO regeneration is usually carried out at low $CO_2$ partial pressure in lab-scale tests. Novel results reported in this paper show the opposite when the sorbent is regenerated by calcination at high $CO_2$ concentration, which is arguably due to the diverse mechanisms that rule decarbonation depending on the $CO_2$ concentration in the calciner atmosphere. Dynamic and reversible adsorption/desorption of $CO_2$ is thought to govern decarbonation during calcination at high $CO_2$ partial pressure, which would be hindered by the introduction of a recarbonation stage before carbonation. Moreover, carbonation in the fast phase is severely hampered as a result of the marked loss of reactivity of the surface of CaO regenerated under high $CO_2$ partial pressure. On the other hand, heat pretreatment and harsh calcination conditions lead to a notable enhancement of diffusion, which would favor the process efficiency. In these conditions, diffusion controlled carbonation becomes a significant contribution to CaO conversion, which is notably increased by prolonging the carbonation stage. Heat pretreatment allows also reducing the calcination temperature at high $CO_2$ partial pressure while still achieving full decarbonation in short residence times.

## Wall paintings studied using Raman spectroscopy: A comparative study between various assays of cross sections and external layers

Perez-Rodriguez, JL; Robador, MD; Centeno, MA; Siguenza, B; Duran, A

*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **120** (2014) 602-609
February, 2014 | **DOI:** 10.1016/j.saa.2013.10.052

This work describes a comparative study between in situ applications of portable Raman spectroscopy and direct laboratory measurements using micro-Raman spectroscopy on the surface of small samples and of cross sections. The study was performed using wall paintings from different sites of the Alcazar of Seville.

Little information was obtained using a portable Raman spectrometer due to the presence of an acrylic polymer, calcium oxalate, calcite and gypsum that was formed or deposited on the surface. The pigments responsible for different colours, except cinnabar, were not detected by the micro-Raman spectroscopy study of the surface of small samples taken from the wall paintings due to the presence of surface contaminants.

The pigments and plaster were characterised using cross sections. The black colour consisted of carbon black. The red layers were formed by cinnabar and white lead or by iron oxides. The green and white colours were composed of green emerald or atacamite and calcite, respectively. $Pb_3O_4$ has also been characterised. The white layers (plaster) located under the colour layers consisted of calcite, quartz and feldspars. The fresco technique was used to create the wall paintings.

A wall painting located on a gypsum layer was also studied. The Naples yellow in this wall painting was not characterised due to the presence of glue and oils.

This study showed the advantage of studying cross sections to completely characterise the pigments and plaster in the studied wall paintings.

## Self-propagating combustion synthesis via an MSR process: An efficient and simple method to prepare (Ti, Zr, Hf)B2–Al2O3 powder nanocomposites

Sayagues, MJ; Aviles, MA; Cordoba, JM; Gotor, FJ
*Powder Technology*, **256** (2014) 244-250
April, 2014 | **DOI:** 10.1016/j.powtec.2014.02.031

The synthesis of $(Ti_{1-x}Zr_x)B_2$–$Al_2O_3$, $(Ti_{1-x}Hf_x)B_2$–$Al_2O_3$ and $(Zr_{1-x}Hf_x)B_2$–$Al_2O_3$ (x = 0, 0.5 and 1) powder nanocomposites via a mechanochemical method using $TiO_2$, $ZrO_2$, $HfO_2$, $HBO_2$ and Al as the raw materials was investigated. The formation of the nanocomposites proceeds via a mechanically-induced self-sustaining reaction (MSR) process that involves several simultaneous reactions. The aluminothermic reductions of the $TMO_2$ and $HBO_2$ produce $Al_2O_3$ and transition metal and boron elements, which in turn react to yield the diboride phase. The ignition of the complex combustion reaction occurred after a short milling time (15–30 min), instantly transforming most of the reactants into products. The sample composition was marked by the stoichiometry of the combustion reaction, and the resulting nanocomposites were analysed using XRD, ED, SEM, TEM and EDX techniques. The X-ray results confirmed the biphasic character of the prepared composite powder ($TMB_2$ and $Al_2O_3$ structures); minor amounts of the Zr and Hf oxides were also observed. The achieved microstructure was characterised by the agglomeration of $Al_2O_3$ nanocrystallites and diboride crystals with a diffraction domain size ranging between 100 and 300 nm.

## Study and restoration of the Seville City Hall façade

Robador, MD; Arroyo, F; Perez-Rodriguez, JL
*Construction and Building Materials*, **53** (2014) 370-380
February, 2014 | **DOI:** 10.1016/j.conbuildmat.2013.11.088

Before restoring the Seville City Hall façade, a study of the original materials and the compounds added or formed was performed. The stone is fine-grained carbonate rock. Gypsum and mortars were used to restore stone fragments. A black crust was also found the wall was covered with an acrylic resin. A layer of lime on the surface was also detected. The restoration was intended to preserve the artistic quality and uniqueness of this building. The cleaning, reinforcing and innovatively consolidating and protecting the stone using suitable materials similar to those used in the original construction are described in this study.

## CdSe@ZnS nanocomposites prepared by a mechanochemical route: No release of $Cd^{2+}$ ions and negligible in vitro cytotoxicity

Balaz, P; Sayagues, MJ; Balaz, M; Zorkovska, A; Hronec, P; Kovac, J; Kovac, J; Dutkova, E; Mojzisova, G; Mojzis, J
*Materials Research Bulletin*, **49** (2014) 302-309
January, 2014 | **DOI:** 10.1016/j.materresbull.2013.08.070

CdSe@ZnS nanocomposites have been prepared by a two-step solid state mechanochemical synthesis. CdSe prepared from Cd and Se elements in the first step was mixed with zinc acetate and sodium sulphide in the second step of milling to prepare a CdSe@ZnS nanocomposite. In the third step, the obtained nanocomposite was coated with l-cysteine to prepare a biocompatible system. The crystallite size of the new type of nanocomposite was 20–35 nm for cubic CdSe and 3–8 nm for hexagonal ZnS as calculated from XRD, TEM and SEM data. The synthesised samples show good crystallinity and have been tested for dissolution and cytotoxicity. The dissolution of cadmium from CdSe@ZnS was less than 0.05 µg $mL^{-1}$, whereas a value of 0.8 µg $mL^{-1}$ was measured for CdSe alone. The binding of ZnS with CdSe in the nanocomposite practically eliminated the release of cadmium into solution. As a consequence, a very low cytotoxic activity has been evidenced for CdSe@ZnS. The nanocomposites coated with l-cysteine have a great potential as fluorescent labels in biomedical engineering.

### Scission kinetic model for the prediction of polymer pyrolysis curves from chain structure

Perez-Maqueda, LA; Sanchez-Jimenez, PE; Perejon, A; Garcia-Garrido, C; Criado, JM; Benitez-Guerrero, M

*Polymer Testing*, **37** (2014) 1-5

August, 2014 | **DOI:** 10.1016/j.polymertesting.2014.04.004

There is a significant interest in correlating polymer structure with thermal degradation behavior. Thus, polymer pyrolysis curves could be predicted from the chemical structure of the polymer. Recent proposals correlate the kinetic temperature function directly with the chemical structure of the polymer by means of the dissociation energy while assuming a semi-empirical first order model for the reaction fraction function. However, a first order model lacks physical meaning and produces significant deviations of the predicted curves, mostly under isothermal conditions. Thus, in this work, an upgrade of the method is proposed by using a new random scission kinetic model. The newly proposed kinetic equation has been checked by fitting the experimental data reported by different authors for the thermal pyrolysis of polystyrene. It has been demonstrated that it accounts for the experimental data of polymer degradation under different heating schedules with considerably higher precision than the previously assumed first order kinetics.

### Comparison of thermal behavior of natural and hot-washed sisal fibers based on their main components: Cellulose, xylan and lignin. TG-FTIR analysis of volatile products

Benitez-Guerrero, M; Lopez-Beceiro, J; Sanchez-Jimenez, PE; Pascual-Cosp, J

*Thermochimica Acta*, **581** (2014) 70-86

April, 2014 | **DOI:** 10.1016/j.tca.2014.02.013

This paper presents in a comprehensive way the thermal behavior of natural and hot-washed sisal fibers, based on the fundamental components of lignocellulosic materials: cellulose, xylan and lignin. The research highlights the influence exerted on the thermal stability of sisal fibers by other constituents such as non-cellulosic polysaccharides (NCP) and mineral matter.

Thermal changes were investigated by thermal X-ray diffraction (TXRD), analyzing the crystallinity index (%Ic) of cellulosic samples, and by simultaneous thermogravimetric and differential thermal analysis coupled with Fourier-transformed infrared spectrometry (TG/DTA-FTIR), which allowed to examine the evolution of the main volatile compounds evolved during the degradation under inert and oxidizing atmospheres. The work demonstrates the potential of this technique to elucidate different steps during the thermal decomposition of sisal, providing extensible results to other lignocellulosic fibers, through the analysis of the evolution of $CO_2$, CO, $H_2O$, $CH_4$, acetic acid, formic acid, methanol, formaldehyde and 2-butanone, and comparing it with the volatile products from pyrolysis of the biomass components. The hydroxyacetaldehyde detected during pyrolysis of sisal is indicative of an alternative route to that of levoglucosan, generated during cellulose pyrolysis.

Hot-washing at 75 °C mostly extracts non-cellulosic components of low decomposition temperature, and reduces the range of temperature in which sisal decomposition occurs, causing a retard in the pyrolysis stage and increasing TbNCP and TbCEL, temperatures at the maximum mass loss rate of non-cellulosic polysaccharides and cellulose decompositions, respectively. However, enriching sisal fibers in cellulose produces a decrease of TbCEL under an oxidizing atmosphere, and furthermore, a delay of the combustion process, displacing TbCOM to higher temperatures.

The results and findings of the paper would help further understanding of thermal processes where Agave fibers are involved, as the decomposition of their composites.

### Properties of mechanochemically synthesized nanocrystalline $Bi_2S_3$ particles

Dutkova, E; Sayagues, MJ; Zorkovska, A; Real, C; Balaz, P; Satka, A; Kovac, J

*Materials Science in Semiconductor Processing*, **27** (2014) 267-272

November, 2014 | **DOI:** 10.1016/j.mssp.2014.05.057

Nanocrystalline $Bi_2S_3$ particles have been synthesized from Bi and S powders by high-energy milling in a planetary mill. Structural and microstructural characterization of the prepared particles, including phase identification, specific surface area measurement and particle size analysis has been carried out. The optical properties were measured by spectroscopic methods and the structural stability up to 500 °C was studied by thermal analysis. The production of orthorhombic $Bi_2S_3$ with crystallite size of about 26 nm was confirmed by X-ray diffraction. The nanocrystals tend to agglomerate due to their large specific surface area. Accordingly, the average hydrodynamic diameter of the mechanochemically synthesized particles is 198 nm. EDS analysis shows that the synthesized material is pure $Bi_2S_3$. The band gap of the $Bi_2S_3$ nanoparticles is 4.5 eV which is wider than that in bulk materials. The nanoparticles exhibit good luminescent properties with a peak centered at 490 and 390 nm. Differential scanning calorimetry curves exhibit a broad exothermic peak between 200 and 300 °C, suggesting recovery processes. This interpretation is supported by X-ray diffraction measurements that indicate a 10-fold increase of the crystallite size to about 230 nm. The controlled mechanochemical synthesis of $Bi_2S_3$ nanoparticles at ambient temperature and atmospheric pressure remains a great challenge.

### Mechanochemical Processing of $CaCu_3Ti_4O_{12}$ with Giant Dielectric Properties

Espinoza-Gonzalez, R; Vega, E; Tamayo, R; Criado, JM; Dianez, MJ

*Materials and Manufacturing Processes*, **29** (2014) 1179-1183

October, 2014 | **DOI:** 10.1080/10426914.2014.921702

The dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramic prepared by mechanochemical synthesis (MCS) were investigated. The effect on dielectric properties of ball-to-powder weight ratio and milling time was investigated and compared to the behavior of CCTO prepared by conventional solid state reaction (CSSR). CCTO ceramic was partially obtained after 6h of the milling process, while complete transformation was obtained during the sintering step of milled powders. It was shown that the dielectric properties of CCTO processed by MCS are dramatically improved compared with samples prepared by CSSR.

### Materials characteristics of Roman and Arabic mortars and stuccoes from The Patio de Banderas in the Real Alcazar of Seville (SPAIN)

Garofano, I; Robador, MD; Duran, A
*Archaeometry*, **56** (2014) 541-561
June, 2014 | **DOI:** 10.1111/arcm.12041

This study discusses the materials and traditional knowledge used in the manufacture and application of lime mortars and stuccoes by Romans and Arabs in Seville (southern Iberian Peninsula). All of the samples studied contain calcite as a binder, combined with aggregates based on river sand from the filling materials of the Guadalquivir River's depression, located in the vicinity of the Real Alcazar Palace in Seville, Spain, where the artefacts were discovered. The Romans used high-quality production technology, as evidenced by the careful selection of raw materials as well as by the adequate binder-to-aggregate ratio and the elevated homogeneity of the mortars and stuccoes. The suitable distribution of aggregates resulted in higher density values for Roman fragments than for Arabic ones. Results derived from Arabic samples suggest a decline in technology manufacture over time. This work provides useful information, particularly regarding the Roman and Arabic periods in the Iberian Peninsula. The analytical techniques employed in this study were X-ray diffraction (XRD), X-ray fluorescence (XRF)—using conventional and portable systems, scanning electron microscopy (SEM), petrographic microscopy, differential thermal analysis/thermogravimetry (DTA/TG), particle-size analysis and mercury intrusion porosimetry.

### Mineralogical Characterization of the Polychrome in Cultural Heritage Artifacts (Antiquity to Date) from Southern Spain Using Micro-Raman Spectroscopy and Complementary Techniques

Perez-Rodriguez, JL; Duran, A
*Spectroscopy Letters: An International Journal for Rapid Communication*, **47** (2014) 223-237
March, 2014 | **DOI:** 10.1080/00387010.2013.791857

This work reports on the use of micro-Raman spectroscopy for the characterization of materials used for producing the polychrome in cultural heritage artifacts from southern Spain. The micro-Raman technique was applied for the characterization of several types of artworks or for cross-sections from these works, which were produced along different historical epochs. This technique was demonstrated to be valuable for the characterization of compounds, which were all detected within the artworks studied. The identification of all of these compounds by micro-Raman was confirmed by other complementary techniques, such as micro-X-ray diffraction and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy.

### Mechanochemically synthesized nanocrystalline $Sb_2S_3$ particles

Dutkova, E; Sayagues, MJ; Real, C; Zorkovska, A; Balaz, P; Satka, A; Kovac, J; Ficeriova, J
*Acta Physica Polonica A*, **126** (2014) 943-946
October, 2014 | **DOI:** 10.12693/APhysPolA.126.943

Nanocrystalline $Sb_2S_3$ particles have been synthesized from Sb and S powders by high-energy milling in a planetary mill using argon protective atmosphere. X-ray diffraction, particle size analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, electron diffraction, high resolution transmission electron microscopy, UV-VIS, and differential scanning calorimetry methods for characterization of the prepared particles were applied. The powder X-ray diffraction pattern shows that $Sb_2S_3$ nanocrystals belong to the orthorhombic phase with calculated crystallite size of about 36 nm. The nanocrystalline $Sb_2S_3$ particles are constituted by randomly distributed crystalline nanodomains (20 nm) and then these particles are forming aggregates. The monomodal distribution of $Sb_2S_3$ particles with the average hydrodynamic parameter 210 nm was obtained. The quantification of energy dispersive X-ray spectroscopy analysis peaks give an atomic ratio of 2:3 for Sb:S. The optical band gap determined from the absorption spectrum is 4.9 eV, indicating a considerable blue shift relative to the bulk $Sb_2S_3$. Differential scanning calorimetry curves exhibit a broad exothermic peak between 200 and 300°C, suggesting recovery processes. This interpretation is supported by X-ray diffraction measurements that indicate a 23-fold increase of the crystallite size to about 827 nm as a consequence of application of high temperature process. The controlled mechanochemical synthesis of $Sb_2S_3$ nanoparticles at ambient temperature and atmospheric pressure remains a great challenge.

## LIBROS Y OTRAS PUBLICACIONES / BOOKS AND OTHER PUBLICATIONS

### Electron Microscopy for the evaluation of particle size evolution of the layer silicate pyrophyllite subjected to mechanical treatment by dry grinding

Sánchez-Soto P.J., Garzón E., Martínez S., Carrasco B., Pérez-Villarejo L.
En: *Electron Microscopy for the evaluation of particle size evolution of the layer silicate pyrophyllite subjected to mechanical treatment by dry grinding,* (Microscopy Book Series VI), A. Méndez-Vilas (Ed.) págs. 803-812 (2014)

### Application of Hot Stage Microscopy (HSM) to the thermal study of two binary systems of pharmaceutical interest: Triamterene-Polyethyleneglycol (PEG) 6000 and Triamterene-beta-Cyclodextrin

Ginés-Dorado J.M., Arias M.J., Rabasco-Alvarez A.M., González-Rodríguez M.L., Cózar-Bernal M.J., Sánchez-Soto P.J.

En: *Electron Microscopy for the evaluation of particle size evolution of the layer silicate pyrophyllite subjected to mechanical treatment by dry grinding,* (Microscopy Book Series VI), A. Méndez-Vilas (Ed.) págs. 1015-1019 (2014)

**Thermal Analysis of Albendazole investigated by HSM, DSC and FTIR**
Moyano J.R., Liró J., Pérez J.I., Arias M.J, Sánchez-Soto P.J.
En: *Electron Microscopy for the evaluation of particle size evolution of the layer silicate pyrophyllite subjected to mechanical treatment by dry grinding,* (Microscopy Book Series VI), A. Méndez-Vilas (Ed.) págs. 1043-1050 (2014)

**Optical and Electron Microscopy studied of glass as artistic and industrial support**
Durán-Domínguez G., Sánchez-Soto P.J.
En: *Electron Microscopy for the evaluation of particle size evolution of the layer silicate pyrophyllite subjected to mechanical treatment by dry grinding,* (Microscopy Book Series VI), A. Méndez-Vilas (Ed.) págs. 1090-1095 (2014)

**Mechanochemical Treatment of Clay Minerals by Dry Grinding: Nanostructured Materials with Enhanced Surface Properties and Reactivity**
Pérez-Villarejo L., Martínez S., Eliche D., Carrasco B., Sánchez-Soto P.J.
En: *Clays and Clay Minerals: Geological Origin, Mechanical Properties and Industrial Applications,* Editor: Liam R. Wesley. Editorial: Nova Publishers NY, (2014) págs. 67-114

**The representation of Cultural Heritage: Methodologies for digital characterization**
Durán-Domínguez G., Felicísimo A.M., Sánchez-Soto P.J.
En: *Science, Technology and Cultural Heritage,* Editor: R. Candelera. Editorial: CRC PressTaylor and Francis Group, London, UK, (2014) págs. 363-368

**Caracterización mineralógica y físico-química de las imitaciones de vajilla de tipo Kuass en el Valle del Guadalquivir**
Moreno Megías V., Sánchez-Soto P.J., Ruiz-Conde A., García Fernández F.J.
En: *Monografías exoficina Hispania II 'As produçoes cerámicas de imitação na Hispania,* Tomo II, Editor: R. Candelera. Editores: R. Morais, A. Fernández, M.J. Sousa, Sociedad de Estudios de Cerámica Antigua en Hispania (SECAH), impreso por Faculdade de Letras da Universidade do Porto (FLUP), O Porto, Portugal, (2014) págs. 11-18

**El patrimonio arquitectónico rural: modelo para la evaluación del potencial de su rehabilitación**
M. Cano García, E. Garzón Garzón, P.J. Sánchez Soto
Editorial Universidad de Almería (2014) 208 páginas
ISBN: 978-84-616-9904-9

**Análisis de pinturas murales góticas en Eslovenia del maestro Bolfgang y su discípulo maestro de Mače (siglo XV)**
Kriznar A., Ruiz-Conde A., Sánchez-Soto P.J.
Revista ph investigación, 3 (2014) 21-33

**Evaluación de las posibilidades de Rehabilitación para la Conservación del Patrimonio Arquitectónico Tradicional**
Cano-García M., Garzón E., Sánchez-Soto P.J.
Macla, 18 (2014) 36-37

**Mineralogy of Supports and Selected Pigments in Mediaeval Churches of Slovenia**
Kriznar A., Ruiz-Conde A., Sánchez-Soto P.J.
Macla, 18 (2014) 77-78

**Caolín de Poveda de la Sierra (Guadalajara): Caracterización, Propiedades Cerámicas y Análisis de Fases con la Temperatura**
Sánchez-Soto P.J., Ruiz-Conde A., Pérez-Villarejo L., Martínez S., Morales L., Garzón E.
Macla 18 (2014) 99-101

**Fabricación de recubrimientos nanoporosos mediante pulverización por plasma: una técnica innovadora para producir materiales avanzados**
Alvarez R., Sánchez-Soto P.J., Palmero A.
Acta Científica y Tecnológica 24 (2014) 40-41

## CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

### COMUNICACIONES / COMMUNICATIONS

**Electronic Materials and Applications 2013**
23 - 25 enero [Orlando, Florida, Estados Unidos de América]

**Electrical properties of stoichiometric $BiFeO_3$ prepared by mechanosynthesis with either conventional or spark plasma sintering**
A. Perejon; L.A. Perez-Maqueda; N. Maso; A. R. West
Comunicación oral

**13th International ceramics congress | CIMTEC 2014**
8 - 13 junio [Montecatini Terme, Italia]

**Electro Discharge Machinable Alumina-based Nanocomposites**
L.A. Díaz; S. Rivera; A.A. Okunkova; YU.G. Vladimirov; F.J. gotor; R. Torrecillas
Comunicación oral

**VIII International conference on mechanochemistry and mechanical alloying | income 2014**
22 - 26 junio [Cracovia, Polonia]

**Mechanochemically synthesized nanocrystalline Sb2S3 particles**
E.Dutkova; M.J.Sayagues; C.Real; A.Zorkovska; P.Balaz; A.Satka; J.Kovac; J.Ficeriova
Póster

## Second International Congress Science and Technology for the Conservation of Cultural Heritage

24 - 27 junio [Sevilla, España]

**Punic and Turdetan amphorae in the Guadalquivir Valley (5th-1st Centuries B.C.): Technological and Compositional Characterization**
F.J. García Fernández; P.J. Sánchez-Soto; A. Ruiz-Conde; V. Moreno Megías; E. Ferrer Albelda; J.J. Martín del Río
Comunicación oral

**The representation of Cultural Heritage for Conservation: standard photographic processes applied to museographic spaces and methodologies for digital characterization**
G. Durán Domínguez; A.M. Felicisimo; P.J. Sánchez-Soto
Póster

## Processing ceramics from wastes: A new raw material source for a global change. Environment Workshops 2014

29 septiembre – 1 octubre [Baeza, Jaén, España]

**Application of carbonaceous slates and coal wastes from different coal mines located in Andalusia Region (Western of Sierra Morena) as ceramic raw materials**
Martínez S., Pérez-Villarejo L., Eliche D., Garzón, E., Sánchez-Soto P.J.
Póster

## Congreso Internacional de metalúrgia y materiales

21 - 24 octubre [Santa Fé, Argentina]

**Caracterización cinética de la precipitación en una aleación de Cu-11Ni-20Zn y Cu-12Ni-17Zn-2Al**
E. Donoso; M.J. Diánez; J.M. Criado; M.J. Sayagués
Póster

# CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESS AND MEETINGS

## COMUNICACIONES / COMMUNICATIONS

### XIII Congreso Nacional de Materiales

18 - 20 junio [Barcelona, España]

**Sustratos cerámicos densos y porosos de mullita y mullita-alúmina procesados a partir de caolinita**
P.J. Sánchez-Soto; E. Garzón-Garzón; R. Gómez Bonilla; B. Carrasco-Hurtado; L. Pérez-Villarejo
Póster

### LIV Congreso Anual de la Sociedad Española de Cerámica y Vidrio

19 - 22 noviembre [Badajoz, España]

**La interdisciplinariedad en los estudios arqueométricos: alteración de pigmentos y materiales cerámicos afectados por cambios degenerativos**
Durán G., Pérez-Villarejo L., Lupión J., Sánchez-Soto P.J.
Póster

**Influencias italiana y norte-europea en los materiales (pigmentos y morteros) de pinturas murales medievales (s. XV) en la zona litoral de Eslovenia**
Kriznar A., Sánchez-Soto P.J.
Póster

**Valorización e inertización de un residuo de galvanizado en pastas cerámicas de arcillas: Caracterización físico-química y propiedades tecnológicas de los materiales cerámicos obtenidos**
Pérez-Villarejo L., Martínez S., Eliche D., Carrasco B., Garzón E., Sánchez-Soto P.J.
Póster

**Caracterización y estudio de las propiedades cerámicas de una materia prima que contiene feldespato sódico y cuarzo procedente de sienitas alteradas**
Sánchez-Soto P.J., Martínez S., Pérez-Villarejo L.
Póster

**Estudio arqueométrico comparativo de materiales cerámicos procedentes de intervenciones arqueológicas del Antiguo Hospital de la Encomienda de la Orden Militar de San Juan de Jerusalem (Cedillo del Condado, Toledo)**
Domínguez E.G., Pérez-Villarejo L., Sánchez-Soto P.J. Póster

### CONAMA 2014: Congreso Nacional del Medio Ambiente
24 - 27 noviembre [Madrid, España]

**Aplicación de pizarras carboníferas y residuos de explotaciones de carbón de diversos yacimientos de Sierra Morena Occidental como materias primas cerámicas**
Pérez-Villarejo L., Martínez S., Carrasco B., Garzón E., Sánchez-Soto P.J.
Póster

**Valorización de lodos rojos residuales de la producción de aluminio para la fabricación de cementos belíticos**
Martínez S., Pérez-Villarejo L., Eliche D., Garzón E., Sánchez-Soto P.J.
Póster

## FORMACION / TRAINING

### TESIS DOCTORALES/ DOCTOR DEGREE THESIS

| | |
|---|---|
| **Título:** | **Desarrollo de cermets basados en soluciones sólidas mediante procesos mecanoquímicos** |
| **Autor:** | Ernesto Chicardi Augusto |
| **Directores:** | Francisco José Gotor Martínez y José Manuel Córdoba Gallego |
| **Calificación:** | Sobresaliente “Cum Laude” |
| **Centro:** | Universidad de Sevilla |

### FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

| | |
|---|---|
| **Título:** | **Síntesis y caracterización de materiales biocompatibles tipo hidrotalcita** |
| **Autor:** | Zaineb Debbagh |
| **Directores:** | María Isabel Domínguez Leal y Regla Ayala Espinar |
| **Grado:** | Trabajo Fin de Master |
| **Año Académico:** | 2013-2014 (19 septiembre 2014) |

## EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Microdurómetro FM700 Future-Tech
- Máquina de ensayo universal AGS-J, Shimadzu
- 3 Termobalanzas CI Electronics
- Dilatómetro diferencial ADAMEL LHOMARGY DI-24
- 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)
- Calorímetro SETARAM differential scanning DSC 111
- 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)

# MATERIALES FUNCIONALES NANOESTRUCTURADOS
# NANOSTRUCTURED FUNCTIONAL MATERIALS

## PERSONAL / PERSONNEL

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Dr. Manuel Ocaña Jurado
Dr. Agustín Rodríguez González-Elipe

**Catedráticos**
Dr. José Cotrino Bautista

**Investigadores Científicos**
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Dr. Francisco Yubero Valencia

**Científicos Titulares**
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Dra. Ana Isabel Becerro Nieto
Dra. Ana Isabel Borrás Martos
Dra. María Aránzazu Díaz Cuenca
Dra. Nuria O. Núñez Álvarez
Dr. Alberto Palmero Acebedo

**Profesor Visitante**
Dr. Richard M. Lambert

**Investigadores Contratados**
Dr. Rafael Álvarez Molina
Dr. Francisco J. Aparicio Rebollo
Dr. Mauricio E. Calvo Roggiani
Dra. Sol Carretero Palacios
Dr. Alberto Escudero Belmonte
Dr. Juan F. Galisteo López
Dr. Francisco J. García García
Dra. Ana María Gómez Ramírez
Dr. Yuelong Li
Dr. Gabriel Lozano Barbero
Dra. M. Carmen López Santos
Dr. Pedro A. Salazar Carballo
Dr. Juan Ramón Sánchez Valencia

**Becarios Predoctorales**
Lda. María Alcaire Martín
Ldo. Miguel Anaya Martín
Lda. Sara Borrego González
Ldo. Gabriel Castillo Dali
Ldo. Pedro Castillero Durán
Ldo. José Raúl Castro Smirnov
Lda. Victoria Esteso Carrizo
Ldo. Alejandro N. Filippin Emilio
Ldo. Alberto Jiménez Solano
Ldo. Mariano Laguna Moreno
Ldo. Manuel Oliva Ramírez
Ldo. Noe Orozco Corrales
Ldo. Julián Parra Barranco
Lda. Liliam Beatriz Romero Sánchez

**Personal Contratado**
Dra. Ana García Navarro
Dr. Jorge Gil Rostra
Lda. M. Carmen Gutiérrez Lázaro
Ldo. Antonio Méndez Montoro de Damas

# PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

## Láminas flexibles nanoestructuradas de polímeros inorgánicos para el control de la luz Polymer-Inorganic Flexible Nanostructured Films for the Control of Light (POLIGHT)

Código/Code: 307081
Periodo/Period: 01-01-2012 / 30-11-2017
Organismo Financiador/Financial source: Unión Europea. Starting Grant
Importe total/Total amount: 1.497.000 €
Investigador responsable/Research head: Hernán R. Míguez García

### RESUMEN / ABSTRACT

El proyecto POLIGHT se centra en la integración de una serie de materiales inorgánicos nanoestructurados que poseen propiedades plasmónicas y/o fotónicas en películas poliméricas, los cuales constituyen un avance significativo con respecto al estado actual de la técnica en materiales fotónicos flexibles. Estas láminas, altamente adaptables, pueden actuar como espejos o filtros pasivos, selectivos en frecuencia en el rango espectral UV-visble-infrarrojo cercano, así como matrices en las que incluir especies absorbentes de luz u ópticamente activas capaces de adaptar su respuesta óptica.

El objetivo de este proyecto es doble. Por un lado se va a llenar un agujero existente en la actualidad en el campo de los materiales para la protección de radiación, que es la ausencia de láminas flexibles y adaptables en las que se puedan seleccionar de una manera drástica y precisa los rangos de longitudes de onda que se deseen bloquear o dejar pasar, según las necesidades de cada aplicación concreta.

Por otro lado el proyecto POLIGHT pretende ir un paso más allá en la integración de nanomateriales absorbentes o emisores de luz dentro de matrices poliméricas flexibles, mediante la fabricación de capas fotónicas jerárquicamente estructuradas que permiten el ajuste fino de las propiedades ópticas del conjunto. Esto se consigue como resultado de las interacciones materia-radiación, intensificadas a raíz de los efectos de localización del campo en los modos resonantes específicos.

El proyecto surge como resultado del reciente desarrollo de una serie de robustas estructuras fotónicas inorgánicas conformadas por redes porosas interconectadas capaces de alojar polímeros y heredando así las propiedades mecánicas características de los mismos.

The POLIGHT project will focus on the integration of a series of inorganic nanostructured materials possessing photonic or combined photonic and plasmonic properties into polymeric films, providing a significant advance with respect to current state of the art in flexible photonics. These highly adaptable films could act either as passive UV-Vis-NIR selective frequency mirrors or filters, or as matrices for light absorbing or optically active species capable of tailoring their optical response. The goal of this project is two-fold. In one aspect, the aim is to fill a currently existing hole in the field of materials for radiation protection, which is the absence of highly flexible and adaptable films in which selected ranges of the electromagnetic spectrum wavelengths can be sharply blocked or allowed to pass depending on the different foreseen applications. In another, the POLIGHT project seeks to go one step beyond in the integration of absorbing and emitting nanomaterials into simple flexible polymeric matrices by including hierarchically structured photonic lattices that provide fine tuning of the optical properties of these hybrid ensembles. This will be achieved by means of enhanced matter-radiation interactions that result from field localization effects at specific resonant modes. The opportunity arises as a result of the recent development of a series of robust inorganic photonic structures that present interconnected porous networks susceptible of hosting polymers and thus inheriting their mechanical properties.

## Arquitecturas SOFC innovadoras basadas en operación "Triodo"
## Innovative SOFC Architecture based on Triode Operation

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|---|---|
| Código/Code: | FCH-JU-2011-1 |
| Periodo/Period: | 01-09-2012 / 31-08-2015 |
| Organismo Financiador/Financial source: | Unión Europea |
| Importe total/Total amount: | 256.363 € |
| Investigador responsable/Research head: | Agustín R. González-Elipe |
| Componentes/Research group: | Francisco Yubero Valencia, Juan Pedro Espinós Manzorro, Angel Barranco Quero, Richard Lambert, Victor J. Rico, Ana Borrás Martos, José Cotrino, Jorge Gil, Pedro Castillero, Fran J. García, Alberto Palmero |

RESUMEN / ABSTRACT

El desarrollo de celdas de combustible de óxido sólido (SOFCs) que operen con hidrocarburos como combustibles (gas natural, biocompustibles, LPG) es esencial para la comercialización a plazos cortos y medios. El desarrollo de HC SOFCs directas se enfrenta todavía a numerosos retos y problemas que surgen del hecho que los materiales del anodo operan bajo condiciones muy severas. Estas limitan el rendimiento con reacciones de reformado u oxidación, producen una desactivación rápida debido a la contaminación con carbón y generan inestabilidad asociada a la presencia de compuestos de azufre. Aunque la investigación en estos temas es intensa, no se han producido avances tecnológicos significativos respecto a mejorar la robustez del proceso, el incremento de su tiempo de vida y a la disminución de su costo.

T-CELL propone una aproximación electroquímica novedosa con el fin de abordar estos problemas mediante un esfuerzo integrado para definir, explorar, caracterizar, desarrollar y ejecutar una aproximación a la tecnología SOFC radicalmente nueva basada en una aproximación tipo “triodo”. Para ello se desarrollará una aproximación integrada basada en el desarrollo de materiales y en la aplicación de un diseño de celda innovador que permite el control efectivo de la actividad electrocatalítica bajo vapor o condiciones de reformado en seco.

La novedad del trabajo propuesto reside en el esfuerzo pionero para desarrollar nuevos materiales a base de Ni que actúen como ánodo y que presenten tolerancia al envenenamiento, así como en el desarrollo del concepto de triodo aplicado a celdas SOFC para incorporar una nueva variable en la operación de celdas de combustible.

Para demostrar la posibilidad de apilamiento en las celdas triodo, se desarrollará un apilamiento SOFC tipo triodo formado por cuatro unidades repetidas. Este sistema se evaluará con metano y vapor en presencia de una pequeña concentración de compuestos de azufre.

The development of Solid Oxide Fuel Cells (SOFCs) operating on hydrocarbon fuels (natural gas, biofuel,LPG) is the key to their short to medium term broad commercialization. The development of direct HC SOFCs still meets lot of challenges and problems arising from the fact that the anode materials operate under severe conditions leading to low activity towards reforming and oxidation reactions, fast deactivation due to carbon formation and instability due to the presence of sulphur compounds. Although research on these issues is intensive, no major technological breakthroughs have been so far with respect to robust operation, sufficient lifetime and competitive cost.

T-CELL proposes a novel electrochemical approach aiming at tackling these problems by a comprehensive effort to define, explore, characterize, develop and realize a radically new triode approach to SOFC technology means of an integrated approach based both on materials development and on the deployment of an innovative cell design that permits the effective control of electrocatalytic activity under steam or dry reforming conditions.

The novelty of the proposed work lies in the pioneering effort to apply Ni-modified materials electrodes of proven advanced tolerance, as anodic electrodes in SOFCs and in the exploitation of our novel triode SOFC concept which introduces a new controllable variable into fuel cell operation.

In order to provide a proof of concept of the stackability of triode cells, a triode SOFC stack consisting of at least 4 repeating units will be developed and its performance will be evaluated under methane and steam co-feed, in presence of a small concentration of sulphur compound.

## Integración de Nanoestructuras Fotónicas en Celdas Solares de Colorante Integration of Photonic Nanostructures in Flexible Dye Solar Cells

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| Código/Code: | FP7-PEOPLE-2013-IIF Marie Curie Actions |
| Periodo/Period: | 01-07-2014 / 30-06-2016 |
| Organismo Financiador/Financial source: | Unión Europea |
| Importe total/Total amount: | 173.370 € |
| Investigador responsable/Research head: | Hernán Míguez García |
| Componentes/Research group: | Yuelong Li |

RESUMEN / ABSTRACT

El proyecto INPHOFLEX se enmarca en la búsqueda de ese aumento de eficiencia sin alterar completamente las propiedades de transparencia y flexibilidad. El grupo liderado por el Dr. Míguez en el Instituto de Ciencia de Materiales de Sevilla ha conseguido recientemente un aumento significativo sin perder la transparencia, mediante la introducción de estructuras fotónicas en la celda. Este proyecto continúa en esa senda de investigación y se basa en la hipótesis de que insertando nuevas estructuras ópticas flexibles en la celda se conseguirá el aumento deseado de eficiencia sin perder transparencia ni flexibilidad. Es en este contexto que se incorpora al grupo el Dr. Yuelong Li, experto en el desarrollo de celdas solares flexibles y autor de los principales trabajos en ese campo. El objetivo general del proyecto se afrontará a través de los siguientes objetivos y líneas de investigación integradas en el presente proyecto:

- Objetivo 1. Preparación de las celdas solares flexibles altamente eficientes y transparentes a través de la integración de nuevas estructuras fotónicas flexibles porosas sobre la capa de recolección de luz. Se prepará la nanoestructura óptica sobre el electrodo flexible. Las propiedades mecánicas de la estructura han de ser tales que la celda resultante debe ser estable contra la flexión y estiramiento.
- Objetivo 2. Preparación de las celdas solares flexibles altamente eficientes y transparentes a través de la integración de nanoestructuras fotónicas flexibles de polímero para que actúen como espejos traseros. Se fabricará una nanoestructura fotónica flexible para ser transferida sobre la parte trasera de la celda de manera que actúe como retroreflector. Se trata de un espejo de bajo peso y capaz de resistir la flexión de la misma sin perder calidad óptica.
- Objetivo 3. Preparación de las celdas solares altamente eficientes y flexibles mediante la integración de dispersores aleatoriamente distribuidos: diseño de una estructura desordenada que maximice la absorción de la luz y la captura electrónica a la vez que preserve parcialmente la transparencia. Se introducirán en el electrodo centros dispersores, desordenadamente distribuidos y de un tamaño y forma bien definidos, con el propósito de controlar el transporte difuso de luz a través de la celda para maximizar la probabilidad de absorción así como la eficiencia de captura electrónica. Se trabajará también para que los diseños de dispersión propuestos preserven una buena parte de la transmisión de la luz de forma difusa, de manera que la celda solar resultante deje pasar parte de la claridad.

El presente proyecto comprende el desarrollo de tanto del diseño teórico óptico de las nanoestructuras fotónicas optimizado para la obtención de la máxima eficiencia, así como la realización experimental de las nanoestructuras y de los ulteriores dispositivos fotovoltaicos.

It is the main goal of this project to bring to the host institution and the European Research Area the knowledge and technology to prepare current record flexible dye sensitized photovoltaic devices, previously developed by the candidate in South Korea and then the USA, in order to be able to further improve them, while endowing them with semi-transparency, using stretchable and bendable optical materials. The candidate has demonstrated that several key materials and processes provide better

performance of bendable dye solar cells, i.e., enhanced efficiency and flexibility, by allowing the preparation of electrodes in which the electron diffusion length is longer and charge collection efficiency is consequently enhanced. However, highly efficient dye solar cells are opaque as a consequence of the particular diffuse scattering design employed to improve light absorption, which limits their application in building or automotive integrated photovoltaics. This proposal seeks to solve such drawback by

introducing photonic nanostructures in different configurations, yielding both light harvesting enhancement and preserving transparency, hence placing Europe at the forefront of research in this specific area within the field of renewable energy. This final goal will be attempted through different approaches, each one challenging from the materials science perspective. Preparation of such highly efficient and transparent devices will combine the flexible solar cell processing tools previously developed by the candidate with the versatile optical material preparation techniques pioneered by the host institution. More specifically, integration of novel porous flexible photonic structures into the light harvesting layer, use of flexible mirrors attached to the back of the counter-electrode, and designed distribution of scatterers will be employed to reach the target.

## Nuevos materiales para envasado, etiquetado inteligente, control de fraudes y monitorización visual del estado de los productos New materials for advanced packaging, intelligent labeling, anti-counterfeiting and monitoring of agricultural and livestock products

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|---|---|
| Código/Code: | RECUPERA2020 - 1.4.2 |
| Periodo/Period: | 02-12-2013 / 31-12-2015 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 454.239,23 € |
| Investigador responsable/Research head: | Angel Barranco Quero |
| Componentes/Research group: | Ana Isabel Borrás, Francisco Yubero, José Cotrino, Juan Pedro Espinós, Juan Ramón Sánchez Valencia, Francisco Javier Aparicio Rebollo |

En esta actividad se pretende desarrollar una serie de nuevos materiales y procesos basados en marcado por láser para el desarrollo de un nuevo sistema de marcaje y etiquetado "inteligente" capaz de lograr una mejora en los procesos de control y de la trazabilidad de productos agropecuarios.

This Project intends the development of novel materials and processes for intelligent labeling of agricultural and livestock products to improve their traceability. The project is based on the development of active optical structures, laser processing strategies and the fabrication of practical testing prototypes.

## Purificación del aire en invernaderos y centros de tratamiento de alimentos Purification of air in greenhouses and food processing centers

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| Código/Code: | RECUPERA2020 - 2.2.3 |
| Periodo/Period: | 02-12-2013 / 31-12-2015 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 454.239,23 € |
| Investigador responsable/Research head: | José Cotrino Bautista |
| Componentes/Research group: | Ana María Gómez Ramírez, Antonio Méndez Montoro de Damas |

### RESUMEN / ABSTRACT

Este proyecto está relacionada con una tecnología para generar un plasma frío a presión atmosférica con aire que fluye a través de un reactor. El objetivo específico de esta actividad es el desarrollo de un sistema prototipo de purificación de aire para invernaderos, centros de procesamiento de alimentos, recintos para el ganado u otros tipos similares en mercados o recintos donde la concentración de gases nocivos para la salud de los trabajadores puede ser muy significativa por el uso de insecticidas, fungicidas, desinfectantes y otros compuestos. El sistema desarrollado debe ser capaz de purificar el aire en instalaciones cerradas y donde un gran número de productos químicos, compuestos orgánicos volátiles, principalmente, se acumulan en el aire del establecimiento. El diseño de la tecnología del reactor de plasma frío sigue las características de descarga de barrera dieléctrica con dieléctrico en forma de lecho empaquetado utilizando materiales dieléctricos de carácter ferroeléctrico con elevada constante dieléctrica.

This project is related with a technology to generate a cold plasma at atmospheric pressure with air flowing through a reactor. The specific objective of this activity is the development of a prototype air purification system for greenhouses, food processing centers, livestock enclosures, or other similar types of markets or enclosures where the concentration of gases harmful to the health of the workers can be very significant by the use of insecticides, fungicides, disinfectants or other compounds. The developed system should be able to purify the air in closed installations and where a large number of chemicals, mainly volatile organic compounds, accumulate in the air that is handled. The cold plasma reactor technology design follows the characteristics of packed-bed dielectric barrier discharge by using ferroelectric dielectric.

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## Sensores micro-fluídicos integrados para el control de la fermentación Microfluidic integrated sensors for the control of fermentation

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| Código/Code: | RECUPERA2020 – 1.4.1 |
| Periodo/Period: | 02-12-2013 / 31-12-2015 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 454.539,23 € |
| Investigador responsable/Research head: | Agustín R. González-Elipe |
| Componentes/Research group: | Juan Pedro Espinós Manzorro, José Cotrnio Bautista, Francisco Yubero Valencia, Alberto Palmero Acebedo, Angel Barranco Quero, Ana I. Borrás Martos, Victor J. Rico Gavira, Rafael Alvarez Molina, Pedro Angel Salazar Carballo |

### RESUMEN / ABSTRACT

El objetivo de este proyecto es el desarrollo de nuevos sistemas micro/nano fluídicos integrados y robustos que permitan la incorporación fiable de tests de control, sensorización y/o análisis rápido de productos agroalimentarios, fundamentalmente líquido o productos solubles. La tecnología a desarrollar se intenta aplicar tanto para el control de productos finales como durante las etapas de elaboración de los mismos. En concreto, un nicho de aplicación que directamente que se abordará dentro del proyecto es el control de procesos de fermentación, con el desarrollo de nuevos transductores fluídicos integrados que permitan la detección cuantitativa de glucosa y/o otros azúcares mediante desarrollos electroquímicos y fotónicos en dispositivos microfluídicos y similares.

The objective of this Project is the development of new integrated and robust micro/nano- fluidic systems that enable the reliable incorporation of control tests, sensorization and rapid analysis of agrofood products, mainly liquids or soluble. The technology to be developed should be applied to final products, as well as during their different elaboration steps. IN particular, a niche of application that will be directly addressed in the project is the control of fermentation process with the development of new integrated fluidic transductors that permit the quantitative detection of glucose and/or other sugars by means of electrochemical and photonic developments integrated in microfluidic and similar devices.

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## Control de la Absorcion y la Emisión Ópticas de Nanomateriales integrados en Estructuras Fotónicas Porosas Multifuncionales

## Control of the Optical Emission and Absorption properties of Nanomaterials Integrated in Multifunctional Porous Photonic Structures

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|---|---|
| Código/Code: | MAT2011-23593 |
| Periodo/Period: | 01-01-2012 / 31-12-2014 |
| Organismo Financiador/Financial source: | Ministerio de Economia y Competitividad |
| Importe total/Total amount: | 210.000 € |
| Investigador responsable/Research head: | Hernán R. Míguez García |
| Componentes/Research group: | Nuria Nuñez Alvarez, Mauricio Calvo Roggiani, Carmen López López, Sonia Rodríguez Liviano, Manuel Ocaña Jurado, Silvia Colodrero Pérez, José Raúl Castro Smirnov |

RESUMEN / ABSTRACT

En este proyecto se estudiarán las modificaciones que tienen lugar tanto en la absorción como en la emisión ópticas de nanomateriales de diverso tipo (nanopartículas dopadas con tierras raras, nanopartículas semiconductoras, nanopartículas metálicas, films de colorantes orgánicos de grosor nanométrico) por el hecho de encontrarse éstos formando parte de

una estructura fotónica en la que tienen lugar fenómenos ópticos complejos. El estudio se realizará tanto desde el punto de vista fundamental como aplicado, centrándose en materiales que tengan interés en distintos campos de la tecnología actual tales como células solares, sensores o dispositivos emisores de luz. La motivación principal de este proyecto desde el punto de vista aplicado radica en la posibilidad de modificar controladamente estos procesos de absorción y emisión, de tal modo que puedan inhibirse o amplificarse según convenga a un fin determinado. En concreto, se pretende poner en práctica estos nuevos fenómenos para el diseño de células solares más eficientes, capaces de recolectar una mayor cantidad de la radiación incidente, y en el desarrollo de films para sensores sensibles a modificaciones de distinto tipo en su entorno, tales como presencia de analitos de distinto tipo, variaciones en la presión del vapor ambiente, etc.... Del mismo modo, y basándonos en los exitosos resultados del proyecto MAT que ahora termina, pretendemos preparar materiales en los que tengan lugar mecanismos más eficientes de extracción de luminiscencia y que puedan emplearse en dispositivos emisores de luz. Nuestro proyecto incluye en esta ocasión como objetivo el desarrollo de pequeños dispositivos prototipo en los que se pongan en práctica los conceptos que están siendo investigados.

En su aspecto más fundamental, nuestra propuesta ahonda en el análisis de la interacción entre luz y materia en sistemas en los que existe una fuerte dispersión y anisotropía de la constante dieléctrica, y en los que es posible obtener bajas velocidades de propagación de fotones. Para este análisis se emplearán distintos tipos de estructuras fotónicas porosas, tales como cristales fotónicos con orden uni- y tri-dimensional o materiales formados por partículas desordenadas, como matrices en los que se infiltrarán nanomateriales tanto orgánicos como inorgánicos en diferentes configuraciones y cuya absorción y emisión serán estudiadas.

Aunque este proyecto tiene un carácter fundamental tanto por la naturaleza de las técnicas de preparación como de los complejos fenómenos ópticos que pretenden explorarse, es nuestro objetivo estratégico continuar generando y transfiriendo propiedad intelectual basada en los nuevos conceptos, propiedades y diseños objeto de nuestra investigación.

In this project the modifications of both optical emission and absorption of nanomaterials of different sort (rare earth doped nanoparticles, semiconductor quantum dots, metallic nanoparticles, and films of organic dyes of nanometer dimensions) that occur when they are embedded in different types of photonic structures will be investigated. Both fundamental and applied aspects of the subject will be analysed. Efforts will be mainly focused on materials of current technological interest for solar cells, sensors and light emitting devices. From the applied point of view, this project finds its motivation in the possibility that photonic structures offer of modifying absorption and emission processes in a controlled manner so that they can be inhibited or amplified depending on the specific goal pursued. Particularly, we seek to put into practice these concepts to generate new designs of more efficient solar cells, capable of harvesting a larger amount of the incident radiation, and in the development of films for sensing devices responsive to modifications of different kind, such as presence of targeted molecules, variations of ambient gas pressure, etc... Also, more efficient or controlled light extraction from light emitting devices is sought after. The development of small prototype devices to prove the novel concepts under research is also an objective of this grant proposal.

In its more fundamental aspect, our project aims at deepening our knowledge of the interaction between light and matter in systems in which there exists a strong dispersion and anisotropy of the dielectric constant, and in which it is possible to attain very low photon propagation speeds. For this analysis, we will employ different types of porous photonic structures, such as one-dimensional and three-dimensional photonic crystals, as well as disordered assemblies of particles, as hosts in which a wide range of organic and inorganic nanomaterials will be integrated in different configurations and whose absorption and emission will be experimentally and theoretically studied.

Although this project has a fundamental character due to the nature of the preparation techniques and complex optical properties we seek to analyze, it is our aim to continue generating and transferring intellectual property based on the novel concepts, properties and designs which are the subject of our research.

## Nuevas nanoestructuras 1d-híbridas multifuncionales para el desarrollo de nanosistemas autoalimentados New multi-functional 1D hybrid nanostructures for selfpowered nanosystems

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| Código/Code: | MAT2013-42900-P |
| Periodo/Period: | 1-01-2014 / 31-12- 2016 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 54.326,53 € |
| Investigador responsable/Research head: | Ana Isabel Borrás Martos |
| Componentes/Research group: | José Cotrino Bautista, Ricardo Molina Mansilla, Juan Pedro Espinós Manzorro, Ana Isabel Borrás Martos, Angel Barranco Quero |

RESUMEN / ABSTRACT

HYBR(1)D es un proyecto de carácter multidisciplinar en el que se persigue el desarrollo de nuevos materiales nanoestructurados multifuncionales que encuentren aplicación final en campos como las energías renovables, fotónica y la miniaturización de dispositivos. En el proyecto se plantea como principal objetivo el desarrollo de métodos de fabricación de nuevos materiales unidimensionales nanoestructurados como nanocables orgánicos e inorgánicos y sistemas unidimensionales heteroestructurados e híbridos. Haciendo especial hincapié en sistemas compuestos del tipo coaxial "core@shell/multi-shell" que integren componentes orgánicas, metales y óxidos. Estos materiales serán fabricados mediante una innovativa metodología que permiten su formación sobre sustratos procesables de distinta naturaleza involucrando tecnologías escalables industrialmente. Además se propone de forma exploratoria la fabricación de membranas "compuestas" que permitan el uso de estas nanoestructuras embebidas de forma autosoportada. El segundo objetivo de este proyecto es probar la funcionalidad de estas nuevas nanoestructuras en distintas aplicaciones atendiendo al concepto de “nanosistema autoalimentado”: como sistemas de generación de energía (celdas solares y piezoelectricidad) y nanosensores. Cabe resaltar que aunque los materiales a fabricar son muy diversos, desde nanotubos de semiconductores inorgánicos (TiO2 y ZnO) a nanohilos orgánicos ("small-molecule single crystal nanowires) híbridos y heteroestruturados, los métodos de fabricación que se pretenden utilizar se basan en técnicas de vacío muy similares y facilmente acoplables. Así, las distintas nanoestructuras y heteroestructuras se fabricarán mediante cuatro técnicas principales y combinaciones de las mismas: deposición física desde fase vapor aplicada a moléculas orgánicas, deposición química desde fase vapor asistida por plasma de moléculas orgánicas y óxidos semiconductores, sputtering-dc de metales y "etching" por plasma de oxígeno. El IP y el grupo Nanotechnology on Surfaces del ICMS tienen un amplio background en la aplicación de estas técnicas para el desarrollo de sistemas del tipo láminas delgadas y recubrimientos funcionales, experiencia que se ha extendido en los últimos años al estudio de nanoestructuras 1D soportadas. El proyecto aborda toda la cadena de valor que lleva desde la síntesis de nuevos materiales a sus aplicaciones, incluyendo su caracterización avanzada e integración en dispositivos y prototipos a escala de laboratorio.

HYBR(1)D is a multidisciplinary Project that aims the development of novel multifunctional nanostructured materials for applications as renewable energy devices, photonics and device miniaturization. The main objective of the project is the development of original synthetic strategies for nanostructured 1D materials like organic and inorganic nanowires and other hybrid hetero-structured systems. Special attention will be paid to the development of coaxial "core@shell/multi-shell" structures integrating organic, metallic and oxide nanostructured components. These materials will be synthesized using an innovative methodology compatible with processable substrates of different nature that will be fully scalable to industrial production. In addition, the project also included exploratory studies about self-supported composite membranes where the nanostructured 1D materials will be embedded.

A second project objective is to probe the functionality of the novel 1D nanostructures in different applications under the global strategy that we defined as development of "self-powered nanosystems". These applications are: energy power generation devices (solar cells and piezoelectric nanogenerators) and nanosensors. It is worthy to notice that although the materials under study are relatively diverse, from semiconducting inorganic nanotubes (TiO2, ZnO) to organic single-crystal nanowires ("small molecules") or hybrid heterostructures, the synthetic vacuum methodologies are, in all the cases, very similar and easily adaptable. These methodologies are physical vapor deposition (organic molecules), plasma assisted vacuum deposition (organic molecules and inorganic oxides), metal dc-sputtering and oxygen plasma etching. All of them can be used sequentially or in combination and are integrated in the same reactors. The project PI and the Nanotechnology on Surface group from the ICMS-CSIC have a solid background in the use of plasma and vacuum technology for the study of functional thin films and devices that is being extended to the field of 1D supported nanostructures in the recent years. HYBR(1)D project intend to cover all the scientific-technological chain from the materials development to the final applications including advanced characterization, flexible synthetic routes, device integration and testing at laboratory scale.

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## Unidad altamente optimizada para un Sistema solar sostenible y mejorado Highly optimized unit for a sustainable enhanced solar system HOUSESS

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| Código/Code: | RTC-2014-2333-3 (Programa Retos) |
| Periodo/Period: | 3-02-2014 / 31-12- 2017 |

Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 244.204,44 €
Investigador responsable/Research head: Hernán Míguez García
Componentes/Research group: Juan Francisco Galisteo López, José María Miranda Muñoz

## RESUMEN / ABSTRACT

El objetivo del proyecto es el diseño, desarrollo, prototipado y validación de un sistema híbrido de cilindro parabólico termosolar- fotovoltaico que permita el almacenamiento y la gestionabilidad de la energía solar generada. Dicho sistema estará caracterizado por generar electricidad a menores costes que la tecnología estándar termosolar, de forma que el sistema integrado de concentración posea una mayor eficiencia.

El sistema híbrido consiste en un sistema cilindro parabólico termosolar y un receptor fotovoltaico de baja concentración. Entre estos dos componentes se sitúa un filtro dicroico de separación espectral, que recibe la luz reflejada del espejo primario del cilindro parabólico y permite la separación selectiva del espectro solar, dirigiendo una parte del mismo hacia el receptor fotovoltaico y el resto hacia el tubo absorbedor térmico. Dicho filtro dicroico se caracteriza por enviar al receptor fotovoltaico los fotones de luz con una longitud de onda a la cual dicho semiconductor opera más eficientemente, lo que conlleva a que el sistema integrado propuesto posee una mayor eficiencia que las tecnologías convencionales actuales, redundando en una mayor competitividad en costes. El sistema presenta además, por su parte termosolar, la capacidad de entrega de la energía de manera gestionable, permitiendo su almacenamiento para su introducción en la red eléctrica durante las franjas horarias en los que es más conveniente para el sistema.

The aim of the project is the design, development, prototyping and validation of a hybrid photovoltaic-thermosolar system that allows the storage and manageability of the generated solar energy. This integrated system will generate electricity at lower costs than standard thermosolar technology.

The hybrid system consists of a parabolic cylinder system and a low concentration photovoltaic solar receiver. Between these two components a dichroic filter is placed, which receives the reflected light from the parabolic cylinder primary mirror and allows the selective separation of the solar spectrum, letting pass a portion of the light to the photovoltaic receiver and reflecting the rest to the thermal tube receiver. Said dichroic filter sends to the photovoltaic receiver photons with wavelengths which are more efficiently absorbed by the solar cell. The thermal part of the system also shows the ability to controllably deliver power, allowing energy storage for its use in the most suitable moment of the day.

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## Sol y Visión par la energía térmica actual
## Sun and vision for the present thermal energy

Código/Code: IPT-2011-1425-920000
Periodo/Period: 04-05-2011 / 31-12-2014
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 246.992,80 €
Investigador responsable/Research head: Agustín R. González-Elipe
Componentes/Research group: Francisco Yubero Valencia, Juan Pedro Espinós Manzorro, Angel Barranco Quero, Victor J. Rico, Ana Borrás Martos, José Cotrino, Jorge Gil, Pedro Castillero, Fran J. García

RESUMEN / ABSTRACT

Este proyecto persigue el desarrollo de una serie de equipos y dispositivos para la monitorización de las condiciones de funcionamiento de plantas termosolares de concentración con espejos cilíndrico-parabólicos. La participación del ICMSE se centra en la aplicación tecnologías de plasma y el desarrollo de sistemas en lámina delgada capaces de diagnosticar las condiciones de funcionamiento de dichas instalaciones.

This Project aims at the development of a series of equipment and devices to monitor the working conditions of solar thermal plants based on light concentration with cylindrical parabolic mirrors. The role of ICMSE in this project focusses on the application of plasma technology systems and the development of thin films able to determine the working conditions of these facilities.

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## Control ambiental y de procesos con dispositivos responsivos con capas nanoestructuradas fabricadas por tecnologías innovadoras de vacio y plasmas Environmental and process monitoring with responsive devices integrating nanostructured thin films grown by innovative vacuum and plasma technologies

Código/Code: MAT2013-40852-R
Periodo/Period: 01-01-2014 / 31-12-2016
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 227.183,67 €
Investigador responsable/Research head: Agustín R. González-Elipe
Componentes/Research group: José Cotrino Bautista, Ricardo Molina Mansilla, Victor Rico Gavira, Francisco Yubero Valencia, Juan Pedro Espinós Manzorro, Alberto Palmero Acebedo, Angel Barranco Quero, Fernando Lahoz Zamarro

RESUMEN / ABSTRACT

Este proyecto persigue el desarrollo de una nueva generación de sistemas responsivos y sensores de baja dimensión que integren capas delgadas nanoestructuradas con propiedades ópticas y eléctricas controladas preparadas mediante técnicas innovadoras de vacío y plasma. Los principios básicos de la deposición física en fase vapor (PVD) en configuración oblicua (OAD) se extenderán a técnicas de plasma y de pulverización catódica para producir capas con porosidad controlada que interactúen eficientemente con el medio. Se propone también la combinación de estas técnicas con otras tecnologías novedosas de plasma, como la deposición por plasma a presión atmosférica o mediante evaporación-polimerización, para conseguir un control estricto sobre la nanoestructura y las propiedades finales de sistemaas complejos. Mediante estas tecnologías se prepararán capas finas nanoestructuradas de metales y óxidos, multicapas apiladas y nanoestructuras tipo "composites" e híbridas que, a continuación, se caracterizarán mediante microcopías electrónicas avanzadas y de proximidad, entre otras técnicas. Para encontrar nuevas rutas de procesado de capas porosas con morfologías y propiedades "a medida" y posibilitar su escalado a nivel industrial, se propone estudiar los mecanismos fundamentales que gobiernan el crecimiento de las películas a fin de modificarlos convenientemente. Conjuntos ordenados y homogéneos de estas estructuras se emplearán como sensores de gases y líquidos a temperatura ambiente, dispositivos microfluídicos responsivos y etiquetas inteligentes. Para estas y otras aplicaciones, las capas finas porosas soportadas se funcionalizarán convenientemente con nanopartículas metálicas, cadenas moleculares ancladas o capas de materiales poliméricos. Asímismo, se contempla su apilamiento en forma de estructuras fotónicas verticales. Para la implementación de estas estructuras en forma de micro-dispositivos que actúen como sensores avanzados, se desarrollarán microreactores y sistemas responsivos mediante estrategias novedosas de integración, basadas en la deposición mediante evaporación de capas eliminables de NaCl. Estos sistemas incluirán también transductores fotónicos, eléctricos y/o electroquímicos que permitan el desarrollo de dispositivos finales capaces de detectar i) oxígeno y cloro en disolución, ii) glucosa y materia orgánica en el agua, iii) vapores y gases en aire, o iv) etiquetas inteligentes que cambien como respuesta al medio. Se prevén aplicaciones específicas para el control del medio ambiente en aire y aguas, emplazamientos industriales e invernaderos, procesos agroindustriales tales como la fermentación, así como para el seguimiento y la trazabilidad de diferentes tipos de mercancías y alimentos. Se espera que la combinación de nuevos descubrimientos científicos en el campo de la tecnología de capas delgadas y el de nuevos principios de integración a las escalas micro y nano abran nuevas áreas de investigación con alto impacto en diversos campos y tecnologías facilitadoras tales como la fotónica, la nanotecnología o los materiales avanzados, así como en tecnología de plasma y microfluídica.

This project aims at the development of a new generation of low dimensional responsive systems and sensors that integrate nanostructured layers with well-controlled electrical and optical properties which, prepared by innovative vacuum and plasma methods, present a tunable and high porosity and are able to actively interact with the environment. The basic principles of the oblique angle approach (OAD) during the physical vapor deposition (PVD) of evaporated thin films will be extended to the fabrication of similar layers by plasma and magnetron sputtering techniques. Combination of these techniques along with other innovative plasma technologies, including atmospheric pressure plasma deposition or plasma-evaporation polymerization will be employed to achieve a strict control over the nanostructure and properties of final films and complex systems . Supported metal and oxide nanostructured thin films, stacked multilayers and hybrid and composite suported nanostructures will be prepared and thereafter characterized by advanced electron and proximity microscopies and other techniques. Process-control strategies will be implemented in order to understand the fundamental mechanisms governing the film structurations and to propose new synthetic routes scalable to industrial production so as to achieve tailored morphologies and properties for these porous thin film materials. Highly ordered and homogenous arrays of these nanostructures will be used as ambient temperature gas and liquid sensors, microfluidic responsive devices and intelligent labelling tags. For these applications the supported porous thin films will be suitably functionalized with metal nanoparticles, grafted molecular chains or layers of other polymeric materials. They will be also stacked in the form of vertically ordered photonic structures. Innovative device integration approaches including the water removal of evaporated sacrificial layers of NaCl and their integration in the form of microdevices will be carried out to fabricate advanced sensors, microreactors and responsive systems. Photonic, electrical and/or electrochemical principles of transduction will be implemented into the devices for detecting and/or fabricating i) oxygen and chlorine in solutions, ii) glucose and organic matter in water iii) gas and vapor sensors or iv) inteligent labels. Specific applications are foressen for the control of the outside environment (air and waters), industrial and greenhouse locations, agroindustrial processes such as fermentation and the tracking and trazability of different kinds of goods and foods.

It is expected that the combination of scientific breakthroughs in thin film technology and new film engineering principles at the micro- and nano-scales will open new areas of research with a high impact in key enabling technologies such as photonics, nanotechnology, advanced materials and in other fields like plasma technology and microfluidics.

JUNTA DE ANDALUCIA

## Desarrollo de recubrimientos y andamios bioactivos de material cerámico nanoestructurado para la regeneración ósea (BIOCEREG) Development of Nanostructured Ceramic Coatings and Scaffolds for Bone Regeneration (BIOCEREG)

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| Código/Code: | CTS-661 (Proyecto de Excelencia) |
| Periodo/Period: | 06-07-2011 / 05-06-2015 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 240.497 € |
| Investigador responsable/Research head: | M. Aránzazu Díaz Cuenca |
| Componentes/Research group: | M. Lourdes Ramiro Gutiérrez, Sara Borrego González |

### RESUMEN / ABSTRACT

Este Proyecto pretende contribuir al avance en el desarrollo de nuevos biomateriales con bioactividad mejorada para su aplicación en la reparación y regeneración ósea. Se propone la preparación de nuevos recubrimientos y andamios cerámicos mediante técnicas de procesado láser a partir de materiales cerámicos particulados, nanoestructurados de composición bioactiva en el sistema SiO2-CaO-P2O5 sintetizados en el ICMS por la Dra. Díaz (IP de esta solicitud). La hipótesis de partida es que las características nanoestructurales y texturales del material cerámico particulado en combinación con la fuente láser tiene un gran potencial para resultar en deposiciones con microestructura y nanoestructura controlada. Se plantea procesar dos tipos de pieza prototipo: i) piezas de sustrato metálico (de titanio) con recubrimiento cerámico de composición bioactiva y ii) piezas monolito (andamio) solo cerámica bioactiva con geometría controlada. Hay que distinguir por tanto la persecución de dos hitos. Un primer Hito es la obtención de materiales prototipo (recubrimientos y andamios) con unos requerimientos de micro y nanoestructura, superficie, propiedades mecánicas, homogeneidad y reproducibilidad mínimas. Y un segundo Hito consistente en la verificación de sus propiedades biológicas in vitro e in vivo. El éxito en ambos hitos es lo que finalmente denominaremos biomaterial prototipo. La obtención de los recubrimientos tendría una translación muy directa para implementarse en distintas partes de los componentes de implantes ortopédicos. En este sentido el equipo de investigación integra a biólogos de regeneración esquelética y clínicos de cirugía ortopédica y traumatología que van a estudiar la bioactividad y biocompatibilidad de estos recubrimientos sobre sustratos de titanio suministrados por Synthes, empresa líder en fabricación y comercialización de implantes para ortopedia, que participa en esta propuesta como EPO. Por otra parte y desde el punto de vista del procesado de materiales, la aplicación del procesado láser a los materiales cerámicos nanoestructurados SiO2-CaO-P2O5 es totalmente novedoso y creemos que puede optimizarse para obtener recubrimientos y también andamios tridimensionales, conformados con macroporosidad interconectada pero a su vez con microestructura fina y nanoestructura, que culminen en la obtención de piezas prototipo con alta reproducibilidad y de calidad e innovación tecnológica elevada. El Proyecto se encuadra en áreas de investigación fuertemente innovadoras y pujantes como son la nanotecnología y la medicina regenerativa ambas con un carácter multidisciplinar intrínseco donde la frontera entre las distintas disciplinas científicas tradicionales aparece difuminada. El Proyecto aúna esfuerzos de investigadores con formación básica en las disciplinas de química (ICMS), física e ingeniería (Empresa Subcontratada AIMEN), biología (UMA-CIBER-BBN) y medicina clínica y traslacional (HCS). Creemos que la integración de estos tres pilares i) síntesis, procesado y caracterización de materiales, ii) biología de la regeneración e ingeniería tisular y iii) práctica clínica ofrece una propuesta con capacidad para aportar resultados de impacto trasferibles a la industria y que puede por tanto ayudar al desarrollo de productos para aplicaciones en la reparación y regeneración esquelética en Andalucía.

The aim of this Project is to advance in the development of new biomaterials with improved bioactivity for their application in bone repair and regeneration. The goal is the preparation of new coatings and scaffolds of ceramic materials using laser processing techniques from nanostructured ceramic particulates in the SiO2-CaO-P2O5 system which will be synthesised at the ICMS. The hypothesis is the compositional properties and the textural parameters of the particulates in combination with the laser source have potential for processing depositions with controlled macro-nanostructure. It is programmed to prepare two types of prototype pieces: i) Titanium metallic substrates with bioactive ceramic coatings and ii) monolith scaffolds of bioactive ceramic with controlled geometry. There are two milestones to highlight. The first one is the fabrication of prototype pieces (coatings and scaffolds) with reproducibility, homogeneity, micro-nanostructural features, and surface and mechanical properties requirements. A second milestone will be the evaluation of their in vitro an in vivo biological properties. The achievement of both mentioned milestones will lead to the final biomaterial prototype. Bone regeneration biologists and orthopaedic surgeons will study the bioactivity and biocompatibility of the coatings on titanium substrates provided by Synthes which is a leader Company in orthopaedic trauma devices for internal and external fixation and is included in the proposal as EPO. The application of the laser processing to the SiO2-CaO-P2O5 nanostructured ceramic materials is completely new and we believe that it could be optimised for obtaining coatings and reticulated scaffolds while keeping their nanostructural features. The Project integrates material scientist, laser engineers, biologists and orthopaedic surgeons. We believe that this multidisciplinary approach with work in the i) synthesis, processing and characterisation of materials, ii) regeneration biology and tissue engineering and iii) medical practise could achieve results with potential to be transferred to the industry to promote the orthopaedic products to improve Andalusian bone repair and regeneration therapies.

## Control de procesos en plasmas para la síntesis de materiales nanoestructurados en forma de láminas delgadas (PLASMATER) Process-control in plasmas for the synthesis of nanostructured thin films (PLASMATER)

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| Código/Code: | P09-FQM-6900 (Proyecto de Excelencia) |
| Periodo/Period: | 15-03-2011 / 14-03-2014 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 167.209,71 € |
| Investigador responsable/Research head: | Alberto Palmero Acebedo |
| Componentes/Research group: | José Cotrino Bautista, Ana Borrás Martos, Francisco Yubero Valencia, Rafael Alvarez Molina, Juan Carlos González González, Carmen López Santos |

RESUMEN / ABSTRACT

En el proyecto PLASMATER abordamos el desarrollo de nuevos procesos basados en plasmas para controlar la nanoestructura, porosidad y morfología superficial de películas delgadas, con el objetivo de mejorar sus funcionalidades para aplicaciones finales. En las técnicas de deposición de películas delgadas asistida por plasma, las cantidades que definen la deposición, tales como la potencia electromagnética empleada, presión de los gases, etc., definen las propiedades del plasma, que a su vez, y a través de procesos no-lineales y fuertemente acoplados entre sí, producen el crecimiento de la película delgada en un porta-substrato. La complejidad de todos estos procesos ha dado lugar a que existan multitud de relaciones de carácter empírico entre cantidades controlables experimentales y las nanoestructuras crecidas, sin que haya una explicación clara sobre los mecanismos que controlan dicho crecimiento, y la conexión entre ambas. Este conocimiento es esencial para proponer modificaciones en las condiciones de la deposición que permitiesen un mayor control y versatilidad a la hora de sintetizar películas delgadas nanoestructuradas.

En PLASMATER nos proponemos desarrollar herramientas para controlar procesos en plasmas y obtener capas nanoestructuradas y sistemas 1D de TiO2 y ZnO soportados en substratos, para mejorar propiedades funcionales tales como foto-actividad o propiedades de mojado, entre otras. Se explorarán tres aspectos relacionados entre sí: i) diagnosis completa de la fase gaseosa (plasma y vaina) y caracterización de la nanoestructura de los materiales depositados, ii) estudio de las funcionalidades de dichos materiales, y iii) el desarrollo de códigos

numéricos predictivos, a partir de los cuales se desarrollen nuevos protocolos que permitan un mayor control sobre la nanoestructura del material y, por lo tanto, sobre las funcionalidades. El uso de modelos predictivos tiene una gran relevancia debido a que, hasta nuestro conocimiento, i) será la primera vez en la literatura que se dé una visión completa del proceso de deposición y nanoestructuración de estas películas delgadas basada en fenómenos fundamentales, a partir del valor de las cantidades experimentales de control (potencia electromagnética empleada, presión de los gases, etc.), y ii) se utilizará el modelo para proponer modificaciones en el proceso de deposición que ayuden a controlar los procesos de nanoestructuración de la película y proveer de más flexibilidad y versatilidad a los materiales depositados con vista a mejorar sus funcionalidades.

Para desarrollar el proyecto PLASMATER nos proponemos seguir una estrategia mixta simulación/diagnosis experimental del proceso de deposición para desarrollar interactivamente los modelos de crecimiento en múltiples condiciones. Se considerará el estudio de las diferentes escalas espaciales en el problema, desde el propio plasma (escala típica de decenas de centímetros), la vaina del plasma (por debajo de 1 milímetro), y la superficie del material (decenas de nanometros), y se utilizarán herramientas de diagnostico avanzado del plasma y de la película delgada que ayudarán al desarrollo del proyecto. Por último, la investigación también se centrará en encontrar las condiciones experimentales que permitan obtener la mejores propiedades de las capas con vista a optimizar sus aplicaciones tecnológicas e industriales.

Project PLASMATER aims at developing new plasma-based procedures to control the nanostructure, porosity and morphology of deposited thin films, and optimize the material functionalities and applications. From an experimental point of view, plasma-assisted thin film deposition techniques make use of various quantities to define the deposition conditions, such as the electromagnetic power, pressure in the reactor, etc. These quantities controls the plasma properties, which at the same time conditions the growth mechanism of the films. The complexity of the relation between experimentally controllable quantities and growth processes has produced the existence of empirical relations between experimental conditions and final film structure and composition, whose justification from a fundamental point of view is unclear.

In PLASMATER we propose to analyze three related aspects of the deposition of TiO2 and ZnO thin films assisted by plasmas: i) complete diagnosis of the plasma bulk and sheath in connection with the material microstructure, ii) functionality of the material, and iii) the development of predictive numerical codes that calculate the final film microstructure as a function of experimentally controllable quantities. This last part is of relevance because to our knowledge, i) it is the first time in the literature the deposition is fully characterized from a fundamental point of view, ii) this knowledge can be applied to suggest modifications in the deposition reactor in order to enhance different structural properties of the films.

In order to carry out the PLASMATER project, we aim at following at mixed theoretical and experimental strategy in order to interactively develop numerical codes of the thin film growth in multiple conditions. All the spatial scales involved in the description must be studied, from the plasma bulk itself (typically of few tens cm), the plasma sheath (below 1 mm), and the surface of the material (tens nm). Advanced diagnosis techniques will be employed to understand the plasma behavior and the film growth. Finally, PLASMATER will focus on the experimental conditions that lead to an optimized performance of the studied materials for advance applications in technology and industry.

## Síntesis y propiedades de nanopartículas luminiscentes basadas en tierras raras para aplicaciones biomédicas Synthesis and properties of luminiscent nanoparticles based on rare earth for biological applications

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|---|---|
| Código/Code: | FQM6090 (Proyecto de Excelencia) |
| Periodo/Period: | 15-03-2011 / 14-03-2014 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 100.000 € |
| Investigador responsable/Research head: | Manuel Ocaña Jurado |
| Componentes/Research group: | Angel Justo Erbez, Nuria O. Núñez Alvarez,<br>Fernando Cussó, Jesús Martínez de la Fuente,<br>Vanesa Sanz Beltrán, Sonia Rodríguez Liviano |

RESUMEN / ABSTRACT

El trabajo de investigación que se propone en esta memoria está dirigido al desarrollo de nuevos métodos de síntesis, poco agresivos para el medioambiente, de materiales nanoestructurados luminiscentes constituidos por partículas uniformes con forma y tamaño de partícula controlados de fluoruros, vanadatos y fosfatos de Gd, Y o La dopados con diversos cationes lantánidos, así como al análisis de sus propiedades ópticas y magnéticas (en compuestos de Gd) y de sus posibles aplicaciones biomédicas. En concreto, se abordará el dopado con diversos cationes con luminiscencia convencional y emisión en el visible (Eu, Tb, etc.) o infrarrojo (Nd, Er, Pr) y el codopado con pares Er/Yb, Tm/Yb o Ho/Yb con luminiscencia "up-conversion". Las principales ventajas que presentan estos materiales basados en tierras raras frente a otros materiales fluorescentes propuestos para las aplicaciones mencionadas son su menor toxicidad, su mayor estabilidad química y sobre todo, en el caso de los materiales con fluorescencia "up-conversion", su excitación con radiación infrarroja evita que se dañen los tejidos biológicos. Las muestras preparadas se caracterizarán en términos de sus propiedades estructurales, morfológicas y composicionales y se evaluarán sus propiedades ópticas (absorción y luminiscencia) y magnéticas en relación con sus características morfológicas y estructurales. Posteriormente, se desarrollarán procedimientos de funcionalización de las nanopartículas obtenidas para obtener materiales estables en condiciones fisiológicas. Por último, se analizará la biocompatibilidad de las nanopartículas obtenidas y su eficacia para la detección de tumores.

This project is devoted to the development of new methods, environmentally friendly, for the synthesis of nanostructured luminescent materials consisting of uniform particles with controlled size and shape, based on a Gd, Y or La matrix (fluoride, vanadate or phosphate) doped with different lanthanide (Ln) cations, as well as to the analysis of theirs optical and magnetic (Gd compounds) properties and the evaluation of theirs biomedical applications. Several Ln cations with down-conversion and emissions in the visible (Eu, Tb) or near-infrared (NIR) (Nd, Er, Pr) and up-coversion (Er/Yb, Tm/Yb, Ho/Yb) luminescence have been selected. The main advantages that these Ln based nanomaterials present over other luminescent systems with potential bioapplications are their lower toxicity and higher chemical stability. In addition, in the case of up-converting nanophosphors, they are excited with NIR radiation which, in contrast with ultraviolet excitation, does not cause damage to biological tissues. Several procedures for the functionalization of the obtained nanoparticles will be essayed in order

to obtain stable dispersions in physiological media. Finally, the nanophosphors biocompatibility and their efficiency for the detection of tumors will be also evaluated.

JUNTA DE ANDALUCIA

## Dispositivos luminiscentes basados en láminas delgadas con tierras raras depositadas mediante tecnología de plasma (LUMEN) Luminescent devices based on rare earth containing thin films deposited by plasma technology (LUMEN)

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| Código/Code: | P11-TEP-8067 (Proyecto de Excelencia Motriz) |
| Periodo/Period: | 16-05-2013 / 15-05-2016 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 143.750 € |
| Investigador responsable/Research head: | Angel Barranco |
| Componentes/Research group: | Agustín R. González-Elipe, Juan Pedro Espinós, Richard Lambert, Juan Carlos González-González, Francisco J. García García, Victor J. Rico Gavira, , Jorge Gil Rostra, Lola González García, F. Javier Ferrer (CNA), Fabián Frutos Rayego |

RESUMEN / ABSTRACT

El presente proyecto persigue el desarrollo de una serie de dispositivos luminiscentes basados en láminas delgadas con tierras raras depositadas mediante tecnologías de plasma. Las láminas delgadas luminiscentes se fabricarán mediante un nuevo procedimiento desarrollado por el grupo investigador que combina procesos clásicos como "magnetrón sputtering" o deposición por plasma y la evaporación de compuestos metalorgánicos de baja o nula tensión de vapor a temperatura ambiente pero fácilmente sublimables en la cámara de reacción. Esta metodología ofrece la oportunidad de integrar uno o varios elementos de tierras raras dentro de la capa formada, controlando perfectamente su concentración en la misma. Dada la versatilidad del proceso, se plantea fabricar capas delgadas luminiscentes de interés para tres campos de aplicación: procesos de "up conversión", detectores de ion-luminiscencia y sistemas de señalización. Los materiales a desarrollar deben permitir superar algunas de las limitaciones existentes con los materiales actualmente existentes, proporcionando nuevas funcionalidades y mejoras sustanciales en sus prestaciones en relación con aplicaciones como detectores en procesos de fusión nuclear, cambiadores de longitud de onda en sistemas para comunicaciones ópticas y señalización en automoción. Dadas las características del nuevo método propuesto, el proceso de síntesis de las capas luminiscente es compatible con otros procesos en línea proponiéndose la integración de las capas luminiscentes en dispositivos fotónicos simples formadas por estructuras multicapa tipo reflectores de Bragg o similares. El proyecto aborda todo la cadena de valor que lleva de la síntesis de los materiales a sus aplicaciones, incluyendo su caracterización avanzada, el análisis de sus propiedades ópticas y de luminiscencia, su integración en dispositivos y el análisis de su resistencia medioambiental.

The objective of the LUMEN project is the development of luminescent devices incorporating as active layers rare earth containing thin films deposited by plasma CVD. The thin films will be deposited by novel synthetic approaches that combined classic approaches as magnetron sputtering and plasma CVD with the sublimation of functional molecules. This methodology is very effective to introduce a controlled amount of functional elements (i.e., rare earth cations of functional organic groups) in the growing film. Due to the full compatibility of the proposed methodology with optoelectronics processes the active layers will be directly incorporated in photonic structures as Bragg reflectors and photonic crystals to fabricate prototype devices. Thus, the LUMEN projects start with the development of new materials but also intend to study the functionality of devices that integrates these novel materials in real life conditions. These devices are intelligent label structures, up-converters and ion detectors.

## Plasmas de Descarga de Barrera Dieléctrica para el Desarrollo de Procesos Industriales a Presión Atmosférica (DBD-Tech) Dielectric Barrier Discharge plasma for the developing of industrial process at atmospheric pressure (DBD-Tech)

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| Código/Code: | P12-FQM-2265 (Proyecto de Excelencia) |
| Periodo/Period: | 30-01-2014 / 29-01-2017 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 143.750 € |
| Investigador responsable/Research head: | José Cotrino Bautista |
| Componentes/Research group: | Francisco García García, Jorge Gil Rostra, Richard M. Lambert, Manuel J. Macías Montero, Alberto Palmero Acebedo, Victor Rico Gavira |

RESUMEN / ABSTRACT

La presente propuesta de proyecto de investigación persigue en primera instancia abordar una serie de aspectos básicos no resueltos relacionados con los mecanismos de la descarga barrera, las condiciones óptimas que deben cumplir los electrodos, la definición de un diseño óptimo de los mismos y el establecimiento de las mejores condiciones para la descarga.

En una segunda instancia y desde una perspectiva aplicada, se pretende la fabricación de dos tipos de reactores de descarga barrera mejorados para dos aplicaciones tecnológicas de gran impacto industrial. Primeramente para la funcionalización superficial de materiales avanzados persiguiendo, entre otros, el control lateral de la funcionalización según patrones litográficos. En segundo término, para el desarrollo de procesos de “plasma-catálisis” tendentes a aumentar la selectividad y disminuir el consumo energético de una serie de reacciones químicas de alto valor añadido e impacto industrial. Se prevé que, para ambos tipos de aplicaciones, los estudios básicos planteados permitan avanzar de manera clara en la optimización de los procesos finales con perspectivas de uso industrial.

This research project aims first the study of different unknown basic aspects of the construction of the dielectric barrier discharge, better design conditions for: barrier electrodes, the design of the metallic electrodes and dielectrics and to know the best working conditions (size and operation frequency) for the plasma. One goal is to control the lateral functionalization of advanced materials and other objective, is the discovering of new plasma catalysis processes that can increase selectivity and the reduction of energy consumption by plasma chemical reactions in controlled industrial processes of high added value and/or impact. It is expected for both applications, a clear advance in optimization of the industrial process.

JUNTA DE ANDALUCIA

## **Síntesis y propiedades de nanopartículas luminiscentes para aplicaciones biomédicas** **Synthesis and properties of luminescent nanoparticles for biomedical applications**

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| Código/Code: | TAPOST-234 |
| Periodo/Period: | 01-10-2014 / 30-09-2016 |
| Organismo Financiador/Financial source: | Junta de Andalucía /Unión Europea |
| Importe total/Total amount: | 155.008,57 € |
| Investigador responsable/Research head: | Alberto Escudero Belmonte |

RESUMEN / ABSTRACT

Las nanopartículas luminiscentes resultan de interés en Nanobiomedicina debido a sus diferentes aplicaciones, que incluyen sensores ópticos para la imagen de tejidos o estructuras intracelulares y para la detección y cuantificación de moléculas de interés biológico. En este proyecto se desarrollan nuevos métodos de síntesis de nanoestructuras uniformes de diferentes materiales inorgánicos (vanadatos, fluoruros, fosfatos y molibdatos dopados con cationes lantánidos) más económicos y respetuosos con el medio ambiente. También se evalúan las aplicaciones biomédicas de estos materiales, con especial atención al diseño de sensores y a su potencialidad como dispositivos para la detección e imagen de células cancerígenas. Este proyecto incluye la caracterización de los materiales obtenidos, la optimización de sus propiedades ópticas y magnéticas, el desarrollo de nuevos métodos de funcionalización y conjugación con moléculas de interés biológico, el análisis de la citotoxicidad de los materiales resultantes y el estudio de la interacción de las diferentes nanoestructuras funcionalizadas con células de distinta naturaleza, con especial atención al efecto de la morfología y composición química de las nanopartículas.

Luminescent nanoparticles are currently attracting wide research interest in Nanobiomedicine due to their applications, ranging from optical biolabels for imaging of tissues or intracellular structures to sensors to detect biological molecules, and as tracking devices. This project is focused on the design of new, cheaper, and environmentally friendly synthesis methods of uniform luminescent nanoparticles, such as rare earth doped fluorides, phosphates, molybdates, and vanadates. It also evaluates their biomedical applications, with special attention to their sensing properties and their ability to detect tumour cells. This scientific work includes the characterization of the resulting materials, the optimization of their optical and magnetic properties, and the development of different functionalization processes. The final step of this research project deals with the study of the interaction of the functionalised nanoparticles with cells of different nature, and includes cytotoxicity studies, with special attention to the role played by the morphology and chemistry of the particles.

## PROYECTOS EN LOS QUE PARTICIPAN INTEGRANTES DE LA UNIDAD

### Nuevas técnicas de procesado de cerámica y vidrio respuestas con el medio ambiente (CERAMGLASS) Environmentally friendly processing of ceramics and glass (CERAMGLASS)

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|---|---|
| Código/Code: | LIFE11 ENV/ES/560 |
| Periodo/Period: | 01-01-2011 / 31-12-2014 |
| Organismo Financiador/Financial source: | Unión Europea |
| Importe total/Total amount: | 1.456.870 € |
| Investigador responsable/Research head: | Germán de la Fuente Leis |
| Componentes/Research group: | ICMS: Agustín R. González-Elipe, Victor J. Rico, Angel Barranco Quero, Juan Pedro Espinós Manzorro, Jorge Gil, Francisco Yubero Valencia |

RESUMEN / ABSTRACT

El objetivo general del proyecto CERAMGLASS es disminuir el impacto al medio ambiente durante los tratamientos térmicos en la industria cerámica mediante la aplicación de una tecnología innovadora de horno láser a cerámica plana y vridrio. El proyecto persigue construir una planta piloto basada en la combinación innovadora de un horno continuo y un láser que barra la superficie. El propósito es probar que esta combinación permite una reducción significativa en el consumo energético y la escalabilidad industrial del proceso.

En primer lugar, el proyecto persigue demostrar que es posible producir placas cerámicas robustas de sólo 4 mm de espesor. Esto significaría una reducción del 50% en el espesor, con la consiguiente reducción en el consumo de materias primas. El proyecto persigue también adaptar las composiciones decorativas incorporando el uso de materiales menos agresivos al uso del procesado láser. En concreto, se tratará de adaptar los procesos de decorado “screen printing” a productos de tercer fuego con lustre y efectos metálicos, así como el de tintas decorativas al vidrio plano. La sustitución de productos iniciales tóxicos permitirá una disminución en la generación de CO2 y otras emisiones gaseosas, residuos tóxicos y la reducción de los requerimientos energéticos del proceso.

The general objective of the 'CERAMGLASS' project is to reduce the environment impact of thermal treatment of ceramics by the successful application of an innovative laser-furnace technology on planar ceramics and glass. The project plans to construct a pilot plant based on the innovative combination of a continuous furnace and a scanning laser. It aims at demonstrating a considerable reduction in energy consumption and the industrial scalability of the process.

The project primarily aims at showing that it is feasible to produce robust ceramic tile of only 4 mm thick. This would represent a 50% reduction in tile thickness, with consequent reduction in consumption of raw source materials. The project will adapt decoration compositions with more environmentally friendly materials by using the laser processing. Specifically it will adapt screen printing decorations to third-fire products with lustre and metallic effects and decoration inks for planar glass. The replacement of toxic starting materials will allow a minimisation of CO2 and other gas emissions, toxic residues and a reduction of the energy consumption of the process.

## Convenios y Contratos / Contracts and Agreements

### Evaluación de la aplicabilidad de diversas estructuras inorgánicas como matriz huésped en el desarrollo de nuevos pigmentos inorgánicos

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| Periodo/Period: | 01-01-2013 / 30-09-2014 |
| Organismo Financiador/Financial source: | AL-FARBEN, S.A. |
| Importe total/Total amount: | 177.870 € |
| Investigador responsable/Research head: | Manuel Ocaña Jurado |
| Componentes/Research group: | Ana Isabel Becerro Nieto, Nuria Núñez Álvarez, Alberto Escudero Belmonte |

### Promover el progreso científico en líneas de investigación de común interés y favorecer la transferencia de nuevo conocimiento a los sectores productivos

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| Periodo/Period: | 02-08-2012 / 01-08-2016 |
| Organismo Financiador/Financial source: | ABENGOA RESEARCH, S.L. |
| Importe total/Total amount: | 290.400 € |
| Investigador responsable/Research head: | Agustín R. González-Elipe |

### MTA “A suspensión of titanium oxide nanoparticles synthesised”

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| Periodo/Period: | 08-06-2012 / 08-06-2017 |
| Organismo Financiador/Financial source: | COPSAFE BVBA |
| Investigador responsable/Research head: | Hernán Míguez García |

### Fabricación de láminas de subóxidos de Silicio como sustratos para descomposición espinodal por procesado láser

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| Periodo/Period: | 01-01-2011 / 31-12-2014 |
| Organismo Financiador/Financial source: | ABENGOA RESEARCH, S.L. |
| Importe total/Total amount: | 36.300 € |
| Investigador responsable/Research head: | Ana Borrás Martos |

### Validación de la tecnología “Thin Film” (lámina delgada) fotovoltáica a escala piloto

Periodo/Period: 30-04-2010 / 1-09-2014
Organismo Financiador/Financial source: Ghenova Ingenieria, S.L.U.
Importe total/Total amount: 918.624,07 €
Investigador responsable/Research head: Agustín R. González-Elipe
Componentes/Research group: José Cotrino Bautista, Juan Pedro Espinós Manzorro, Angel Barranco Quero, Francisco Yubero

### Desarrollo de Added Value New CPVs enhanced developtments (ADVANCED)

Periodo/Period: 23-07-2013 / 31-12-2014
Organismo Financiador/Financial source: ABENGOA SOLAR NEW TECHNOLOGIES, S.A.
Importe total/Total amount: 302.500 €
Investigador responsable/Research head: Agustín R. González-Elipe
Componentes/Research group: José Cotrino Bautista, Angel Barranco Quero, Ana Isabel Borrás Martos, Francisco Yubero Valencia, Juan Pedro Espinós Manzorro, Alberto Palmero Acebedo, Victor R. Rico Gavira

### Ensamblaje de un equipo comprobador del estado de vacío en el espacio anular de los tubos receptores en colectores cilindro parabólicos

Periodo/Period: 24-01-2014 / 23-07-2014
Organismo Financiador/Financial source: ABENGOA Solar New Technologies, S.A.
Importe total/Total amount: 10.890 €
Investigador responsable/Research head: Francisco Yubero Valencia
Componentes/Research group: José Cotrino Bautista, Juan Pedro Espinós Manzorro, Agustín R. González-Elipe, Angel Barranco Quero

### Recubrimientos ópticos para sistemas fotovoltáicos de concentración

Periodo/Period: 15-05-2014 / 31-03-2015
Organismo Financiador/Financial source: ABENGOA Solar New Technologies, S.A.
Importe total/Total amount: 181.500 €
Investigador responsable/Research head: Hernán Míguez García
Componentes/Research group: Mauricio Calvo Roggiani, Juan F. Galisteo López, Alberto Jiménez Solano, Miguel Anaya Martín

### Acuerdos de colaboración para producir espejos de alta reflectavidad a los fines de reducir costes en la tecnología cilindro parabólica

Periodo/Period: 9-10-2014 / 8-07-2015
Organismo Financiador/Financial source: ABENGOA SOLAR LLC
Importe total/Total amount: 30.000 €
Investigador responsable/Research head: Hernán Míguez García

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| Componentes/Research group: | Mauricio Calvo Roggiani, Juan F. Galisteo López, Gabriel Lozano Barbero, Alberto Jiménez Solano, Miguel Anaya Martín |

## EXPERIMENTOS EN GRANDES INSTALACIONES / LARGE FACILITY EXPERIMENTS

### Sincrotrón ALBA / ALBA Synchrotron

### Unraveling the wetting properties of TiO2 under UV Irradiation

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| Código/Code: | 2012010293 |
| Periodo/Period: | 14-10-2014 / 21-10-2014 |
| Organismo Financiador/Financial source: | Sincrotrón ALBA |
| Instalación Científica: | ALBA línea BL24. Cerdanyola del Vallés, Barcelona (España) |
| Investigadores/Researchers: | Juan Pedro Espinós, Victor Rico Gavira, M. Carmen López Santos |

## PATENTES / PATENTS

### Detector de partículas ionizantes

Inventores: Angel Barranco Quero, Jorge Gil Rostra, Juan Pedro Espinós Manzorro, Francisco Yubero Valencia, José Cotrino Bautista, Agustín R. González-Elipe, F. Javier Ferrer Fernández
Tipo de Patente: Nacional
Número de Solicitud: 201430394
Fecha Solicitud: 20 Marzo 2014
Entidad/es Titular/es: Universidad Complutense de Madrid y CSIC

### Implantes biocompatibles de titanio nanoestructurado con propiedades antibacterianas

Inventores: Rafael Alvarez Molina, Alberto Palmero Acebedo, José Miguel García Martín (IMM-CNM)
Tipo de Patente: Nacional
Número de Solicitud: 201430616
Fecha Solicitud: 25 Abril 2014
Entidad/es Titular/es: CSIC

### Espejo para aplicaciones de energía solar y método de fabricación de dicho espejo

Inventores: Keith Boyle; Carlos Alcañiz García; Mercedes Alcón Camas; Juan Pablo Núñez Bootello; Hernán Ruy Míguez García; Mauricio Ernesto Calvo Roggiani; Alberto Jiménez Solano; Miguel Anaya Martín
País de inscripción: España
Número de Solicitud: P201431774
Fecha Solicitud: 28 noviembre 2014
Entidad/es Titular/es: ABENGOA SOLAR NEW TECHNOLOGIES, S.A.

## ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

### Dye sensitized solar cells as optically random photovoltaic media

Galvez, FE; Barnes, PRF; Halme, J; Miguez, H
*Energy & Environmental Science*, **6** (2014) 1260-1266
February, 2014 | **DOI:** 10.1039/C3EE42587H

In order to enhance optical absorption, light trapping by multiple scattering is commonly achieved in dye sensitized solar cells by adding particles of a different sort. Herein we propose a theoretical method to find the structural parameters (particle number density and size) that optimize the conversion efficiency of electrodes of different thicknesses containing spherical inclusions of diverse composition. Our work provides a theoretical framework in which the response of solar cells containing diffuse scattering particles can be rationalized. Optical simulations are performed by combining a Monte Carlo approach with Mie theory, in which the angular distribution of scattered light is accounted for. Several types of scattering centers, such as anatase, gold and silver particles, as well as cavities, are considered and their effect compared. Estimates of photovoltaic performance, insight into the physical mechanisms responsible for the observed enhancements, and guidelines to improve the cell design are provided. We discuss the results in terms of light transport in weakly disordered optical media and find that the observed variations between the optimum scattering configurations attained for different electrode thicknesses can be understood as the result of the randomization of the light propagation direction at different depths within the active layer. A primary conclusion of our study is that photovoltaic performance is optimised when the scattering properties of the film are adjusted so that the distance over which incident photons are randomized is comparable to the thickness of the film. This simple relationship could also be used as a design rule to attain the optimum optical design in other photovoltaic materials.

### Low Temperature Production of Formaldehyde from Carbon Dioxide and Ethane by Plasma-Assisted Catalysis in a Ferroelectrically Moderated Dielectric Barrier Discharge Reactor

Gomez-Ramirez, A; Rico, VJ; Cotrino, J; Gonzalez-Elipe, A; Lambert, RM
*ACS Catalysis*, **4** (2014) 402-408
February, 2014 | **DOI:** 10.1021/cs4008528

Plasma-assisted catalysis of the reaction between $CO_2$ and $C_2H_6$ in a single-pass, ferroelectrically moderated dielectric barrier discharge reactor has been studied at near ambient temperature as a function of physicochemical and electrical reaction variables. The presence of small amounts of a vanadia/alumina catalyst dispersed on the $BaTiO_3$ ferroelectric markedly enhanced the production of formaldehyde, the focus of this work. A maximum HCOH selectivity of 11.4% (defined with respect to the number of ethane carbon atoms consumed) at 100% ethane conversion was achieved, the other products being CO, $H_2O$, $H_2$, $CH_4$ and a small amount of $C_3H_8$. $N_2O$ was also an effective partial oxidant (HCOH selectivity 8.9%) whereas use of $O_2$ led to complete combustion, behavior that may be rationalized in terms of the electron impact excitation cross sections of the three oxidants. Control experiments with the coproducts $CH_4$ and $C_3H_8$ showed that these species were not intermediates in HCOH formation from $C_2H_6$. Analysis of reactor performance as a function of discharge characteristics revealed that formaldehyde formation was strongly favored at low frequencies where the zero-current fraction of the duty cycle was greatest, the implication being that plasma processes also acted to destroy previously formed products. A tentative reaction mechanism is proposed that accounts for the broad features of formaldehyde production.

## Tailor-made directional emission in nanoimprinted plasmonic-based light-emitting devices

Lozano, G; Grzela, G; Verschuuren, MA; Ramezani, M; Rivas, JG
*Nanoscale*, **6** (2014) 9223-9229
August, 2014 | **DOI:** 10.1039/c4nr01391c

We demonstrate an enhanced and tailor-made directional emission of light-emitting devices using nanoimprinted hexagonal arrays of aluminum nanoparticles. Fourier microscopy reveals that the, luminescence of the device is not only determined by the material properties of the organic dye molecules but is also strongly influenced by the coherent scattering resulting from periodically arranged metal nanoparticles. Emitters can couple to lattice-induced hybrid plasmonic-photonic modes sustained by plasmonic arrays. Such modes enhance the spatial coherence of an emitting layer, allowing the efficient beaming of the emission along narrow angular and spectral ranges. We show that tailoring the separation of the nanoparticles in the array yields an accurate angular distribution of the emission. This combination of large-area metal nanostructures fabricated by nanoimprint lithography and light-emitting devices is beneficial for the design and optimization of solid-state lighting systems.

## Bending Induced Self-Organized Switchable Gratings on Polymeric Substrates

Parra-Barranco, J; Oliva-Ramirez, M; Gonzalez-Garcia, L; Alcaire, M; Macias-Montero, M; Borras, A; Frutos, F; Gonzalez-Elipe, AR; Barranco, A
*ACS Applied Materials & Interfaces*, **6** (2014) 11924-11931
August, 2014 | **DOI:** 10.1021/am5037687

We present a straightforward procedure of self-surface patterning with potential applications as large area gratings, invisible labeling, optomechanical transducers, or smart windows. The methodology is based in the formation of parallel micrometric crack patterns when polydimethylsiloxane foils coated with tilted nanocolumnar $SiO_2$ thin films are manually bent.

The $SiO_2$ thin films are grown by glancing angle deposition at room temperature. The results indicate that crack spacing is controlled by the film nanostructure independently of the film thickness and bending curvature. They also show that the in-plane microstructural anisotropy of the $SiO_2$ films due to column association perpendicular to the growth direction determines the anisotropic formation of parallel cracks along two main axes. These self-organized patterned foils are completely transparent and work as customized reversible diffraction gratings under mechanical activation.

### Tuning the transmittance and the electrochromic behavior of CoxSiyOz thin films prepared by magnetron sputtering at glancing angle

Gil-Rostra, J; Garcia-Garcia, F; Yubero, F; Gonzalez-Elipe, AR
*Solar Energy Materials and Solar Cells*, **123** (2014) 130-138
April, 2013 | **DOI:** 10.1016/j.solmat.2013.12.020

This work reports the synthesis and the characterization of amorphous CoxSiyOz thin films prepared by magnetron sputtering from a single cathode. Porous layers with outstanding electrochromic properties are obtained at room temperature in one step by performing the deposition at a glancing angle configuration. The electrochromic behavior of these layers in a basic aqueous medium was dependent on the Co/Si ratio in the films and in all cases was characterized by a fast response, a high coloration efficiency and a complete reversibility after several hundred cycles. A characteristic feature of these electrochromic layers is that, for a similar thickness, the range of transmittance modulation can be tuned by changing the Co/Si ratio in the films and, specifically for films with a high concentration of silicon, to change their aspect from an almost transparent to a full colored state.

### Role of crystal structure on $CO_2$ capture by limestone derived CaO subjected to carbonation/recarbonation/calcination cycles at Ca-looping conditions

Valverde, JM; Sanchez-Jimenez, PE; Perez-Maqueda, LA; Quintanilla, MAS; Perez-Vaquero, J
*Applied Energy*, **125** (2014) 264-275
July, 2014 | **DOI:** 10.1016/j.apenergy.2014.03.065

Large scale pilot plants are currently demonstrating the feasibility of the Calcium-looping (CaL) technology built on the multicyclic calcination/carbonation of natural limestone for post-combustion and precombustion $CO_2$ capture. Yet, limestone derived CaO exhibits a drop of conversion when subjected to multiple carbonation/calcination cycles, which lessens the efficiency of the technology. In this paper we analyze a novel CaL concept recently proposed to mitigate this drawback based on the introduction of an intermediate stage wherein carbonation is intensified at high temperature and high $CO_2$ partial pressure. It is shown that carbonation in this stage is mainly driven by solid-state diffusion, which is determined by the solid's crystal structure. Accordingly, a reduction of crystallinity by ball milling, which favors diffusion, serves to promote recarbonation. Conversely, thermal annealing, which enhances crystallinity, hinders recarbonation. An initial fast phase has been identified in the recarbonation stage along which the rate of carbonation is also a function of the crystal structure indicating a relevant role of surface diffusion. This is consistent with a recently proposed mechanism for nucleation of $CaCO_3$ on the CaO surface in islands with a critical size determined by surface diffusion. A further issue analyzed has been the effects of pretreatment and cycling on the mechanical strength of the material, whose fragility hampers the CaL process efficiency. Particle size distribution of samples dispersed in a liquid and subjected to high energy ultrasonic irradiation indicate that milling promotes friability whereas thermal annealing enhances the resistance of the particles to fragmentation even though pretreatment effects become blurred after cycling. Our study demonstrates that recarbonation conditions and crystal-structure controlled diffusion are important parameters to be considered in order to assess the efficiency of $CO_2$ capture in the novel CaL concept.

### Bifunctional, Monodisperse $BiPO_4$-Based Nanostars: Photocatalytic Activity and Luminescent Applications

Becerro, AI; Criado, J; Gontard, LC; Obregon, S; Fernandez, A; Colon, G; Ocana, M
*Crystal Growth & Design*, **14** (2014) 3319-3326
July, 2014 | **DOI:** 10.1021/cg500208h

Monodisperse, monoclinic $BiPO_4$ nanostars have been synthesized by a homogeneous precipitation reaction at 120 °C through controlled release of $Bi^{3+}$ cations from a Bi–citrate chelate, in a mixture of glycerol and ethylene glycol, using $H_3PO_4$ as the phosphate source. The set of experimental conditions necessary to obtain uniform nanoparticles is very restrictive, as the change in either the polyol ratio or the reactant concentrations led to ill-defined and/or aggregated particles. The morphology of the particles consists of a starlike, hierarchical structure formed by the ordered arrangement of nanorod bundles. Transmission electron tomography has revealed that the nanostars are not spherical but flattened particles. Likewise, Fourier transform infrared spectroscopy and thermogravimetry have shown that the synthesized nanostars are functionalized with citrate groups. The mechanism of formation of the nanostars has been analyzed to explain their morphological features. The as-synthesized BiPO4 nanostars exhibit an efficient photocatalytic performance for the degradation of Rhodamine B. Finally, it has been demonstrated that the stars can be $Eu^{3+}$-doped up to 2 mol % without any change in the particle morphology or symmetry, and the doped samples show emission in the orange-red region of the visible spectrum after ultraviolet excitation. These experimental observations make this material a suitable phosphor for biotechnological applications.

### New Single-Phase, White-Light-Emitting Phosphors Based on delta-Gd2Si2O7 for Solid-State Lighting

Fernandez-Carrion, AJ; Ocana, M; Garcia-Sevillano, J; Cantelar, E; Becerro, AI
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August, 2014 | **DOI:** 10.1021/jp505524g

Two new white-light (WL)-emitting phosphors ($\delta$-$Gd_2Si_2O_7$:Dy and $\delta$-$Gd_2Si_2O_7$:Eu,Tb) have been synthesized by the sol–gel method. The Gd-$Ln^{3+}$ ($Ln^{3+}$= $Dy^{3+}$, $Tb^{3+}$, $Eu^{3+}$) energy-transfer band has been used to excite both phosphors, which provides an enhancement of the Ln3+ emissions. First, WL was generated from $\delta$-$Gd_2Si_2O_7$:xDy thanks to the particular ratio of the blue and yellow emissions observed in all three compositions, which had chromatic coordinates of x = 0.30, y = 0.33 and CCT values of between 7077 and 6721 K. The decay curves of the main transitions of $Dy^{3+}$ showed a maximum lifetime value for δ-$Gd_2Si_2O_7$:0.5%Dy, which is, therefore, the most efficient doping level. Second, a broad spectral range, single-phase, WL-emitting phosphor was generated by codoping δ-$Gd_2Si_2O_7$ with $Tb^{3+}$ and $Eu^{3+}$. The composition δ-$Gd_2Si_2O_7$:0.3%$Eu^{3+}$;0.8%$Tb^{3+}$ showed CIE coordinates well inside the ideal WL region of the CIE diagram and a CCT value of 5828 K. The single-phase WL-emitting phosphors presented in this paper are promising materials to be used in white solid-state lighting systems and field-emission displays due to the advantages provided both by $Gd^{3+}$ ions and by the high thermal and chemical stabilities of the rare earth disilicate matrix.

### Oxygen Optical Sensing in Gas and Liquids with Nanostructured ZnO Thin Films Based on Exciton Emission Detection

Sanchez-Valencia, JR; Alcaire, M; Romero-Gomez, P; Macias-Montero, M; Aparicio, FJ; Borras, A; Gonzalez-Elipe, AR; Barranco, A

*Journal of Physical Chemistry C*, **118** (2014) 9852-9859

May, 2014 | **DOI:** 10.1021/jp5026027

Transparent nanocolumnar porous ZnO thin films have been prepared by plasma-enhanced chemical vapor deposition. By controlling the H-2/O-2 ratio in the plasma gas, the deposition conditions were optimized to obtain an intense exciton emission at around 381 nm and virtually no luminescence in the visible region associated with electronic states in the gap. The intensity of the exciton band varied significantly and reversibly with the partial pressure of oxygen in the environment. This behavior and its variations with temperature and water vapor sustain the use of these thin films as photonic sensors of oxygen. Further experiments in liquid water show that fluorescence intensity also varies with the amount of dissolved oxygen even for concentrations lower than 0.02 mg/L where commercial oxygen galvanic sensors show limited sensitivity. These results and the use of ZnO as photonic sensor of oxygen are discussed by assuming a classical mechanism involving the photoactivated adsorption of oxygen when this oxide is irradiated with UV light during its fluorescence interrogation.

### The Flexible Surface Revisited: Adsorbate-Induced Reconstruction, Homocoupling, and Sonogashira Cross-Coupling on the Au(100) Surface

Sanchez-Sanchez, C; Yubero, F; Gonzalez-Elipe, AR; Feria, L; Sanz, JF; Lambert, RM

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Phenylacetylene (PA) and iodobenzene (IB) are prototypical reactants in Sonogashira cross-coupling. Their adsorption behavior and reactivity on the Au(100) surface were studied by STM, temperature-programmed desorption and reaction, and DFT calculations that included the effect of dispersion forces. The two species exhibited very different behavior. Thus, even at 200 K, PA rearranged Au surface atoms so as to lift the hex reconstruction and adsorb in 4-fold-symmetric islands on the unreconstructed 100 surface. On the other hand, IB adsorbed on the reconstructed hex surface, again as islands, forming three different coexisting close-packed structures. The DFT results are in good accord with these findings, demonstrating the strong preference of PA and IB for the (100) and hex surfaces, respectively. Moreover, the calculated adsorption energies were in satisfactory agreement with values estimated from the desorption data. Adsorbed separately, both PA and IB underwent homocoupling yielding diphenyl diacetylene and biphenyl, respectively; in the former case, reaction appeared to originate at island boundaries. On the well-annealed surface, coadsorbed PA and IB behaved independently, generating only products of homocoupling. However, on the Ar+ roughened surface, Sonogashira cross-coupling also occurred, yielding diphenyl acetylene. These findings are discussed in terms of the island-forming propensity of the reactants, amplified by the labile nature of the Au 100 surface under adsorption and the marked preference of the two reactants for different substrate structures, factors that act to inhibit the formation of a mixed adlayer and suppress reactivity. The implications for the behavior of practical Au nanoparticle catalysts are considered.

### Luminescent 3-hydroxyflavone nanocomposites with a tuneable refractive index for photonics and UV detection by plasma assisted vacuum deposition

Aparicio, FJ; Alcaire, M; Borras, A; Gonzalez, JC; Lopez-Arbeloa, F; Blaszczyk-Lezak, I; Gonzalez-Elipe, AR; Barranco, A

*Journal of Materials Chemistry C*, **2** (2014) 6561-6573

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Luminescent organic-thin-films transparent in the visible region have been synthesized by a plasma assisted vacuum deposition method. The films have been developed for their implementation in photonic devices and for UV detection. They consist of a plasma polymeric matrix that incorporates 3-hydroxyflavone molecules characterized by absorption of UV radiation and emission of green light. The present work studies in detail the properties and synthesis of this kind of transparent and luminescent material. The samples were characterized by X-ray photoemission (XPS), infrared (FT-IR) and secondary ion mass (ToF-SIMS) spectroscopies; and their optical properties were analysed by UV-Vis absorption, fluorescence and ellipsometry (VASE) spectroscopies. The key factors controlling the optical and luminescent properties of the films are also discussed. Indeed, our experimental results show how the optical properties of the films can be adjusted for their integration in photonic devices. Moreover, time resolved and steady state fluorescence analyses, including quantum yield determination, indicate that the fluorescence efficiency is a function of the deposition parameters. An outstanding property of these materials is that, even for high UV absorption values (i.e. large layer thickness and/or dye concentration), the emitted light is not reabsorbed by the film. Such highly UV absorbent and green emitting films can be used as UV photodetectors with a detection threshold smaller than 10 mu W cm(-2), a value similar to the limit of some commercial UV photodetectors. Based on these properties, the use of the films as visual tags for the detection of solar UV irradiation is proposed.

### Morphological and structural behavior of $TiO_2$ nanoparticles in the presence of $WO_3$: crystallization of the oxide composite system

Kubacka, A; Iglesias-Juez, A; di Michiel, M; Becerro, AI; Fernandez-Garcia, M

*Physical Chemistry Chemical Physics*, **16** (2014) 19540-19549

September, 2014 | **DOI:** 10.1039/c4cp02181a

Composite $TiO_2$-$WO_3$ oxide materials were prepared by a single pot microemulsion method and studied during calcination treatments under dry air in order to analyze the influence of tungsten on the behavior of the dominant titania component. To this end, the surface and bulk morphological and structural evolution of the solid precursors was studied using X-ray diffraction and infrared spectroscopy. In the calcination process, differences in the dominant titania component behavior appeared as a function of the W/Ti atomic ratio of the precursor. First, the crystallization of the anatase phase is affected by tungsten through an effect on the primary particle size growth. Furthermore, such an effect also influences the anatase to rutile phase transformation. The study provides evidence that the W-Ti interaction develops differently for a low/high W/Ti atomic ratio below/above 0.25 affecting fundamentally the above-mentioned anatase primary particle size growth process and the subsequent formation of the rutile phase and showing that addition of tungsten provides a way to control morphology and phase behavior in anatase-based oxide complex materials.

### Panchromatic porous specular back reflectors for efficient transparent dye solar cells

Lopez-Lopez, C; Colodrero, S; Miguez, H
*Physical Chemistry Chemical Physics*, **16** (2014) 663-668
January, 2014 | **DOI:** 10.1039/C3CP53939C

A panchromatic specular reflector based dye solar cell is presented herein. Photovoltaic performance of this novel design is compared to that of cells in which standard diffuse scattering layers are integrated. The capability of the proposed multilayer structures to both emulate the broad band reflection of diffuse scattering layers of standard thickness (around 5 microns) and give rise to similarly high light harvesting and power conversion efficiencies, yet preserving the transparency of the device, is demonstrated. Such white light reflectors are comprised of stacks of different porous optical multilayers, each one displaying a strong reflection in a complementary spectral range, and are designed to leave transmittance unaltered in a narrow red-frequency range in which the sensitized electrode shows negligible absorption, thus allowing us to see through the cell. The reflectance bandwidth achieved is three times as broad as the largest bandwidth previously achieved using any photonic structure integrated into a dye solar cell.

### A study of the optical properties of metal-doped polyoxotitanium cages and the relationship to metal-doped titania

Lv, YK; Cheng, J; Matthews, PD; Holgado, JP; Willkomm, J; Leskes, M; Steiner, A; Fenske, D; King, TC; Wood, PT; Gan, LH; Lambert, RM; Wright, DS
*Dalton Transactions*, **43** (2014) 8679-8689
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To what extent the presence of transition metal ions can affect the optical properties of structurally well-defined, metal-doped polyoxotitanium (POT) cages is a key question in respect to how closely these species model technologically important metal-doped $TiO_2$. This also has direct implications to the potential applications of these organically-soluble inorganic cages as photocatalytic redox systems in chemical transformations. Measurement of the band gaps of the series of closely related polyoxotitanium cages $[MnTi_{14}(OEt)_{28}O_{14}(OH)_2]$ (1), $[FeTi_{14}(OEt)_{28}O_{14}(OH)_2]$ (2) and $[GaTi_{14}(OEt)_{28}O_{15}(OH)]$ (3), containing interstitial Mn(II), Fe(II) and Ga(III) dopant ions, shows that transition metal doping alone does not lower the band gaps below that of $TiO_2$ or the corresponding metal-doped $TiO_2$. Instead, the band gaps of these cages are within the range of values found previously for transition metal-doped $TiO_2$ nanoparticles. The low band gaps previously reported for 1 and for a recently reported related Mn-doped POT cage appear to be the result of low band gap impurities (most likely amorphous Mn-doped $TiO_2$).

## Multidirectional Light-Harvesting Enhancement in Dye Solar Cells by Surface Patterning

Lopez-Lopez, C; Colodrero, S; Jimenez-Solano, A; Lozano, G; Ortiz, R; Calvo, ME; Miguez, H
*Advanced Optical Materials*, **2** (2014) 879-884
September, 2014 | **DOI:** 10.1002/adom.201400160

One dimensional gratings patterned on the surface of nanocrystalline titania electrodes are used as a light harvesting strategy to improve the overall performance of dye solar cells under both frontal and rear illumination conditions. A soft-lithography-based micromoulding approach is employed to replicate a periodic surface relief pattern onto the surface of the electrode, which is later sensitized with a dye. As the patterned surface acts as an optical grating both in reflection and transmission modes, its effect is to increase the light path of diffracted beams within the absorbing layer when it is irradiated either from the electrode or the counter electrode for a broad range of angles of incidence on each surface. Full optical and photovoltaic characterization demonstrates not only the optical quality of the patterned surfaces but also the multidirectional character of the enhancement of light harvesting and conversion efficiency. The approach herein presented thus permits to preserve the operation of the cell when irradiated from its two faces while increasing its overall power conversion efficiency. This feature is a key advantage over other light harvesting efficiency enhancing methods, such as the deposition of a back diffuse scattering layer, in which the performance of the cell under illumination from one of its sides is enlarged at the expense of reducing the output under reverse irradiation conditions.

## Synthesis and luminescence of uniform europium-doped bismuth fluoride and bismuth oxyfluoride particles with different morphologies

A. Escudero; E. Moretti; M. Ocaña
*CrysEngComm*, **16** (2014) 3274-3283
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Facile synthesis routes have been developed for the preparation of uniform cubic bismuth fluoride and bismuth oxyfluoride particles. The synthesis methods are based on homogeneous precipitation reactions at 120 °C in solutions of bismuth nitrate and sodium tetrafluoroborate precursors in polyol-based solvents. Both the nature of the solvent and the heating modes (conventional or microwave-assisted heating) have a remarkable effect on the morphology and crystallinity of the resulting particles. Thus, polycrystalline spheres of $\alpha$-$BiF_3$ with a mean diameter ranging from 1.2 to 2 µm could be obtained by heating solutions with the appropriate reagent concentrations in a mixture of ethylene glycol and glycerol (1 : 1 by volume) using a conventional oven, whereas octahedral single crystals of α-$BiO_yF_{3-2y}$ with mean edges ranging from 250 nm to 920 nm precipitated when using a diethylene glycol–water mixture (8 : 2 in volume) as solvent and a microwave reactor for heating. To explain these different morphological and structural features, the mechanism of formation of such particles was investigated. Both kinds of particles were also doped with $Eu^{3+}$, and both the morphological and luminescence properties of the resulting materials were evaluated. It was found that the luminescence intensity of the europium-doped α-$BiO_yF_{3-2y}$ nanoparticles was higher than that of the europium-doped α-BiF3 sub-micrometric spheres, which was associated with the higher crystallinity of the former. Moreover, the presence of oxygen in the europium-doped α-$BiO_yF_{3-2y}$ samples permits the excitation of the europium cations through an Eu–O energy transfer process, which results in a much higher luminescence intensity with respect to that corresponding to the direct excitation of the europium cations. Finally, the effect of the amount of dopant on the luminescence properties of the phosphors was also evaluated.

### Anchoring effect on (tetra)carboxyphenyl porphyrin/$TiO_2$ composite films for VOC optical detection

Roales, J; Pedrosa, JM; Cano, M; Guillen, MG; Lopes-Costa, T; Castillero, P; Barranco, A; Gonzalez-Elipe, AR

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January, 2014 | **DOI:** 10.1039/C3RA42443J

The optical gas sensing properties of Zn-(II)-5,10,15,20-tetra(3-carboxyphenyl)porphyrin (m-ZnTCPP) and Zn-(II)-5,10,15,20-tetra(4-carboxyphenyl)porphyrin (p-ZnTCPP) bound to microcolumnar $TiO_2$ thin films have been compared and explained in terms of their different molecular structure and anchoring to the titania surface. This different binding has been confirmed by specular reflectance FTIR revealing that m-ZnTCPP is bound by its four carboxylic groups in contrast to p-ZnTCPP where two or three of these groups remain unanchored. As a consequence, the Soret band of the para derivative is blue shifted with respect to the solution, indicating H aggregation, while m-ZnTCPP remained in its monomeric form due to the planar anchoring by the four COOH groups to the titania matrix that would avoid porphyrin aggregation. The sensing performance of the two systems has been assessed by analyzing the spectral changes in their UV-visible spectra under exposure to six volatile organic compounds. Although the highly porous and non-dispersive $TiO_2$ matrix allow good sensing ability in both cases, the response of the m-ZnTCPP/$TiO_2$ composite has been found to be more intense and faster than that of p-ZnTCPP. Moreover, the use of identification patterns also indicates that the meta derivative achieves a more selective recognition of the selected analytes. This improvement in the sensing capabilities of m-ZnTCPP has been attributed to the absence of aggregation between adjacent macrocycles.

### Synthesis of antibacterial silver-based nanodisks and dendritic structures mediated by royal jelly

Mendoza-Resendez, R; Gomez-Trevino, A; Barriga-Castro, ED; Nuñez, NO; Luna, C

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The one-step preparation of silver nanoparticles and dendritic structures mediated by aqueous royal jelly solutions has been investigated for the first time. It has been found that royal jelly (RJ) is a complex organic matrix that can be simultaneously used as a reducing and stabilizing agent in the chemical synthesis of colloidal silver-based nanostructures from aqueous $AgNO_3$ solutions, without the requirement of additional reagents or heating sources to initiate the oxidation–reduction reactions. The resulting product consisted of very fine single-crystal disks of Ag and silver 4,4′-dimethyldiazoaminobenzene (a triazenic compound). Both kinds of particles tended to coalesce and form supramolecular dendritic structures, the $AgNO_3$/RJ weight ratio chosen in the synthesis being a key parameter to control the crystal growth and the microstructural properties of the Ag nanodisks. Data obtained from Fourier transform infrared and Raman spectroscopy analysis indicated that these nanostructures are coated by RJ biomolecules (residues of proteins and carbohydrates). In vitro biological assays showed that these nanostructures exhibit a promising enhanced antibacterial activity against both Gram-positive and Gram-negative bacteria.

## On the formation of the porous structure in nanostructured a-Si coatings deposited by dc magnetron sputtering at oblique angles

Godinho, V; Moskovkin, P; Alvarez, R; Caballero-Hernandez, J; Schierholz, R; Bera, B; Demarche, J; Palmero, A; Fernandez, A; Lucas, S
*Nanotechnology*, **25** (2014) 355705
September, 2014 | **DOI:** 10.1088/0957-4484/25/35/355705

The formation of the porous structure in dc magnetron sputtered amorphous silicon thin films at low temperatures is studied when using helium and/or argon as the processing gas. In each case, a-Si thin films were simultaneously grown at two different locations in the reactor which led to the assembly of different porous structures. The set of four fabricated samples has been analyzed at the microstructural level to elucidate the characteristics of the porous structure under the different deposition conditions. With the help of a growth model, we conclude that the chemical nature of the sputter gas not only affects the sputtering mechanism of Si atoms from the target and their subsequent transport in the gaseous/plasma phase towards the film, but also the pore formation mechanism and dynamics. When Ar is used, pores emerge as a direct result of the shadowing processes of Si atoms, in agreement with Thornton's structure zone model. The introduction of He produces, in addition to the shadowing effects, a new process where a degree of mobility results in the coarsening of small pores. Our results also highlight the influence of the composition of sputtering gas and tilt angles (for oblique angle deposition) on the formation of open and/or occluded porosity.

## Mechanisms of Electron Transport and Recombination in ZnO Nanostructures for Dye-Sensitized Solar Cells

Vega-Poot, AG; Macias-Montero, M; Idigoras, J; Borras, A; Barranco, A; Gonzalez-Elipe, AR; Lizama-Tzec, FI; Oskam, G; Anta, JA
*Chemphyschem*, **15** (2014) 1088-1097
April, 2014 | **DOI:** 10.1002/cphc.201301068

ZnO is an attractive material for applications in dye-sensitized solar cells and related devices. This material has excellent electron-transport properties in the bulk but its electron diffusion coefficient is much smaller in mesoporous films. In this work the electron-transport properties of two different kinds of dye-sensitized ZnO nanostructures are investigated by small-perturbation electrochemical techniques. For nanoparticulate ZnO photoanodes prepared via a wet-chemistry technique, the diffusion coefficient is found to reproduce the typical behavior predicted by the multiple-trapping and the hopping models, with an exponential increase with respect to the applied bias. In contrast, in ZnO nanostructured thin films of controlled texture and crystallinity prepared via a plasma chemical vapor deposition method, the diffusion coefficient is found to be independent of the electrochemical bias. This observation suggests a different transport mechanism not controlled by trapping and electron accumulation. In spite of the quite different transport features, the recombination kinetics, the electron-collection efficiency and the photoconversion efficiency are very similar for both kinds of photoanodes, an observation that indicates that surface properties rather than electron transport is the main efficiency-determining factor in solar cells based on ZnO nanostructured photoanodes.

### Quinone-Rich Poly(dopamine) Magnetic Nanoparticles for Biosensor Applications

Martin, M; Orive, AG; Lorenzo-Luis, P; Creus, AH; Gonzalez-Mora, JL; Salazar, P
*ChemPhysChem*, **15** (2014) 3742-3752
December, 2014 | **DOI:** 10.1002/cphc.201402417

Novel core-shell quinone-rich poly(dopamine)–magnetic nanoparticles (MNPs) were prepared by using an in situ polymerization method. Catechol groups were oxidized to quinone by using a thermal treatment. MNPs were characterized by using X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscopy, magnetic force microscopy, UV/Vis, Fourier-transform infrared spectroscopy, and electrochemical techniques. The hybrid nanomaterial showed an average core diameter of 17 nm and a polymer-film thickness of 2 nm. The core-shell nanoparticles showed high reactivity and were used as solid supports for the covalent immobilization of glucose oxidase (Gox) through Schiff base formation and Michael addition. The amount of Gox immobilized onto the nanoparticle surface was almost twice that of the nonoxidized film. The resulting biofunctionalized MNPs were used to construct an amperometric biosensor for glucose. The enzyme biosensor has a sensitivity of 8.7 mA $\mathrm{M}^{-1}$ $\mathrm{cm}^{-2}$, a low limit of detection (0.02 mM), and high stability for 45 days. Finally, the biosensor was used to determine glucose in blood samples and was checked against a commercial glucometer.

### Reticulated bioactive scaffolds with improved textural properties for bone tissue engineering: Nanostructured surfaces and porosity

Ramiro-Gutierrez, ML; Will, J; Boccaccini, AR; Diaz-Cuenca, A
*Journal of Biomedical Materials Research Part A*, **102** (2014) 2982-2992
September, 2014 | **DOI:** 10.1002/jbm.a.34968

Organised nanoporous SBA-15 type silica precursor (SP) particulate material has been processed into three-dimensional macroporous, reticulated structures using a novel strategy consisting of blending increasing percentages of SP with a $SiO_2$-$CaO$-$P_2O_5$ (80Si15Ca5P) mesoporous bioactive glass (MBG) sol. The procedure successfully produced consolidated and functionally competent open-cell scaffolds while preserving the nanoporous order of the SP. Scaffolds were prepared using four different (MBG)/(SP) ratios. These structures were then characterized using field emission gun scanning electron microscopy, X-ray diffraction (XRD), nitrogen adsorption-desorption measurements, and compressive strength testing. Open-cell interconnected structures with dual macro (150-500 µm) and nano (4-6 nm)-organised porosity were produced. Both the textural and mechanical properties were found to improve with increasing SBA-15 content. The in vitro bioactive response using simulated body fluid confirmed high reactivity for all prepared scaffolds. In addition, the SBA-15 containing scaffolds exhibited a superior ability to delay the pH-triggered lysozyme release with antibiotic activity.

### Perovskite Solar Cells Based on Nanocolumnar PlasmaDeposited ZnO Thin Films

Ramos, FJ; Lopez-Santos, MC; Guillen, E; Nazeeruddin, MK; Gratzel, M; Gonzalez-Elipe, AR; Ahmad, S
*Chemphyschem*, **15** (2014) 1148-1153
April, 2014 | **DOI:** 10.1002/cphc.201301215

ZnO thin films having a nanocolumnar microstructure are grown by plasma-enhanced chemical vapor deposition at 423 K on pre-treated fluorine-doped tin oxide (FTO) substrates. The films consist of c-axis-oriented wurtzite ZnO nanocolumns with well-defined microstructure and crystallinity. By sensitizing $CH_3NH_3PbI_3$ on these photoanodes a power conversion of 4.8 % is obtained for solid-state solar cells. Poly(triarylamine) is found to be less effective when used as the hole-transport material, compared to 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD), while the higher annealing temperature of the perovskite leads to a better infiltration in the nanocolumnar structure and an enhancement of the cell efficiency.

### The Use of Fluorocarbons to Mitigate the Oxygen Dependence of Glucose Microbiosensors for Neuroscience Applications

Martin, M; O'Neill, RD; Gonzalez-Mora, JL; Salazar, P
*Journal of The Electrochemical Society*, **161** (2014) H689-H695
October, 2014 | **DOI:** 10.1149/2.1071410jes

First-generation amperometric glucose biosensors are the most commonly used method for glucose monitoring in neuroscience. Nevertheless, biosensors of this genre suffer from the so-called "oxygen deficit". This problem is particularly acute when the oxygen concentration is low, as is the case in brain extracellular fluid. In the present work we use different fluorocarbons, such as Nafion and H700, to mitigate the oxygen deficit. These fluorocarbon-derived materials display a remarkable solubility for oxygen, and are able to act as oxygen reservoirs supporting the enzymatic reaction. Different biosensor configurations are presented, evaluating their sensitivity, linear range and oxygen dependence. Optimized Nafion- and H700-modified biosensors displayed a remarkable oxygen tolerance, with K-M(O-

2) values as low as 11 and 4 mu mol $L^{-1}$, respectively, and an appropriate sensitivity for in-vivo applications. Finally, in-vivo data are reported in order to illustrate the application of such devices in neuroscience applications.

### Structure determination and electronic structure of $Cu_3Au_{0.5}N$

Soto, G; Ponce, I; Moreno, MG; Yubero, F; De la Cruz, W

*Journal of Alloys and Compounds*, **594** (2014) 48-51

May, 2014 | **DOI:** 10.1016/j.jallcom.2014.01.113

This study investigated the formation of a $Cu_3Au$-nitride alloy using both experimental and computational methods. The alloy was produced as thin film by sputtering a $Cu_3Au$ target in a nitrogen atmosphere. The films were characterized for structure and composition by spectroscopic and diffraction techniques. The structure was established by Rietveld and ab inito methods. The structure is cubic and of the Fm3m space group, with a composition close to $Cu_6AuN_2$. Relative to the $Cu_3N$ structure, the Cu atoms occupy the faces, Au the half corners, and N the centers. The compound is a narrow-gap semiconductor with a positive hall coefficient that could be used for infrared detection.

### One-Step Synthesis and Polyacrylic Acid Functionalization of Multifunctional Europium-Doped $NaGdF_4$ Nanoparticles with Selected Size for Optical and MRI Imaging

Nunez, NO; Garcia, M; Garcia-Sevillano, J; Rivera-Fernandez, S; de la Fuente, JM; Ocana, M

*European Journal of Inorganic Chemistry*, **35** (2014) 6075-6084

December, 2014 | **DOI:** 10.1002/ejic.201402690

Multifunctional Eu:$NaGdF_4$ nanospheres functionalized with polyacrylic acid (PAA) polymer have been prepared for the first time by a simple one-pot method that consists of a homogeneous precipitation reaction at 120 °C. The size of the nanospheres, which were polycrystalline and crystallized into a hexagonal structure, could be altered in the 60–95 nm range by adjusting the amount of polyacrylic acid added. The effects of Eu content and particle size of these nanomaterials on their optical properties (emission intensity and lifetime) as well as on their relaxivity (r1 and r2) values were also analyzed to find the optimum system for optical bioimaging and as a positive contrast agent for magnetic resonance imaging (MRI) applications. Finally, such optimum nanoparticles showed negligible cytotoxicity for Vero cells for concentrations up to 0.5 mg $mL^{-1}$ and a high colloidal stability in 2-morpholinoethanesulfonic acid solutions, thereby satisfying the most important requirements for their use in biotechnological applications.

### Influence of thickness and coatings morphology in the antimicrobial performance of zinc oxide coatings

Carvalho, P; Sampaio, P; Azevedo, S; Vaz, C; Espinos, JP; Teixeira, V; Carneiro, JO

*Applied Surface Science*, **307** (2014) 548-557

July, 2014 | **DOI:** 10.1016/j.apsusc.2014.04.072

In this research work, the production of undoped and silver (Ag) doped zinc oxide (ZnO) thin films for food-packaging applications were developed. The main goal was to determine the influence of coatings morphology and thickness on the antimicrobial performance of the produced samples. The ZnO based thin films were deposited on PET (Polyethylene terephthalate) substrates by means of DC reactive magnetron sputtering. The thin films were characterized by optical spectroscopy, X-Ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The antimicrobial performance of the undoped and Ag-doped ZnO thin films was also evaluated. The results attained have shown that all the deposited zinc oxide and Ag-doped ZnO coatings present columnar morphology with V-shaped columns. The increase of ZnO coatings thickness until 200 nm increases the active surface area of the columns. The thinner samples (50 and 100 nm) present a less pronounced antibacterial activity than the thickest ones (200–600 nm). Regarding Ag-doped ZnO thin films, it was verified that increasing the silver content decreases the growth rate of Escherichia coli and decreases the amount of bacteria cells present at the end of the experiment.

### Osteoblasts Interaction with PLGA Membranes Functionalized with Titanium Film Nanolayer by PECVD. In vitro Assessment of Surface Influence on Cell Adhesion during Initial Cell to Material Interaction

Terriza, A; Vilches-Perez, JI; Gonzalez-Caballero, JL; de la Orden, E; Yubero, F; Barranco, A; Gonzalez-Elipe, AR; Vilches, J; Salido, M

*Materials*, **7(3)** (2014) 1687-1708

March, 2014 | **DOI:** 10.3390/ma7031687

New biomaterials for Guided Bone Regeneration (GBR), both resorbable and non-resorbable, are being developed to stimulate bone tissue formation. Thus, the in vitro study of cell behavior towards material surface properties turns a prerequisite to assess both biocompatibility and bioactivity of any material intended to be used for clinical purposes. For this purpose, we have developed in vitro studies on normal human osteoblasts (HOB®) HOB® osteoblasts grown on a resorbable Poly (lactide-co-glycolide) (PLGA) membrane foil functionalized by a very thin film (around 15 nm) of $TiO_2$ (i.e., TiO2/PLGA membranes), designed to be used as barrier membrane. To avoid any alteration of the membranes, the titanium films were deposited at room temperature in one step by plasma enhanced chemical vapour deposition. Characterization of the functionalized membranes proved that the thin titanium layer completely covers the PLGA foils that remains practically unmodified in their interior after the deposition process and stands the standard sterilization protocols. Both morphological changes and cytoskeletal reorganization, together with the focal adhesion development observed in HOB osteoblasts, significantly related to $TiO_2$ treated PLGA in which the Ti deposition method described has revealed to be a valuable tool to increase bioactivity of PLGA membranes, by combining cell nanotopography cues with the incorporation of bioactive factors.

## FRET-Tuned Resonant Random Lasing

Galisteo-Lopez, JF; Ibisate, M; Lopez, C
*Journal of Physical Chemistry C*, **118** (2014) 9852-9859
May, 2014 | **DOI:** 10.1021/jp501101a

We report the fabrication and characterization of a novel type of optical gain material. A biopolymeric matrix (DNA-lipid complex) doped with two families of organic dyes is combined with a strongly scattering medium. While the optical gain of the biopolymer complex is controlled via the FRET efficiency between the incorporated dyes, multiple scattering provides the necessary feedback to achieve lasing. This introduces two mechanisms to control the lasing wavelength: optical gain (via resonant energy transfer) and resonant scattering. In this way, an organic laser with a spectral tunability range over 40 nm is demonstrated.

## Fully stable numerical calculations for finite one-dimensional structures: Mapping the transfer matrix method

Luque-Raigon, JM; Halme, J; Miguez, H
*Journal of Quantitative Spectroscopy and Radiative Transfer*, **134** (2014) 9-20
February, 2014 | **DOI:** 10.1016/j.jqsrt.2013.10.007

We design a fully stable numerical solution of the Maxwell's equations with the transfer matrix method (TMM) to understand the interaction between an electromagnetic field and a finite, one-dimensional, non-periodic structure. Such an exact solution can be tailored from a conventional solution by choosing an adequate transformation between its reference systems, which induces a mapping between its associated TMMs. The paper demonstrates theoretically the numerical stability of the TMM for the exact solution within the framework of Maxwell's equations, but the same formalism can efficiently be applied to resolve other classical or quantum linear wave-propagation interaction in one, two, and three dimensions. This is because the formalism is exclusively built up for an in depth analysis of the TMM's symmetries.

## c- C4F8 Plasmas for the Deposition of Fluorinated Carbon Films

Terriza, A; Macias-Montero, M; Lopez-Santos, MC; Yubero, F; Cotrino, J; Gonzalez-Elipe, AR
*Plasma Processes and Polymers*, **11** (2014) 289-299
March, 2014 | **DOI:** 10.1002/ppap.201300129

Highly fluorinated polymeric (CFX), fluorine containing diamond-like carbon (F-DLC) and, for comparison, diamond-like carbon (DLC) films have been plasma deposited in a RF parallel plate reactor by using c-$C_4F_8$ as fluorine precursor and different mixtures of argon, $C_2H_2$, and $H_2$. Plasmas have been characterized by optical emission spectroscopy, mass spectrometry, and Langmuir probe measurements. Differences in the film composition and structure have been related with the type of species formed in the plasma and with the self-bias potential developed at the deposition electrode. Additional experiments using $CF_4$ have confirmed that the formation in the plasmas of neutral or ionized CxFy species with $x > 2$ is a critical factor for the synthesis of fluorine rich films.

### On the Deposition Rates of Magnetron Sputtered Thin Films at Oblique Angles

Alvarez, R; Garcia-Martin, JM; Lopez-Santos, MC; Rico, V; Ferrer, FJ; Cotrino, J; Gonzalez-Elipe, AR; Palmero, A
*Plasma Processes and Polymers*, **11** (2014) 571-576
June, 2014 | **DOI:** 10.1002/ppap.201300201

We describe here the deposition of thin films using magnetron sputtering at oblique angles. General relations between the deposition rates of the films and experimental parameters, such as gas pressure or substrate tilt angles, are deduced and experimentally tested. The model also permits the direct determination of the thermalization mean free path of the sputtered particles in the plasma gas, a key parameter defining the balance between ballistic and diffusive flows in the deposition reactor. The good agreement between experimental and calculated results supports the validity of our description, which becomes a useful tool to explain the main features of the magnetron sputtering deposition of thin films at oblique angles.

### Plasma Deposition of Superhydrophobic Ag@ $TiO_2$ Core@ shell Nanorods on Processable Substrates

Macias-Montero, M; Borras, A; Romero-Gomez, P; Cotrino, J; Frutos, F; Gonzalez-Elipe, AR
*Plasma Process and Polymers*, **11** (2014) 164-174
February, 2014 | **DOI:** 10.1002/ppap.201300112

This work reports the low temperature plasma formation of Ag@$TiO_2$ nanorods (NRs) on processable substrates. The layers have been analyzed by electron microscopy and secondary ion mass spectroscopy. The NRs morphologies suggest that the plasma sheath, the high mobility of the silver and the incoming direction of the precursor moieties are key factors determining their shape, dimensions, and tilting orientation. Both amorphous and anatase Ag@$TiO_2$ NRs surfaces are superhydrophobic, and turn into superhydrophilic by irradiation with UV light. This wetting behavior is discussed by considering the water penetration in the inter-NR space during the light-mediated transformation.

### On the kinetic and thermodynamic electron temperatures in non-thermal plasmas

Alvarez, R; Cotrino, J; Palmero, A
*EPL (Europhysic Letters)*, **105** (2014)
January, 2014 | **DOI:** 10.1209/0295-5075/105/15001

The framework to describe the out-of-equilibrium free electrons in cold plasmas is developed assuming the electron entropy is defined through the Boltzmann H-theorem. Our theory explains why the Saha-Boltzmann relation among higher-lying excited states by means of the electron kinetic temperature is fulfilled, even when free electrons are far from equilibrium. The thermodynamic electron temperature, pressure and chemical potential have been introduced through the derivatives of the electron entropy. It is demonstrated that under usual conditions in cold plasmas, e.g. when the electron distribution function possesses the

Maxwellian, Druyvestein or Kappa functional forms, kinetic and thermodynamic electron temperatures yield the same value.

### LMM Auger primary excitation spectra of copper

Pauly, N; Tougaard, S; Yubero, F
*Surface Science*, **630** (2013) 294-299
December, 2014 | **DOI:** 10.1016/j.susc.2014.08.029

The shape and intensity of measured Auger peaks are strongly affected by extrinsic excitations due to electron transport out of the surface and to intrinsic excitations induced by the sudden creation of the two static core holes. Following a method developed for XPS in a previous work [N. Pauly, S. Tougaard, F. Yubero, Surf. Sci. 620 (2014) 17], we have calculated the effective energy-differential inelastic electron scattering cross-sections, including the effects of the surface and of the two core holes, within the dielectric response theory by means of the QUEELS-XPS software (QUantitative analysis of Electron Energy Losses at Surfaces for XPS). The Auger spectra are then modeled by convoluting this energy loss cross section with the primary excitation spectrum that accounts for all effects which are part of the initial Auger process, i.e. L–S coupling and vacancy satellite effects. The shape of this primary excitation spectrum is fitted to get close agreement between the theoretical and the experimental spectra obtained from X-ray excited Auger electron spectroscopy (XAES). We have performed these calculations of XAES spectra for various LMM Auger transitions of pure Cu ($L_3M_{45}M_{45}$, $L_3M_{23}M_{45}$, $L_3M_{23}M_{23}$ and $L_2M_{45}M_{45}$ transitions). We compare the resulting primary excitation spectra with theoretical results published in the literature and obtain reasonable quantitative agreement. In particular, we extract from experimental spectra quantitative intensities due to Coster–Kronig, shake-off and shake-up processes relative to the intensity from the “normal” Auger process.

### The growth of cobalt oxides on HOPG and $SiO_2$ surfaces: A comparative study

Diaz-Fernandez, D; Mendez, J; Bomati-Miguel, O; Yubero, F; Mossanek, RJO; Abbate, M; Dominguez-Canizares, G; Gutierrez, A; Tougaard, S; Soriano, L
*Surface Science*, **624** (2014) 145-153
June, 2014 | **DOI:** 10.1016/j.susc.2014.02.007

The growth of cobalt oxides by reactive thermal evaporation of metallic cobalt on highly oriented pyrolytic graphite (HOPG) and $SiO_2$ (X cut quartz surface), in an oxygen atmosphere at room temperature, has been chemically and morphologically studied by means of X-ray photoelectron spectroscopy and atomic force microscopy. The chemical analysis, which also includes cluster calculations, reveals that for the early deposition stages on both substrates, $Co_2$ + species are stabilized at the surface up to a coverage which depends on the substrate. Further coverages lead to the formation of the spinel oxide $Co_3O_4$. The results are discussed in terms of the dependence of the surface energy on the size of the CoO deposited moieties. On the other hand, it has been found that the initial way of growth of cobalt oxides on HOPG is of Stranski–Krastanov mode whereas on $SiO_2$ the growth is of Volmer–Weber mode. The differences in the growth morphology have been discussed in terms of the surface diffusivity of the CoO deposits on the substrates.

## Nanoindentation of nanocolumnar $TiO_2$ thin films with single and stacked zig-zag layers

Jimenez-Pique, E; Gonzalez-Garcia, L; Rico, VJ; Gonzalez-Elipe, AR
*Thin Solid Films*, **550** (2014) 444-449
January, 2014 | **DOI:** 10.1016/j.tsf.2013.10.022

This paper reports a systematic analysis of the mechanical properties of nanocolumnar $TiO_2$ thin films prepared by evaporation at a glancing geometry. A systematic study of the mechanical properties is carried out by comparing the hardness and the Young's modulus determined by nanoindentation for thin films prepared at different deposition angles and characterized by a tilted nanocolumnar structure and others where the nanocolumns are perpendicular to the substrate or are arranged as zig-zag stacked layers. A correlation between mechanical properties and glazing angle geometry is proposed. Differences in the results are discussed in view of the cross section images obtained by focused ion beam and of the deformed areas. Zig-zagged layers present lower values of hardness and Young's modulus due to the collapse of the angles of the columns, but at the same time this configuration impedes the appearance of fracture or delamination, as observed for tilted columns.

## Osteoconductive Potential of Barrier Nano$SiO_2$ PLGA Membranes Functionalized by Plasma Enhanced Chemical Vapour Deposition

Terriza, A; Vilches-Perez, JI; de la Orden, E; Yubero, F; Gonzalez-Caballero, JL; Gonzalez-Elipe, AR; Vilches, J; Salido, M
*BioMed Research International*, **2014** (2014) 253590
May, 2014 | **DOI:** 10.1155/2014/253590

The possibility of tailoring membrane surfaces with osteoconductive potential, in particular in biodegradable devices, to create modified biomaterials that stimulate osteoblast response should make them more suitable for clinical use, hopefully enhancing bone regeneration. Bioactive inorganic materials, such as silica, have been suggested to improve the bioactivity of synthetic biopolymers. An in vitro study on HOB human osteoblasts was performed to assess biocompatibility and bioactivity of $SiO_2$ functionalized poly(lactide-co-glycolide) (PLGA) membranes, prior to clinical use. A 15 nm $SiO_2$ layer was deposited by plasma enhanced chemical vapour deposition (PECVD), onto a resorbable PLGA membrane. Samples were characterized by X-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy, and infrared spectroscopy (FT-IR). HOB cells were seeded on sterilized test surfaces where cell morphology, spreading, actin cytoskeletal organization, and focal adhesion expression were assessed. As proved by the FT-IR analysis of samples, the deposition by PECVD of the $SiO_2$ onto the PLGA membrane did not alter the composition and other characteristics of the organic membrane. A temporal and spatial reorganization of cytoskeleton and focal adhesions and morphological changes in response to $SiO_2$ nanolayer were identified in our model. The novedous $SiO_2$ deposition method is compatible with the standard sterilization protocols and reveals as a valuable tool to increase bioactivity of resorbable PLGA membranes.

### Nanocolumnar growth of thin films deposited at oblique angles: Beyond the tangent rule

Alvarez, R; Lopez-Santos, C; Parra-Barranco, J; Rico, V; Barranco, A; Cotrino, J; Gonzalez-Elipe, AR; Palmero, A

*Journal of Vacuum Science & Technology B*, **32** (2014) 041802

July, 2014 | **DOI:** 10.1116/1.4882877

The growth of nanostructured physical vapor deposited thin films at oblique angles is becoming a hot topic for the development of a large variety of applications. Up to now, empirical relations, such as the so-called tangent rule, have been uncritically applied to account for the development of the nanostructure of these thin films even when they do not accurately reproduce most experimental results. In the present paper, the growth of thin films at oblique angles is analyzed under the premises of a recently proposed surface trapping mechanism. The authors demonstrate that this process mediates the effective shadowing area and determines the relation between the incident angle of the deposition flux and the tilt angle of the columnar thin film nanostructures. The analysis of experimental data for a large variety of materials obtained in our laboratory and taken from the literature supports the existence of a connection between the surface trapping efficiency and the metallic character of the deposited materials. The implications of these predictive conclusions for the development of new applications based on oblique angle deposited thin films are discussed.

### Interpretation of electron Rutherford backscattering spectrometry for hydrogen quantification

Alvarez, R; Yubero, F

*Surface and Interface Analysis*, **46** (2014) 812-816

October, 2014 | **DOI:** 10.1002/sia.5486

In the last few years, several papers have appeared showing the capabilities of electron Rutherford backscattering spectrometry (eRBS) to quantify the H content at surfaces. The basis of the H detection in this technique relies on the difference in recoil energy of the incident electrons depending on the mass of the atoms located at the surface that act as scatter centers. In this paper, we address the interpretation of eRBS spectra of hydrogen containing surfaces. The aim is to compare the naive single elastic scattering approximation with a more realistic description of eRBS spectra including multiple elastic scattering using the HQ-eRBS (hydrogen quantification eRBS) software based on a Monte Carlo algorithm. It is concluded that multiple elastic scattering is a significant contribution to experimentally measured eRBS spectra of a polyethylene surface. It induces significant broadening of the distribution of the maximum elastic scattering angle along the electron trajectories contributing to the measured spectra. However, it has weak effect in the energy distribution of the collected electrons (about 10% overestimation of the H content in the particular case of a polyethylene surface with respect to the corresponding ratio of elastic scattering cross sections).

### Modeling of X-ray photoelectron spectra: surface and core hole effects

Pauly, N; Tougaard, S; Yubero, F

*Surface and Interface Analysis*, **46** (2014) 920-923

October, 2014 | **DOI:** 10.1002/sia.5372

The shape and intensity of photoelectron peaks are strongly affected by extrinsic excitations due to electron transport out of the surface and by intrinsic excitations induced by the sudden creation of the static core hole. Besides, elastic electron scattering may also be important. These effects should be included in the theoretical description of the emitted photoelectron peaks. To investigate the importance of surface and core hole effects relative to elastic scattering effect, we have calculated full XPS spectra for the Cu 2p emissions of Cu and CuO with the simulation of electron spectra for surface analysis (SESSA) software and with a convolution procedure using the differential inelastic electron scattering cross-section obtained with the quantitative analysis of electron energy loss in XPS (QUEELS-XPS) software. Surface and core hole effects are included in QUEELS-XPS but absent in SESSA while elastic electron scattering effects are included in SESSA but absent in QUEELS-XPS. Our results show that the shape of the XPS spectra are strongly modified because of surface and core hole effects, especially for energy losses smaller than about 20eV.

### Study of the early stages of growth of Co oxides on oxide substrates

Diaz-Fernandez, D; Mendez, J; Yubero, F; Dominguez-Canizares, G; Gutierrez, A; Soriano, L
*Surface and Interface Analysis*, **46** (2014) 975-979
October, 2014 | **DOI:** 10.1002/sia.5366

The growth of Cobalt oxides by reactive thermal evaporation of metallic Cobalt in an oxygen atmosphere on a series of oxide substrates, namely $SiO_2$, $Al_2O_3$ and MgO, has been chemically and morphologically studied by means of XPS and atomic force microscopy (AFM). The XPS results reveal that cobalt oxide grows as CoO ($Co^{2+}$) for coverages up to some tens of equivalent monolayers on all substrates. For larger coverages, the formation of the spinel oxide $Co_3O_4$ has been observed. AFM and XPS quantification allowed us to determine the way of growth of CoO on all substrates, being of Volmer-Weber (i.e. islands) mode for $SiO_2$, whereas for $Al_2O_3$ and MgO, the growth follows the Frank-van der Merwe (i.e. layer-by-layer) mode. The results are discussed in terms of the mismatch of the lattice parameters of the CoO adsorbates with the substrates.

### Simultaneous quantification of light elements in thin films deposited on Si substrates using proton EBS (Elastic Backscattering Spectroscopy)

Ferrer, FJ; Alcaire, M; Caballero-Hernandez, J; Garcia-Garcia, FJ; Gil-Rostra, J; Terriza, A; Godinho, V; Garcia-Lopez, J; Barranco, A; Fernandez-Camacho, A
Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with *Materials and Atoms*, **332** (2014) 449-453
August, 2014 | **DOI:** 10.1016/j.nimb.2014.02.124

Quantification of light elements content in thin films is an important and difficult issue in many technological fields such as polymeric functional thin films, organic thin film devices, biomaterials, and doped semiconducting structures.
Light elements are difficult to detect with techniques based on X-ray emission, such as energy dispersive analysis of X-rays (EDAX). Other techniques, like X-ray photoelectron spectroscopy

(XPS), can easily quantify the content of light elements within a surface but often these surface measurements are not representative of the lights elements global composition of the thin film. Standard Rutherford backscattering spectroscopy (RBS), using alpha particles as probe projectiles, is not a good option to measure light elements deposited on heavier substrates composed of heavier elements like Si or glass. Nuclear Reaction Analysis (NRA) offers a good quantification method, but most of the nuclear reactions used are selective for the quantification of only one element, so several reactions and analysis are necessary to measure different elements.

In this study, Elastic Backscattering Spectroscopy (EBS) using proton beams of 2.0 MeV simultaneously quantified different light elements (helium, carbon, nitrogen, oxygen, and fluorine) contained in thin films supported on silicon substrates. The capabilities of the proposed quantification method are illustrated with examples of the analysis for a series of thin film samples: amorphous silicon with helium bubbles, fluorinated silica, fluorinated diamond-like carbon and organic thin films. It is shown that this simple and versatile procedure allows the simultaneous quantification of light elements in thin films with thicknesses in the 200–500 nm range and contents lower than 10 at.%.

## CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

## COMUNICACIONES / COMMUNICATIONS

### TNT Japan 2014 | Trends in NanoTechnology

29 – 31 enero [Tokio, Japón]

**Versatility and Multifunctionality of Porous Photonic Structures**
Hernán Míguez
Conferencia invitada

### NanoSpain Conference 2014

11 – 14 marzo [Madrid, España]

**Flexible nanostructured optical material**
Hernán Míguez
Comunicación oral

**Surface modified Eu:GdVO$_4$ nanocrystals for optical and MRI imaging**
Nuria Núñez; Sara Rivera; David Alcantara; Jesus M. de la Fuente; Jorge García-Sevillano; Manuel Ocaña
Póster

## HOPV Conference 2014
11 – 14 mayo [Lausana, Suiza]

**Photonic structures for highly efficient and transparent dye solar cells**
Hernán Míguez; Carmen López; Silvia Colodrero; Miguel Anaya; Mauricio Calvo Roggiani
Comunicación oral

**Proving the existence of slow photons using dye sensitized periodic multilayer structure**
Miguel Anaya; Mauricio E. Calvo; Hernán Míguez
Póster

## 5th International workshop on photoluminescence in rare earths PRE’14
14 – 16 mayo [San Sebastián, España]

**Up-conversion in $Er^{3+}$/$Yb^{3+}$ co-doped $LaPO_4$ submicron-sized spheres**
J. García-Sevillano; E. Cantelar; F. Cussó; M. Ocaña
Póster

## E-MRS 2014 Spring Meeting
26 – 30 mayo [Lille, Francia]

**Laser processing of ceramic substrates modified by deposition of metals and oxides**
V. Rico Gavira; J. Gil Rostra; F. Yubero; J. P. Espinós; A. R. González-Elipe; R. Lahoz; F. Rey García; G. F. de la fuente
Comunicación oral

## 4th International Colloids Conference: Surface Design &Engineering
15 – 18 junio [Madrid, España]

**Bifunctional, monodisperse $BiPO_4$-based nanostars: Photocatalytic activity and luminescent applications**
Ana Isabel Becerro; Joaquín Criado; Lionel C. Gontard; Sergio Obregón; Asunción Fernández; Gerardo Colón; Manuel Ocaña
Póster

## Sungkyun International Solar Forum 2014 (SISF 2014)
5 julio [República de Corea]

**Optical designs of dye solar cell**
H. Míguez
Conferencia invitada

## Nanotexnology 2014 | 11th International Conferences & Exhibition on Nanotechnologies & Organic Electronics

5 - 12 julio [Tesalónica, Grecia]

**Synthesis of nanoporous materials by magnetron sputtering at oblique incidence**
J.M. García-Martín; R. Alvarez; A. Palmero
Comunicación oral

## Al-NanoFunc Final Conference

7 - 11 julio [Sevilla, España]

**Optical design of hematite layers for optimized water splitting performance**
Miguel Anaya; Alberto Jiménez-Solano; Mauricio E. Calvo; Hernán Míguez
Comunicación oral

**Random scatterers by design for enhancing light harvesting efficiency in dye solar cells**
Gabriel Lozano; Francisco E. Gálvez; Jose M. Miranda; Sol Carretero-Palacios; Mauricio E. Calvo; Alberto Jiménez; Miguel Anaya; Hernán Míguez
Comunicación oral

## Nano 2014 | XII International Conference on Nanostructured Materiales

13-18 julio [Moscú, Rusia]

**Synthesis and surface modification of multifunctional mesoporous Eu:$GdF_3$ nanoparticles for biomedical applications**
Sonia Rodriguez-Liviano; Nuria O. Núñez; Sara Rivera; Jesus M. de la Fuente; Manuel Ocaña
Póster

## The 35th PIERS | Progress in Electromagnetics Research Symposium

25 – 28 agosto [Guangzhou, Canton, China]

**Optical materials by design for enhancing light harvesting in dye solar cells**
G. Lozano, C. López-López, F.E. Galvez, S. Colodrero, A. Jiménez-Solano, M.E. Calvo, H. Míguez
Conferencia invitada

## E-MRS 2014 Fall Meeting

15 – 18 septiembre [Varsovia, Polonia]

**Nanostructured Biocompatible coatings to prevent orthopedic implant infections**
R. Alvarez; A. Palmero; J.M. García-Martín
Comunicación oral

### 14th International Conference on Plasma Surface Engineering
15 – 19 septiembre [Stuttgart, Alemania]

**On the Deposition Rate of Magnetron Sputtered Thin Films at Oblique Angles**
R. Alvarez; J. M. Garcia-Martin; C. Lopez-Santos; V. Rico; F. J. Ferrer; J. Cotrino; A. R. Gonzalez-Elipe; A. Palmero
Comunicación oral

### Xtreme COAT 2014 | Surface Engineering for Functional Applications under Extreme Conditions
20 – 21 octubre [Madrid, España]

**Nanostructured Biocompatible coatings to prevent orthopedic implant infections**
R. Alvarez; A. Palmero; J.M. García-Martín
Comunicación oral

**On the deposition rate of magnetron sputtered thin films at oblique angles**
R. Alvarez; J.M. Garcia-Martin; M.C. Lopez-Santos; V.Rico; F.J. Ferrer; J. Cotrino; A.R. Gonzalez-Elipe; A. Palmero
Póster

### 8th CIBER-BBN Annual Conference
10 – 11 noviembre [Girona, España]

**Synthesis and proccessing of biopolymer/bioceramic hybrid systems for bone tissue engineering applications**
Borrego-González, Sara; Romero-Sánchez, Lilian Beatriz; Becerra, José; Díaz-Cuenca,A
Póster

## CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESS AND MEETINGS

## COMUNICACIONES / COMMUNICATIONS

### Conferencia Española de Nanofotónica (CEN) 2014
14-16 mayo [Santander, España]

**Optical trapping and manipulation of nano- and micro-objects**
Sol Carretero Palacios
Conferencia invitada

**Metallic particle arrays for directional light-emitting devices**
Gabriel Lozano Barbero
Conferencia invitada

### Seminarios de Investigación Básica en Odontología
4 diciembre [Sevilla, España]

**Materiales biocerámicos: nuevos desarrollos para su aplicación en terapias de regeneración en Odontología**
Aránzazu Díaz-Cuenca
Comunicación oral

## FORMACION / TRAINING

### TESIS DOCTORALES/ DOCTOR DEGREE THESIS

**Título:** **Síntesis y Procesado de Materiales Mesoporosos Ordenados y Estudio de su Funcionalidad para Aplicación en Regeneración Ósea**
**Autor:** María Lourdes Ramiro Gutiérrez
**Directores:** María Aránzazu Díaz Cuenca
**Calificación:** Apto "Cum Laude"
**Centro:** Universidad de Sevilla

**Título:** **Disilicatos de tierras raras simples y sus soluciones sólidas: Estructura cristalina y propiedades físicas**
**Autor:** Alberto José Fernández Carrión
**Directores:** Ana Isabel Becerro Nieto
**Calificación:** Apto "Cum Laude"
**Centro:** Universidad de Sevilla

### FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

**Título:** **Síntesis y caracterización de partículas monodispersas luminiscentes basadas en $LuF_3$**
**Autor:** Daniel González Mancebo
**Directores:** Hernán Ruy Míguez García y Mauricio Calvo Roggiani
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (17 Julio 2014)

**Título:** **Síntesis y funcionalización de nanopartículas luminiscentes de $CaF_2$ dopadas con $Eu^{3+}$**
**Autor:** Mariano Laguna Moreno
**Directores:** Manuel Ocaña Jurado
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (26 Septiembre 2014)

**Título:** **Síntesis y propiedades de nanopartículas uniformes luminiscentes basadas en $NaGd(MoO_4)_2$**
**Autor:** Verónica Rodriguez Bravo
**Directores:** Nuria O. Núñez Álvarez
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (26 Septiembre 2014)

**Título:** **Estudio de fuerzas de Casimir en sistemas plano-paralelos reales**
**Autor:** Victoria Esteso Carrizo
**Directores:** Hernán Ruy Míguez García y Sol Carretero Palacios
**Grado:** Trabajo Fin de Master
**Año Académico:** 2013-2014 (26 Septiembre 2014)

## DOCENCIA / TEACHING

### Máster Oficial y Doctorado en “Biotecnología Avanzada”

**Módulo de Nanotecnología**
Dra. Aránzazu Díaz Cuenca
**Lugar:** Universidad de Málaga
Organizado por la Universidad de Málaga y la Universidad Internacional de Andalucía

## PREMIOS Y RECONOCIMIENTOS / PRIZES AND ACKNOWLEDGEMENTS

**Manuel Macías Montero, Premio CicCartuja Ebro Foods** 2014. Un estudio sobre materiales nanométricos firmado por Manuel Macías Montero, investigador del Instituto de Ciencia de Materiales de Sevilla (ICMS), ha obtenido el Premio de Investigación cicCartuja Ebro Foods en su quinta edición. Este galardón, que pretende reforzar la carrera de los investigadores noveles, se ha entregado hoy en el Centro de Investigaciones Científicas Isla de la Cartuja (cicCartuja), centro mixto del Consejo Superior de Investigaciones Científicas (CSIC), Junta de Andalucía y Universidad de Sevilla.

### Nuevo material en forma de nanocable híbrido

En esta ocasión, el primer premio ha recaído en Manuel Macías por un trabajo en el que se ha sintetizado por primera vez un material en forma de nanocable híbrido. Los nanocables híbridos son estructuras alargadas con apenas unos cuantos nanómetros de espesor que integran un cristal orgánico en el núcleo y una capa inorgánica como envoltura exterior.

Según ha explicado Manuel Macías, esta combinación permite que la luz pueda ser transportada por su interior sin apenas registrar pérdidas, de modo que los nanocables actúan como una fibra óptica 10.000 veces más pequeña que las utilizadas actualmente en los hogares. Ello implica que el material hallado pueda tener múltiples aplicaciones en la microelectrónica –por ejemplo, en los circuitos fotónicos de los smartphones–, pero también en el terreno de las energías renovables, como alternativa en la nueva generación de celdas solares.

**Rafael Álvarez, premio a la "Investigación en Innovación"**, El científico del Instituto de Ciencia de Materiales de Sevilla, Rafael Álvarez Molina, ha sido galardonado con el III Premio Manuel Losada Villasante en la categoría de ‘Investigación en Innovación’.

Este reconocimiento, convocado por la Cadena SER en Sevilla y el Ayuntamiento de Carmona con la colaboración de la Universidad de Sevilla, la Fundación Cajasol y el Foro Interalimentario, está dotado con 4000 euros, y tiene como principal objetivo apoyar a los jóvenes investigadores que desarrollan su labor en Sevilla.

La línea de investigación de Rafael Álvarez se enmarca dentro de la problemática de la síntesis de películas delgadas con nanoestructuras “a la carta” para aplicaciones funcionales. Entre sus resultados más destacables se encuentra el desarrollo de un protocolo de síntesis general de estos materiales mediante técnicas de plasma en un solo paso, a temperatura ambiente, y sin necesitar reactivos de alto coste.

El jurado del III Premio Manuel Losada Villasante a la Excelencia en la Investigación ha estado compuesto por el rector de la Universidad de Sevilla, Antonio Ramírez de Arellano; el director de Radio Sevilla, Antonio Yélamo; el alcalde de Carmona, Juan Ávila; la catedrática de Química Orgánica de la US, Rosario Fernández; la directora de Relaciones Institucionales de la Fundación Cajasol, Pilar Lacasta; el profesor titular de Obstetricia y Ginecología de la US, Guillermo Antiñolo y el director-general del Foro Interalimentario, Víctor Yuste; y el periodista de Radio Sevilla Salomón Hachuel.

**Premio Real Academia Sevillana de Ciencias 2014,** Al Doctor D. Juan Ramón Sánchez Valencia, Licenciado en Ciencias Físicas por la Universidad de Granada (2005) e Ingeniero de Materiales y Doctor (2010) por la Universidad de Sevilla. Buena parte de su carrera investigadora se ha desarrollado en el Instituto de Ciencias Materiales de Sevilla.

Su actividad como investigador se concentra en el estudio de nanomateriales funcionales con aplicaciones en fotónica, sensórica y electrónica. Se trata de materiales de alto interés técnico que se preparan mediante técnicas de laboratorio de vacío y de procesado de plasma, que pueden asimismo desarrollarse a escala industrial, y que son compatibles con los métodos actuales de fabricación de dispositivos microelectrónicos.

**Rafael Alvarez Molina, PLACA DE HONOR AEC-2014 como JOVEN CIENTIFICO**. El Dr. Rafael Álvarez Molina ha sido galardonado con la Placa de Honor AEC-2014 en reconocimiento por sus méritos como joven científico. La Junta de Gobierno de la Asociación Española de Científicos ha decidido concedérsela por sus aportaciones internacionales en los campos de la nanociencia y nanotecnología a lo largo de su carrera investigadora.

Los trabajos de Rafael se centran en la elaboración de nanomateriales “a la carta” para el desarrollo de aplicaciones tecnológicas avanzadas. En sus investigaciones combina la simulación por ordenador con la realización de experimentos de tipo fundamental para analizar el ensamblaje atómico en la nanoescala. Los procedimientos que desarrolla en su laboratorio pueden utilizarse en la fabricación de un gran número de materiales con aplicaciones para la industria medioambiental y biomédica, entre otras.

Asimismo es coinventor, junto a otros investigadores, de varias patentes en el área de la biomedicina y de las células fotovoltaicas, y también es autor de diferentes programas de ordenador especializados para el estudio de los nanomateriales. Los resultados de sus estudios le han hecho merecedor del reconocimiento internacional en multitud de publicaciones científicas, que han sido destacadas en numerosos medios de comunicación y divulgación europeos y americanos.

## ESTANCIAS Y VISITAS DE PERSONAL DEL ICMS EN OTROS CENTROS
## PERSONNEL OF THE ICMS IN OTHER LABORATORIES

**Photovoltaic and Optoelectronic Device Group, Departament of Physics, University of Oxford**

| | | |
|---|---|---|
| Oxford, Reino Unido | **Miguel Anaya Martín** | 1 mes |

**Philipps Universität Marburg**

| | | |
|---|---|---|
| Marburg, Alemania | **Alberto Escudero Belmonte** | 3 meses |

**Photonics Group del departament of physics, University of York**

| | | |
|---|---|---|
| York, Reino Unido | **Alberto Jiménez Solano** | 3 meses |

## 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).

# DISEÑO DE NANOMATERIALES Y MICROESTRUCTURAS

# TAILORED NANOMATERIALS AND MICROSTRUCTURE

## PERSONAL / PERSONNEL

**Profesores de Investigación**

Dra. Asunción Fernández Camacho

**Catedráticos**

Dr. Luis M. Esquivias Fedriani
Dr. Diego Gómez García

**Investigadores Científicos**

Dr. Juan Carlos Sánchez López

**Científicos Titulares**

Dra. Rosalía Poyato Galán
Dra. T. Cristina Rojas Ruiz

**Investigadores Contratados**

Dra. Gisela M. Arzac Di Tomaso
Dra. Vanda C. Fortio Godinho
Dr. Eugenio Zapata Solvas
Dr. Miguel Castillo Rodríguez

**Becarios Predoctorales**

Ldo. Jaime Caballero Hernández
Ldo. Carlos Andrés García Negrete
Ldo. Santiago Domínguez Meister
Lda. Mariana Paladini San Martin

**Personal Contratado**

Lda. Lucia T. Castillo Flores
Ldo. Dirk Hufschmidt
D. Miguel Nieto Redondo
Ing. Tec. M. Rocío García Gil
Dr. Bertrand Lacroix

## PROYECTOS DE INVESTIGACIÓN / RESEARCH PROJECTS

### Laboratorio avanzado para el análisis de nanomateriales funcionales Advanced laboratory for the nano-analysis of novel functional materials (AL-NANOFUNC)

| | |
|---|---|
| Código/Code: | REGPOT-CT-2011-285895 |
| Periodo/Period: | 01-10-2011 / 30-03-2015 |
| Organismo Financiador/Financial source: | Unión Europea |
| Importe total/Total amount: | 2.687.409 € |
| Investigador responsableICMS Research head ICMS: | Asunción Fernández Camacho |
| Componentes/Research group: | Cristina Rojas, M. Carmen Jiménez, Gisela Arzac, Olga Montes, Inmaculada Rosa, Rafael Alvarez, Vanda Godinho, Juan Carlos Sánchez-López, Hernán Míguez, Agustín R. González-Elipe, Manuel Ocaña, M. Jesús Sayagués, Lionel Cervera, Roland Schierholz, Salah Rouillon, Lucia Castillo, Rocío García, Carlos García-Negrete, Jaime Caballero |

RESUMEN / ABSTRACT

El proyecto AL-NANOFUNC ha sido diseñado para poner en marcha en el Instituto de Ciencia de los Materiales de Sevilla (ICMS, CSIC-Univ.Sevilla, España) un laboratorio avanzado para el Nano-análisis de nuevos materiales funcionales. Las técnicas de Nanoscopía avanzada, basadas en equipos de microscopía electrónica de última generación, se dedicarán a la investigación de vanguardia en temas específicos de gran interés: i) Nanomateriales para aplicaciones energéticas sostenibles; ii) películas delgadas multifuncionales y recubrimientos nanoestructurados; iii) materiales nano-estructurados para fotónica y sensores.

Para situar a los laboratorios del ICMS en una posición de liderazgo que sea competitiva en un escenario mundial, el proyecto AL-NANOFUNC contempla la puesta al día del potencial investigador actual en varias direcciones: i) Mejorar las capacidades de equipamiento en relación a la microscopía electrónica analítica de alta resolución; ii) mejorar el impacto de la investigación básica a través de la contratación de investigadores especializados y el intercambio transnacional con los centros de referencia en Europa, iii) desarrollar y mejorar el potencial de innovación de la investigación del ICMS abriendo las nuevas instalaciones a empresas y centros relacionados; iv ) organizar talleres, conferencias y actividades de difusión para mejorar la visibilidad de la investigación.

En el proyecto se propone también una estrecha colaboración con centros de referencia y empresas de Lieja (Bélgica), Graz (Austria), Jülich (Alemania), Oxford (Inglaterra), Cambridge (Inglaterra), Dübendorf (Suiza) y Rabat (Marruecos), así como con laboratorios de Universidades Andaluzas.

Cinco empresas en Andalucía colaborarán también en estrecha sinergia para promover las líneas estratégicas de interés a largo plazo de la región en los productos de piedra natural y artificial y los sectores de energía solar y energías renovables.

The AL-NANOFUNC project has been designed to install and fully develop at the Materials Science Institute of Seville (ICMS, CSIC-Univ.Seville, Spain) an advanced laboratory for the Nano-analysis of novel functional materials. Advanced Nanoscopy facilities, based on latest generation electron microscopy equipments, will be devoted to breakthrough research in specific topics of high interest: i) Nanomaterials for sustainable energy applications; ii) protective and multifunctional thin film and nanostructured coatings; iii) nanostructured photonic materials and sensors.

To take the ICMS laboratories to a leading position that is competitive in a world-wide scenario, the AL-NANOFUNC project is contemplated to up-grade the actual research potential in several directions: i) improve equipment capabilities regarding the Analytical High Resolution Electron Microscopy facilities; ii) improve the impact and excellence of basic research through hiring of experienced researchers and transnational exchange with the reference centers in Europe; iii) develop and improve the innovation potential of the ICMS's research by opening the new facilities to companies and stakeholders; iv) organize workshops and conferences, dissemination and take-up activities to improve research visibility.

Close collaborations with reference centers and companies in Liège (Belgium), Graz (Austria), Jülich (Germany), Oxford (England), Cambridge (England), Dübendorf (Switzerland) and Rabat (Morocco), as well as with laboratories at Andalucian Universities, are foreseen in this project.

Five companies in Andalusia will also collaborate in close synergies to promote the long-term strategic lines of interest for the region in the natural and artificial stone products and solar and renewable energy sectors.

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## Desarrollo de recubrimientos nanoestructurados protectores para su uso en condiciones extremas (NANOPROTEXT) Development of nanostructured protective coatings for extreme environmental conditions (NANOPROTEXT)

Código/Code: MAT2011-29074-C02
Periodo/Period: 01-10-2012 / 31-12-2014
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
Importe total/Total amount: 129.999,98 €
Investigador responsable/Research head: Juan Carlos Sánchez López
Componentes/Research group: T. Cristina Rojas Ruiz; Francisco Javier Pérez Trujillo;Maria del Pilar Hierro de Bengoa;Germán Alcalá Penades; Maria Sonia Mato Díaz; Marta Brizuela; Pablo Corengia; José Luis Viviente; Alberto García;Daniel González

## RESUMEN / ABSTRACT

En muchas operaciones industriales, los componentes de las máquinas o piezas que están en contacto se hallan sometidos a condiciones extremas de carga, fricción, temperatura o atmósfera variable. La investigación dirige sus esfuerzos hacia al desarrollo de nuevos recubrimientos multicomponentes capaces de aumentar su eficiencia protegiendo su superficie contra el desgaste y la oxidación, que ocasionan fallos ulteriores de funcionamiento. Mediante el control del tamaño y distribución de las fases componentes, la composición química y su microestructura en el rango nanométrico es posible obtener propiedades multifuncionales tales como baja fricción, dureza y estabilidad térmica.

En este proyecto se propone el desarrollo de tres tipos de recubrimientos nanoestructurados mediante el proceso de magnetron sputtering para aplicaciones protectoras en condiciones extremas o singulares de funcionamiento (presión, temperatura, atmósferas oxidantes, vacío, etc). Los sistemas elegidos comprenden cristales de materiales duros (nitruros o carburos) combinados con una segunda fase o elemento que mejore su comportamiento. De este modo se ensayarán recubrimientos nanocomposite formados por nanocristales de WC dispersos en una segunda fase amorfa de tipo calcogenuro (WS2 or WSe2) para su uso como lubricante sólido en aplicaciones espaciales o bajo atmósferas inertes. En el segundo caso, Y ó Zr serán usados como elementos dopantes dentro de recubrimientos de CrAlN con objeto de incrementar la resistencia a la oxidación a baja y alta temperatura, y el comportamiento tribológico, muy válido en numerosos sectores industriales tales como (herramientas de mecanizado, metalúrgico, aeronaútico, automoción, etc.). Finalmente, se desarrollaran recubrimientos nanocomposite duros y transparentes basados en la familia del Al-Si-N para protección de sistemas ópticos.

En todos los casos, el proyecto comprende su síntesis, caracterización estructural y química, así como su validación práctica en ensayos tribológicos y de oxidación que simulan las condiciones finales de operación. En el caso concreto de las capas duras y transparentes también se evaluarán sus propiedades ópticas. El estudio de la relación existente entre la microestructura y las propiedades medidas será un objetivo esencial puesto que permitirá una mayor comprensión de los mecanismos de actuación, y por ende, la optimización de tales sistemas nanoestructurados para su mejor aprovechamiento tecnológico.

In many industrial operations, the machines or tool components in contact are submitted to severe conditions of load, friction, temperature or variable atmosphere. The research efforts are directed towards the development of new multiphase coatings capable to increase their performance by protection of the surface against wear and oxidation that cause failure mechanisms. By appropriate control of the size and distribution of phases, chemical composition and microstructure in the nanometric regime it is possible to obtain multifunctionality as low friction, hardness and thermal stability. To achieve excel in this purpose it is necessary to correlate the macroscopic properties of these coated surfaces (mechanical, tribological, oxidation resistance) with these basic phenomena.

In this project, three types of nanostructured coatings will be prepared using a magnetron sputtering process for protection in running operations under extreme or singular conditions (pressure, temperature, oxidant atmospheres, vacuum, etc.). The chosen systems are constituted by crystals of hard materials (nitrides or carbides) in combination with a second element or phase that improves the practical performance. Thus, nanocomposite coatings

consisting of WC nanocrystals dispersed in an amorphous dichalcogenide phase (WS2 or WSe2) are proposed as solid lubricant coatings to run under high vacuum conditions useful for spatial applications or inert environments. In the second case, Y or Zr will be tested as dopant elements in CrAlN coatings with the aim of increasing the corrosion and oxidation resistance and tribological behaviour useful for many industrial fields (machining tools, metallurgy, aeronautic, automotive, etc…). Finally, hard and transparent nanocomposite coatings based on the Al-Si-N system are suggested as protective coatings for optical systems.

In all cases, the project comprises their synthesis, chemical and structural characterization, and validation in tribological and oxidation under extreme condition tests that simulate the final operation conditions. In the case of the hard and transparent coatings, their optical properties will be also analysed. The establishment of the relationships between microstructure and measured properties will be an essential objective, since it enables the better understanding of the action mechanisms, and thus, the optimisation of such nanostructured multifunctional systems for an improved technological benefit.

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## Estudio de las interacciones intermoleculares entre hidroxiácidos carboxílicos de cadena larga como modelo para el diseño de poliésteres biomiméticos Fatty hydroxyacids molecular interactions as model for biomimetic polyester design

| | |
|---|---|
| Código/Code: | CTQ2011-24299 |
| Periodo/Period: | 01-01-2012 / 31-12-2014 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 99.220 € |
| Investigador responsable/Research head: | Benítez Jiménez, José Jesús |
| Componentes/Research group: | Alejandro Heredia Guerrero, Miguel Angel San Miguel Barrera, Jaime Oviedo López, Miguel Salmerón Batalle |

RESUMEN / ABSTRACT

El objetivo de este proyecto de investigación es el estudio y determinación de las interacciones que se ponen de manifiesto entre las moléculas de ácidos carboxílicos lineales de cadena larga en función del nivel y tipo de funcionalización con grupos hidroxilos. Para ello se proponen sistemas modelos basados en capas autoensambladas de estas moléculas sobre un soporte plano de baja energía de interacción para que sean las propias interacciones intermoleculares las que condicionen la estructura del empaquetamiento. La metodología de estudio de estos sistemas confinados combinará, fundamentalmente, las microscopías de sonda de proximidad, las simulaciones atomísticas de dinámica molecular y el análisis químico por espectroscopía infrarroja. La información fundamental obtenida se empleará para el diseño de una ruta de síntesis química de poliésteres miméticos a la cutina vegetal, un biopolímero de barrera hidrófobo, inocuo y completamente biodegradable. Se determinarán las propiedades

físicas (mecánicas, permeabilidad, de transporte iónico, etc…) y químicas (grado de esterificación, degradabilidad, etc…) de estos materiales sintéticos y se relacionarán con sus estructuras primarias (red de enlaces ester) y secundarias (interacciones por puente de hidrógeno entre grupos hidroxilos remanentes). A partir de esta relación estructura-función, se modificará el protocolo de síntesis empleando elementos no propagadoras del entrecruzamiento de la red primaria (moléculas con bajo grado de hidroxilación) y modificadores de la red secundaria (ácidos carboxílicos con distinto grado de hidroxilación), con vistas a la obtención de polímeros con propiedades "a la carta". Finalmente, se explorará el potencial de aplicación de estos poliésteres sintéticos como sustitutos de plásticos obtenidos a partir de hidrocarburos con vistas a reducir residuos, tanto en el proceso de fabricación como los asociados a su desecho.

The objective of this Project is to study and characterize the specific interactions between fatty carboxylic acids molecules arising from selective hydroxylation of the alkyl chain. To address this issue, molecular self-assembled systems showing a low interaction with an atomically flat support are proposed as models. The use of low binding energy supports is to ensure the packing structure to be mainly driven by the molecule to molecule interactions rather than the molecule to substrate adsorption. These self-assembled systems will be characterized by scanning probe microscopies such as AFM and STM and infrared spectroscopy. Results will be complemented with molecular dynamics atomistic simulations. Basic information obtained from self-assembled models will be used to design the in-vitro chemical synthesis of cutin mimetic polyesters. Cutin is a non toxic, fully biodegradable barrier biopolymer present at the skin of fruits, leaves and non lignified stems of higher plants. Physical (mechanical, water permeability, ionic transport, etc…) and chemical (ester yield, controlled chemical degradation rate, etc…) properties of synthetic polyesters will be determined. Material features will be related with both, the main structure arising from the ester bonds formation and the secondary network resulting from hydrogen bonding between spare non reacted hydroxyl groups. Structure-function patterns will be used to redesign the synthesis route to obtain polymeric esters with tailored properties. To achieve this goal, both the primary and secondary structural networks will be manipulated. In the first case non hydroxylated molecules will be used to prevent ester bonding propagation. To modify hydrogen bonding crosslinking, additives with selected hydroxylation (primary or secondary) will be employed. The final motivation of this research is to explore the applicability of such mimetic polyester as substitutes for the highly contaminant hydrocarbon based plastics.

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## Desarrollo de nuevos materiales y procesos para la generación y uso del hidrógeno principalmente en aplicaciones portátiles Development of novel materials and processes for the generation and use of hydrogen mainly in portable applications

Código/Code: CTQ2012-32519
Periodo/Period: 01-01-2013 / 31-12-2015
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad

| | |
|---|---|
| Importe total/Total amount: | 190.710 € |
| Investigador responsable/Research head: | Fernández Camacho, Asunción |
| Componentes/Research group: | Gisela Arzac, Jaime Caballero, Lionel Cervera, Vanda Fortio, Carlos Negrete, Dirk Hufschmidt, Cristina Rojas Ruiz, Roland Schierholz |

## RESUMEN / ABSTRACT

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 el presente proyecto se abordará el estudio de los distintos procesos que conducen a la configuración final integrada de sistemas de generación y uso del hidrógeno principalmente en aplicaciones portátiles (y potencialmente escalables para aplicaciones estacionarias). En particular se trabajará en este proyecto en las siguientes líneas de actuación:

a) Investigación en nuevos compuestos ligeros para su uso en procesos de generación de hidrógeno en pequeña escala por vía química (hidrólisis). Típicamente reacciones de hidrólisis de borohidruros (i.e. NaBH4) y compuestos tipo borano de amoníaco, hidrazinas ó borano hidrazina. Este area incluye el desarrollo de catalizadores en la nanoescala utilizando métodos de vía húmeda para su síntesis: Nanoestructuras metal-metaloide (tipo Co-B, Co-B-P y similares) y catalizadores bimetálicos (que incluyan ó no metaloide) de bajo coste potenciando efectos sinérgicos (tipo CoRu, NiPt ó Co-Ru-B). Incluye también el desarrollo de reactores portátiles para estos procesos y el desarrollo de nuevos sustratos y monolitos, estudios de adherencia del catalizador y durabilidad.

b) Investigación en nuevos sistemas anfitrión-huésped (host-guest) que contengan hidrógeno para el almacenamiento reversible (carga/descarga). Principalmente soportes (anfitrión) porosos del tipo “nanoscaffolds” (basados en C ó BN) infiltrados con borohidruros (huésped) (i.e. borohidruro de titanio) típicamente utilizados para el almacenamiento reversible de hidrógeno. Estos nuevos materiales deben presentar cinéticas de carga y descarga mejoradas.

c) Estudios de acoplamiento de un sistema generador de hidrógeno de bajo coste a una celda de combustible. Típicamente un reactor continúo para la hidrólisis del NaBH4 con catalizador Co-B que suministra H2 en condiciones de flujo constante para alimentar directamente una pila de combustible tipo PEM de 60 W.

d) Estudios fundamentales para el desarrollo de catalizadores y soportes para la combustión controlada de hidrógeno. Es una línea nueva en el grupo de investigación que se basa en preparar por vía húmeda catalizadores nanoparticulados de metal noble sobre soportes comerciales de cerámicas porosas (tipo SiC). Incluye el diseño de un reactor para el estudio en escala laboratorio de la producción de calor por combustión controlada de hidrógeno.

e) Desarrollo de la tecnología de pulverización catódica (“magnetrón sputtering”) para la preparación de catalizadores y nano-estructuras sobre diversos sustratos de aplicación en los procesos desarrollados en los apartados anteriores. El grupo tiene una amplia experiencia en esta tecnología que se aplicaría de manera novedosa en este proyecto permitiendo una gran versatilidad en cuanto a la nanoestructura, composición y aditivos para mejorar la actividad, durabilidad y selectividad de los catalizadores.

f) Caracterización microestructural y química de los nuevos materiales y catalizadores desarrollados en el proyecto. Se trata típicamente de materiales con una nanoestructura con-

trolada en donde las modernas técnicas nanoscopicas van a jugar un papel fundamental en la fabricación a medida de estos materiales.

Hydrogen as a vector of transport and storage of energy is a very attractive candidate in the context of increased use of renewable and clean energies. This project will address the study of the different processes that lead to the final configuration of an integrated systems for hydrogen generation and use mainly in portable applications (and potentially scalable for stationary applications). In particular, work will be carried out in this project in the following lines:

a) Research on new lightweight compounds for use in hydrogen generation processes on a small scale by chemical routes (hydrolysis). Typically hydrolysis reactions of borohydrides (i.e. NaBH4) and compounds like ammonia borane, hydrazine borane or hydrazine. This line includes the development of catalysts at the nanoscale using wet chemical methods for their synthesis: Metal-metalloid nanostructures (i.e. Co-B, Co-B-P and similar ones) and bimetallic catalysts (including or not metalloid) of low cost which potentiate synergistic effects (i.e. CoRu, NiPt or Co-Ru-B). The topic also includes the development of portable reactors for these processes and the development of new substrates and monoliths, studies of adherence and durability of the catalyst.

b) Research on new host-guest systems containing hydrogen for reversible storage (loading / unloading). Mainly porous supports (host) like the so called "nanoscaffolds" (based on C or BN) infiltrated with borohydrides materials (guest) (i.e. titanium borohydride) typically used for reversible hydrogen storage. These new materials must present improved charging and de-charging kinetics.

c) Studies of coupling a hydrogen generator system with a low cost fuel cell. Typically a continuous reactor for the hydrolysis of NaBH4 with Co-B catalyst for providing H2 at constant flow rate conditions to directly feed a PEM fuel cell of 60 W.

d) Fundamental studies for the development of catalysts and supports for the controlled combustion of hydrogen. It's a new line in the research group based on wet chemical preparation of noble metal nanoparticle catalysts on commercial porous ceramic supports (i.e. SiC). The line also includes the design of a reactor for laboratory-scale study of heat production by controlled combustion of hydrogen.

e) Development of sputtering technology ("magnetron sputtering") for the preparation of catalysts and nano-structures on various substrates for use in the processes developed in the previous sections. The group has extensive experience in this technology to be applied in novel ways in this project leading to a great versatility regarding nanostructure, composition and addition of additives to improve catalytic activity, durability and selectivity of catalysts.

f) Microstructural and chemical characterization of new materials and catalysts developed in the project. We are dealing typically with materials of controlled nanostructure where modern nanoscopic techniques will play a key role in the custom manufacturing of these materials

# Desarrollo de recubrimientos composite de carbono para aplicaciones biomédicas

# Development of carbón-based composites for biomedical applications

| | |
|---|---|
| Código/Code: | P10-TEP 06782 (Proyecto de Excelencia) |
| Periodo/Period: | 15-03-2011 / 15-03-2014 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 96.000 € |
| Investigador responsable/Research head: | Juan Carlos Sánchez López |
| Componentes/Research group: | T. Cristina Rojas, Carlos López Cartes, David Abad, Vanda Godinho, Santiago Domínguez, Inmaculada Rosa |

## RESUMEN / ABSTRACT

El proyecto comprende el desarrollo de recubrimientos basados en carbono desde su síntesis a medida, caracterización, evaluación en tests de desgaste y estudios de biocompatibilidad para su uso en implantes artificiales. El control del tipo de enlace químico del carbono (sp2/sp3) y la composición química, incluyendo metales como (Ag, Ti) u otros elementos (B, N, O), permitirá modular las propiedades mecánicas y tribológicas (dureza, fricción y resistencia al desgaste) con objeto de incrementar su comportamiento final. Para ello se propone el empleo de la técnica de pulverización catódica (del inglés magnetron sputtering) para depositar estos recubrimientos avanzados sobre los materiales usados en los implantes (acero, aleaciones de Ti o polímeros) bajo diferentes condiciones de síntesis. Seguidamente, éstos composites de carbono serán evaluados de forma comparativa en ensayos de fricción y desgaste que simulen las condiciones que estos materiales se encontrarán en la aplicación final. De esta manera será posible establecer una correlación entre el comportamiento observado y las características químicas y estructurales de las capas preparadas bajo diferentes condiciones de síntesis. Finalmente, la biocompatibilidad será estudiada en ensayos de adhesión celular, citotoxicidad y actividad antibacteriana. Este completo conjunto de análisis aportará una excelente perspectiva de las posibilidades de transferencia tecnológica de estos materiales avanzados a la biomedicina.

This project pursues the development of carbon-based coatings including the tailored synthesis, characterization, evaluation in wear tests and biocompatibility study for the application in artificial implants. The control of the carbon chemical bonding (sp2/sp3) and the chemical composition, including metals as (Ag, Ti) or other elements (B, N, O) will enable to tune the mechanical and tribological properties (hardness, friction and wear resistance) with the aim of improving the final performance. To achieve this goal, the use of magnetron sputtering technique is envisaged to deposit advanced coatings under different synthesis conditions. Next, these carbon composites will be evaluated comparatively in friction and wear tests that simulate the conditions that these materials will face in the final application. In this way, it will be possible to establish the correlation between the observed behavior and chemical and structural characteristics of the prepared layers in cell adhesion tests, cytotoxicity and antibacterial

activity. This complete characterization will provide an excellent overview of the possibilities of technological transfer of these advanced materials to the biomedicine.

## Desarrollo de procesos de combustión catalítica de hidrógeno y estudio de su integración en dispositivos para aplicaciones portátiles Development of processes for the catalytic combustion of hydrogen and study of the integration in devices for portable applications

| | |
|---|---|
| Código/Code: | P12-TEP-862 (Proyecto de Excelencia) |
| Periodo/Period: | 16-05-2014 / 15-05-2016 |
| Organismo Financiador/Financial source: | Junta de Andalucía |
| Importe total/Total amount: | 153.025 € |
| Investigador responsable/Research head: | Asunción Fernández Camacho |
| Componentes/Research group: | Julián Martínez, Gisela Arzac, Dirk Hufschmidt, Joaquín Ramírez, M.Carmen Vera, Vanda Godinho, Lionel Cervera, T.Cristina Rojas, Olga Montes, Mariana Paladini, Jaime Caballero-Hernández |

RESUMEN / ABSTRACT

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. La producción y el uso de la energía basada en la tecnología del hidrógeno es de especial relevancia en pequeña escala para aplicaciones portátiles (y potencialmente escalable para aplicaciones estacionarias). En el presente proyecto se abordará el estudio del proceso de combustión catalítica o controlada de hidrógeno en los distintos aspectos que puedan conducir a una configuración final integrada con un sistema de generación de H2 en aplicaciones portátiles. Para ello se aprovecharán las sinergias integrando investigadores de dos grupos del PAI: i) Del grupo TEP217, especialistas en almacenamiento y generación de hidrógeno en sistemas basados en hidruros metálicos, hidruros complejos y composites de hidruros reactivos; así como en el uso de catalizadores y aditivos para controlar y mejorar las cinéticas de estos procesos. ii) Del grupo FQM342, especialistas en la obtención de cerámicos porosos de alto interés como soportes de catalizadores en entornos agresivos de combustión. Además la colaboración se completa con la participación de la empresa Abengoa Hidrógeno S.A. que participa en calidad de subcontratada como especialistas en sistemas de producción y almacenamiento de hidrógeno.

En particular se trabajará en este proyecto en las siguientes líneas de actuación:

1.- Desarrollo de catalizadores y soportes para la combustión controlada. Típicamente cerámicas porosas biomórficas de carburo de silicio y catalizadores clásicos tipo metal noble y nuevos catalizadores de bajo coste a desarrollar en el proyecto.

2.- Desarrollo de los reactores necesarios para el estudio de la combustión controlada. Típicamente para flujos de hidrógeno de unos pocos ml/min y para la escala de un generador de H2 ya disponible de 0.5 a 1.5 L/min.

3.- Acoplamiento al sistema de combustión controlada de los sistemas portátiles de generación de hidrógeno que hemos desarrollado en proyectos anteriores.

4.- Aplicación de la tecnología de pulverización catódica de una manera exploratoria en este proyecto para depositar los catalizadores de combustión catalítica en sustratos porosos.

5.- Caracterización microestructural y química de los soportes y catalizadores en la nanoescala para seguir los procedimientos de síntesis y evolución en operación.

Hydrogen is an attractive candidate as a vector for storage and transport of energy in the context of an increased use of renewable and clean energies. The production and use of energy based on hydrogen technology is particularly important for small-scale portable (and potentially scalable for stationary) applications. In this project the process of catalytic (controlled) combustion of hydrogen will be investigated in the various aspects that could lead to a final integrated configuration with a H2 generation system for portable applications. For that the project will take advantage of the synergy of integrating two researcher groups from the PAI: i) The TEP217 group, specialists in storage and generation of hydrogen based on metal hydrides, complex hydrides and hydride composites reactive systems; and in the use of catalysts and additives to control and improve the kinetics of these processes. ii) The FQM342, specialist group for the fabrication of porous ceramics of high interest as catalyst supports for harsh combustion environments. Further collaboration is completed with the participation of the company Abengoa Hidrógeno SA that will be involved as sub-contractor as specialist in systems for the production and storage of hydrogen.

In particular we will work on this project in the following lines:

1.- Development of catalysts and supports for catalytic combustion. Typically porous biomorphic silicon carbide ceramics and classic noble metal catalysts, as well as new low cost catalysts to be developed in the project.

2.- Development of reactors needed for the study of the catalytic combustion. Typically hydrogen flows from a few ml/min to the scale of a H2 generator already available in the range 0.5 to 1.5 L/min.

3.- Coupling the catalytic combustion system with a portable hydrogen generation systems that we have developed in previous projects.

4.- Application of the sputtering technology in an exploratory manner in this project to deposit the catalyst materials for the H2 catalytic combustion on porous substrates.

5.- Microstructural and chemical characterization of the supports and catalysts in the nanoscale to follow the procedures of synthesis and evolution in operation.

## Convenios y Contratos / Contracts and Agreements

### Research on tribological systems. Functional coatings and their characterization

| | |
|---|---|
| Periodo/Period: | 23-10-2014 / 28-02-2016 |
| Organismo Financiador/Financial source: | Robert Bosch Gmbh |
| Importe total/Total amount: | 23.320 € |
| 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: | 18-01-2010 / 31-12-2014 |
| Organismo Financiador/Financial source: | Clarton Horn |
| Importe total/Total amount: | 14.916,75 € |
| Investigador responsable/Research head: | Asunción Fernández Camacho |
| Componentes/Research group: | Vanda Fortio Godinho, M. Carmen Jiménez de Haro, Inmaculada Rosa Cejudo |

### Caracterización microstructural y química de materiales por microscopía electrónica

| | |
|---|---|
| Periodo/Period: | 14-02-2014 / 15-02-2016 |
| Organismo Financiador/Financial source: | ABENGOA RESEARCH S.L. |
| Importe total/Total amount: | 15.125 € |
| Investigador responsable/Research head: | Asunción Fernández Camacho |
| Componentes/Research group: | Vanda Fortio Godinho, M. Carmen Jiménez de Haro, Inmaculada Rosa Cejudo |

### Caracterización microstructural y química de materiales en células CIGSe

| | |
|---|---|
| Periodo/Period: | 13-05-2014 / 12-05-2017 |
| Organismo Financiador/Financial source: | ABENGOA Solar New Technologies, S.A. |
| Importe total/Total amount: | 55.660 € |
| Investigador responsable/Research head: | Asunción Fernández Camacho |
| Componentes/Research group: | Vanda Fortio Godinho, M. Carmen Jiménez de Haro, Inmaculada Rosa Cejudo, Olga Montes Amorín |

## PATENTES / PATENTS

### Polyester films obtained by noncatalyzed Melt-condensation polymerization of aleuritic (9,10,16-trihydroxyhexadecanoic) acid in air

Inventores: José Jesús Benítez Jiménez, José Alejandro Heredia Guerrero, Antonio Heredia Bayona
Tipo de Patente: Nacional
Número de Solicitud: 201401057
Fecha Solicitud: 25 Diciembre 2014
Entidad/es Titular/es: Universidad de Málaga y CSIC

### Procedimiento de fabricación de materiales avanzados por concentración de corriente eléctrica

Inventores: Diego Gómez García y Eugenio Zapata Solvas
Tipo de Patente: Nacional
Número de Solicitud: 201400347
Fecha Solicitud: 24 Abril 2014
Entidad/es Titular/es: Universiad de Sevilla y CSIC

## COOPERACIÓN INTERNACIONAL Y OTROS INTERNATIONAL COOPERATION AND OTHERS

### Mise au point de revêtements bactéricides sur microbilles de verre par technique plasma base pression - ABBEADS

| | |
|---|---|
| Periodo/Period: | 1-10-2012 / 30-09-2014 |
| Código/Code: | ECV320600FD013F/1217577 |
| Entidad Financiadora/Financial source: | Direction des Progammes Regionaux de Wallonie (Bélgica) |
| Investigador responsable/Research head: | Fabian Renaux |
| Participantes/Participants: | Juan Carlos Sánchez López |

## ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

### Supported Co catalysts prepared as thin films by magnetron sputtering for sodium borohydride and ammonia borane hydrolysis

Paladini, M; Arzac, GM; Godinho, V; De Haro, MCJ; Fernandez, A
Applied Catalysis B: Environmental, 158-159 (2014) 400-409
October, 2014 | DOI: 10.1016/j.apcatb.2014.04.047

Supported Co catalysts were prepared for sodium borohydride and ammonia borane hydrolysis by magnetron sputtering for the first time under different conditions. Ni foam was selected as support. Deposition conditions (time, pressure, and power) were varied to improve catalytic activity. A decrease in deposition power from 200 to 50 W, leads to a decrease in crystallite and column size and a higher activity of catalysts. The increase in deposition pressure from 1.5 × 10−2 to 4.5 × 10−2 mbar produces same effect but in this case the enhancement in activity is higher because amorphous materials were obtained. The highest activity for SB hydrolysis was 2650 ml min−1 gcat−1 for the 50 W Co 4.5 (4 h) sample (Ea = 60 ± 2 kJ mol−1). For AB hydrolysis activity for the 50 W Co 3.2 (4 h) sample was similar. Durability of the thin films was tested for both reactions upon cycling (14 cycles). Diluted acid washing was effective to recover the activity for sodium borohydride reaction but not for ammonia borane hydrolysis. The strong Co–NH3 interactions explain the non-efficiency of the acid washing.

### Shape-defined nanodimers by tailored heterometallic epitaxy

Garcia-Negrete, Carlos A; Rojas, Teresa C; Knappett, Benjamin R; Jefferson, David A; Wheatley, Andrew E H; Fernandez, Asuncion

*Nanoscale*, **6** (2014) 11090-11097

October, 2014 | **DOI:** 10.1039/C4NR01815J

The systematic construction of heterogeneous nanoparticles composed of two distinct metal domains (Au and Pt) and exhibiting a broad range of morphologically defined shapes is reported. It is demonstrated that careful Au overgrowth on Pt nanocrystal seeds with shapes mainly corresponding to cubeoctahedra, octahedra and octapods can lead to heterometallic systems whose intrinsic structures result from specific epitaxial relationships such as {111} + {111}, {200} + {200} and {220} + {220}. Comprehensive analysis shows also that nanoparticles grown from octahedral seeds can be seen as comprising of four Au tetrahedral subunits and one Pt octahedral unit in a cyclic arrangement that is similar to the corresponding one in decahedral gold nanoparticles. However, in the present case, the multi-component system is characterized by a broken five-fold rotational symmetry about the [011] axis. This set of bimetallic dimers could provide new platforms for fuel cell catalysts and plasmonic devices.

### A General Perspective of the Characterization and Quantification of Nanoparticles: Imaging, Spectroscopic, and Separation Techniques

Lapresta-Fernandez, A; Salinas-Castillo, A; de la Llana, SA; Costa-Fernandez, JM; Dominguez-Meister, S; Cecchini, R; Capitan-Vallvey, LF; Moreno-Bondi, MC; Marco, MP; Sanchez-Lopez, JC; Anderson, IS

*Critical Reviews in Solid State and Materials Sciences*, **39** (2014) 423-458

June, 2014 | **DOI:** 10.1080/10408436.2014.899890

This article gives an overview of the different techniques used to identify, characterize, and quantify engineered nanoparticles (ENPs). The state-of-the-art of the field is summarized, and the different characterization techniques have been grouped according to the information they can provide. In addition, some selected applications are highlighted for each technique. The classification of the techniques has been carried out according to the main physical and chemical properties of the nanoparticles such as morphology, size, polydispersity characteristics, structural information, and elemental composition. Microscopy techniques including optical, electron and X-ray microscopy, and separation techniques with and without hyphenated detection systems are discussed. For each of these groups, a brief description of the techniques, specific features, and concepts, as well as several examples, are described.

## Impregnation of carbon black for the examination of colloids using TEM

Gontard, LC; Knappett, BR; Wheatley, AEH; Chang, SLY; Fernandez, A

*Carbon*, **76** (2014) 464-468
September, 2014 | **DOI:** 10.1016/j.carbon.2014.05.006

Nanoparticles are frequently synthesised as colloids, dispersed in solvents such as water, hexane or ethanol. For their characterisation by transmission electron microscopy (TEM), a drop of colloid is typically deposited on a carbon support and the solvent allowed to evaporate. However, this method of supporting the nanoparticles reduces the visibility of fine atomic details, particularly for carbonaceous species, due to interference from the 2-dimensional carbon support at most viewing angles. We propose here the impregnation of a 3 dimensional carbon black matrix that has been previously deposited on a carbon film as an alternative means of supporting colloidal nanoparticles, and show examples of the application of this method to advanced TEM techniques in the analysis of monometallic, core@shell and hybrid nanoparticles with carbon-based shells.

Nanoparticles represent one of the most studied structures in nanotechnology and nanoscience because of the wide range of applications arising from their unique optical, physical and chemical properties [1]. Often they have core@shell structures, or are coated with organic molecules. Nanoparticle functionality is largely affected by the specific configuration of the outer surface atoms. For example, in heterogeneous catalysis activity and selectivity are mostly determined by the type of atomic defects present at the surface of metallic nanoparticles, and in the field of biomedicine the surface coating of hybrid (inorganic core@organic shell) nanoparticles regulates their stability, solubility and targeting.

Nanoparticles are frequently synthesised using solution techniques that yield colloids, i.e., a solid–liquid mixture containing solid particles that are dispersed to various degrees in a liquid medium; most frequently water, ethanol or hexane. Colloid characterisation generally employs a variety of techniques to establish understanding and control over nanoparticle synthesis and properties. Electron microscopy in transmission mode (TEM) and in scanning transmission mode (STEM) are widely used for particle characterisation, and advances in these techniques mean that it is now routinely possible to resolve single atoms at the surfaces of nanoparticles using aberration-corrected microscopes, to elucidate the three-dimensional shapes of nanoparticles using electron tomography, and to enhance the contrast in very low density materials (e.g., carbonaceous materials) using electron holography [2] and [3]. However, the significant potential of these (S)TEM techniques is ultimately limited by the sample and the techniques available for sample preparation.

Typically, examination by (S)TEM requires that a nanoparticulate sample be prepared by depositing a drop of colloid on a thin, electron-transparent support. It is usual that an amorphous carbon film, silicon nitride film or graphene layers deposited on a copper grid constitute the support [4]. Crucially, these sample preparation techniques suffer from the major limitation that the contrast from the support often shadows atomic details at the particle surface. Moreover, it has been established that the thinnest supports can degrade under electron-beam irradiation, affecting particle stability [5], and also that hydrocarbon contamination can be an issue [6]. The most widely used commercially available TEM support is holey carbon, which comprises of a perforated carbon thin film. In this case, sample preparation aims to locate at least some of the nanoparticles of interest at the edges of the perforations. However, the concave nature of the holes means that solvent contaminants tend to accumulate preferentially at these sites. Moreover, if the TEM sample holder is tilted a particle attached to the edge of a hole is very likely to be shadowed by the carbon film. Taken together, these drawbacks significantly limit the application of techniques such as electron tomography [6].

We propose here a method of circumventing some of these fundamental problems by developing a technique for mounting nanoparticulate samples using a carbon matrix that is inspired by the way samples used in electrocatalysis are prepared [7]. Fig. 1 shows an image of a typical Pt-based electrocatalyst supported on carbon black as used in proton-electron membrane fuels cells, and which consists of Pt nanoparticles formed by calcination of a carbon black impregnated with a solution of salt precursor. Carbon black is a low-grade form of graphite, which is composed of nanocrystallites and no long-range order [8]. In Fig. 1 the carbon black is Vulcan XC-72R, which is widely used as a catalyst support in fuel cells because it provides high electrical conductivity, good reactant gas access, adequate water handling and good corrosion resistance, whilst allowing high dispersion of the particles. In electrocatalyst samples it is common to find particles, like the 5 nm Pt particle shown in Fig. 1, attached strongly to the surface of the support and viewed edge-on against a vacuum so as to provide optimal conditions for high-resolution TEM (HRTEM). Fig. 1B is a quantitative phase image of a Pt particle obtained from a defocus series of 20 images at intervals of 5 nm acquired in a FEGTEM JEOL 2020 at 200 kV with spherical aberration of −30 μm and applying the exit-wave restoration technique [2]. The contrast between details of the particle finestructure is very high compared to conventional HRTEM images, and details such as the presence of monoatomic carbon ribbons surrounding the particle can be seen.

## Bifunctional, Monodisperse $BiPO_4$-Based Nanostars: Photocatalytic Activity and Luminescent Applications

Becerro, AI; Criado, J; Gontard, LC; Obregon, S; Fernandez, A; Colon, G; Ocana, M
*Crystal Growth & Design*, **14** (2014) 3319-3326
July, 2014 | **DOI:** 10.1021/cg500208h

Monodisperse, monoclinic $BiPO_4$ nanostars have been synthesized by a homogeneous precipitation reaction at 120 °C through controlled release of $Bi^{3+}$ cations from a Bi–citrate chelate, in a mixture of glycerol and ethylene glycol, using $H_3PO_4$ as the phosphate source. The set of experimental conditions necessary to obtain uniform nanoparticles is very restrictive, as the change in either the polyol ratio or the reactant concentrations led to ill-defined and/or aggregated particles. The morphology of the particles consists of a starlike, hierarchical structure formed by the ordered arrangement of nanorod bundles. Transmission electron tomography has revealed that the nanostars are not spherical but flattened particles. Likewise, Fourier transform infrared spectroscopy and thermogravimetry have shown that the synthesized nanostars are functionalized with citrate groups. The mechanism of formation of the nanostars has been analyzed to explain their morphological features. The as-synthesized BiPO4 nanostars exhibit an efficient photocatalytic performance for the degradation of Rhodamine B. Finally, it has been demonstrated that the stars can be $Eu^{3+}$-doped up to 2 mol % without any change in the particle morphology or symmetry, and the doped samples show emission in the orange-red region of the visible spectrum after ultraviolet excitation. These experimental observations make this material a suitable phosphor for biotechnological applications.

### Long-term high temperature oxidation of CrAl(Y)N coatings in steam atmosphere

Mato, S; Alcala, G; Brizuela, M; Galindo, RE; Perez, FJ; Sanchez-Lopez, JC
*Corrosion Science*, **80** (2014) 453-460
March, 2014 | **DOI:** 10.1016/j.corsci.2013.11.066

The oxidation resistance of CrAl(Y)N coatings deposited by reactive magnetron sputtering on P92 steel substrates was tested at 650 °C in 100% steam atmosphere up to 2000 h of oxidation. Mass gain measurements and characterisation of coatings and scales after oxidation show the enhanced oxidation resistance provided by the coatings with respect to that of the substrate. The dominant influence of the film microstructure developed due to the presence of an adhesion interlayer of CrN at the coating/substrate interface over Y additions is evidenced. The best performance is achieved by a CrAlN dense coating of around 6 µm without adhesion interlayer.

### Chemistry, nanostructure and magnetic properties of Co-Ru-B-O nanoalloys

Arzac, GM; Rojas, TC; Gontard, LC; Chinchilla, LE; Otal, E; Crespo, P; Fernandez, A
*RSC Advances*, **4** (2014) 46576-46586
Septiembre, 2014 | **DOI:** 10.1039/C4RA05700G

In our previous works, Co–B–O and Co–Ru–B–O ultrafine powders with variable Ru content (xRu) were studied as catalysts for hydrogen generation through sodium borohydride hydrolysis. These materials have shown a complex nanostructure in which small Co–Ru metallic nanoparticles are embedded in an amorphous matrix formed by Co–Ru–B–O based phases and $B_2O_3$. Catalytic activity was correlated to nanostructure, surface and bulk composition. However, some questions related to these materials remain unanswered and are studied in this work. Aspects such as: 3D morphology, metal nanoparticle size, chemical and electronic information on the nanoscale (composition and oxidation states), and the study of the formation or not of a CoxRu1−x alloy or solid solution are investigated and discussed using XAS (X-ray Absorption Spectroscopy) and Scanning Transmission Electron Microscopy (STEM) techniques. Also magnetic behavior of the series is studied for the first time and the structure–performance relationships discussed. All Co-containing samples exhibited ferromagnetic behavior up to room temperature while the Ru–B–O sample is diamagnetic. For the xRu = 0.13 sample, an enhancement in the Hc (coercitive field) and Ms (saturation magnetization) is produced with respect to the monometallic Co–B–O material. However this effect is not observed for samples with higher Ru content. The presence of the CoxB-rich (cobalt boride) amorphous ferromagnetic matrix, very small metal nanoparticles (Co and CoxRu(1−x)) embedded in the matrix, and the antiferromagnetic CoO phase (for the higher Ru content sample, xRu = 0.7), explain the magnetic behavior of the series.

### On the formation of the porous structure in nanostructured a-Si coatings deposited by dc magnetron sputtering at oblique angles

Godinho, V; Moskovkin, P; Alvarez, R; Caballero-Hernandez, J; Schierholz, R; Bera, B; Demarche, J; Palmero, A; Fernandez, A; Lucas, S

*Nanotechnology*, **25** (2014) 355705
September, 2014 | **DOI:** 10.1088/0957-4484/25/35/355705

The formation of the porous structure in dc magnetron sputtered amorphous silicon thin films at low temperatures is studied when using helium and/or argon as the processing gas. In each case, a-Si thin films were simultaneously grown at two different locations in the reactor which led to the assembly of different porous structures. The set of four fabricated samples has been analyzed at the microstructural level to elucidate the characteristics of the porous structure under the different deposition conditions. With the help of a growth model, we conclude that the chemical nature of the sputter gas not only affects the sputtering mechanism of Si atoms from the target and their subsequent transport in the gaseous/plasma phase towards the film, but also the pore formation mechanism and dynamics. When Ar is used, pores emerge as a direct result of the shadowing processes of Si atoms, in agreement with Thornton's structure zone model. The introduction of He produces, in addition to the shadowing effects, a new process where a degree of mobility results in the coarsening of small pores. Our results also highlight the influence of the composition of sputtering gas and tilt angles (for oblique angle deposition) on the formation of open and/or occluded porosity.

### Additive-free superhard $B_4C$ with ultrafine-grained dense microstructures

Moshtaghioun, BM; Cumbrera, FL; Ortiz, AL; Castillo-Rodriguez, M; Gomez-Garcia, D

*Journal of the European Ceramic Society*, **34** (2014) 841-848
March, 2014 | **DOI:** 10.1016/j.jeurceramsoc.2013.10.006

A unique combination of high-energy ball-milling, annealing, and spark-plasma sintering has been used to process superhard $B_4C$ ceramics with ultrafine-grained, dense microstructures from commercially available powders, without sintering additives. It was found that the ultrafine powder prepared by high-energy ball-milling is hardly at all sinterable, but that $B_2O_3$ removal by gentle annealing in Ar provides the desired sinterability. A parametric study was also conducted to elucidate the role of the temperature (1600–1800 °C), time (1–9 min), and heating ramp (100 or 200 °C/min) in the densification and grain growth, and thus to identify optimal spark-plasma sintering conditions (i.e., 1700 °C for 3 min with 100 °C/min) to densify completely (>98.5%) the B4C ceramics with retention of ultrafine grains (∼370 nm). Super-high hardness of ∼38 GPa without relevant loss of toughness (∼3 MPa m1/2) was thus achieved, attributable to the smaller grain size and to the transgranular fracture mode of the B4C ceramics.

### Effect of high SWNT content on the room temperature mechanical properties of fully dense 3YTZP/SWNT composites

Poyato, R; Gallardo-Lopez, A; Gutierrez-Mora, F; Morales-Rodriguez, A; Munoz, A; Dominguez-Rodriguez, A

*Journal of the European Ceramic Society*, **34** (2014) 1571-1579

June, 2014 | **DOI:** 10.1016/j.jeurceramsoc.2013.12.024

This paper is devoted to correlate the microstructure and room temperature mechanical properties of single-wall carbon nanotube (SWNT) reinforced 3 mol% yttria stabilized tetragonal zirconia with high SWNT content (2.5, 5 and 10 vol%). Fully dense composites were prepared by using a combination of aqueous colloidal powder processing and Spark Plasma Sintering. SWNTs were located at the ceramic grain boundaries and they were not damaged during the sintering process. The weak interfacial bonding between SWNTs and ceramic grains together with the detachment of SWNTs within thick bundles have been pointed out as responsible for the decrease of hardness and fracture toughness of the composites in comparison with the monolithic 3YTZP ceramic.

### Effect of $La_2O_3$ addition on long-term oxidation kinetics of $ZrB_2$-SiC and $HfB_2$-SiC ultra-high temperature ceramics

Zapata-Solvas, E; Jayaseelan, DD; Brown, PM; Lee, WE

*Journal of European Ceramic Society*, **34** (2014) 3535-3548

December, 2014 | **DOI:** 10.1016/j.jeurceramsoc.2014.06.004

Long-term oxidation kinetics of SiC-reinforced UHTCs and $La_2O_3$-doped UHTCs over an intermediate temperature range (1400-1600 degrees C) reveal partially protective behavior for the former characterized by an oxidation kinetic exponent $1 < n < 2$. In addition, unstable oxidation behavior was observed in HfB2-based UHTCs due to the presence of SiC agglomerates. On the other hand, $La_2O_3$-doped UHTCs were found to be protective over the whole temperature range studied ($n = 2$), in particular at 1600 degrees C, where oxidation kinetic exponents as high as 8 were observed as a consequence of formation of new oxidation protective particles, MeOxCy, where Me is Zr, Hf or Si. Adsorption of oxygen-containing species formed protective MeOxCy), phases, which enhanced the thermal stability of the oxide scale as well as providing protection against oxidation for long exposure times at 1600 degrees C.

### High temperature internal friction measurements of 3YTZP zirconia polycrystals. High temperature background and creep

Simas, P; Castillo-Rodriguez, M; No, ML; De-Bernardi, S; Gomez-Garcia, D; Dominguez-Rodriguez, A; Juan, JS

*Journal of the European Ceramic Society*, **34** (2014) 3859-3863

December, 2014 | **DOI:** 10.1016/j.jeurceramsoc.2014.05.016

This work focuses on the high-temperature mechanic properties of a 3 mol% yttria zirconia polycrystals (3YTZP), fabricated by hot-pressureless sintering. Systematic measurements of mechanical loss as a function of temperature and frequency were performed. An analytical method, based on the generalized Maxwell rheological model, has been used to analyze the high temperature internal friction background (HTB). This method has been previously applied to intermetallic compounds but never to ceramics, except in a preliminary study performed on fine grain and nanocrystalline zirconia. The HTB increases exponentially and its analysis provides an apparent activation enthalpy which correlates well with that obtained from creep experiments. This fact shows on the one hand the plausibility of applying the generalized Maxwell model to ceramics, and on the other hand indicates the possibility of using mechanical spectroscopy as a complementary helpful technique to investigate the high temperature deformation mechanism of materials.

### Improvement of Vickers hardness measurement on SWNT/$Al_2O_3$ composites consolidated by spark plasma sintering

Rodriguez, AM; Lopez, AG; Fernandez-Serrano, A; Poyato, R; Munoz, A; Dominguez-Rodriguez, A
*Journal of the European Ceramic Society*, **34** (2014) 3801-3809
December, 2014 | **DOI:** 10.1016/j.jeurceramsoc.2014.05.048

Dense alumina composites with different carbon nanotube content were prepared by colloidal processing and consolidated by Spark Plasma Sintering (SPS). Single-wall carbon nanotubes (SWNTs) were distributed at grain boundaries and also into agglomerates homogeneously dispersed. Carrying out Vickers hardness tests on the cross-section surfaces instead of top (or bottom) surfaces has shown a noticeable increase in the reliability of the hardness measurements. This improvement has been mainly attributed to the different morphology of carbon nanotube agglomerates, which however does not seem to affect the Vickers hardness value. Composites with lower SWNT content maintain the Vickers hardness of monolithic alumina, whereas it significantly decreases for the rest of compositions. The decreasing trend with increasing SWNT content has been explained by the presence of higher SWNT quantities at grain boundaries. Based on the results obtained, a method for optimizing Vickers hardness tests performance on SWNT/$Al_2O_3$ composites sintered by SPS is proposed.

### Hardness and flexural strength of single-walled carbon nanotube/alumina composites

Gallardo-Lopez, A; Poyato, R; Morales-Rodriguez, A; Fernandez-Serrano, A; Munoz, A; Dominguez-Rodriguez, A
*Journal of Materials Science*, **20** (2014) 7116-7123
October, 2014 | **DOI:** 10.1007/s10853-014-8419-5

This work adds new experimental facts on room temperature hardness and flexural strength of alumina and composites with 1, 2, 5 and 10 vol% single-walled carbon nanotubes (SWNT) with similar grain size. Monolithic $Al_2O_3$ and composites were spark plasma sintered (SPS) in identical conditions at 1300 A degrees C, achieving high density, submicrometric grain size and a reasonably homogeneous distribution of SWNT along grain boundaries for all compositions with residual agglomerates. Vickers hardness values comparable to monolithic alumina were obtained for composites with low (1 vol%) SWNT content, though they decreased for higher concentrations, attributed to the fact that SWNT constitute a softer phase. Three-point bending flexural strength also decreased with increasing SWNT content. Correlation between experimental results and microstructural analysis by electron microscopy indicates that although SWNT agglomerates have often been blamed for detrimental effects on the mechanical properties of these composites, they are not the main cause for the reported decay in flexural strength.

## Phase assembly and electrical conductivity of spark plasma sintered $CeO_2$-$ZrO_2$ ceramics

Poyato, R; Cruz, SA; Cumbrera, FL; Moreno, B; Chinarro, E; Odriozola, JA
*Journal of Materials Science*, **49** (2014) 6353-6362
June, 2014 | **DOI:** 10.1007/s10853-014-8361-6

$Ce_xZr_{1-x}O_2$ (x = 0.10, 0.16 and 0.33) nanocrystalline powders were obtained by a two-step synthesis technique and sintered by spark plasma sintering (SPS). As consequence of the reduction of $Ce^{4+}$ to $Ce^{3+}$ species by carbon in the graphite environment in SPS, phase assemblies including tetragonal, monoclinic and pyrochlore phases were generated in the ceramics during the sintering process. The electrical conductivity was highly dependent on phase assembly and atmosphere ($N_2$, $H_2$ and $O_2$). A significant decrease in the activation energy was noticed in the ceramics with high pyrochlore content when measuring the conductivity in H2 atmosphere, consequence of the strong reduction promoted in these ceramics during the measurement. Equal conduction behavior with similar activation energy was observed in all the ceramics when measuring in $O_2$ atmosphere.

## Mechanical and phase stability of TiBC coatings up to 1000 degrees C

Abad, MD; Veldhuis, SC; Endrino, JL; Beake, BD; Garcia-Luis, A; Brizuela, M; Sanchez-Lopez, JC
*Journal of Vacuum Science & Technology A*, **32** (2014) 021508
March, 2014 | **DOI:** 10.1116/1.4861365

TiBC coatings with different phase compositions (nanocrystalline $TiB_xC_y$ or $TiB_2$ phases mixed or not with amorphous carbon, a-C) were prepared by magnetron sputtering. These coatings were comparatively studied in terms of phase stability after thermal annealing at 250, 500, 750, and 1000 °C in argon using Raman and x-ray absorption near-edge spectroscopy techniques. The main differences were observed at temperatures above 500 °C when oxidation processes occur and the mechanical properties deteriorate. At 1000 °C, the samples were fully oxidized forming a-C, $TiO_2$, and $B_2O_3$ as final products. Higher hardness and reduced indentation modulus values and better tribological properties were observed at 750 °C for nanocomposite structures including amorphous carbon and ternary TiBxCy phases. This behavior is attributed to a protective effect associated with the a-C phase which is achieved by the encapsulation of the nanocrystals in the coating and the better hard/lubricant phase ratio associated with this type of coating.

## Thermal properties of $La_2O_3$-doped ZrB2- and HfB2-based ultra-high temperature ceramics

Zapata-Solvas, E; Jayaseelan, DD; Brown, PM; Lee, WE
*Journal of the European Ceramic Society*, **33** (2013) 3467-3472
December, 2013 | **DOI:** 10.1016/j.jeurceramsoc.2013.06.009

Thermal properties of $La_2O_3$-doped $ZrB_2$- and $HfB_2$-based ultra high temperature ceramics (UHTCs) have been measured at temperatures from room temperature to 2000 °C and compared with SiC-doped $ZrB_2$- and $HfB_2$-based UHTCs and monolithic $ZrB_2$ and $HfB_2$. Thermal conductivities of $La_2O_3$-doped UHTCs remain constant around 55–60 W/mK from 1500 °C to 1900 °C while SiC-doped UHTCs showed a trend to decreasing values over this range.

## Tribological comparison of different C-based coatings in lubricated and unlubricated conditions

Ciarsolo, I; Fernandez, X; de Gopegui, UR; Zubizarreta, C; Abad, MD; Mariscal, A; Caretti, I; Jimenez, I; Sanchez-Lopez, JC

*Surface and Coatings Technology*, **257** (2014) 278-285
October, 2013 | **DOI:** 10.1016/j.surfcoat.2014.07.068

The use of carbon-based coatings (hydrogenated and non-hydrogenated DLC, doped and alloyed-DLC) is of wide interest due to its applications in mechanical components submitted to friction and wear including sliding parts in automotive engines. A tribological comparative analysis using a reciprocating (SRV) tester in lubricated and unlubricated conditions with a 4-stroke motor oil has been carried out on six currently relevant state-of-the-art coatings (namely WC/a-C, TiBC/a-C and TiC/a-C:H nanocomposites, Ti-doped DLC, BCN film and a crystalline monolithic TiC film as reference). The quantification of the fraction of the sp(2)-bonded matrix has been done by fitting of C 1s XPS peak and the mechanical properties evaluated by nanoindentation. The comparative analysis has allowed us to identify the capabilities of each system depending on the testing conditions and the possible synergies as a function of the chemical composition and film nature. Under lubricated harsh conditions (max. contact pressure 1.7 GPa) only coatings displaying hardness superior to 20 GPa could stand the sliding motion without failure. At lower contact pressures, a significant fraction of sp(2) carbon (>= 75%) is advantageous for reducing wear in boundary lubrication. WC/a-C, BCN and Ti-DLC films showed the best tribological response in dry sliding conditions. This fundamental information would be of relevance for assisting engineers in selecting best partnership for lubrication systems.

## Transmission electron microscopy of unstained hybrid Au nanoparticles capped with PPAA (plasma-poly-allylamine): Structure and electron irradiation effects

Gontard, LC; Fernandez, A; Dunin-Borkowski, RE; Kasama, T; Lozano-Perez, S; Lucas, S

*Micron*, **67** (2014) 1-9
December, 2014 | **DOI:** 10.1016/j.micron.2014.06.004

Hybrid (organic shell–inorganic core) nanoparticles have important applications in nanomedicine. Although the inorganic components of hybrid nanoparticles can be characterized readily using conventional transmission electron microscopy (TEM) techniques, the structural and chemical arrangement of the organic molecular components remains largely unknown. Here, we apply TEM to the physico-chemical characterization of Au nanoparticles that are coated with plasma-polymerized-allylamine, an organic compound with the formula C3H5NH2. We discuss the use of energy-filtered TEM in the low-energy-loss range as a contrast enhancement mechanism for imaging the organic shells of such particles. We also study electron-beam-induced crystallization and amorphization of the shells and the formation of graphitic-like layers that contain both C and N. The resistance of the samples to irradiation by high-energy electrons, which is relevant for optical tuning and for understanding the degree to which such hybrid nanostructures are stable in the presence of biomedical radiation, is also discussed.

### A Nanoscale Characterization with Electron Microscopy of Multilayered CrAlYN Coatings: A Singular Functional Nanostructure

Rojas, TC; Dominguez-Meister, S; Brizuela, M; Garcia-Luis, A; Fernandez, A; Sanchez-Lopez, JC
*Microscoy and Microanalysis*, **20** (2014) 14-24
February, 2014 | **DOI:** 10.1017/S1431927613013962

A combination of transmission electron microscopy techniques and spatially resolved microanalysis is used to investigate the nanostructure, constituting phases, and chemical elemental distribution in CrAlYN multilayered coatings. The location of the metallic elements and their chemical state are needed to understand their functional properties. Samples were prepared with variable Al (4-12 at%) and Y (2-5 at%) contents by direct current reactive magnetron sputtering on silicon substrates using metallic targets and Ar/N-2 mixtures under different deposition parameters (power applied to the target and rotation speed of the sample holder). The changes produced in the nanostructure and chemical distribution were investigated. Nanoscale resolution electron microscopy analysis has shown that these coatings present a singular nanostructure formed by multilayers containing at a certain periodicity nanovoids filled with molecular nitrogen. Spatially resolved energy dispersive spectroscopy and electron energy loss elemental mappings and profiles showed that the chromium, aluminum, and yttrium atoms are distributed in a sequential way following the position of the targets inside the deposition chamber. Analysis of the different atomic distribution and phases formed at the nanoscale is discussed depending on the deposition parameters.

### Tomographic Heating Holder for In Situ TEM: Study of Pt/C and PtPd/$Al_2O_3$ Catalysts as a Function of Temperature

Gontard, LC; Dunin-Borkowski, RE; Fernandez, A; Ozkaya, D; Kasama, T
*Microscoy and Microanalysis*, **20** (2014) 982-990
June, 2014 | **DOI:** 10.1017/S1431927614000373

A tomographic heating holder for transmission electron microscopy that can be used to study supported catalysts at temperatures of up to similar to 1,500 degrees C is described. The specimen is placed in direct thermal contact with a tungsten filament that is oriented perpendicular to the axis of the holder without using a support film, allowing tomographic image acquisition at high specimen tilt angles with minimum optical shadowing. We use the holder to illustrate the evolution of the active phases of Pt nanoparticles on carbon black and PtPd nanoparticles on gamma-alumina with temperature. Particle size distributions and changes in active surface area are quantified from tilt series of images acquired after subjecting the specimens to increasing temperatures. The porosity of the alumina support and the sintering mechanisms of the catalysts are shown to depend on distance from the heating filament.

### Tribological behaviour at high temperature of hard CrAlN coatings doped with Y or Zr

Sanchez-Lopez, JC; Contreras, A; Dominguez-Meister, S; Garcia-Luis, A; Brizuela, M

*Thin Solid Films*, **550** (2014) 413-420

January, 2014 | **DOI:** 10.1016/j.tsf.2013.10.041

The tribological properties of CrAlN, CrAlYN and CrAlZrN coatings deposited by direct current reactive magnetron sputtering are studied by means of pin-on-disc experiments at room temperature, 300, 500 and 650 °C using alumina balls as counterparts. The influence of the metallic composition (Al, Y and Zr) on the friction, wear properties and oxidation resistance is studied by means of scanning electron microscopy, energy dispersive X-ray analysis and Raman analysis of the contact region after the friction tests. The results obtained allow us to classify the tribological behaviour of the CrAl(Y,Zr)N coatings into three groups according to the nature of the dopant and aluminium content. The sliding wear mechanism is characterized by the formation of an overcoat rich in chromium and aluminium oxides whose particular composition is determined by the initial chemical characteristics of the coating and the testing temperature. The fraction of $Cr_2O_3$ becomes more significant as the Al content decreases and the temperature increases. The addition of Y, and particularly Zr, favours the preferential formation of $Cr_2O_3$ versus $CrO_2$ leading to a reduction of friction and wear of the counterpart. Conversely, the tribological behaviour of pure CrAlN coatings is characterized by higher friction but lower film wear rates as a result of higher hardness and major presence of aluminium oxides on the coating surface.

### Calcium silicates synthesised from industrial residues with the ability for $CO_2$ sequestration

Morales-Florez, V; Santos, A; Lopez, A; Morina, I; Esquivias, L

*Waste Management & Research*, **32** (2014) 1178-1185

December, 2014 | **DOI:** 10.1177/0734242X14542148

This work explored several synthesis routes to obtain calcium silicates from different calcium-rich and silica-rich industrial residues. Larnite, wollastonite and calcium silicate chloride were successfully synthesised with moderate heat treatments below standard temperatures. These procedures help to not only conserve natural resources, but also to reduce the energy requirements and $CO_2$ emissions. In addition, these silicates have been successfully tested as carbon dioxide sequesters, to enhance the viability of $CO_2$ mineral sequestration technologies using calcium-rich industrial by-products as sequestration agents. Two different carbon sequestration experiments were performed under ambient conditions. Static experiments revealed carbonation efficiencies close to 100% and real-time resolved experiments characterised the dynamic behaviour and ability of these samples to reduce the $CO_2$ concentration within a mixture of gases. The $CO_2$ concentration was reduced up to 70%, with a carbon fixation dynamic ratio of 3.2mg$CO_2$ per g of sequestration agent and minute. Our results confirm the suitability of the proposed synthesis routes to synthesise different calcium silicates recycling industrial residues, being therefore energetically more efficient and environmentally friendly procedures for the cement industry.

### Comparative Study of Micro- and Nano-structured Coatings for High-Temperature Oxidation in Steam Atmospheres

Perez, FJ; Castaneda, SI; Hierro, MP; Galindo, RE; Sanchez-Lopez, JC; Mato, S
*Oxidation of Metals*, **81** (2014) 227-236
February, 2014 | **DOI:** 10.1007/s11085-013-9447-2

For many high-temperature applications, coatings are applied in order to protect structural materials against a wide range of different environments: oxidation, metal dusting, sulphidation, molten salts, steam, etc. The resistance achieved by the use of different kind of coatings, such as functionally graded material coatings, has been optimized with the latest designs. In the case of supercritical steam turbines, many attempts have been made in terms of micro-structural coatings design, mainly based on aluminides, and other diffusion coating systems in order to consider alternatives, nano-structured coatings based on Cr and Al compositions and deposited by a physical vapor deposition technique, were assessed to high-temperature oxidation resistance in steam environments. The oxidation kinetics where analyzed for up to 2,000 h at 650 °C by means of gravimetric measurements. The evaporation behavior was also analyzed by thermogravimetric-mass spectrometry. Excellent results where observed for some of the nano-structured coatings tested. Those results where compared to results obtained for micro-structured coatings. Based on that comparison, it was deduced that the nano-structured coatings have a potential application as protective systems in high-temperature steam environments.

### Simultaneous quantification of light elements in thin films deposited on Si substrates using proton EBS (Elastic Backscattering Spectroscopy)

Ferrer, FJ; Alcaire, M; Caballero-Hernandez, J; Garcia-Garcia, FJ; Gil-Rostra, J; Terriza, A; Godinho, V; Garcia-Lopez, J; Barranco, A; Fernandez-Camacho, A
Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with *Materials and Atoms*, **332** (2014) 449-453
August, 2014 | **DOI:** 10.1016/j.nimb.2014.02.124

Quantification of light elements content in thin films is an important and difficult issue in many technological fields such as polymeric functional thin films, organic thin film devices, biomaterials, and doped semiconducting structures.

Light elements are difficult to detect with techniques based on X-ray emission, such as energy dispersive analysis of X-rays (EDAX). Other techniques, like X-ray photoelectron spectroscopy (XPS), can easily quantify the content of light elements within a surface but often these surface measurements are not representative of the lights elements global composition of the thin film. Standard Rutherford backscattering spectroscopy (RBS), using alpha particles as probe projectiles, is not a good option to measure light elements deposited on heavier substrates composed of heavier elements like Si or glass. Nuclear Reaction Analysis (NRA) offers a good quantification method, but most of the nuclear reactions used are selective for the quantification of only one element, so several reactions and analysis are necessary to measure different elements.

In this study, Elastic Backscattering Spectroscopy (EBS) using proton beams of 2.0 MeV simultaneously quantified different light elements (helium, carbon, nitrogen, oxygen, and fluorine) contained in thin films supported on silicon substrates. The capabilities of the proposed quantification method are illustrated with examples of the analysis for a series of thin film samples: amorphous silicon with helium bubbles, fluorinated silica, fluorinated diamond-like carbon and organic thin films. It is shown that this simple and versatile procedure allows the simultaneous quantification of light elements in thin films with thicknesses in the 200–500 nm range and contents lower than 10 at.%.

### Detecting single-electron events in TEM using low-cost electronics and a silicon strip sensor

Gontard, LC; Moldovan, G; Carmona-Galn, R; Lin, C; Kirkland, AI
*Microscopy*, **63(2)** (2014) 119-130
April, 2014 | **DOI:** 10.1093/jmicro/dft051

There is great interest in developing novel position-sensitive direct detectors for transmission electron microscopy (TEM) that do not rely in the conversion of electrons into photons. Direct imaging improves contrast and efficiency and allows the operation of the microscope at lower energies and at lower doses without loss in resolution, which is especially important for studying soft materials and biological samples. We investigate the feasibility of employing a silicon strip detector as an imaging detector for TEM. This device, routinely used in high-energy particle physics, can detect small variations in electric current associated with the impact of a single charged particle. The main advantages of using this type of sensor for direct imaging in TEM are its intrinsic radiation hardness and large detection area. Here, we detail design, simulation, fabrication and tests in a TEM of the front-end electronics developed using low-cost discrete components and discuss the limitations and applications of this technology for TEM.

### Technological Proposals for Recycling Industrial Wastes for Environmental Applications

Romero-Hermida, I; Morales-Florez, V; Santos, A; Villena, A; Esquivias, L
*Minerals*, **4** (2014) 746-757
September, 2014 | **DOI:** 10.3390/min4030746

A two-fold objective is proposed for this research: removing hazardous and unpleasant wastes and mitigating the emissions of green house gasses in the atmosphere. Thus, the first aim of this work is to identify, characterize and recycle industrial wastes with high contents of calcium or sodium. This involves synthesizing materials with the ability for $CO_2$ sequestration as preliminary work for designing industrial processes, which involve a reduction of $CO_2$ emissions. In this regard, phosphogypsum from the fertilizer industry and liquid wastes from the green olive and bauxite industries have been considered as precursors. Following a very simple procedure, Ca-bearing phosphogypsum wastes are mixed with Na-bearing liquid wastes in order to obtain a harmless liquid phase and an active solid phase, which may act as a carbon sequestration agent. In this way, wastes, which are unable to fix $CO_2$ by themselves, can be successfully turned into effective $CO_2$ sinks. The $CO_2$ sequestration efficiency and the $CO_2$ fixation power of the procedure based on these wastes are assessed.

## CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

### COMUNICACIONES / COMMUNICATIONS

**EHEC 2014 European Hydrogen Energy Conference**
12 – 14 marzo [Sevilla, España]

**Hydrogen storage by sodium borohydride: Development of versatile and fast responding reactors for the release of Hydrogen in mobile applications**
D. Hufschmidt; G. Arzac; G. Adame; M. A. Jiménez; A. Fernández
Comunicación oral

**Understanding the role of additives/catalysts in H2 storage processes based on borohydride materials**
A. Fernández; E. Deprez; G. Arzac; D. Hufschmidt
Comunicación oral

**Hydrogen production through sodium borohydride ethanolysis**
G.M. Arzac; A. Fernández
Póster

**SETAC Europe 25th Annual Meeting**
11 – 15 mayo [Basilea, Suiza]

**A comprehensive review of tribological behavior of TiBC coatings**
J.C. Sánchez-López, M.D. Abad
Conferencia invitada

**Environmental dependence on the tribology of tailored WSex coatings prepared by magnetron sputtering**
S. Dominguez-Meister, M. Conte, T.C. Rojas, A. Igartúa, J.C. Sánchez-López
Comunicación oral

**Nanoscale TEM characterization of the oxidation process of CrAlN coating grown on steel**
T. C. Rojas, S. Domínguez-Meister, M. Brizuela, J. C. Sánchez-López
Comunicación oral

**Hydrogen storage by sodium borohydride: Development of versatile and fast responding reactors for the release of Hydrogen in mobile applications**
D. Hufschmidt; G. Arzac; G. Adame; M.A. Jiménez; A. Fernández
Comunicación oral

**Citrate gold nanoparticle exposure in the marine clam Ruditapes philippinarum: Uptake, elimination and effect**
M. Volland; M. Hampel; C. Trombini; C. García-Negrete; A. Fernández; T. Gomes; M. Bebianno; J. Blasco
Póster

## International Discussion on Hydrogen Energy and Applications (IDHEA)

11 – 15 mayo [Basilea, Suiza]

**Co and Co-B films deposited by magnetron sputtering on PTFE membranes for the catalytic hydrolysis of sodium borohydride**
A. Fernández; D. Hufschmidt; V. Godinho; G.M. Arzac; M. Paladini; M.C. Jimenez De Haro; O. Montes
Comunicación oral

## 3rd European Conference on NanoFilms & Al-NanoFunc Final Conference: Microstructural and Chemical Characterization in the Nano-Scale

7 – 11 julio [Sevilla, España]

**STEM in SEM imaging of gold nanoparticles in tissular ecotoxicity experiments**
C.A. García-Negrete; M.C. Jiménez de Haro; J. Blasco; M. Soto; A. Fernández
Comunicación oral

**Co and Co-B films deposited by magnetron sputtering on PTFE membranes for the catalytic hydrolysis of sodium borohydride**
D. Hufschmidt; V. Godinho; M. Paladini; G.M. Arzac; M.C. Jimenez; O. Montes; A. Fernández
Comunicación oral

**Formation of oxidatively stable M@Fe3O4 and MPt@Fe3O4 (M = Fe, Co) core@shell nanoparticles using a simple and versatile synthetic procedure**
Benjamin R. Knappett; Lionel C. Gontard; Emilie Ringe; Edward W. Tait; Asunción Fernandéz; Andrew EH Wheatley
Comunicación oral

**Hybrid bioactive coatings on 316L stainless by sol-gel technique**
Claudia García; Ma Asunción Fernández; Carlos Pauca R.
Comunicación oral

**Influence of deposition parameters on the microstructure of magnetron sputtered amorphous silicon coatings with closed porosity**
J. Caballero-Hernández; R. Schierholz; B. Lacroix; V. Godinho; A. Fernández
Comunicación oral

**Modeling of energetic ion bombardment of Si growing films by kinetic Monte Carlo method**
P. Moskovkina; S. Lucas; V. Godinho; R. Álvarez; A. Palmero; A. Fernandez
Comunicación oral

**Nanocomposite MoCN/Ag and TiAlSiCN/MoSeC coatings for tribological applications in wide temperature ranges**
Shtansky D.V.; Bondarev A.V.; Kiryukhantsev-Korneev Ph.V.; Rojas T.C.; Godinho V.; Fernandez A
Comunicación oral

**On the formation of the porous structure in nanostructured a-Si coatings deposited by DC magnetron sputtering at oblique angles**
V. Godinho; P. Moskovkin; R. Álvarez; J. Caballero-Hernández; R. Schierholz; B. Bera; J.Demarche; A. Palmero; A. Fernández; S. Lucas
Comunicación oral

**Spectrum imaging of Helium pores in amorphous Silicon-coatings**
Roland Schierholz; Bertrand Lacroix; Jaime Caballero; Vanda Godinho; Martial Duchamp; Asuncion Fernandez
Comunicación oral

**Microstructural and Catalytic characterization of a Pt containing washcoat on SiC foams for hydrogen combustion applications**
A. Fernández; U.F. Vogt; F. Hosoglu; M.C. Jiménez de Haro; O.M. Montes; A. Borgschulte; A. Züttel
Póster

**(S)TEM of organic-inorganic nanoparticles: limitations and prospects**
Lionel C Gontard; Stéphane Lucas; Rafal E Dunin-Borkowski; Asunción Fernández
Póster

**Probing the pore structure of cobalt coatings grown by magnetron sputtering using TEM and spatially resolved EELS**
B. Lacroix; V. Godinho; A. Fernández
Póster

**Nanoscale chemical characterization of multicomponent nanocrystals: Shape-defined Pt-seeds and AuPt heterodimers**
C. A. García-Negrete; B. R. Knappett; F. Schmidt; T. C. Rojas; A. E. H. Wheatley; F. Hofer; A. Fernández
Póster

**Supported Co catalyst prepared as thin films by magnetron sputtering for sodim borohydride and ammonia borane hydrolysis**
M. Paladini; G. M. Arzac; V. Godinho; M. C. Jiménez De Haro; A. Fernández
Póster

## IMC-2014 | 18th International Microscopy Congress
7 – 12 septiembre [Praga, República Checa]

**Spatially resolved EELS to probe the pore structure of porous coatings grown by magnetron sputtering**
Lacroix B; Godinho V.; Fernández A.
Póster

**STEM in SEM imaging of gold nanoparticles in tissular ecotoxicity experiments**
García-Negrete C. A.; Jiménez de Haro M. C; Blasco J.; Soto M.; Fernández A.
Póster

**Amorphous Silicon-coatings with high amount of closed porosity**
Schierholz R; Lacroix B.; Caballero-Hernández j.; Godinho V.; Duchamp M.; Fernández A.
Póster

## 14th International Conference on Plasma Surface Engineering, PSE2014
15 – 19 septiembre [Garmisch-Partenkirchen, Alemania]

**Environmental dependence on the tribology of tailored WSex coatings prepared by magnetron sputtering**
J.C. Sánchez-López, S. Dominguez-Meister, M. Conte, T.C. Rojas, A. Igartua
Comunicación oral

**Influence of the target distribution on the nanostructure and oxidation protection of sputtered CrAlYN coatings**
J.C. Sánchez-López, T.C. Rojas, S. Dominguez-Meister, M. Brizuela
Póster

## XtremeCOAT2014 Workshop: Surface engineering for functional applications under extreme conditions
20 – 21 octubre [Madrid, España]

**Influence of the microstructure in the high temperature corrosion resistance of CrAl(Y)N coatings deposited by PVD**
S. Mato, J.C. Sánchez-López, G. Alcalá, M. Brizuela, R. Escobar Galindo, F.J. Pérez
Comunicación oral

**On the nanostructure and oxidation protection of CrAlN and CrAlYN coatings**
T. C. Rojas, S. Domínguez-Meister, M. Brizuela, J. C. Sánchez-López
Comunicación oral

**High temperature oxidation in steam atmosphere of nanostructured transition metal nitrides coatings on steel**
A. Illana, M. A. Sánchez-Mancilla, M. Brizuela, J.C. Sánchez-López, F.J. Pérez, S. Mato
Póster

**Ag-containing diamond-like carbon coatings: on their microstructure and tribo-mechanical properties**
S. Domínguez-Meister, T. C. Rojas, J. C. Sánchez-López
Póster

**Tribocorrosion behavior of TiBxCy/a-C nanocomposite coating in strong oxidant disinfectant solutions**
E. Gracia-Escosa, I. García, J.C. Sánchez-López, M. D. Abad, A. Mariscal, M. A. Arenas, J. de Damborenea, A. Conde
Póster

### 9èmes Journées Maghreb-Europe Materiaux et applications aux dispositifs et capteurs, MADICA2014
5 – 7 noviembre [Mahdia, Tunez]

**Synthesis of CNx films by fs-PLD for electrochemical detection of pollutants**
C. Maddi, N. Zehani, T. Tite, A. S. Loir, V. Barnier, K. Wolski, C. Chaix, P. Fortang, J. C. Sanchez-Lopez, T.C. Rojas, N. Jaffrezic- Renault, C. Donnet, F. Garrelie
Póster

# CONGRESOS Y REUNIONES NACIONALES / NATIONAL CONGRESSES AND MEETINGS

## COMUNICACIONES / COMMUNICATIONS

### XIII Congreso Nacional de Materiales
18 – 20 junio [Barcelona, España]

**Effect of processing and microstructure on the electrical properties of 3YTZP/1.5 vol%SWNT ceramic nanocomposites**
R. Poyato; J. Macías-Delgado; A. Gallardo-López; A. Muñoz; A. Domínguez-Rodríguez
Póster

**Enhancement of carbon nanotube dispersión in 3YTZP/SWNT composites**
A. Gallardo-López; R. Poyato; A. Morales-Rodríguez; A. Muñoz; A. Domínguez-Rodríguez
Póster

### XIV Congreso Nacional de Propiedades Mecánicas de Sólidos

17 – 19 septiembre [Jaén, España]

**Procesado de Nanocompuestos de 3YTZP/SWCNT. Optimización de la dispersión de los CNTs y su relación con la resistencia a la fluencia**
M. Castillo-Rodríguez; A. Muñoz; A. Morales-Rodríguez; R. Poyato; A. Gallardo-López; A. Domínguez-Rodríguez
Comunicación oral

**Comportamiento tribológico de cerámicos estructurales avanzados con distinto contenido de nanotubos de carbono (SWCNTs)**
F. Gutiérrez-Mora; R. Poyato; A. Gallardo-López; A. Muñoz; A. Domínguez-Rodríguez
Comunicación oral

**Estudio de composites de 3YTZP/SWNT como material multifuncional: Procesado y caracterización microestructural, mecánica y eléctrica**
R. Poyato; J. Macías-Delgado; A. García-Valenzuela; Á. Gallardo-López; A. Morales-Rodríguez; A. Muñoz; A. Domínguez-Rodríguez
Comunicación oral

**Compuestos alúmina: nanotubos de carbono monocapa: Efecto de la aglomeración de nanotubos en la resistencia a la flexión**
A. Gallardo-López; A. Morales-Rodríguez; R. Poyato; A. Fernández-Serrano; A. Muñoz; A. Domínguez-Rodríguez
Póster

## FORMACION / TRAINING

## FORMACIÓN DE GRADUADOS / MASTER DEGREE THESIS

| | |
|---|---|
| **Título:** | **Procesado y microestructura: su efecto sobre las propiedades eléctricas de compuestos de 3YTZP con nanotubos de carbono monocapa** |
| **Autor:** | Julio Macías Delgado |
| **Directoras:** | Dra. Rosalía Poyato Galán y Dra. Ángela Gallardo López |
| **Grado:** | Trabajo Fin de Master (Máster en Ciencia y Tecnología de Nuevos Materiales) |
| **Año Académico:** | 2013-2014 (Junio 2014) |

## ESTANCIAS Y VISITAS DE INVESTIGADORES EN EL ICMS
## PERSONNEL OF THE OTHER LABORATORIES IN THE ICMS

| | | |
|---|---|---|
| **Université de Mons (UMONS)** | | |
| Mons, Bélgica | **Rémy Francq** | 3 semanas |

## PREMIOS Y RECONOCIMIENTOS / PRIZES AND ACKNOWLEDGEMENTS

**Premio Real Maestranza de Caballería de Sevilla 2014,** Al Doctor D. **Eugenio Zapata Solvas**, investigador contratado por el Instituto de Ciencia de Materiales de Sevilla, dentro del grupo de investigación Diseño de Nanomateriales y Microestructuras. Formado en la Universidad de Sevilla y, después de diversas estancias en prestigiosos centros científicos extranjeros, el doctor Zapata ha dedicado su atención a las propiedades mecánicas y térmicas de compuestos cerámicos nanoestructurados y a "composites" con matriz cerámica. El resultado de su investigación ha sido difundido preferentemente mediante veintiún artículos científicos publicados en diversas e importantes revistas internacionales de la especialidad.

El jurado ha destacado, entre otras, sus importantes contribuciones al desarrollo de sensores fotónicos (por ejemplo de oxígeno o de dióxido de nitrógeno), al de fuentes portátiles de rayos X basadas en nanotubos de carbono, así como sus trabajos relacionados con la fabricación de nanotubos de carbono con precisión atómica.

## EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

Spin coater
UV/Ozonone cleaner
Horno a vacío de baja temperatura
Cromatógrafo
Pila de combustible (100W)
Medidor y sonda de temperatura por fluorescencia
Cabeza magnetrón de 2”
Bomba FLODOS
Electrónica y controladores de flujo másico para gases

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.

Cámaras de deposición
Tres cámaras de deposición de recubrimientos y películas delgadas por la técnica de pulverización catódica (magnetrón sputtering). Con una dotación de 7 cabezas magnetrón, 2 fuentes DC, 2 fuentes RF y 1 fuente pulsada, portamuestras girables y calentables.

Laboratorio de síntesis de NPs y catalizadores por vía química
Reactores y material de vidrio convencional
Rotavapor, sistemas de filtrado
Cámara seca MBRAUN
Reactores de producción de hidrógeno

# 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. 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

## Proyectos de Investigación / Research Projects

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

### Propiedades termomagnéticas de materiales y optimización de su eficiencia energética Thermomagnetic properties of materials and optimization of energy efficiency

| | |
|---|---|
| Código/Code: | MAT2010-20537 |
| Periodo/Period: | 01-01-2011 / 30-06-2014 |
| Organismo Financiador/Financial source: | Ministerio de Economía y Competitividad |
| Importe total/Total amount: | 121.000 € |
| Investigador responsable/Research head: | Alejandro Conde Amiano |
| Componentes/Research group: | Clara F. Conde Amiano, Josefa María Borrego Moro, Victorino Franco García, Javier S. Blázquez Gámez, Rafael Caballero Flores, Jhon J. Ipus Bados |

RESUMEN / ABSTRACT

Se propone un estudio de propiedades termomagnéticas de materiales magnéticos blandos, preparados por técnicas de solidificación rápida y aleado mecánico. Se trata de profundizar en la relación composición-microestructura-propiedades como vía para la optimización de materiales en dos direcciones: magnéticos blandos para aplicaciones a alta temperatura y materiales para refrigeración magnética en el entorno de la temperatura ambiente. En el primer caso se trata de aumentar el límite térmico de comportamiento blando del material y de disminuir el coeficiente de temperatura de sus propiedades. En el segundo caso se trata de acercar la temperatura de transición magnética del material a la temperatura ambiente y de maximizar su respuesta magnetocalórica. Se abordará también la modelización de diferentes procesos implicados en la formación de aleaciones (aleado mecánico, cinética de nanocristalización), de las interacciones entre partículas y sus efectos en el comportamiento termomagnético del material, de la dependencia de la respuesta magnetocalórica con el campo magnético aplicado, etc.

A study of the thermomagnetic properties of soft magnetic materials obtained by rapid quenching and mechanical alloying techniques is proposed. The aim of the project is to improve the knowledge of the composition-microstructure-properties relationship as a way to optimize the material properties in two lines: soft magnetic materials for high temperature applications and materials for magnetic refrigeration near room temperature. In the first case, the aim is to enhance the thermal limit for the soft magnetic behavior of the materials and to decrease the temperature coefficient of their properties. In the second case, the aim is to bring the magnetic transition temperature of the material close to room temperature and to maximize the magnetocaloric response. It will be also contemplated modeling of different processes involved in the alloy formation (mechanical alloying, nanocrystallization kinetics), of the interactions between particles and their effects on the thermomagnetic behavior of the material, of the dependency of the magnetocaloric response with the applied magnetic field, etc.

Unión Europea
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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

# 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 / 31-12-2016
Organismo Financiador/Financial source: Ministerio de Economía y Competitividad
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.

### Materiales magnéticos blandos; su optimización para un uso eficiente de la energía Soft magnetic materials; their optimization for an efficient use of energy

Código/Code: P10-FQM-6462 (Proyecto de Excelencia)
Periodo/Period: 15-03-2011 / 31-12-2014
Organismo Financiador/Financial source: Junta de Andalucía
Importe total/Total amount: 153.190,75 €
Investigador responsable/Research head: Alejandro Conde Amiano
Componentes/Research group: Clara F. Conde Amiano, Josefa María Borrego Moro, Victorino Franco García, Javier S. Blázquez Gámez, Jhon J. Ipus Bados

RESUMEN / ABSTRACT

El proyecto plantea abordar problemas relativos al comportamiento termomagnético de materiales amorfos y nanocristalinos magnéticamente blandos, preparados por técnicas de solidificación rápida y de aleado mecánico. En las aleaciones nanocristalinas obtenidas por desvitrificación parcial de un amorfo precursor se trata de profundizar en los mecanismos de formación de los nanocristales, analizando los efectos composicionales en la cinética del proceso y en la microestructura resultante.

The aim is to optimize in terms of composition and microstructure the thermomagnetic behaviour of materials in two directions: a) extension of the high temperature limit for soft magnetic behaviour, and b) optimization of the magnetocaloric properties in order to their use for magnetic refrigeration at room temperature. Also, in the context of the relation microstructure-properties, we will try to modelize the involved processes in the formation of the alloys, the particle interactions and thir effects on the thermomagnetic behaviour of materials, the field dependence of the magnetocaloric effects, etc. following previous results of the group.

## CONVENIOS Y CONTRATOS / CONTRACTS AND AGREEMENTS

### Caracterización de aceros eléctricos

Periodo/Period: 01-09-2014 / 30-09-2015
Organismo Financiador/Financial source: ThyssenKrupp Steel Europe AG
Investigador responsable/Research head: Victorino Franco García

### Characterization of magnetocaloric materials

Periodo/Period: 14-05-2013 / 13-05-2014
Organismo Financiador/Financial source: ERASTEEL
Investigador responsable/Research head: Victorino Franco García

### Magnetocaloric research with vibrating sample magnetometers: Algorithms for data analysis and development of new measuring protocols

| | |
|---|---|
| Periodo/Period: | 20-01-2014 / 30-06-2015 |
| Organismo Financiador/Financial source: | Lake Shore Cryotronics Inc. (EE.UU.) |
| Investigador responsable/Research head: | Victorino Franco García |

## ARTÍCULOS PUBLICADOS EN REVISTAS SCI / PAPERS IN SCI JOURNALS

**Influence of the demagnetizing factor on the magnetocaloric effect: Critical scaling and numerical simulations**

C. Romero-Muñiz, J.J. Ipus, J.S. Blázquez, V. Franco and A. Conde

*Applied Physics Letters,* **104** (2014) 252405

**DOI:** 10.1063/1.4885110

In recent years, the magnetocaloric effect is studied not only for the search of potential magnetic refrigerant materials but also for the analysis of critical phenomena. In both cases, the demagnetizing field might have a notable influence on the results. In this work, we carry out a systematic study, based on theoretical simulations, of the influence of the demagnetizing factor on the magnetocaloric properties. On the one hand, we show that demagnetizing factor affects only slightly the magnetic entropy change ($\Delta S_M$), reducing its magnitude and shifting the peak to higher temperatures. On the other hand, it dramatically affects the exponent n of field dependence ($\Delta S_M \propto H^n$) at temperatures below the peak. We demonstrate that scaling of the magnetocaloric curves can be used to remove the influence of the demagnetizing field and, to which extent, critical exponent determination can be affected. Results of numerical simulations are compared with experimental data from a ball milled powder alloy.

**A procedure to extract the magnetocaloric parameters of the single phases from experimental data of a multiphase system**

J.J. Ipus, L.M. Moreno-Ramírez, J.S. Blázquez, V. Franco and A. Conde

*Applied Physics Letters,* **105** (2014) 172405

**DOI:** 10.1063/1.4900790

In this work, we propose a method to extract the individual parameters that describe the field dependence of magnetic entropy change of each phase in a multiphase system. This method makes use of the scaling laws of the magnetocaloric effect and can help us to determine the behavior of individual phases and to predict their critical exponents. The accuracy of the procedure is illustrated applying it to ball milled powders, in which an amorphous phase with TC around room temperature coexists with bcc-Fe type crystallites. The obtained values are in good agreement with those reported in the literature for single phase systems. The proposed method could be applied to other systems where single phase materials cannot be easily obtained in order to characterize the effect of impurities.

**Evolution of Fe environments in mechanically alloyed Fe–Nb–(B) compositions**
J.S. Blázquez, J.J. Ipus, C.F. Conde, A. Conde
*Journal of Alloys and Compounds,* **615** (2014) S555-S558
**DOI:** 10.1016/j.jallcom.2013.11.118

Nanocrystalline alloys of nominal composition $Fe_{85}Nb_5B_{10}$ were produced by mechanical alloying from a mixture of elemental powders. Two commercial boron structures were used: amorphous and crystalline. In addition, a third composition $Fe_{94.4}Nb_{5.6}$ was prepared for comparison. X-ray diffraction and Mössbauer spectroscopy were used to describe the evolution of the microstructure and Fe environments as a function of the milling time. Whereas Nb is rapidly incorporated into the nanocrystalline matrix, boron inclusions remain even after long milling times. The presence of boron is found to enhance the comminuting of crystallites.

**Amorphization and evolution of magnetic properties during mechanical alloying of $Co_{62}Nb_6Zr_2B_{30}$: Dependence on starting boron microstructure**
L.M. Moreno, J.S. Blázquez, J.J. Ipus, A. Conde
*Journal of Alloys and Compounds,* **585** (2014) 485-490
**DOI:** 10.1016/j.jallcom.2013.09.191

$Co_{62}Nb_6Zr_2B_{30}$ composition was mechanically alloyed using three different types of boron powders in the starting mixture: crystalline β-B, commercial amorphous B and optimized amorphous B via ball milling. Using optimized amorphous B, amorphization process of the alloy is more efficient but milling to optimize amorphous B introduces some iron contamination. Boron inclusions (100–150 nm in size) remain even after long milling times. However, using amorphous boron reduces the fraction of boron distributed as inclusions to ~40% of the total B. Thermal stability at the end of the milling process is affected by the initial boron microstructure. Coercivity is reduced a half using amorphous B instead of crystalline B in the starting mixture.

**Structural relaxation in Fe(Co)SiAlGaPCB amorphous alloys**
J.M. Borrego, J.S. Blázquez, S. Lozano-Pérez, J.S. Kim, C.F. Conde, A. Conde
*Journal of Alloys and Compounds,* **684** (2014) 607-610
**DOI:** 10.1016/j.jallcom.2013.09.074

The structural relaxation of multicomponent Fe(Co)SiAlGaPCB amorphous alloys was investigated calorimetrically for annealed samples over a wide temperature range below the glass transition temperature. Upon heating, the annealed samples exhibit an endothermic reaction (enthalpy relaxation) starting around the annealing temperature and continuing over a temperature range of about 50–140 K, that it is followed by a broad exothermic reaction. Changes in the heat flow curves with annealing temperature and time were analyzed. Experimental values of the overall enthalpy change, $\Delta H$, the peak temperature of the difference in heat flow between the annealed and the as-quenched samples, $T_p$, and Curie temperature, $T_C$, were fitted by exponential functions including two relaxation times. Values of the two relaxation times are the same for different annealing temperatures regardless the considered property. Saturation values of these magnitudes show a linear dependence with the inverse of the annealing temperature. Tiny domains (2–3 nm in diameter) in the matrix observed by spherical aberration corrected high-resolution transmission electron microscopy could be attributed to some medium-range order in the atomic structure of these quenched alloys.

### Crystallization kinetics and soft magnetic properties in metalloid-free (Fe, Co)$_{90}$Zr$_{10}$ amorphous and nanocrystalline alloys

J.S. Blázquez, J.J. Ipus, C.F. Conde, D. Cabrera, V. Franco, A. Conde
*Journal of Alloys and Compounds,* **615** (2014) S213-S216
**DOI:** 10.1016/j.jallcom.2014.01.095

Microstructure and magnetic properties of metalloid-free $(Fe_{100-x}Co_x)_{90}Zr_{10}$ amorphous and nanocrystalline alloys were characterized. Devitrification of these amorphous alloys occurs in two overlapped transformations leading to the formation of α-Fe(Co) and Fe(Co)Zr$_2$ phases. Constant local Avrami exponents have been found for each individual process. Although Co-free alloy shows a larger grain size, crystalline fractions are similar for both alloys after equivalent annealing. Good soft magnetic properties at room temperature have been observed for amorphous and nanocrystalline alloy with $x = 30$, which exhibits an amorphous Curie temperature of 735 K. The $x = 0$ amorphous alloy is paramagnetic at room temperature and nanocrystalline samples exhibit a transition to superparamagnetic behavior.

### Extracting the composition of nanocrystals of mechanically alloyed systems using Mossbauer spectroscopy

J.S. Blázquez, J.J. Ipus, V. Franco, C.F. Conde, A. Conde
*Journal of Alloys and Compounds,* **610** (2014) 92-99
**DOI:** 10.1016/j.jallcom.2014.04.195 *

Determining the composition at the nanoscale generally requires the use of experimental techniques such as 3D atom probe or nanoanalysis, which have limited availability, involve high economic cost and, moreover, imply aggressive sample preparations. However, the combination of Mössbauer spectrometry (MS), X-ray diffraction (XRD) and magnetization measurements can supply very detailed information on the average values of composition of tiny elements of the microstructure such as nanocrystals and boundary regions. Unlike nanoscale techniques, those techniques are widely accessible to most of the scientific community and do not require any special sample preparation, especially for powder samples. Two methods are proposed: the first method uses the ratio between the high field contributions to the MS spectra to extract the composition of the nanocrystals and allows us to follow its evolution; the second method uses average values of the hyperfine field and XRD data to study nanocrystalline samples. These procedures have been applied to two FeNb(B) powder samples obtained by mechanical alloying. The proposed procedures can be easily extended to systems containing other isotopes suitable for Mössbauer spectroscopy or to data from nuclear magnetic resonance experiments.

### Magnetocaloric effect and critical behavior in $Pr_{0.5}Sr_{0.5}MnO_3$: an analysis of the validity of the Maxwell relation and the nature of the phase transitions

R. Caballero-Flores, N.S. Bingham, M.H. Phan, M.A. Torrija, C. Leighton, V. Franco, A. Conde, T.L. Phan, S.C. Yu and H. Srikanth

*Journal of Physics: Condensed Matter,* **26** (2014) 286001

**DOI:** 10.1088/0953-8984/26/28/286001

The Maxwell relation, the Clausius–Clapeyron equation, and a non–iterative method to obtain the critical exponents have been used to characterize the magnetocaloric effect (MCE) and the nature of the phase transitions in $Pr_{0.5}Sr_{0.5}MnO_3$, which undergoes a second-order paramagnetic to ferromagnetic (PM-FM) transition at $T_C \sim 247$ K, and a first-order ferromagnetic to antiferromagnetic (FM-AFM) transition at $T_N \sim 165$ K. We find that around the second-order PM-FM transition, the MCE (as represented by the magnetic entropy change, ΔSM) can be precisely determined from magnetization measurements using the Maxwell relation. However, around the first-order FM-AFM transition, values of ΔSM calculated with the Maxwell relation deviate significantly from those calculated by the Clausius–Clapeyron equation at the magnetic field and temperature ranges where a conversion between the AFM and FM phases occurs. A detailed analysis of the critical exponents of the second-order PM-FM transition allows us to correlate the short-range type magnetic interactions with the MCE. Using the Arrott–Noakes equation of state with the appropriate values of the critical exponents, the field- and temperature-dependent magnetization $M(T, H)$ curves, and hence the $\Delta S_M(T, H)$ curves, have been simulated and compared with experimental data. A good agreement between the experimental and simulated data has been found in the vicinity of the Curie temperature $T_C$, but a noticeable discrepancy is present for $T << T_C$. This discrepancy arises mainly from the coexistence of AFM and FM phases and the presence of ferromagnetic clusters in the AFM matrix.

### Avalanche correlation in the martensitic transition of a Cu-Zn-Al shape memory alloy: analysis of acoustic emission and calorimetry

Baro, J; Martin-Olalla, JM; Romero, FJ; Gallardo, MC; Salje, EKH; Vives, E; Planes, A

*Journal of Physics: Condensed Matter,* **26** (2014) 125401

**DOI:** 10.1088/0953-8984/26/12/125401

The existence of temporal correlations during the intermittent dynamics of a thermally driven structural phase transition is studied in a Cu-Zn-Al alloy. The sequence of avalanches is observed by means of two techniques: acoustic emission and high sensitivity calorimetry. Both methods reveal the existence of event clustering in a way that is equivalent to the Omori correlations between aftershocks in earthquakes as are commonly used in seismology.

### Relationship between mechanical amorphization and boron integration during processing of FeNbB alloys

J.J. Ipus, J.S. Blázquez, C.F. Conde, J.M. Borrego, V. Franco, S. Lozano-Pérez, A. Conde

*Intermetallics,* **49** (2014) 98-105

**DOI:** 10.1016/j.intermet.2014.01.018

$Fe_{75}Nb_{10}B_{15}$ alloys were prepared by mechanical alloying using different boron powders (crystalline B, commercial amorphous B, optimized amorphous B and intermetallic FeB) in the initial mixture in order to study the boron incorporation into the Fe matrix and its influence on the amorphization of the alloys. Another composition with the same Fe/Nb ratio but without boron was prepared in order to differentiate between the influence of B and Nb in the evolution of microstructure and magnetic properties. Amorphization of samples was followed by X-ray diffraction and Mössbauer spectroscopy, concluding that only B-containing alloys develop an amorphous phase, while for the B-free alloy a supersaturated solid solution was observed as the final microstructure. Nb is rapidly incorporated into the matrix whereas remaining B inclusions are found at the end of the explored milling range for all B-containing samples. The amount of dissolved boron into the amorphous matrix was estimated from magnetic measurements, being the alloy prepared using FeB powder the one that most effectively dissolves this element.

**Milling effects on magnetic properties of melt spun Fe-Nb-B alloy**
J.J. Ipus, J.S. Blázquez, V. Franco, M. Stoica, A. Conde
*Journal of Applied Physics,* **115** (2014) 17B518
**DOI:** 10.1063/1.4866700

$Fe_{75}Nb_{10}B_{15}$ amorphous ribbons were grinded via ball milling to produce powder samples preserving the amorphous microstructure. A continuous increase of the Curie temperature with the milling time is observed as well as an enhancement of spontaneous magnetization, average hyperfine field, and magnetocaloric effect. This enhancement in the magnetic character of the samples as milling progresses is ascribed to an increase of the Fe-Fe distance. However, the peak entropy change reduces after grinding the ribbon sample. This effect could be related to a broader distribution of Curie temperatures in powdered samples.

**On the broadening of the magnetic entropy change due to Curie temperature distribution**
Pablo Alvarez-Alonso, José L. Sánchez Llamazares, César F. Sánchez-Valdés, Gabriel J. Cuello, Victorino Franco, Pedro Gorria, and Jesús A. Blanco
*Journal of Applied Physics,* **115** (2014) 17A929
**DOI:** 10.1063/1.4867346

We have studied the correlation between the broadening of the isothermal magnetic entropy change and the Curie temperature (T C) distribution in nanostructured $Pr_2Fe_{17}$ and $Nd_2Fe_{17}$ alloys produced by high-energy ball-milling after milling times of 10, 20, and 40 h. The changes in the microstructure affect the Fe local environments and as a consequence the magnetic interactions, giving rise to T C distributions centered around 285 K and 330 K for the $Pr_2Fe_{17}$ and $Nd_2Fe_{17}$ alloys, respectively. The width of the distributions enlarges (up to 60 K) as the milling-time increases, and consequently, the isothermal magnetic entropy change curves show an extended full width at half maximum.

### Magnetocaloric effect of $Co_{62}Nb_6Zr_2B_{30}$ amorphous alloys obtained by mechanical alloying or rapid quenching

L.M. Moreno, J.S. Blázquez, J.J. Ipus, J.M. Borrego, V. Franco and A. Conde
*Journal of Applied Physics,* **115** (2014) 17A302
**DOI:** 10.1063/1.4857595

Amorphous samples of nominal composition $Co_{62}Nb_6Zr_2B_{30}$ have been prepared using mechanical alloying (MA) and rapid quenching (RQ) techniques. Differences appear in Curie temperature and the phases developed after crystallization. Refrigerant capacity is enhanced 20% in the MA-sample with respect to that of RQ-sample. Neglecting the demagnetizing factor of powder samples significantly affects the exponent n characterizing the field dependence of the maximum magnetic entropy change.

### Impact of structural disorder on the magnetic ordering and magnetocaloric response of amorphous Gd-based microwires

Anis Biswas, Y.Y. Yu, N.S. Bingham, H. Wang, F.X. Qin, J.F. Sun, S.C. Yu, V. Franco, H. Srikanth and M.H. Phan
*Journal of Applied Physics,* **115** (2014) 17A318
**DOI:** 10.1063/1.4864143

We have studied the impact of structural disorder on the magnetic ordering and magnetocaloric response of amorphous $Gd_{68}Ni_{32}$ and $Gd_{53}Al_{24}Co_{20}Zr_3$ microwires. We find that the presence of structural disorder significantly broadens the paramagnetic to ferromagnetic (PM-FM) transition and the temperature-dependent magnetic entropy change, while the nature of the second-order magnetic transition and long-range ferromagnetic order are not essentially affected by this effect. The large magnetic moment of Gd and the presence of the long-range ferromagnetic order are believed to result in a large magnetic entropy change, which together with the broadening of the PM-FM transition due to structural disorder contribute to a large refrigerant capacity. The excellent magnetocaloric properties of the amorphous microwires make them very promising candidates for active magnetic refrigeration.

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

### Optimizing the Curie temperature of pseudo-binary RxR'2-xFe17 (R,R' = rare earth) for magnetic refrigeration

Pablo Álvarez-Alonso, Pedro Gorria, Gabriel Cuello, Inés Puente Orench, José L. Sánchez Llamazares, Victorino Franco, Marian Reiffers, Jesús A. Blanco
*Journal of Physics: Conference Series,* **549** (2014) 012019

## CONGRESOS Y REUNIONES INTERNACIONALES / INTERNATIONAL CONGRESS AND MEETINGS

## COMUNICACIONES / COMMUNICATIONS

### TMS 2014 143rd Annual Meeting & Exhibition
16 – 20 febrero [San Diego, California, Estados Unidos de América]

**The Magnetocaloric Effect in Nanostructured Materials**
V. Franco, A. Conde
Conferencia invitada

### INTERMAG 2014
4 – 8 mayo [Dresden, Alemania]

**Influence of demagnetizing factor on the magnetocaloric effect of a cobalt-based powder alloy**
L.M. Moreno, C. Romero-Muñiz, J.J. Ipus, V. Franco, J.S. Blázquez, A. Conde
Póster

**Anomalous enhancement of magnetocaloric effect in B-rich FeZrBCu amorphous alloys**
L.F. Kiss, T. Kemény, V. Franco, A. Conde
Póster

### INCOME 2014
22 – 26 junio [Cracovia, Polonia]

**Compositional distribution of nanocrystalline phases developed by mechanical alloying using Mössbauer spectroscopy**
J.S. Blázquez, J.J. Ipus, V. Franco, C. F. Conde, A. Conde
Conferencia invitada

**Effect of hot compaction on the microstructure and magnetic properties of mechanically alloyed Fe-Co-Nb-B system**
J.S. Blázquez, J.J. Ipus, M. Stoica, V. Franco, A. Conde
Comunicación oral

### The European Conference Physics of Magnetism 2014
23 – 27 junio [Poznan, Polonia]

**The magnetocaloric effect: A useful tool for the characterization of phase transitions**
V. Franco, A. Conde

Conferencia Invitada

**Normal and inverse magnetocaloric effects in amorphous R8Co62B30 (R = Y, Ho, Tb) alloys**
Z. Śniadecki, V. Franco, J. Marcin, I. Škorvánek, N. Pierunek, B. Idzikowski
Póster

**Spin reorientation and magnetocaloric properties of Y1−xGdxCo2 (0 ≤ x ≤ 1) compounds**
Z. Śniadecki, N. Pierunek, V. Franco, R. Puźniak, A. Wiśniewski, B. Idzikowski
Póster

## THERMAG VI

7 – 10 septiembre [Victoria, Canadá]

**Effect of the demagnetizing factor on the magnetic entropy change of powders and composites**
L.M. Moreno-Ramírez, C. Romero-Muñiz, J.J. Ipus, J.S. Blázquez, V. Franco, A. Conde
Comunicación oral

## 59th Annual Magnetism and Magnetic Materials (MMMM) Conference

3 – 7 noviembre [Honolulu, Hawaii, Estados Unidos de América]

**Influence of microstructure on the enhancement of soft magnetic character and the induced anisotropy of field annealed HITPERM-type alloys**
J. S. Blázquez, J. Marcin, M. Varga, V. Franco, A. Conde, I. Skorvanek
Comunicación oral

**Characterization of the interphase interactions of multiphase magnetocaloric materials using FORC analysis**
V. Franco, F. Béron, K.R. Pirota, M. Knobel, M.A. Willard
Comunicación oral

## Avalanches in Functional Materials and Geophysics

4 – 8 diciembre [Magdalene College, University of Cambridge, Reino Unido]

**Dynamic heat flux measurments on Cu-Zn-Al and Cu-Al-Ni shape memory alloys**
José María Martín Olalla
Conferencia invitada

# Congresos y Reuniones Nacionales / National Congress and Meetings

## Comunicaciones / Communications

### XXXVII Encontro Nacional de Fisica da Matéria Condensada

12 – 16 mayo [Costa do Sauipe, Brasil]

**The magnetocaloric effect: A useful tool for the characterization of phase transitions**
V. Franco, A. Conde
Conferencia invitada

# Formacion / Training

## Formación de Graduados / Master Degree Thesis

| | |
|---|---|
| **Título:** | **Preparación por molienda mecánica de la aleación amorfa Co62Nb6Zr2B30: caracterización magnética y microestructural** |
| **Autor:** | Luis Miguel Moreno Ramírez |
| **Directores:** | Javier S. Blázquez Gámez / Jhon J. Ipus Bados |
| **Grado:** | Trabajo Fin de Master (Ciencia y Tecnología de Nuevos Materiales) |
| **Año Académico:** | 2013-2014 (27 Junio 2014) |

# Docencia / Teaching

**Máster Oficial y Doctorado en “Biotecnología Avanzada”**
**Máster Profesorado de ESO y Bachillerato, FP**
Dr. Javier S. Blázquez
**Lugar:** Universidad de Sevilla

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

**Universidad Estadual de Campinas**

| | | |
|---|---|---|
| Campinas, Brasil | **Victorino Franco García** | 1 mes |

**University of Science and Tecnology Beijing**

| | | |
|---|---|---|
| Beijing, China | **Victorino Franco García** | 1 semana |
| **Institute of Experimental Physics, Slovak Academy of Sciences**<br>Kosice, Eslovaquia | **Javier S. Blázquez Gámez** | 2 semanas |
| **TU-Darmstadt**<br>Darmstadt, Alemania | **Victorino Franco García** | 2 meses |

## ESTANCIAS Y VISITAS DE INVESTIGADORES EN EL ICMS
## PERSONNEL OF THE OTHER LABORATORIES IN THE ICMS

| | |
|---|---|
| **Wigner Institute, Hungarian Academy of Sciences**<br>Budapest, Hungria | **Laszlo F. Kiss** |

## EQUIPAMIENTO CIENTÍFICO AVAILABLE EQUIPMENT

- Calorímetro de barrido diferencial (Perkin-Elmer DSC7)
- Criostato para espectrómetro Mόssbauer
- 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 de Resonancia Magnética Nuclear, 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: Nuclear Magnetic Resonance Spectroscopy, Raman Spectroscopy, Infrared Spectroscopy and Ultraviolet-Visible Spectroscopy. It is devoted to the determination of molecular structure of chemical compounds and materials.

## RESONANCIA MAGNÉTICA NUCLEAR EN SU CONFIGURACIÓN DE ESTADO SÓLIDO / NUCLEAR MAGNETIC RESONANCE IN ITS SOLID-STATE CONFIGURATION

La Resonancia Magnética Nuclear en estado sólido se utiliza, fundamentalmente, para el estudio de la estructura atómica de materiales amorfos o poco cristalinos. Se basa en el comportamiento de los momentos magnéticos de ciertos núcleos atómicos bajo la influencia de un campo magnético externo y de los campos locales creados por los núcleos vecinos y por la distribución de carga electrónica en torno al núcleo. Los espectros más comunes son representaciones de la intensidad de absorción frente a la frecuencia de resonancia y presentan señales cuya posición, forma y tamaño están íntimamente relacionados con el entorno químico del núcleo estudiado. Permite el estudio del orden a corto alcance de materiales estructuralmente desordenados y diferencia átomos con números atómicos similares.

Solid State Nuclear Magnetic Resonance is a widely use technique to study the structural properties of materials, including amorphous and not very crystalline solids. This technique is based on the behavior of the magnetic moments of the nuclei under an external magnetic field and the local magnetic field due to the environment. Thus, the position, shape and intensity of the signals inform of the chemical environment of the nuclei.

## INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Espectrómetro de RMN multinuclear Bruker, mod. DRX-400
  Multinuclear RMN Spectrometer (Bruker, mod. DRX-400)
- Sonda CP/MAS de 4 mm dotada de doble canal, 1H y BB (en el rango de frecuencia desde 15N a 31P)
  CP/MAS sound of 4 mm with double channel, 1H and BB (at a frequency range from 15N to 31P)
- Unidad neumática, que permite alcanzar velocidades de giro bajo ángulo mágico de hasta 15000 Hz
  Neumatic unit, that allows to reach turn velocities under a magic angle up to 15000 Hz

- Accesorio de temperatura variable dotado de una línea propia de $N_2$, así como de un sistema de control de temperatura que permite trabajar en un rango entre 223 K y a 373 K.
  Accessory of variable temperature with a line of its own of $N_2$, and with a temperature control system that allows to work at a range of 223 K - 373 K.

**Responsable Científico/Scientific Responsible:** Dra. María Dolores Alba Carranza
**Personal Técnico/Technical Assistant:** Dr. Miguel Angel Avilés Escaño

## 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. Manuel Ocaña Jurado y Dr. Ángel Barranco Quero
**Personal Técnico/ Technical Assistant:** Dr. Miguel Angel Avilés Escaño

## ESPECTROSCOPÍA ULTRAVIOLETA / ULTRAVIOLET-VISIBLE SPECTROSCOPIES

La espectroscopía Ultravioleta-Visible (UV-Vis) informa sobre las diferencias de energía existentes entre los niveles electrónicos ocupados más externos y los desocupados más próximos.
Se dispone en el ICMS de dos equipos que cubren el rango de longitudes de onda que va desde 190 nm hasta 900 nm. Se puede trabajar tanto en el modo de Transmisión como en el de Reflectancia Difusa.

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 two 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
- Perkin Elmer Lambda 12
  Perkin Elmer Lambda 12

**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), acopladas una y otra con las Espectroscopías de Energía Dispersiva de Rayos X (EDS) y de Pérdida de Energía de Electrones (EELS).
Las tareas ofrecidas por el personal técnico comprenden la preparación de muestras, su estudio por la batería de técnicas disponibles (TEM, SEM, HRTEM, SAED, EDS, EELS), la adquisición de imágenes y espectros, y en algunos casos, la interpretación de los datos experimentales.

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 and Scanning Electron Microscopy, which are equipped with a Electron Energy Loss Spectrometre and a Energy Dispersive X-ray Analyser, respectively.
The technicians working on this service carryied out different tasks, as sample preparation, image and spectral adquisition, and in some particular cases, interpretation of experimental results.

## MICROSCOPÍA ELECTRÓNICA DE BARRIDO / SCANNING ELECTRON MICROSCOPY

La microscopía electrónica de barrido proporciona información microestructural, morfológica y de composición química en escala microscópica (hasta una resolución lateral de ~ 5 nm). 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.

The scanning electron microscopy provides information about the microstructure, morphology and chemical composition at the microscopic scale of solid samples (upto a lateral resolution of ~ 5 nm). 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.

### INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Microscopio SEM, modelo Hitachi S4800 SEM-FEG de alta resolución (1-3 nm). Dotado de analizador EDX Bruker X Flash Detector 4010 con una resolución de 133 eV. Cañón de emisión de campo y detector STEM
  Hitachi S4800 SEM-FEG microscope of high resolution (1-3 nm). Equipped with a Bruker X flash 4010 EDX detector with a resolution of 133 eV, field emission gun and STEM detector.

- Equipamiento anexo para la preparación de muestras: metalizadores, cortadoras, etc.
  Sample preparation equipment: metallization devices, cutting tools, etc.

**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, pudiéndose obtener información sobre morfología, tamaño de grano, composición química, grado de cristalinidad e identificación de fases cristalinas en todo tipo de materiales. La espectroscopia de pérdida de energía de electrones (EELS) acoplada al microscopio TEM constituye una herramienta adicional para determinar la estructura electrónica, el tipo de enlace y la formación de fases.

The transmission electron microscopy is a widely used technique for the microstructural and chemical characterization at micro and nanoscales, giving information about morphology, grain size, chemical composition, crystallinity and identification of crystalline phases in all type of materials. The energy loss spectroscopy (EELS), coupled to the TEM microscope, constitutes an additional tool for the determination of electronic structure, type of bond and phase formation.

### INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

- Microscopio JEM-2000EX con una resolución estructural de 2.1 Å
  JEM-2000EX microscope with a structural resolution of 2.1 Å.
- Microscopio Philips CM200 con una resolución estructural entre puntos de 2.3 Å, portamuestras de uno y dos giros, calentamiento y enfriamiento. Acoplado al equipo se dispone de un sistema de análisis por Energías Dispersivas de Rayos X (EDX) y Espectrómetro de Pérdidas de Energía Electrónica (PEELS), de GATAN modelo 766-2 keV
  Philips CM200 microscope with a structural resolution of 2.3 Å. Sample holder with one and two angles, heating and cooling. It is equipped with a X-ray Energy Dispersive Analyser (EDX) and a Electron Energy Loss Spectrometre (PEELS) (Gatan, model 766-2 keV.
- Laboratorio de preparación de muestras para microscopía, que comprende: Evaporador de carbón, pulidora, cortadoras de disco y ultrasónica, adelgazador cóncavo-convexo, adelgazadores iónicos: Balttec (modelo RES 100) y Fischione (modelo 1010)
  Sample preparation laboratory, equipped with carbón evaporator, cutting and polishing tools, dimple, ion milling guns Balttec (model RES100) and Fischione (model 1010)

**Responsable Científico/ Scientific Responsible:** Dra. Asunción Fernández Camacho
**Personal Técnico/ Technical Assistant:** Dª Olga Montes Amorín (CicCartuja) y Dª María Inmaculada Roja Cejudo

## 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 ($\theta$-2$\theta$), 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 ($\theta$-2$\theta$), 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, AlK$\alpha$ y MgK$\alpha$, 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, Alk$\alpha$ y MgK$\alpha$).
  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
**Personal Técnico/Technical Assistant:** D. David Benítez Sánchez

## SERVICIO DE MECANIZADO/ MECHANICAL WORKSHOP

Se trata de un servicio horizontal fundamental para el Instituto y unidades externas adscritas al mismo, puesto que, además del mantenimiento del material y equipamiento científico, permite su mejora y adaptación a los distintos experimentos en curso, y de acuerdo con las necesidades de los investigadores y/o los proyectos que se llevan a cabo.

The Machining workshop is a basic and essential service that provides technical support to the maintenance, change, fitting and development of simple scientific equipments, according with the current requirements of the experiments and projects carried out by the researchers at the ICMS.

### INSTRUMENTAL DISPONIBLE / AVAILABLE EQUIPMENT

Además de otras herramientas menores para cortar, soldar, doblar, taladrar, etc., el taller de mecanizado cuenta con los siguientes equipos:
Besides other minor tools for cutting, soldering, folding, drilling, etc, this workshop is equipped with:

- Centro de mecanizado de control numérico computerizado (CNC), modelo HASS TM1P
  A computer numeric control turing machine, model HASS TM1P

- Taladro vertical, modelo ERLO TSAR32
  A vertical drill, model ERLO TSAR32
- Torno paralelo manual EMCO SUPER 11CD y torno semiautomático PINACHO SMART TURN180
  A couple of turning machines: models PINACHO TURN180 and SUPER 11 CD EMCO

**Responsable/ Responsible:** D. Enrique Jiménez Roca
**Personal Técnico:** D. Juan Carlos Sánchez Martín

# 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 2010

Métodos Físicos de Análisis de Capas Finas y Superficies de Sólidos

Sevilla, del 28 de Junio al 2 de Julio de 2010

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

Aplicaciones Tecnológicas de las Películas Delgadas
Técnicas de Preparación de Películas y Recubrimientos (CVD, PVD)
Espectroscopías de Fotoemisión (XPS, UPS)
Microscopías Electrónicas de Transmisión y Barrido (TEM y SEM) Espectroscopías Electrónicas (Auger, REELS, EDX, PEELS)
Difracción de Rayos X
Absorción de Rayos X (EXAFS, XANES)
Dispersión de Iones (ISS, RBS)
Microscopías de Aproximación de puntas (AFM, STM)

Directores:
Dr. Juan Pedro Espinós Manzorro
Instituto de Ciencia de Materiales de Sevilla
jpespinos@icmse.csic.es

Dr. Guillermo Munuera Contreras
Instituto de Ciencia de Materiales de Sevilla
Dpto. Química Inorgánica

Instituto de Ciencia de Materiales de Sevilla
c/ Américo Vespucio, 49, 41092 (Sevilla)
Telf: 954 48 95 27 • Fax: 954 46 06 65
http://www.icmse.csic.es/cursocapas.htm
CUOTA DE INSCRIPCIÓN: 300 €

Hay disponible un número limitado de becas para alumnos de tercer ciclo (adjuntar curriculum vitae y una carta de presentación de un investigador cualificado)

**Organizado por el Instituto de Ciencia de Materiales de Sevilla**
**Directores:** Dr. Juan Pedro Espinós y Dr. Guillermo Munuera
**Fecha de Celebración:** 23 al 27 de junio de 2014
**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
**Determinación de Perfiles de Composición mediante TOF-SIMS** | Dr. Daniel Gamarra
**Microscopía Electrónica de Efecto Túnel** | Dr. Juan Ramón Sánchez Valencia
**Plasmas en la Tecnología de Materiales**| Dr. José Cotrino Bautista
**Microscopía Electrónica de Transmisión: Fundamentos y Aplicaciones Generales** | Dra. Asunción Fernández Camacho

**Microscopía Electrónica: PEELS y EFTEM**| Dra. Cristina Rojas Ruiz
**Microscopía Electrónica de Barrido**| Dra. María del Carmen Jiménez de Haro
**Microscopías de Fuerzas Atómicas** | Dra. Carmen López Santos
**Análisis Tribológico y Mecánico de Capas Delgadas** | Dr. Juan Carlos Sánchez López
**La Difracción de Rayos X: Generalidades** | Dr. Antonio Ruiz Conde
**Determinación de Perfiles de Composición a partir del Análisis de Forma de Pico en XPS: Método de Tougaard** | Dr. Francisco Yubero Valencia
**Retrodispersión Rutherford: Perfiles de Composición** | Dr. Javier García

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 Espinós | Ldo. Davíd Benítez | Dr. Juan Pedro Holgado
**c. Difracción de Rayos X** | Dr. Angel Justo | Ldo. José M. Martínez Blanes
**d. Retrodispersión Rutherford** | Dr. Javier García
**f. Microscopía de Fuerzas Atómicas y Túnel** | Dr. Carmen López Santos | Dr. Juan Ramón Sánchez Valencia

## 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 2014-15
**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
**Recuperación y Transformación de Materiales** (Créditos: 5) | Dra. Svetlana Ivanova
**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. Hernán Míguez García | Dr. Francisco Javier Romero Landa | Dra. Carmen Gallardo Cruz
**Computación en Ciencia de Materiales** (Créditos: 5) | Dra. Regla Ayala Espinar | Dr. Antonio Córdoba Zurita (US) | Dr. Felipe Gutiérrez Mora

■■■■■■

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

**The magnetocaloric effect of multiphase materials and nanostructures**
Dr. Victorino Franco
Universidad Estadual de Campinas. Campinas (Brasil)

**The Magnetocaloric Effect: From Energy Efficient Refrigeration to Fundamental Studies of Phase Transitions**
Dr. Victorino Franco
University of Science and Technology Beijing (China)

**The Magnetocaloric Effect in amorphous and multiphase materials: phenomenological models to describe its field dependence**
Dr. Victorino Franco
VACUUMSCHMELZE GmbH & Co. KG (Alemania)

**Gaining information of phase transitions and critical phenomena via magnetocaloric studies**
Dr. Victorino Franco
TU-Darmstadt, Darmstadt (Alemania)

2 de abril | **Biodegradable Polyesters from Natural Occurring Fatty Hydroxyacids. The Synthesis and Characterization of Polyaleuritate**
Dr. José Jesús Benítez
Istituto Italiano di Tecnologia (IIT), Genova (Italia)

## CONFERENCIAS Y SEMINARIOS IMPARTIDOS EN EL ICMS
## CONFERENCES AND SEMINAR IN THE ICMS

12 de junio| **Casimir force between real materials for device applications**
Dr. George Palasantzas
Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, The Netherlands

Using the measured optical response and surface roughness topography as inputs, we perform realistic calculations of the influence of Casimir forces on the actuation dynamics of micro/nanoelectromechanical systems (MEMS/NEMS). Amorphous to crystalline phase transitions in phase change materials can have strong influence on the actuation of microelectromechanical systems under the influence of Casimir forces. Indeed, the phase portraits of the actuation dynamics show strong sensitivity to changes of the Casimir force as the stiffness of the actuating component decreases and/or the effective interaction area of the Casimir force increases, which can also lead to stiction. Introduction, however, of intrinsic energy dissipation (associated with a finite quality factor of the actuating system) can prevent stiction by driving the system to attenuated motion towards stable equilibrium. It is also found that even though surface roughness appears to have a detrimental effect on the availability of stable equilibria, it ensures that those equilibria can be reached more easily than in the case of flat surfaces. Hence our findings play a principal role for the stability of micro/nanodevices and architectures operating at distances below 200 nm. Finally, new investigations for the Casimir force from conductive SiC and their implications for MEMS/NEMS will also be discussed.

## Otras Actividades / Other Activities

### Feria de la Ciencia / Fair of Science

La Feria de la Ciencia (15 al 17 de mayo de 2014, 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: “De la Microscopía óptica a la microscopía electrónica: Un sorprendente viaje del micro al nanomundo”.
Coordinadora: Asunción Fernández Camacho. Participaron un total de 16 monitores.

The Fair of Science (15 to 17 May 2014, 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: “From optical to electron microscopy. A voyage from the micro- to the nano-world”
Coordination: Asunción Fernández Camacho.

## SEMANA DE LA CIENCIA Y LA TECNOLOGÍA / SCIENCE AND TECHNOLOGY WEEK

Jornadas de puertas abiertas (Semana del 11 al 14 de Noviembre de 2014, en Sevilla). La Semana de la Ciencia y la Tecnología está dirigida a todos los públicos. 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.

### Visitas guiadas

Coordinador Dr. A. Ruiz Conde

### Charlas

11 de Noviembre de 2014. Dr. José Luis Pérez Rodríguez

Titulo: "La Ciencia de Materiales en el Patrimonio Histórico-Artístico”

13 de Noviembre de 2014. Dr. José Cotrino Bautista

Titulo: “Tecnología de plasma y materiales”

14 de Noviembre de 2014. Dra. Gisela Arzac Di Tomaso

Titulo: “El hidrógeno como combustible sostenible”

### 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:** Dr. Alberto Palmero Acebedo. Coloquio con estudiantes. Tema: “Nanotecnología del siglo XXI. Una visita al nanomundo”

IES Las Encinas (10 alumnos). IES Jacarandá (15 alumnos)

**Mesa:** Dra. Sol Carretero Palacios. Coloquio con estudiantes. Tema: “Controlando la luz en el mundo nano y microscópico”

IES Las Encinas (10 alumnos)

### Exposición de Fotografías

En esta duodécima edición de la Semana de la Ciencia, se ha incluido en su programa de actividades una muestra de fotografía científica, titulada “Microscopía electrónica: todo un arte”. Esta exposición se desarrollará en el hall de cicCartuja, entre el 12 y el 16 de noviembre, y estará coordinada por Asunción Fernández Camacho, investigadora del Instituto de Ciencia de Materiales de Sevilla (ICMS) y responsable de la Red Al-NanoFunc (dedicada al estudio internacional de los nanomateriales funcionales).

La muestra consistirá en un conjunto de imágenes obtenidas por técnicas de microscopía electrónica. Estas micrografías corresponden a materiales con variada funcionalidad: desde catalizadores hasta dispositivos ópticos, pasando por sensores de diversas sustancias. Dichos materiales han sido preparados previamente por científicos (en su mayoría, del ICMS) como parte de su trabajo de investigación. Las micrografías expuestas, retocadas y coloreadas con fines artísticos, han sido seleccionadas teniendo en cuenta su apariencia y la relevancia del material que representan.

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