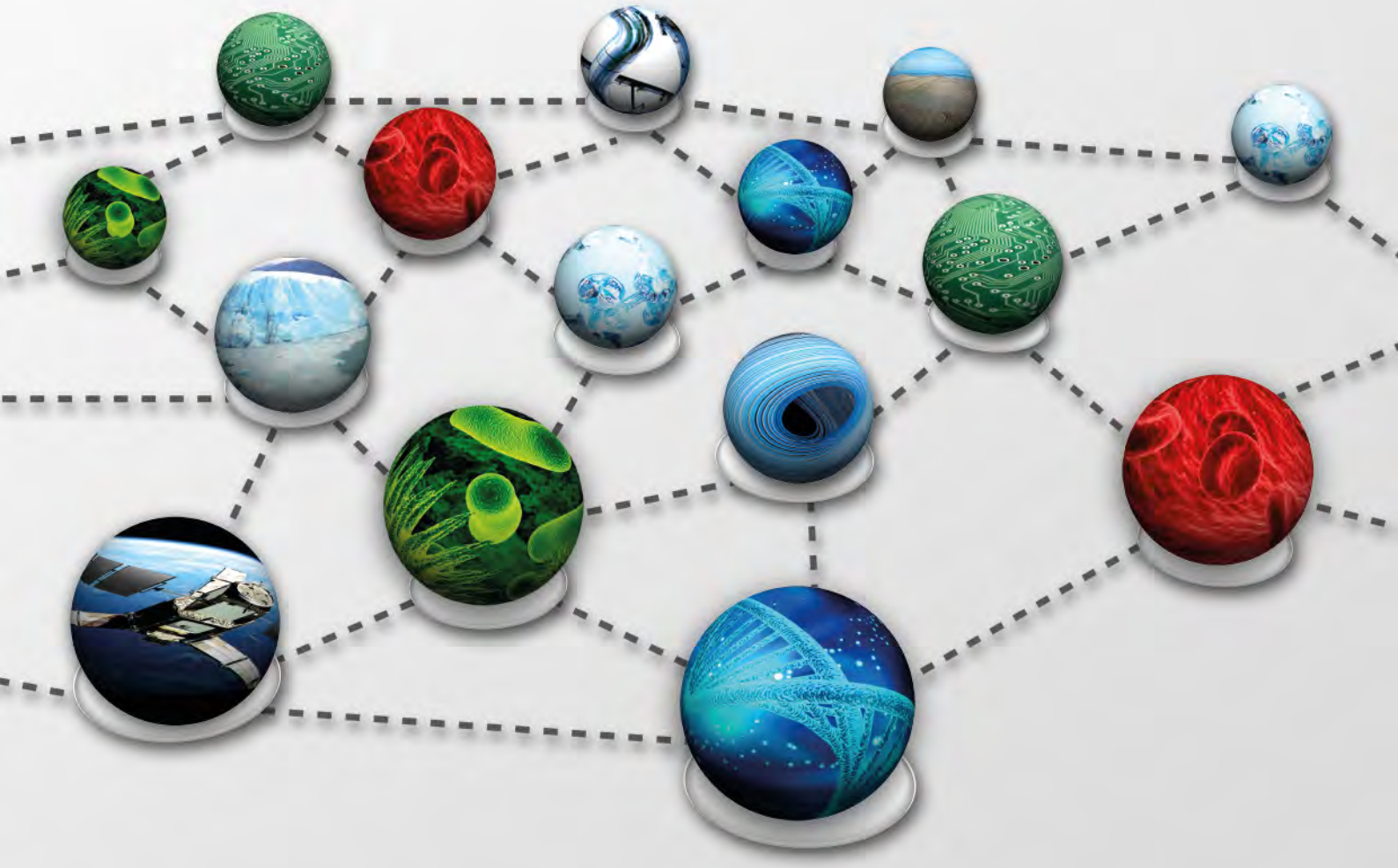
2018
Martxoak
14 - 15 de Marzo

Zientzia eta Teknologia Fakultateko VI. Ikerkuntza Jardunaldiak

VI Jornadas de Investigación de la Facultad de Ciencia y Tecnología

www.ztf-fct.org

Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares



eman ta zabal zazu

Universidad del País Vasco
Euskal Herriko Unibertsitatea

CIP. Biblioteca Universitaria

Universidad del País Vasco/Euskal Herriko Unibertsitatea. Facultad de Ciencia y Tecnología. Jornadas de Investigación. (6ª. 2018. Leioa)

Diziplina anitzeko sareak ehunduz [Recurso electrónico]: Zientzia eta Teknologia Fakultateko VI. Ikerkuntza Jardunaldiak = Tejiendo redes multidisciplinares : VI Jornadas de Investigación de la Facultad de Ciencia y Tecnología, 2018 Martxoak 14-15 de Marzo. – Datos. - Bilbao : Universidad del País Vasco / Euskal Herriko Unibertsitatea, Argitalpen Zerbitzua = Servicio Editorial, [2018]. – 1 recurso en línea : PDF (164 p.)
Abstracts de las comunicaciones en inglés.
Modo de acceso: World Wide Web.
ISBN: 978-84-9082-836-6.

1. Investigación. 2. Ciencias - Congresos. I. Título: Tejiendo redes multidisciplinares: VI Jornadas de Investigación de la Facultad de Ciencia y Tecnología. II. Título: VI Jornadas de investigación de la Facultad de Ciencia y Tecnología.

(0.034)001.891(063)
(0.034)5/6(063)

ISBN: 978-84-9082-836-6

Dear colleagues:

As you know, the **6th Research Conference of the Faculty of Science and Technology** is to take place on 14-15 March.

On Wednesday, 14 March, at 9 a.m., the Conference will start with oral presentations by young researchers from the area of **Biosciences** and **Chemical Engineering,** in the Adela Moyua Room, in the Classroom 0.22 and in the Lecture Hall of the Faculty. At 11.30 a.m., once these presentations are finished, coffee will be served at the Grande Salle and the posters can be viewed.

Also on the 14th, at 12 noon, the Official Inauguration of the 6th Conference will be held in the Main Auditorium, with the presence of the Director of Scientific Policy of the Basque Government, Amaia Esquisabel, the Vice Rector of the Bizkaia Campus, Patxi Juaristi and of the Dean of the Faculty, Esther Domínguez.

Following that, Dr. Margarita Salas will give the Opening Keynote **'From Molecular Biology to Biotechnology'**.

In the afternoon of the 14th (3–5.30 p.m.) oral presentations will continue in the areas of I) **Physics and Electronic Engineering,** II) **Mathematics** and III) **Geology** in the Graduation Hall, Adela Moyua Room and Classroom 1.1, respectively.

In the morning of the 15th (11.45 a.m.–2 p.m.) oral presentations will continue in the area of **Chemistry** in the Adela Moyua Room and in the Lecture Hall.

During the whole morning, there will be guided tours of the posters and, at 11.30 a.m., coffee will be served in the Grande Salle.

Esther Domínguez
The dean of the Faculty of Science and Technology

Lankideok:

Dakizuen moduan, martxoaren 14an eta 15ean **Zientzia eta Teknologia Fakultateko VI. Ikerketa Jardunaldiak** izango dira.

Jardunaldiok martxoaren 14an hasiko dira (asteazkena) goizeko 9:00etan, fakultateko Adela Moyua Aretoan, 0.22 gelan eta Hitzaldia Aretoan **Biozientzien** eta **Ingeniaritza Kimikoa** arloko ikertzaile gazteen ahozko aurkezpenekin. Hitzaldi horiek amaituta, 11:30ean kafea egongo da Grande Sallen eta posterrak bisitatu ahal izango dira.

Egun horretan bertan, eguerdiko 12:00etan, VI. Jardunaldiei hasiera emateko ekitaldi ofiziala izango da Paraninfoan. Bertan izango dira Amaia Esquisabel, Eusko Jaurlaritzako Zientzia Politikarako zuzendaria; Patxi Juaristi, Bizkaiko Campuseko errektoreordea; eta Esther Domínguez, Fakultateko dekanoa.

Horren ostean, Margarita Salas doktoreak hasiera emango die jardunaldiei hitzaldi honekin: **"De la Biología Molecular a la Biotecnología".**

Egun horretako arratsaldean (15:00etatik 17:30etara) ahozko aurkezpen gehiago egongo dira 1) **Fisika eta Ingeniaritza Elektronikoa** arlokoak, Gradu Aretoan, II) **Matematika** arlokoak, Adela Moyua Aretoan eta III) **Geologia** arlokoak, 1.1. gelan.

Martxoaren 15ean, goizean (11:45-14:00) ahozko aurkezpen gehiago egongo dira **Kimika** arlokoak, Adela Moyua Aretoan eta Hitzaldi Aretoan.

Goiz osoan zehar bisita gidatuak egingo dira posterretara eta 11:30ean kafea egongo da Grande Sallen.

Ahozko aurkezpenen ostean **«Zientzia eta Teknologia Fakultateko VI. Ikerketa Jardunaldietako Poster Onenaren Saria»** emateko ekitaldia izango da. Jarraian, fakultateko dekanoak amaiera emango die jardunaldiei.

Aurreko edizioetako arrakasta ikusita, eta kontuan hartuta ikasleek interes handia erakutsi dutela fakultatean egiten den ikerketaren errealitatea ezagutzeko, arren eskatzen dizuet anima ditzazuen jardunaldietan parte hartzera; horretarako, eskatuko nizueke egun horietako eskola orduetan jardunaldietan programatutako ekimenetara joateko.

Proposamen honetan zuen laguntza izango dugulakoan, eskerrik asko aldez aurretik eta ondo izan.

Esther Domínguez
Zientzia eta Teknologia Fakultateko Dekanoa Andrea

Estimados compañeros y compañeras:

Como sabéis, durante los próximos días 14 y 15 de marzo se celebrarán las **VI Jornadas de Investigación de la Facultad de Ciencia y Tecnología**.

El miércoles, 14 de marzo, a las 9:00 h darán comienzo las Jornadas con las presentaciones orales de jóvenes investigadores de las áreas de **Biociencias** e **Ingeniería Química** en la Sala Adela Moyua, aula 0.22 y Sala de Conferencias de la Facultad. A las 11:30 h, una vez finalizadas dichas presentaciones, se servirá un café en la Grande Salle y se podrán visitar los pósteres.

El mismo día 14, a las 12:00 h, se celebrará en el Paraninfo, la Inauguración oficial de las VI Jornadas con la presencia de la Directora de Política Científica del Gobierno Vasco, Amaia Esquisabel, del Vicerrector del Campus de Bizkaia, Patxi Juaristi y de la Decana de la Facultad, Esther Dominguez.

Seguidamente, la Dra. Margarita Salas impartirá la Conferencia Inaugural **"De la Biología Molecular a la Biotecnología"**.

Durante la tarde del día 14 (15:00 – 17:30 h) continuarán las presentaciones orales en las áreas de I) **Física e Ingeniería Electrónica,** II) **Matemáticas** y III) **Geología** en el Salón de Grados, Sala Adela Moyua y Aula 1.1 respectivamente.

Durante la mañana del día 15 (11:45-14:00 h) continuarán las presentaciones orales en el área de **Química,** en la Sala Adela Moyua y en la Sala de Conferencias**.**

Durante toda la mañana se realizarán visitas guiadas a los pósteres y a las 11.30 h se servirá un café en la Grande Salle.

Al término de las comunicaciones orales se procederá a la entrega del **"Premio al Mejor Póster de las VI Jornadas de Investigación de la Facultad de Ciencia y Tecnología".** A continuación la Decana de la Facultad procederá al cierre de las mismas.

El éxito de las ediciones anteriores y el interés mostrado por el alumnado en conocer la realidad de la investigación que se lleva a cabo en el Centro, me motiva para pediros que impulséis su participación, trasladando la presencialidad del aula a las actividades programadas.

En la confianza de que contaremos con vuestro apoyo, recibid mi agradecimiento y mi saludo más cordial.

Esther Domínguez
Decana de la Facultad de Ciencia y Tecnología

Egitaraua / Programa

Martxoaren 14a, asteazkena

9:00 - 19:00 Egun osoan zehar **posterren saio jarraia**.

9:00 - 11:30 **Ahozko komunikazioak**: **Biozientziak** eta **Ingeniaritza Kimikoa** Adela Moyua gelan, 0.22 gelan eta Hitzaldi Aretoan.

11:30 - 12:00 Grande Sallen kafea eta posterren bisita.

12:15 - 14:00 **Jardunaldien aurkezpena** egingo da Fakultateko Paraninfoan Eusko Jaurlaritzako Zientzia Politikarako zuzendaria, Bizkaiko Campuseko errektoreordea eta Fakultateko Dekanordearen eskutik.

Inaugurazio-hitzaldia **Margarita Salas doktorearen** eskutik. Hitzaldiaren izenburua: "**De la Biología Molecular a la Biotecnología**".

15:00 - 17:30 **Ahozko komunikazioak**: I) **Fisika eta Ingeniaritza Elektronikoa**, II) **Matematika** eta III) **Geologia** fakultateko Gradu Aretoan, Adela Moyua gelan eta 1.1. gelan.

Martxoaren 15a, osteguna

9:00 - 19:00 Egun osoan zehar **posterren saio jarraia.**

11:30 - 12:00 Kafea Grand Sallen eta posterren bisita.

12:00 - 14:00 **Ahozko komunikazioak**: **Kimika** Adela Moyua gelan eta Hitzaldi Aretoan.

14:00 VI. Ikerkuntza Jardunaldietako poster onenari saria ematea.

14:15 Jardunaldien itxiera Zientzia eta Teknologia Fakultateko Dekanoaren partetik.

Miércoles 14 de marzo

9:00 - 19:00 **Sesión continua de pósteres** durante toda la jornada.

9:00 - 11:30 **Comunicaciones Orales: Biociencias e Ingeniería Química** en la sala Adela Moyua, aula 0.22 y Sala de Conferencias de la Facultad.

11:30 - 12:00 Café en la Grande Salle y visita a los pósteres.

12:15 - 14:00 **Inauguración de las Jornadas** en el Paraninfo de la Facultad a cargo de la de la Directora de Política Científica del Gobierno Vasco, del Vicerrector del Campus de Bizkaia y de la Decana de la Facultad.

Conferencia inaugural impartida por la **Dra. Margarita Salas**, con el título: "**De la Biología Molecular a la Biotecnología**".

15:00 - 17:30 **Comunicaciones Orales**: I) **Fisica e Ingeniería Electrónica**, II) **Matemáticas** y III) **Geologia** en el Salón de Grados de la Facultad, Sala Adela Moyua y aula 1.1.

Jueves 15 de marzo

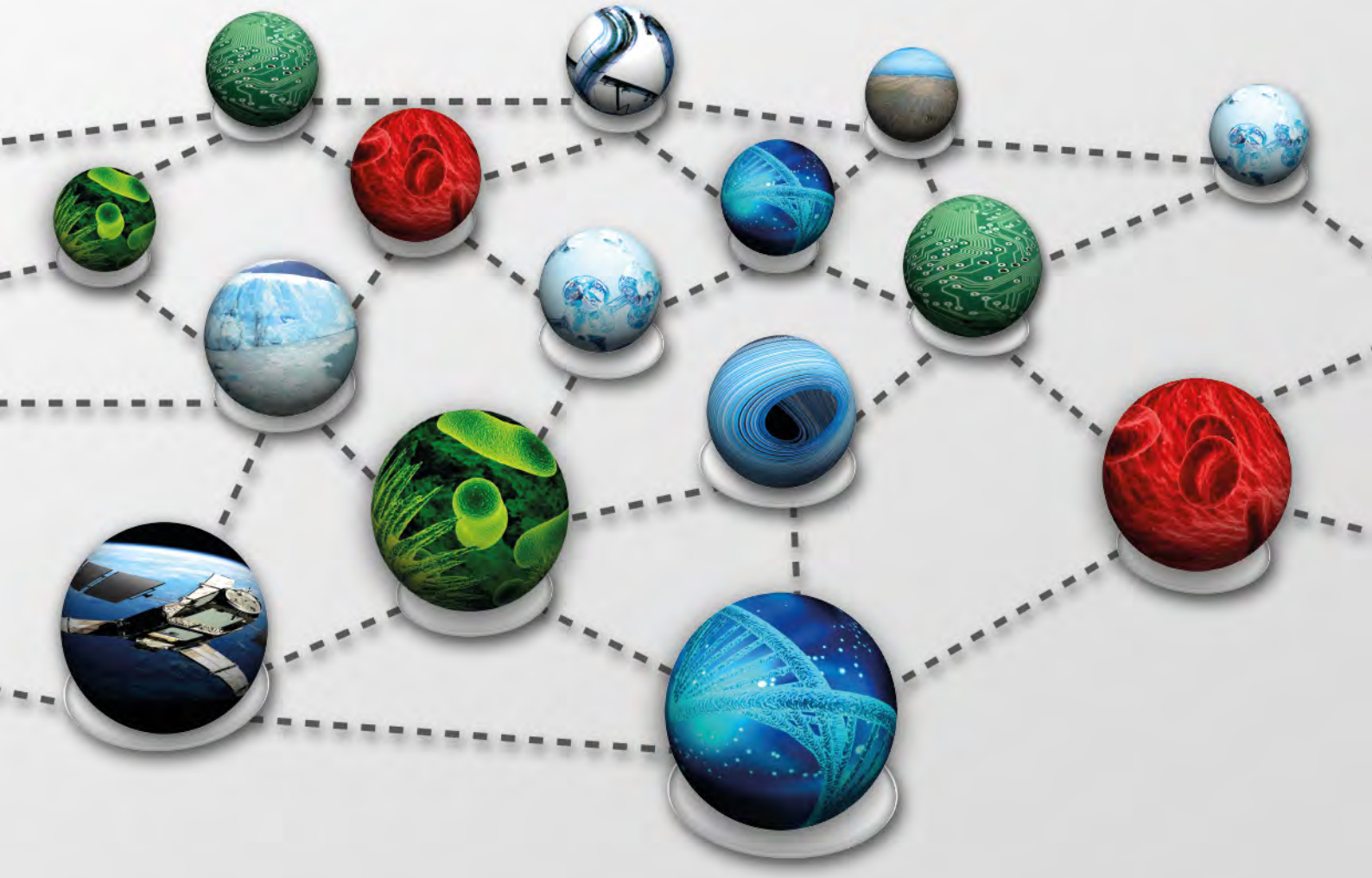
9.00 - 19:00 **Sesión continua** de pósteres durante toda la jornada.

11:30 - 12:00 Café en la Grande Salle y visita a los pósteres.

12:00 - 14:00 **Comunicaciones Orales: Química** en la Sala Adela Moyua y Sala de Conferencias de la Facultad.

14:00 Entrega del premio al mejor póster de las VI Jornadas de Investigación.

14:15 Cierre de las Jornadas por la decana de la Facultad de Ciencia y Tecnología.



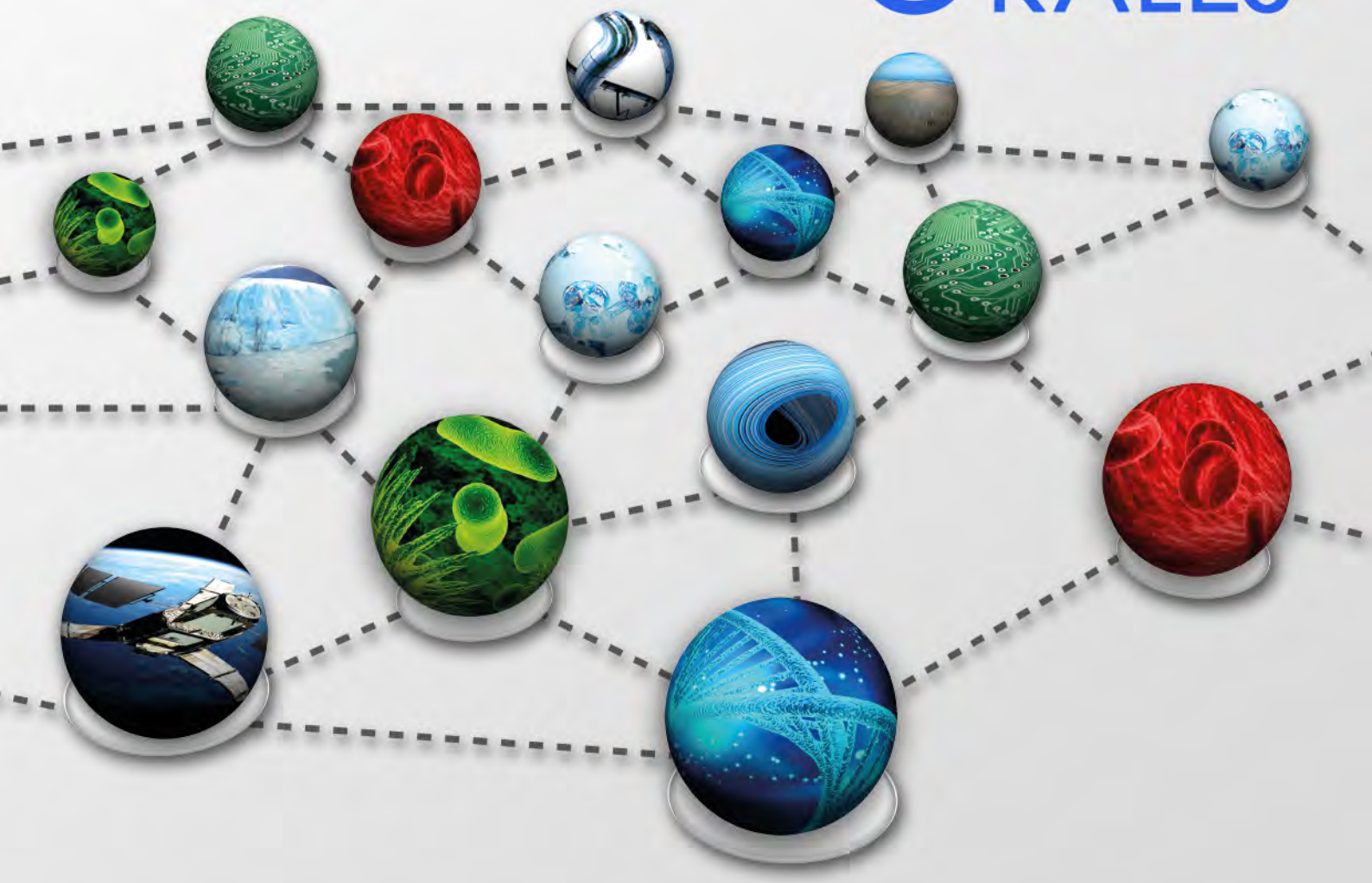
Diziplina Anitzeko Sareak Ehunduz

Tejiendo Redes Multidisciplinares

ABSTRACTS

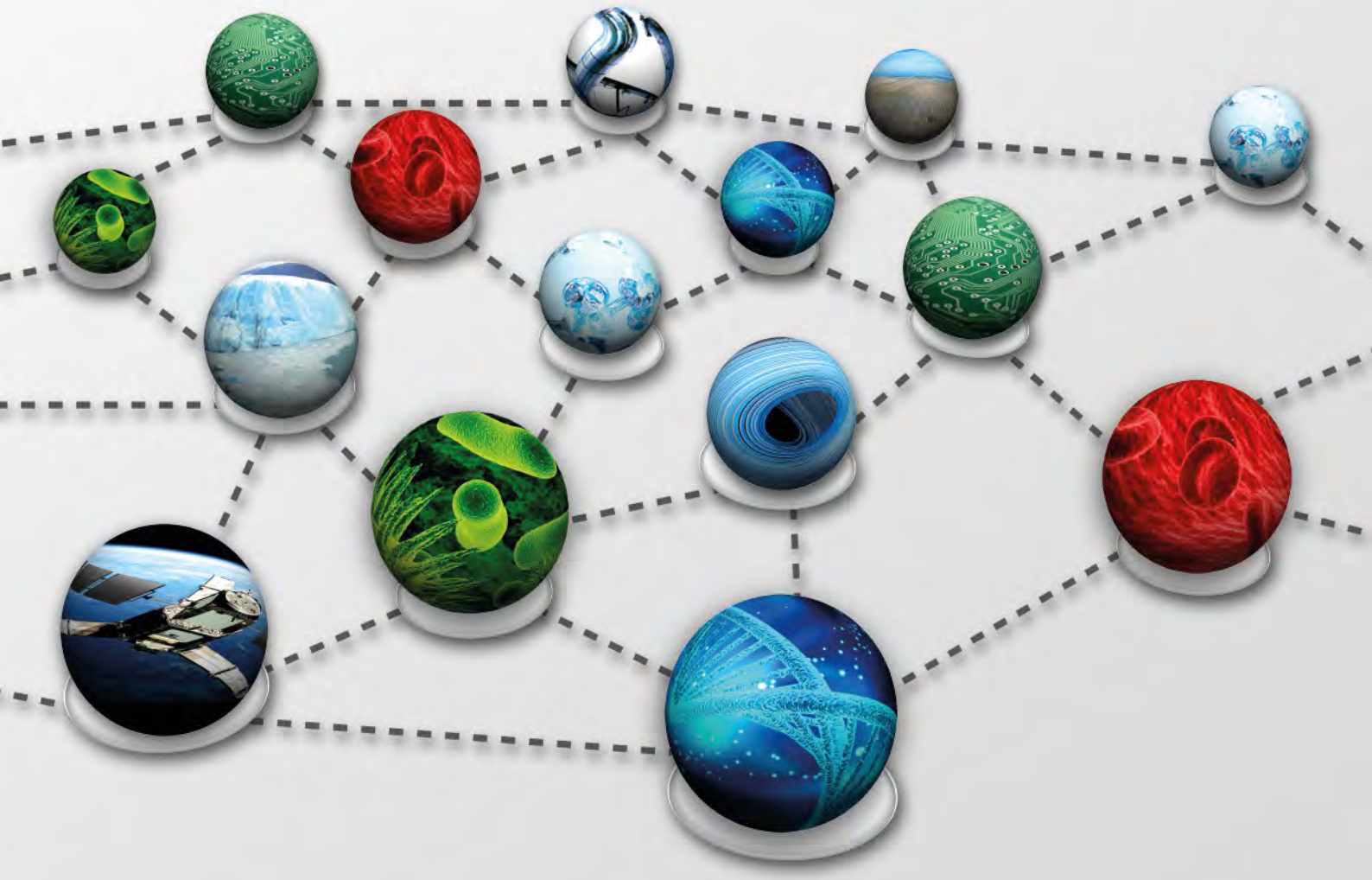
AHOZKO KOMUNIKAZIOAK

COMUNICACIONES ORALES



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

BIOZIENTZIAK
BIOCIENCIAS



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Identification of antigens of *Mucor circinelloides* recognized by sera from infected immunosuppressed mice

Arbizu-Delgado A, Guruceaga X, Antoran A, Martin-Souto L, Buldain I, Aparicio L. Rementeria A, Hernando FL, Ramirez-Garcia A.
Fungal and Bacterial Biomics Research Group, Department of Immunology, Microbiology and Parasitology, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Leioa, Spain.

KEY WORDS: *Mucor*, *Mucor circinelloides*, mucromycosis, antigen, secretome

Mucormycosis, infections caused by fungi of the order *Mucorales*, are a group of emerging infectious diseases characterized by rapid progression and high aggressiveness. The genera *Mucor* is one of the most common etiological agents, being *Mucor circinelloides* the most frequently isolated species. Moreover, their virulence mechanisms are still unknown and there is no effective diagnostic method for this disease apart from classical methods.

In this context, the aim of this study was to identify the antigens from the secretome and cell extracts of *M. circinelloides* recognized specifically by immunosuppressed infected mice sera.

To do that, *Mucor circinelloides* was grown into potato dextrose broth at 37ºC with 120 rpm agitation for 24 hours. Then, to obtain the secretome extracts the fungal material was separated from the medium by filtration and incubated at 37ºC with 120 rpm agitation in PBS 2% glucose for 20 hours. Then, the supernatant was filtered, sterilized and dialyzed, and finally, proteins were precipitated and resuspended in 2-DE buffer.

On the other hand, to obtain cell extracts the fungal material was separated from the medium by filtration, resuspended with phosphate buffered saline (PBS) in a proportion of volume of 1:1 and disrupted by bead beating. Afterwards, the solution was centrifugated and the supernatant separated from the pellet, keeping the supernatant. Finally, proteins were precipitated and resuspended in 2-DE buffer.

Protein separation was carried out by two-dimensional electrophoresis and antigen detection was performed by Western Blot against a pool of sera obtained from 5 mice infected intravenously with $1x10^5$conidia of *M. circinelloides* NRRL 3631 and 5 control sera from non-infected mice. These mice had been previously immunosuppressed by giving them 100 mg/kg cyclophosphamide intraperitoneally at -4 days and, then, every three days until the day 20 in which the mice were sacrificed and the sera was obtained.

Several immunoreactive proteins were specifically detected by sera from infected immunosuppressed mice. The reactivity of these antigens was also observed when sera of infected mice were tested individually. This study identifies some antigens of *M. circinelloides*, which are recognized by sera from infected mice even in an immunosuppressant state. The study of the reactivity of those antigens might be very useful to develop a sensitive and specific serological diagnostic test, taking into account that these fungal infections occur mainly in immunosuppressed patients.

Analysis of mechanisms involved in *Vibrio harveyi* adaptation to stress and their regulation by antisense RNAs

Ander Hernández Plágaro [1], Vladimir R. Kaberdin[1,2,3]
[1] Universidad del País Vasco UPV/EHU, Immunology, Microbiology and Parasitology, Leioa, Spain;
[2] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain;
[3]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV), Plenzia Marine Station

KEY WORDS: Vibrio, RNA, transcriptome, regulation.

BACKGROUND

The genus *Vibrio* comprises a large group of ubiquitous aquatic bacteria. Previous studies highlighted their capacity to survive under different adverse conditions including starvation, drastic temperature shifts and solar radiation. Previous studies disclosed that the resistance to stress can be controlled at the post-transcriptional level through regulation of gene expression mediated by small RNAs (sRNAs). These regulatory molecules specifically recognize their target mRNAs and subsequently alter their stability and/or translation.

OBJECTIVES

The aim of this project was to use *Vibrio harveyi* as a model organism to monitor gene expression changes at the whole transcriptome level and discover novel putative sRNAs potentially involved in adaptation of this marine bacterium to changing environments.

MATERIALS AND METHODS

Total *Vibrio harveyi* RNA was isolated and subjected to differential RNA sequencing to map transcription start sites (TSS) within the genome. The data obtained were further analyzed *in silico* and a number of new sRNAs were identified and validated by northern blotting.

RESULTS AND CONSLUSIONS

Differential RNA sequencing revealed 3900 TSS in total. They were placed in 4 arbitrary groups including:

- Intergenic TSS preceding genes on the same strand (group A)
- Intergenic TSS mapped downstream of genes located on the opposite strand (group B)
- Introgenic TSS mapped within genes on the same strand (group C)
- Introgenic TSS mapped within genes on the opposite strand (group D)

Study of regions flanking TSS associated with canonical mRNAs revealed motifs possibly associated with sigma factor recognition sequences normally present in -35 and -10 regions. Moreover, we found that the first nucleotide transcribed by *V. harveyi* RNA polymerase is usually represented by purine bases (i.e. guanosines or adenosines).

Due to its nature, group B TSS could be associated with new genes overlooked in the annotation of the reference genome. Indeed, bioinformatic analysis revealed a number of putative protein-coding and sRNA genes. Expression of some putative sRNA genes (23 in total) was further validated by northern blotting. The result of this analysis confirmed the existence of several unknown putative sRNAs.

We also found that TSS in group C defined transcripts whose transcription could be initiated within the protein-coding sequences yielding either leaderless mRNA or their truncated forms potentially encoding protein isoforms.

Finally, some TSS in group D were likely associated with *cis*-encoded antisense RNAs whereas others could represent the results of pervasive transcription.

Development of a serological diagnostic kit for the detection of *Scedosporium* in cystic fibrosis pacients

Leire Martin-Souto, Idoia Buldain, Aize Pellon, Aitziber Antoran, Xabier Guruceaga, Aitana Arbizu-Delgado, Leire Aparicio, Uxue Perez-Cuesta, Aitor Rementeria, Fernando L. Hernando and Andoni Ramirez-Garcia.

University of the Basque Country UPV/EHU, Fungal and Bacterial Biomics Research Group. Dept. of Immunology, Microbiology and Parasitology, Leioa, Spain

KEY WORDS: Cystic fibrosis, *Scedosporium*, serodiagnosis, proteome

OBJECTIVES

Species of the genera *Scedosporium* and *Lomentospora* are emergent pathogens ranking the second, only behind *Aspergillus* spp., among filamentous fungi causing a chronic colonization of the airways of cystic fibrosis (CF) patients. This may lead to chronic inflammation or even to life-threatening invasive disease in cases of severe immunosuppression.

The detection of these fungi relies upon low sensitivity and specificity procedures, which results in a delayed diagnosis and inadequate monitoring of the patients. Furthermore, their virulence is quite high due to intrinsic multidrug resistance, which contributes, as a whole, to an inefficient treatment.

To contribute to the finding of new diagnostic targets, our aim is to identify the most immunoreactive antigens of *Scedosporium boydii* recognized specifically by serum IgGs from CF patients colonized by *Scedosporium* spp. in order to develop a diagnosis kit, which allows detection and discrimination of *Scedosporium* species.

METHODS

Sera from CF patients without fungal colonization, CF colonized by *Scedosporium* spp. and CF colonized by *Aspergillus* spp. were used to carry out the experiments. To compare the serological response against *S. boydii* and *A. fumigatus*, an ELISA (Enzyme-Linked ImmunoSorbent Assay) was performed with serial dilutions of the sera to calculate the titer of IgG and IgE antibodies against both fungal species.

Moreover, a total protein extract from *S. boydii* cultured during 24 h at 37 ºC into potato dextrose broth was obtained and separated by two dimensional gel electrophoresis. Then, proteins were transferred to PVDF membranes to perform immunoblotting with the different sera. Comparative image analysis of the results obtained with the sera from the three groups of CF patients allowed characterizing the antigens of *S. boydii* cross-reacting with sera from CF patients colonized by *Aspergillus* spp., as well as those specifically detected by sera from CF patients colonized by *Scedosporium* spp. Among the latter, the most immunoreactive ones were identified by LC-MS/MS (Liquid chromatography-tandem mass spectrometry).

RESULTS

The ELISA test revealed that IgG antibody titer against both fungi, *S. boydii* and *A. fumigatus*, in CF patients sera with *Scedosporium* was higher (1/2000) than in those with *Aspergillus* (1/500). Conversely, the measure of IgE levels showed very low titers in both sera types, similar to the control sera values.

Regarding the immunoproteomics study, different serological profiles were obtained. On the one hand, sera from CF patients colonized by *Scedosporium* reacted with a great number antigens of high molecular weight (Mr 75-250 kDa) located in the acid region of the gel (pI 3-5), while with the control sera no recognition was detected. On the other hand, sera from patients colonized by *Aspergillus* showed cross-reactivity with some antigens of *S. boydii*, but the immunomic pattern was quite different.

CONCLUSION

This study characterizes the most immunoreactive *S. boydii* antigens specifically recognized by sera from CF patients colonized by *Scedosporium* spp. These proteins should be studied further in order to develop a sensitive and specific serological test for improved detection of *Scedosporium* species in CF patients.

Sex differentiation and xenoestrogenic effects in fish: in search of suitable molecular markers

Ainara Valencia, Anthony Nzioka, Oihane Diaz de Cerio, Ibon Cancio and Maren Ortiz-Zarragoitia
Cell Biology in Environmental Toxicology Research Group, Dept. Zoology and Animal Cell Biology and Technology and Research Centre for Experimental Marine Biology and Biotechnology (PiE).

KEY WORDS: sex differentiation, xenoestrogenicity, fish reproduction, intersex, BPG axis.

During the last decade, several studies have been performed in different Basque estuaries, demonstrating the presence of environmental pollutants such as endocrine disrupting chemicals (EDCs) and their effects on aquatic organisms. EDCs are able to interact with the endocrine system of fish and can affect processes as important as sex differentiation and reproduction capacity. In the Basque Coast, such effects have been detected in thicklip grey mullets (*Chelon laborsus*) from several estuaries. These fish show alterations at different levels of biological organization, being the most severe effect the appearance of intersex males, which show oocytes within their testes.

In the last years, we have been studying molecular biomarkers of xenoestrogenicity, sex differentiation and intersex condition. Well-known biomarkers of xenoestrogenicity such as up-regulation of brain and gonad aromatase and hepatic vitellogenin transcription levels have shown altered levels in males and intersex mullets from polluted environments. 5S rRNA levels (which is accumulated in the oocytes for a rapid ribosome assemblage in case of fertilization) can be used as female sex differentiation marker, as allows the identification of oocytes in the testis of intersex males. Moreover, we have also measured transcription levels of other genes related to female sex differentiation (*foxl2*) and male sex differentiation (*dmrt1, sox9, amh*) in mullets. Up-regulation of female related genes and down-regulation of male related genes has been observed in intersex males. Recently, we have focused our attention on the Brain-Pituitary-Gonad axis (BPG axis) as it is the main coordinator, through the gonadotropin hormones (FSH and LH), of the correct timing and functioning of gametogenesis and reproduction in fish. Gonadotropins are directly related to steroidogenesis, as they activate steroid production in the gonads regulating gametogenesis. In addition, steroids can act on the BPG axis modulating the production of gonadotropic hormones. We have analyzed the transcription levels of several genes in the brain (*kiss2, gpr54, gnrh1*), pituitary (*fshβ, lhβ)* and gonads (*lhr, fshr*). Results have shown that transcription alterations are localized mainly at the level of the gonads, suggesting that regulation of such genes occurs at gamete level during intersex condition in testis.

The Oka estuary in Gernika has gained attention, as lately the prevalence of intersex males has been rising, while in female ovaries high prevalences of atresia have been identified. Follicular atresia can be caused by several environmental factors and can compromise the reproductive capacity of a fish population. In fish, oocyte atresia can be regulated by apoptotic and/or autophagocytic events. In this sense, the transcription pattern of *p53*, involved in regulating apoptosis, and of *mdm2*, which regulates *p53* turnover, have been measured in mullet gonads. Moreover, in the BPG axis, FSH has often been defined as an anti-apoptotic hormone, due to its ability to regulate genes involved in cell surviva and linking the gonadotropic system to the atretci responsel. All the obtained results together with the ones yet to come will provide a global overview on the processes that command oocyte differentiation and survival within the testis of thicklip grey mullets under exposure to xenoestrogens.

ACKNOWLEDGEMENTS
Basque Government (IT810-13), UPV/EHU (UFI 11/37), Spanish MINECO and EU-FEDER/ERDF (AGL2015-63936-R).

Vitamin E alleviates non-alcoholic fatty liver disease in phosphatidylethanolamine *N*-methyltransferase deficient mice. The implication of ceramide metabolism

Natalia Presa[1], Robin D. Clugston[2,3], Susanne Lingrell[2,4], Samuel Kelly[6], Alfred H. Merrill Jr.[6], Antonio Gómez-Muñoz[1], Dennis E. Vance[2,4], Rene L. Jacobs[2,4,5], Jelske N. van der Veen[2,4].
[1]Department of Biochemistry and Molecular Biology. Faculty of Science and Technology. EHU/UPV (Basque Country, Spain). [2]Group of Molecular and Cell Biology of Lipids, and Departments of [3]Physiology, [4]Biochemistry, and [5]Agricultural, Food and Nutritional Sciences. University of Alberta (Edmonton, Canada). [6]Schools of Chemistry and Biochemistry, Petit Institute for Bioengineering and Bioscience, Georgia Institute of Technology (Atlanta, USA)

KEY WORDS: non alcoholic fatty liver disease; oxidative stress; vitamin E, antioxidant; ceramide, ceramide kinase.

Phosphatidylethanolamine *N*-methyltransferase (PEMT) enzyme converts phosphatidylethanolamine (PE) to phosphatidylcholine (PC), mainly in the liver. *Pemt*$^{-/-}$ mice are protected from high-fat diet (HFD) induced obesity ans insulin resistance, but develop severe **non-alcoholic fatty liver disease** (NAFLD) when fed a HFD, in part due to an impaired VLDL secretion. Oxidative stress is thought to be an essential factor in the progression from simple steatosis to steatohepatitis. **Vitamin E** is a lipid-soluble antioxidant that has been clinically used to improve NAFLD pathology. Besides, sphingolipids are a major class of membrane lipids that play a fundamental role in membrane architecture and in the regulation of key physiologic processes. Among the sphingolipid family, **ceramides** have been linked to insulin resistance, oxidative stress, and inflammation processes, which suggest that ceramides may play a critical role in development of fatty liver disease.

Our aim was to determine whether supplementation of the diet with vitamin E could attenuate HFD-induced NAFLD and its progression to NASH in *Pemt*$^{-/-}$ mice, and to study whether ceramide metabolism was altered in the disease. Treatment with vitamin E (0.5g/kg) for 3 weeks normalized liver weight, improved VLDL-TG secretion and recovered cholesterol metabolism, but failed to reduce hepatic TG content. Moreover, vitamin E treatment was able to reduce hepatic oxidative stress, inflammation and fibrosis. We also observed abnormal ceramide metabolism in mice lacking PEMT fed a HFD, where acid ceramidase (*Asah1*) and ceramide kinase (*Cerk*) genes were upregulated. This indicates that both genes might be used as novel markers for the disease. Interestingly, vitamin E supplementation also restored *Asah1* and *Cerk* mRNA levels. Together these data suggest that vitamin E treatment efficiently prevented the progression from simple steatosis to steatohepatitis in mice lacking PEMT.

ACKNOLEDGEMENTS: This research was supported by grants IT-1106-16 from 'Departamento de Educación, Universidades e Investigación del Gobierno Vasco (Basque Country, Spain)', SAF2016-79695-R from 'Ministerio de Economía y Competitividad (Madrid, Spain)', and the Canadian Institutes of Health Research (MOP 5182).

Role of Chk2 kinase in G1 checkpoint maintenance after DNA damage

Iraia García-Santisteban[1,2], Alba Llopis[2], Bram van den Broek[2], René H. Medema[2] and Ana Maria Zubiaga[1]
[1]Department of Genetics, Physical Anthropology and Animal Physiology, University of the Basque Country (UPV/EHU);
[2]Division of Cell Biology, The Netherlands Cancer Insitute (NKI).

KEY WORDS: cell cycle, DNA damage, phosphatases.

DNA damage checkpoints are of crucial importance for maintaining genomic stability. Following DNA damage, cells must stop cell cycle progression, maintain the arrest until the repair has been completed, and finally restart the cell cycle. Although the basic machinery that detects the damage is common throughout the cell cycle, subsequent checkpoint establishment and maintenance are different in G1 and G2. In sharp contrast to G2 cells, which lose their ability to recover within a few hours after irradiation-induced DNA damage, G1 cells maintain the recovery competence for several days.

After DNA damage in G1, ATM kinase phosphorylates and activates Chk2, triggering a downstream signaling cascade that prevents cell cycle progression. An initial ATM-dependent response is essential to install a checkpoint arrest. By contrast, ATM is dispensable to perpetuate it, even after one hour following damage. Instead, checkpoint maintenance mainly depends on the downstream target Chk2, which keeps its own activity and sustains the arrest independently of ATM, even when most of the DNA lesions are already resolved. These data suggest that Chk2 might be activated in a DNA damage template-independent manner.

Importantly, fluorescence-activated cell sorting (FACS) experiments reveal that Chk2 activity is specifically lost in those cells that re-enter the cell cycle after the damage. These results suggest the presence of an active phosphatase that inactivates Chk2 to allow cell cycle recovery. To test this hypothesis, we set up a screen with a siRNA library spanning all phosphatases and regulatory proteins. Silencing the phosphatase that dephosphorylates Chk2 could potentially prevent the cell cycle recovery of G1 cells following DNA damage. Results from this screen, which are being validated using deconvoluted siRNA and CRISPR/Cas9 approaches, are enabling us the identification of novel phosphatases required for checkpoint recovery after DNA damage in G1.

Metabolomics, Life Sciences and Analytical Chemistry

Oskar González [1], Oihane Abóniga[1] Maria Encarnación Blanco[2] and Rosa M. Alonso[1]
[1]Analytical Chemistry Department, Faculty of Science and Technology, UPV/EHU
[2]D3 PharmaChemistry Department, Istituto Italiano di Tecnologia,

KEY WORDS: metabolomics, analytical chemistry, health, LC-MS

Metabolomics is the omic science that studies the metabolites, i.e. the organic compounds below <1200 Da present in the biological systems. As the rest of omics it is an holistic science, considering the living systems as a whole and not as the bare sum of the parts. Metabolites are strongly correlated with the phenotype, and therefore, with the actual characteristics of a biological system.

The study of the metabolites can offer useful information about the state of living systems and allow to better understand them. For instance, metabolomics could help to detect illnesses in an early stage or explain the mechanism behind a metabolic process. Metabolomics opens a world of possibilities in Life Sciences and has become a main research target in this field.

Nevertheless, studying a broad range of metabolites in a single analysis is a challenge, especially from the Analytical Chemistry point of view. First, analytical methods that allow the simultaneous detection of those metabolites are required. Then, data treatment capable of distinguishing the metabolites that really matter should be applied. Finally, after identifying those metabolites, a biological explanation can be proposed.

In our research group, we develop Liquid Chromatography-Mass Spectrometry methods for the analysis of biological matrices (plasma, liver, saliva) and we apply them to the metabolomic study of different challenges in Life Sciences. In this moment, we are using animal models to study how organs develop during the first years of life in order to find a solution to one of the main problems in paediatric medicine: adjustment of drug dosage. Nowadays, it is performed using non-reliable methodologies, but if a simple way to know the actual state of development of organs was available, a safer and more effective drug administration could be possible.

An E2F7-dependent transcriptional program modulates DNA damage repair and genomic stability

Jone Mitxelena[1, §, #], Aintzane Apraiz[2, §], Jon Vallejo-Rodríguez[1, §], Iraia García-Santisteban[1], Asier Fullaondo[1], Mónica Alvarez-Fernández[3], Marcos Malumbres[3], Ana M. Zubiaga[1]

[1] Department of Genetics, Physical Anthropology and Animal Physiology, University of the Basque Country UPV/EHU, 48080 Bilbao, Spain

[2] Department of Cell Biology and Histology, University of the Basque Country UPV/EHU, 48080 Bilbao, Spain

[3] Cell Division and Cancer Group, Spanish National Cancer Research Centre (CNIO), 28029 Madrid, Spain.

[§]: The authors wish it to be known that, in their opinion, the first 3 authors should be regarded as joint First Authors

[#] Present address: Department of Molecular Mechanisms of Disease, University of Zurich, Switzerland.

KEY WORDS: E2F, DNA repair, interstrand cross-links.

The cellular response to DNA damage is essential for maintaining the integrity of the genome. Recent evidence has identified E2F7 as a key player in DNA damage-dependent transcriptional regulation of cell cycle genes. However, the contribution of E2F7 to cellular responses upon genotoxic damage is still poorly defined.

Here we show that E2F7 represses the expression of a set of genes involved in the maintenance of genomic stability, both throughout the cell cycle and upon induction of DNA lesions that interfere with replication fork progression.

Acute depletion of E2F7 leads to a reduction in 53BP1 and FANCD2 foci and to fewer chromosomal aberrations following treatment with agents that cause interstrand cross-link (ICL) lesions but not upon ionizing radiation. Accordingly, E2F7-silenced cells exhibit enhanced cell cycle re-entry and clonogenic survival after exposure to ICL-inducing agents.

We further report that expression and functional activity of E2F7 are p53-independent in this context. Using a cell-based assay, we show that E2F7 restricts homologous recombination through the transcriptional repression of RAD51.

Finally, we present evidence that downregulation of E2F7 confers an increased resistance to chemotherapy in recombination-deficient cells.

Taken together, our results reveal an E2F7-dependent transcriptional program that contributes to the regulation of DNA repair and genomic integrity.

Plants, earthworms and bacteria: an integrated approach to assess and recover the health of soils contaminated with chromium (VI) and lindane

Rafael G. Lacalle[a], J.D. Aparicio[b,c], U. Artetxe[a], C. Garbisu[d], M. Soto[c] and J.M. Becerril[a]
[a] *Dpt. Plant Biology and Ecology, University of the Basque Country, Spain*
[b] *PROIMI-CONICET, Argentina*
[c] *Dpt. Zoology and Animal Cell Biology, University of the Basque Country, Spain*
[d] *Soil Microbial Ecology Group, NEIKER-Tecnalia, Spain*

rafael.gomezl@ehu.eus

Industrial activity is responsible for a great variety of contamination scenarios, often including the presence of more than one type of contaminant. Complex environmental problems can be generated when inorganic and organic compounds are simultaneously found in the same site. Tanning industries use compounds containing Cr(VI), an extremely toxic and carcinogenic element. The gamma isomer of hexachlorocyclohexane (lindane), used as insecticide, is an extremely hazardous contaminant. Rhizoremediation is a technology that combines phytoremediation and bioremediation strategies. This technology is most suitable to simultaneously remove organic and inorganic contaminants, while recovering the health of the soil. The aim of this work was to test an integrated methodological approach combining three taxa (plants, earthworms and bacteria), to assess and recover the health of soils contaminated with organic and inorganic compounds.

A greenhouse experiment was carried out using soil, amended or not with organic matter. Both soils were artificially contaminated with lindane (15 mg kg^{-1}) and two different concentrations of Cr(VI) (100 and 300 mg kg^{-1}), keeping non polluted soils as control. The following treatments were applied: i) inoculation of a resistant actinobacteria consortium; ii) growth of *Brassica napus*; iii) application of *Eisenia fetida* earthworms; iv) combination of bacterial consortium and *B. napus*; v) combination of bacterial consortium and worms; vi) combination of bacteria, plant and worms; vii) no biological treatment. Pots were kept in the greenhouse for two months and then plants and soils were sampled. Chromium and lindane concentration in soils and plants was determined. Soil ecotoxicology was evaluated using three types of biological indicators: soil bacterial respiration, root elongation bioassay with *Cucumis sativus*, and Neutral Red Uptake assay in extruded coelomocytes of *E. fetida*.

Organic matter amendment was the most effective treatment recovering soil health, due to a decrease of Cr(VI) bioavailability. Among the biological treatments, the inoculation of the actinobacteria consortium in the presence of plants and earthworms was most effective. When applied singly the inoculation of the consortium was more effective than the plants or earthworms alone. The inoculation of the consortium decreased lindane concentrations, especially in the presence of plants and/or earthworms. Although Cr phytoextraction was negligible, soil ecotoxicity was decreased in all treatments that included the actinobacteria consortium. No correlation was observed between lindane concentration and soil ecotoxicity. Even when contaminants are not fully removed, soil health can be improved by the combination of the three taxa. In conclusion, organic matter and the bacteria consortium are two effective factors on health recovery of soils polluted with Cr (VI) and lindane.

Acknowledgements: This work was financially supported by the projects AGL 2015-64481-C2-1-R and AGL2016-76592-R from MINECO and IT018-16 from the Basque Government. R.G. Lacalle is the recipient of a predoctoral grant from the Basque Government.

Presence of *Vibrio* spp in the Basque coastal area and influence of environmental factors on their survival

Elixabet Ogayar[1]
Maite Orruño[1,2] *and Inés Arana*[1,2]
[1]Department of Immunology, Microbiology and Parasitology (UPV/EHU), [2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV/EHU; Plentzia Marine Station)

KEY WORDS: *Vibrio*, distribution, survival.

The survival of bacteria in changing environments such as natural aquatic systems largely depends on their ability to cope with variations in nutrient availability, temperature, salinity or exposure to solar radiation, being all superimposed on the complex interactions established between microbial populations. Changes in temperature determine the permanence of bacteria in aquatic environments by inducing survival strategies as the entry into viable but nonculturable state (VBNC), the adhesion to biotic and abiotic surfaces and others.

Vibrio genus is a ubiquitous microorganism, inhabiting aquatic ecosystems and, in the last years, its detection in unusual areas and the incidence of *Vibrio*-borne diseases related to contaminated seafood or water consumption have increased.

To determine the importance and space-temporal distribution of this genus in Basque Coastal area, monthly and during an annual cycle, we have collected samples from 3 coastal stations in Bizkay. Samples were used to determined total and culturable heterotrophic bacteria and culturable presumptive *Vibrio* spp. Moreover, some isolates were identified *via* biochemical- and molecular probes (like the 16S rRNA and multilocus sequencing analysis –MLSA-) as *Vibrio* species related with different clades (*V. harveyi*, *V. cyclitrophicus*, *V. tubiashi* and *V. kanaloe*).

Currently, a larger study area comprising coast, estuaries and open water in the Basque coastal area (16 sampling stations) is being sampled quarterly. We are adapting the Fluorescence *in situ* hybridization (FISH) standard technique, widespreadly used for the enumeration of specific microorganisms throughout the detection of ribosomal RNA. The two main reasons for this preliminary work are the diversity of the genus *Vibrio* and the insufficient sensitivity due to the low number of target molecules in marine bacteria. To solve the first problem we are testing different fluorescent probes, recommended in the bibliography, alone and in combination, and to address the question of sensitivity of the technique, we have selected the signal amplification (catalyzed reporter deposition, CARD-FISH) technique. Therefore, we are developing a suitable protocol for the *Vibrio* genus detection in natural habitats.

Moreover, for the environmental *Vibrio* isolates, we have determined survival patterns under stress (starvation, changes in temperature and/or salinities and continuous light radition) and we have compared these patterns with that previously obtained for a control strain, *V. harveyi* ATCC14126^T. Our results indicate that adaptation to starvation is a temperature-dependent process which is accompanied by a reduction of cell size and occasionally leads to the acquisition of the VBNC phenotype. However, the survival pattern differs between species and with the origin of the strain.

This work will be completed by verifying the changes at the level of expression of genes related to the morphology and cell size (such as the mreB gene) and the determination of the variation of the outer membrane proteome attributable to the upshift of temperature.

In vitro models of infection to study the virulence of the pathogenic fungus *Aspergillus fumigatus*

Guruceaga X., Perez-Cuesta U., Arbizu-Delgado A., Martin-Souto L., Buldain I., Antoran A., Aparicio L., Pellon A., Hernando F.L., Ramirez-Garcia A.& Rementeria A.

University of the Basque Country UPV/EHU, Fungal and Bacterial Biomics Research Group. Dept. of Immunology, Microbiology and Parasitology, Leioa, Spain

KEY WORDS: *Aspergillus fumigatus*, RAW 2647.7, A549, Microarray.

BACKGROUND

Aspergillus fumigatus is a greater conidia producer saprophytic mold. These conidia can maintain during long time in the air and could reach the lung epithelium through the airways. Once in this site the fungus could avoid the weak macrophage response in immunosuppressed patients and finally penetrates the alveolar epithelium and germinate creating invasive hyphae that are able to disseminate trough the bloodstream causing fungal disseminated diseases, named invasive aspergillosis (IA). The better knowledge of the fungal virulence mechanism and its behavior during the first steps of an infection is important in order to improve the understanding of the infection. Classically, these studies have been developed using animal models that requires the approval of the Ethics Committees, which recommend that animal models are replaced or limited. Our purpose is study the first steps of the fungal infection using cell cultures as an alternative method through transcriptomic studies using the microarray technology.

METHODS

Two independent *in vitro* models of infection were developed. For that, *A. fumigatus* conidia were incubated with the murine macrophages RAW264.7 or the bronchial epithelium cell line A549 in a multiplicity of infection of 10 and 5 respectively. Cell cultures were grown in RPMI 1640 medium (10% of fetal bovine serum, 2 mM of glutamine and 2 mM of Penicillin-Streptomycin mix) and were incubated at 37ºC in presence of 5% of CO_2. When the fungus reached 30% of germination, cell lines were lysed and fungal cells were recovered in order to carry out a total RNA extraction. The fungus growing alone was used as control.

Fungal RNA was extracted and hybridized with the whole genome microarray *Agilent Whole A. fumigatus Genome Expression 44k v.1* (AWAFUGE v.1). The dataset were analyzed following an own programation code based in Bioconductor using a combination of *normexp* and *quantile* routines followed by a linear model with Benjamini-Hochberg correction. Differentially expressed genes (DEGs) were defined by comparison with the control situation ($p < 0.05$) and the results were expressed in $\log_2$FC.

RESULTS

Among the 9,630 fungal genes represented in the microarray, 22.2% and 55.3% of them were DEGs in contact with macrophages and bronchial epithelium respectively. Among those genes up-regulated we highlight genes related with tyrosine metabolism, and in consequence, with pyomelanin production, acidic phosphatases related with thiamine metabolism and genes related with fumagillin production. In previous studies carry out by our group after mice infections some of this genes were also detected.

CONCLUSIONS

During the *in vitro* contact between *A. fumigatus* with the principal cell line types present in the pulmonary environmental, several metabolic pathways and virulence factors, previously detected during a mice infection, showed an up-regulation pattern of expression. This fact make interesting the using of the *in vitro* models to study the virulence factors of the fungus in a reliable way.

FINANCIAL SUPPORT

This work was partly funded by the UPV/EHU grants (GIU15/36 and PPG17/41). Xabier Guruceaga, Leire Martin Souto and Idoia Buldain have been supported by Pre-doctoral Research Grants of the Government of the Basque Country.

Chemical interactions behind toxicological effects: sorption of persistent organic pollutants to plastics and carbon nanomaterials

Ignacio Martínez-Álvarez[1,2], Hélène Budzinski[2], Miren P. Cajaraville[1], Amaia Orbea[1]

[1]CBET Res Group, Dept. Zoology and Animal Cell Biology, Faculty of Science and Technology and Research Centre for Experimental Marine Biology and Biotechnology PiE, University of the Basque Country UPV/EHU; [2]Environnements et Paléoenvironnements Océaniques et Continentaux (EPOC), Equipe de Physico et Toxico-Chimie (LPTC)- UMR 5805 CNRS, Université de Bordeaux.

KEY WORDS: persistent organic pollutants, micro- and nanoplastics, carbon nanomaterials, chemical interactions, biological effects.

Presence of plastic debris at sea is being perceived as a global-scale problem and is increasingly attracting the attention of the media and society. It has become evident that large pieces of plastics, such as bottles, bags and fishing nets, pose a risk for marine mammals and for big and medium-size fish. But this is just the tip of the iceberg. Plastic items at sea undergo a series of transformation processes, including mechanical breakage, photo- and bio-degradation. This results in the appearance of small plastic pieces known as micro- (MPs, <5 mm) or nanoplastics (NPs, <100 nm), depending on their size. MPs and NPs can also be specifically manufactured for industrial and domestic applications, which results in an additional source of pollution. Once at sea, MPs and NPs become available to biota and enter into the food web.

Plastic is not an inert polymer, but it contains a complex mixture of chemical substances added during its manufacture to achieve desired plastic properties (color, malleability, etc). Many of these substances, which can be released from plastics during weathering, are well known by toxicologists due to their toxic effects on biota, often related to reproduction impairment or cancer development.

MPs and NPs are not the only particulate hazard to aquatic wildlife. Nanomaterials are emerging as new concerning pollutants and their presence in aquatic environments is thought to raise in the near future. The amazing development of Nanotechnology is leading to the design and fabrication of new materials with applications in all imaginable fields, including environmental protection and remediation. In the later field, carbon-based nanomaterials (CNMs), such as graphene or carbon nanotubes, are very promising tools for innovative water cleaning technologies. These are based on the the physico-chemical properties shared by CNMs and MPs and NPs: their large surface to volume ratio and high hydrophobicity allow them to adsorb dissolved pollutants from the water column, mainly hydrophobic organic contaminants known for their persistence in the environment. As a result, plastic particles and CMNs could act as Trojan horses by delivering adsorbed persistent organic pollutants (POPs) to aquatic organisms.

Thus, the present research aims to address the potential risks for the aquatic environment posed by CNMs, MPs and NPs alone and in combination with POPs. For this, first we characterised the adsorption of POPs to selected CNMs and plastics, for which a specific methodology was developed. Our initial results with the model polycyclic aromatic hydrocarbon (PAH) benzo(a)pyrene (BaP) and polystyrene MPs and NPs show that the capacity of ad/absorption of polystyrene microbeads is directly dependent on their size. The percentages of ad/absorbed B(a)P from the total B(a)P solution were 90.88% and 37.18% for 0.5 µm and 4.5 µm MPs, respectively. Currently, similar studies are being carried out using a complex mixture of PAHs, such as that present in the water accommodated fraction of a crude oil. 4.5 µm MPs were able to ad/absorb between 17 and almost 80% of the compound depending on the PAH. All this chemical characterisation of the interactions between POPs and particulate pollutants are the basis for the design of the studies focused to address the potential modulatory capacity of plastics and CNMs on the bioavailability of POPs to aquatic organisms.

Funded by Spanish MINECO (NACE project — CTM2016-81130-R), Basque Government (consolidated research group IT810-13), UPV/EHU (UFI 11/37 and PhD fellowship to Ignacio Martínez-Álvarez) and French ANR (No.–10-IDEX-03-02 and Cluster of Excellence COTE (ANR-10-LABX 45).

Eclosion, survival and individual growth of Eisenia andrei in soil from three different vegetation units

Esther Iparraguirre-Bolaños and M. Mercedes Ortega-Hidalgo
University of the Basque Country, Faculty of Science and Technology, Animal Physiology.
esther.oparraguirre@ehu.eus; mercedes.ortega@ehu.eus

KEY WORDS: *Eisenia andrei*, Growth, Survival, Vegetation units, Soil respiration

Edaphic organisms are considered keystone species in the maintenance of soil health and, among them, earthworms cause special interest for their role in the conservation of edaphic properties, helping to maintain soil structure, and for their positive interactions with soil microbiota and plants. For this reason, in this work our aim has been to analyse the suitability of soils from different vegetation units to support active populations of the earthworm *Eisenia andrei* using soil from *Eucalyptus globulus* plantation (EP), forest dominated by *Quercus robur* (FQR) and Scrub dominated by *Crataegus monogyna* (SC) focusing on the nutritional value of their litter layer for epigeic earthworms. Two control substrates were employed: Horse manure (HM) and Coconut coir (CC). Eclosion success, survival and growth of newly hatched *Eisenia andrei* specimens were analysed. Initial characteristics of substrates displayed the highest organic matter percentage in CC, followed by HM and the lowest organic content was obtained in SC; however, CC displayed the lowest figures for soil respiration (virtually zero). A negative relation was established between substrate respiration ($\mu LO_2\ h^{-1}\ g^{-1}$) and fibre (% of organic matter), with the exception of HM. Regarding eclosion success, a significant influence of the substrate was found in the initial biomass and the total biomass per cocoon, observing the highest figures in CC and SC, which is explained by the increment in the rendering time in the cocoon associated with an unfavourable environment. Survival percentage differed highly between substrates being 100 %, 90 %, 80 %, 67 % and 60 % in HM, EP, FQR, SC and CC respectively. Growth patterns also differed largely among substrates and we obtained average maximal live weights (MLW) of 247, 117, 56, 19 and 10 mg in HM, EP, FQR, SC and CC respectively. Survival and growth were positively related to substrate organic matter percentage (except CC) and to substrate respiration ($\mu LO_2\ h^{-1}\ g^{-1}$). Overall, a decrease of the non-fibre organic content (% of dry matter) of substrates and an increase in the proportion of their fiber content (% of organic matter), would account for the lower digestibility of the organic matter for both soil microorganisms and earthworms, redounding in lower live expectancy and growth for epigeic earthworms.

Does genetic influence Cross training athletes´anaerobic power and capacity?

Ramírez de la Piscina X[1,2], Diaz J.[1] Larruskain J[1], Castañeda[3], bores A[4]. Muñoz I[4], Álvarez J[1]., Martínez I[2], Antúnez A[2]., Odriozola I[2], Ruiz de Gauna N[1], Caballero A[1,5]., Irazusta J[5]., Lleida A[1], Buide E[1], Ahedo L[1]., Ascension A[1], Revilla M[1], and Odriozola A. [1,2]

Corresponding author: adrian.odriozola@ehu.eus

[1]Department of Genetics, Physical Antrhopology and Animal Physiology. University of Basque Country; [2]KDNA Genomics; [3]Sport Sciences. University of Deusto.; [4]Sport Sciences. University of Atlantic; [5]Department of Physiology, Faculty of Medicine and Nursing, University of the Basque Country

KEY WORDS: Sport, Lactate, Performance, Cross training, training, SNP, Genetics

Cross training or concurrent training, was originally designed to train individuals such as police officers and military Special Forces, who requires physical fitness and muscle strength, to transform from low to high levels of effort in a second. So and to improve movement efficiency, the cross training programs incorporates functional movements to promote muscle strength and cardiorespiratory fitness.

FROM SCIENCE TO PERFORMANCE

Our aim is to determine the association between genetic factors and inter individual variability in endurance, strength, power, flexibility, neuromuscular coordination and nutrition, in order to use this molecular tool in individualization of training programs.

For that reason, we carried out in a population of cross training amateur athletes, the following analytical tests:

- Wingate Anaerobic Test (WAnt): The WAnT is an “all out” 30 s cycling maximal effort test, to evaluate anaerobic performance. The absolute and the relative (per body weight in kg) mean power and the peak power over the entire 30 s were calculated for each participant.
- Anthropometric measurements: height, weight, body mass (BM) and body fat Percentage based on 8 skin folds. These variables are indicators of the athletic status of the subject.
- Lactate measurements: lactate is the final metabolite of glycolysis and is a good indicator of muscle fatigue. Capillary blood samples were taken from the ear lobe in different moments around the Wingate Test, and blood lactate was immediately determined using portable lactate monitors.
- Benchmark workouts questionnarie: participants had to fill in a questionnaire about common workouts in CrossFit and Powerlifting.

Finally and on the practical implications, coaches will can consider this knowledge to design personalized recovery times, both during training and in competition. In this sense, looking for the polymorphisms associated with anaerobic metabolism can provide a valuable tool to individualize training programs aimed at improving health and performance.

BIBLIOGRAPHY

- Cupeiro, R, Benito, PJ, Maffulli, N, Calderón, FJ, and González-Lamuño, D. MCT1 genetic polymorphism influence in high intensity circuit training: A pilot study. J Sci Med Sport 13: 526–530, 2010.
- Brooks, GA. The lactate shuttle during exercise and recovery. Med Sci Sports Exerc 18: 360–8, 1986
- Fedotovskaya, ON, Mustafina, LJ, Popov, D V., Vinogradova, OL, and Ahmetov, II. A Common Polymorphism of the MCT1 Gene and Athletic Performance. Int J Sports Physiol Perform 9: 173–180, 2014.

Bacterial resistance to stress. *Vibrio* spp. in the aquatic systems

Maite Orruño[1,2], Vladimir Kaberdin[1-3] and Inés Arana[1,2]
Elixabet Ogayar[1], Alba Pascual[1], Ana Lomba[1] and Natalia González[1]
[1]Department of Immunology, Microbiology and Parasitology (UPV/EHU), [2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV/EHU; Plentzia Marine Station), [3]IKERBASQUE, Basque Foundation for Science

KEY WORDS: *Vibrio*, adverse environments, ocean warming

In the last decade, presumably as a result of the increase in surface water temperature, the detection of facultative pathogenic *Vibrio* strains and the incidence of *Vibrio*-borne diseases related to water use have increased. Some adaptation mechanisms have been proposed to promote the persistence of *Vibrio* spp. in marine systems under starvation by means of induction of the viable but nonculturable state (VBNC) or by increasing bacterial adhesion to biotic and abiotic surfaces or morphological changes. At the same time, bacteria-controlling microorganisms are also affected by global warming, which control their own survival and predatory/lytic activity on bacteria.

In the Basque Country, there are no studies focused on analyzing the distribution and survival of *Vibrio* spp. present in our coasts, although, considering our geographical situation and the coastal water uses, the changes in their distribution could have an important health, tourism and environmental impact. In this context, our group has initiated the study of the temporal/spatial distribution of *Vibrio* spp. in the coast, estuaries and open water of the Basque coastal area.

For comparison, we study the survival patterns developed by a *V. harveyi* type strain and other environmental *Vibrio* species, isolated from seawater. Our recent work on survival of *Vibrio* spp. has shown that survival under starvation conditions is a temperature-dependent process, which is accompanied by a reduction of cell size, proteomic changes and, occasionally, leads to the acquisition of the VBNC phenotype. In a similar way, solar radiation and other essential abiotic factors, such as salinity, also affect survival of *Vibrio* spp.; nevertheless, we observed differences in the survival patterns of laboratory and environmental strains wich can be attributed to the complexity and diversity of *Vibrio* genus.

Despite significant progress achieved in testing survival capacities of *Vibrio* species, relatively little is known about the effect of biotic factors on *Vibrio* populations. Our data show that predation by protozoa is the main factor eliminating *Vibrio* spp., and temperature modulates the complex interrelationships that are established between the bacterivorous protozoa and their preys.

In the environment, numerous vibrios remain attached to the surface of marine organisms (crustacean, zooplancton and others); this constitutes a defensive strategy to escape protozoan grazing and enables their mechanical translocation to other areas. Therefore, our future studies will be focused on the study of *Vibrio* spp. adhesion ability to marine organisms and on the comparative analysis of the survival responses developed by planktonic and adhered populations under stress conditions.

The techniques and methodologies used include epifluorescence microscopy, fluorescence *in situ* hybridization, analysis of bacterial proteome, etc.

Using biogenic magnetic nanoparticles in magnetic hyperthermia for cancer treatment

David Muñoz[1,2], Lourdes Marcano[2], Iñaki Orue[3], Javier Alonso[4], Ana García Prieto[5,6], Alicia Muela[1,6] and Mª Luisa Fdez-Gubieda[2,6]

[1]Departamento de Inmunología, Microbiología y Parasitología (UPV/EHU); [2]Dpto. Electricidad y Electrónica (UPV/EHU); [3]SGIker Medidas Magnéticas; [4]Dpto. Ciencias de la Tierra y Física de la Materia Condensada (UC); [5]Dpto. Física Aplicada I (UPV/EHU); [6]Basque Center for Materials, Applications and Nanostructures (BCMaterials).

KEY WORDS: Magnetotactic bacteria, magnetosomes, magnetic hyperthermia, antitumoral treatment.

Magnetotactic bacteria are ubiquitous aquatic microorganisms able to produce genetically controlled intracellular magnetic nanoparticles called magnetosomes. These organelle-like nanostructures show several outstanding physical and magnetic properties, such as an uniform morphology, a narrow size distribution or a high biocompatibility due to the presence of a lipid bilayer surrounding the mineral core of the nanoparticle, that make them suitable for biomedical applications [1].

In particular, magnetosomes have attracted great attention since they have shown high potential in magnetic hyperthermia for cancer treatment. In this technique, the treatment makes use of the heat-releasing power of magnetic nanoparticles when exposed to an alternating magnetic field (AMF). This toxic heat can kill the cancer cells by reaching temperatures around 42-45 °C, without affecting the healthy tissue, due to the higher sensitivity of tumoral cells to temperature increase [2].

The goal of our work is to check the efficiency of magnetosomes as magnetic hyperthermia agents, trying to understand the main mechanism of their heat production. Moreover, we analyze their impact on cell viability *in vitro*. Regarding the first question, the heat production or specific absorption rate (SAR) is based on intrinsic hysteresis losses -related to magnetic properties of the magnetosomes-, obtaining high values under concrete conditions of the AMF. Concerning the effect on cell viability, our results show cell death caused by the hyperthermia treatment, as well as cell growth inhibition provoked by the presence of the magnetosomes inside the cells. Specifically, only around 25% of the treated cells remained alive 24 h after AMF exposure [3].

These promising results open up the possibility of using magnetosomes as effective agents in hyperthermia-based anticancer therapies.

[1] E. Alphandéry, *Front. Bioeng. Biotechnol.* **2** (2014)

[2] D. Ortega Ponce, Q. Pankhurst, *Nanoscience*. **60** (2012)

[3] A. Muela, et al., *J. Phys. Chem. C.* **120** (2016)

Understanding disorders of the visual system and promoting repair and regeneration

Xandra Pereiro[1], Noelia Ruzafa [1] Arantxa Acera[1], Haritz Urcola[2] Alex Fonollosa[2], Itziar Martinez[2], Roberto Fernandez[2], Jimena Baleriola[3], Javier Araiz[2], Juan Durán de la Colina[2], Elena Vecino[1]
[1]Dept. Cell Biology and Histology UPV/EHU, [2]Dept. Ophthalmology UPV/EHU, [3]Achucarro Centre for Neurosci.

KEY WORDS: visual system, eye, glaucoma, repair, tears, reina, regeneration, GOBE.

The GOBE (Grupo de Oftalmo Biología Experimental) www-ehu.es/GOBE is a multidisciplinary research group interested in eye research. The group are integrated by ophthalmologists, biologists and veterinarians. Currently, GOBE have 17 members: 10 doctors and 2 PhD students, 3 TFG and 2TFM students.
The PI of the group is Elena Vecino Full Professor at the Faculty of Science and Technology. The laboratory is placed in the Faculty of Medicine in the Dept. of Cell Biology and Histology. The group is a consolidated group that has been collaborating for 23 years. During that period, the members of the group have published more than 150 papers and 20 Doctors have been trained, some of them are Ophthalmologist that works in Hospitals such as Cruces, San Eloy, Donostia and Txagorritxu. The members of the group are also attached to Biocruces, Biodonosti and BioAraba and collaborate with national and international groups in Universities of Munich, New York and Cambridge among others.
The methods and techniques that we use include animal models of glaucoma, primary cell culture, immunohistochemistry, proteomic, lipidomic, electron microscopy, use of biomaterials etc.

Our objective is to understand the cellular and molecular basis of a disease with the idea of future clinical applications.

The group have 4 principal lines of research:
1-Neuroprotection and Glaucoma (Prof. Elena Vecino and Prof. Javier Araiz). The retina is composed of groups of highly specialised cells that convert light energy into visual signals. Retinal ganglion cells (RGCs) collectively transmit visual information from the retina to several regions in the brain. Glaucoma is a neurodegenerative disease and cause leading of irreversible blindness that it is caused by the death of RGCs. Retinal glia-neuronal ganglion cells relations are important for normal function, and by studying their molecular interactions, we hope to understand how we can prevent cell death and thus, blindness.

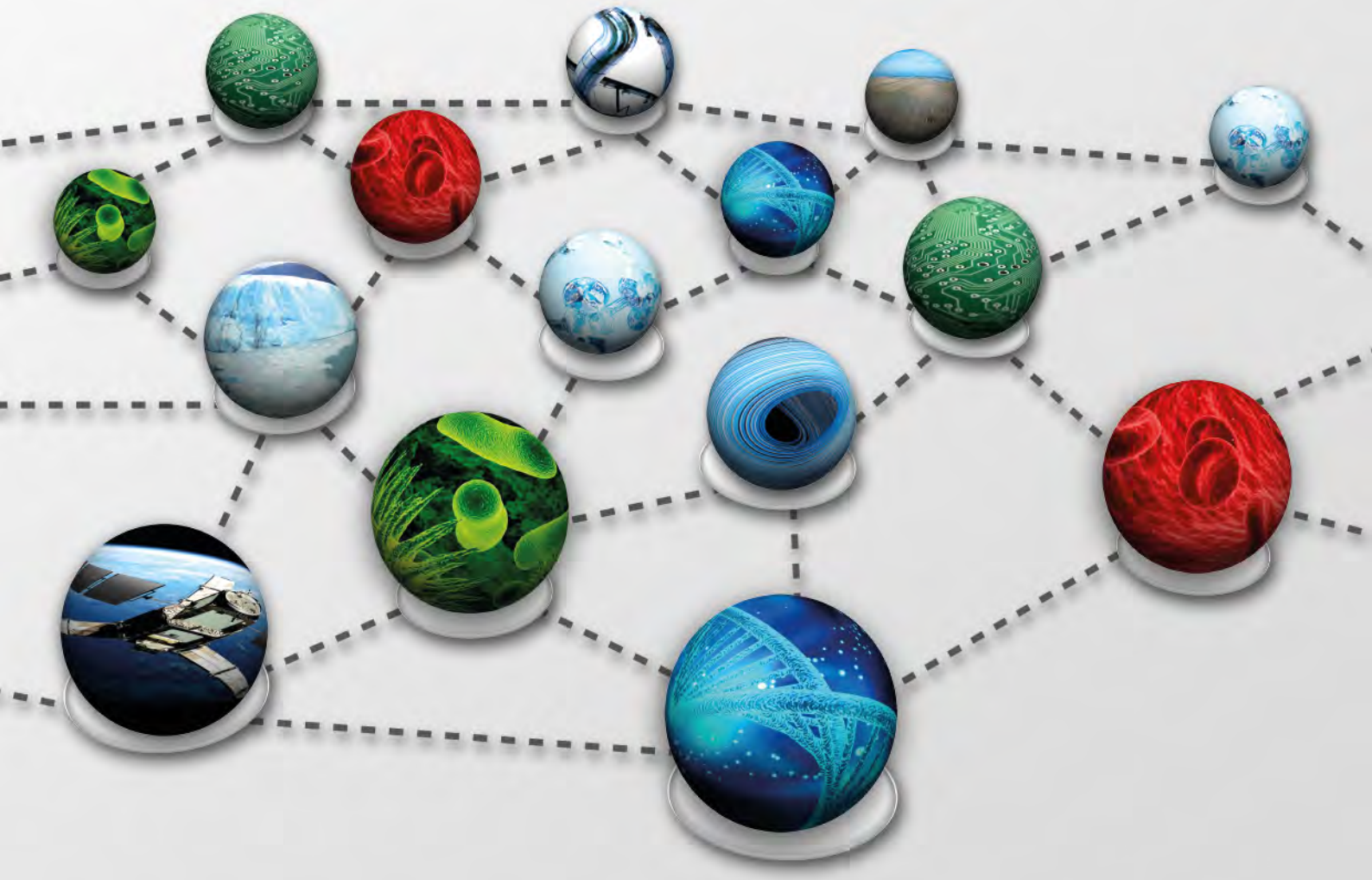
2- Ocular Surface (Prof. Juan Durán and Dra. Arantxa Acera). The main objective is to identify biomarkers in tears, as a source of information for the ocular surface in different diseases with the idea to design artificial tears that could promote the repair of the injured ocular surface.

3- Analysis of aqueous humor in glaucoma (Dr.Haritz Urcola). Aqueous humour is a transparent, gelatinous fluid that is located in the space between the lens and the cornea. Lack of circulation of aqueous humour is one factor that increases intraocular pressure in glaucoma. We analyse the biophysical properties of aqueous humour in patients with glaucoma to detect changes compared with healthy eyes. Alterations in its composition may help us understand more about how glaucoma progresses

4- Uveitis (Dr. Alex Fonollosa) Uveitis is a term describing a group of inflammatory diseases that produces swelling and destroys eye tissues. This line studies cultured cells to test the possible action of somatostatin in the tight junctions formed in the retina-pigment epithelium with the aim of developing clinical applications. Moreover we are testing the effect of anti-inflammatory substances in different ocular tissues in vitro.

FISIKA ETA INGENIERITZA ELEKTRONIKA

FÍSICA E INGENIERÍA ELECTRÓNICA



Diziplina Anitzeko Sareak Ehunduz

Tejiendo Redes Multidisciplinares

Radiative heat losses of V-4Cr-4Ti candidate alloys for fusion reactors

I. González de Arrieta [1], T. Echániz[2], R. Fuente[2], I. Urcelay-Olabarria[1], M.J. Tello[3] and G.A. López[1]
[1]Applied Physics II, University of the Basque Country UPV/EHU, Leioa, 48940, Spain;
[2]Faculty of Engineering, University of the Basque Country UPV/EHU, Bilbao, 48013, Spain;
3 Condensed Matter Physics, University of the Basque Country UPV/EHU, Leioa, 48940, Spain.

KEY WORDS: infrared emissivity, vanadium alloys, fusion energy.

V-4Cr-4Ti alloys are the most advanced candidates for structural applications in the first wall/blanket of nuclear fusion reactors. The directional spectral emissivities of two V-4Cr-4Ti alloys have been measured between 200 ºC and 750 ºC, before and after a high-temperature treatment was performed. Both alloys show a weak temperature dependence, and no significant differences were found between the shapes of their directional spectra. Nevertheless, the thermal treatment above 1000 ºC induced an emissivity increase, particularly in one of the samples, which was alloyed with a dispersion of Ti_3SiC_2 nanoparticles. This could enhance the refrigerating capability at high temperature of these alloys by means of thermal radiative heat loss. The directional results have been integrated in order to estimate the total hemispherical emissivity, which is the key heat transfer parameter in the high-temperature high-vacuum environments of fusion reactors.

Relativistic effects and many-body interactions in systems with strong spin-orbit coupling

Peio Garcia-Goiricelaya [1,2], Jon Lafuente-Bartolome [1,2], Haritz Garai-Marin [1,2], Idoia G. Gurtubay [1,2] and Asier Eiguren [1,2]

[1] Materia Kondentsatuaren Fisika Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, 644 Postakutxatila, E-48080 Bilbao, Basque Country, Spain.
[2] Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 Donostia, Basque Country, Spain.

KEY WORDS: Computational many-body physics, electron-plasmon, electron-phonon, spin-orbit coupling.

Theoretical condensed-matter physics involves the use of mathematical and computational models in order to understand and describe the physical properties of materials. These models have as starting point an *ab-initio* description of matter, that is, a definition based on first-principles: the quantum mechanics of electrons and atomic nuclei.

However, solving many-body problem is a challenging task, requiring the use of wise approximations and complex mathematical tools, as well as high-performance supercomputing. In our research group we develop efficient numerical methods and implement novel theoretical and computational techniques for solving interesting and challenging problems in solid state physics.

We are particularly interested in materials whose surfaces are composed of heavy atoms, in which strong relativistic spin-orbit coupling (SOC) introduce new and interesting physics arising from significant SOC-induced splitting of the surface bands. Likewise, surface states acquire a well defined spin-polarized texture even in nominally nonmagnetic systems, as a result of the consideration of non-collinear spinor wave functions. Indeed, in these materials the spin degree of freedom does not remain just as a trivial integrable magnitude, but it is at the origin of exceptional spin-related conduction properties, as happens, for instance, in the promising field of spintronics (electronics based on the electron spin). Nevertheless, such features can be strongly influenced by many-body effects.

In this sense, we focus on the many-body interactions that lead to collective oscillations of the electronic charge and/or spin density (plasmons and spin-plasmons) and collective oscillations of the crystal lattice (lattice vibrational modes or phonons). We also study how these collective oscillations affect, at its turn, the electron dynamics, that is, the electron-plasmon and electron-phonon coupling. For this purpose, we employ a formulation of the many-body problem based on Green's functions, obtained by solving the Dyson equation, which incorporate the many-body interactions by treating the interacting particles as dressed independent particles with modified or renormalized properties.

Simulating the early universe

Joanes Lizarraga [1], Asier Lopez-Eiguren [1,2], Jon Urrestilla [1]
[1]Department of Theoretical Physics, University of the Basque Country UPV/EHU [2]Department of Physics and Helsinki Institute of Physics, University of Helsinki

KEY WORDS: cosmology, early universe, inflation, topological defects, CMB, gravitational waves.

The physics behind some of the processes that took place at the early universe, such as inflation, reamains as one of the biggest questions of the contemporary cosmology. Even though there exists a variety of different proposals based on high energy physics, the correct physical model for the first moments of the universe has not been discovered yet.

The events ocurred at the early universe involved extremely high energetic processes, which would have created an unequivocal imprint on some cosmological observables such as potentially measurable backgrounds of gravitational waves or anisotropies on the Cosmic Microwave Background (CMB).

Some of the most interesting candidates to uncover the physics behind those events are the cosmological phase transitions and the topological defects (cosmic strings, monopoles, textures...) that are inevitably created after them. Despite their microscopical origin, they can create potentially observable cosmological signals like those mentioned previously.

Our research, in collaboration with international groups, aims to improve the understanding of the early universe studying the physics of cosmological phase transitions and topological defects. In order to accomplish that we perform massice numerical simulations to try to reproduce the conditions under which those processes took place. In this respect we have developed powerful simulations based on the most modern numerical technics. Our main objectives can be summarized as follows:

1. Improve the understanding of the evolution of cosmological phase transitions as well as of different topological defects.

2. Calculate as accurately as possible the potentially observational signals that they could have created. Especially we focus on the computation of the cosmological graviational background and the anisotropies of the temperature and polarization of the CMB.

3. Evaluate the validity of the physical models under study comparing our predictions with the most modern cosmological data, *e.g.* LIGO, VIRGO and LISA for gravitational waves and Planck for the CMB.

Gaussian Random Fields as toy models for the String Theory Landscape

Mikel A. Urkiola[1], Jose Juan Blanco-Pillado[1] and Kepa Sousa[2]
[1]UPV/EHU, Theoretical Physics and History of Science dept.; [2]Instituto de Física Teórica, Madrid

KEY WORDS: String Theory, landscape, cosmology, inflation, false vacuum decay

String Theory has acquired an ever increasing popularity as a candidate for a unified theory of Fundamental Physics at high energy scales. One of the central statements of the theory is the existence of more than 4 spacetime dimensions, which in turn requiere *compactification methods*, techniques to contract extra dimensions so as to make them directly unobservalble, for the explanation of our low-energetical 4-dimensional spacetime.

The main consequence of the application of these mechanisms is the arisal of a high-dimensional scalar potential, known as the *String Theory Landscape,* whose properties not only characterize fundamental particles, but also other big-scale processes such as Cosmological Inflation or the formation of vacuum bubbles via *False Vacuum Decay.*

The main objective of this research is the elaboration of Landscape models using different statistical tools such as Gaussian Random Fields and Slepian models, along with Flux Compactification models, in order to characterize these models both from the analytical and statistical point of view and to check for viability for Inflation and False Vacuum decay in them.

Magnetotactic bacteria as theranostics agents

Lucía Gandarias [1,2], David Gandia [2,3], Mª Luisa Fernández-Gubieda [2,3], Alicia Muela [1,3], Ana García [3,4] and Javier Alonso [5]

[1]Inmunología, Microbiología y Parasitología (UPV/EHU); [2]Electricidad y Electrónica (UPV/EHU); [3]Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park; [4]Física Aplicada I (UPV/EHU); [5]Ciencias de la Tierra y Física de la Materia Condensada (UC).

KEY WORDS: Magnetotactic bacteria, microrobot, biomedicine, magnetosomes, hyperthermia, magnetism, anticancer.

Magnetotactic bacteria are aquatic microorganisms that swim along the Earth's magnetic field lines towards low oxygen regions, using chains of magnetic nanoparticles biomineralized internally, called magnetosomes. The bacteria use the chain as a compass needle. The different species of magnetotactic bacteria synthesize perfectly stoichiometric magnetite nanocrystals, with genetically controlled sizes and shapes, surrounded by a biocompatible membrane, making them ideal for biomedical use. Our projects are oriented in two complementary directions: first, the thorough study of the magnetic properties of the magnetosomes and its relation with other nanoparticle systems, and second, the exploitation of magnetotactic bacteria for biomedical applications.

Lucía´s PhD project: The main objective is to use the magnetosomes, as anticancer agents. In fact, magnetosomes are magnetic and as such can be heated up by the effect of alternating magnetic fields. If they are placed close to the tumour cells, they can heat up these cells debilitating them. This technique is called magnetic hyperthermia. Alternatively, being magnetic means that the magnetosomes and the bacteria themselves, with the magnetosomes inside, can be guided to the tumour site by external magnetic fields. If drugs are attached to the magnetosomes or to the bacteria, the drug delivery can be localized avoiding undesired effects on healthy tissues. These potentialities of magnetosomes as anticancer agents are to be developed in this project at an *in vitro* level. This main aim will imply culturing and standardizing the bacterial production and magnetosome isolation of three species of magnetotactic bacteria, studying the cytotoxicity and interaction with tumour cells, functionalizing the magnetosomes with drugs or tumour specific ligands, and finding the optimal technical parameters (magnitude of the applied field, frequency, concentration, etc.) that optimize the anticancer performance of magnetosomes.

David´s PhD project: The aim of this PhD project is to take advantage of the magnetic and oxygen sensing of the magnetotactic bacteria in order to develop biological nanorobots capable of targeting and killing cancer cells in a controlled and highly efficient way, by releasing anticancer drugs and heat in the tumour area. The project brings together condensed matter physics, magnetism, microbiology, nanomedicine, and robotics, and it will clearly have a broad positive impact on the modern society. The interdisciplinary research programme includes the magnetic and structural characterization of magnetotactic bacteria, the study of their movement under applied magnetic fields and oxygen gradients in a microfluidic chip fabricated by photolithography, and the design and implementation of a workstation to monitor, guide, and heat up the bacteria, aimed at assessing the suitability of magnetotactic bacteria as potential cancer therapy agents.

Artificial Neural Networks and their applications on pattern recognition and function approximation for autonomous vehicles

Óscar Mata Carballeira[1]
[1]Digital Electronics Design Group (GDED)
Department of Electricity and Electronics

KEY WORDS: autonomous vehicle, advanced driving assistance systems, computational intelligence, artificial neural networks, machine learning, function approximation, image recognition, data reduction.

Autonomous vehicles and Advanced Driving Assistance Systems (ADAS) are incipient industrial and research topics on which pattern recognition and approximation of functions play an important role. In this context, Artificial Neural Networks (ANNs) have consolidated in the last decades as an accurate way of performing tasks requiring image recognition, i.e. pedestrian and traffic sign identification, as well as driver profiling from driving data.

Basically, ANNs emulate structures of biological brains, with discrete units (neurons) organized in layers and interconnected between them. Each neuron is mathematically modeled as a sum of products which excites an activation function. Once the neurons are modeled, the structure is defined depending on the application. There are, eventually and very simplistically, two families of structures:

1. **Shallow Networks:** On which, added to the input and output nodes, only one layer of neurons is placed between them.
2. **Deep Networks (Deep Learning):** More than one layer of neurons is placed between input and output nodes.

Evidently, the more layers between input and output nodes, the more complex and time consuming the ANN becomes, so, deciding the adequate structure is one of the keys to meet the objectives of accuracy and speed (usually set in advance).

On the other hand, not only is the structure important to reach an adequate trade-off between velocity and precision, but also the algorithm we select to solve the problem. There are two approaches on this topic:

1. **Traditional algorithms:** Which are based on minimizing a cost function in order to tune the parameters of each neuron individually. These algorithms are usually very sensitive to local minima.
2. **Extreme machine learning (ELM):** Assumes that the parameters of the intermediate layers are randomly generated, and the only weights that need to be tuned are those of the output nodes.

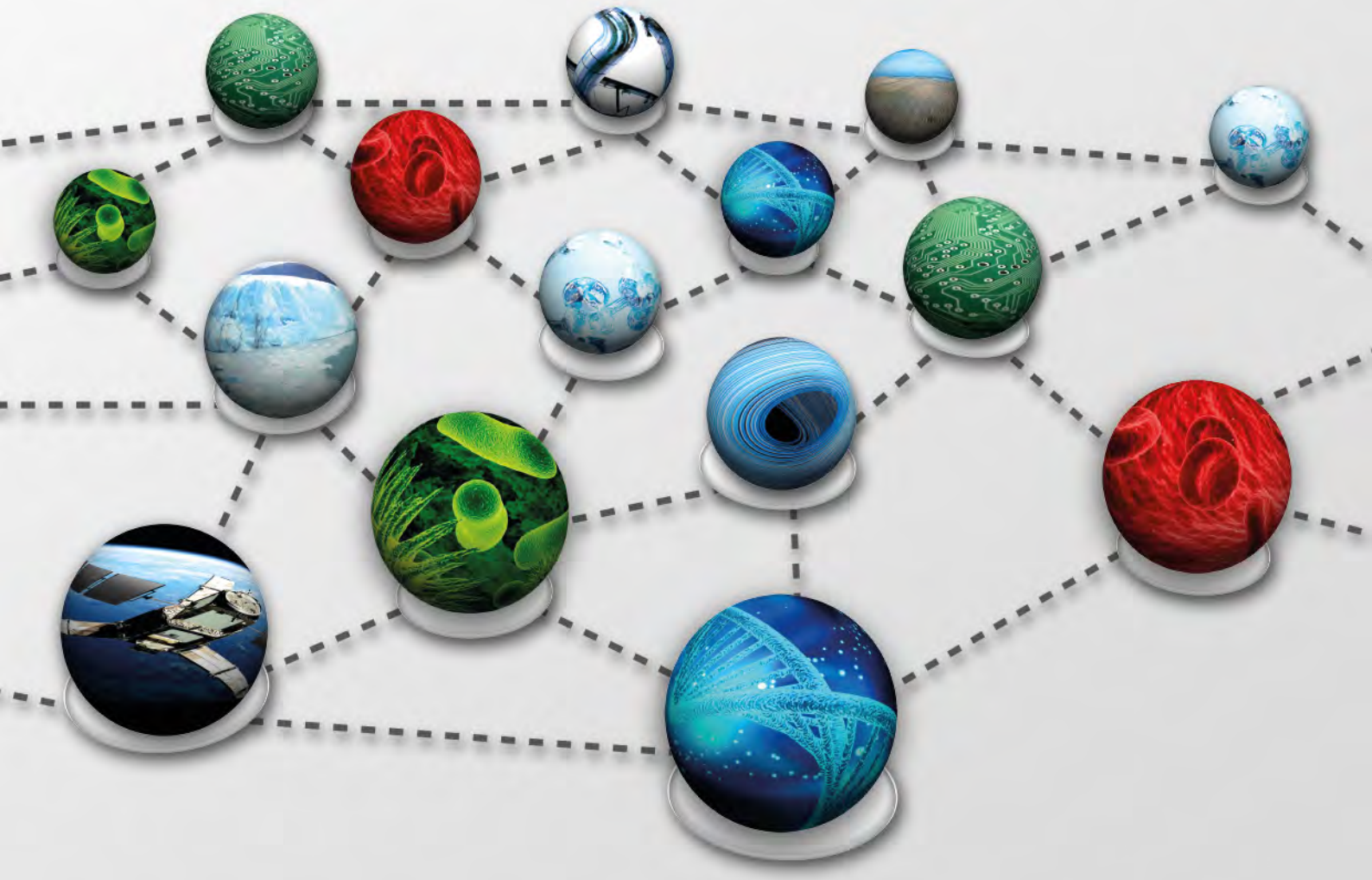
In addition, the format of the data we introduce in an ANN has an important role on its performance. Usually, performing some transformations on the data makes the whole ANN perform much better than if we had input the same data in a non-transformed format. These modifications are known as data reduction and they are related to introducing the main characteristics instead of raw data. This is crucial, for example, in handwritten character and traffic signs recognition. For this task, we have been working on two methods:

1. **Principal Component Analysis (PCA):** Which uses Algebra concepts (eigenvalues and eigenvectors) to reduce problems' dimensionalities.
2. **Extreme Learning Machine-Autoencoder (ELM-AE):** This is a particular application of a Shallow-ELM based on making the intermediate layer contain a certain family of input data features.

Combining all these tools, we develop applications based on real world data collected from a variety of sources, ranging from the MNIST handwritten characters database to real driving data collected from instrumented cars. Finally, ANNs have proved their performance as reliable tools for facing the challenge of autonomous driving.

GEOLOGIA

GEOLOGÍA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

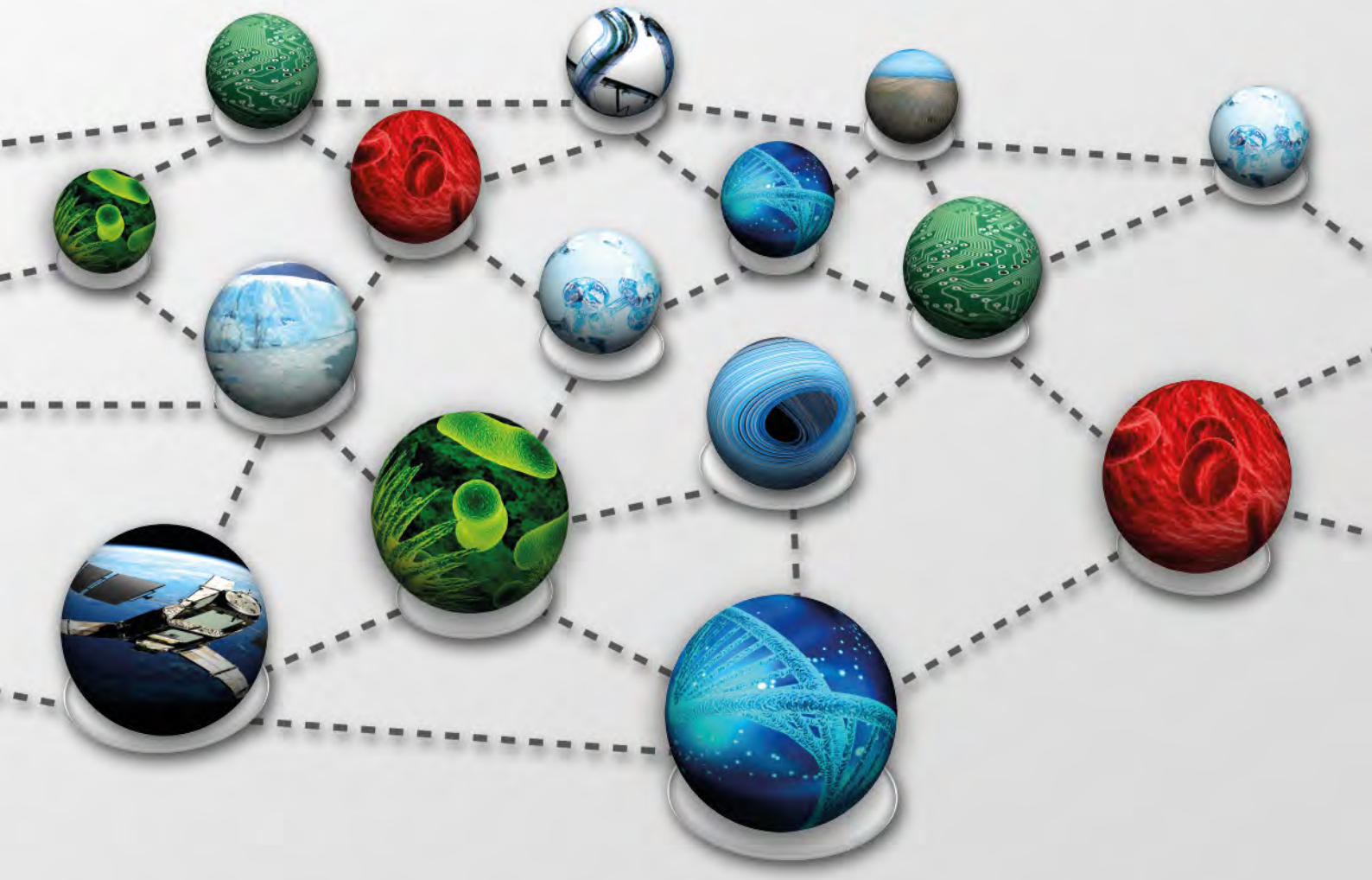
A geochemical and microfaunal approach to the recent environmental transformation of the Bilbao and Urdaibai estuaries

Humberto Serrano[1], Alejandro Cearreta[1]and María Jesús Irabien[2]
[1]Departamento de Estratigrafía y Paleontología, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, Apartado 644, 48080 Bilbao; [2]Departamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, Apartado 644, 48080 Bilbao.

KEY WORDS: sediments, estuaries, metals, benthic foraminifera, Anthropocene.

The combined estudy of hevy metals and benthic foraminifera in surficial and cored sediments has allowed the reconstruction of the environmental history of the Bilbao and the Urdaibai estuaries to be made. While the former appears as an example of a very deteriorated area, due the to complete reclamation of the original estuarine domains, the severe pollution of waters and sediments and the degradation of biota, the latter is one of the best preserved coastal environments of the Basque Country. However, even in this exceptional area, it can be recognized the fingerprint of ancient reclamation processes for agricultural activities.
Notwithstanding that Earth has probably entered a new geological epoch, the Anthropocene, defined by human impact, evidences of ongoing processes of environmental regeneration can be also found in both estuaries.

MATEMATIKA
MATEMÁTICAS



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Comparison of the performance of different correction methods when correcting for the optimism of the AUC

Amaia Iparragirre[1], Irantzu Barrio[1,3] and María Xosé Rodríguez-Álvarez[2,4]
[1]Departamento de Matemática Aplicada, Estadística e Investigación Operativa (UPV/EHU); [2]BCAM – Basque Center for Applied Mathematics; [3]Red de Investigación y Servicios de Salud en Enfermedades Crónicas (REDISSEC); [4]IKERBASQUE, Basque Foundation for Science.

KEY WORDS: logistic regression, AUC, optimism correction.

Prediction models play an important role in daily clinical practice. Their use has increased during the last years. Prediction models provide clinicians with a tool to identify individuals at higher risk, and thus help in the decision making process. When a prediction model is developed, the aim is usually to apply it into new patients in order to make predictions for them. During the development process of a prediction model, if the same data is used to fit the model and to evaluate its predictive performance (which is usually denoted as apparent performance), an optimism could appear given that the most model fitting strategies rely on optimality criteria for the data used. Therefore, in order to guarantee model's usefulness and accuracy when applied to new patients, the validation or correction of this optimism is required. The best strategy to evaluate the performance of a prediction model, is to apply it into new data (i.e., to apply the model to individuals that have not been used in the development process of the model). Unfortunately, in practice, most of the times it is not possible to obtain new data for that purpose given that it is often not available or difficult and expensive to collect. For this reason, some approaches have been proposed in the literature to correct for the optimism internally (i.e., re-using the available data). The most popular approaches are the split-sample (which is probably the most commonly used method in medical research), cross-validation and bootstrap techniques.

This study, focuses on logistic regression models where we measure model's predictive performance by means of the area under the receiver operating characteristic (ROC) curve (AUC). The performance of different correction methods has been compared in previous studies, when correcting for the optimism of the apparent AUC. In particular, Austin and Steyerberg (2017), Smith et al. (2014) and Steyerberg et al. (2001,2003) all focus on logistic regression models and they study the impact of different events per variable (EPV) on the performance of the methods. Nevertheless, in practice, other factors besides of the EPV could affect the behavior of the methods. Thus, in this study, we aim to go further. An extensive simulation study has been conducted considering different scenarios taking into account a) the number of covariates in the model, b) the available sample size, c) the prevalence; and/or d) the correlation among covariates. In addition, in contrast to the above-mentioned studies, this simulation study has been conducted in a situation where the theoretical logistic regression model is known.

The results of the simulation study suggest that the optimism of the apparent AUC increases as the sample size and prevalence decrease, and the number of covariates and correlation among covariates increase. The results also suggest the use of *k*-fold cross-validation with replication and bootstrap. In particular, for small sample size and low prevalence the bootstrap is the most appropriate correction method, according to these results. We do not recommend the use of the split-sample validation and the *k*-fold cross-validation without replication because of the large variability or the worse performance of the final model obtained with the split-sample validation.

Funding: This study was partially supported by grants Severo Ochoa Program SEV-2013-0323, Basque Government BERC Program 2014-2017, IT620-13 from the Departamento de Educación, Política Lingüística y Cultura del Gobierno Vasco and MTM2016-74931-P from the Ministerio de Economía y Competitividad and FEDER.

On solving the Orienteering Problem via an efficient Evolutionary Algorithm

Gorka Kobeaga [1,3], María Merino[1] and Jose A. Lozano[2,3]
[1] Dep. of Applied Mathematics and Statistics and Operations Research, UPV/EHU;
[2]Dep. of Computer Science and Artificial Intelligence, UPV/EHU
[3]BCAM - Basque Center for Applied Mathematics

KEY WORDS: orienteering problem, combinatorial optimization, evolutionary algorithm.

The Orienteering Problem (OP) is a relevant problem in network optimization. It considers a full graph, where the nodes have an associated profit and the edges a weight representing the distance between the nodes. The goal of the OP is to find a single route that maximizes the total collected profit subject to a total distance limitation; therefore, it is not mandatory to visit all the nodes. OP is a mixture between two classical combinatorial problems, the Travelling Salesperson Problem (TSP) and the Knapsack Problem (KP). In fact, it is NP-hard problem. Since [1] first introduced the term OP, several variants have been added, such as the Team OP, the OP with Time Windows, the Time-Dependent OP and the Stochastic OP. These problems have many applications in production management, e-commerce and tourist tour planning, see [2].

In order to solve this problem, we have developed an evolutionary algorithm, whose key characteristic is to maintain unfeasible solutions during the search, the so-called Evolutionary Algorithm for the Orienteering Problem (EA4OP). We propose a novel solution codification for the Orienteering Problem, a novel heuristic for node inclusion in the route, an adaptation of the Edge Recombination crossover developed for the TSP [3], specific operators to recover the feasibility of solutions when required, and the use of the Lin-Kernighan heuristic to improve the route lengths.

We compare EA4OP on 344 benchmark instances [4], with up to 7397 nodes, with three state-of-the-art algorithms for the problem, one exact and two heuristics. Specifically, we compare our approach with a Branch-and-Cut [5], a two-parameter iterative algorithm described in [6] and the Greedy Randomized Adaptive Search Procedure with Path Relinking [7]. The results [8] show a competitive behavior of our methodology in instances of low-medium dimensionality (up to 400 nodes), and outstanding results in the large dimensionality instances reaching new best-known solutions with lower computational time than the state-of-the-art algorithms.

References:
[1] B.L. Golden, L. Levy and R. The orienteering problem. Naval Research Logistics, 34 (3) (1987), pp. 307-318.
[2] A. Gunawan, H. ChuinLau and P. Vansteenwegen. Orienteering Problem: A survey of recent variants, solution approaches and applications. European Journal of Operational Research, 225 (2016), pp. 315-332.
[3] D. L. Whitley, T. Starkweather, and D. Fuquay, Scheduling problems and travelling salesman: The genetic edge recombination operator, Proc. of the Third Int. Conf. on Genetic Algorithms (San Mateo, CA) (J. David Schaffer, ed.), Morgan Kaufmann (1989), pp. 133–140.
[4] G. Reinelt, TSPLIB - A Traveling Salesman Problem Library, ORSA Journal on Computing 3 (1991), no. 4, 376–384.
[5] M. Fischetti, J. J. Salazar-González, and P. Toth, Solving the orienteering problem through branch-and-cut, INFORMS Journal on Computing 10 (1998), 133–148.
[6] J. Silberholz and B. Golden, The effective application of a new approach to the generalized orienteering problem, Journal of Heuristics 16 (2010), no. 3, 393–415.
[7] V. Campos, R. Martí J. Sánchez-Oro, and A. Duarte, Grasp with path relinking for the orienteering problem, Journal of the Operational Research Society 65 (2014), no. 12, 1800–1813.
[8] G. Kobeaga, M. Merino and J.A. Lozano, An efficient evolutionary algorithm for the orienteering problem, Computers & Operations Research 90, pp. 42-59.

Mathematical Control Theory for Evolution Equations

Jone Apraiz Iza[1], Aingeru Fernández Bertolin[1]
[1]Departamento de Matemáticas, UPV/EHU;

KEY WORDS: Control theory, parabolic evolution equations, null-controllability

We will divide this talk in two parts. First, we will outline the research lines of the "Mathematical Analysis and Applications" research group at the Math Section of the UPV/EHU, where we focus on several branches of mathematical analysis and mathematical physics, included in 6 different national and international projects.

To give a few examples, our group is currently working on the development of methods for the analysis, numerical approximation and control of partial differential equations in natural processes. We are also interested in problems related to harmonic analysis and their interactions with partial differntial equations, such as the uncertainty principle and the study of the vortex filament equation, and in the theoretical and numerical analysis of evolution equations.

As an example of the latter, in the second part of this talk we will see some ideas about the mathematical control theory applied to evolution equations. The purpose of this topic is to drive the solution to an evolution equation to a prescribed state starting from certain initial condition. One acts on the equation through a source term, a so-called distributed control, or through a boundary condition. To achieve general results one wishes for the control to only act in part of the domain or its boundary and to have as much latitude as possible in the choice of the control region: location, size, shape.

We will see some results we obtained where we proved the interior and boundary null-controllability of some parabolic evolutions with controls acting over measurable sets. This is a joint work with professor Luis Escauriaza.

On the Evolution of the Vortex Filament Equation for Initial Polygonal Data

Francisco de la Hoz
Dpto. Matemática Aplicada y Estadística e Investigación Operativa (UPV/EHU)

KEY WORDS: Vortex filament equation, PDEs, Numerical Analysis, Generalized quadratic Gaussian sums, Fractals, Randomness

Abstract

In this talk, we will consider the evolution of the so-called Vortex filament equation:

$$\mathbf{X}_t = \mathbf{X}_s \wedge \mathbf{X}_{ss},$$

taking initial polygonal data. First, we will consider the evolution of a regular planar polygon [1,2,3]; this case is closely related to the generalized quadratic Gaussian sums, exhibits remarkable fractality phenomena, and has a completely random behavior. Then, we will briefly expose how the results can be generalized to more general polygons, which is a topic on which we are currently conducting research.

Acknowledgments

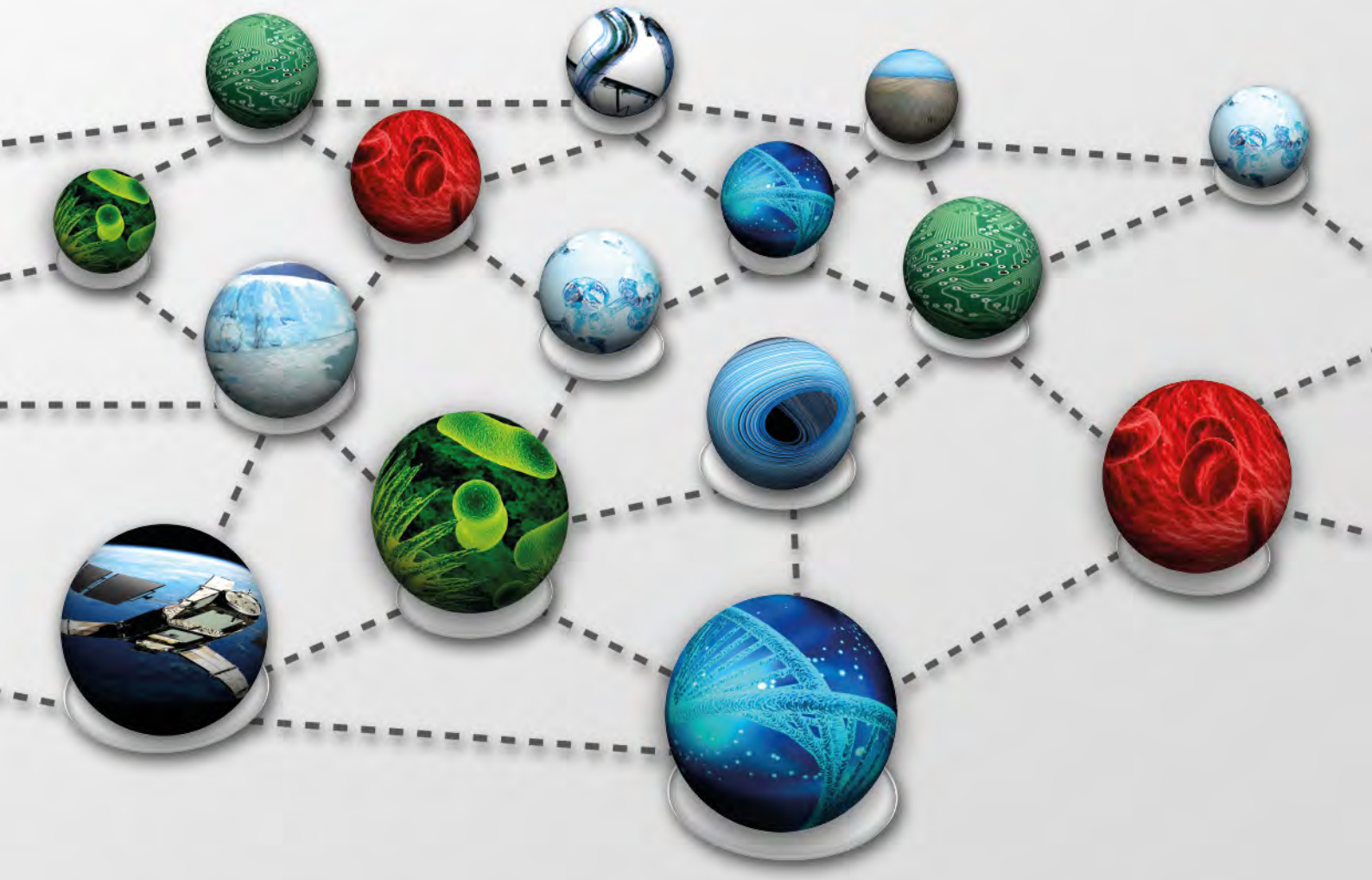
This work was supported by an ERCEA Advanced Grant 2014 669689 - HADE, by the MINECO projects MTM2014-53850-P, MTM2011-24054 and SEV-2013-0323, and by the Basque Government project IT641-13.

References

[1] F. de la Hoz, L. Vega, *On the Relationship between the One-Corner Problem and the M-Corner Problem for the Vortex Filament Equation*, arXiv:1707.09408 (2017).
[2] F. de la Hoz, L. Vega, *The Vortex Filament Equation as a Pseudorandom Generator*, Acta Appl. Math. 138:1 (2015), 135-151.
[3] F. de la Hoz, L. Vega, *Vortex filament equation for a regular polygon*, Nonlinearity 27:12 (2014), 3031-3057.

KIMIKA

QUÍMICA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Two-compartment in vitro PK/PD models to study the resistance of *Candida Glabrata* to antifungal drugs

Beatriz Uribe [1], Oskar González[1] , Boubakar Ba[2] , Rosa M. Alonso[1] and Karen Gaudin[2]
[1]FarmArteM research group, Analytical Chemistry Department, Faculty of Scieence and Technolgy, University of the Basque Country (UPV/EHU)
[2]Chembiopharm research group, Analytical chemistry, UFR Sciences pharmaceutiques, Université de Bordeaux.

KEY WORDS: Antifungals, Caspofungin, HPLC, Fluorescence.Resistance,

During the last three decades, the incidence of invasive fungal infections has drastically increased. Despite the impact of these infections the therapeutic choices are limited. The echinocandin drugs (micafungin, anidulafungin and caspofungin) are the preferred choice to treat a range of candidiasis, but increasing clinical failures due to resistant organisms are appearing, especially among Candida species. The resistance *of candida glabrata* to antifungals as triazoles family is known and now the rising resistance to echinocandins is a cause of alarm.

The challenge of the research presented will be to avoid resistant strain emergence of *candida glabrata* to the echinocandin caspofungin (Image 1). For that, an In vitro pharmacokinetic/pharmacodynamic (PK/PD) model is going to be used to combat the lack of clinical trials and to animal model drawbacks. The two-compartment in vitro PK/PD system simulates human metabolism (absorption, distribution and elimination of plasma kinetic profile) and exposes microorganisms to changing antifungal drug concentrations.

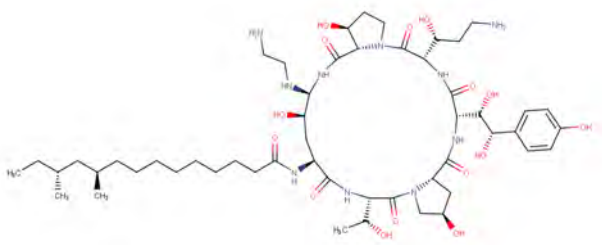


Image 1: Caspofungin molecule

Since the pharmacologically active fraction of drug is the free fraction, simulated profiles in the in vitro PK/PD model must be simulated under these conditions. Taking into account therapeutic caspofungin concentration in human , and its high plasma protein binding (96%), analytical methods able to quantify at least 0.01 µg/ml must be developed.

Therefore, selective and sensitive analytical methods for the quantitative evaluation are required for the successful conduct of PK studies. Because of the high number of samples and the small volume of withdrawn sample from the model (50 µl sample), liquid chromatographic methods with direct injection of culture medium and on-line concentration and extraction are required. An on-line SPE extraction method coupled to a HPLC analysis with fluorescence detection will be developed and optimized.

Restoration and Memory Recovery of high Historical Cultural value building of Punta Begoña Galleries

C. García-Florentino [1], J. A. Carrero[1], O. Gómez-Laserna[1], L. Blanco-Zubiaguirre[1], L. Kortazar[1], H. Morillas[1], I. Marcaida[1], S. Fdez-Ortiz de Vallejuelo[1], A. Gredilla[3], N. Prieto-Taboada[3], I. Martínez-Arkarazo[1],M. Maguregui[2], M. Olivares[1], M. Olazabal[1], K. Castro[1], G. Arana[1], L. A. Fernández[1], J.M. Madariaga[1]

1 Department of Analytical Chemistry, Faculty of Science and Technology, University of Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, 2Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, P.O. Box 450, 01080, Vitoria-Gasteiz,; 3 Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country UPV/EHU, P.C. 2018 San Sebastian, Basque Country, Spain.

KEY WORDS: Material Characterization, Material degradation, Soil, Metals, Particulate Matter, Biocides, Percolation waters, rock cleaning treatments, XRF, ICP-MS, Raman Microscopy

Punta Begoña Galleries were built in 1918 for an important businessman, Horacio Echevarrieta and were abandoned in 1960 and forgotten by society for years. In October 2014, the city council of Getxo promoted a revalorization project together with the Basque government and the University of Basque Country (UPV/EHU) in order to restore and recover their value for the citizens. Punta Begoña Galleries are located in Getxo, in front of Ereaga beach and the Arriluze harvour. Inside this interdisciplinar project researchers from different fields (chemistry, (hidro)geology, architecture, archaeology, history, etc.) are developing different research works. In particular, IBeA research group has been encharged of the following studies:

1. Material original composition characterization: The multianalytical approach employed showed that the main composition of the mortars was calcite, gypsum and quartz. In addition, alite and belite were also identified in rendering mortars, which are specific compounds of Portland Cement (maybe one of the first places in Spain where this Cement was used).

2. Chemical and biological degradation processes of the materials: The most important chemical pathologies identified were, loss of original material because of solubilization processes, hydration and dehydration cycles of gypsum giving rise to fractures. Aesthetic impact of material surfaces due to different biological colonizations (algae, yeast, fungi, lichens, bacteria, etc.) and growing of black crusts (gypsum crusts with airborne particulate matter trapped in their porous structure).

3. Cleaning treatments for different ornamental rock types (lithotypes) affected by the biological colonizations. First of all a chemical treatments based on the application of several biocides were studied. However these chemical treatments were very aggresive for some of the materials. On the other hand, the mechanical polishing turned out to be more appropiate, which only implied 1 mm of surface erosion.

4. Study of the contamination impact. On the one hand, the atmospheric particulate matter was studied. With this aim, two different passive samplers were designed for the fast and easy collection of the suspended particulate matter. The colllected filters were analysed by Raman Microscopy, SEM-EDS and micro-XRF. These analyses showed the major presence of NaCl due to the marine aerosol, gypsum and other sulphates. The elemental characterization suggested the major presence of Fe particle depositions together with some Zn and Cu. A second study of the atmospheric contamination characterization and effect was carried out for the quantification of dicarboxylic acids in marine aerosol and mortar samples using a new developed mixed mode SPE-GC-MS method. Different seasonal sampling campaings were performed during 2017. Oxalic acid was the major compound found in both kind of samples. All these identified contaminants in the atmosphere can induce an impact on the building materials of the Galleries. On the other hand, the presence of metals (depth profiles) in the soils of the gardens above the Galleries and in the percolation water flowing through the Galleries was evaluated. High concentrations of Pb, Zn, As, Cr, Cu, Cd and Ni were idenfied in the surface of the soils coming from the deposition of contaminats from the industrial and portuary activities. Whereas Al, Mo, Sb, Ba and Pb were the metals with the highest concentrations in the percolation waters.

Feasability of passive dosing methods for in vitro toxicological tests risk of petroleum hydrocarbons in accidental spills

Denis Bilbao[1], Amaia Igartua[1], Laura de Miguel[3], Nagore Gonzalez[3], Tamer Hafez[3], Xabier Lekube[2-3], Urtzi Izagirre[2-3], Amaia Orbea[2-3], Maitane Olivares[1-3], Aresatz Usobiaga[1-3], Ailette Prieto[1-3] and Nestor Etxebarria[1-3]
[1]Department of Analytical Chemistry UPV/EHU
[2]Department of Zoology and Animal Cell Biology, UPV/EHU
[3]Plentzia Marine Station, UPV-EHU

KEY WORDS: Accidental oil-spills, Arctic environment, Ecotoxicological assessment, Water Accomodated Fraction, Passive dosing

Marine traffic in arctic seas shows a growing trend and the effects on the arctic environment are a matter of increasing concern, especially due to the high probability of accidental oil spills. As a consequence of the environmental threats, international institutions and governments are fostering the study of marine oil spill response technologies in the cold climate area and the assessment on the impacts on fish, invertebrates and macro algae of naturally and chemically dispersed oil, in situ burning residues and non-collected oil using highly sensitive biomarker methods.

One of the typical approaches to study the toxicological effect of oil emulsions in marine biota is the use of the water accommodated fraction (WAF) prepared according to standard procedures. In addition to this, the assurance of long and stable exposures to very hydrophobic compounds such as the polycyclic aromatic hydrocarbons (PAHs) for in-vivo and in-vitro tests requires the use of sensitive and precise analytical techniques.

In order to overcome the difficulties of classical approaches, we have explored the feasibility of the passive dosing approach. Within this context, the main aims of this work were to study the features of the WAF prepared according to the agreed procedures and to study the feasibility of a passive dossing method to run in-vitro essays.

All the analysis was carried out by gas chromatography coupled to mass spectrometer in order to analyse PAHs and lineal aliphatic hydrocarbons. In this sense, the most abundant PAH of the raw oil was phenantrene at a concentration of 209 µg/g. The rest of the PAHs were detected between 4 and 108 µg/g. In the case of lineal aliphatic hydrocarbons, the most important one was the C34 at 37 mg/g. On the contrary, the rest of the aliphatic compounds were detected between 2.0 and 9.5 mg/g.

Regarding to the preparation of the WAF, a small and handy procedure was designed allowing the preparation of up to 130 ml of WAF at different temperatures and including the loading of a small sheet (1 cm^2) of polydimethylsiloxane (PDMS) as a passive sampler. The kinetics of the oil-water-PDMS sheet partitioning was studied and it was concluded that the steady state was achieved after 150 h of soft stirring. The composition of the WAF at this steady-state was measured by solid-phase microextraction (SPME). Finally, the stability of the WAFs at room temperature was also studied and, according to the preliminary results, the most abundant PAHs are lost in the early five hours.

Based on the loaded PDMS sheets during the preparation of the WAFs, the feasibility of these sheets to run in-vitro tests is being studied. The preliminary results show very low concentrations of the most abundant PAHs in both the sheets and the obtained water solutions, but compared to the standard WAFs longer stable exposures are observed. In addition to this, fish embryo tests were carried out to support this feasibility study.

In order to achieve higher loadings and doses, a new procedure is being also tested. In this case, instead of PDMS sheets, O- rings are used and instead of being loaded when WAFs are prepared, methanolic oil solutions will be used. The results obtained through this approach will be discussed.

ACKNOWLEDGEMENTS

This work is being carried out through funding provided by the GRACE project (Integrated oil spill response actions and environmental effects). H2020-BG-2015-2

Development of microfluidics Devices for Biomedical Applications: Surface Engineering and Integration of Smart Materials

Maite Garcia-Hernando, Alba Calatayud-Sanchez, Marina Oronoz, Jaione Etxebarría-Elezgarai, Lourdes Basabe-Desmonts and Fernando Benito-Lopez

Microfluidics Cluster UPV/EHU, University of the Basque Country UPV/EHU, Spain

KEY WORDS: microfluidics, Lab-on-a-chip, smart materials, surface engineering.

Lab-on-a-Chip" (LOC) has the greatest potential for integrating multiple functional elements into a small device to produce truly sample-in/answer-out systems. The design, fabrication, flow control, analysis and connection techniques are under continuous development improving among others, throughput and automation while at the same time leading to reduced costs [1]. Here we present the development of micro-technologies based on surface engineering, for biomedical applications in LOC devices.

Surface engineering within the channel of the microfluidic device enables the study of cellular behaviour, since it is possible to adequately position cells in an array format, in a controlled manner. Figure 1 (left) presents a "lauburu" shaped protein pattern for cell adhesion. Figure 1 (right) shows the integration of smart materials into microfluidic devices also with defined structures (in this case a start shaped array).

Then, cell adhesion happen on the functionalised surface of the microfluidic device and biological studies could be performed on a highly controlled environment within the microfluidic device, Figure 2 [2, 3].

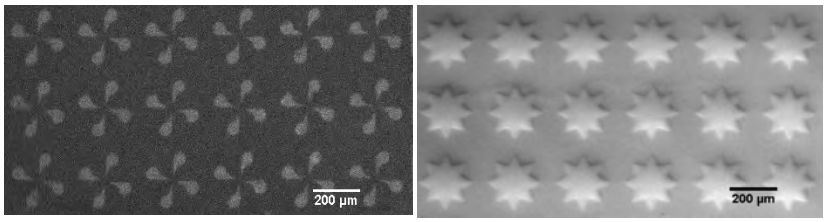


Figure 1. Pictures of patterns of different compositions. Fluorescence microscopy picture of a fluorescent protein pattern done by Microcontact Printing (left) and Optical Microscopy picture of ionogel microestructures fabricated by photolithography (right).

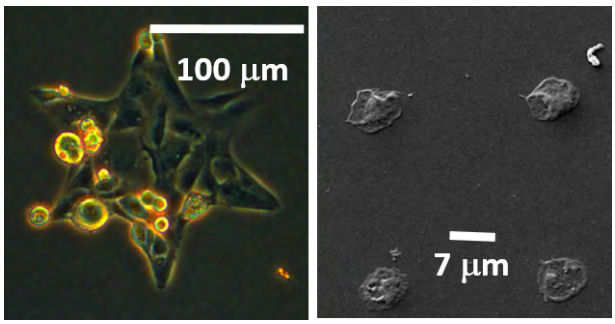


Figure 2. Pictures of patterned surfaces with fibroblast within a start shape adhesion protein surface (left), and a single platelet array (right).

References:

[1] Low Cost Origami Fabrication of 3D Self-aligned Hybrid Microfluidic Structures, J. Saez, L. Basabe-Desmonts,* F. Benito-Lopez, *Microfluidics and Nanofluidics*, **2016**, 116, 1-7.

[2] Cyrille Hamon, Malou Henriksen-Lacey, Andrea La Porta, Melania Rosique, Judith Langer, Leonardo Scarabelli, Ana Belén Serrano Montes, Guillermo González-Rubio, Marian M. de Pancorbo, Luis M. Liz-Marzán, Lourdes Basabe-Desmonts **T**unable Nanoparticle and Cell Assembly Using Combined Self-Powered Microfluidics and Micro-contact Printing *Advanced Functional Materials*, **2016**, 26, 8053 – 8061.

[3] C. Hamon, S. Novikov, L. Scarabelli, L. Basabe-Desmonts, L.M. Liz-Marzán Hierarchical self-assembly of gold nanoparticles into patterned plasmonic nanostructures *ACS Nano*, **2014**, 8, 10694 – 10703.

Development and extension of new analytical methods for dating documents applying invasive and non-invasive techniques

Laura Ortiz Herrero[1], María Luz Alonso Alonso[1], Miren Itxaso Maguregui Olabarria[2]
[1]Analytical Chemistry Department, Faculty of Science and Technology, UPV/EHU, Bizkaia. [2]Painting Department, Faculty of Fine Arts, UPV/EHU, Bizkaia.

KEY WORDS: forensic science, questioned document, ink dating, GC/MS, DR-UV-vis-NIR, chemometrics

Written documents have always played an important role as they are the primary source of information and they are used as a medium of communication in many areas. Questioned document examinations are highly demanded in civil and criminal cases related to the manipulation and falsification of documents. Counterfeit the signatures, inscriptions and dates with ink pens are typical ways of forgery. Forensic document examiners handle different types of questioned documents such as checks, contracts, testaments, acknowledgments of debt, threatening letters, which can be found in a variety of criminal investigations. The legitimacy of an ink entry is often an important question during forensic investigation of questioned documents. In this way, the ability to determine the approximate age of an ink stroke when it was deposited on the document would help to solve this problem. For this reason, significant research effort has been directed towards development of ink dating methods.
Pen inks are multicomponent chemical systems and the specific composition of the ink is often unknown. All ink components can yield important analytical information. Ink components undergo various physical and chemical transformations over time. Moreover, the mechanism of ink ageing is influenced by interactions with the support and external factors. In real casework, no information about these factors is generally available. Three main approaches can be applied for ink dating: static, absolute dynamic and relative dynamic. In these approaches, accelerated artificial aging treatments can be used to imitate the degradation processes, using them as reference materials to naturally aged documents.

This work aims to develop and extend new analytical methodologies that allow to move forward in questioned document examination; without document destruction and extending the application range to documents older than 2 years and to different pen brands, and in that way overcome forensic caseworks. Analytical methods that include chromatographic techniques, i.e. HPLC and GC, and spectroscopic techniques, i.e. FTIR, Raman and UV-vis-NIR, coupled with chemometrics have been used for ink dating and examination. These methods will help to respond with greater confidence to judicial issues of great relevance and economic and social impact.

In this work an ink dating method using multivariate chemometrics based on the monitoring of the UV-vis-NIR diffuse reflectance spectra modifications over time was developed. Inks were exposed to accelerated aging, their reflectance spectra were measured and a PLS multivariate regression model was performed. Mathematical treatments of the spectroscopic data were carried out to enhance the prediction ability of the model and the qualitative interpretation of the spectra. This way, a prediction model capable of dating inks up to five years (RSD of 25 %) was developed and the relation between the natural and the accelerated aging was determined. Moreover, the regions of the spectra influenced by the aging mechanisms of ink components was identified. Inks sharing a common dye chromatographic profile showed to fit well in the predictive model, implying that the method shows a great potential for future applications in the field of questioned documents dating.

Food Safety: Analytical methodologies applied to quality control of meat products

O. de la Hera, N.Ayarza, R.M: Alonso
Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU)

KEY WORDS: Efflorescences, Pork Sausage, Lactate, Metallic ions, Creatine

Nowadays, the food safety is a discipline which has a great impact for consumers. Despite of great advances in the quality control systems in food industry, problems can be produced. In this sense, in the pork sausage production occasionally can be observed the existence of different white crystals (efflorescences) on sausage surface. This fact makes consumers reject these products and provokes important economics losses for meat industry.

Different types of efflorescences can be observed on the surface of pork sausages with have different chemical composition and its formation can be a reversible or irreversible process. Phosphates, lactates and creatine are the main components of those deposits.

Analytical methodologies need to be developed to characterize those efflorescences and also find the sources of their appearence, since industry needs to fulfill all the requirements of food quality and safety directives.

In this research the characterization of the different tpes of efflorescences and the analysis of ingredients and also additives used in the production of pork sausages will be carried out. Different spectroscopic and also chromatogrpahic techniques wil be used for this purpose.

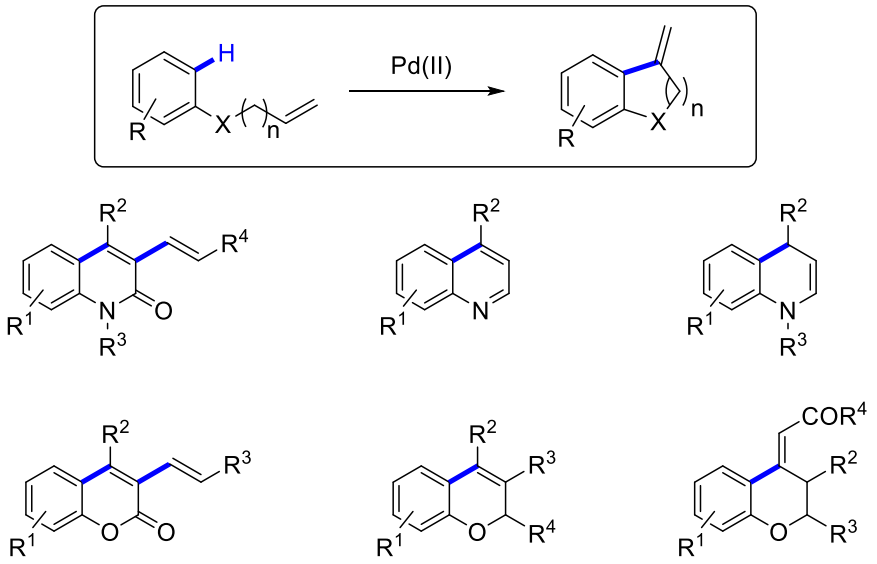
Palladium catalyzed C-H activation reactions. The intramolecular Fujiwara-Moritani reaction in synthesis of nitrogen and oxygen heterocycles

A. Carral-Menoyo, M. Martínez-Nunes, M. Gómez Redondo, C. Santiago, N. Sotomayor, E. Lete
Departamento de Química Orgánica II, Facultad de Ciencia y Tecnología, Universidad del País Vasco / EuskalHerriko Unibertsitatea (www.ehu.es/oms)

KEY WORDS: organometallics, C-H activation, heterocycles

Pd(II)-catalyzed C-H alkenylation of arenes, known as Fujiwara-Moritani reaction, has attracted much attention as an efficient atom-economical synthetic tool for the preparation of functionalized molecules. Although the intramolecular version has been successfully applied to the formation of five-member rings through 5-*exo* processes, the generation of six-member heterocycles still remains a challenge in terms of controlling reactivity and regioselectivity.

In this context, we have reported an efficient approach to the synthesis of 3-alkenyl-4-substituted quinolin-2(1*H*)-ones that involves a Pd(II)-catalyzed selective 6-*endo* intramolecular C-H alkenylation of *N*-phenylacrylamides, which could be further functionalized in C-3 through a second intermolecular C-H alkenylation reaction [1]. This procedure can also be extended to the synthesis of quinolines[2] and chromanes, through 6-*exo* processes. The application of these methodologies to the synthesis of nitrogen and oxygen heterocycles, privileged structures with many interesting biological properties, will be presented.



[1] V. Ortiz de Elguea, N. Sotomayor, E. Lete, *Adv. Synth. Catal.* **2015**, *357*, 463-473.
[2] A. Carral-Menoyo, V. Ortiz de Elguea, M. Martínez-Nunes, N. Sotomayor, E. Lete, *Mar. Drugs* **2017**, *15*, *276*

Heterocycle formation through intramolecular Pd-catalyzed alkenyl-aryl and aryl-aryl Cross-Coupling Reactions

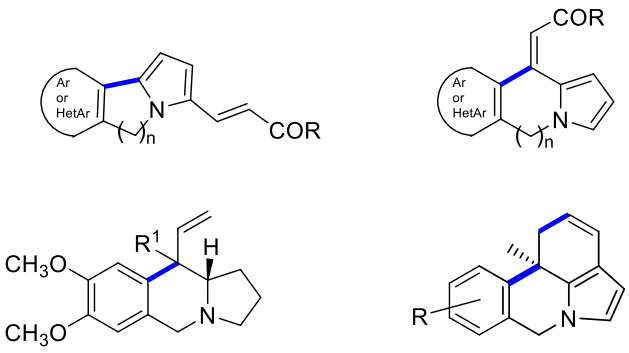
I. Barbolla, A. R. Azcargorta, N. Sotomayor, E. Lete
Departamento de Química Orgánica II, Facultad de Ciencia y Tecnología, Universidad del País Vasco / EuskalHerriko Unibertsitatea (www.ehu.es/oms)

KEY WORDS: organometallics, palladium-catalyzed cross coupling reactions, heterocycles

The Mizoroki-Heck (M-H) reaction is one of the most important carbon-carbon bond-forming reactions in organic synthesis. The intramolecular variant represents an extremely powerful method for the construction of small and medium-size rings. More recently, this procedure has become an effective method for the formation of tertiary and quaternary stereocenters in an asymmetric fashion [1]. The control of the *syn* ß-hydride elimination step is crucial to generate tertiary and quaternary stereocenters. Different strategies have been developed to avoid the elimination on the carbon directly involved in bond formation.

On the other hand, the intramolecular C-H arylation reaction is an interesting alternative to the classical cross-coupling reactions in the formation biarylic bonds on (hetero)aromatic systems. Both the direct arylation and the Mizoroki-Heck reactions use similar palladium-based catalytic systems, so the control of the chemoselectivity on polyfunctionalized substrates would allow the synthesis of different heterocyclic systems with interesting biological properties [2].

We have studied the possibility of generating quaternary or tertiary stereocenters on the pyrroloisoquinoline skeleton using an asymmetric Mizoroki-Heck cyclization [3], as well as asymmetric palladium-catalyzed cascade processes [4]. Besides, the C-H arylation reaction has been applied on both aromatic and heteroaromatic systems. Both approaches allow the straightforward assembly of complex heterocyclic systems.



[1] Larhed, M. Ed., *Science of Synthesis - Cross Coupling and Heck-Type Reactions, Vol. 3* Thieme: Stuttgart, 2013.
[2]. a) Lage, S.; Martínez-Estibalez, U.; Sotomayor, N.; Lete, E. *Adv. Synth. Catal.* **2009**, 351, 2460; b) Coya, E.; Sotomayor, N.; Lete E. *Adv. Synth.* Catal. **2014**, *356*, 1853.
[3] Azcargorta, A. R.; Barbolla, I.; Coya, E.; Lete, E.; Sotomayor, N. *Eur. J. Org. Chem.* **2016**, 2054.
[4] Coya, E.; Sotomayor, N.; Lete E. *Adv. Synth.* Catal. **2015,** *357,* 3206.

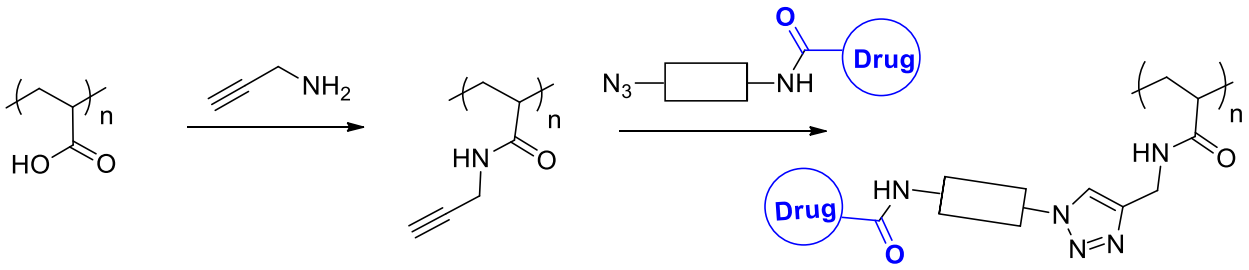
Azide-alkyne “click” reaction: A suitable methodology for drug immobilization in polymeric materials

Julia Sánchez Bodón[1], Isabel Moreno[1] and José L. Vilas[2]
[1]Macromolecular Chemistry Research Group, Dept. of Organic Chemistry II, Faculty of Science and Technology; [2]Macromolecular Chemistry Research Group, Dept. of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Leioa 48940, Spain.

KEY WORDS: antibacterial property, “click” reaction.

In recent years, hip or knee replacements, fracture fixation, ligament and tendon reconstruction and other surgical implant procedures have become common strategies to restore the function of affected traumatological injuries.[1]These implants placement require the administration of antibiotic prophylaxis due to the possible presence of bacteria or other microorganism in patients. In addition, bacteria, normally adsorbed on the implant surface, often form an adherent biofilm which exhibits increased protection from host defenses and improves resistance to antibiotic treatments.[2] As a result, almost half of nosocomial infections are related to the use of these implants. Furthermore, in some cases, these devices can lead to patient death.[3]Therefore, medical devices with intrinsic antibacterial properties are highly desirable. However, the addition of antibiotics on the material such as ß-lactam, vancomycin, ciprofloxacin is not easy to design due to additional structural restrictions that may compromise the bioactivity of these drugs. Because of this, we wanted to design a permanent immobilization of the antibiotic compounds to the polymeric material to maintain its function over a prolonged period. Thus, we considered the “click” reaction could be an excellent methodology for the conjugation of complex organic structures on the surface of many materials,[4] since it can be carried out in practically quantitative yield at room temperature, using water as a solvent and physiological-like conditions.[5]

For this reason, in this communication we report a method for the immobilization in a polyacrilic surface of different compounds based on azide-alkyne “click” reactions.



***Scheme 1*. General immobilization procedure of antibiotic compounds and analogous in polyacrilic surface.**

[1] Campoccia, D.; Montanaro, L.; Arciola, C. R. *Biomaterials* **2006**, *27*, 2331.
[2] Reid, G. *Int. J. Antimicrob. Agents* **1999**, *11*, 223.
[3] Zilberman, M.; Elsner, J. J. *J. Control. Release* **2008**, *130*, 202.
[4] Dijk, M.; Rijkers, D. T. S.; Liskamp, R. M. J.; Nostrum, C. F.; Hennink, W. E. *Bioconjug. Chem.* **2009**, *20*, 2001.
[5] Riva, R.; Lussis, P.; Lenoir S.; Jeróme, C.; Jeróme, R.; Lecomt, P. *Polymer* **2008**, *49*, 2023.

Aryl halides as convenient arylating agents for the “on water” efficient functionalization of deoxybenzoin

Iratxe Astarloa[1], Raul SanMartin[1], Aimar Garcia[1], Garazi Urgoitia[1], Galder Llorente[1], Maria Teresa Herrero[1] and Esther Domínguez[1]

[1]Department of Organic Chemistry II, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Sarriena auzoa, 48940 Leioa (Bizkaia).

KEY WORDS: haloarenes, deoxybenzoin, water, palladium.

One of the main methods for C-C bond formation relies on the nucleophilic attack of enolate-type species to alkyl halides and other alkylating agents. When aryl halides are involved these protocols fail, and therefore alternative strategies have been developed. However, serious limitations have been encountered for the arylation at the α-position of carbonyl compounds: strong electronwithdrawing substituents are required in the aryl halide, and lack of regioselectivity and dehalogenation side-reactions are common features. Besides, procedures based on diazonium salts, organolead compounds, zinc enolates, silylenol ethers, etc. have also been developed, but in general theses specific reagents are toxic and stoichiometric amounts are required, among other drawbacks.[1]

Metal-catalyzed arylation of carbonyl compounds has evolved into several variants, including changes in the arylating agent, enolate and metal catalyst. However, palladium-catalyzed arylation of ketone enolates is still the main methodology, although bidentate phosphine ligands or more complex phosphine derivatives, which are relatively expensive or require tedious preparative methods, are still needed.[2] Moreover, hazardous and relatively harmful organic solvents (DMF, THF, toluene…) are still prevalent in these reaction, so it is not surprising that the use of aqueous reaction media has gained much attention, despite the few examples reported up to date.[3]

We wish to present a very efficient palladium-catalyzed arylation of deoxybenzoin with haloarenes using commercially available, stable and easy to handle phosphine derivatives as ligands in aqueous media. Reaction conditions, substrate scope and several mechanistic studies will be discussed.

ACKNOWLEDGEMENTS:

This research was supported by the Basque Government (IT-774-13) and the Spanish Ministry of Economy and Competitiveness (CTQ2013-46970-P and CTQ2017-86630-P). I. A. thanks the Basque Government for a predoctoral scholarship. Finally, the technical and human support provided by SGIker of UPV/EHU is gratefully acknowledged.

REFERENCES:

1. Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108-11109.
2. Johansson, C. C. C.; Colaot, T. *Angew. Chem.* **2010**, *122*, 686-718.
3. a) Bellina, F.; Masini, T.; Rossi, R. *Eur. J. Org. Chem.* **2010**, 1339-1344; b) Lessi, M.; Masini, T.; Nucara, L.; Bellina, F.; Rossi, R. *Adv. Synth. Catal.* **2011**, *353*, 501-507.

Norbornene-mediated reactions with difuctionalized alkylating and acylating reagents

Galder Llorente[1], Xabier Guarrochena[1], Raul SanMartin[1], Garazi Urgoitia[1], María Teresa Herrero[1] and Esther Domínguez[1]

[1] Department of Organic Chemistry II, University of Basque Country (UPV/EHU), Faculty of Science and Technology, Sarriena auzoa z/g, 48940 Leioa, Spain.

KEY WORDS: Norbornene, C-H activation, palladium catalysts.

Transition metal-catalyzed reactions are a powerful tool in organic and organometallic chemistry due to their ability to perform unique transformations. Among many of these reactions, those based on C-H bond activation have gained much attention owing to the improvement in atom economy. In this regard, norbornene-mediated reactions provide an efficient approach the selective functionalization of the *ipso* and *ortho* positions of haloarenes. Indeed, the cooperative catalysis between a palladium source with such a rigid and strained alkene as norbornene is the key for a number of one-pot transformations that combine cross-coupling reactions, alkylations, aminations and cyanations, *inter alia*.

Since the first examples of the norbornene-mediated transformations,[1] this family of reactions has demonstrated its ability to offer more molecular diversity. Thus, polycycles such as phenantridines,[2] dibenzopyrans[3] or dibenzoazepines[4] have been synthesised from consecutive reactions based on initial norbornene-mediated transformations. From a mechanistic point of view, it is commonly proposed that of Pd^{IV} species participate in norbornene mediated reactions.[5]

Herein, we wish to report some unprecedented norbornene-mediated alkenylation/acylation and alkenylation/benzylation reactions involving iodoarenes, acrylates and *ortho*-functionalized benzyl or acyl halides. In addition, cyanation/benzylation between *o*-bromobenzyl halides and 2-iodotoluene will be also discussed.

Acknowledgements: This research was supported by the Basque Government (IT-774-13) and the Spanish Ministry of Economy and Competitiveness (CTQ2013-46970-P and CTQ2017-86630-P). Finally, technical and human support provided by SGIker of UPV/EHU is gratefully acknowledged.

References:

(1) Catellani, M.; Frignani, F.; Rangoni, A. *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 119–122.
(2) Della Ca', N.; Motti, E.; Catellani, M. *Adv. Synth. Catal.* **2008**, 350, 2513–2516.
(3) Motti, E.; Faccini, F.; Ferrari, I.; Catellani, M.; Ferraccioli, R. *Org. Lett.* 2006, 8, 3967–3970.
(4) Della Ca', N.; Maestri, G.; Malacria, M.; Derat, E.; Catellani, M. *Angew. Chem. Int. Ed.*, **2011**, 50, 12257–12261.
(5) Della Ca', N.; Fontana, M.; Motti, E.; Catellani, M. *Acc. Chem. Res.*, **2016**, 49, 1389–1400.

Palladium-catalyzed Glaser-Hay coupling of arylacetylenes

Maria Obieta[1], Garazi Urgoitia[1], Raul SanMartin[1], María Teresa Herrero[1] and Esther Domínguez[1]
[1] Department of Organic Chemistry II, University of Basque Country (UPV/EHU), Faculty of Science and Technology, Sarriena auzoa z/g, 48940 Leioa, Spain.

KEY WORDS: Glaser-Hay coupling, palladium catalysts.

The history of the preparation of diynes began back in the XIX century when Carl Glaser[1] reported the synthesis of 1,3-diynes from terminal alkynes through an oxidative process mediated by copper(I) chloride exposed to air. Even Glaser is considered as the father of this transformation, Baeyer[2] showed the synthetic utility of the methodology by expanding the coupling to various organic compounds possessing terminal ethynyl groups. Eglington improved the procedure by the use of a copper(II) salt in acidic media, thus providing a new procedure to prepare a variety of unsaturated macrocycles.[3] Later Hay described the use of a copper(I) salt and catalytic amounts of the bidentate ligand TMEDA as an alternative for the classical Glaser coupling of alkynes.[4] Regarding the oxidant, several oxidizing agents (I_2,sodium percarbonate, Ag and others)[5] have been explored although molecular oxygen is still the oxidant of choice.
The importance of 1,3-diynes as building blocks in many biologically active molecules and as precursors of polymers, macrocycles and supramolecular structures prompted us to study the above reaction. Herein we wish to present an efficient Glaser-Hay type coupling procedure mediated solely by palladium and molecular oxygen in an environmentally friendly media.

Acknowledgements: This research was supported by the Basque Government (IT-774-13) and the Spanish Ministry of Economy and Competitiveness (CTQ2013-46970-P and CTQ2017-86630-P). Finally, technical and human support provided by SGIker of UPV/EHU is gratefully acknowledged.

References:

1. Glaser, C. *Ber. Dstch. Chem. Ges.* **1869**, *2*, 422-424.
2. Baeyer, A. *Ber. Dstch. Chem. Ges.* **1882**, *15*, 50-56.
3. Eglington, G.; Galbraith, R. *J. Chem. Soc.* **1959**, 889-896.
4. Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275: *J. Org. Chem.* **1962**, *27*, 3320-3321.
5. a) Yan, J.; Wu, J.; Jin, H. *J. Organomet. Chem.* **2007**, *692*, 3636-3639. b) Zhou, L.; Zhan, H. Y.; Liu, H. L.; Jiang, H. F. *Chin. J. Chem.* **2007**, *25*, 1413-1416. c) Feng, X.; Zhao, Z.; Yang, F.; Jin, T.; Ma, Y.; Bao, M. *Organomet. Chem.* **2011**, *696*, 1479-1482. d) Li, J. H.; Liang, Y.; Zhang, X. D. *Tetrahedron* **2005**, *61*, 1903-1907. e) Chalifoux, W. A.; Ferguson, M. J.; Tykwinski, R. R. *Eur J. Org. Chem.* **2007**, 1001-1006.

Palladium-catalyzed hydro-oxycarbonylation leading to alkylidene lactones

Aimar García[1], Nerea Conde[1], Raul SanMartin[1], María Teresa Herrero[1], Garazi Urgoitia[1], and Esther Domínguez[1]

[1] Department of Organic Chemistry II, University of Basque Country (UPV/EHU), Faculty of Science and Technology, Sarriena auzoa z/g, 48940 Leioa, Spain.

KEY WORDS: alkylidene lactone, γ-alkynoic acid, hydroxycarbonylation, palladium catalysts

The alkylidene lactone scaffold can be found in a plethora of natural products, isolated from bacteria, algae and plants (*cyanobacterin*, *fimbrolide* derivatives and sesquiterpene lactone derivatives, respectively), which have shown appealing biological activities in diverse fields.[1] Moreover, enol lactones are known to be useful synthetic intermediates and consequently, it is not surprising that new and more effective syntheses leading to these cores are being pursued.[2]

The scientific community has striven to develop cleaner chemical reactions in which minimization of waste-generation and the employment of highly efficient catalytic systems have earned huge relevance.[3] In this regard, high atom economy reactions have gained much attention due to their inherent lower residue formation. Relating to the synthesis of alkylidene lactones, several synthetic routes have been reported amongst which alkyne hydro-oxycarbonylation must be remarked on account of its high atom economy. This reaction has been successful in the formation of the desired enol lactone moiety employing different metals (Ru, Rh, Pd, Au, Ag, Cu…), according to the number of stablished protocols.[4] However, most of these procedures required relatively high catalyst-loadings, long reaction times or even high temperatures.

In the present work, the successful implementation of a palladacyclic catalyst in the intramolecular alkyne-acid to alkylidene lactone reaction is described.

ACKNOWLEDGEMENTS

This research was supported by the Basque Government (IT-774-13) and the Spanish Ministry of Economy and Competitiveness (CTQ2013-46970-P and CTQ2017-86630-P). A. G. thanks the Spanish Ministry of Economy and Competitiveness for a predoctoral scholarship. Finally, technical and human support provided by SGIker of UPV/EHU is gratefully acknowledged.

REFERENCES

1. (a) Ishibashi, F.; Park, S.; Kusano, T.; Kuwano, K. *Biosci. Biotechnol. Biochem.* **2005**, *69*(2), 391–396. (b) Zhao, W.; Lorenz, N.; Jung, K.; Sieber, S. A. *Angew. Chem. Int. Ed.* ***2016***, *55*, 1187-1191. (c) Schepetkin, I. A.; Kirpotina, L. N.; Mitchell, P. T.; Kishkentaeva, A. S.; Shaimerdenova, Z. R.; Atazhanova, G. A.; Adekenov, S. M.; Quinn, M. T. *Phytochemistry* **2018**, *146*, 36-46.
2. (a) Goh, W. K.; Iskander, G.; Black; D. St C.; Kumar, N. *Tetrahedron Lett.* **2007**, *48*, 2287–2290. (b) Lu, B.; Zhao, M.; Ding, G.; Xie, X.; Jiang, L.; Ratovelomanana-Vidal, V.; Zhang, Z. *ChemCatChem* **2017**, *9* (20), 3989–3996.
3. Anastas, Paul T.; Warner, John C. *Green chemistry: theory and practice* **1998** New York: Oxford University Press.
4. Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079-3159.

Unraveling non-covalent interactions: mass-resolved laser spectroscopy as a tool for studying biological systems

A. Camiruaga [1], I. Usabiaga[1], I. Insausti[1] and J. A. Fernández[1]
1 Dpto. Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco-UPV/EHU, Bº Sarriena s/n, Leioa 48940, Spain.

KEY WORDS: Laser Spectroscopy, UV, REMPI, Double Resonance UV/IR, Non-covalent interactions, Molecular aggregates.

The intra- and inter-molecular interactions represent one of the main forces involved in the stabilization of molecular systems. In particular, non-covalent interactions are ubiquitous in Nature, and govern most fundamental processes in biological systems. These interactions have a pure quantum chemical nature because they originate in the interaction between the elctronic clouds of neighbour molecules. Among these non-covalent interactions, hydrogen bond deserves special mention because of its high covalent character, making it the strongest intermolecular interaction. However, non-covalent interactions are very weak in comparison with a covalent bond (about %5 of the strenght), and any perturbation in the enviroment could result in a problem for its characterization.

Generating molecular beams in supersonic expansions allow us to form isolated molecular aggregates, free from solvent effects, helping us to fully characterization of non-covalent interactions and their intrinsic properties. Furthermore, the combination of jet science with clasiccal spectroscopy techniques and mass-selective detection results in a powerfull tool for studying aggregates of biological interest.

Our group has developed a sophisticated methodology to fully characterize molecular aggregates of biological relevance. This methodology includes a number of spectroscopic techniques: REMPI, 2-color REMPI, double resonance techniques, such as UV/UV hole burning, IR/UV, IR/IR/UV/UV and IR^3, which allows us to tackle the mass-resolved IR spectroscopy of systems without a chromophore. Interpretation of the experimental information obtained using such techniques is not straightforward and requires of theoretical predictions to understand the conformational preferences of biological aggregates. The systems studied using this methodology include aggregates of DNA bases, xanthynes, sugars, drugs and their cross-aggregates. In the following work we characterize the interaction of a monosaccharide (Phenyl-β-D-glucopyranoside) with a “peptidic bond” as a model system for understanding the stabilization of sugar units in specific receptors.

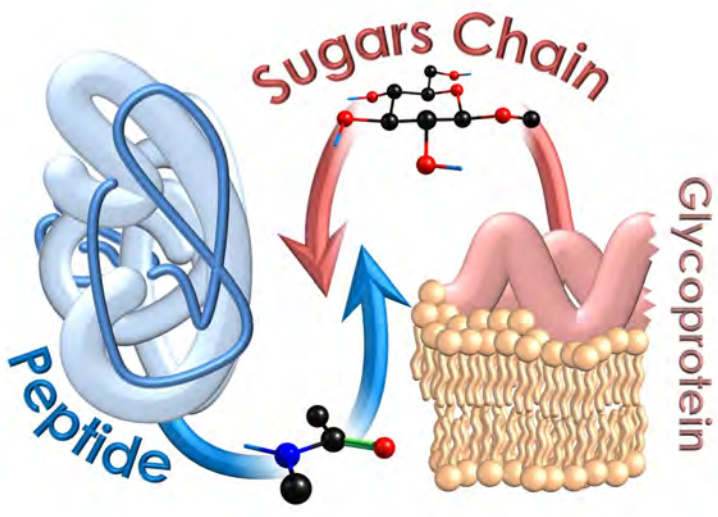


Fig. 1 Model system of an interaction between a sugar unit and a peptide bond

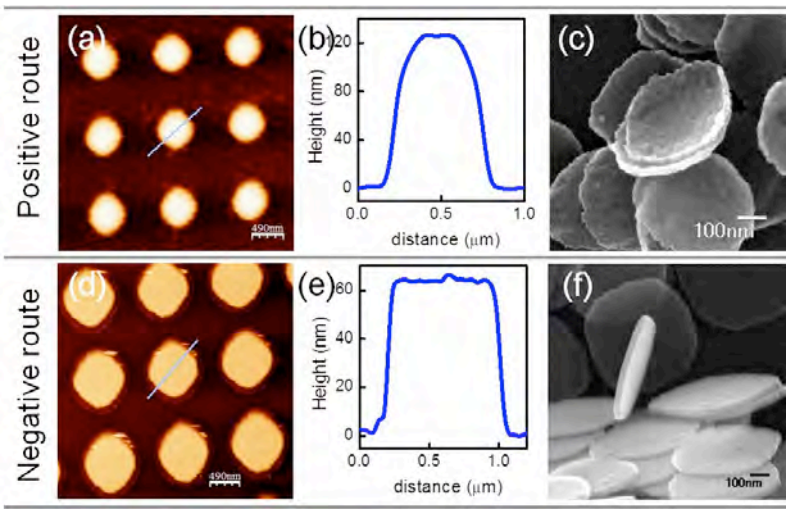
Interference lithography fabrication of magnetic nanostructures suitable for biomedical applications

C. Redondo[1], B. Mora[1], A . Perez-Valle[2], M. Boyano[2,3], and R. Morales[4,5]
[1] Department of Chemical-Physics, University of the Basque Country UPV/EHU
[2] Department of Cell Biology and Histology, University of the Basque Country UPV/EHU
[3] Biocruces Health Research Institute, 48903 Barakaldo, Spain.
[4] Department of Chemical-Physics & BCMaterials, University of the Basque Country UPV/EHU,
[5] IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain.

KEY WORDS: magnetic nanostructures, Interference Lithography, cell viability, nanomedicine, biomedical applications

In recent years, magnetic nanostructures have attracted the attention of a broad community of researchers from a wide variety of fields. In particular, disk-shaped magnetic nanostructures, which due to their unique properties and dimensions comparable to biological systems, present distinctive features for novel biomedical applications. These characteristics can be exploited to develop new diagnostic and therapeutic approaches such as promoting magnetomechanically tumor cell destruction or improving detection limits of cancer biomarkers through magnetoresistance sensor devices.

In order to evaluate the efficiency and capability of such applications, fine tuning of geometry and dimensions is mandatory. This contribution addresses cost-effective, versatile and maskless fabrication processes of biocompatible high-magnetic moment elements at the submicrometer scale[1]. First, advantages and disadvantages of two high throughput fabrication routes using interference lithography were evaluated. Then, cell viability of the nanostructures was assessed in primary melanoma cultures. No toxicity effects were observed, validating the potential of these nanostructures in biotechnological applications.



[1] ACS Appl. Mater. Interfaces, Manuscript, DOI: 10.1021/acsami.7b16779 *"in press"*

Fig.1-. Morphological characterization of Permalloy disks obtained from the positive and negative resist route. Positive route: (a) AFM image after thermal evaporation of Permalloy on top of resist pillars, (b) AFM profile along the blue line in (a), (c) SEM image of nanodisks after lift-off of the resist.
Negative resist route: (d) AFM image after Permalloy deposition and lift-off of the resist, (e) AFM profile along the blue line in (d), (f) SEM image of nanodisks after etching of the sacrificial layer.

Unravelling the Ultrafast Photophysics of the Isolated 7-Azaindole Molecule

Iker Lamas[1], Raúl Montero[2] and Asier Longarte[1]
[1]Spectroscopy Laboratory, Department of Physical Chemistry, University of the Basque Country UPV/EHU, Aptdo. 644, 48080 Bilbao, Spain.
[2]SGIKER Laser facility, University of the Basque Country UPV/EHU, Aptdo. 644, 48080 Bilbao, Spain.

KEY WORDS: Laser spectroscopy, Photodissociation dynamics.

Azaindole has attracted a great deal of attention as a chemical analogue of the nucleic bases adenine and guanine. Indeed, its doubly hydrogen bonded dimer undergoes a double proton transfer reaction upon excitation with light, so it has been taken as an ideal model system for DNA base pairs.[1] Nevertheless, the electronic structure and relaxation pathways of azaindole monomer have not been studied deeply enough. The present work focuses on the relaxation dynamics of the isolated 7-azaindole molecule, which has been tracked by femtosecond time-resolved ionization. The electronic excitation region explored (289-256 nm) covers three electronic excited states: the two ππ* L_a and L_b states, and the dark πσ* state with dissociative character.[2,3] The study has provided a comprehensive picture of the photophysics of the molecule, which is driven by the interplay between these three excited surfaces and the ground state.

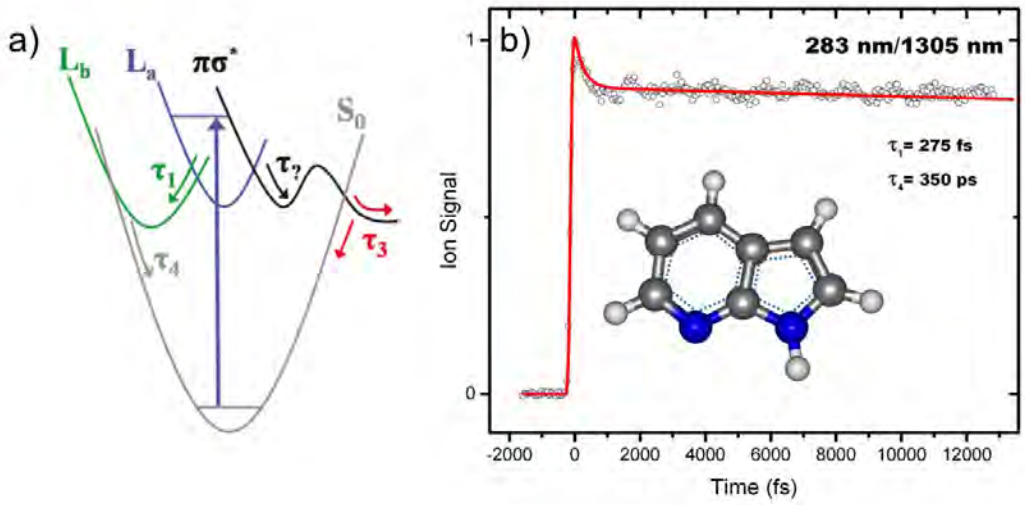


FIG. 1. a) Cartoon of the relaxation processes observed for 7-azaindole. b) Transient collected at the azaindole$^+$ channel by exciting at 283 nm while probing with the 1305 nm radiation.

REFERENCES

[1] A. Douhal, S. K. Kim, A. H. Zewail, Nature 378, 260 (1995)

[2] L. Serrano-Andrés, M. Merchán, A. C. Borín, J. Stålring, Int. J. Quantum Chem. 84, 181 (2001)

[3] S. Arulmozhiraja, M. L. Coote, J. Hasegawa, J. Chem. Phys. 143, 204304 (2015)

A brief history of 3D printing polymers: the future technology to obtain smart and multifunctional materials

Cristian Mendes-Felipe[1,2], José M. Laza[1] and José L. Vilas[1,2]
[1]Grupo de Química Macromolecular (Labquimac), Dpto. Química Física; [2]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.

KEY WORDS: 3D printing, photopolymerization, smart and multifunctional materials.

Additive manufacturing (AM), commonly known as 3D printing, can be defined as the "process of joining materials to make parts from 3D model data, usually layer by layer, as opposed to subtractive manufacturing and formative manufacturing methodologies".[1] 3D printing processes can be classified into seven categories (Fig. 1a) in which ink photopolymerization, specifically UV radiation induced polymerization (Fig. 1b), is the most efficient method for the generation of highly cross-linked polymer networks from liquid resin systems.

In recent years, due to increasing demand for both complex and multi-functionality products, many new materials, such as nanomaterials, functional materials, biomaterials, smart materials or even fast drying materials, have been developed for 3D printing and to be use as feed materials for printing real application parts. Smart materials are a driving force for the fabrication of wireless, sustainable and interconnected autonomous smart devices.[2]

Printing of smart materials, besides allowing a more environmental friendly production and implementation into devices, also offers several advantages over other large-scale production methods, such as patterning capability, high speed, low cost and ability to produce specific parts with complex geometries at low costs. Polymers offer excellent advantages for printable smart materials based technologies, since they are relatively low cost materials, are more versatile than inorganics, their fabrication techniques are simple and there is a wide possibility of ways to adapt their structures that allows to produce materials with specific physical and chemical properties. Despite the large evolution of 2D and 3D printed technologies, the number of materials with suitable properties to be printed is still small.[3] In addition, most of those materials are printed after melting or solvent based processes, limiting fabrication speed, definition and the introduction of specific functionalities. These limitations must be addressed to meet the requirements of industrial applications.

In this way, the manufacture of polymer based inks and resins that can provide specific functionality or active behavior is a highly interesting method of printing smart materials. However, the development of this kind of materials for 3D printing technologies remains in its preliminary state; there are only few studies carried out but the industrial interest has arisen the investigation on these materials.

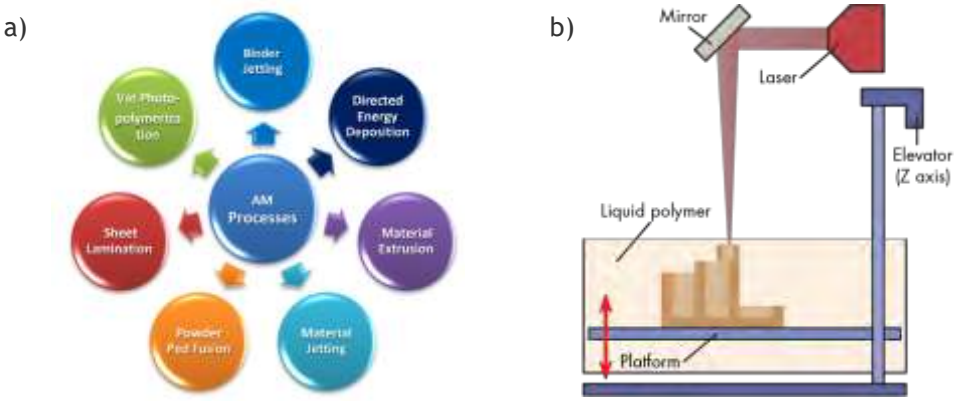


Fig. 1. a) Classification of AM processes, b) Scheme of stereolithography process (UV radiation induced polymerization).

(1) Lee, J. Y.; An, J.; Chua, C. K. Appl. Mater. Today 2017, 7, 120–133.
(2) Xu, Y.; Wu, X.; Guo, X.; Kong, B.; Zhang, M.; Qian, X.; Mi, S.; Sun, W. The Boom in 3D-Printed Sensor Technology; 2017; Vol. 17.
(3) Tiwari, A.; Polykarpov, A. Photocured Materials RSC Smart; Royal Society of Chemistry: Cambridge, UK, 2014.

Poly-L-isomer of lactic acid (PLLA) for active packaging of food

Jon Andrade del Olmo[1], *Leyre Pérez Álvarez*[1] *and Leire Ruiz Rubio*[1]
[1]Macromolecular Chemistry Research Group (LABQUIMAC), Department of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU)

KEY WORDS: Poly-*L*-isomer of lactic acid (PLLA), antibacterial properties, β-cyclodextrins.

The improvement of ecofriendly polymers with lower environmental impact is important because it offers us the possibility of replacing current petroleum-based plastic by biodegradable and renewable materials. One of these polymers is the poly-*L*-isomer of lactic acid (PLLA) which is derived from natural sources and it is used to replace the polymers derived from petrochemicals for the packaging industry because of its good properties such as non-toxicity and biodegradability. PLLA can be specifically modified in order to develop new materials for active packaging in which packaging system plays an active role providing PLLA, on the one hand, antibacterial properties to increase the durability of food, and on the other hand, the capacity to encapsulate flavors and fragrances.

Regarding antibacterial properties PLLA is blended with ZnO nanoparticles.[1] In addition, the antibacterial capacity of PLLA can be enhanced by functionalization with chitosan, a biopolymer that has shown an exceptional ability to cause the disruption of bacteria cells.[2] So, surfaces of PLLA-ZnO films can be modified in order to improve final antibacterial properties. For this, different modification methods will be studied, such as covalent bonding and electrostatic interactions.[3]

On the other hand, cyclodextrins are starch derivatives which present a cylindrically shaped cavity with a hydrophobic inner surface and a hydrophilic outer surface. This hydrophobic pocket is able to form inclusion complexes with a wide range of organic guest molecules. As a consequence, cyclodextrins are employed in the food sector to obtain cholesterol free products and for the encapsulation of flavors or antioxidants.[4] According to this, PLLA surfaces can be also derivatized with cyclodextrins enhancing loading and release of flavors, fragrances and natural antibacterial compounds. The layer by layer deposition of anionic cyclodextrins and cationic chitosan is a simple and inexpensive methodology that allows compiling above proposed modifications of PLLA to get a new active packaging material that improves the organoleptic properties and increase the durability of food.

References

[1] Pantani, R.; Gorrasi, G.; Vigliotta, G.; Murariu, M.; Dubois, P. *Eur. Polym. J.* **2013**, *49* (11), 3471–3482.
[2] Del Hoyo Gallego, S.; Pérez Álvarez, L.; Gómez Galván, F.; Lizundia, E.; Kuritka, I.; Sedlarik, V.; Laza, J.M.; Vilas Vilela, J.L. *Carbohydr. Polym.* **2016**, *143*, 35-43.
[3] Goddard, J. M.; Hotchkiss, J. H. *Prog. Polym. Sci.* **2007**, *32* (7), 698–725.
[4] López-de-Dicastillo, C.; Catalá, R.; Gavara, R.; Hernández-Muñoz, P. *J. Food Eng.* **2011**, *104*, 380-386.

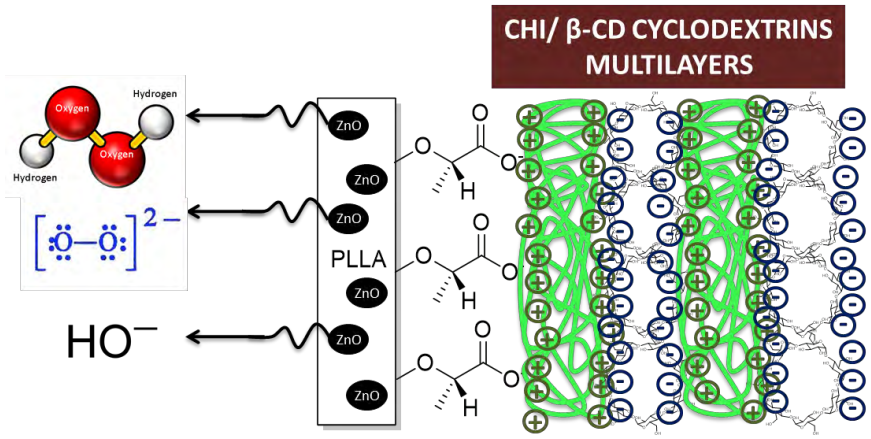


Figure 1 – PLLA modified with ZnO, chitosan (CHI) and ß-cyclodextrins (ß-CD).

Nanotechnology inspired by nature: from photoactive nanomaterials to molecular assemblies

Leire Gartzia-Rivero[1], Rebeca Sola-Llano[1], Eduardo Duque[1], Ruth Prieto[1], Edurne Avellanal[1], Ainhoa Oliden[1], Jorge Bañuelos[1], Virginia Martínez-Martínez[1], Hegoi Manzano[1], Teresa Arbeloa[1], and Iñigo López-Arbeloa[1]
[1]Department of Physical Chemistry (Group of Molecular Spectroscopy), University of the Basque Country (UPV/EHU), Aptdo. 644 48080 Bilbao

KEY WORDS: luminiscent antennas, laser dyes, energy transfer, porous materials, nanoparticles, white-light

The herein reported work describes the development of hierarchically-organized fluorescent nanomaterials inspired by plant antenna systems. These photosynthetic microorganisms consist of thousands of chlorophyll molecules embedded in a protein matrix. Their main characteristic relies on the capability to harvest solar energy in a broad spectral range and transport it by means of multiple and efficient energy transfer processes to a specific reaction centre, where it is finally turned into chemical energy. Taking inspiration from them, we aim to create artificial antenna systems capable to mimic functions and mechanisms present in the natural systems.

To this aim, a wide variety of luminescent fluorophores encapsulated into either inorganic or organic hosts, as well as molecular systems based on scaffolding of suitable laser dyes have been deeply studied. The main goal is to design systems that harvest the light over a broad spectral region (in particular the ultraviolet-visible section of the electromagnetic spectrum) and transfer it to the target place and with a desired energy (especially in the red edge of the visible) via successive energy transfer hops.

To this purpose, three different approaches have been considered to develop optical antennas: (i) hybrid materials based on LTL zeolite aluminosilicate doped with laser dyes absorbing and emitting in different regions of the visible (blue, green or red); (ii) dye-doped latex nanoparticles; (iii) molecular antennas based on donor and acceptor dyes covalently linked through a spacer. The protein matrix of the natural systems has been replaced by synthetic hosts of nanometric dimensions which protect the dyes and provide a significant arrangement that will help to make the energy transfer processes viable and efficient. Furthermore, with respect to the photoactive part, which is responsible for interacting with the light, the chlorophyll molecules have been replaced by fluorescent molecules many of which have been customized à la carte. These luminescent antennas have been designed for photonic purposes such as tunable dye lasers, light modulators or polarity probes.

[1] L. Gartzia-Rivero, J. Bañuelos, I. López-Arbeloa, *Int. Rev. Phys. Chem.*, 34, 517-558 (2015).

MALDI IMS: Mapping Metabolites

Lucía Martín, Jone Garate [1], Roberto Fernández[1], Sergio Lage[2], Igor Galetich and Jose A. Fernández[1]
[1]Department of Physical Chemistry; [2]Department of histology and cellular biology, University of Basque Country

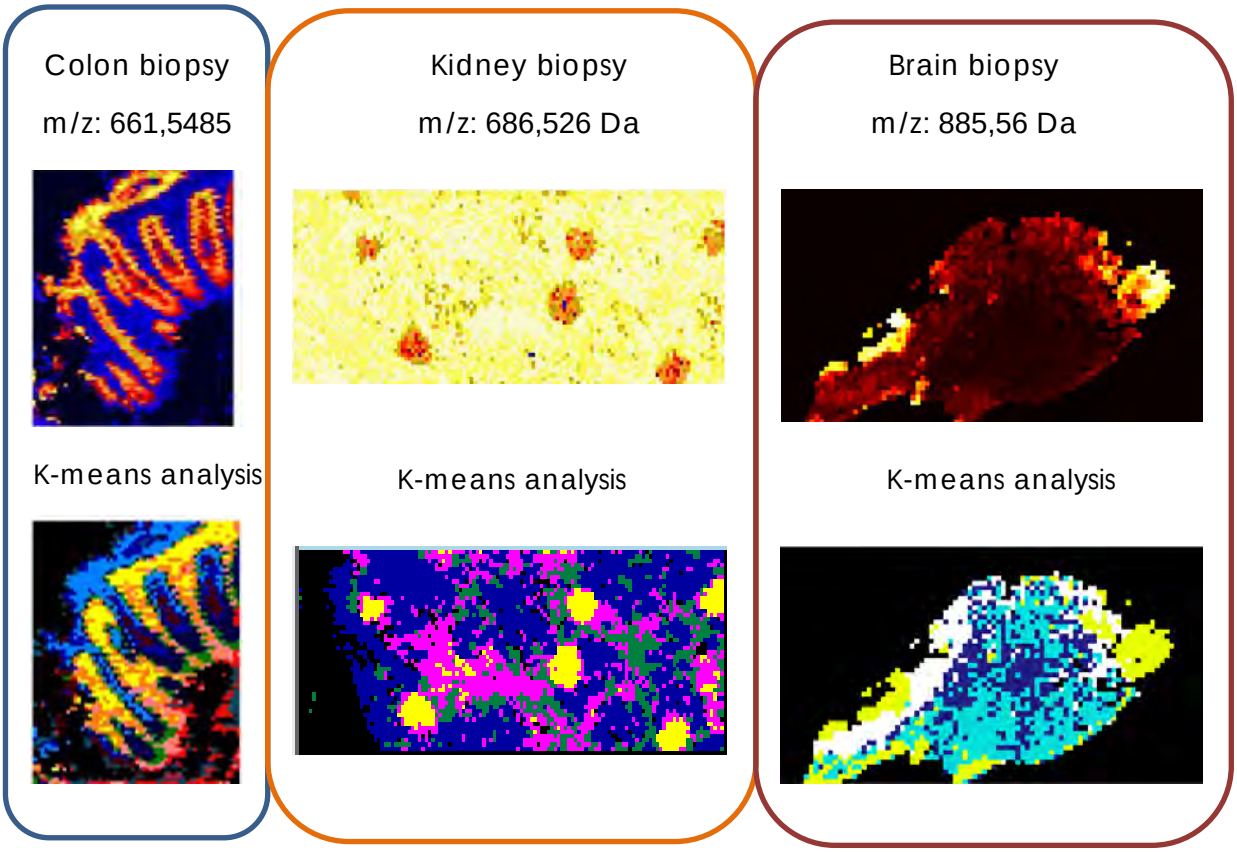
KEY WORDS: MALDI, Imaging Mass Spectrometry, Lipids, Lipidomics, Orbitrap, MS.

The "omic" studies involve large number of non-targeted measurements (genes, proteins, lipids), which are chemical markers indicative of biological events (High-dimensional Biology). The main goal of these studies is to acquire comprehensive knowledge of biological processes not only in normal physiological state, but also in different pathologies. One of the research lines in our group is the use of mass spectrometry in lipidomics to understand complex biological problems

Lipids play an important role at cellular and whole organism level and therefore their metabolism is altered even in the first instants of pathological states, such as in cancer. However, identifying and understanding such changes is not an easy task, due to the large number of lipid species in any cell at any instant.
Mass spectrometry has gained considerable relevance on lipidomics with Imagining Mass Spectrometry due to its ability to obtain the spatial distribution of lipids in tissue sections. Thus, in addition to the lipid identity, it gives also information about its location in a cell or a tissue, adding very relevant information to understand the role each lipid species play.

Advantages of this analytical technique are high sensitivity, robustness, high-throughput capacity and applicability to a wide range of molecules. Moreover, this method is label-free, so there is no need of any kind of chemical marker that could alter the lipidome of the tissue. However, there are still a number of factors limiting its use. Challenges remain in the areas of higher spatial resolution, normalization, ionization method and quantification.

Here we present, some examples of lipid distribution of human biopsies using the equipment available at the analytical services of the UPV/EHU.



Organometallic complexes for Photodynamic Therapy

Rebeca Sola-Llano[1], Eduardo Duque[1], Ruth Prieto[1], Ainhoa Oliden[1], Edurne Avellanal[1], Leire Gartzia[1], Virginia Martínez-Martínez[1], Jorge Bañuelos[1], Hegoi Manzano[1], Teresa Arbeloa[1] and Iñigo López-Arbeloa[1]
[1]Department of Physical Chemistry, University of the Basque Country (UPV/EHU), P. O. B. 644, 48080 Bilbao.

KEY WORDS: Photodynamic Therapy, singlet oxygen generation, fluorescence, organometallic complexes, photosensitizers.

Photodynamic Therapy (PDT) agents are undergoing intensive research because they appear as highly promising in biomedicine as an approach for cancer treatment. Indeed, PDT through singlet oxygen generation enables the use of light to promote cell-death in a minimally invasive way. In this process, chromophores acting as singlet oxygen photosensitizers are capable of generating the cytotoxic singlet oxygen species ($^1O_2$) after photoexcitation.

In this work, efficient singlet oxygen photosensitizers (PS) are obtained through the rational design of BODIPY-linked biscyclometalated Iridium (III) complexes. Furthermore, owing to the incorporation of the BODIPY-type chromophores into the molecular structure of the hybrid PSs, the light harvesting capacity is enhanced, reaching more appealing ranges of the electromagnetic spectrum for biomedicine, *i.e.* close to the clinic window (650-800 nm). Note that typical organometallic complexes usually absorb light in the UV region, which is not optimum in terms of light penetration in tissues.

In addition to the demonstration of the high singlet oxygen generation efficiency of the compounds herein presented, a complete photophysical characterization has been carried out, evidencing the dual behavior of one of the organometallic compounds that, besides absorbing light towards the red range of the electromagnetic spectrum and producing the cytotoxic species, it shows fluorescent emission, being very interesting also for bioimaging.

With the aim of supporting the conclusions derived from the experimental results, theoretical calculations were also carried out, shedding light on the mechanism that takes place in the process of the singlet oxygen production for these particular complexes.

Finally, in order to analyze the viability of the BODIPY-linked biscyclometalated complexes as biomedical tools, *in vitro* cytotoxicity studies with and without light exposure were carried out. The hybrid complexes showed extremely low dark toxicity, an essential property for their use in PDT, and triggered phototoxicity on HeLa cells, which revealed apoptotic morphologies after the photodynamic treatment (incubation and irradiation).

Functional open-frameworks based on isopolyoxometalates and Cu(cyclam) complexes: single-crystal-to-single-crystal transformations

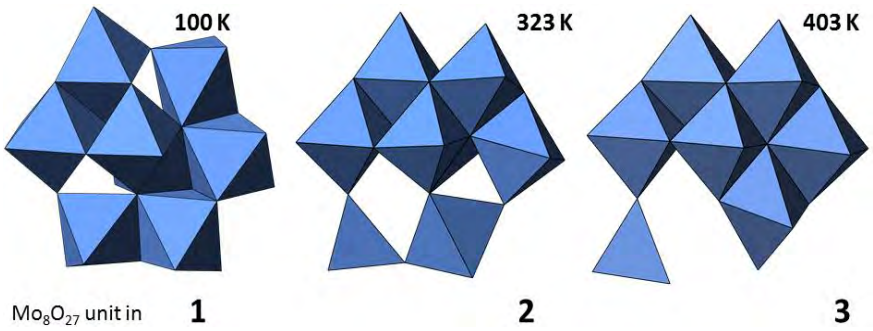
Estibaliz Ruiz-Bilbao, Beñat Artetxe, Luis Lezama, Juan M. Gutiérrez-Zorrilla
Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, P. O. Box 644, 48080 Bilbao, Spain

KEY WORDS: Polyoxometalates, metalorganic complexes, SCSC transformations.

Polyoxometalates (POMs) are a family of anionic-oxo clusters of d-block transition metals in their highest oxidation states (traditionally M = V^V, Mo^{VI} and W^{VI}) that exhibit a huge structural diversity and remarkable electronic properties. In the last few years, the possibility of combining the multifunctional nature of the POM clusters (e.g. photoluminescence, magnetism, redox activity) with the characteristics related to open-framework materials with high internal surface area have gained great attention. The combination of POM anions with copper(II) complexes of the macrocyclic N_4-donor cyclam (1,4,8,11-tetraazacyclotetradecane) ligand has been identified in our group as a suitable method to prepare such POM-based porous crystalline materials (POMOFs).

In this context, we have recently explored the reactivity of vanadates toward the $\{Cu(cyclam)\}^{2+}$ complex, which resulted in two different open-framework materials as a function of the pH. Moderately acidic conditions (pH = 4-6) afforded the $[Cu(cyclam)][\{Cu(cyclam)\}_2(V_{10}O_{28})]\cdot 10H_2O$ supramolecular POMOF-like material, the architecture of which remains virtually unaltered upon thermal evacuation of solvent molecules leading to a system of microporous channels operative for the selective adsorption of CO_2 over N_2.[1] In contrast, basic conditions (pH = 9) yielded the $[\{Cu(cyclam)\}(VO_3)_2]\cdot 5H_2O$ three-dimensional open-framework hybrid, the porous structure of which collapses upon thermal dehydration and does not show any applicability in gas sorption as a result.[1] In both cases, the crystallinity was fully retained throughout the whole dehydration process, and this fact allowed us to unequivocally prove the robustness of the decavanadate-based architecture, as well as the dynamic nature of the metavanadate-based structure, which undergoes as much as three sequential single-crystal-to-single-crystal (SCSC) transitions. Such studies provide direct insight into the exact location of atoms and molecules within the crystal packing of the activated form of a given material, as well as for correlating how any property of interest (sorption ability in our case, but also color, magnetism, luminescence, etc) is modified and tuned as a result of such structural changes.

Studies were later expanded to tungstate and molybdate systems. For the former, the hybrid $[\{Cu(cyclam)\}_3(W_7O_{24})]\cdot 15.5H_2O$ constitutes the first example of a 3-D polyoxometalate–metalorganic extended framework that exhibits both thermally-triggered crystal dynamics and permanent microporosity with associated gas sorption (N_2 and CO_2) capability. [1] In the case of molybdates, the POMOF $[\{Cu(cyclam)\}_3Mo_8O_{27}]\cdot 14H_2O$ (**1**) was obtained, which undergoes, upon thermal evacuation of guest solvent molecules, two sequential SCSC transformations, the partially dehydrated (**2**) and the anhydrous phase (**3**). These transitions involve modifications in the crystal packing as well as isomerization of the octamolybdate anions though migration of some of the metal centers with associated changes in their coordination numbers.



REFERENCES:
[1] Martin-Caballero, J. *Hybrid polyoxometalates: Synthesis, Crystal Structures, Thermostructural Behaviour and Anchoring to Tailored Polymeric Surfaces*, Ph.D. Thesis, UPV/EHU, Leioa, **2017**.

Supramolecular compounds based on π-stacking interactions between metal-adenine entities and theobromine/caffeine methylxanthines

J. Pascual-Colino[1], G. Beobide[1], O. Castillo[1], A. Luque[1], M. Perfecto[1], P. Roman[1] and S. Pérez-Yáñez[2]
[1]Departament of Inorganic Chemistry, University of the Basque Country, UPV/EHU, PO Box 644, 48080 Bilbao, Spain; [2]Departament of Inorganic Chemistry, University of the Basque Country, UPV/EHU, 01006 Vitoria-Gazteiz, Spain.

KEY WORDS: SMOFs, Supramolecular interactions, π-π stacking, adenine, theobromine, caffeine.

We analyse the π-π stacking interactions as alternative to more directional hydrogen bonding interactions to develop porous supramolecular metal-organic frameworks (SMOFs).[1] The blue compound $[Cu_7(\mu\text{-ade})_6(\mu_3\text{-OH})_6(\mu\text{-}H_2O)_6](theo)_2{\cdot}28H_2O$ (**1**) (ade: adeninato, theo: theobrominate) is formed by wheel-shaped cationic units where the Cu(II) atoms are bridged by hydroxide anions, water molecules, and adeninato ligands with a μ-κN3:κN9 coordination mode. The supramolecular assembly *(Figure 1)* takes place mainly through π-π stacking interactions involving the adeninato ligands of the rigid heptameric entities and theobrominate moieties. Compound **1** exhibits an open-framework with voids representing 37% of the unit cell volume, but the plasticity of the π-π interactions causes a reversible shrinkage of the porous system upon activation that precludes the adsorption of gas molecules.

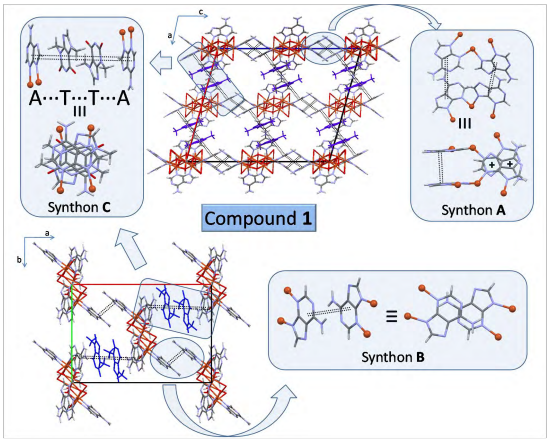


Figure 1: Supramolecular interactions connecting heptanuclear entities in the ac (top) and ab (bottom) crystallographic planes.

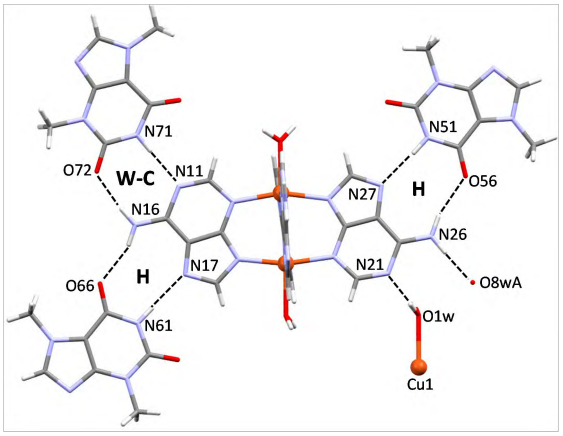


Figure 2: Theobromine molecules anchored to the dimeric entities by means of complementary hydrogen bonding interactions.

Dark purple compounds $[Cu_2(\mu\text{-ade})_4(H_2O)_2]{\cdot}3Htheo{\cdot}7H_2O$ (**2**), $[Cu_2(\mu\text{-ade})_4(H_2O)_2]{\cdot}2Htheo{\cdot}18H_2O$ (**3**) and $[Cu_2(\mu\text{-ade})_4\ (H_2O)_2]{\cdot}(caf){\cdot}\sim6H_2O$ (**4**) (Htheo: theobromonine , caf: caffeine) contain neutral windmill units in which two copper atoms are bridged by four μ-κN3:κN9 adeninato ligands. Their crystal structures highly depend on the supramolecular interactions of the theobromine and caffeine bases. In compound **2**, two theobromine molecules are hydrogen bonded to the Hoogsteen face of two trans-arranged adeninato ligands, whereas a third theobromine molecule is joined to the Watson-Crick face of one of the previous adeninato ligand *(Figure 2)*. In compound **3**, with a lower amount of theobromine, the Watson-Crick interaction is not present. In both compounds, the 3D crystal structure requires the additional presence of π-π stacks between the theobromine molecules.

In compound **4**, as the methyl groups of the caffeine molecule do not allow hydrogen bond interactions, the adeninato ligands are hydrogen bonded among them to generate, together with π-stacking interactions, supramolecular sheets containing rectangular windows in which the caffeine molecules are located. Only compound **4** showed permanent porosity, adsorbing a significant amount of CO_2 (0.88 mmol of CO_2/g at 5 bar and 273 K). The magnetic characterization of the compounds indicate a ferromagnetic behaviour for **1** and strong intradimeric antiferromagnetic interactions in compounds **2** and **4**.

References:

[1] (a) Thomas-Gipson,J.; Pérez-Aguirre, R.; Beobide,G.; Castillo,O.; Luque,A.; Pérez-Yáñez,S.; Román,P. *Cryst. Growth Des.*, **2015**, 15, 975-983. (b) Beobide,G.; Castillo,O.; Luque,A.; Pérez-Yáñez,S.; *CrystEngComm*, **2015**, 17, 3051-3059.

Advanced cathode composites for Li and Na-ion batteries

A. Iturrondobeitia[a], A. Goñi[a,b], V. Palomares[a,b], I. Gil de Muro[a,b], L. Lezama[a,b] and T. Rojo[a,c]
[a] Dept. Química Inorgánica, Facultad de Ciencia y Tecnología, UPV/EHU, Bº Sarriena, 48940 Leioa, Spain.
[b]BCMaterials, UPV/EHU Scientific Park,E-48940 Leioa, Spain.
[c] CIC ENERGIGUNE, Parque Tecnológico de Álava, Albert Einstein 48, ED. CIC, 01510, Miñano, Spain.

KEY WORDS: Li-ion and Na ion batteries, electrochemistry, spinel, lithium manganese phosphate, sodium vanadium fluorophosphates, sodium iron sulphates.

As one of the most important and widely used rechargeable power sources, lithium ion batteries (LIBs) have been widely used in portable electronics, electric vehicles (EVs), and hybrid electric vehicles (HEVs) [1]. Additionally, they are supposed to be one of the most promising candidates for next generation power sources. Besides of LIBs, recently, sodium ion batteries (NIBs) have received increased attention as an alternative to LIBs for stationary storage due to the abundance and low cost of Na [2].

Regarding to lithium ion batteries, lithium manganese oxide spinel is especially interesting for use in hybrid electric vehicles and electric vehicles due to its low cost and high safety. However, the main problem for application is the capacity fading caused by the instability of Mn(III). In order to improve that factor, in this report we investigate the effect of substitution of a small quantity of Mn by p-block elements such as Ga^{3+} or Si^{4+}. The $Li(Mn,M)_2O_4$ (M = Ga^{3+},Si^{4+}) phases have been synthesized by the freeze-drying method and calcinated at 700ºC [1]. Another interesting material is the LiMnPO4 olivine compound. Unfortunately, the electronic and ionic conductivity of LiMnPO4 is insufficient for good electrochemical performance. The most widespread solutions are reduction of the particle size to nanometric scale, surface coating by an electronic conductor, or structural substitution by small amounts of metallic cations. In this work, nanosizing, carbon coating, and substitution have been combined in order to produce new and better-performing cathode materials based on $Li(Mn_{0.8}Fe_{0.1}M_{0.1})PO_4/C$ (M = Fe, Co, Ni, Cu) composites [3].

On the other hand, the most important cathodic materials employed in sodium ion batteries can be classified into two main groups: 1) transition metal oxides (Na_xMO_2) and 2) $Na_xM_y(XO_4)_n$ (M= Mn, Fe, Ni, Co; X=Si, P, S) type polyanionic compounds. In this sense, inside the polyanionic compounds, transition metal (TM) fluorophosphates and sulphates are among the most promising cathode materials for NIBs. In this regard, $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ sodium-vanadium fluorophosphates have high reaction voltages (at 3.6 and 4.1 V *vs.* Na/Na^+) and their good specific capacity values in sodium half-cells (theoretical specific capacity of about 130 mAh/g) leads to high energy density compounds (*ca.* 500 Wh/kg) [4] .Among the $Na_xM_y(SO_4)_3$ compounds, $Na_2Fe_2(SO_4)_3$ seems to be a good candidate as it has register high redox potentials at 3.8V along with fast kinetics. Moreover, this phase posses an inherent deviation from stoichiometry leading to $Na_{2+2x}Fe_{2-x}(SO_4)_3$ compound, which has emerged as a more cathode material due to its enhanced compositional, structural and electrochemical flexibility [5].

In this study, we report on the synthesis and exhaustive characterization of an advanced cathode composite for SIBs: $Na_{2.5}Fe_{1.75}(SO_4)_3$/Ketjen/rGO. The morphology, spectroscopic and electrochemical properties have been studied obtaining excellent results. Moreover, a post mortem study of the cycled electrodes has been performed by EPR and XPS techniques in order to further analyze the SEI formation so as to design a next generation SIB.

[1] A. Iturrondobeitia, A. Goñi, V. Palomares, I. Gil de Muro, L. Lezama, T. Rojo, *J. of Power Sources*, 2012, **216**, 482-488.
[2] P. A. Adelhelm, P. Hartmann, C. L. Bendar, M. Busche, C. Enfinger, J. Janek, *Beilstein JNanotechnol*. 2015, **6**, 1016-55
[3] A. Iturrondobeitia, A. Goñi, I. Gil de Muro, L. Lezama, C. Kim, M. Doeff, J. Cabana, T. Rojo, *Inorganic Chemistry*, 2015, DOI:10.1021/ic5028306.
[4] P. Serras, V. Palomares, A. Goñi, I. Gil de Muro, P. Kubiak, L. Lezama, T. Rojo, *J. Mater. Chem.*, 2012, **22**, 22301
[5] A. Goñi, A. Iturrondobeitia, I. Gil de Muro, L. Lezama, T. Rojo, *j. Power Sources*, 2017, **369**, 95-102.

Magnetic Nanoparticles for Biomedical Applications

I. Castellanos-Rubio [1], O.K. Arriortua[1], I. Galarreta [1], I. Gil de Muro [1,2], I. Ruiz de Larramendi [1], M. Insausti [1,2], L. Lezama [1,2]

[1]Faculty of Science and Technology, University of the Basque Country, UPV/EHU, E-48080, Bilbao, Spain;
[2]BC Materials, Parque Científico de UPV/EHU, E-48940, Leioa, Spain.

KEY WORDS: magnetic nanoparticles, magnetite, colloidal stability, biomedicine, magnetothermal therapies.

The size reduction of materials involves a noticeable change in their physicochemical properties, and this fact has driven the development of Nanoscience and Nanotechnology. Biomedicine stands among the fields that have most benefited from the new potentials of nanomaterials. In these sense, the main advantage of the synthetic nanostructures is that they can interact with fundamental biological entities (macromolecules of life and cells) locally and precisely in the nanoscopic scale. Consequently, the current research in this field is making great progress towards more sophisticated diagnosis and therapy models.

Specifically, magnetic nanoparticles (MNP) arouse enormous interest for their ability to generate heat under alternating magnetic fields (AMF). These heat nanoinductors can remotely release drugs, stimulate cellular signaling or induce tumor necrosis without damaging healthy cells. Magnetite (Fe_3O_4) nanoparticles are excellent candidate due to their good biocompatibility, low toxicity and suitable magnetic properties. The maximal heating power (at clinically safe AMF conditions) for Fe_3O_4 nanoparticles is achieved in the ferromagnetic regime (d>25nm). However, growing the size of these inorganic NPs over 15 nm, while keeping a narrow size distribution and preventing the formation of secondary phases, remains a challenge to synthetic chemistry. Moreover, as ferromagnetic nanoparticles exhibit permanent magnetization, special care needs to be taken in order to avoid agglomeration of NPs during the biomedical application.

Our group has optimized the chemical synthesis to obtain highly crystalline monodomain Fe_3O_4 ferromagnetic NPs with exceptional heating potential. These NPs have been prepared by thermal decomposition of iron (III) oleate precursor, in a mixture of solvents with high boiling points and in the presence of oleic acid capping agent. In addition, we have developed two approaches to prevent MNP clustering: Firstly, the as-synthesized Fe_3O_4 NPs have been coated with an amphiphilic copolymer (PMAO-g-PEG) that offers the necessary steric hindrance so as to display colloidal stability in physiological media. The second approach has consisted on incorporating the ferromagnetic Fe_3O_4 nanoparticles in inorganic-polymeric microdisks in uniform and flat arrangement. It is worthwhile to mention that these magnetic hybrid microdisks have been proved to act as long lasting sub-cellular implants for efficient magnetothermal actuation.

Our final goal through the design, fabrication, characterization and optimization of these magnetic nano- and micromaterials is to contribute to the development of biomedical fields that make use of magnetic induction heating such as magnetic hyperthermia therapies and magnetothermal neuromodulation. The efficacy of these materials is already being tested within the scope of the therapy for hepatic malignancy and within the framework of neuroscience research.

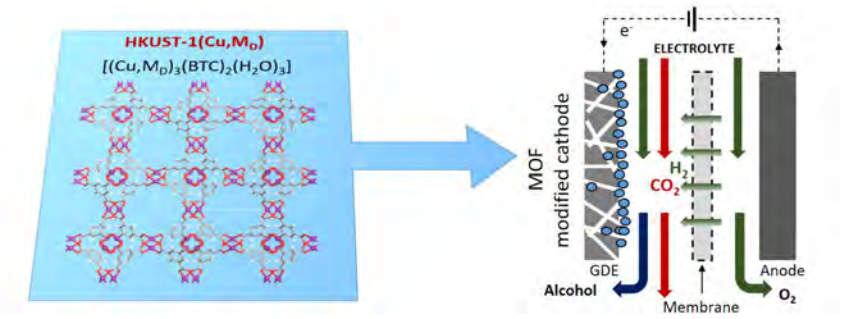
Electrocatalytical evaluation of heterometallic porous coordination polymers for CO_2 conversion

Maite Perfecto-Irigaray[1], Jonathan Albo[2], Garikoitz Beobide[1], Ángel Irabien[2], Sonia Pérez-Yáñez,[1], Óscar Castillo[1], Jon Pascual-Colino[1], Antonio Luque[1], Pascual Román[1].

[1]Department of Inorganic Chemistry, University of the Basque Country (UPV/EHU), PO Box. 644, 48080, Bilbao (Spain); [2]Department of Chemical & Biomolecular Engineering, University of Cantabria (UC), Avda. Los Castros, 39005, Santander (Spain).

KEY WORDS: CO_2, electroreduction, heterogeneous catalysis, solvent-less synthesis, heterometallic MOFs.

Nowadays the catalytic conversion of CO_2 into added-value products can be regarded as hot topic that awakens the interest of both scientific and industrial community. Particularly, the challenges for converting CO_2 into high-energy density alcohols, such as methanol, are great, but the potential rewards are also enormous.[1] A recent research work[2] has reported the first evidence that proofs the aptitude of homometallic Cu(II) based MOFs in the electroreduction of CO_2 to methanol. Based on it, herein we report the solvent-less synthesis and doping of the benchmark HKUST-1(Cu) as a facile route to afford heterometallic MOFs and their proficient behaviour as electrocatalytic materials in the carbon dioxide reduction to alcohols. Precisely, Zn(II), Ru(III), Rh(II), Pd(II) and Bi(III) were selected as doping metals (M_D) with the aim of partially replacing the Cu(II) atoms of the pristine structure to afford HKUST-1(Cu,M_D) type materials. It deserves to note that solvent-less synthesis procedures have demonstrated to be high yield routes to render crystalline MOFs.[3] Nonetheless, the extremely high reagent concentration that imply the reaction conditions can also make feasible the herein aimed doping.



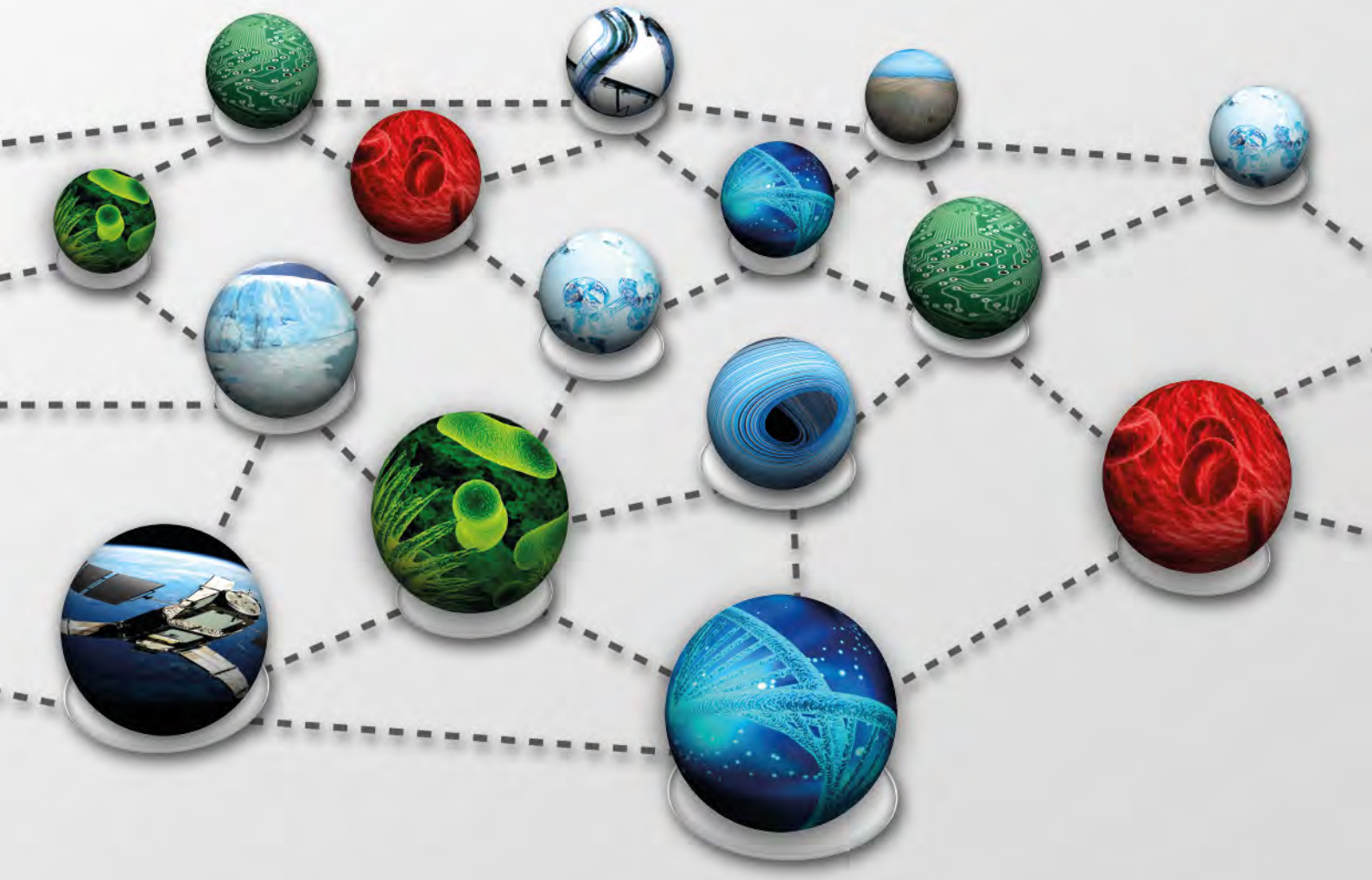
The doping process was initially monitored by X-ray diffraction on polycrystalline sample and by X-ray fluorescence. This analysis demonstrates that Zn(II), Ru(III) and Pd(II) are satisfactorily incorporated, controlling dopant/copper ratio, while incorporation of Rh(II) is very low and uncontrollable. In the case of Bi(III), it appears segregated as a different crystalline phase. The analysis of the microstructure has been made by scanning electron microscopy, which has also allowed to discuss on the homogeneity of the samples. Finally, herein prepared materials have been evaluated as catalyst in the electroreduction of CO_2 to alcohols in terms of efficiency of the process. Faradaic efficiencies range from 6 to 60 %, which are values comparable or greater than those provided by conventionally used elemental copper and copper oxides. The interplay of the dopant metal and copper(II) is discussed by comparing the results with those provided by homometallic HKUST-1(Cu). Furthermore, long-term performance and stability of MOFs during the electrochemical process are also discussed.

References:

[1] Albo, J.; Alvarez-Guerra, M.; Castaño, P.; Irabien, A. *Green Chem.* **2015**, 17 (4), 2304–2324.
[2] Albo, J.; Vallejo, D.; Beobide, G.; Castillo, O.; Castaño, P.; Irabien, A. *ChemSusChem* **2016**, 1–11.
[3] Lanchas, M.; Arcediano, S.; Aguayo, A. T.; Beobide, G.; Castillo, O.; Cepeda, J.; Vallejo-Sánchez, D.; Luque, A. *RSC Adv.* **2014**, 4 (104), 60409–60412.

INGENIERITZA KIMIKOA

INGENIERÍA QUÍMICA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Workflow for the CFD-DEM simulation of a conical spouted bed

Aitor Atxutegi, RobertoAguado and Martin Olazar
Department of Chemical Engineering (CPWV Group), University of the Basque Country,
P.O. Box 644, 48040, Bilbao, Spain

KEY WORDS: CFD, DEM, Spouted-Bed

Spouted beds are type of fluidized beds that are suitable for handling a range of particle sizes and specially those coarse, irregular or sticky materials. Its flexibility has created the need to use various internal devices for the stabilization of the spouting regimes such as draft tubes or fountain containment devices [1]. The complexity and high nonlinearity of system parameters make prediction of cycle times, fountain height, pressure drop and minimum spouting velocity increasingly difficult, given that traditional correlations are bounded by the operational limits at which they were obtained. Lately, CFD-DEM coupling has emerged as an appropriate model for the simulation of a range of gas-solid contacts. This approach solves the Navies Stokes equations for the continuous phase, whilst the solid particles are tracked individually solving Newton's second law [2]. In this case, the fact that particles are tracked individually directly makes available information such as the particles cycle time distribution.

In this work, OpenFOAM® has been used for the simulation of the continuous phase through PIMPLE pressure-velocity coupling and LIGGGHTS® has been used for the simulation of the discrete phase. The coupling of both phases is accomplished through semi-implicit source terms in the momentum equation of each phase, mainly; drag and turbulence terms. The Figure shows the fluidization of particles and height distribution.

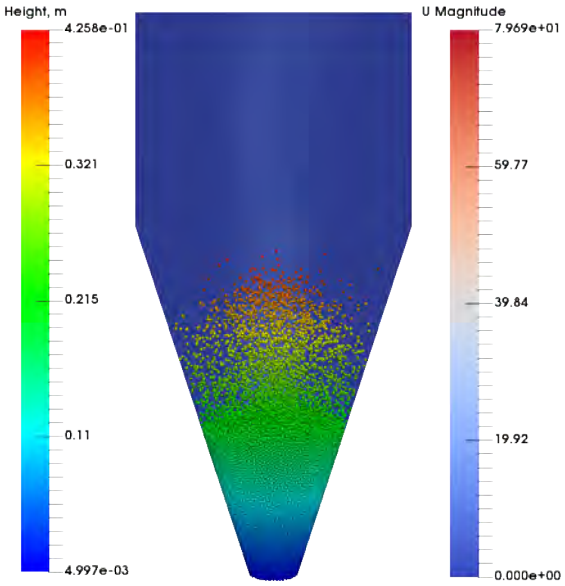


Figure. Particles height distribution and gas velocity magnitude snapshot.

The use of the lagrangian framework requires the description of the contacts between the materials in the system, i.e., particle-particle and particle-wall collisions. In this case they are characterized by the Hertz model with the resistance dashpot model in a soft sphere fashion. This model requires the input of the restitution coefficients in each collision type, which are calculated by test drops of each pair of materials and comparison of the kinetic energy before and after the collision. In order to measure the kinetic energy of the particle a high-speed camera has been employed and the detected optical flow is related to the frame by frame speed, hence obtaining the amount of kinetic energy lost on each impact.

[1] H. Altzibar *et al*, *Powder Technol.*, 312 (2017) 334-346.
[2] S. Pietsch *et al.*, *Powder Technol.*, 316 (2017) 245-255.

CO_2 methanation: carbon neutral and renewable energy source

A. Bermejo, A. Quindimil, U. De La Torre, B. Pereda-Ayo, J.M. Castresana, J.A. González-Marcos, J.R. González-Velasco
Group of Chemical Technologies for Environmental Sustainability, Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country, UPV/EHU, Bº Sarriena, Leioa, Bizkaia

KEY WORDS: Climate change, renewable energy, CO_2 recycling, catalytic CO_2 hydrogenation into CH_4

The main cause of climate change is anthropogenic CO_2 emissions from an energy system based on fossil fuels. It is estimated that annual CO_2 emissions will continue to increase due to the global growing energy demand linked to the exponential increase in population. In fact, the International Energy Agency (IEA) foresees 35.7 Gt of emitted CO_2 for 2040, a quantity far from enough to avoid severe climate change. In recent decades, many efforts have been made to develop efficient renewable energy sources that reduce the amount of CO_2 emitted. The major drawback of renewable energy is its intermittency; wind and solar energy are fluctuating and have to be balanced for electric grid stability purposes. Consequently, large capacity electricity storage is required, as well as reserve production capacity.

Nowadays, the electrical power obtained from wind turbines and solar panels can be stored in form of energy vector such as H_2 or CH_4. Hydrogen has a higher calorific value than methane (33,900 vs. 13,249 kcal·kg-1) and no CO_2 is formed during H2 combustion. However, hydrogen also presents some drawbacks compared to methane: (i) very low density, thus its storage is considerably more expensive and (ii) infeasibility of large-scale transport due to incompatibility of the current gas grid. Thus, the conversion of renewable energy into methane seems to be by now a more suitable technology.

Valorization of CO_2 by hydrogenation is a promising alternative, not only because of the use of renewable energy, but also because CO_2 anthropogenic emissions are reduced. Carbon dioxide from flue gas can be combined with H_2 generated from renewable energies and converted catalytically into methane or synthetic natural gas (SNG), according to the Sabatier reaction: $CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O$. In fact, as a proof of concept, the e-gas plant of Audi Motor Company located in Werlte (Germany) efficiently produces 1000 tons of SNG per year, combining renewable hydrogen and concentrated CO_2 from a nearby biogas plant.

CO_2 methanation catalysts reported in literature normally consists of an active metal supported on a metal oxide. Ru and Ni have been the most studied metals. Ruthenium is the most active and selective metal in CO_2 hydrogenation into methane. The only disadvantage against nickel is the highest cost. Nickel seems to be the most active and selective among the non-noble metals and is widely used in the industry due to its low cost. The main reported disadvantage of Ni-based catalysts versus those based on Ru is deactivation due to interaction with CO and formation of mobile nickel carbonyls that results in the metal sintering.

On the one hand, our research has focused on the design of supported active catalysts for the methanation of CO_2 in steady state, such as Ru/ and Ni/Al_2O_3 or Ru/ and Ni/CeO_2. In addition to alumina and ceria supports, the use of BETA type zeolite has been considered due to its high specific surface area and mechanical resistance. The main drawback of this support is that is not able to adsorb CO_2. However, it has been demonstrated that both the number and the strength of basic sites notably increase if H-BETA zeolite is exchanged with Na^+ and impregnated with 10% of La_2O_3, which leads to a higher activity. On the other hand, we are developing catalysts with the ability to capture CO_2 and simultaneously convert it into CH_4 (Dual Function Materials). For that purpose, $Ru\text{-}CaO/Al_2O_3$ and $Ru\text{-}Na_2CO_3/Al_2O_3$ catalysts are being investigated. $4\%Ru\text{-}15\%CaO/Al_2O_3$ and $4\%Ru\text{-}10\%Na_2CO_3/Al_2O_3$ catalysts are the most active, with high ability to store CO_2, 558,4 μmol/g and 416,6 μmol/g, and a high CH_4 yield, 74.2% and 92.0%, respectively. The utilization of Na_2CO_3 as a CO_2 sorbent material is more suitable because the operation is carried out at somewhat lower temperatures (280 ºC) in comparison to CaO based catalysts (400 ºC).

Controlling the environmental impact of natural gas engines: Catalytic combustion of residual methane

A.Choya, Z. Boukha, B. de Rivas, J.L. Ayastuy, A. Aranzabal, M.A. Gutiérrez-Ortiz, J.I. Gutiérrez-Ortiz and R. López-Fonseca
Group of Chemical Technologies for Environmental Sustainability, Dept. of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Leioa, Bizkaia, Spain

KEY WORDS: methane, catalytic combustion, cobalt, spinel oxide

Natural gas is considered a versatile and environmentally friendly alternative fuel for automotive applications. It has been estimated that proven natural gas resources are enough for 250 years, which guarantees its availability in the medium and long term. Natural gas as a fuel for vehicles (also called VNG or vehicular natural gas) is considered a reliable technology with respect to gasoline and diesel engines. Besides, natural gas is safer and cheaper than gasoline or diesel and the driving autonomy is 1.6-2.5 times longer.

Comparing with other automotive fuels, VNG poses a smaller impact to the environment. From all the hydrocarbons, methane (main component of natural gas) has the lower C/H ratio. This means a lower CO_2 emission per unit of energy generated, comparing to gasoline or diesel. Besides, the lower operation temperature of GNV engines helps in limiting the emission of NO_x and the relative cleanliness of natural gas results in virtually no particle emissions. The main technological limitation of VNG engines lies on the emission of residual methane not burned in the engine. Although methane does not contribute to tropospheric ozone formation, it is a powerful greenhouse effect gas, with an estimated effect of 25-30 times that of CO_2. This requires the application of a effective post-treatment system for the exhaust gases.

Catalytic oxidation is an attractive alternative to convert trace amounts of methane into carbon dioxide and water. It is a notably difficult process due to the high relative stability of the methane molecule, and the low temperature of the exhaust gases from the engine (500 °C at most). Mostly used commercial catalysts are based on highly active noble metals such as palladium. However, these materials are often very expensive and their activity decreases with time due to sintering and ageing. For this reason, finding cheaper and more available alternatives is an interesting challenge that can in turn increase the economic attractiveness of VNG systems.

Cobalt spinel oxides are considered a promising alternative to noble metals for catalytic oxidation of methane due to their relatively low cost, high stability and selectivity to CO_2. However, their main limitation is their low activity at low temperatures. For this reason, the main objective of this project is to find suitable cobalt spinel oxide catalysts that are active enough at the operational temperatures of VNG engines, while maintaining good thermal and hydrothermal stability. For that purpose, different cobalt oxide formulations and configurations have been synthesised and investigated.

Up to date, it has been found that the bulk Co_3O_4 oxide prepared by precipitation is the most active spinel oxide, due to its good redox properties, operating with a relatively high space velocity under both dry and humid conditions. However, remarkable efforts are being made on improving its structural and textural properties with different approaches, such as supporting it on a porous media (modified alumina) or doping its lattice with other chemical elements. Recent results have shown that the latter strategy promotes the intrinsic activity of these catalysts by improving their redox properties, but only specific elements (cerium) are capable of inducing such beneficial effect. Alternatively, nanocasted Co_3O_4 with controlled morphology (nanorods) will be examined with the aim of increasing the number of more catalytically active exposed crystalline planes.

Catalyst selection and kinetic modeling for the production of olefins from oxygenated compounds and paraffins

Tomás Cordero-Lanzac, Pedro Castaño and Javier Bilbao

Department of Chemical Engineering (CPWV Group), University of the Basque Country (UPV/EHU), P.O. Box 644, 48040, Bilbao, Spain

KEY WORDS: Olefins, DTO, Catalytic cracking, Acid catalysts, HZSM-5

The chemical industry needs non-conventional processes to be developed, which should be environmentally friendly and based on renewable sources in order to meet the growing demand for fuels and chemicals. In this scenario, the production of olefins (particularly propylene) receives great attention aiming to substitute the conventional steam cracking of naphtha. This process presents high energetic requirement, low selectivity of propylene and high CO_2 emissions. Some of the most studied alternatives to this process are: (i) the methanol (or dimethyl ether)-to-olefins (MTO or DTO) process [1]; and (ii) the catalytic cracking (CC) of naphtha [2]. The ultimate aim of the work is synthesizing novelty acid catalyst, proposing kinetic models that explain their behavior and simulating reactors for the industrial implementation of DTO and CC processes.

Particularly, the hereby presented reaction runs were carried out in a fixed bed reactor using a HZSM-5 based catalyst, which was agglomerated with pseudoboehmite. The results obtained for both processes are displayed in the Figure. As observed, the conversion obtained for the dimethyl ether (DME) is higher than that for n-pentane (nC_5, as model molecule of naphtha) at the conditions detailed in the Figure caption. The yield of olefins in both cases is the highest one in comparison with the yield of other lumps of compounds. Moreover, HZSM-5 zeolite, which exhibits a MFI structure, allows for producing propylene as the main olefin in both reactions. This was not possible using catalysts with different structures (as SAPO-18 or -34).

From the data collected using different temperatures and space times, a kinetic scheme based on mechanistic consideration have been proposed for the DTO process and the CC of n-pentane with a HZSM-5 based catalyst. The kinetic schemes consider olefins as the primary products and then intermediates of the mechanism. As it is detailed in the Figure, DME forms olefins (O) by dehydration, whereas nC_5 undergoes a sequenced protolytic cracking/ß-scission (*ßs*) pathway in order to yield O. Afterwards, short paraffins (P), long paraffins (C5+) and BTX are formed through hydride transfer (*Ht*), oligomerization-cracking (*oc*) and cyclization-aromatization (*ca*) pathways, respectively. After adjusting the kinetic constant for the kinetic steps in the Figure, it is noteworthy the values registered for the *Ht* and *oc* pathways at the reference temperature of 400 ºC: 65.9 and 123.4 molC g^{-1} h^{-1} bar^{-1} for DTO and 95.3 and 12.9 molC g^{-1} h^{-1} bar^{-1} for CC, respectively. These results are in concordance with the product distribution of the Figure, where C5+ is the main sub-product in the DTO process, meanwhile the yield of P is the second highest one in the CC of nC_5 These preliminary mechanistic advances will be used as the grounds for developing kinetic models, proposing novel catalysts and designing optimized reactors for DTO and CC processes.

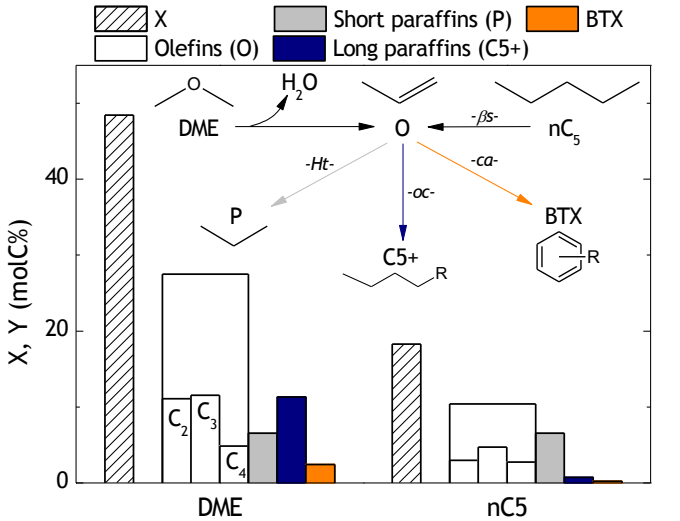


Figure. Product lumps distribution and conversion (X) of DME and nC_5

DME: 375 ºC, 1.5 bar, 0.5 g_{cat} h $molC^{-1}$

nC_5: 550 ºC, 1.5 bar, 1.0 g_{cat} h $molC^{-1}$

[1] Pérez-Uriarte et al. *Chem Eng. J.*, 311 (2017) 367-377.
[2] Cordero-Lanzac et al. *Chem. Eng. J.*, 331 (2018) 818-830.

Catalysts for automobile exhaust control: improving activity and durability, and reducing costs

U. De-La-Torre, J.A. Onrubia-Calvo, M. Urrutxua, B. Pereda-Ayo, Z. Boukha, R. López-Fonseca, M.P. González-Marcos, J.A. González-Marcos, M.A. Gutiérrez-Ortiz, J.R. González-Velasco
Group of Chemical Technologies for Environmental Sustainability, Dept. of Chemical Engineering, University of the Basque Country, UPV/EHU, Bº Sarriena, Leioa, Bizkaia

KEY WORDS: NO_X removal, diesel engines, NSR-SCR, Pt group, perovskites.

Increased environmental awareness, legislative measures and public demand for environmental sustainability are leading to an increase in diesel engines in developed countries. The operation with higher air/fuel ratios results in a higher fuel efficiency and lower greenhouse gases emission. Nevertheless, NO_X are particularly difficult to remove from oxidizing exhausts such as those in diesel vehicles

Over the last years, the TQSA research group has focused its efforts on the development of catalytic systems for the two main technologies proposed for the removal of NO_X from exhaust gases released by diesel engines: NO_X storage and reduction (NSR) and NO_X selective catalytic reduction (SCR). SCR technology consists of using ammonia (NH_3), produced by hydrolysis of urea that is stored into an on-board tank in the vehicle, to reduce NO_x selectively to nitrogen (N_2). This technology uses zeolitic structures interchanged with metals as catalysts and a model SCR catalyst could consists of a Cu-zeolite.

In the NSR strategy, the conversion of NO_x into N_2 occurs through a two-step cyclic operation. During the fuel-lean stage, the NO_x is trapped on the catalyst; then, the engine is switched to a fuel-rich condition where NO_x is released and reduced preferentially to N_2, although some NH_3 can also be produced. Therefore, NSR technology requires a catalyst combining sites for NO_X adsorption and metallic sites able to favor oxidation and reduction reactions. A model NSR catalyst consists of platinum and barium supported on alumina.

The concept of coupling NSR with SCR is based on tuning the operation of the NSR catalyst to produce a controlled amount of ammonia, which is stored on the SCR catalyst during the fuel-rich stage, and used to reduce remaining NO_x to N_2 on the SCR catalyst, placed downstream of the NSR catalyst in a sequential NSR-SCR configuration, which allows for virtually zero-emission exhausts.

In this sense, NSR formulations developed up to date allow to achieve strict standards emission levels. However, important loads of Pt group metals (PGMs) with high price and poor thermal stability are required. For the total implementation of these technologies it is necessary to develop sustainable alternatives, with higher durability and less expensive. Perovskites oxides described by general formula (ABO_3) have been proposed as an alternative which reduces costs comparing to PGMs catalysts in many heterogeneous catalysis processes. More than 90% of the metallic elements from the periodic table can enter the perovskite structure. That way, one of the main advantages of perovskite structures is the possibility to adopt a wide range of different compositions, changing either A or B cations or partially substituting each cation by others of the same or different valences to adjust their redox and surfaces properties.

Lanthanum based perovskites with Co or Mn as B cation have been synthesized for NSR process because of their high NO oxidation capacity. In order to improve redox and surfaces properties, some La is partially substituted by Sr. As a consequence; there is an improvement in NO to NO_2 oxidation and NO_x storage capacity, achieving higher or similar values to Pt-based catalysts. Recently, a combination of 30% of $La_{0,7}Sr_{0,3}CoO_3$ and 70% Pt-Ba/Al_2O_3 has shown similar activity to 100% Pt-based catalysts with lower cost and more durability.

New approaches in the production of TiO_2/GAC composites for ozonation

C. Ferreiro [1], J.I. Lombraña [1] and M.J. Rivero [2]
[1] Department of Chemical Engineering. University of the Basque Country UPV/EHU. P.O. Box 644. E-48080 Bilbao, Spain;
[2]Department of Chemical and Biomolecular Engineering, University of Cantabria, 39005 Santander, Spain.

KEY WORDS: catalytic ozonization, TiO_2, granular activated carbon GAC, aniline, industrial wastewater.

The increase of industrial production has generated large amounts of waste by-products that have to be treated before their discharge into the environment. It has been proven that many of these industrial compounds such as aniline affect the health of aquatic organisms and the quality of water. Catalytic ozonation can arise as a suitable technology for the degradation of aniline, compared to any other conventional treatment [1]. The objective of this research is the synthesis of a novel composite based on the in-situ generation and deposition of nanocrystals of TiO_2 on two types of granular activated carbon GAC (Norit 1240 Plus and Norit ROX 0.8), which can be used as catalytic support in heterogeneous ozonation.

The composite materials have been prepared using several experimental methods such as precipitation in alcoholic medium, impregnation by immersion or the hydrothermal method.

The main results showed that the composites obtained by precipitation had an homogeneous distribution of TiO_2 particles on the external surface of the GAC. However, in the obtained catalysts by both the immersion and the hydrothermal impregnation method, large amounts of TiO_2 covering surface of the GAC as a film were observed, causing a significant lost of the porosity and surface area. The best method was precipitation in alcoholic medium, using Norit 1240 Plus. However, this synthesis route led to a low percentage of TiO_2 deposition inside the GAC (less than 0.1%). Currently, a new synthesis method based on the precipitation of TiO_2 in acid medium from a $TiCl_4$ precursor agent is being developed. It is expected to obtain a carbonaceous material with a good distribution and penetration of TiO_2 nanocrystals of the order of 5-10 nm and TiO_2 content higher than 0.5%. This new approach is based on the formation of $[TiCl_6]^{2-}$ by stabilizing $TiCl_4$ in HCl solution. Subsequently, with the addition of NaOH $Ti(OH)_4$ gel is obtained. As a result of the calcination of the hydroxide, nanocrystals of TiO_2 of anatase crystalline structure are predominantly obtained. Table 1 shows the variables under study to intensify the TiO_2 content deposited on the GAC.

Table 1. Experimental conditions of TiO_2/GAC composite preparation by precipitation of TiO_2 in acid medium.

	Order of the reagents						*Temperature*	
$TiCl_4$/GAC ratio	**1st**	**2nd**	**[HCl], mol/L**	**[NaOH], mol/L**	**[$TiCl_4$] 1st, mol/L**	**[$TiCl_4$] 2nd, mol/L**	**1st, ºC**	**2nd, ºC**
0.61	HCl	NaOH	6.02	3.82	0.09	$1.06 \cdot 10^{-4}$	15	15
0.61	HCl	NaOH	6.02	19.10	0.09	$1.06 \cdot 10^{-4}$	15	15
0.61	HCl	NaOH	6.02	6.36	0.09	$7.08 \cdot 10^{-5}$	15	15
0.61	HCl	NaOH	6.02	19.10	0.09	$1.06 \cdot 10^{-4}$	0	50
0.61	NaOH	HCl	6.02	9.55	0.09	$1.06 \cdot 10^{-4}$	15	15
0.61	NaOH	-	-	5.00	0.09	-	15	90

REFERENCES

[1] Orge, C.A., Faria, J.L., Pereira, M.F.R., Photocatalytic ozonation of aniline with TiO_2-carbon composite materials, J. Environ. Manage., 195 (2017), 208-215.

Simultaneous catalytic abatement of NO_x and dioxins: A novel alternative for gas cleaning in MWI plants

J.A. Martín, M.J. Cano, J.I. Álvarez, J.I. Gutiérrez-Ortiz, J.A. González-Marcos, J.R. González-Velasco, M.P. González-Marcos, A. Aranzabal
Group of Chemical Technologies for Environmental Sustainability, Dept. of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Leioa, Bizkaia, Spain

KEY WORDS: MWI plants, NO_x, dioxins, simultaneous catalytic removal, VO_x catalyst, MnO_x-CeO_2 catalyst

This research line studies the simultaneous catalytic abatement of nitrogen oxides (NO_x), dioxins (PCDD), furans (PCDF) and volatile organic compounds (VOCs) in exhaust gases from municipal waste incineration (MWI) plants.

Nowadays, the management of waste generated by society has become one of our biggest challenges. Incineration in MWI plants is a good alternative, since it allows for energy recovery from waste through electric power production. However, the emission of gases with a high polluting power, derived from combustion, is its biggest drawback. As a result, the gas cleaning line is the most important part of the plant, from an environmental point of view. This line is composed of several stages, including: removal of ashes and heavy metals through an electrostatic precipitator; neutralization of acid gases, such as HCl and SO_2, by dry and wet scrubbers; removal of NO_x and retention of VOC and PCDD/Fs.

Up to now, the typical way to abate NO_x from combustion gases of MWI plants was non-catalytic reduction with NH_3. However, this technique presents a low efficiency. On the other hand, PCDD/Fs are separated by adsorption, which has the problem of transferring PCDD/Fs from the gas phase to a solid phase which requires further treatments.

The tightening of emission regulation limits has promoted the search for alternative processes which allow the removal of pollutants more efficiently. In this way, catalytic technology has been incorporated into the abatement of NO_x (SCR). The reaction is based on the reduction of NO_x with NH_3 over VO_x/TiO_2-based catalyst. Previous works show that this catalyst has good properties in oxidation reactions. Therefore, TQSA research group proposes the simultaneous abatement of NO_x and PCDD/Fs in a single catalytic bed (dDiNO_x process).

The results obtained with VO_x/TiO_2 catalyst show that the simultaneous abatement of both pollutants is possible. SCR reaction occurs at lower temperature than oxidation reaction. Moreover, at high temperature, parallel reactions, such as NH_3 oxidation, take place and because of them it is difficult to obtain high conversion of both reactions at the same temperature. Regarding the reaction mechanism, it has been concluded to be quite complex, and the reaction pathway changes with reaction temperature and VO_x species in the catalyst surface.

The study of alternative catalysts shows that metal-interchanged zeolites (with Cu, Fe and Mn) improve activity in SCR reaction due to their higher acidity, although the oxidation activity decreases due to diffusion problems related to catalyst pore size. On the other hand, the use of MnO_x-based catalysts shows the best activity in the abatement of both components at low temperature. This behaviour improves with the addition of CeO_2, which increases oxygen mobility thus improving the redox properties of the catalyst.

Currently, our research is focused on MnO_x-CeO_x-based catalyst. In the future, the main objective is to propose a mechanistic equation to describe reaction kinetics. For this purpose, it will be important to find an adequate reaction pathway, by means of *in-situ* FTIR experiments, describing how reactants and products interact with the catalyst. This will help to solve one of the biggest handicaps of MnO_x-CeO_2 catalyst: their deactivation at low temperature.

Catalytic valorisation of biomass-derived organic waste: a contribution to the hydrogen economy

A.J. Reynoso[1], J. L. Ayastuy[1], A. Morales-Marín[1], U. Iriarte-Velasco[2], M. Gil-Calvo[1], A. Sanz[1], Z. Boukha[1], B. De Rivas[1], A. Aranzabal[1], M.P. González-Marcos[1], J.I. Gutiérrez-Ortiz[1], R. López-Fonseca[1], M.A. Gutiérrez-Ortiz[1]

Group of Chemical Technologies for Environmental Sustainability.

[1]Dept. of Chemical Engineering, Faculty of Science and Technology, UPV/EHU, Leioa, Bizkaia, Spain; [2] Dept. of Chemical Engineering, Faculty of Pharmacy, UPV/EHU, Vitoria-Gasteiz, Spain

KEY WORDS: Hydrogen production, fuel cell, catalytic processes, aqueous phase reforming, biomass, waste valorization.

The increasing economic development in the world has notably increased energy consumption, accelerating the depletion of fossil fuels. Additionally, there is a need for developing alternative energy supply strategies, which protect the environment and promote a transition from the actual fossil-fuel based economy to renewable energy based one. In this context, hydrogen is taking a relevant place as energy vector, promoting the development of fuel cell technology, with an added value of neutral net CO_2 balance whenever they are fed by hydrogen produced from biomass–derived oxygenated hydrocarbons.

A fossil fuel economy is totally non-sustainable in our society due to the lessening of fossil sources and increase of environmental, economic and political problems driven by this economic model. Hydrocarbons cause huge negative impact on public health due to its polluting gas emission. The increasing emission of greenhouse gas introduced by burning fossil fuel leads to global warming. In recent years, new technologies have been developed to promote the transition from the fossil-based to a bio-based economy.

Hydrothermal processes have been applied to convert biomass or intermediate products with high water content into biochemicals and biofuels. Among these processes, aqueous phase reforming (APR), introduced in 2002, produces hydrogen and other value-added chemicals from biomass derived feedstock under significantly mild reaction conditions. It can be carried out in a single-step chemical reactor, though various reversible chemical reactions like Water-Gas Shift (WGS) reaction, dehydration, carbon bond cleavage, etc. can take place simultaneously. APR has been proven energetically more efficient than the other technologies. Its higher efficiency derives from its lower energy requirements by the suppression of the water evaporation step. Also, it is one of the most technically feasible approaches to produce hydrogen streams with trace amounts of CO. In general, oxygenated hydrocarbons such as sugars (glucose, fructose) and alcohols (sorbitol, xylitol, glycerol, ethylene glycol, ethanol, methanol, acetic acid) can be valorised into hydrogen and carbon dioxide among other gaseous and liquid products.

TQSA group has focused the present research in the development of active catalysts for obtaining hydrogen-rich streams from the aqueous phase reforming of biomass-derived glycerol. Nowadays, there exists a surplus of glycerol on the market as a result of the ever increasing biodiesel production promoted by firmer regulations for fuels. The interest of the project is oriented to the non-conventional design (preparation, composition and activation protocol) of new transition metal cost-effective catalysts (Co,Ni) whose catalytic behaviour can be comparable to that of the benchmark noble metal catalysts.

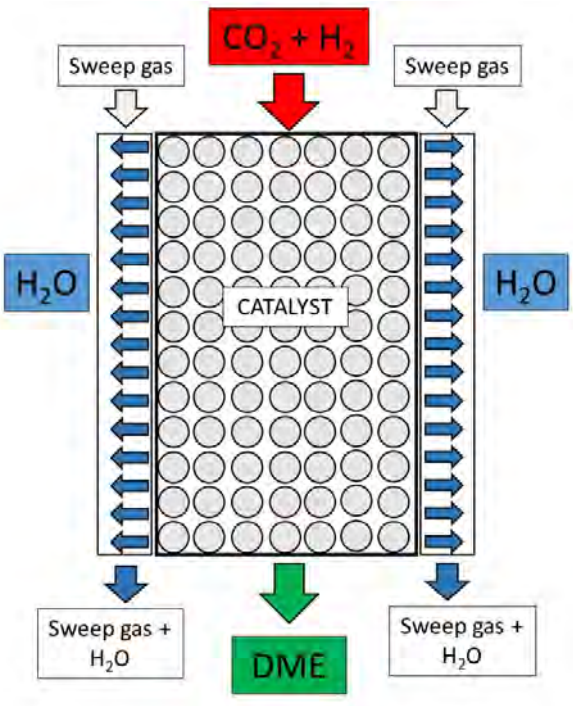
The physico-chemical characterisation of the prepared samples involved a wide number of techniques for the determination of their composition, surface properties, morphology, structure etc., either for the fresh or spent catalysts. The evaluation of the catalytic performance is carried out in a bench-scale fixed-bed up-flow reactor and the reaction products analysed by chromatographic methods.

CO_2 valorization enhancement in the one-step DME synthesis using a packed bed membrane reactor

Pablo Rodriguez-Vega, Andrés T. Aguayo and Javier Bilbao
Chemical Engineering Department (CPWV Group), University of the Basque Country (UPV/EHU),
P.O. Box 644, 48080 Bilbao, Spain

KEY WORDS: Dimethyl Ether, CO_2, Membrane reactor.

Dimethyl Ether (DME) has become a great interest as an environment-friendly alternative fuel with similar characteristics to diesel fuel, as raw material for the synthesis of chemicals (olefins, aromatics) and as vector for H_2 production. Besides, using the DME direct synthesis process (STD process), the thermodynamical limitations of methanol and of the two-step process are reduced. This facilitates the conversion of CO_2 co-feeded with syngas and the syngas valorization with a low H_2/CO ratio, like the one obtained from biomass gasification [1]. Through the last few years important contributions in the improvement of catalysts and kinetic modeling have been made, focused on the co-feeding of CO_2. The most recent innovations address two main aspects: 1) the preparation of the bifunctional catalyst with a core-shell like configuration of the particles, dividing in two domains the reactions on the metallic function (methanol synthesis and WGS) and on the acid function (methanol dehydration); 2) the use of a membrane reactor. Both strategies facilitate the separation of the water formed in the dehydration, promoting the progress of the methanol synthesis. However, it results more effective the separation within the whole reactor (Figure 1), which has been cuantified by simulation in previous studies by simulation [2]. Membrane reactors have been widely studied during the last two decades due to their high potential for the production of fuels from alternative sources and, particularly, for the Fischer-Tropsch synthesis.



In this study, the experimental implementation of the membrane reactor to produce DME has been described. The originality of this objective has required the following work steps: 1) Selection of the zeolite membrane, suitable for high pressure, temperature and selective separation of water from DME and methanol; 2) LTA membranes synthesis (Scrubbing and Vacuum Seeding methods); 3) Characterization of its properties (hydrothermal and mechanical resistance, hydrophilicity and H_2O/DME permselectivity); 4) Instalation of the fixed bed membrane reactor system, external gas-inlet equipment, sweep gases and analysis.

The performance of the membrane reactor with a conventional fixed bed reactor has been compared, for quantifying the CO_x conversion ($CO+CO_2$), DME yield and selectivity and stability). The reaction runs were carried out under the following conditions: Catalyst, CuO-ZnO-ZrO_2/SAPO-11, with a high stability co-feeding CO_2 [3]; Feed gas, $H_2+CO+CO_2$; H_2/CO_x ratio in the feed, 3; CO/CO_2 ratio, 0.5; temperature, 275-325 ºC; pressure, 20- 40 bar; space time, 10 $g_{cat}h\ (mol_C)^{-1}$.

Figure 1. Fundamentals of the packed bed membrane reactor en el STD process

The results show a considerable enhancement in the DME yield (greater than 50 % within a wide range of reaction conditions) using a membrane reactor in comparison with a conventional fixed bed reactor. Additionaly, they expose a greater capacity of the new reactor to produce DME valorizing CO_2 and a huge step to enable its industrial application.

[1] Ateka, A. Pérez-Uriarte, P., Gamero, M., Ereña, J., Aguayo, A.T., Bilbao, J. Energy, 120 (2017) 796-804.
[2] Diban, N., Aguayo, A.T., Bilbao, J., Urtiaga, A., Ortiz, I. Ind. Eng. Chem. Res., 52 (2013) 10342-10354.
[3] Sánchez-Contador, M., Ateka, A., Aguayo, A.T., Bilbao. J. Ind. Eng. Chem. Res., 57 (2018) 1169-1178.

Hydrogen production from biomass pyrolysis/steam reforming on different Ni supported catalysts

L.Santamaria, G. Lopez and M. Olazar
Department of Chemical Engineering (CPWV Group), University of the Basque Country (UPV/EHU),
P.O Box 644, 48080 Bilbao, Spain

KEY WORDS: Hydrogen, Reforming, Pyrolysis, Biomass, Catalyst

In-line reforming of the volatiles has been proposed as an adequate strategy for H_2 production from biomass that involves several operational advantages, as are: (i) separate optimization of pyrolysis and reforming conditions, (ii) lower temperature than gasification, which reduces material costs and catalyst sintering problems, (iii) avoids the direct contact of the catalyst with the inorganics contained in biomass. The aim of this research was to study the influence the support (Al_2O_3, MgO, SiO_2, TiO_2, and ZrO_2) has on the performance of Ni catalysts used and their relation on the basis of the characterization result (N_2 adsorption-desorption, XRF, TPR and XRD).

The bench scale plant used is made up of two reactors connected in line (Figure): A conical spouted bed reactor (CSBR) in which the pine sawdust pyrolysis was carried out at 500ºC, and a fluidised bed reactor (FBR) for the reforming of pyrolysis volatiles at 600ºC [1]. A steam/biomass (S/B) ratio of 4 was used in all the experiments, with continuous biomass feed rate being 0.75 g min^{-1} and that of the steam 3 ml min^{-1}. In addition, two different space time values (10 and 20 g_{cat} min $g_{volatiles}^{-1}$) were assayed. The products were quantified on-line by means of a GC Varian 3900, and the permanent gases in a microGC (Varian 4900).

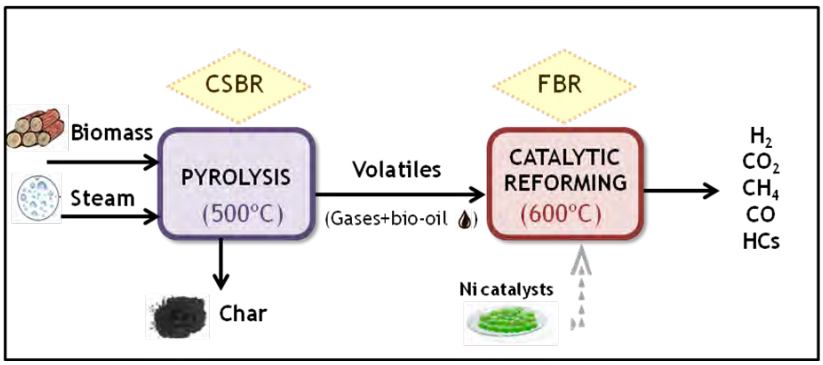


Figure. Reaction steps

The results obtained for the space time of 20 g_{cat} min $g_{volatiles}^{-1}$ showed almost full conversion (>98%) for Ni/Al_2O_3, Ni/MgO and Ni/ZrO_2 catalysts. In the case of Ni/TiO_2 catalyst, conversion was 91 %, whereas Ni/SiO_2 had a low reforming activity, with conversion being 23 %. In this case, although Ni/SiO_2 catalyst showed an adequate Ni dispersion and low crystalline size, the microporous structure of the support hinders the accessibility and diffusion of bio-oil molecules to Ni sites, explaining the low reforming activity observed. In Ni/TiO_2 catalyst the low Ni dispersion may be responsible for the limited activity of this catalyst. For MgO support, a suitable activity is obtained in spite of its low surface area and metal dispersion, since Ni is located mainly on the external surface of the support, making active sites highly accessible to pyrolysis volatiles and thus, improving catalyst activity.

It can be concluded that the continuous reforming of biomass fast pyrolysis volatiles in a CSBR-FBR system is a suitable process for the direct H_2 production from biomass. Ni/Al_2O_3 and Ni/ZrO_2 present the best activity with a hydrogen production above 10 wt% (referred to biomass mass unit), as a consequence of the suitable physical properties of the support, whereas TiO_2 and SiO_2 supports lead to a markedly reduced activity.

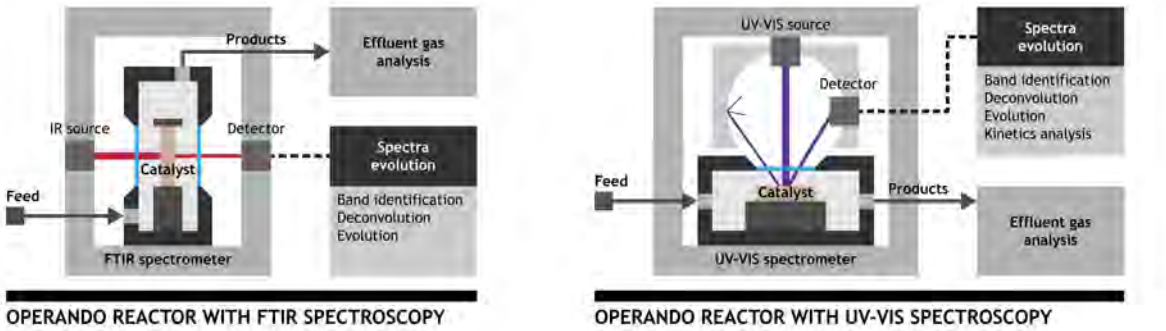
[1] Santamaria, L., Lopez, G., Arregi, A., Amutio, M., Artetxe, M., Bilbao, J. and Olazar, M., Applied Catalysis B: Environmental 229 (2018) 105-113.

Advances in understanding catalyst deactivation using operando reactors

José Valecillos, Andrés T. Aguayo and Pedro Castaño
Department of Chemical Engineering (CPWV Group), University of the Basque Country (UPV/EHU),
P.O. Box 644, 48040, Bilbao, Spain

KEY WORDS: Catalyst Deactivation, Operando Reactors, FTIR, UV-VIS, Methanol-to-Olefins

Catalysts are the cores of catalytic processes as they accelerate the reactions of desired products. However, in many processes, the catalyst also undergoes rapid deactivation affecting process economy due to complementary process equipment needed for catalyst regeneration or dead time for production. Catalysts deactivation strongly depends on the process nature. For example, in the hydrocarbons conversion, catalysts commonly deactivate due to the formation and deposition of heavy carbonaceous species, namely coke, that block catalyst pores and active sites for further reactions. This sets out the research challenge of better understanding the deactivation phenomena in order to optimize catalyst design to prevent deactivation. For this purpose, operando reactors are powerful tools as they offer the possibility of observing what happens to the catalyst surface as the reaction is taking place (*in situ*) by means of diverse spectroscopies techniques. Particularly, infrared (FTIR) and ultraviolet-visible (UV-VIS) spectroscopies are suitable techniques to study catalyst deactivation caused by coke as they allow detecting a wide range of hydrocarbon species that remain in the catalyst. The following chart summarizes our experimental strategy for testing catalysts and reaction conditions in operando reactors:



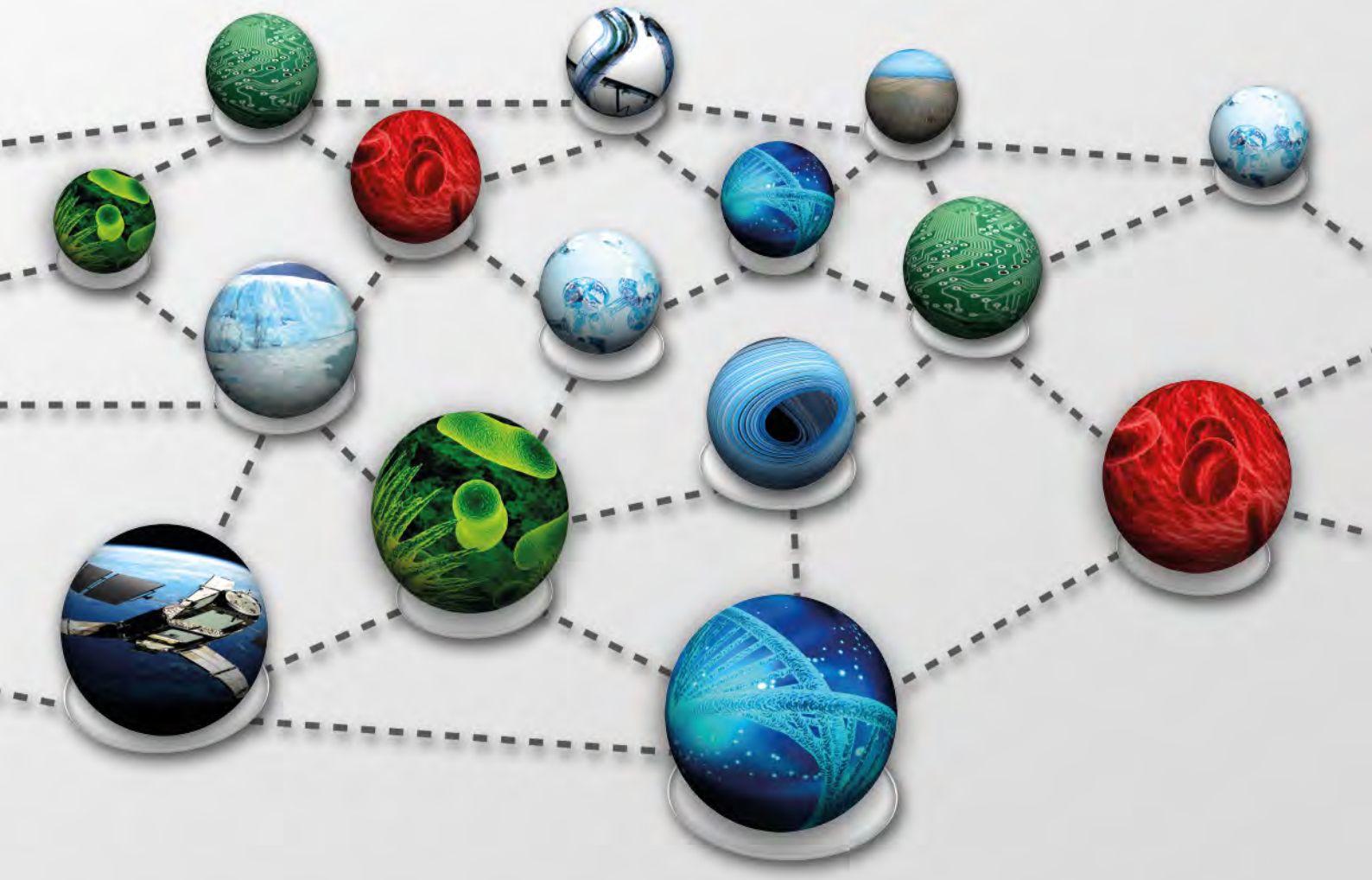
One relevant case study is the alternative catalytic process for olefins production by the methanol-to-olefins (MTO) conversion. This conversion takes place in acid catalysts, mostly based on HZSM-5 zeolites, and it involves three stages: initiation, autocatalysis and deactivation. The autocatalytic stage is key because it involves joint reactions assisted by active species formed from olefins, called hydrocarbon pool (HCP), which evolve and eventually end up being the species (coke) that deactivate the catalyst. In order to prevent the catalyst deactivation in the MTO conversion, we have aimed to study the modification of HZSM-5 zeolite (HZ5) by H_3PO_4 impregnation (PZ5) or $ZnCl_2$ ion exchange (ZnZ5) monitoring the retained products in operando reactors. The results evidenced the formation of HCP and coke species determined by the appearance and rising of absorption bands associated with aliphatic or aromatic species, through which we observe that:

- Carbocations of alkylated benzenes, alkylated naphthalene and anthracene/phenanthrene are present during the MTO conversion. The former are active species to form olefins whereas two- and three-ring aromatics are active and deactivating species.
- The formation of these species corresponds with an autocatalytic kinetic and the rate constant of each species decreases with P or Zn modifications. Zn is more effective to retard coke precursors formation.

The results are promising to improve catalyst design and they open an opportunity to study other process conditions, such as the effect of adding water in the feed, and other hydrocarbons conversion processes.

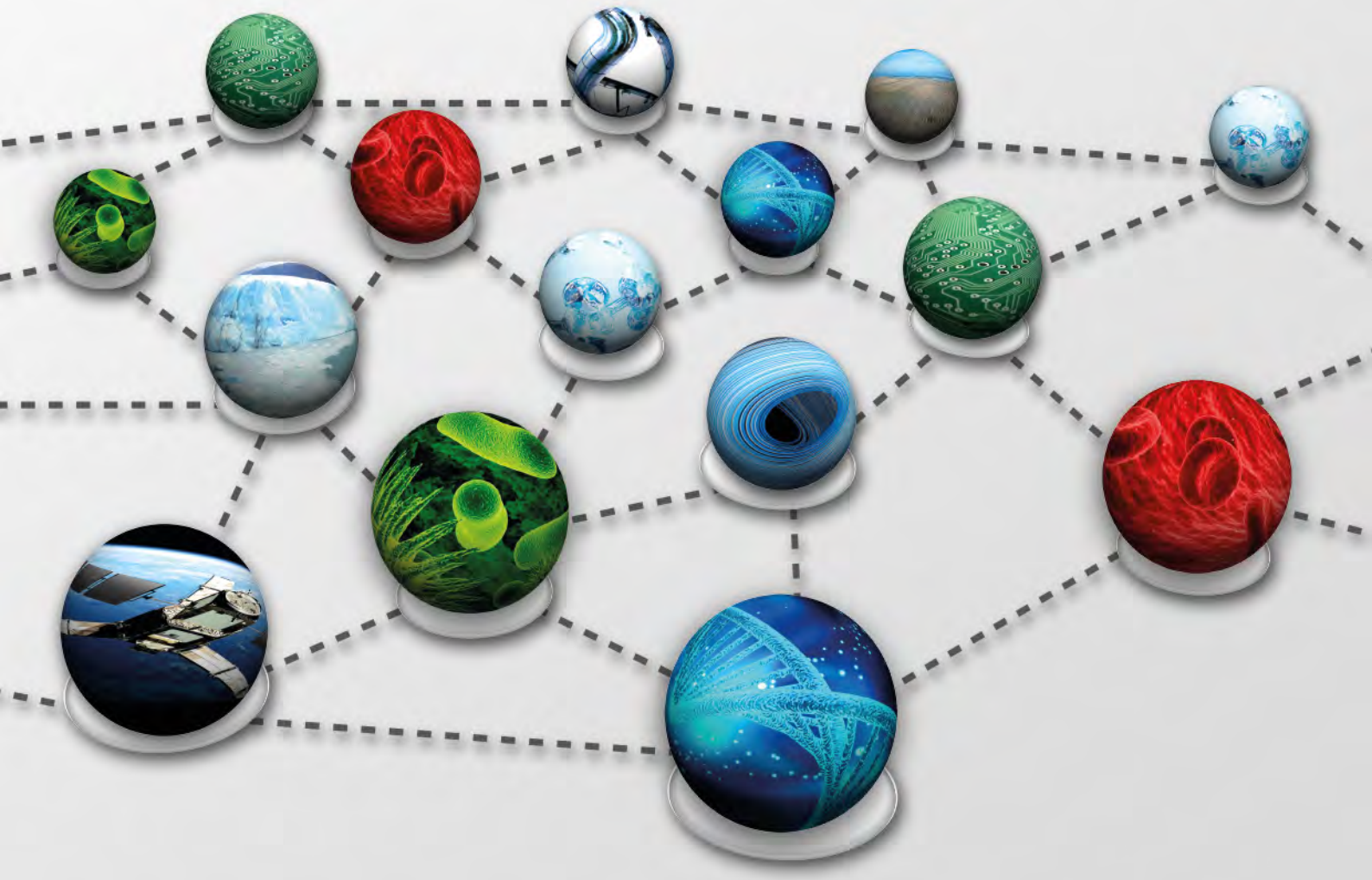
Beste Ikergune Batzuk

Otros Centros de Investigación



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

BCMATERIALS



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

A new generation of multifunctional materials based on silk fibroin

Ander Reizabal, Leire Pérez, Senen Lanceros, Jose Luis Vilas

KEY WORDS: Silk, Bombyx mori, Fibroin, film, scaffold, membranes, multifunctional, sensor, actuators, biomedicine

Bombyx mori (silkworm) silk is a unique material, which has historically been highly regarded for its strength and luster. Chinese legend gives the title Goddess of Silk to Lady Hsi-Ling-Shih, wife of the mythical Yellow Emperor, who was said to have ruled China in about 3000 BC. Since then and during centuries silk threads were used in the manufacturing of high quality woven. High demand and value of silk-based textiles promoted its expansion and use along the world, giving a name to one of the best-known trade routes, the silk road. Besides the textile application, high mechanical properties of silk fibres and biocompatibility promote their use as surgical sutures during centuries, but the appearance of low-cost synthetic polymers replace it and reduce their use to the high-quality clothes confection.

Industrial revolution together with the scientific advances minimised the use of natural materials during XX century but actually, green transition demands the substitution of actually based petrochemical compounds by environmental low impact materials.

This project proposed silk as a natural resource for advanced applications in high impact areas: technological products and biomedical area. In this context, the long range of morphological variations of silk, its functional characteristics and processability situate this product as a new and promising material for the becoming revolution. This work is proposed as a contribution to the advanced manufacturing and circular economy, enhancing the technological transition while fuel based material substitutions is promoting.

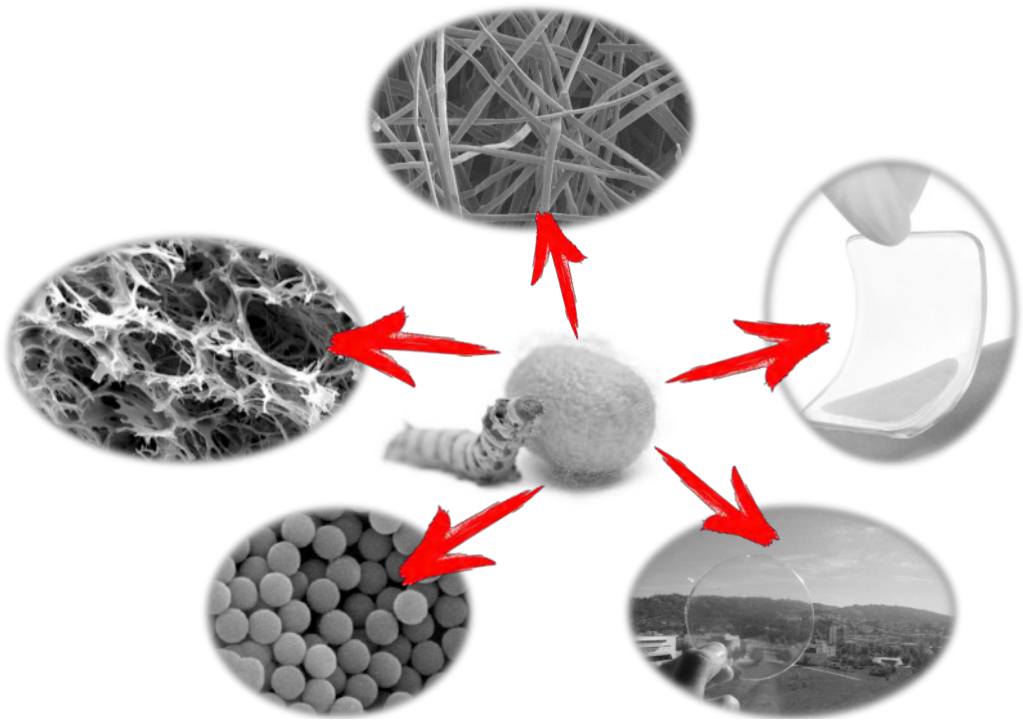
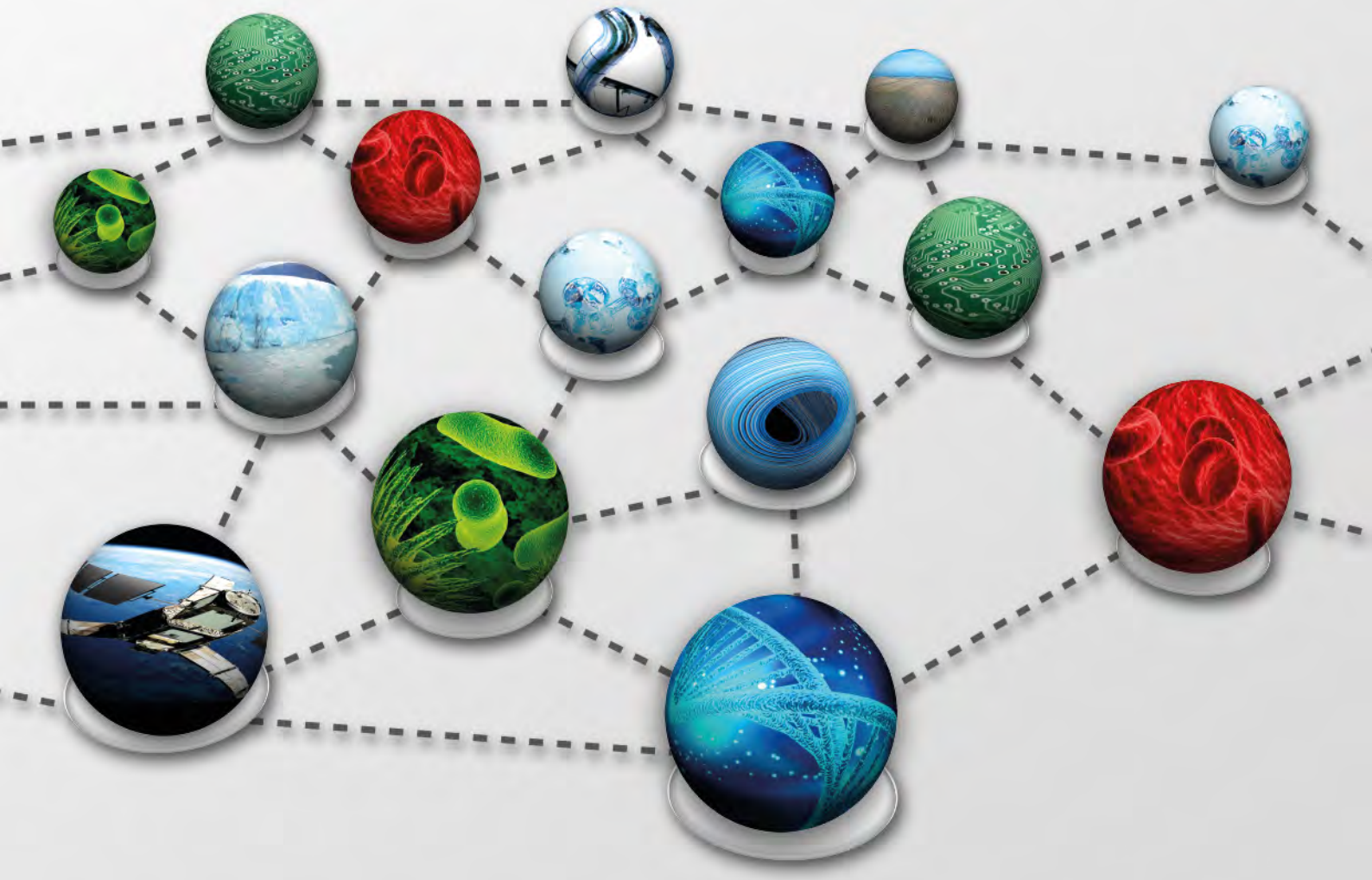


Fig 1. An example of the different morphological variations of silk fibroin.

SGIKER



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Advanced research facilities of the UPV/EHU SGIker

Echeverria-Machado I.[1]*, Arriortua MI*[2]
[1]Advanced research facilities, UPV/EHU, SGIker; [2]Univ Basque Country, Fac Ciencia & Tecnol, Sarriena S-N, Leioa 48940, Spain.

KEY WORDS: Advanced, research, facility.

Advanced Research Facilities, SGIker, created by the University of the Basque Country / Euskal Herriko Unibertsitatea, UPV/EHU, were born in 2002 with the vocation to respond and provide support for research, being available to the university itself, other Public Institutions and Business.

SGIker have front-line technical and human resources, and aims to offer research support at the highest level, with modern equipment and high technology equipment. This infrastructure allows SGIker to respond to a variety of problems in the field of research and technological development.

SGIker units are present in the three Campus of the UPV/EHU and are distributed in the following scientific areas:

- Materials and Surfaces
- Biotechnology and Biomedicine
- Environment
- Common Services
- Geographical-Historical Sciences
- Social Sciences
- Technological support

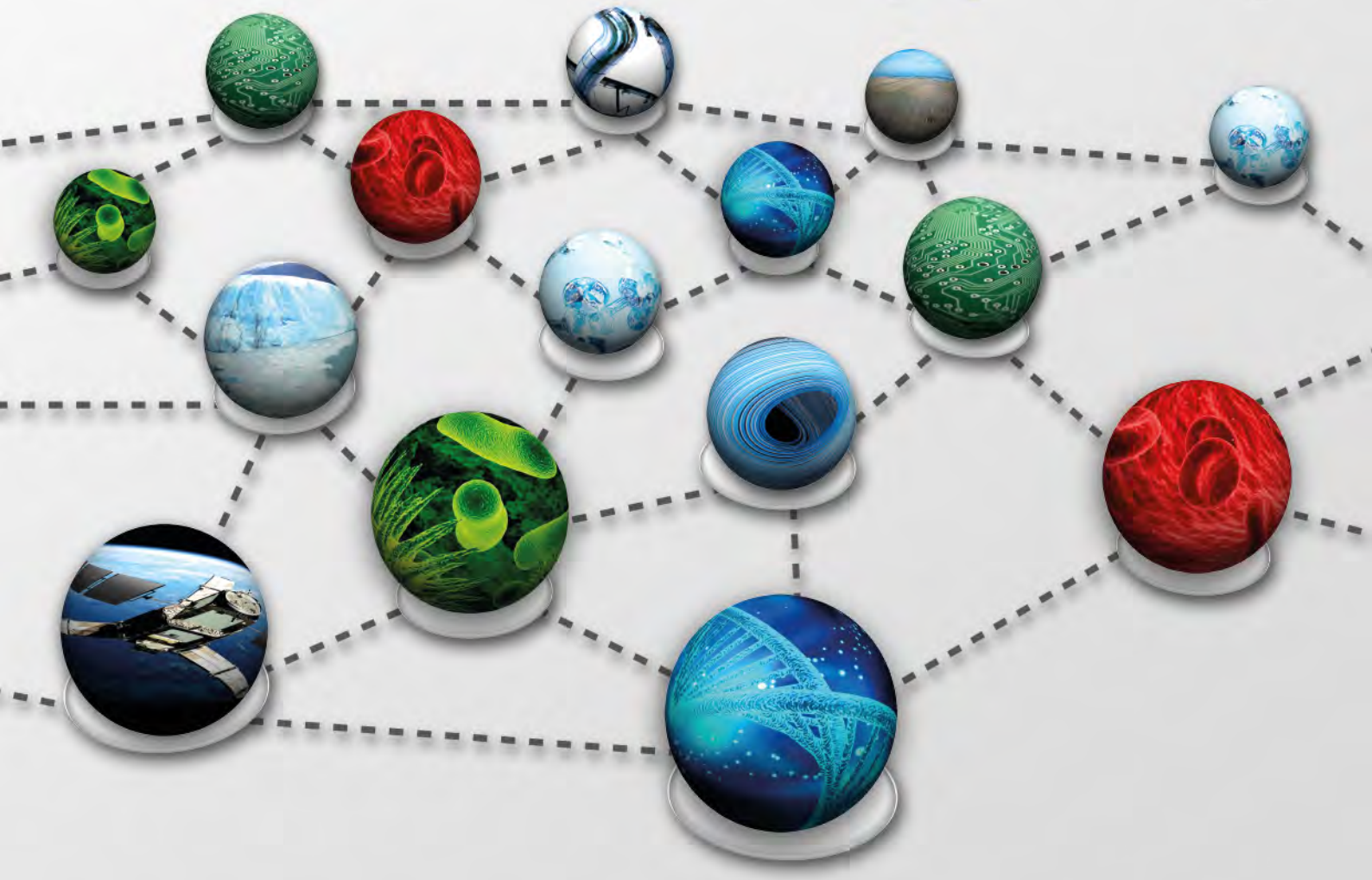
As a result of this proposal of the university, the scientific indicators of the UPV/EHU have increased, mainly the publications indexed in JCR in the fist quartile or decile.

This actions have been possible thanks of the efforts of the SGIker staff, other university's departments, the Basque Government and the corresponding Spanish Ministry.

ABSTRACTS

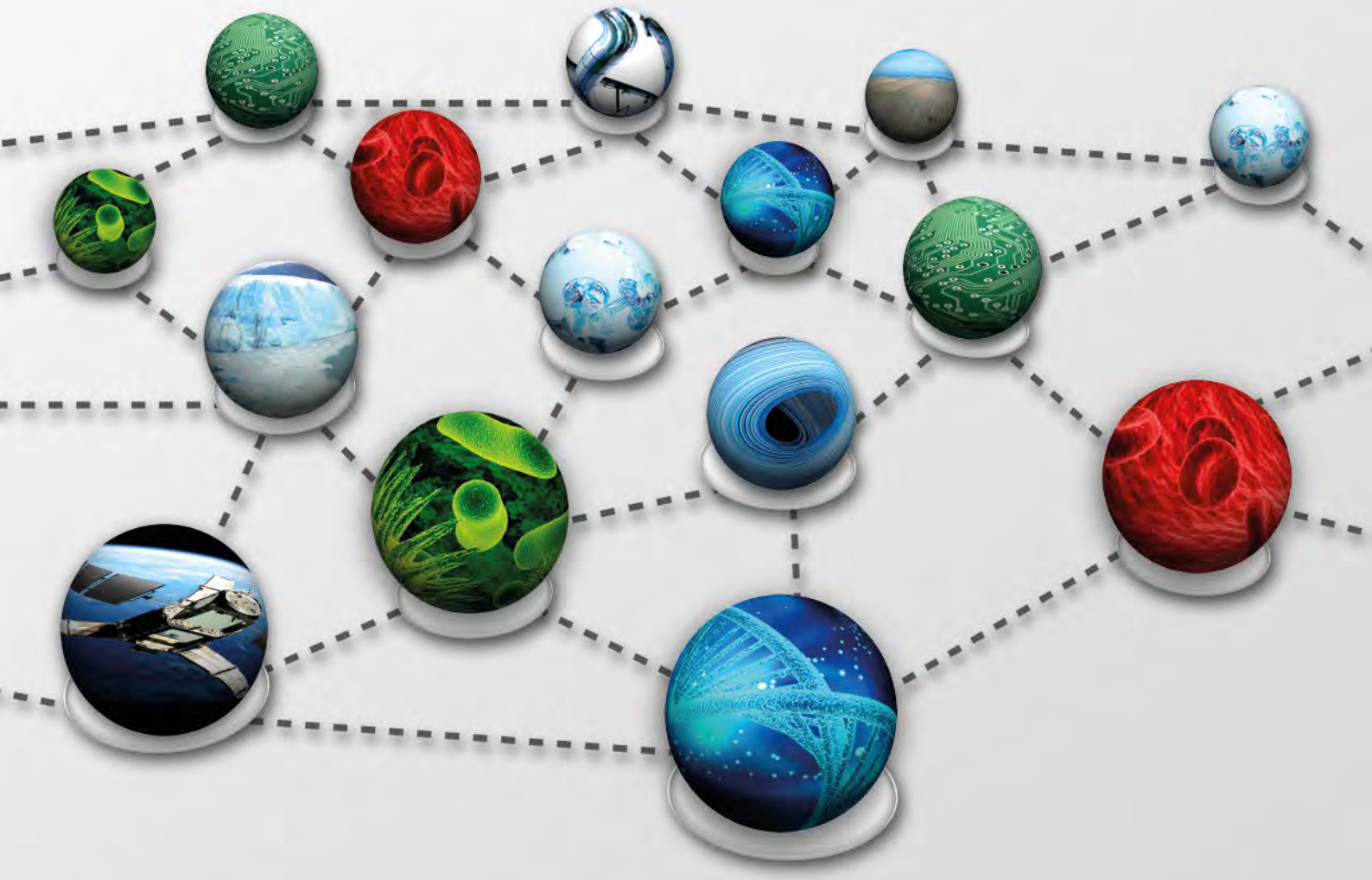
IDATZIZKO KOMUNIKAZIOAK

COMUNICACIONES ESCRITAS



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

BIOZIENTZIAK
BIOCIENCIAS



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Ceramide 1-phosphate is a novel regulator of adipocyte proliferation

Asier Domínguez, Natalia Presa, Miguel Trueba and Antonio Gómez-Muñoz
Department of Biochemistry and Molecular Biology, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48080 Bilbao, Spain

KEY WORDS: adipocytes, cell proliferation, ceramide 1-phosphate (C1P), obesity, sphingolipids.

Sphingolipids have been considered for many years as structural components of cell membranes. However, it is now well established that some sphingolipids are bioactive molecules that are capable of regulating essential biological functions. A particularly important bioactive sphingolipid is ceramide 1-phosphate (C1P), which is synthesized by phosphorylation of ceramide in a reaction catalyzed by ceramide kinase (CerK). C1P was first shown to stimulate cell growth and survivial in different cell types including fibroblasts, myoblasts and macrophages, and was later shown to be implicated in inflammatory responses. In this study, we show that C1P promotes proliferation of 3T3-L1 preadipocytes, an action that may be associated with adipocyte expansion and increased risk of obesity and obesity-associated illnesses. In addition, we show that C1P stimulates the phosphorylation of protein kinase B (also known as Akt), extracellularly regulated kinases 1 and 2 (ERK1-2) and signal transducer and activator of transcription 3 (STAT-3), suggesting that phosphatidylinositol 3-kinase (PI3K)/PKB, mitogen activated protein kinase kinase (MEK)/ERK1-2 and janus kinase (JAK)/STAT3 pathways might be involved in the mitogenic effect of C1P. To test this, we used selective inhibitors of these kinases. Noteworthy, we found that the inhibitors of PI3K, MEK and STAT-3 (LY294002, PD98059 and Stattic, respectively) as well as specific siRNAs to silence the genes encoding PI3K, MEK and STAT-3, attenuated C1P-stimulated adipocyte proliferation thereby implicating these pathways in the mitogenic effects of C1P in preadipocytes. The present study highlights new aspects on the control of preadipocyte proliferation implicating C1P as a novel regulator of this process. These actions may be important in the onset or development of obesity and obesity-associated disseases such as diabetes, cardiovascular disease or cancer.

ACKNOWLEDGEMENTS: This research was supported by grants IT-1106-16 from ‘Departamento de Educación, Universidades e Investigación del Gobierno Vasco (Basque Country, Spain)’, and SAF2016-79695-R from ‘Ministerio de Economía y Competitividad (Madrid, Spain). AD is a recipient of a fellowship from the Basque Government.

Pharmacological chaperoning and binding impairment, two therapeutic approaches involving nucleophosmin as target in antitumoral treatments

David J. López, Marián Alonso-Mariño, María A. Urbaneja and Sonia Bañuelos.
Biofisika Institute (UPV/EHU-CSIC) and Department of Biochemistry and Molecular Biology, University of the Basque Country (UPV/EHU), Leioa, Spain.

KEY WORDS: NPM1, APE1, acute myeloid leukemia, pharmacological chaperones.

Nucleophosmin (NPM1), also known as nucleolar phosphoprotein B23, NO38 or Numatrin, is a protein preferentially localized in nucleoli of cells. It is found in animals, but not in bacteria or yeast. NPM1 is a homopentameric protein composed of a compact, β-structured and highly conserved N-terminal domain (core) which is responsible for oligomerization. The core is connected to the corresponding α-helical C-terminal domains through flexible, unstructured linkers. NPM1 functions as ribosome and histone chaperone, by participating in the ribogenesis and chromatin remodeling, respectively. Besides, it takes part in other cell processes such as DNA replication, transcription and repair, centrosome duplication and nucleocytoplasmic transport. This protein is also related to cancer and its levels are generally elevated in tumor cells, presumably due to a higher demand of ribosome synthesis and the fact that its transcription is regulated by the oncogene Myc.

NPM1 has become an interesting target in antitumor therapies since it is implicated in several cell functions affecting cell growth, cell survival and apoptosis. In 2005, a mutation of the C-terminal domain of NPM1 was observed in ~30% of adult acute myeloid leukemia (AML) patients. The mutation correlates with structural destabilization of the C-terminal domain and aberrant cytoplasmic localization of the protein. Refolding of this domain by the so-called pharmacological chaperones may constitute a therapeutic approach to revert the delocalization of mutant NPM1. Here, we show the chaperoning potential of two compounds, namely C1 and C3, to restore the nucleolar localization of misfolded mutants. Biophysical techniques (fluorimetry, circular dichroism and molecular dynamics) showed the binding and the stabilization effect of these compounds on misfolded NPM1, while microscopy analyses validated their potential to relocate the mutant protein to the nuclei.

On the other hand, another antitumoral approach is related to the DNA repair function of NPM1. NPM1 has been described to interact with apurinic/apyrimidinic endonuclease 1 (APE1), a protein implicated in the “base excision repair” pathway. Since this protein-protein interaction regulates the localization and enzymatic activity of APE1, any impairment of the NPM1/APE1 interaction has been raised as an alternative antitumoral treatment. Specifically, it may be useful as a synergistic therapy to enhance the effect of molecules aimed to induce genotoxicity, that is, DNA damage in cancer cells. Here, as a first step towards targeting the NPM1/APE1 interaction, we present data describing the binding affinity between APE1 and NPM1 (Kd ~0.5 μM), which will serve as valuable reference in the search of molecules for a binding impairment therapeutical approach.

Structure and lipid specificity support adaptation of pestivirus p7 c-terminal helix to permeabilizing secretory compartments

Eneko Largo[1], Douglas P. Gladue[2], Nerea Huarte[1], Antonio Alcaraz[3], Vicente M. Agilella[3], Manuel V. Borca[2], and José L. Nieva[1]

[1]Biofisika Institute (CSIC-UPV/EHU) and Biochemistry and Molecular Biology Department, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080 Bilbao, Spain. [2]Plum Island Animal Disease Center, ARS, USDA, Greenport, NY 11944, USA.[3]Laboratory of Molecular Biophysics, Department of Physics, Universitat Jaume I, 12071 Castelló, Spain.

KEY WORDS: Viroporin, CSFV, Membrane permeabilization.

Classical swine fever virus (CSFV) protein p7 possesses two hydrophobic domains intervened by a short polar loop, predicted to span the membrane as a helix-turn- helix hairpin. Here, we use a combined lipid monolayer, planar bilayer and vesicle analysis to characterize the insertion and permeabilization of membranes by constituent CSFV p7 helices. Structural data and the dependence on lipid composition of these processes support that the C-terminal helix is a poreforming protein adapted to permeabilizing membranes of the secretory compartments or mitochondria. Together with the observed pH-dependence and inhibition pattern, our data suggest that CSFV p7 relies on genus-specific structures-mechanisms to perform its viroporin function.

Remodeling of RepE conformation by DnaK and DnaJ

Judit Perales-Calvo, Garbiñe Celaya, José Angel Fernández-Higuero, Arturo Muga, David Rodriguez-Larrea and Fernando Moro
Biofisika Institute (UPV/EHU, CSIC) and Department of Biochemistry and Molecular Biology, Faculty of Science and Technology, University of Basque Country, Barrio Sarriena S/N, 48940 Leioa, Spain

KEY WORDS: Molecular chaperones, DnaK, DnaJ, single molecule.

Hsp70 chaperones, together with their Hsp40 cochaperones and nucleotide exchange factors, are essential components of the cellular protein homeostasis network. The Hsp70 chaperone system is involved in multiple essential functions as protein folding, transport across membranes, prevention of protein aggregation and reactivation of aggregates in cooperation with bacterial and fungi Hsp100, and metazoan Hsp110 chaperones. Especially interesting is the ability to modify the function of naturally occurring proteins by conformational remodeling. A good model to study this process is the bacterial protein RepE, the initiation factor of mini F plasmid replication. RepE can act as repressor or activator of plasmid replication depending in its oligomeric state (dimer or monomer respectively). Monomerization of RepE is facilitated by DnaK and DnaJ, the main bacterial representatives of the Hsp70 and Hsp40 families. Here we present bulk biochemical and biophysical data, as well as nanopore single molecule studies of the interaction of RepE with the chaperones and DNA.

Solid Lipid Nanoparticles, smart drug carries that improve drug delivery into cells

Lide Arana, Laura Bayón, Laura Sarasola and Itziar Alkorta [1]
[1] Insituto Biofísica (CSIC, UPV/EHU), and Departamento de Bioquímica y Biología Molecular. Faculty of Science and Technology (UPV/EHU), Leioa.

KEY WORDS: Solid Lipid Nanoparticles, controlled drug delivery, polyethilenglycol, cell uptake.

In the recent years it has been highlighted the relevance of drug nanocarriers in order to improve bioavailability of drugs that, although have been proven to be effective against a particular disease, present bad solubility, poor absorption or low cell membrane permeability. Improving drug stability and solubility in aqueous dispersions could increase their efficiency and reduce solvent-related degradation and high dose-related side effects.
In this regard, Solid Lipid Nanoparticles (SLN) are one of the most promising nanocarriers for controlled drug delivery because of their multiple advantages. They are able to incorporate hydrophilic and lipophilic drugs, present no biotoxicity and drug release kinetic is controlled thanks to their solid core. Moreover, their most important characteristics are their ability to pass through some biological barriers, such as the blood-brain barrier and their tendency to accumulate around solid tumor areas.
Many SLN compositions have been developed and tested and it has been demonstrated that interactions of these nanoparticles and cells depend on the SLN characteristics. Therefore, systematic determination of nanoparticle application is not possible and each preparation should be analyzed independently. In the present work, we have prepared and characterized SLN composed of stearic acid, Epikuron 200, and sodium taurodeoxycholate covered by different amounts of phosphatidilethanolamine-polyethilenglycol (PE-PEG). It has been demonstrated that this polymer stabilizes different nanoparticle suspensions and it can improve the nanocarrier biocompatibility. In order to analyze the effect of PE-PEG addition into SLN, different compositions were prepared and characterized by the analysis of the following parameters: z-size, polidispersity index, z-potential, cell toxicity and cell incorporation pathway. We have observed that PE-PEG covering reduces cell toxicity without affecting significantly SLN physicochemical characteristics. In addition, our results suggest that this surface functionalization modifies cell internalization pathway, which could be a profitable characteristic for the selective drug delivery.
In conclusion, the PEG-SLN nanoparticles developed here present promising characteristics as controlled drug delivery systems because of their low toxicity, proper size and stability and advantageous cell uptake mechanisms. This system offers the possibility of applying smart nanocarries to challenging drugs in which bad solubility, poor absorption or low cell membrane permeability represent a burden to their good a priori therapeutic behavior.

Imaging the Packing State and Lateral Organization of the HIV-1 Membrane Lipids by Two-Photon and Atomic Force Microscopy

Nerea Huarte[1], Pablo Carravilla[1], Antonio Cruz[2], Maier Lorizate[1], Jon A. Nieto-Garai[1], Hans-Georg Kräusslich[3], Jesús Pérez- Gil[2], José Requejo-Isidro[1], José Luis Nieva[1].

[1] 1Biophysics Unit (CSIC, UPV/EHU) and Department of Biochemistry and Molecular Biology, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080 Bilbao, Spain. [2]Department of Biochemistry, Faculty of Biology, and Research Institute Hospital 12 de Octubre, Universidad Complutense, Madrid, Spain.[3]3Department of Infectious Diseases, Virology, University Hospital Heidelberg, 69120 Heidelberg, Germany.

KEY WORDS: HIV, membrane, lipids, microscopy.

The chemical composition of the human immunodeficiency virus type 1 (HIV-1) membrane is critical for fusion and entry into target cells, suggesting that preservation of a functional lipid bilayer organization may be required for efficient infection. HIV-1 acquires its envelope from the host cell plasma membrane at sites enriched in raft-type lipids. Furthermore, infectious particles display aminophospholipids on their surface, indicative of dissipation of the inter-leaflet lipid asymmetry metabolically generated at cellular membranes.

By combining two-photon excited Laurdan fluorescence imaging and atomic force microscopy, we have obtained unprecedented insights into the phase state of membranes reconstituted from viral lipids (i.e., extracted from infectious HIV-1 particles), established the role played by the different specimens in the mixtures, and characterized the effects of membrane-active virucidal agents on membrane organization.

In determining the molecular basis underlying lipid packing and lateral heterogeneity of the HIV-1 membrane, our results may help develop compounds with antiviral activity acting by perturbing the functional organization of the lipid envelope.

Conclusions:

- The HIV lipid envelope is a highly ordered structure.
- The viral membrane may be organized in nanophases as suggested by the presence of nanoscopic rigid domains in HIV lipid monolayers at every measured lateral pressure.
- Anti-viral membrane active compounds decrease lipid packing and induce macroscopic phase separation, indicating this organization may be essential for viral infection.

Unravelling the molecular mechanisms of action of BCL2-related ovarian killer (BOK)

Itsasne Bustillo-Zabalbeitia[1,2], Hector Flores[1,2], Olatz Landeta[1,2], Gorka Basañez[2] and Oihana Terrones[1,2]
[1]Department of Biochemistry and Molecular Biology, University of the Basque Country (UPV/EHU); [2]Biofisika Institute (UPV/EHU, CSIC).

KEY WORDS: apoptosis, mitochondria, BCL2.

Apoptosis is a morphologically distinct and genetically controlled form of cell death that is essential for human development and physiology. Aberrant regulation of this pathway is linked to multiple human diseases, most prominently cancer. The ‘‘point of no return’’ in the mitochondrial apoptotic pathway is the mitochondrial outer membrane permeabilization (MOMP) process that allows release of cytochrome c (cyt. c) and other toxic mitochondrial apoptogenic factors. BCL2 family proteins have long been considered the main regulators of MOMP and cellular commitment to apoptosis, and were more recently found to have additional roles in non-apoptotic cellular processes including mitochondrial dynamics and mitochondrial metabolism. The identification of BCL2 as an inhibitor of cell death not only marked recognition of the first component of cell death mechanism in any organism, but also established a new universal hallmark of cancer cells: evasion of apoptosis. Moreover, BCL2 family proteins are essential contributors to tumor resistance to chemotherapy, as well as promising clinical predictive biomarkers of anticancer chemoterapeutic success.

Over the past three decades, research in hundreds of laboratories has identified and characterized around 20 members of the BCL2 family in humans, and categorized them into three groups: (1) proapoptotic BAX-type protein effectors (BAX, BAK, and perhaps BOK), which form pores directly responsible for MOMP; (2) proapoptotic BH3-only protein ligands (such as BID, BIM, PUMA, NOXA, and BIK), which trigger functional activation of BAX-type proteins; and (3) antiapoptotic BCL2-type proteins (BCL2, MCL1, and others), which inhibit MOMP by sequestering proapoptotic members.

Although BOK was identified almost two decades ago, it remains as one of the least understood BCL2 family members and it is currently the focus of vigorous investigations. Of note, BOK is widely and highly expressed in mammalian tissues, and a global genomic screen of multiple human cancers found that the BOK gene is amongst the most frequently inactivated or deleted genes during tumorigenesis. Because BOK present certain similarities with pro-apoptotic proteins (BAX/BAK), it has been often been assumed that BOK is functionally and mechanistically redundant with BAX/BAK. However, this assumption remains to be explicitly proven. Here, we present distinct lines of evidence indicating that similar to BAX/BAK, BOK: (i) can induce cell death and (ii) binds specifically to cardiolipin (CL) containing membranes. But in contrast to BAX/BAK, BOK: (iii) does not form large scale membrane openings, (iv) induces mitochondrial membrane remodeling in the absence of mitochondrial fission protein DRP1 and (v) is not activated by any BH3-only protein. In conclusion, we have found that the cellular behaviour of BOK shares some common features but also important differences with BAX/BAK.

Selected apoptosis-related lipids regulate BAX/BAK activation and action

Ane Landajuela[*1], Olatz Landeta*[*,2,3], Itsasne Bustillo-Zabalbeitia[2,3], Juan Garcia Valero[4], Hector Flores-Romero[2,3], Miguel Garcia Porras[2], Oihana Terrones[2,3], and Gorka Basañez[2].*

**Both authors contributed equally to this work.*

[1]Department of Cellular and Molecular Physiology Yale University (West Haven, USA); [2] Biofisika Institut (CSIC-UPV/EHU) (Leioa); [3] Department of Molecular Biology and Biochemistry, UPV/EHU (Leioa); [4]Division of Hematology and Oncology, Institut d'Investigacions Biomèdiques (IDIBAPS), (Barcelona).

KEY WORDS: BCL2 family proteins, mitochondrial lipids, cardiolipin, BAX, BAK.

INTRODUCTION:

The BCL-2 protein family is the key regulator of mitochondrial outer membrane (MOM) permeabilization (MOMP), the commitment point in most forms of apoptotic cell death in vertebrates. Activated BCL2 family proapoptotic proteins, BAX and BAKΔC, form a lipidic pore at the MOM allowing apoptogenic factors to be released into the cytosol leading to cellular apoptosis. Therefore, deciphering the mechanisms of action of BAX and BAKΔC is pivotal for understanding how the cell regulates its fate.

A growing number of evidence indicates that selected MOM lipids specifically interact with BCL-2 family proteins to regulate the MOMP pathway. Interaction with mitochondrial lipids is indeed an important parameter to consider in the regulation of these protein functions, as the conformational rearrangements that many BCL-2 family members undertake to become active occur in a lipid bilayer environment. However, the mechanistic roles of apoptosis-related mitochondrial lipids (e.g. cardiolipin (CL), monolysocardiolipin (MLCL), sphingosine-1-phosphate (S1P), ceramide (CER)…) in BCL-2 family protein function are still poorly understood. The main aim of our work is to try elucidating whether and how a variety apoptosis-related lipids regulate the conformation and action of BAX and BAKΔC.

RESULTS:

We have undertaken a systematic analysis to determine whether and how a variety of apoptosis-related mitochondrial lipids interacts physically and functionally with proapoptotic BAX and BAKΔC. We used a combination of biophysical and biochemical techniques mainly applied to *in vitro* reconstituted systems due to the complex network of intermolecular interactions of BCL2 family proteins to regulate MOMP pathway in intact cells. Our studies reveal that CL, MLCL, and S1P, but not other apoptosis-related mitochondrial lipids studied (CER, HEX…), physically interact with recombinant BAX and BAKΔC inducing analogous localized structural rearrangements in the two proapoptotic proteins. In addition, we show that the same subset of apoptosis-related mitochondrial lipids stimulates membrane-permeabilizing (pore formation) activities of BAX and BAKΔC allowing for the release of differently-sized molecules from MOM-like vesicles. Furthermore, we have observed that active apoptosis-related lipids could regulate pore-size triggered by BAX and BAKΔC.

CONCLUSION:

Studies with *in vitro* reconstituted systems indicate that selected apoptosis-related mitochondrial lipids (CL, MLCL and S1P) modulate BCL-2 protein family function through both lipid:protein and lipid:lipid interactions. We propose that specific mitochondrial lipids and BCL2 family proteins intersect mechanistically at the MOM level to regulate apoptosis.

Sport Genomics research Group

Ramírez de la Piscina X[1,2], Larruskain J[1], Castañeda[3], bores A[4]. Muñoz I[4], Álvarez J[1]., Martínez I[2], Odriozola I[2], Antúnez A[2]., Ahedo L[1]., Ascension A[1], Ruiz de Gauna .N[1], Lleida A[1] Buide E[1], Caballero A.[1], Revilla M[1], and Odriozola A. [1,2]

[1]Department of Genetics, Physical Antrhopology and Animal Physiology. University of Basque Country; [2]KDNA Genomics; [3]Sport Sciences. University of Deusto.; [4]Sport Sciences. University of Atlantic.

KEY WORDS: Sport, Genetics, SNP, trainability, injury, polymorphism, performance, Nutrigenetics

SPORT GENOMICS IN A FEW WORDS

Sport Genomics is a research Group focused in:

- studying genetic, epigenetic, microbiomic and metabolomic factors associated with personal injury risk, trainability and the response to nutrition.
- Developing bioinformatic and molecular tools for the individualization of programs focused on the improvement of health and sport performance.

There is a growing evidence about the impact of OMICS (genome, epigenome, microbiome and metabolome) in the human variability to respond differently to each training or diet program.

It implies, determining OMICS related markers associated with this variability, as well as to understand how they interact to each other. This knowledge, would not only improve performance of elite athletes and would reduces their injury risk in a natural way, but also would have a great positive influence in public health, as it would promote general population to acquire and maintain personalized healthy habits, by preventing unsuccessful strategies.

Therefore, our aim is to develop biologically personalized training and nutrition programs, by using markers associated with the variability in response of training programs of three main types of sports focused respectively on power, endurance, and power-endurance.

FROM SCIENCE TO PERFORMANCE

Research activity of Sport Genomics group is done in very close collaboration with K-DNA Genomics, a spin-off of the University of the Basque Country, which invests nearly the 100% of its profit to University R&D. K-DNA Genomics is focused on Development of Bio-technological solutions for Sport Sciences, in sport specific Genetic Analysis & Online Apps, and Education in Nutrition and Sport Genetics.

EUSKADI INNOVATION AWARD BECAUSE OF "INTERACTIVE R&D" (Research and Development)

Sport Genomics and K-DNA Genomics collaborate through an innovative concept called "Interactive R&D", awarded with the Euskadi Innovation prize in 2017.

In interactive R & D, the athlete becomes an active agent in R & D related to Development and continuous improvement of his own Genetic Analysis, donating his genetic results anonymously, performing physical tests and completing questionnaires through the exclusive online application.

In this way, in interactive R & D, the participating athletes collaborate directly with researchers and sports professionals; invest in the improvement of the R&D, and in the permanent updating of the Genetics Services that they themselves enjoy.

Genomics and Health, and Biotechnology

Begoña M. Jugo[1], Elena Díaz-Ereño[2], Ana María Valle[3], Jaime Zubero[4], Naiara Abendaño[1], Itxazne García-Ceciaga[2], Endika Varela-Martínez[1], Martín Bilbao-Arribas[1], Ainhoa Arrieta-Gisasola[1]
[1]Genetics, P. Anthropology and Animal Physiology Dpt. and [3]Mathematics, Statistics and Operational Research Dpt., Fac. of Science and Technology; [2]Physiology Dpt. and [4]Nursery Dpt., Fac. of Medicine and Dentistry

KEY WORDS: genomics, obesity, physical activity, dietary patterns, gene-environment interactions, infectious diseases, vaccine adjuvants, autoimmunity, RNA-seq, miRNAs, aluminium

Our research interests include both animal and human health.

Animal Health and biotechnological applications: Characterization of the mechanism of action of aluminium as adjuvant in vaccines.

In relation to animal health, we are involved in different works. One of them is based on the analysis of the mechanism of action of aluminium as adjuvant. Aluminium compounds, especially aluminium hydroxide, are the most widely used adjuvant in human and animal vaccines. In spite of its wide use, the mechanism of how they exert beneficial effects is still not fully understood. Moreover, sometimes they can cause adverse reaction. In sheep, a form of autoimmune/autoinflammatory syndrome induced by adjuvants (ASIA) has been described, linked to the repetitive inoculation of aluminium-containing adjuvant vaccines. Our main interest is the study of the mechanism of action of aluminium hydroxide adjuvant and their relationships with the autoimmune disease.
For that, total RNA sequencing and miRNA sequencing are performed. RNA-seq is an optimal tool for a precise and real holistic analysis of the loci expressed in cells and tissues due to its large dynamic range and its low technical variability.
This study can help to identify molecular signatures activated by vaccines and their adjuvants, providing insight into the mechanism that underlie the immune response, by combining the molecular information provided by RNA sequencing of both miRNA and mRNA in an in vivo experiment.

Human health: life style and genetics in obesity

Obesity and its associated comorbidities represent one of the biggest public health challenges today. The marked rise in obesity observed over the last years suggests that behavioral and environmental factors underpin the mismatch between energy intake and energy expediture. Our main interest in human health is the disentangling of environment-genes interaction in relation to obesity in work environments. During the 2011-2013 period, we have been involved in the OSAGEIN study (Osasuna+ Genetika+ Ingurumena). The main objective of this study was to improve the health of people who work in our University. Furthermore, this study took into account the differential morbidity of women and gender segregation in working environments.
As a part of this OSAGEIN study we have analyzed the prevalence of overweight, obesity and the fulfillment of international physical activity recommendations. Analyses were conducted regarding the associations between body mass index (BMI) and physical activity (PA) level, recommendations, daily habits, work activity, and bio-socio-demographic factors. The prevalence of weight overload was 42% but overweight and obesity in the university workers was lower than in the general population. The overload increases with age and is greater in men, except for women ≥55 years old. Sleep duration seems to be a possible PA level determinant, as does BMI.

We are now analyzing the results obtained from dietary habits and patterns. Our next aim is to define the dietary patterns, which represent a broader picture of food and nutrient consumption, and may thus be more predictive of disease risk than individual foods or nutrients. Lastly we will try to associate all this information with genetic polymorphisms of selected candidate genes.

Human Molecular Evolution

Concepción de la Rúa[1], Neskuts Izagirre[1], Montserrat Hervella[1], Imanol Martín[1], Nerea G. Ventades[1], Cristina Claver[1]
Santos Alonso[1], Isabel Smith[2], Arrate Sevilla[1].
[1]UPV/EHU. FCyT. Dpto. de Genética, Antropología Física y Fisiología Animal.
[2]UPV/EHU. Dpto. Zoología y Dinámica Celular.

KEY WORDS: Neanderthal, archaic and modern humans, Next Generation Sequencing, Paleogenomics, bioinformatics, skin pigmentation, melanoma, genetic expression, human diversity, resequencing, aptamer.

PALEOGENOMICS: RECONSTRUCTION OF THE HUMAN EVOLUTIONARY HISTORY

The aim of our research is to understand the evolutionary success of our species using paleogenomics analysis. The development of the Next Generation Sequencing (NGS) techniques allows the comparison of the genomic data of our species with other closely related extinct species as Neanderthals. Up to the present we have recovered the complete genome of both the first *Homo sapiens* in Europe (35 kya) and the most ancient human (at least 165 kya) in the Basque Country (Lezetxiki, Gipuzkoa). The human of Lexetxiki is related to ancestor species of Neanderthals. Another field of research is the genetic and environmental influence in the genesis of rheumatological diseases. The study of both present-day patients and past populations allowed us to understand environmental factors (such as "Little Ice Age" period) in relation to the genetic susceptibily of Basque population to rheumatic patologies. Methodological innovation in ancient DNA analysis is being carried out through the design of genotyping chip, which includes a hundred SNPs associated to several rheumatologic diseases (Arthritis Rheumatoid, Ankylosing Spondylitis, Psoriatic Arthritis, Reactive Arthritis, among others). The aim of this study is to design a risk haplotype in order to establish an early diagnosis of a heterogeneous group of rheumatic pathologies. Regarding environmental changes, we are also studying animal domestication in Paleolithic through the genomic analysis of *Canis lupus familiaris* remains from Magdalenian period recovered in the Basque Country.

PIGMENTATION OF SKIN AND MELANOMA

There are genetic and environmental factors that determine the risk to melanoma susceptibility. In particular, light-skinned individuals are less protected against photocarcinogenesis and/or photoaging after solar irradiation. Therefore, we are trying to identify genetic variation associated with skin pigmentation in humans in order to infer its adaptive value and assess its biomedical implications. For that reason, we are focusing on the detection of differentially expressed genes in melanocytic cell lines from individuals with different skin pigmentation, using expression chips. We are also analysing the effect of vitamin D on pigmentation using different techniques: RNA-seq., ChIP-seq and methylation analysis by MeDIP-Seq. Subsequently, a subset of loci is selected to analyse their sequence diversity by resequencing and their variation in the copy number of their exons. The variability discovered is analysed in collaboration with other laboratories, in melanoma patients and healthy individuals. We are evaluating the adaptive value of these polymorphisms by means of bioinformatics trying to infer the potential biomedical implications (predisposition to/protection against cutaneous melanoma). On the other hand, we design aptamers, single-stranded oligonucleotides that bind with high affinity to metabolites of interest, like the alfa-MSH hormone, a ligand of *MC1R*. These aptamers will allow the detection and the quantification of biomarkers in individuals of light and dark skin pigmentation, and they may also serve as tumour markers for clinical diagnosis of melanoma. Besides, we are analysing the mutational load of driver mutations in melanoma biopsies and in serum of melanoma patients (cell-free DNA) by Digital PCR so as to determine if the mutational load can be used as a diagnosis or prognosis biomarker.

Flow-Through Chamber vs. Biodeposition Method. Comparison of methods to estimate the clearance rate in bivalve mollusks

Kristina Arranz, Iñaki Urrutxurtu, Irrintxi Ibarrola, Miren Bego Navarro and Enrique Navarro
University of the Basque Country, Faculty of Science and Technology, Animal Physiology.

KEY WORDS: Clearance rate, Bivalves, Flow-through chamber, biodeposition.

Flow-through chamber (CRf) and biodeposition (CRb) are among the most used methods of recording clearance rate. Fast and instantaneous measurements provided by the first method contrasts with integrated measurements over longer periods provided by the second. CRf is based in computing the proportion of particles removed from the water by the animal while CRb is based on rates of inorganic biodeposition assuming conservation of this diet component within the gut. Given that each method is useful depending on the context, we aimed to (a) determine the differences between CRf and CRb as well as (b) to analyze both endogenous (age/size and species) and exogenous factors (diet and individual vs. group determinations) which could alter the relationship between the results obtained under each method. Adults and juveniles of both Ruditapes decussatus and R. philippinarum were exposed to 5 different diets. Measurement with both methods were carried out at the same time on ca. 400 individuals/groups. CRf determinations were taken 12-16 times during the daytime while CRb was computed for 24h. CRf values approximately doubled CRb values, which could be attributed both to endogenous activity rhythms and to methodological reasons, since CRf determinations represent the mean of the data in which activity is present, while CRb integrates the whole activity in 24h. Among the aforementioned factors studied, only species and individual vs. group differences were significant. R. decussatus is expected to experience a more discontinuous activity than R. philippinarum, leading to a higher ratio between CRf and CRb. Similarly, homogenization of filtering behavior inside groups resulted in CR ratios with both methods that were closest to 1 than those recorded for individuals.

Feeding, growth and reproduction in animals

M. Mercedes Ortega-Hidalgo [1], Esther Iparraguirre-Bolaños[1], Samuel Aguirre[1], J.M. Txurruka[1], Solveig Haukeland [2], E. Txurruka[1].
1 University of the Basque Country (UPV/EHU) Faculty of Sciences and Technology, Animal Physiology
2 ICIPE International Centre for insect physiology and ecology. Nairobi, Kenya.

KEY WORDS: Earthworms, terrestrial slugs, anemones, biometry.

Objectives:

The group works mainly on soft body invertebrates conducting studies involving a physio-ecological approach to the analysis of patterns of feeding responses of organisms in response to variable foodstuffs, evaluation of metabolic expenditure and examining life cycle traits in the search of descriptors that would reliably associate to environmental changes.

At present our work deals with

1. Analysing the response of an epigean earthworm (*Eisenia andrei*) in the earliest stages of the life cycle (cocoons, hatchlings and, pre-reproductive juveniles) to variable substrates: manure, composting grass, and a variety of natural soils. Particular traits of the life cycle may be an approach to defining biological quality of soils.
2. Comparative studies of life cycles, growth and metabolism in terrestrial slugs (*Arion ate*r) in a latitudinal gradient: north of the Iberian Peninsula and Norway. The study deals with the role of temperature on defining limits to active stages of the life cycle with the aim of understanding changes related to on-going climatic change.
3. Surveys on growth and reproductive dynamics of an intertidal sea anemone (*Actinia equina*) both in laboratory and field populations. Being a ubiquitous species inhabiting the rocky shores worldwide and occupying a large range of air exposure periods (from medium intertidal to mostly subtidal), it offers good possibilities to explore resources to survive increasing warming of oceans and land. Particularly regarding the maintenance of appropriate recruiting rates to guarantee population endurance.
4. Biometry of different class ages of anchovy in the Gulf of Biscay. Present studies have found good relationship between liver size in females and reproductive stage suggesting a connexion with oocyte production.

Methods

1. Field surveys and growth models to evaluate growth and reproductive patterns.
2. Respirometric techniques to evaluate metabolic expenditure in animals and tissues.
3. Analytics of Biochemical Composition of tissues, faeces, foodstuffs and substrates.
4. Laboratory experiments in growth chambers (terrestrial invertebrates) and aquaria (sea anemones) in monitored conditions of environmental variable and feeding regime. Determination of ingestive and digestive parameters and potential growth (SFG).

Make the small great again in a warmer world

N. Abad[1], A. Uranga[1], Z. Baña[1], I. Artolozaga[1], B. Ayo[1, 2], I. Azúa[1] M. Unanue1, J. Iriberri[1, 2]
[1]Dept. of Immunology, Microbiology and Parasitology. Faculty of Science and Technology. University of the Basque Country UPV/EHU. Leioa, Spain; [2]Research Center for Experimental Marine Biology and Biotechnology PiE-UPV/EHU, Plentzia-Bizkaia, Spain.

KEY WORDS: extracellular enzymatic activities, global climate change, marine bacterial community.

Our planet is undergoing a period of climate change that has resulted in an increase of the sea surface temperature in the global ocean. A warming of 1 °C to 3 °C is expected by the end of the XXI century and this process is being more intense in coastal areas. In this context, it is challenging to know the response of the microorganisms to warming from a functional point of view.

Among the physiological traits, the synthesis and release of extracellular enzymes by bacteria is a critical step in regulating the biogeochemical functioning of the marine environment. Recently, in a global study in the tropical and subtropical ocean performed within the MALASPINA 2010 Project, our research group demonstrated the different temperature sensitivity of several extracellular enzymatic activities that hydrolyze specific dissolved organic matter compounds. Ultimately, this could lead to i) substantial stoichiometric shifts toward more nutrient-poor organic matter and ii) the expansion of low-nutrient regions in the ocean.

Currently, we are working on the ENZYME Project, which aims to acquire predictive power on the response of extracellular enzymatic activities to rising temperatures in surface waters of a coastal marine ecosystem under the different environmental conditions that occur throughout a seasonal cycle. The main goals of the project are:

- To assess the temperature sensitivity of both the hydrolytic activity and substrate-affinity in a set of model extracellular enzymes that hydrolyze organic compounds rich in carbon, nitrogen and phosphorus in coastal waters.
- To analyze how the substrate-affinity of the produced enzymes can regulate the resulting hydrolytic activity.
- To assess the possible shifts of the C:N, C:P and N:P stoichiometric ratios in the resulting organic material that is available for remineralization by bacteria.
- To identify links between the enzymatic extracellular activities and fundamental properties of the ecosystem, such as seawater temperature, the composition and activity of the microbial communities, and the concentration of inorganic nutrients and dissolved organic material.

Biology of the pathogenic fungus *Aspergillus fumigatus* using omic techniques and different models of infection

Guruceaga X.[1], Abad-Díaz-de Cerio A.[2], Buldain I.[1], Arbizu-Delgado A.[1], Martin-Souto L.[1], Perez-Cuesta U.[1], Antoran A.[1], Sevilla M.J.[1], Ramírez-García A.[1], Garaizar J.[3], Hernando F.L.[1] & Rementeria A.[1]

Fungal and Bacterial Biomics Research Group. Departamento de Inmunología, Microbiología y Parasitología. [1]Facultad de Ciencia y Tecnología, [2]Facultad de Medicina y Enfermería, y [3]Facultad de Farmacia, Universidad del País Vasco/Euskal Herriko Unibersitatea (UPV/EHU).

KEY WORDS: Aspergillus fumigatus, omic techniques, infection models, virulence, diagnosis, antifungal treatment.

Aspergillus fumigatus, one of the most prevalent airborne pathogenic fungi, causes a variety of diseases in immunocompromised patients. Invasive aspergillosis, the most severe of them, presents mortality rates of 70-90%, due to the weakened immune status of the patients, the virulence of the fungus and the late diagnosis. In the last few years, whole genome transcriptomic studies using both microarray and RNA-seq have deepened in the genomic expression dataset allowing us to know more about its virulence mechanisms and select new therapeutic and diagnostic targets. Our purpose is to delve into the knowledge of the infection by *A. fumigatus* and contribute to the general knowledge of this fungus.

GENERAL TECHNIQUES

- Conventional microbiological techniques.
- Animal model and cell line infections.
- Immunological and histological techniques.
- Trancriptomic studies using microarray technology and RT-qPCR.
- Mutant strains generation.
- Sequecing and bioinformatics.

TRANSCRIPTOMIC TECHNIQUES

Our group performs different transcriptomic assays using the AWAFUGE v.1 microarray, a whole genome custom microarray designed by us. For that purpose, we have established different infection models by *A. fumigatus*:

- *In vitro* infections using different cell lines: macrophages (RAW 264.7) and type II pneumocytes (A549).
- *In vivo* infection models using immunosuppressed mice and *Galleria mellonella* larvae.

DELETION MUTANT STRAINS GENERATION

We are developing different deletion mutant strains by the Double-joint PCR method using, as target, the most outstanding genes detected by transcriptomic analysis. Particularly, we highlight a pectin lyase mutant strain, a tryptophan degradation mutant strain and a thiamine degradation mutant strain among others.

GROUP PUBLICATIONS

- Abad *et al. Medical mycology* 51:545-554 (2013)
- Ramirez-García *et al. PLOS ONE* 8(1): e53584 (2013)
- Fernandez-Molina *et al. Diagnostic Microbiology and Infectious Disease* 80: 111-118 (2014)
- Sueiro-Olivares *et al. Microbiology* 161:490-502 (2015)
- Pellon *et al. Journal of Proteome Research* 15: 595-607 (2016)
- Ramirez-Garcia *et al. Critical Review in Microbiology* 42: 181-193 (2016)
- Bulbain *et al. Proteomics Clinical Applications* 10: 1058-1067 (2016)
- Ramirez-Garcia *et al. Mycopathologia* 183(1): 273-289 (2018)

GROUP PATENTS

- Fernandez *et al.* N. de solicitud: P201131497 (15/11/2011) Entidad titular: UPV/EHU.

The underrated assassins: Virulence mechanisms of fungal pathogens

A. Ramirez-Garcia, A. Antoran, I. Buldain, X. Guruceaga, A. Arbizu-Delgado, L. Martin-Souto, L. Aparicio, U. Perez-Cuesta A. Abad-Díaz-de-Cerio, A. Rementeria and F.L. Hernando
Fungal and Bacterial Biomics Research Group. Department of Immunology, Microbiology and Parasitology. Faculty of Science and Technology. University of the Basque Country (UPV/EHU)

KEY WORDS: fungal pathogens, antigens, cancer, diagnosis, treatment.

The incidence of fungal infections is suffering an important global increase in the last years. In fact, infections caused by microscopic fungi affect millions of individuals, mainly immunocompromised, every year with unacceptable mortality rates, which usually exceed 50%.

One of the main factors that causes these fatal results is the delay in diagnosis due to the lack of rapid, specific, and sensitive detection methods. Furthermore, it is worth highlighting the increasing resistances of many of these fungi to the commonly used antifungal drugs.

Therefore, the *Fungal and Bacterial Biomics Research Group* focuses its efforts on shedding light on the pathobiology of the most important fungal pathogens, mainly the genera *Candida*, *Aspergillus*, *Scedosporium*/*Lomentospora*, and *Mucor*, with the aim of increasing the knowledge of the virulence mechanism. To do that, we use omics techniques in order to identify and characterize molecular and diagnostic targets, and we perform recombinant proteins and monoclonal antibodies for using in therapeutic treatment.

Moreover, the group has been studying for several years the role of *C. albicans* on tumor adhesion. In this sense, we have demonstrated that the inflammatory response produced by *C. albicans* in the hepatic endothelium favors the adhesion of tumor cells to the endothelial cells, leading to liver metastasis in vitro and in vivo. Furthermore, we identified several molecules as putative candidates to be enhancers of the response and receptors involved in the process. We have also produced monoclonal antibodies to inhibit the effect of the identified molecules.

Most recently published manuscripts:

- Ramirez-Garcia *et al.* Med Mycol. 2018; doi: 10.1093/mmy/myx113
- Ramirez-Garcia *et al.* Mycopathologia. 2018;183:273-289
- Pellon *et al.* Int J Antimicrob Agents. 2018;12(3): e0174885
- Pellon *et al.* PLOSone. 2017;51:10-15
- Buldain *et al.* Proteomics Clin Appl. 2016;10: 1058-1067
- Pellon *et al.* J Proteome Res. 2016;15:595-607
- Ramirez-Garcia *et al.* Crit Rev Microbiol. 2016;42:181-193

Bacterial resistance to stress. *Vibrio* spp. in the aquatic systems

Maite Orruño[1,2], Vladimir Kaberdin[1-3] and Inés Arana[1,2]
Elixabet Ogayar[1], Alba Pascual[1], Ana Lomba[1] and Natalia González[1]
[1]Department of Immunology, Microbiology and Parasitology (UPV/EHU), [2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV/EHU; Plentzia Marine Station), [3]IKERBASQUE, Basque Foundation for Science

KEY WORDS: *Vibrio*, adverse environments, ocean warming

In the last decade, presumably as a result of the increase in surface water temperature, the detection of facultative pathogenic *Vibrio* strains and the incidence of *Vibrio*-borne diseases related to water use have increased. Some adaptation mechanisms have been proposed to promote the persistence of *Vibrio* spp. in marine systems under starvation by means of induction of the viable but nonculturable state (VBNC) or by increasing bacterial adhesion to biotic and abiotic surfaces or morphological changes. At the same time, bacteria-controlling microorganisms are also affected by global warming, which control their own survival and predatory/lytic activity on bacteria.

In the Basque Country, there are no studies focused on analyzing the distribution and survival of *Vibrio* spp. present in our coasts, although, considering our geographical situation and the coastal water uses, the changes in their distribution could have an important health, tourism and environmental impact. In this context, our group has initiated the study of the temporal/spatial distribution of *Vibrio* spp. in the coast, estuaries and open water of the Basque coastal area.

For comparison, we study the survival patterns developed by a *V. harveyi* type strain and other environmental *Vibrio* species, isolated from seawater. Our recent work on survival of *Vibrio* spp. has shown that survival under starvation conditions is a temperature-dependent process, which is accompanied by a reduction of cell size, proteomic changes and, occasionally, leads to the acquisition of the VBNC phenotype. In a similar way, solar radiation and other essential abiotic factors, such as salinity, also affect survival of *Vibrio* spp.; nevertheless, we observed differences in the survival patterns of laboratory and environmental strains wich can be attributed to the complexity and diversity of *Vibrio* genus.

Despite significant progress achieved in testing survival capacities of *Vibrio* species, relatively little is known about the effect of biotic factors on *Vibrio* populations. Our data show that predation by protozoa is the main factor eliminating *Vibrio* spp., and temperature modulates the complex interrelationships that are established between the bacterivorous protozoa and their preys.

In the environment, numerous vibrios remain attached to the surface of marine organisms (crustacean, zooplancton and others); this constitutes a defensive strategy to escape protozoan grazing and enables their mechanical translocation to other areas. Therefore, our future studies will be focused on the study of *Vibrio* spp. adhesion ability to marine organisms and on the comparative analysis of the survival responses developed by planktonic and adhered populations under stress conditions.

The techniques and methodologies used include epifluorescence microscopy, fluorescence *in situ* hybridization, analysis of bacterial proteome, etc.

Analysis of bacterial stress responses and their regulation by small RNAs

Vladimir R. Kaberdin[1,2,3], Inés Arana[1,2], Maite Orruño[1,2], Itxaso Montánchez[1], Ander Hernández Plágaro[1], Ion Luis Abad[1], Kaan Gundogdu[1], Adela Olcina Aguado[1], Paula Martin de Prado[1], Aránzazu González Arce[1], Guillermo Ledesma Domínguez[1]

[1]Department of Immunology, Microbiology and Parasitology, Faculty of Science and Technology,
[2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV), Plenzia Marine Station,
[3]Basque Foundation for Science (IKERBASQUE), Bilbao; e-mail: vladimir.kaberdin@ehu.eus

KEY WORDS: small RNAs, RNase E, post-transcriptional control, *Vibrio harveyi*, *Escherichia coli*, stress responses.

The ubiquitous presence of microorganisms is largely conferred by their unique abilities to adapt and successfully strive under adverse conditions. In our work, we use various Gram-negative bacteria (e.g. *Escherichia coli* (*E. coli*), *Vibrio harveyi* (*V. harveyi*) as well as some environmental isolates) to study microbial responses to diverse environmental signals (e.g. temperature up- and downshifts, limitation of nutrients *etc.*) at the transcriptional and post-transcriptional levels. Our major lines of research are briefly outlined below.

1. Identification of regulatory factors playing the key role in the temperature-dependent adaptation of *Vibrio harveyi* in aquatic systems

Vibrio species including *Vibrio harveyi* constitute one of the most diverse genera of Gram-negative bacteria ubiquitously present in natural aquatic systems. We use *V. harveyi* as a model organism to unveil the cellular strategies enabling this marine gammaproteobacterium to cope with limitation of nutrients during its persistence in seawater microcosm. In particular, our study is focused on: (i) physiological responses and morphological changes of *V. harveyi* during its short- and long-term incubation in seawater microcosms; (ii) analysis of *V. harveyi* adaptation at the whole transcriptome level and identification of the key metabolic pathways and cellular factors playing the major roles in the adaptation process; (iii) comparison of adaptation mechanisms, physiological and phenotypic changes triggered in *V. harveyi* during its incubation in seawater microcosms at optimal and suboptimal temperatures.

2. High-throughput screening and analysis of antisense RNAs with new roles in *E. coli* and *V. harveyi* stress responses

Recent studies revealed a new class of small antisense RNAs (sRNAs) that are involved in regulatory mechanisms controlling bacterial responses to environmental changes. We have recently employed RNA sequencing to discover a number of new sRNAs in *E. coli* and *V. harveyi*. While anticipating important roles for the newly discovered sRNAs in bacterial adaptation and virulence, we employ a combination of genetic, molecular biology and biochemical tools to address the biological functions of these regulatory RNAs and their possible contribution to cell adaptation and survival.

3. Analysis of subcellular localization and protein-protein interactions of glycolytic enzymes in *E. coli*

Our previous work has shown that the glycolytic enzyme enolase is a major component of the degradosome, a multienzyme complex controlling RNA processing and decay in *Escherichia coli* (*E. coli*) and additionally containing RNase E (Rne), the exoribonuclease PNPase (Pnp) and DEAD-box helicase RhlB (RhlB). While association of RNase E with RhlB and PNPase was shown to be critical for the normal efficiency of the degradosome-mediated RNA decay, the function(s) of enolase in the degradosome remains uncertain. The long-term goal of our study is to perform in-depth analysis of the protein-protein network that control glycolysis and link this process to RNA turnover and sugar transport in *E. coli*.

Some of the most recent results include:

- Characterization of the long-term response of *V. harveyi* to starvation at moderate and elevated temperatures;
- Identification of numerous protein-coding (e.g. genes encoding transporters, transcription factors and essential metabolic enzymes) and sRNA (e.g. genes encoding GcvB and Qrr1) genes important for adaptation of *V. harveyi* in natural aquatic systems;
- Design and use of new custom microarray for sRNA profiling in *E. coli*;
- Isolation of *Pseudomonas fluorescens* species highly resistant to pentachlorobenzene.

Impact of climate change on agro-pastoral systems: sustainable production and food security

Aldezabal, A.[1], Andonegi, A.[1], Del Canto-Romero, A.[2], García-Baquero, G.[1], Herrero, A.[1], Lacuesta, M.[2], Laskurain, N.A.[2], Mena-Petite, A.[1], Miranda-Apodaca, J.[1], Muñoz-Rueda, A.[1], Odriozola, I.[1], Pérez-López, U.[1], Sanz-Sáez, A.[2], Sarrionandía-Areitio, E.[2], Yoldi-Achalanbaso, A.[1]
Dpto. Biología Vegetal y Ecología, [1]FCyT y [2]Fac. Farmacia, UPV/EHU

KEY WORDS: Biodiversity, cereals, climate change (drought, elevated CO_2 and high temperature), ecosystem management, legume-rhizobium symbiosis, soil-plant-herbivore interaction.

The increase in CO_2 and other greenhouse gasses are provoking a rise of global temperature, and soil drought and salinization, among others. These changes modify plant physiology, altering plant growth and productivity, and also food quality, threatening food supply. In fact, climate change is transforming food production systems, from agricultural crops to extensive grazing in mountain, altering species distribution, production practices and land use.

These effects should be considered from different perspectives to avoid, or at least minimize, the impact of climate change on biological systems, biodiversity, plant production and food supply. Basic and applied research are needed to understand, not only the impact of climate change on plant production and quality, but also the adaptation capacity of agricultural crops and grassland resources to climate change, seeking new strategies to minimize its negative impact and to favor production sustainability under the future climatic conditions.

Our research group (IT1022-16) analyzes the effect of elevated CO_2 and the main stresses associated (Tª, drought, nitrogen fertilization, and its interaction) on the growth and productivity of diverse crops. In addition, our group evaluates biotic interactions among plant species and their functional ecology in semi-natural mountain grassland communities, evaluating the plant-herbivore interactions and the optimal use of food resources. The research tries to improve the understanding of the impact of climate change on agro-pastoral systems and to find solutions that respond to society demands for food security and environmental sustainability, both present and future. To that end, three lines of investigation are carried out with specific objectives:

Line 1: To study the impact of climate change on barley, identifying agronomical, physiological, biochemical and molecular traits to select cultivars able to adapt to future climate conditions.

Line 2: To look for strategies for increasing legumes' productivity under climate change, selecting cultivars and Rhizobium strains of high symbiotic efficiency under controlled and field conditions either in organic or conventional farming.

Line 3: To analyze the impact of extensive grazing abandonment on soil functions, biodiversity and forage quality in mountain grasslands under different changes in land use and climate change scenarios from a multidisciplinary perspective.

The main objectives of the research group are: (a) to improve understanding of the adaptation mechanisms of species to climate change identifying plant physiological and molecular tolerance traits; (b) to evaluate the effect of climate change on plant production and nutraceutical quality; and (c) to search strategies to minimize the impact of climate change and to obtain sustainable plant production to achieve present and future food security.

Acknowledgements: IT1022-16, EHUA16/17, AGL2013-48361-C2-1-R and Project 32-2016-00043 from Departamento de Desarrollo económico e Infraestructuras del Gobierno Vasco.

Ecosystem Services and Green Infrastructures

Miren Onaindia, Ibone Ametzaga, Lorena Peña, Jasone Unzueta, Beatriz Fernández, Nekane Castillo
Capital Natural Assessment Research Group. Department of Plant Biology and Ecology. Basque Country University (UPV/EHU)

KEY WORDS: Indicators, Mapping, Integration, Management

Ecosystem services are the many and varied benefits that humans freely gain from the natural environment and from properly-functioning ecosystems. The aim of our research group is to integrate the concept of ecosystem services into land planning and to provide the information and tools required by the decision-makers for a sustainable land management based on ecosystem services. In this context, we are developing the project "Ecosystem Services Assessment of the Basque Country", in which we are performing the following actions:

1. Mapping ecosystem services at different spatial scales and analyzing their trade-offs and synergies to develop a green infrastructure: Basque Country, Biscay, Municipal, City…

2. Integrating the concept of ecosystem services and green infrastructure into different tools of land planning: Revision of Regional Planning Guidelines (DOT), Revision of Partial Territorial Plan (PTP) of Metropolitan Bilbao and Renewal of PRUG of Urdaibai (PRUG).

3. Analyzing the perception and demands of society about ecosystems services by means of interviews in different green infrastructures of different cities: Green-Belt of Bilbao, Green Ring of Vitoria-Gasteiz, Ullia Mountain in Donostia…

4. Developing new tools to facilitate decision making: multi-functionality indicator to be used in payment for services, compensatory measures based on loss of ecosystem services...

5. Disseminating of results of the project: teaching workshops and conferences, attendance at national and international congress, news in press and radio, participation in international networks, typing scientific publications, social networks…

6. Training in ecosystem services and green infrastructures at different levels: in universities (master, postgraduate courses, Biology graduated…), in Vocational training, courses for professors, technicians and general public…

Acknowledgments

We are very greatful to the financial support from the Department of Environment of the County Council of Biscay (*Millennium Ecosystem Assessment of Biscay Project*) and from the Department of Environment and Landscape Policy of the Basque Government (*Millennium Ecosystem Assessment of Basque Country Project*).

Ecophysiology of Plant Stress and Soil Contamination (EKOFISKO)

PROFESSORS: José Mª Becerril (I.P.), José I. García, Antonio Hernández
POSTDOCS: Unai Artetxe, Raquel Esteban, Beatriz Fernández, Mª Teresa Gómez, Fátima Míguez,
PREDOCS: Rafael Gómez, Marina López
Department of Plant Biology and Ecology

KEY WORDS: Environmental Stress, Biomarkers, Nutraceutics, Photoprotection, Phytoremediation, Soil contamination, Desiccation tolerance, Global Change, Phytomanagement.

Since 1990 The EKOFISKO group has developed research and teaching activities on physiological and ecophysiological aspects of natural and anthropic agents causing stress in plants. Our group is a consolidated research group distinguished with the highest grade of the Basque Government classification for Scientific Groups and is composed of 8 PhD and 2 PhD students.

This group has developed a variety of novel methodological tools: (i) determination of plant stress biomarkers, in particular those related to photoprotection and oxidative stress, (ii) set up of plant toxicity bioassays to determine the ecotoxicological effects of pollutants in contaminated soils, and (iii) implementation of physiological parameters to evaluate phytotoxicity or damage caused by natural stress conditions as extreme temperatures, drought, light intensity, nutritional disorders, etc. In collaboration with other groups, we have incorporated genomic methodologies with emphasis in differential gene expression and in the application of DNA microarrays to assess and monitor soil health in a multidisciplinary approach; and developed a procedure to study molecular mobility of photosynthetic tissues, which is relevant to understand the mechanisms that underpin tolerance to desiccation.

All these methodologies have been implemented in several more applied research areas:

- Determination of the role of photoprotective compounds and tolerance to stress conditions (natural or anthropic) with particular emphasis on the acclimation to extreme environmental conditions, such as those prevailing at high altitudes, forest understory or historically polluted sites.
- Use of plant biomarkers to monitor environmental and global change and genotype plant selection for tolerance to adverse climatic agents and to the soil ecotoxicology.
- Identification of environmental agents to enhance nutraceutical compounds (carotenoids and tocopherols) in plant foods.
- Use of plants for ecological restoration of degraded environments, specially polluted soils through ecotechnologies as phytomanagement and bio- and phytoremediation (phytostabilization, phytoextraction and rhizodegradation).
- Assessment and monitoring soil health with biological indicators during remediation processes.

The research indicated above is currently carried out in a multidisciplinary approach in collaboration with relevant national and international scientists, universities (Complutense de Madrid, Autónoma de Barcelona, La Laguna, Helsinki, La Frontera, Tartu, Australian National, Innsbruck, St. Thomas, Florence, etc) and institutions (Neiker, Gaiker, Phytosphere Institute, Royal Kew Gardens, USDA, etc), and supported regularly by competitive projects (EU, Spanish Ministry). The quality of group's achievements is supported by regular publications in international journals, and by regular participation in national and international congresses. We also have a compromise on the cooperation for development, with several projects in Latin American universities (Chile, Nicaragua and Cuba). Besides, not only our group is very active in the formation of PhD students, but also we participate in four Master Programs: "Agrobiología Ambiental", "Environmental Contamination and Toxicology" , "Enología Innovadora" and "Medio Ambiente y Sostenibilidad"; and in the Doctorate Program "Agrobiología Ambiental". The latter has been honored with a quality award by the Ministry of Economy and Competitiveness.

The zooplankton as indicator of ecosystem rehabilitation: the case of the estuary of Bilbao

Fanjul Alvaro1, Barroeta Ziortza1, Txurruka Estibalitz1, Uriarte Ibon2, Villate Fernando1, Iriarte Arantza2
1Laboratory of Ecology, Department of Plant Biology and Ecology, Faculty of Science and Technology, University of the Basque Country, PO Box 644, 48008 Bilbao. 2Laboratory of Ecology, Department of Plant Biology and Ecology, Faculty of Pharmacy, University of the Basque Country, Paseo de la Universidad 7, 01006 Gasteiz.

KEY WORDS: Bilbao estuary, zooplankton ecology, ecosystem restoration, non-native species.

The estuary of Bilbao was once one of the most heavily polluted and degradated estuarine systems of Europe due to the heavy industrialization along its banks. Since the late 20th century, the implementation of the Comprehensive Plan for the Sanitation of the Metropolitan Area of Bilbao, environmental protection policies and the closure of different industries have favored a recovery process, which has led to an improvement in sediment and water quality. Evident decrease in heavy metal, nutrients, and organic matter loadings have been concomitant to the increase in oxygenation levels and biological diversity. Zooplanktonic organisms comprise a key component of estuarine ecosystems, forming a major link between primary producers and upper trophic level consumers. A monthly monitoring of these organisms (mesozooplankton; >200 µm) is being carried out since 1997 in this estuary, gaining a thorough insight into these low trophic level organisms' ecology. This time series has allowed us to study spatial and temporal variations in the distribution and abundance of zooplankton, being able primarily to assess the effect of both pollution and pollution abatement, as well as of climatic variations. Within estuary differences in the seasonal pattern of zooplankton are mainly shown through seaward time-advances in the seasonal peak from summer to late spring along the salinity gradient, linked to differences in phytoplankton availability during the summer, in turn, related to differences in nutrient availability. Regarding interannual variations, during the period of heavy pollution the estuary became almost devoid of zooplankton and through the process of improvement of its health status, total zooplankton abundance has increased. In this recovery process recolonization of estuarine areas by zooplankton has occurred, in which two types of introductions can be distinguished. On the one hand, species present in other nearby estuaries, e.g. Acartia bifilosa and Calanipeda aquaedulcis have arrived. On the other hand, there have also been new records of non-indigenous species occurrences, such as the copepods Acartia tonsa, Pseudodiaptomus marinus and Oithona davisae. These species have Asian (P. marinus), American (O. davisae) or uncertain (A. tonsa) origins and we hypothesize that their colonization could be due to commercial shipping and the release of ballast water. These species have showed a rapid and abrupt increase in abundance, evidencing the availability of unsaturated ecological niches in areas of recent recovery. The introduced species have enriched the overall zooplankton community diversity in this estuary. Therefore, despite the usual negative perception that we have of invasive species, these observations emphasize their potential beneficial effect in a system under recovery.

Are nanomaterials carriers of other relevant toxic pollutants in the aquatic environment? The NAnoCarrierEra (NACE) project

José María Lacave[1], Ignacio Martínez-Álvarez[1], Joseph Hatfield[1], Greta Nicolussi[1], Nagore González-Soto[1], Ada Esteban-Sánchez[1], Nerea Duroudier[1], Alberto Katsumiti[1], Beñat Zaldibar[1], Eider Bilbao[1], Enrique Navarro[2], Radmila Tomovska[3], Hélène Budzinski[4], Amaia Orbea[1], Miren P. Cajaraville[1]

[1] CBET Research Group, Dept. Zoology and Animal Cell Biology; FCT/ZTF and PiE, UPV/EHU, Basque Country, Spain

[2]al Physiology Research Group, Dept. Genetics, Physical Anthropology and Animal PhysiologyFCT/ZTF, UPV/EHU, Basque Country, Spain.

[3] POLYMAT and Dept. Applied Chemistry, Faculty of Chemistry, UPV/EHU, Basque Country, Spain.

[4]Equipe de Physico et Toxico-Chimie LPTC- EPOC-UMR 5805 CNRS, Université de Bordeaux, France.

KEY WORDS: aquatic toxicity, nanomaterials, microplastics, adsorbed persistent organic pollutants, alternative methods

Since the recent development of nanotechnology, nanomaterials (NMs) are increasingly being applied in our daily lives in many consumer products, with domestic, medical and industrial uses. In the aquatic environment, NMs are usually found in complex mixtures with other pollutants and, thus, the aim of the NACE project is to assess the potential risks for the aquatic ecosystems posed by NMs, in combination with other persistent organic pollutants (POPs) already present in the environment. The question is whether NMs can act as carriers of relevant POPs to aquatic organisms (the so-called "Trojan horse" effect) or conversely, they can act as sinks of POPs, thus diminishing the availability of POPs to aquatic organisms. Different groups of NMs have been selected for the study, such as carbon nanotubes, graphene-family nanomaterials (GFNs) and plastics (polystyrene from nano to micro size). A multispecies approach is being employed with a special emphasis on the use of alternative test methods such as embryo toxicity tests with two invertebrate species, mussels (*Mytilus galloprovincialis*) and brine shrimps (*Artemia sp.*), and one vertebrate, the zebrafish (*Danio rerio*), and *in vitro* toxicity tests with isolated mussel cells (hemocytes) and with microalgae (*Isochrysis galbana*). In these alternative models, we are testing the general and acute toxicity of NMs alone and in binary mixtures with the POPs using a range of concentrations covering the environmentally relevant concentrations, if known. Based on the results obtained in the screening assays, several combinations of NM-POPs have been selected for *in vivo* assays with adult mussels and zebrafish. The cellular and molecular biomarkers and histopathological analyses applied in these assays allowed us to dcipher the mechanisms of action of NMs alone and with adsorbed POPs. Moreover, we will address the potential for extrapolation of results from *in vitro* to *in vivo* approaches in mussels or from embryos to adults in the case of zebrafish.

As a first task of the project, the adsorption capacity of NMs such as GFNs and plastics for POPs must be characterized. For this, adsorption assays of the model polyaromatic hydrocarbon benzo(a)pyrene (BaP) to polystyrene micro and nanoplastics are being undertaken. Results indicated that smaller microplastics (0.5 µm) showed a higher capacity of ad/absorption of BaP than larger ones (4.5 µm). This points out that size of plastics is a key parameter driving the bioaccumulation and hence toxicity of adsorbed POPs to aquatic organisms. Results of *in vivo* assays with mussels exposed to MPs alone or to MPs with adsorbed BaP, showed that BaP concentrations in mussels increase with time (up to 150 times greater than background levels) and that smaller MPs pose an increased hazard in terms of the transfer of adsorbed BaP. Increased effects of MPs with sorbed BaP compared to MPs alone were demonstrated in neutral red uptake and catalase activity but there was no additional effect of sorbed BaP on DNA damage. At a whole organism level a general hormetic effect was demonstrated on energy budget following exposure in all MP treatments.

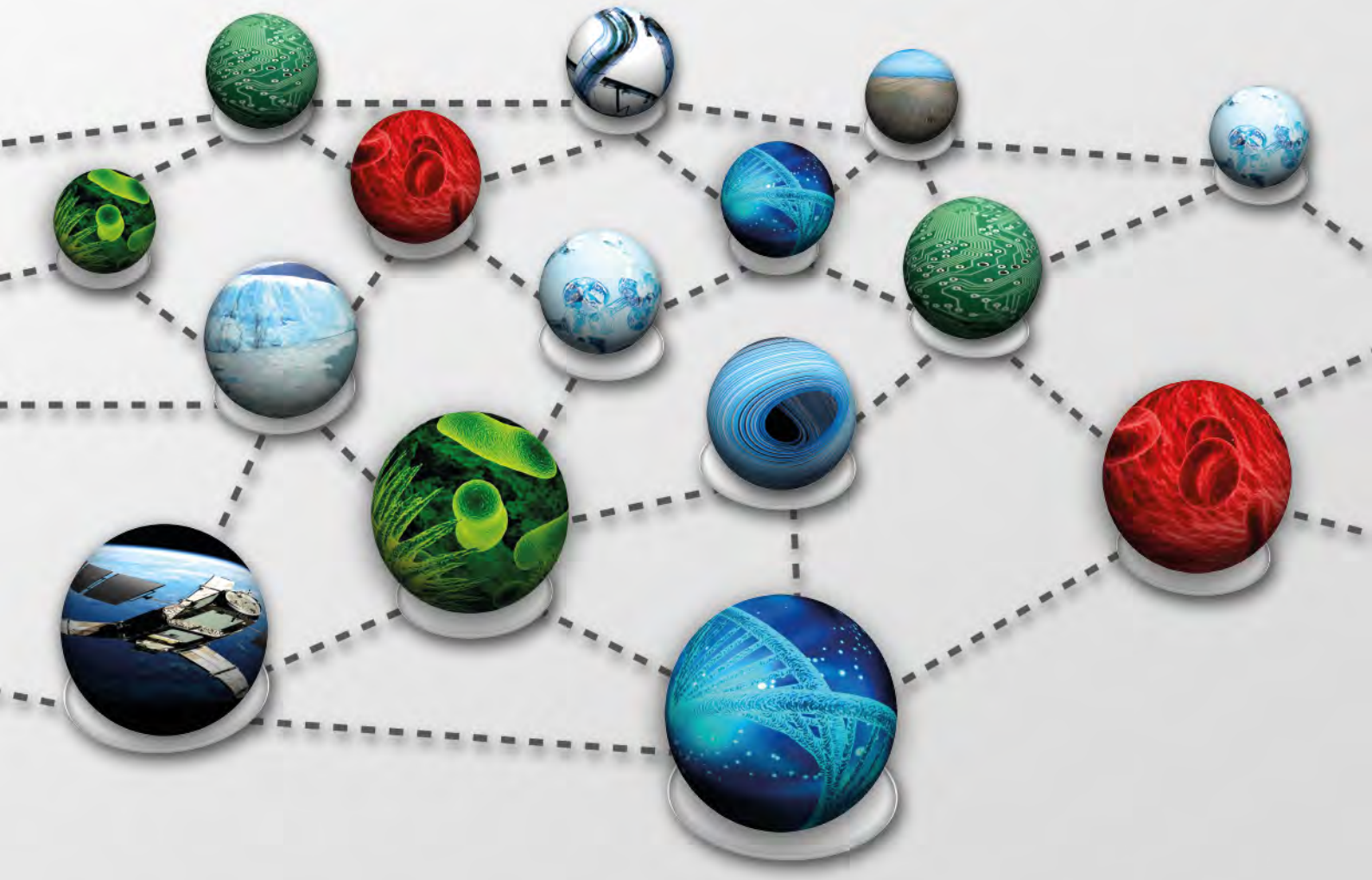
Regarding GFNs, graphene oxide (GO), GO-PVP and reduced GO-PVP nanoplatelets were moderately toxic to mussel hemocytes and produced a significant increase in reactive oxygen species (ROS) production. Exposure to GFNs with adsorbed oil compounds lead to decreased hemocyte viability at similar concentrations as in exposures to nanoplatelets alone. However, ROS production increased in hemocytes exposed to lower concentrations of GFNs (10 mg/L) with adsorbed oil compounds compared to nanoplatelets alone (25 mg/L), indicating that adsorbed oil compounds increased nanoplatelets toxicity, in agreement with the Trojan horse hypothesis.

The present project will enhance our knowledge on the Trojan horse effect of NMs as carriers of other relevant toxic pollutants in the aquatic environment and will provide data for the environmental risk assessment of NMs.

This work was supported by Spanish MINECO (NACE project CTM2016-81130-R), EU H2020 GRACE project (grant 679266), EU project PLASTOX (JPI Oceans 005/2015), Basque Government (consolidated group IT810-13) and UPV/EHU (UFI 11/37, VRI grant PLASTOX) and PhD grants (IMA: UPV/EHU; NGS and ND: BG; AES: FPU-MEC).

FISIKA ETA INGENIERITZA ELEKTRONIKA

FÍSICA E INGENIERÍA ELECTRÓNICA



Diziplina Anitzeko Sareak Ehunduz

Tejiendo Redes Multidisciplinares

Microestructural, magnetic and spectroscopic characterization of materials with high technological applications

Axpe E [1], Merida D[1], Garcia JA[2], Garaio E[1], Garitaonandia JS[2], Perez J[1], Plazaola F[1], Rodrigo I[1] and Unzueta I[1]
[1]Elektrizitatea eta Elektronika Saila; [2]Fisika Aplikatua II Saila.

KEY WORDS: Magnetic Nanoparticles, Hipertermia, MSMA

The group is comprised by several members of two different departments. They carry out different research lines:

1. **Magnetic nanoparticles and their applications in magnetic hyperthermia.** This is an ongoing activity that the research group carries out together with a multidisciplinary team formed by researchers from the BIO Foundation (Hospital Galdakao-Usansolo), and research groups of the UPV/EHU of the Faculties of Science and Technology and Medicine. The fundamental objective is the development of a therapeutic modality to provoke the selective thermal ablation of tumor tissue in colorectal cancer, by means of magnetic nanoparticles when exposed to an external radiofrequency inductor. So far, several objectives have been achieved. Among them the design and manufacture of several magnetic applicators for hyperthermia both in-vitro and in-vivo, obtaining hyperthermia temperatures in ex-vivo experiments in rat livers WAG infused with Fe3O4 nanoparticles.
2. **Nanoparticles of noble metals.** The experimental confirmation of the genesis of magnetism in nanoparticles (NP) of Au has symbolized a definitive and irreversible break with the most classical magnetism that divides magnetic materials exclusively between electron transition metals 3d unpaired and rare earths. Behind this magnetism lies a new type of magnetic anisotropy, which has been called charge-induced. This magnetism is very localized. Thus in Au NPs is achieved by chemically surrounding Au NPs with certain chemical agents of strong interaction such as thiols. A similar effect has been achieved by mechanically introducing Al atoms into ZnO NP. The coexistence of magnetism and semiconductivity in the same material is the foundation on which the spintronics would be based on these materials.
3. **Magnetic materials for technological applications.** At present, and within this line of research, we are studying alloys that are source of the magnetic form memory alloys (MSMA) and the magnetocaloric effect (EMC). The first present thermoelastic martensitic transformation and when it takes place at temperatures lower than the Curie temperature, the application of an external magnetic field in the structural phase of low temperature can induce a redistribution of crystalline domains, and even the martensitic transformation, causing a great macroscopic deformation. The magnetocaloric effect (EMC) is the change in temperature which corresponds to a change in the magnetic entropy of a material due to the application or elimination of an external magnetic field. These phenomena have aroused great interest as they open the door to a new type of magnetic actuator-controllers (capable of working at high frequencies and without variation of external temperature) and new materials for heat pumps or refrigerators. In this sense, alloys of the type Heusler, Ni-Mn-Ga next to the stoichiometry and different non-stoichiometric compositions are being studied because of the high values of mechanical deformation that can be obtained after the application of low magnetic fields. Likewise, Heusler metamagnetic Ni-Mn-X alloys (X = In, Sn, Sb) are very important for their potential for magneto-caloric applications.
4. **New positron annihilation spectroscopy (PALS) applications.** Our group has been a worldwide pioneer in the use of positron annihilation spectroscopy (PALS) to investigate the physical and mechanical properties of nanomaterials, biomaterials and biological systems. These new applications have been developed mainly in the fields of: i) polymeric materials and biopolymers, ii) biomimetic nanocomposites, iii) biomenbranas and iv) three-dimensional cell cultures.

High-accuracy infrared emissivity measurements between room temperature and 1000 ºC for solar energy materials

I. González de Arrieta [1], T. Echániz[2], R. Fuente[2], I. Urcelay-Olabarria[1], M.J. Tello[3] and G.A. López[1]
[1]Applied Physics II, University of the Basque Country UPV/EHU, Leioa, 48940, Spain;
[2]Faculty of Engineering, University of the Basque Country UPV/EHU, Bilbao, 48013, Spain;
3 Condensed Matter Physics, University of the Basque Country UPV/EHU, Leioa, 48940, Spain.

KEY WORDS: infrared emissivity, solar energy, solar selective coatings, thermal energy storage.

The total hemispherical emissivity of materials used in the solar energy industry is a critical parameter in the calculation of the radiative thermal losses and material efficiency, especially in solar thermal collector absorbing surfaces. This is because the radiative heat losses have a significant economic impact on the final cost of the electricity produced in solar plants.

Our laboratory in the University of the Basque Country (UPV/EHU) [1] is the first to have published infrared spectral emissivity measurements in Solar Absorber Surfaces at working temperature [2]. The laboratory allows measuring between room temperature and 1000 ºC in the 0.83-25 μm range and is also capable of doing directional measurements at different angles between 0º and 80º. Therefore, it is suitable for measuring solar selective coatings, for studying high temperature stability and for characterizing thermal energy harvesting materials.

In this presentation, we show the specifications of our laboratory, the results of spectral emissivity measurements in air-resistant solar selective coatings and in eutectic alloys for thermal storage and we demonstrate the necessity of measuring at working temperature in order to possess reliable data.

References:

1. L. del Campo, R.B. Pérez-Sáez, X. Esquisabel, I. Fernández, M.J. Tello. Reviews on Scientific Instruments 77 (2006) 113111.
2. T. Echániz, I. Setién-Fernández, R.B. Pérez-Sáez, C. Prieto, R. Escobar Galindo, M.J. Tello, Solar Energy Materials & Solar Cells 140 (2015) 249-252.

Magnetism and Magnetic Materials Group

[1,6]Mª Luisa Fdez-Gubieda, [1,6]Jose Manuel Barandiarán,[1,6]Jon Gutierrez, [1,6]Alfredo García Arribas, [1,6]Galina, Kurlyandskaya, [2,6]Ana García Prieto, [3,6]Alicia Muela, [4]David de Cos, [5]Andoni Lasheras, [1,6]Patricia Lazpita, [1,6]Volodymyr Chernenko, [6]Eduardo Fernandez , [1]Ivan Rodriguez , [1]Lourdes Marcano, [1,3]David Muñoz, [1]David Gandía, [1,3]Lucia Gandarias

[1]Departamento de Electricidad y Electrónica, [2]Departamento de Física Aplicada I, [3]Departamento de Inmunología, Microbiología y Parasitología, [4]Departamento de Física Aplicada II, [5]Departamento de Matemática Aplicada, [6]BCMaterials, Basque Center for Materials, Applications and Nanostructures

Nanomagnetism, Magnetotactic bacteria, Ferromagnetism shape memory alloys, Thin films, Magnetic sensors and actuators

The Magnetism and Magnetic Materials Group (GMMM) started working at the Faculty 30 years ago. As a result of the consistent and productive research performed, the group is acknowledged as a consolidated research group. The main objective of the group is to prepare and characterize new magnetic materials with special properties for outstanding applications. Nowadays there are three main research lines: Magnetotactic bacteria as theranostic agent, Ferromagnetic shape memory alloys and Magnetic Sensors and Actuators

Magnetotactic bacteria

Magnetotactic bacteria are aquatic microorganisms that swim along the geomagnetic magnetic field lines towards hipoxic regions, using a chains of magnetic nanoparticles biomineralized internally, called magnetosomes). The different species of magnetotactic bacteria synthesize perfectly stoichiometric magnetite nanocrystals, with genetically controlled sizes and shapes, surrounded by a biocompatible membrane, making them ideal for biomedical use. This research line is oriented in two complementary directions: first, the thorough study of the magnetic properties of the magnetosomes and its relation with other nanoparticle systems, and second, the exploitation of magnetotactic bacteria as a therasnostic agent such as a microbot for drug delivery or a hiperthermia agent.

Ferromagnetic Shape Memory Alloys (FSMA) in bulk, composite and thin film form

FSMA are active materials that develop high recoverable shape changes under the effect of mechanical stress or magnetic field in very short times (a few milliseconds). Due to their remarkable properties in actuation, vibration damping and sensing have permeated into many industries, such as the biomedical, energy or aerospace. FSMAs also possess large magnetocaloric properties and could substitute the rare-earth based magnetocaloric materials developed for magnetic refrigeration clean and efficient. The main objective of this research line is the combination of applied and fundamental research to improve the material performances and the comprehension of the involved physical processes

Magnetic Sensors: Giant Magneto Impedance (GMI) and Magnetoelasticity (ME) based devices

The GMI effect produces huge changes in the electric impedance of a soft magnetic material and provides excellent sensitivities to small magnetic fields. It is already used in sensor devices to measure orientation (inside the Earth magnetic field) and other applications. The actual trend is to produce GMI material in the form of thin films to obtain miniaturized devices that can be integrated in microelectronic circuits.

The ME effect consists in the fact that any mechanical action alters the magnetic state of such materials. When driven to resonance it is an extremely sensitive effect, being that resonance frequency specially affected by any external parameter (temperature, humidity, pressure, etc) or agent (biological as bacteria, or chemical as inorganic salts) that alters the magnetic or stress state of the core magnetic material. This property allows to develop extremely sensitive sensing devices based in this ME effect.

The techniques currently employed by the group include:

- Atomic/Magnetic Force Microscopy (AFM/MFM) (in house technique)
- Magneto-optical Kerr effect Microscopy (in house technique)
- On-wafer and in-circuit high frequency characterization facilities (in house techniques)
- Photolitography Laboratory (in house technique)
- SQUID and Vibrating Sample magnetometer (SGiker facility)
- Neutron Techniques (Great European Installation Facilities: ILL, ISIS)
- Synchrotron Radiation Techniques (Great European Installation Facilities: ESRF, Diamond, ALBA, BESSY)

The main founding of the group comes from Ministerio de Economia y Competitividad, Basque Goverment and European Union. If you need more information about the group contact: malu.gubieda@ehu.es

Estimation of the thermodynamic data (ΔH_f^o, ΔS_f^o and ΔG_f^o) of the destinezite originated in the El Laco Volcano (Chile): $Fe_2(PO_4)(SO_4)(OH)\cdot 6H_20$

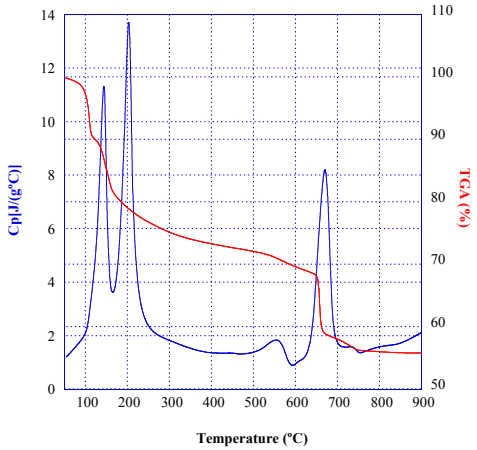
Noelia De La Pinta [1*], *Tomasz Breczewsky*[2] *and Francisco Velasco*[3]

[1]Condensed Materr Physics Department
[2]Applied Physics II Department
[3]Mineralogy and Petrology Department
Facultad de Ciencias y Tecnología Universidad del País Vasco, Apdo. 644, 48-080 Bilbao, Spain

*noelia.delapinta@ehu.eus

Destinezite, Thermodynamic calculations, Calorymetry, Thermogravimetry,

The mineral destinezite $Fe_2(PO_4)(SO_4)(OH)\cdot 6H_20$ is usually difficult to recognize because of the intímate association with other minerals, variable percentages in the mixtures, textural changes in diagenetic or hydrothermal overprinting, and variable origins. We have examined the destinezite nodules that occurs in the unconsolidated tephra forming part of the eruptive products of the El Laco volcano[1-2].
Thermocalorimetric measurements between 25 to 900ºC of these samples supply the enthalpy of formation, entropy and, a combination of these, the Gibbs free energy of formation and the aqueous solubility product of this mineral. These parameters should provides insights about the paths of transformation processes of volcanic rocks and ores of the El Laco, based on the thermodynamic stability of the involved mineral phases including the presence of anhydrous remnants of unknown Fe-phosphates within the nodules. Our interest is, therefore, to attempt the estimation of the thermodynamic data for the destinezite, to help the discussion of its stability conditions in the range of geological conditions underwent by the involved rocks.
Briefly, the results of the thermogravimetric analysis (TGA and DTG) and the calorimetric study, (DSC) show six different transformation steps (Figure 1) in the decomposition of the destinizite with increase of the temperature. These involve, as intermediate and final products, the formation of lipscombite $(Fe2+,Mn2+)(Fe3+)_2(PO_4)_2(OH)_2$, grattarolaite $Fe_3O_3(PO4)$, rodolicoite $Fe(PO4)$, and hematite Fe_2O_3. The control of the above reactions was carried out by X-ray diffraction and SEM techniques which allowed the identification of reaction. For each process and its energy associated. So we have estimated that the values of the thermodynamic data for the destinezite are:



AH_f^o =-4043Kj/mol

AS_f^o=-1515 J/mol·K

AG_f^o= -3592 Kj/mol·K

Figure1. TGA (%) and Cp(J/gºC) for the destinezite in the range 25-900ºC

1. Tornos, F., Velasco, F. and Hanchar, J., 2017. The Magmatic to Magmatic-Hydrothermal Evolution of the El Laco Deposit (Chile) and Its Implications for the Genesis of Magnetite-Apatite Deposits. Economic Geology, 112: 1595-1628.
2. Velasco, F., Tornos, F. and Hanchar, J., 2016. Immiscible iron- and silica-rich melts and magnetite geochemistry at the El Laco volcano (northern Chile): Evidence for a magmatic origin for the magnetite deposits. Ore Geology Reviews, 79: 346-366.

Automatic Control Group GAUDEE

V. Etxebarria, J. Jugo, J. Feuchtwanger, E. Asua, I. Arredondo, I. Badillo, A. García-Arribas, I. Sagastabeitia, I. Lizarraga, S. Alonso;
Departamento de Electricidad y Electrónica, Facultad de Ciencia y Tecnología, UPV/EHU;

KEY WORDS: RF control, particle accelerators, beam diagnostics, EPICS, smart materials

The automatic control group of the University of the Basque Country (UPV/EHU), GAUDEE, carries out research and development of advanced control systems and techniques, combining theoretical work with practical interest applications. The current activities are focused on two main areas. The first one refers to research in the field of particle accelerators science and technology. This is carried out in the IZPILab - Beam Laboratory, which was founded by GAUDEE, in collaboration with the RF and Microwave group of the Department of Electricity and Electronics. The activities in this field include the development of innovative complete key components of particle accelerators, including ion sources, beam diagnostics, RF devices and controls, and the corresponding electronics. Another research field is centered in the research around new advanced sensors and actuators, based on new materials and principles.

PARTICLE ACCELERATOR SCIENCE AND TECHNOLOGY

The group is involved in several projects for particle accelerators. Among these it is worth mentioning:

- Compact ion sources. A new compact proton source for low current low energy applications has been designed and built. All the mechanical, electromagnetic, vacuum, RF and control designs have been in-house completed. The ion source is the first key component of a new generation linac currenty under design.
- Beam diagnostics and related electronics: active projects are related with Beam Position Monitors, for high-accuracy measurement of beam bunches position, key question for the subsequent stages of acceleration.
- RF systems: The RF system is an essential part of modern particle accelerators. Its main task is to transfer energy to the beam. Besides, the RF system has a key role in the stability of the particle beam. A typical RF chain consists of an RF amplifier, a waveguide system, an RF cavity and a Low-Level RF (LLRF) control system. The LLRF consists of fast amplitude and a phase loops to regulate the amplitude and phase of the cavity voltage, and a tuning loop that regulates the resonant frequency of the cavity. The LLRF developed is able to regulate the accelerating fields with a precision of <1% in amplitude and <1° in phase.

  The research group has an on-going a collaboration with the FETS project of Rutherford Appleton Laboratory (RAL) in the UK to integrate a digital LLRF.

SMART MATERIAL BASED ACTUATORS

Ferromagnetic shape-memory alloys (FSMAs) are special smart materials that can experiment huge deformations, have a very fast response and can work at high frequencies when activated with a magnetic field (with the advantage of a contactless activation). A new actuator has been designed and built. This is composed of two pairs of coils: the first one generates a field that causes a deformation in an FSMA monocristal, and the second one actuates in the transversal direction. This way, the actuator can be used in a ”set and forget” mode, which allows to save energy while operating in the micrometric or nanometric range.

RF RESONANT CAVITY BASED SENSORS

Resonant cavities are closed conductive surfaces where the electromagnetic waves are constantly reflecting. Changes in their geometry result in variations in their electromagnetic properties, and more specifically in their resonance frequency. A new displacement sensor, composed of two copper resonant cavities whose dimensions change in opposite directions by means of the displacement of intermediate wall has been developed. Tiny changes in position result in huge resonance frequency shifts that are easily measurable.
This way, the results show that the device can be used as a sub-nanometric precision displacement sensor.

Nanophotonics: Controlling light at the nanoscale

Mattin Urbieta[1,2], Luca Bergamini[1,2] and Nerea Zabala[1,2]
[1]Department of Electricity and Electronics, Faculty of Science and Technology, UPV-EHU, 48940 Leioa
[2]CFM-MPC, Centro MIxto CSIC-UPV-EHU and DIPC, 20018 Donostia

KEY WORDS: light, plasmon, nanoantenna

Propagating electromagnetic waves cannot be focussed to spots much smaller than their wavelength, due to diffraction. However, recent advances in theory and fabrication techniques show how to control light at the nanoscale, provided we can find the correct materials and structures for our devices. Nanophotonics aims to control light on length scales smaller than the wavelength by harnessing the interaction of light with matter. Indeed, metal nanostructures are able to convert Visible–Near-Infrared light into collective excitations of conduction electrons, called plasmons, producing evanescent waves with a decay length of nanometer scale. This allows to mold the flow of light and control its emission and absorption below the diffraction limit, at the length scale of just a few nanometers. At light wavelengths resonant with plasmons, the metallic structures feature a remarkable absorption, and an intense electromagnetic field enhancement and localization around their surface. For this reason they are often referred to as optical antennas or nanoantennas. Optical antennas boost light-matter interaction by bridging the mismatch in length scales between the size of the propagating radiation (around 500 nm for visible light) and that of the emitter or receiver (around 1 nm for a molecule).

Within this framework, we try to shed light on how to describe the phenomena taking place between nanostructures excited by light. As a matter of fact, when irradiated by a laser beam, the plasmon-induced intense electromagnetic field is further enhanced in metallic tips (lightning-rod effect) or intermediate regions between antennas with nanometric separation, so called hot-spots. However, when the gaps are shrunk down to the nanometer, other phenomena start to play a significant role (e.g., tunneling) and a quantum description is required instead of the commonly used classical approach.

The plasmon-excitation can also be exploited in combination with other effects. For instance, under the application of a static magnetic-field, magneto-optical (e.g., nickel) nanoantennas give rise to a component of the electric field in a direction orthogonal to the incident one. When the nanoantennas are placed in a periodic structure, the enhanced field due to the plasmon is also significantly modulated by the diffractive coupling introduced by the periodic arrangement. Metal nanoantennas can also be effectively combined with phase-transition materials, whose optical properties change abruptly on a temperature basis (e.g., vanadium dioxide), to induce light controlled nanometer scale phase transitions.

This vibrant field provides a powerful toolset to create artificial materials and devices molding the flow of light in previously unknown ways, to allow more accurate spectroscopies, molecular and biological sensors, or to create light sources emitting single photons at a high rate.

Digital Electronic Implementations for Data Mining and Machine Learning Applications

Inés del Campo[1], Javier Echanobe[1], Mª Victoria Martínez[1], Estibalitz Asua[1], José Manuel Tarela[1], Óscar Mata Carballeira[1], Koldo Basterretxea[2], Guillermo Bosque[2], Unai Martínez[2] and Naiara Vidal
[1]Department of Electricity and Electronics; [2]*Department of Electronic Technology*.

KEY WORDS: digital electronics, system modelling, embedded systems, field-programmable gate arrays (FPGAs), computational intelligence, machine learning, data mining, driving assistance systems, internet of things (IoT)

The Digital Electronics Design Group (GDED) focuses on two main lines of research aimed at the development of innovative multidisciplinary applications. These lines and their application areas are:

1. **Modelling of complex dynamic systems using data mining and machine learning:** optimization, regression and multiclass classification problems using computational intelligence techniques (neural networks, fuzzy systems, neuro-fuzzy systems, and genetic algorithms).
2. **Design of efficient embedded electronic systems for real-time applications:** systems on a chip (SoCs) based on FPGA devices, hardware/software co-design, high computational efficiency hardware accelerators, device consumption and size reduction techniques, "hardware-in-the-loop" co-simulation, and sensor technologies.

Application areas: ambient intelligence, intelligent agents on a chip, advanced driver assistance systems (ADAS), wireless sensor networks (WSN), environmental and physiological sensors, internet of things (IoT), optimum and predictive controllers, and modelling and optimization of industrial processes (energy co-generation).

RECENT APPLICATIONS DEVELOPED BY THE GROUP AND WORK IN PROGRESS

Innovative applications with the aim of reaching the fully-autonomous self-driving car as well as improving comfort and energetic efficiency are being developed with the ultimate objective of increasing road safety in order to face the “zero accidents” social challenge. Evidently, this horizon cannot be fulfilled immediately, but a step-by-step process of developing incremental, enhanced driving assistance systems must be followed instead for supporting the drivers’ tasks gradually, freeing them from performing the most dangerous operations (on which human factor is the most important safety condition).

On the other hand, Ambient Intelligence proposes a model where people are assisted by an invisible and ubiquitous electronic environment. Intelligent agents have to process a huge amount of signals coming from multiple sensors, and they have to be capable of responding in real-time. The group has developed an autonomous single-chip electronic system, based on FPGA, suitable for integration in a network of cooperative devices.

In addition, the group has participated in an industrial project oriented to improve the efficiency in a cogeneration plant. Industrial processes, such as those in cogeneration plants, involve a large number of pieces of equipment, machinery, and instruments. The group used Computational intelligence (CI) techniques for both modelling and optimisation purposes.

In all these application areas the group works on approaches that process very large and complex data sets and often respond in real-time, by taking advantage of data mining techniques, computational intelligence solutions, machine learning algorithms, and advanced optimization strategies.

RF and microwave group

Lexuri Angulo, Asier Barcenilla, Libe Mori, Javier Alonso, José Manuel González, Nerea Otegi, Aitziber Anakabe, Juan-Mari Collantes, Joaquín Portilla

Departamento de Electricidad y Electrónica, UPV/EHU.

KEY WORDS: high-frequency electronics, solid-state amplifiers, noise characterization, radio-communication systems, instrumentation for LINACs, MRI

The main research topics of the group are the analysis, characterization and design of RF and microwave circuits and systems for radio-communication, radio-navigation and scientific equipment, such as RF linear particle acceleration (LINAC) and magnetic resonance imaging (MRI), among other applications.

We have developed an extensive work on analysis and characterization of solid-state amplifiers, including circuit linearization, circuit modeling and noise characterization. As an example, we can mention the advancements on spurious oscillation detection in power amplifiers for satellite communications achieved in the framework of a project funded by the French Space Agency (CNES, Toulouse, France) in cooperation with Thales Alenia Space (TAS-F). Our group has also a relevant activity in noise characterization of RF circuits and systems, where it is worth mentioning the development of novel techniques for the amplitude noise and phase-noise measurement in the presence of large-signal excitations. We are also involved on RF instrumentation for LINACs. On the other hand, we have a growing activity in RF and microwave sensors and material characterization. Finally, a new researcher has joined us recently thanks to a Marie Skłodowska-Curie Individual Fellowship, introducing our group in the field of MRI.

Early Universe Cosmology and Fundamental Physics

Mikel Alvarez[1], Jose J. Blanco-Pillado[1,2], Igor Bandos[1,2], Sugumi Kanno[1,2], Joanes Lizarraga[1], Juan L. Mañes[3], Eugenio Megias[1], Jon Urrestilla[1], Manuel Valle[1], Jeremy Watcher[1],
[1]Dept. Theoretical Physics and History of Science, UPV/EHU
[2]IKERBASQUE
[3]Dept. Condensed Matter Physics

http://tp.lc.ehu.es/earlyuniverse/

Cosmology, General Relativity, Inflation, String Theory, Multiverse, Cosmic Strings

We are currently investigating several aspects of some of the most interesting topics in Theoretical Cosmology. Here is just a short summary of some of these topics.

- ## Cosmic Strings.

  Cosmic strings are topological defects that may have been created in the early universe. They typically form in a phase transition that gives rise to a complicated network of long strings that stretch across the horizon. One of the most important questions that one needs to address in order to extract predictions on these theories is to understand the cosmological evolution of these networks and its statistical properties. One of the most interesting methods to tackle these questions is the use of computer simulations that evolve the strings from some initial conditions. We are one of the leading research groups on cosmic strings simulations being involved in the largest simulations of a network of strings ever performed.

- ## Cosmological Inflation

  Several cosmological observations suggest that our universe underwent a period of accelerated expansion in its early stages. On the other hand the precise underlying physics of inflation and in particular its embedding within a fundamental theory are still a mystery. In many models inflation is in fact eternal. This would lead to the formation of “pocket universes” that would rise to universes like ours. This view of the universe give some interesting predictions for cosmological observables that allow us to distinguish this scenario from other ones. We are currently following several lines of research to further investigate these issues.

- ## String Theory Cosmology.

  String Theory is today one of the leading candidates for a fundamental theory. It is therefore natural to look for ways to link String Theory and Cosmology. Recent avances on String Theory compactification have allowed us to find some of the most detailed descriptions of Inflation in String Theory. Our group is mainly interested in extracting the observational consequences of the novel ways inflation can occur in String Theory.

- ## The Landscape of String Theory.

  String Theory suggests that there is a large number of ways that one can compactify the original 10d spacetime down to four dimensions. This compactification process gives rise to a complicated multidimensional potential that fixes all the possible degrees of freedom that specify, for example, the geometry of the internal space. Some of the minima of this potential would have a positive value of the cosmological constant and therefore one would expect to have patches of an eternally inflating spacetime. This is an interesting new take on the idea of cosmology within string theory and it is paramount to extract the observational consequences of a multiverse of this kind.

  Our group is currently working on several avenues to explore the consequences of this radical new picture of the spacetime suggested by the existence of a String Theory Landscape.

Theoretical and Phenomenological Cosmology

Mariam Bouhmadi-Lopez[1,2],D. Brizuela[1], T. Broadhurst[1,2], N. Cipriani[1], I. de Martino[1], A. Feinstein[1], F. Fernández-Álvarez[1], I. Garay[1], A. Garcia-Parrado Gomez-Lobo[1], J. Ibáñez[1], P. Jimeno-Romero[1], R. Lazkoz[1], I. Leanizbarrutia[1], M. Ortiz[1], J.M.M. Senovilla[1], B. Reina[1], C. Van-Hulse[1], R. Vera[1], F. Vidotto[1], J. Viegas[1]
[1]Dept. Theoretical Physics and History of Science, UPV/EHU; [2]IKERBASQUE

Cosmology, General Relativity, modified theories of gavity, dark matter, dark energy, gravitational lensing

This line of work focuses on several theoretical and phenomenological aspects of the Universe, both in the context of General Relativity and in the wider context of modified theories. This is an area of research in full swing thanks to the arrival of new observational data. Broadly speaking these data provide surprising conclusions about the possible components of the Universe, whose "presence" is manifested in the kinematics of the Cosmos at different scales. One of the most controversial features is the apparent acceleration of the expansion of the Universe.

Two main sublines:

- Dark matter and energy: observational tests and alternative gravity theories
- Gravitational lensing, galaxy formation and galactic clusters, panoramic surveys and galactic telescopes.

Physical and mathematical fundamentals of the structure of the Universe

Mariam Bouhmadi-Lopez[1,2], D. Brizuela[1], T. Broadhurst[1,2], N. Cipriani[1], I. de Martino[1], A. Feinstein[1], F. Fernández-Álvarez[1], I. Garay[1], A. Garcia-Parrado Gomez-Lobo[1], J. Ibáñez[1], P. Jimeno-Romero[1], R. Lazkoz[1], I. Leanizbarrutia[1], M. Ortiz[1], J.M.M. Senovilla[1], B. Reina[1], C. Van-Hulse[1], R. Vera[1], F. Vidotto[1], J. Viegas[1]
[1]Dept. Theoretical Physics and History of Science, UPV/EHU; [2]IKERBASQUE

Cosmology, General Relativity, Loop Quantum Gravity, Relativistic Astrophysics, neutron stars, black holes, gravitational waves

Einstein's equations of General Relativity (or modifications) link the geometry of spacetime (gravity) with the physics of non-gravitational fields. They constitute the framework for the study of the Universe and relativistic astrophysical objects. A better understanding of the Universe involves deepening the description of its early stages, regimes of high energies, and the principles governing the laws that govern it. Cosmology and physics directed to the description, evolution and emission of gravitational waves of relativistic systems are intimately related to the rest of the aspects of the structure of the Universe, that is to say, with more fundamental aspects, and in general of a more mathematical nature.

Main sublines:

- Dynamics of very compact astrophysical objects and black holes. Emission of gravitational waves, and cosmological gravitational waves. The role of the cosmological constant.
- Quantum cosmology and loop quantum gravity: dynamics, semiclassical approach and physical consequences.
- Mathematical relativity; trapped and umbilical submanifolds, computer algebra, initial data characterisations and exact solutions.

Pulsed dynamical decoupling for fast and robust two-qubit gates with trapped ions

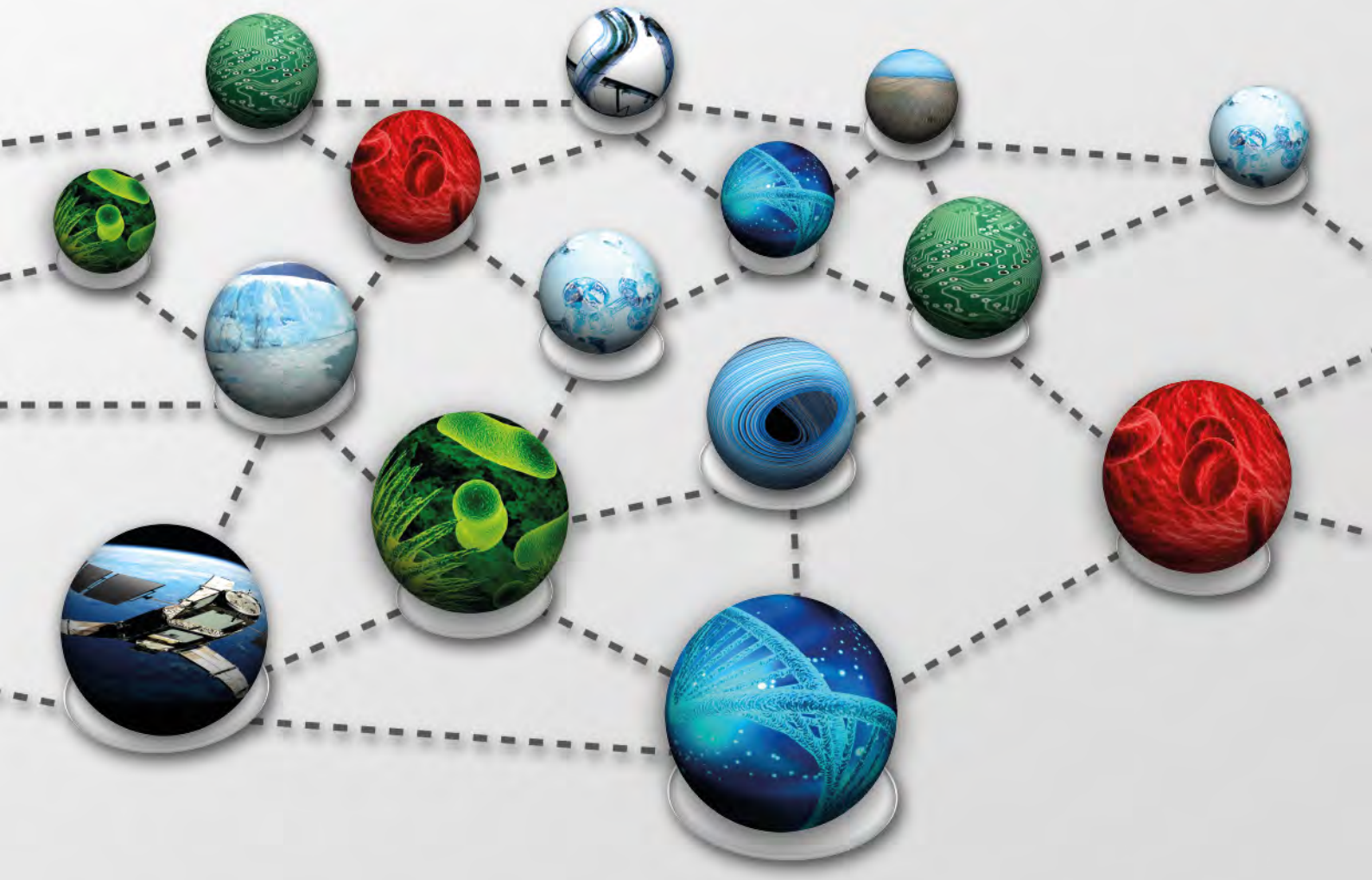
Iñigo Arrazola[1], Jorge Casanova[2], Julen S. Pedernales[2], Zhen-Yu Wang[2], Enrique Solano[1,3,4], and Martin B. Plenio[2]
[1]Deparment of Physical Chemistry, UPV/EHU, Apartado 644, 48080 Bilbao, Spain;
[2]Institute for Theoretical Physics and IQST, Albert-Einstein-Allee 11, Universität Ulm, D-89069 Ulm, Germany;
[3]IKERBASQUE, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain;
[4]Department of Physics, Shanghai University, 200444 Shanghai, China;

KEY WORDS: quantum computation, trapped ions, dynamical decoupling, quantum gates.

We propose a pulsed dynamical decoupling protocol as the generator of tunable, fast, and robust quantum phase gates between two microwave-driven trapped ion hyperfine qubits. The protocol consists of sequences of pi-pulses acting on ions that are oriented along an externally applied magnetic field gradient. In contrast to existing approaches, in our design the two vibrational modes of the ion chain cooperate under the influence of the external microwave driving to achieve significantly increased gate speeds. Our scheme is robust against the dominant noise sources, which are errors on the magnetic field and microwave pulse intensities, as well as motional heating, predicting two-qubit gates with fidelities above 99,9% in tens of microseconds.

GEOLOGIA

GEOLOGÍA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Mineralogical and geochemical approach to the archaeological records

Mª Cruz Zuluaga[1], Luis Ángel Ortega[1], Ainhoa Alonso-Olazabal[1], Iranzu Guede[1], Graciela Ponce-Antón[1] and Haizea Portillo[1]
[1]Dept. Mineralogy and Petrology

KEY WORDS: C isotope, N isotope, Sr isotope; O isotope, bones, teeth, slags, archaeological iron tools mortars, pottery.

Multi-disciplinary research group formed by geologists, archaeologists and anthropologists investigate habit and socio-economics evolution of (pre-)historic epoch from archaeological records. Research team integrates senior and junior members that have been collaborating during several years. Two main research lines according to the studied material are developed in the archaeometric field.

1. **Human bones** allow reconstructing diet and migrations patterns of ancient human by means of carbon, nitrogen, oxygen and strontium isotopes composition.

2. **Archaeological materials** provides clues of human technological evolution, technological skills, and cultural and trade links.

PALAEODIETARY AND MOBILITY PATTENS OF HUMAN POPULATIONS

The analysis of carbon and nitrogen isotope composition in human bone collagen constitutes an approach to palaeodietary reconstruction and provide information about the protein portion of the diet averaged over at least the last 10 years prior to death and also about different protein sources.

Strontium and oxygen isotopes are used to identify migrants and to reconstruct movements of past populations. Both isotopes are two independent isotopic systems in which strontium reflects local geology and oxygen reflects geography. Some cases studied by our team correspond to: Guede et al. (2017) Archaeological and Anthropological Sciences DOI 10.1007/s12520-017-0510-9. Guede et al. (2017) PlosOne, DOI 10.1371/journal.pone.0176572, Ortega et al (2017) BAR International series, S2876

HUMAN TECHNOLOGICAL EVOLUTION

Archaeometric researches are performed on archaeological pottery, lime mortars and historical slags among others. Technique variations between communities and temporal evolution of technologies are valuable topics to get a comprehensive knowledge of social evolution along time. Some case studied can be found in: Portillo et al. (2018) Microchemical Journal 138, 246–25. Grassi et al. (2017) Antiquity, 358

Additionally, new methodologies have been developed to obtain more reliable ages by binder dating since one of the main goals in building archaeology is to determine the age of the structures discovered. In the absence of written records or other archaeological evidence to establish the chronology of the building, it is vital that the historical remains are not affected by the use of older construction materials. In this respect, mortars can provide a potential dating solution, since mortar binder should reflect the time when the building was constructed Ponce et al. (2018) Cement and Concrete (summited).

Contrasting stacking patterns during the growth of a reef-rimmed greenhouse carbonate shelf: Danian of the Urbasa-Andia plateau, Western Pyrenees, N Spain

Baceta, J.I. [1], Wright, V.P. [2], Berreteaga, A.[1]
[1]UPV/EHU, Dpto. Estratigrafía y Paleontología, Leioa; [2]Geology, National Museum of Wales, Cardiff, Walles, UK .

KEY WORDS: Danian, carbonate shelf, sea level changes.

The framework for understanding stratal architecture and stratigraphic sequences in carbonates is now well constrained, both for use in outcrop studies and for reservoir characterization and modelling. One critical factor is that the spatial variability in carbonate production creates different and complex responses to external forcing. To fully assess such factors well constrained large outcrops are needed, and this study focusses on a detailed correlation of numerous vertical sections for more than 90km across an almost complete early Cenozoic tropical platform system in the Danian of the Urbasa-Andia plateau, in the western Pyrenees. This 40-45km wide and 150-300m thick carbonate platform evolved from a ramp to a flat-topped rimmed shelf, following the appearance and spread of coralgal reefs along seaward margins. However, this evolution was discontinuous, punctuated by 3rd and higher order relative sea level changes that created three complete depositional sequences (Ma-Da, Da-1 and Da-2) and a myriad of m-scale shallowing-up units. This contribution focused on the HST of the Da-2 sequence, a 90-200m thick sedimentary package that represents the peak of the rimmed shelf growth stage.

In the large-scale stacking pattern of the upper Danian HST, depending on the position on the shelf, the succession develops three different coeval depositional trends: progradational at the reefal margin, aggradational at the shallow outer shelf lagoon and retrogradational at the interior tidal flat. This divergence in growth pattern, that contradicts the typical aggradational to progradational pattern of facies belts established for third-order highstands, is interpreted in terms of significant variation in the rates of sediment production and accumulation across the shelf, with a highly prolific skeletal factory operating at the margin and a progressively less-productive mixed factory, defined by skeletal and non-skeletal carbonates, dominating the lagoonal and tidal flat areas.

The retrogradational trend seen in the innerrmost tidal flat succession confirms the prevalence of relative rising sea levels. Despite this transgressive trend, rates of carbonate production/accumulation of the reefal factory clearly exceeded any additional accommodation space created, allowing almost continuous basinward progradation of the shelf margin for about 6km. Production rates in the outer shelf lagoonal area were lower but also relatively high, as this setting became progressively wider but was still able to maintain shallow conditions, developing almost continuous aggradation with time. The interior, highly restricted tidal flat deposystem recorded the lowest rates of sediment production and accumulation within the system, only tracking the prevalent rising trend in relative sea level as a retrogradational system.

Acknowledgements: This study is sponsored by BG Group, Carbonate Technology Hub. It is also a contribution to the research projects CGL2014-52096-P and CGL2011-23770 from the Spanish Ministerio de Economía y Competitividad. Also funding from the Basque Government to the Research Group of the Basque University System IT-930-16 has contributed to this research.

Aragonitic oolite and biogenic deposits in lower Palaeocene shelf successions from the western Pyrenees: implications in the secular compositional trends of marine seawater across the Cretaceous-Paleogene boundary

Baceta, J.I. [1], *Wright, V.P.* [2], *Berreteaga, A.*[1]
[1]UPV/EHU, Dpto. Estratigrafía y Paleontología, Leioa; [2]Geology, National Museum of Wales, Cardiff, Walles, UK .

KEY WORDS: Danian, ocean chemistry, oolite.

The Danian shallow-water limestones from the western Pyrenees contain significant amounts of carbonate ooids, a highly striking feature given the global paucity of these non-skeletal grains during the late Cretaceous-Palaeogene interval. The host Danian succession is a 40-45km wide and 150-300m thick carbonate platform that evolved from a ramp to a flat-topped rimmed shelf, following the appearance and spread of coralgal reefs along its seaward margin. This evolution was discontinuous, punctuated by 3rd to 5th order relative sea level changes that created three complete depositional sequences and a myriad of m-scale shallowing up parasequences.

Although present in the whole Danian platform stack, oolites occur concentrated in the 90-100m thick upper interval, the Da-2 sequence of late Danian age, which exemplifies the climax of the rimmed shelf growth stage. They appear forming multiple, massive or cross stratified, sheet-like units, with sharp erosive bases and ranging 0.1-1.5m in thickness and 0.5-3km of average lateral extension, that define the basal parts of the building shelf parasequences. In outer shelf sections oolite beds occur below intervals of subtidal limestones with miliolids and dasycladaleans, capped by fenestral limestones; in the interior shelf underlying intertidal to supratidal fine-grained dolomites (dolomicrites) and laminated dolomitic shales with evaporite remains. Significantly, oolites are very thin or absent in shelf margin reefal successions. This stratigraphic arrangement indicates that the oolite beds are transgressive deposits which developed across the whole shallow shelf during the successive high-frequency marine re-floodings that punctuated the growth of the Danian shelf. This depositional pattern seems to have been also dominant in other greenhouse carbonate shelves.

The petrographic study of the Danian ooids reveals microfabrics and diagenetic alterations indicative of a primary, mostly aragonite composition: strongly neomorphosed tangential fabrics, oomoldic porosity with vadose infillings after early dissolution, and early distortion and moderate to strong compaction are the rule in oolitic beds from outer shelf sections. Although also showing extensive oomoldic porosity by dissolution, fine tangential fabrics after aragonite precursors are also preserved in ooids from units deposited across the interior shelf zone, where the whole Danian succession was affected by widespread early mimetic reflux dolomitisation.

The aragonitic nature of the Danian ooids can be interpreted by the establishment of relatively high Mg-Ca ratios and temperatures across the entire shallow Danian shelf, favoured by a prevalent semiarid to arid climate. However, considering the great abundance of aragonitic fossils in the margin reefal facies (notably of scleractinian corals and peyssonnelid algae) it can be assumed that elevated Mg-Ca ratios also dominated the open waters of the Pyrenean Gulf and adjacent seas. This assumption supports the hypothesis that the Cenozoic aragonite-facilitating sea conditions would have started before than usually stated or, similarly to the Carboniferous to early Jurassic interval, that the transition from the Calcite III to the Aragonite III global phases was likely punctuated by shorter stages of contrasting global ocean chemistry.

Acknowledgements: This study is sponsored by BG Group, Carbonate Technology Hub. It is also a contribution to the research projects CGL2014-52096-P and CGL2011-23770 from the Spanish Ministerio de Economía y Competitividad. Also funding from the Basque Government to the Research Group of the Basque University System IT-930-16 has contributed to this research.

HAREA-Coastal Geology Research Group

Alejandro Cearreta[1], Julio Rodríguez Lázaro[1], Ana Pascual[1], María Jesús Irabien[2], María T. Martín[3], Ane García-Artola[1], Eduardo Leorri[4], Manuel Monge-Ganuzas[5], Humberto Serrano[1], Zeltia Varela[1], Aitor Fernández-Martín Consuegra[1] and Aintzane Goffard[1]

[1]Estratigrafía y Paleontología UPV/EHU; [2]Mineralogía y Petrología UPV/EHU; [3]Ingeniería Minera y Metalúrgica, Ciencia de los Materiales UPV/EHU; [4]East Carolina University (USA); [5]Gobierno Vasco

KEY WORDS: environmental transformation, natural processes, anthropogenic impact

The Harea-Coastal Geology research group (www.ehu.eus/harea-geologialitoral) develops a multidisciplinary approach (sedimentology, geochemistry, micropalaeontology, topography, radiometric chronology) to characterize natural and anthropogenic processes responsible for the environmental transformation of the coastal zone during the last climate cycle (Pleistocene, Holocene and Anthropocene). Its activities can be summarized into the following research lines and recent publications:

1. **Environmental transformation of polluted and regenerated ecosystems.** The coastal area has experienced an intense human pressure that provoked its physical destruction and a significant chemical and biological transformation. The development of environmental conservation and regeneration schemes makes necessary to carry out geological studies to evaluate their modern characteristics, historical alteration processes and the feasibility of improvement proposals (Leorri, E.; Mitra, S.; Irabien, M.J.; Zimmerman, R.; Blake, W.H. and Cearreta, A. 2014. 700 yr record of combustion-derived pollution in northern Spain: tools to identify the Holocene/Anthropocene transition in coastal environments. *Science of the Total Environment* 470-471: 240-247).
2. **Sea-level variations as a consequence of anthropogenic climate change.** An increase in sea-level rise rate is potentially one of the most devastating impacts of the future climate change on coastal areas. Climate change influences the coastline at decadal and centennial scales, and these variations of the relative sea level are registered in the coastal sedimentary sequences. The combined study of historical records and high resolution geological reconstructions of the relative sea level is a powerful tool to assess them (García-Artola, A.; Cearreta, A.; Irabien, M.J.; Leorri, E.; Sanchez-Cabeza, J.A. and Corbett, D.R. 2016. Agricultural fingerprints in salt-marsh sediments and adaptation to sea-level rise in the eastern Cantabrian coast (N. Spain). *Estuarine, Coastal and Shelf Science* 171: 66-76).
3. **Quaternary environmental evolution due to natural processes.** Due to the frequent, rapid and intense climate changes that characterize the late Quaternary, coastal and marine environments have experienced dramatic variations and contain a complete record of the processes and events occurred during this interval. The high-resolution multiproxy study of the sedimentary record allows reconstruction of the past features, to understand the present conditions and to deduce the future environmental variability (Rodriguez-Lazaro, J., Pascual, A., Cacho, I., Varela, Z. and Pena, L. D. 2017. Deep-sea benthic response to rapid climatic oscillations of the last glacial cycle in the SE Bay of Biscay. *Journal of Sea Research* 130: 49-72).
4. **Sedimentary processes with social and economic consequences.** Sedimentary processes in the estuarine areas are frequently altered by human-induced activities (dredgings, dumpings, reclamation, channeling) which can lead to undesirable repercussions. Sedimentological studies contribute to understand the role of the anthropogenic influence and to establish suitable strategies for sustainable development (Leorri, E.; Cearreta, A.; Irabien, M.J.; García-Artola, A.; Corbett, R.; Horsman, E.; Blake, W.H. and Sánchez-Cabeza, J.A. 2014. Anthropogenic disruption of the sedimentary record in coastal marshes: examples from the southern Bay of Biscay. *Continental Shelf Research* 29: 1226-1239).
5. **Anthropocene: a new epoch in the geological scale?** Human activity is leaving a pervasive and persistent signature on Earth. Numerous anthropogenic markers of functional changes in the earth system have been found through the stratigraphic record. These signals render the Anthropocene stratigraphically distinct from the Holocene (Waters, C.N.; Zalasiewicz, J.; Summerhayes, C.; Barnosky, A.D.; Poirier, C.; Galuszka, A.; Cearreta, A.; et al. 2016. The Anthropocene is functionally and stratigraphically distinct from the Holocene. *Science* 351 (6269): aad2622.1-aad2622.10).

This research group has a leading role in the Postgraduate Programmes (Master and Doctorate) and the UFI on Quaternary: Environmental Changes and Human Footprint (www.ehu.eus/mastercuaternario, www.ehu.eus/doctoradocuaternario, www.ehu.eus/uficuaternario). **Acknowledgements:** IT976-16 (Basque Government) and UFI 11/09 (UPV/EHU).

Geobiodiversity: Geology, Fossil record and Palaeontological Heritage from the Mesozoic and Cenozoic of the western Pyrenees

Humberto Astibia[1], Mikel Arlegi[1,2], Ainara Badiola[1], Oscar Bonilla[1], Andrea García Sagastibelza[1,2], Asier Gómez-Olivencia[1,3], Mikel López-Horgue[1], Xabier Pereda Suberbiola[1], Leire Perales[1], Nathalie Bardet[4], J. Carmelo Corral[5], Ester Díaz Berenguer[6], Ignacio Díaz Martínez[7], Javier Elorza[8], Diego Garate[9] & Joseba Rios-Garaizar[10]

[1]UPV/EHU, Dpto. Estratigrafía y Paleontología, Leioa, humberto.astibia@ehu.eus; [2]Université de Bordeaux, PACEA UMR 5199, Pessac 33615, France; [3]Ikerbasque. Basque Foundation for Science; [4]Sorbonne Universités, CR2P-CNRS-MNHN-UPMC Paris 6, Département Histoire de la Terre, Muséum national d'histoire naturelle, Paris; [5]Museo de Ciencias Naturales de Álava/ANZM, Vitoria-Gasteiz; [6]Universidad de Zaragoza, Dpto. Ciencias de la Tierra, Zaragoza; [7]Universidad Nacional de Río Negro, Instituto de Investigación de Paleobiología y Geología, Río Negro, Argentina; [8]UPV/EHU, Dpto. Mineralogía y Petrología, Leioa; [9]Instituto Internacional de Investigaciones Prehistóricas de Cantabria, Universidad de Cantabria, Gobierno de Cantabria, Santander; [10]Centro Nacional de Investigación sobre la Evolución Humana-CENIEH, Burgos.

KEY WORDS: geology, geodiversity, palaeodiversity, vertebrates, invertebrates, Mesozoic, Cenozoic, western Pyrenees,

The Geobiodiversity research group includes palaeontologists and geologists from the Universidad del País Vasco/Euskal Herriko Unibertsitatea, in collaboration with researchers from other centres and institutions (i.e., museums and universities), both national and foreign. Research group IT 1044-16 from the GV/EJ (Basque Gouvernement), Group PPG17-05 from the UPV/EHU.

The main objective of our research is to contribute to the better knowledge of the palaeodiversity of the western Pyrenees from the study of the rocks and the fossil record of marine invertebrates, continental/marine vertebrates and associated biota from the Mesozoic and Cenozoic of the Basque-Cantabrian Region and adjacent sedimentary basins. This knowledge is substantial to understand the geological processes operating in basin development that have occurred throughout the history of the Earth. The fossil record, as a part of the geological record, is a non-renewable historical archive and constitutes the main tool for the study of the biodiversity of the past and of the biosphere evolution.

Main lines of research:

1. Mesozoic and Cenozoic vertebrate faunas and associated biota of the western Pyrenees: Taphonomy, Paleobiology, Geology and Geochronology.
2. Basin analysis, invertebrates and biotic changes in Mesozoic and Cenozoic seas.
3. Human evolution and palaeoecology of the Quaternary.
4. Geodiversity and palaeontological heritage.

The activities of the research group can be summarized into three: A) Research; B) Dissemination of scientific and educational findings; and C) Geoconservation.

Recent publications:

Astibia H., Payros A., Ortiz S., Elorza J., Álvarez-Pérez G., Badiola A., Bardet N., Berreteaga A., Calzada S., Corral J.C., Díaz-Martínez I., Merle D., Pacaud J.-M., Pereda-Suberbiola X., Pisera A., Rodríguez-Tovar F.J. & Tosquella J. (2016). Fossil associations from the middle and late Eocene of the Pamplona Basin and surrounding areas (Navarre, western Pyrenees). *Journal of Iberian Geology*, 41(2): 7-28. https://doi.org/10.5209/rev_JIGE.2016.v42.n1.51601

Badiola A., Gómez-Olivencia A. & Pereda Suberbiola X. (Eds). (2018, in the press). *Registro fósil de los Pirineos occidentales. Bienes de interés paleontológico y geológico. Proyección social*. Gobierno Vasco, Servicio Central de Publicaciones (Eusko Jaurlaritzaren Argitalpen Zerbitzu Nagusia), Vitoria-Gasteiz. ISBN: 978-84-457-3437-7. All members of the research group have participated as authors of different chapters of this book.

López-Horgue, M. A. & Bodego, A. (2017). Mesozoic and Cenozoic record of decapod crustaceans in the Basque-Cantabrian Basin (western Pyrenees): new occurrences and faunal turnovers in the context of the basin evolution. *Bulletin de la Societé Géologique de France*, 188(3): 14, p. 1-28. https://doi.org/10.1051/bsgf/2017180

Gómez-Olivencia A., Sala N., Arceredillo D., García N., Martínez-Pillado V., Rios-Garaizar J., Garate D., Solar G. & Libano I. (2015). The Punta Lucero Quarry Site (Zierbana, Bizkaia): a window into the Middle Pleistocene in the Northern Iberian Peninsula. *Quaternary Science Reviews*, 121: 52-74. https://doi.org/10.1016/j.quascirev.2015.05.001

Materials for the circular flux of energy: crystallographic nets based on metal nodes

IMaCris/MaKrisI Research Team
Maribel Arriortua[1,3], M. Karmele Urtiaga[1], José L. Pizarro[1], Gotzone Barandika[2,3], Begoña Bazán[1,3], Edurne Serrano[1], Roberto Fernández[3], Arkaitz Fidalgo[3], Aroa Morán[1], Eder Amayuelas[1], Laura Bravo[1], Aritza Wain[1], Iñigo Perez[1], Sofia Domínguez[3], Mikel Zarate[1]
[1]Mineralogy and Petrology Department; [2]Inorganic Chemistry Department Science and Technology Faculty. Universidad del País Vasco / Euskal Herriko Unibertsitatea; [3]BCMaterials – Basque Center for Materials, Applications and nanostructures, Martina Casiano Bld., Sarriena s/n, 48940 Leioa, Bizkaia, Spain

KEY WORDS: Energy generation and storage, advanced materials, SOFC cells, batteries, MOFs, sensors, catalysis.

The IMaCris/MaKrisI research group focuses its work on the fields of Materials Science, Crystallography and Solid State Chemistry, having as target the applicability of the developed materials to support circular economy.
Crystallographic networks based on metal nodes can provide efficient solutions to the circular flow of consumer goods, energy and waste. Connecting metal nodes through ligands enables the creation, by a rational design, of complex crystallographic networks in which metals carry out functions beyond the strictly structural ones. This way, the investigation of the redox properties and molecular exchange processes of these networks can target their application to three of the thematic priorities of the challenge on safe, clean and efficient energy contained in the Spanish National Plan for Scientific and Technical Research and Innovation 2013-2016: waste treatment for energetic purpouses, hydrogen and fuel cells and CO_2 reduction, capture and storage.
Specifically, the combination of metals of the first transition series with inorganic ligands (oxides and vanadates, among others) and organic (polycarboxylic, pyridinic and porphyrinic) opens up a range of networks gathered in six categories:

1. Materials scaled for solid oxide fuel cell applications, such as SOFC,
2. High porosity MOFs for CH_4 storage oriented to H_2 production and storage for use as fuel,
3. Heterogeneous catalysts for H_2 production and storage by reduction of water with Mn, Fe and Co and porphyrinic ligands,
4. Heterogeneous catalysts for the transformation of organic waste from refineries with environmentally friendly metals and pyridinic, carboxylic and porphyrinic ligands,
5. MOFs with nodes capable of adsorbing CO_2 and emerging pollutants and transform them into other products of interest,
6. Hybrid adsorbents MOF@IL (IL = ionic liquid) with high porosity and stability networks for adsorption of heavy metals and other pollutants from aqueous media.

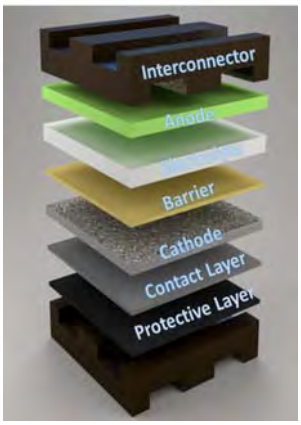


Fig. 1. Schematic stack of a SOFC cell.

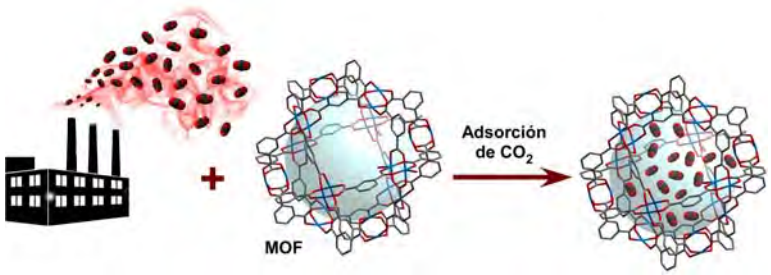


Fig. 2. CO_2 adsorption process into a MOF structure.

Acknowledgements
European Commission: H2020-MSCA-RISE-2017-778412
MINECO: MAT2016-76739-R.
Basque Government: IT-630-13, ELKARTEK KK-2016/00095.
UPV/EHU: UFI11/15.

Latest Publications/Patents of IMaCris/MaKrisI Research Team

Dalton Trans. (2016) 45, 1288-12199; Inorg. Chem. (2016) 55, 11662-11675; Solid State Ionics (2017) 313, 52-57; J. Solid State Chem. (2017) 247, 161-167; Powder Technol. (2017) 322, 131-139; CrystEngComm (2017) 19, 7244-7252; Daton Trans. (2018) 47, 958-970; J. Ceram. Int. (2018) 44, 2240-2248; CrystEngComm (2018) 47, 958-970; Patent: *"Alcohol and water sensor compounds, detection method and device"*, PCT/ES2012/070723.

Deciphering the Quaternary evolution in the Basque Country

Arantza Aranburu[1,6], *Eneko Iriarte*[2,6], *Irantzu Alvarez*[3], *Arantxa* Bodego [4,6], Iñaki Yusta[1], Martin *Arriolabengoa*[1,6], *Miren del Val*[5,6] *and Peru Bilbao*[1,6]

[1]Dept. Mineralogy and Petrology, Science and Technology Fac., UPV/EHU, Bº Sarriena s/n, 48940 Leioa, Bizkaia; [2]Laboratory of Human Evolution, Edificio de I+D+i, Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001, Burgos; [3]Dept. Graphic Design and Engineering Projects, UPV/EHU, Paseo Rafael Moreno "Pitxitxi" nº2, 48013 Bilbao, Bizkaia; [4]Dept. Stratigraphy and Paleontology, Science and Technology Fac., UPV/EHU, Bº Sarriena s/n, 48940 Leioa, Bizkaia; [5]Centro Nacional de Investigación sobre la Evolución Humana (CENIEH). Paseo Sierra de Atapuerca, 3, 09002, Burgos, Spain; [6]Geo-Q Aranzadi, Kortesenabarri Baserria, 48940 Leioa.

KEY WORDS: Quaternary, Karst, Fluvial terraces, Rasas.

The Quaternary period comprises the last 2,58 Ma years of the Earth history. During this period of time, different climatic oscillations between glacial and interglacial phases have led to different scenarios changing from phase to phase variables such as temperature, precipitation, sea level or vegetation. These variations along with tectonic movements, have modeled the landscape that we can see nowadays.

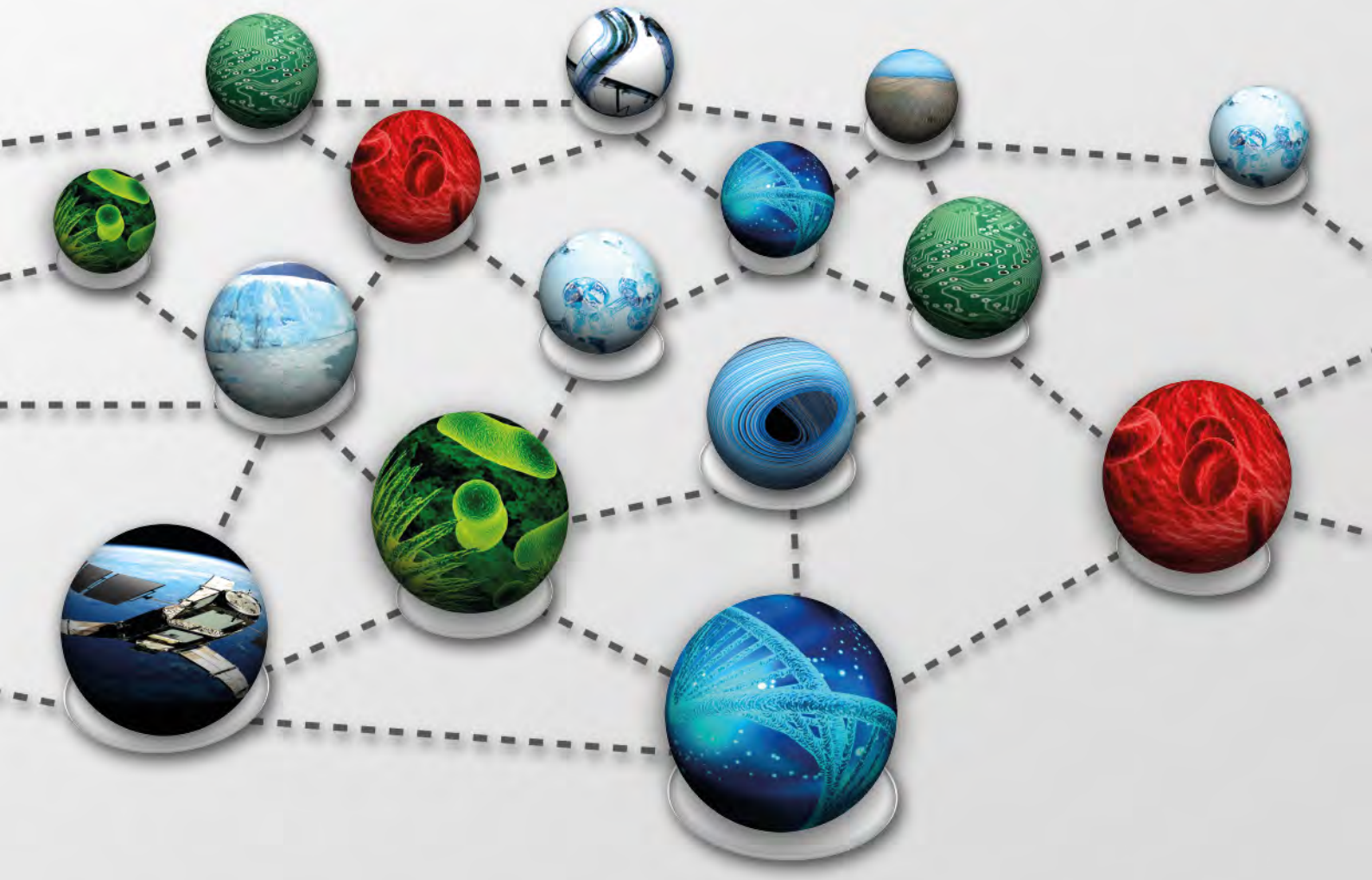
The research of the sub group, now integrated within consolidate Group of *Grupo Procesos Hidro-Ambientales / Hidro-Ingurumeneko Prozesuak Ikertaldea* (HGI) (**IT1029-16**) and lead by Dr. I. Antiguedad, has been mainly focused on analyzing the Quaternary records in order to obtain part of the evolution that has occurred in the Basque Country in the last million years. One of those records is located in the **karstic landscape**. In the Basque Autonomous Community, are known almost 6000 cavities, which act as perfect traps to preserve the detritic and carbonate records from which the different climatic conditions and geological processes can be inferred. The second analyzed records have been the fluvial terraces. **Fluvial terraces** are relatively flat floodplains that have been abandoned and appear in the banks of the current floodplain. The sequence of different terraces in the river profile is mainly controlled by the base level, water discharge and sediment supply. The last analyzed elements are the rasas. **Rasas** are relatively planar surfaces that form due to marine erosion of the continental landmass, when the sea level remains stable during a certain period. Their height will depend on sea level variations and tectonic movements, but their spatial distribution will also be controlled by the type of lithology or orientation of the rock-layers.

To extract information from these records, we use different techniques and methodologies. Direct **field observations** are carried out making different cartographies and stratigraphic columns of the analyzed area. Different **computer softwares** such as Geographical Information Systems (GIS) are also utilized to treat the data obtained from Light Detection and Ranging (LiDAR) techniques. Moreover, different **laboratory techniques** such as X ray diffraction, allow us to obtain information about the granulometry or the mineralogy of the sediments, as well as the analysis of thin sections using the microscope. To date the sedimentary deposits, usually OSL, ESR, or C14 techniques are used, whereas the speleothemes are mainly dated by U/Th techniques.

The members of the group are currently taking part in several projects, such as *Alkerdi II-Aurkikuntza arkeologiko berrien eta labar-artearen babeserako beharezko diren parametro geo-anbientales ikerketaren jarraipena* (funded by *Nafar Gobernua* and *Urdazubiko Udala*), *Estudio Geológico de la Cueva de Nerja: Galerías Turísticas, Galerías Altas y Galerías Nuevas* (funded by *Fundación Cueva de Nerja)* or *Espeleotemas y depósitos de hielo de cuevas del Pirineo: paleoarchivos para la reconstrucción del clima durante las transiciones rápidas* (funded by *Ministerio de Economía, Industria y Competitividad*).

P. Bilbao is beneficiary of a predoctoral grant from the Basque Government (PRE_2017_2_0029).

MATEMATIKA
MATEMÁTICAS



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Optimization and risk management

Unai Aldasoro[3], Larraitz Aranburu[1], Isabel Eguía[3], Laureano F. Escudero[4], M. Araceli Garín[2], Gorka Kobega[6], María Merino[1], Gloria Pérez[1,6], Celeste Pizarro[5] and Aitziber Unzueta[3]
[1]Department of Applied Mathematics, Statistics and Operations Research, UPV/EHU;
[2]Department of Applied Economics III (Econometrics and Statistics), UPV/EHU;
[3]Department of Applied Mathematics, UPV/EHU;
[4]Department of Statistics and Operations Research, URJC;
[5]Applied Mathematics, Materials Science and Engineering and Electronic Technology, URJC;
[6]BCAM-Basque Center for Applied Mathematics.

KEY WORDS: stochastic optimization, network optimization, risk management, parallel computing, CPLEX.

The aim of the Group of Stochastic Optimization (GOE) is the development of methodologies of deterministic and stochastic optimization and the use of High Performance Computing (HPC) for solving very large multiperiod deterministic and multi-stage stochastic mixed 0-1 problems. We implement two types of methodologies: matheuristic algorithms, based on classic branching techniques or advanced decomposition methods, as Branch and Fix Coordination (BFC), Fix and Relax Coordination (FRC) or Cluster Lagrangian Decomposition (CLD); and metaheuristic algorithms for combinatorial optimization as population-based methods (as evolutionary algorithms). Since the 50's, it is well known that traditional deterministic optimization is not appropriate for capturing the uncertain behavior present in most real world applications. And, it was not until the 80's when Stochastic Optimization (SO) was broadly applied in real-world applications. Uncertainty is the key ingredient in many decision problems.

Nowadays, most of the approaches in SO deal with the optimization of the objective function expected value, the risk neutral (RN) environment is assumed. However, there are some approaches that additionally deal with risk averse measures. These measures consider semi-deviations, excess, conditional value-at-risk, or first-order (FSD) and second-order stochastic dominance (SSD) constraints. We have extended the FSD and SSD constraints based measure to the multistage case, and introduced two new multistage risk averse measured based on Time Stochastic Dominance (TSD) and Expected Conditional Stochastic Dominance (ESD) taking into account time inconsistent and consistent risk averse strategies, respectively. We are updating schemes as the Subgradient method the Volume Algorithm, the Lagrangian Progressive Hedging, or the Dynamic Constrained Cutting Plane scheme in a multistage Cluster Lagrangian Decompostion (CLD) methodology and we also working on the multistage matheuristic FRC (Fix-and-Relax-Coordination) multistage for solving multistage mixed 0-1 problems.

Based on the BFC methodology, we are working in the development of matheuristic parallel algorithms for solving very large problems. New branching criteria are considered, based on dynamically-guided and stage-wise ordering schemes, such that fewer Twin Node Families are expected to be visited during the algorithm execution. The optimality gap of the solution value versus the one obtained by a state-of-the-art MIP solver CPLEX, if any, should be very small. The use of parallel computing provides, on one hand, a perspective for solving very large-scale instances and, on the other hand, an expected high elapsed time reduction.

One important application of SO is the stochastic network optimization; in particular, transport and vehicle routing problems with uncertainty in the demand. There is an important subclass of network optimization models that are not easy to solve. Good examples are the Vehicle Routing Problem (VRP) and the Travelling Salesman Problem (TSP). Even though the problems are computationally NP-hard, a large number of heuristics and exact methods are known, so that medium scale instances can be solved completely or even they can be approximated within a very small optimality gap in an affordable computing time. A very interesting modification of the TSP is the so-named Orienteering Problem (OP). It is a combination of vertex selection and determining the shortest Hamiltonian path between the selected vertices. As a consequence, the OP can be considered as a combination between the Knapsack Problem (KP) and the TSP.

This research has been supported by Bizkaia Talent and European Commission through Aid Programme for Researchers AYD-000-280 2015-17; by Spanish Ministry of Economy and Competitiveness MINECO through the BCAM Severo Ochoa excellence accreditation SEV-2013-0323 MINECO 2016-20 and Project I+D Excellence MTM2015-65317-P MINECO/FEDER 2016-18 by the University of the Basque Country UPV/EHU through the GIU17/011: Research Group in Statistics and Optimization, 2018-20. The authors thank the technical and human support provided by IZO-SGI SGIker of UPV/EHU and the European funding (ERDF and ESF).

Mathematical Analysis and Applications

N. Accomazzo[1], J. Apraiz[1], N. Arrizabalaga[1], J.B. Bru[1], J. Cayama[1], C.M. Cuesta[1], F. de la Hoz[2], X. Diez[1], J. Duoandikoetxea[1], L. Escauriaza[1], M. Escobedo[1,3], A. Fernández[1], M. Mourgoglou[1,4], O. Oruetxebarria[1], I. Parissis[1,4], J.C. Peral[1], C. Pérez Moreno[1,3,4], J. Rivas[1], I.P. Rivera[1,3], F. Vadillo[2], L. Vega[1,3], C. Zhang[1].

[1]Depto. De Matemáticas-UPV/EHU;
[2]Depto. De Matemática Aplicada y Estadística e Investigación Operativa-UPV/EHU,
[3]BCAM- Basque Center of Applied Mathematics;
[4]IKERBASQUE, Basque Foundation for Science.

KEY WORDS: PDEs, Dynamics, Harmonic Analysis, Quantum mechanics, Numerical Analysis

Our group focuses on several branches of mathematical analysis and mathematical physics. All represented in the Group lead by L. Vega "Mathematical Physics, mathematical Analysis and PDEs and Numerical Analysis" (IT641-13, Gobierno Vasco). Our lines of research include:

"Methods for numerical simulation platforms and control of the environmental fluids" (MINECO MTM2014-52347-C2-1-R; M. Escobedo, J.C. Peral): Development of methods for the analysis, the numerical approximation and control of partial differential equations, in various geophysical and natural processes such as: fluids in geophysical processes, nonlinear waves in physical processes and climate models and collective behavior of large systems.

"Harmonic measure and quantum mechanics" (MINECO MTM2017-82160-C2-2-P; J.B. Bru, M. Mourgoglou)
Derivation, from first principles of quantum mechanics, of macroscopic behaviours of quantum particles with interactions; the study of one-phase and two-phase free boundary regularity of harmonic measure; study of analytic conditions on maximal operators, defined with respect to general collections of sets, such that the corresponding bases have desirable Lebesgue differentiation properties.

"Quantum mechanics, harmonic analysis and applications to PDE's" (MTM2017-82160-C2; C. Pérez Moreno, L. Roncal): The study of operators that arise from Fourier theory and the study of solutions of elliptical equations such as singular integral operators and their weighted versions. We are interested on the Ap dependence of the Lp norms of these operators, the LlogL A1 conjecture, the two weight problem for singular integrals, commutators and Poincaré and Sobolev type of inequalities. The study of the extension problem for the sublaplacian in the Heisenberg group. The analysis on the infinite dimensional torus, discrete harmonic analysis and the study of generalized spherical means acting on radial functions and their relation to the solution of Euler-Poisson-Darboux equations.

"Theoretical and numerical analysis of evolution equations" (MTM2014-53145-P; L. Vega, C.M. Cuesta):
Unique continuation and Control Theory; uncertainty principles and applications; uniqueness for the Calderón problem; the Dirac equation; randomness in the Vortex Filament Equation; analysis of front solutions in PDEs with dispersion; study of viscous flows; inverse problems and numerical method; Hermite spectral methods; pseudo-spectral numerical methods.

"Harmonic Analysis and Differential Equations: New Challenges (669689 - HADE, H2020 ERC Advanced Grants 2014; L. Vega):This project has mainly 3 parts: Vortex Filament Equation; relativistic and non-relativistic systems with critical electromagnetic Hamiltonians (such as the Schroedinger and Dirac equations) and Uncertainty principles and applications.

Biostatistics Research Group

I. Arostegui[1,7,9], A. Urkaregi[1], F. Aizpuru[2,3,9], J.M. Quintana[4,9], E. Aguirre[5], I. Barrio[1,9], U. Aguirre[4,9], A. Bilbao[6,9], M.X. Rodríguez-Alvarez[7], D.J. Lee[7,] M.J. Legarreta[4,9], M. Mateo-Abad[8,9], A.Iparragirre[1], J. Najera[7].

[1] UPV/EHU. Departamento de Matemática Aplicada y Estadística e IO, [2] UPV/EHU. Departamento de Medicina Preventiva y Salud Pública, [3] Hospital Universitario Araba. Unidad de Investigación, [4] Hospital Galdakao-Usansolo. Unidad de Investigación Clínica, [5] UPV/EHU. Departamento de Didáctica de las Matemáticas y de las CCEE, [6] Hospital Universitario de Basurto. Unidad de Investigación Clínica ,[7] BCAM-Basque Center for Applied Mathematics, [8] Unidad de investigación PC-OSIs Gipuzkoa. [9] Red de Investigación en Servicios de Salud en Enfermedades Crónicas (REDISSEC)

KEY WORDS: Biostatistics; Clinical research; Transfer

The main specific objectives of the group are to detect problems of scientific interest in the biomedical and experimental fields where biostatistics can contribute to their resolution; conduct our own research in biostatistics aimed at generating results for solving the problems; create necessary computer tools and software for its implementation; and apply the proposed methods to the considered problems, helping to interpret the results and draw final conclusions, in collaboration with biomedical and experimental researchers involved.

In the era of Data Science, other objectives of the group are also transversal, such as, to give methodological support in data analysis to other research groups in the fields of biomedicine or experimental sciences; to promote the transfer of the research done at the university in biostatistics to biomedical and experimental fields; to take advantage of the strong demand for support in data analysis to detect future research in biostatistics, that respond to real problems in other fields.

NEW RESEARCH LINES:

1. **Behavior of MCA based score under different patterns of missingness.** MCA can be applied to the analysis of questionnaires; specifically coordinates from the first main component are used as weights of the items' categories in order to obtain an overall score, which resumes the information gathered in the survey. The aim of this work is to analyze the behavior of the MCA-score under different patterns of missing data, missing completely at random (MCAR), missing at random (MAR) and missing not at random (MNAR) by a simulation study.
2. **Longitudinal and multidimensional analysis of patients reported outcomes trough the beta binomial distribution.** In this research line, we have developed a mixed effects model based on the beta binomial distribution for analyzing correlated binomial data.
3. **Correction of the estimated AUC in logistic regression models**. In the development process of a prediction model, if the same data is used to fit the model and estimate its predictive performance, some optimism could appear. We have conducted a large simulation study in order to compare the behavior of different correction methods proposed in the literature to correct for the optimism of the estimated AUC in logistic regression models.
4. **Development of prediction models with complex survey data.** The aim of this work is to develop and validate prediction models with complex survey data incorporating sampling weights to the estimation process. In addition, we are working on the development of a discrimination ability parameter, which can take into account the sampling weight in order to evaluate the discrimination ability of the model either in the survey sample or the whole finite population.

KNOWLEDGE TRANSFER:

- **Software Development. We are working on the implementation of the methodology developed in this group into R or SAS packages.**
  - `CatPredi` an `R` package to categorize continuous variables in prediction models. Available at CRAN.
  - `PROreg` is an `R` package to develop analysis related with patient reported outcomes; such as specific recodes, plots and models. Available at CRAN.
  - `ZScore` an `R` package to develop an overall score of a questionnaire's responses by MCA.

FOR MORE INFORMATION LOOK AT THE FOLLOWING WEB PAGE https://www.ehu.eus/es/web/biostit/home

Transference of mathematical techniques and operations research tools to improve industrial processes

Josu Doncel[1], Carlos Gorria[1], Mikel Lezaun[1]
[1]Dpto. Matemática Aplicada y Estadística e Investigación Operativa (UPV/EHU).

KEY WORDS: Optimization. Linear programming. Operations Research. Industrial Mathematics. Multi skill call centers. Assignment problem

The techniques developed in Applied Mathematics are varied and can be used to find coherent solutions in many contexts. Here we will give a brief description of three different optimization models carried out in collaboration with institutions and enterprises.

SUBTITLE

Here we will describe briefly three different models that have been developed in collaboration with institutions or enterprises. The three problems come from a practical scenario and there can be expressed to a certain degree of precision under a mathematical formulation. The improvement of the results in all the cases is significative.

The first one of the models concerns the call center service that manages the internal incidences of a big distribution company like Eroski S. Coop. The service is made up of three levels, two of which corresponds to own agents. The first level agents manage a flux of general calls that can be satisfactorily managed by the Erlang-C model and its variants. This is a classical problem in operations research related to the queuing theory. When the dynamic can't be reduced to the simplest case with one queue and the time between two arrivals or between two leavings is not exponentially distributed few theoretical results can be used in order to obtain an optimal solution. This is the case at the second level, where the arrivals are distributed in several queues due to its nature. Then the incorporation of multi-skill agents and the use of routing algorithms emerge as essential for improving the management of the service. The results at this stage have to be oriented by numerical simulations because of the complexity of the theoretical formulation.

The second model consists in the management of the stock of certain components of the blood produced for medical uses in the Basque Centre for Transfusion and Human Tissues and the Blood and Tissues Bank of Aragón. Specifically, the blood platelet is a very sensible product due to the short expiry date, between 5 and 7 days from donation to transfusion. However, these components are mostly used in periodic treatments and a good demand forecast can be estimated. This fact is the best ally in order to develop a strategy based on the statistical data for each day of the week, that responds to the calculus of a safety stock. The estimation suggested by mathematical techniques handles with the calendar of the production center, with the expired polls and guarantees a minimum stock every day of the year.

The third scenario is found in an assembly line of tires in the Bridgestone Hispania corporation. The big catalog of types of compounds used and the different combination of machines that can process these compounds arises in a flow problem and an assignment problem. Once more it is a problem in the context of the operations research that can be modeled by linear programming on in which unknowns are binary. The constraints refer to the order of the compounds produced in order to guarantee the stock of a product which is raw material to the following one. On the other hand, the objective function tries to minimize gaps of time in the sequence of steps on the production.

Time-domain methods for efficiently solving challenging geophysical problems: Applications to the oil industry, mining, and earthquake propagation

J. Muñoz Matute[1], E. Alberdi Celaya[1], D. Pardo Zubiaur[1,2,3], V. Darrigrand[2], A. Rodriguez-Rozas[2,1]
[1]University of the Basque Country (UPV/EHU)
[2]Basque Center for Applied Mathematics (BCAM), Bilbao
[3]Ikerbasque, Bilbao

KEY WORDS: Partial Differential Equations, Finite Element Method, geophysics, applications, time-domain problems

The phenomenon of wave propagation and its applications can be found in a variety of disciplines. In aeronautics, acoustic waves are used, for example to reduce the noise generated by aircrafts. Acoustic waves are also used in medicine, to capture internal images of the body by ultrasound imaging. In the field of telecommunications, electromagnetic waves are used to design antennas, radars, and so on.

We can find wave propagation problems also in many geophysical problems, such as, the oil industry, mining and earthquake propagation analysis. These phenomena are modeled using Partial Differential Equations (PDEs), and in general, it is not possible to find an analytic solution of these equations. In this context, it is essential to use accurate numerical methods in order to approximate the solution properly. To solve these problems, we employ a time domain Finite Element (FE) method with goal-oriented adaptivity.

REFERENCES

[1] W. Bangerth, M. Geiger and R. Rannacher. Adaptive Galerkin finite element methods for the wave equation. Computational Methods in Applied Mathematics, 10(1), 3-48, 2010.

[2] V. Darrigrand, D. Pardo and I. Muga. Goal-oriented adaptivity using unconventional error representations for the 1D Helmholtz equation. Computers & Mathematics with Applications, 69(9), 964-979, 2015.

[3] J. Muñoz, E. Alberdi, D. Pardo, Victor M. Calo, Time-Domain Goal-Oriented Adaptivity using Pseudo-Dual Error Representations. Computer Methods in Applied Mechanics and Engineering, 325, 395-415, 2017.

[4] S. Prudhomme and J. T. Oden. On goal-oriented error estimation for elliptic problems: application to the control of pointwise errors. Computer Methods in Applied Mechanics and Engineering, 176(1-4), 313-331, 1999.

[5] P Solin and L Demkowicz. Goal-oriented hp-adaptivity for elliptic problems. Computer Methods in Applied Mechanics and Engineering, 193(6), 449-468, 2004.

[6] J. Tinsley Oden and S. Prudhomme. Goal-oriented error estimation and adaptivity for the finite element method. Computers & Mathematics with Applications, 41(5), 735-756, 2001.

Matrix analysis and applications group

Agurtzane Amparan[1], Gorka Armentia[1], Itziar Baragaña[2], María Asunción Beitia[3], Juan Miguel Gracia[1], Inmaculada de Hoyos[1], Silvia Marcaida[1], Alicia Roca[4], Francisco Enrique Velasco[1] and Ion Zaballa[1]
[1]Departamento de Matemática Aplicada y Estadística e Investigación Operativa (UPV/EHU); [2]Departamento de Ciencia de la Computación e Inteligencia Artificial (UPV/EHU); [3]Departamento de Didáctica de la Matemática y de las Ciencias Experimentales (UPV/EHU); [4]Departamento de Matemática Aplicada (Universidad Politécnica de Valencia).

KEY WORDS: matrix analysis, control theory, linear systems, structure invariants, perturbation, numerical linear algebra, inverse problems, canonical forms, eigenvalues, singular values.

The Group of Matrix Analysis and Applications (GAMA) of the University of the Basque Country UPV/EHU is the result of the evolution of a team that has been working uninterruptedly in research since 1981. The main research areas of this group are:

- Theory of matrices.
- Mathematical control theory.
- Perturbation theory.
- Numerical linear algebra.

The aim of our research is to gain insight into the structure of the linear control systems and matrices and to develop mathematical techniques in order to solve problems in these areas. The following research lines have been designed:

- Study of the structure of control systems and matrices.
- Spectral perturbation of matrices and linear systems.

These research lines are closely related. Nevertheless, in order to clarify the problems that we are interested in, we will state, in a general manner, some of them:

1. Simplify the already obtained characterization of the matrix polynomials with arbitrary degree, rank and size having the same finite and infinite elementary divisors.
2. Parametrize the coprime filters of general quadratic systems, characterize the eigenvectors of classically damping systems and generalize the phase synchronization method.
3. Design a procedure to effectively construct vibrating and gyroscopic systems with prescribed dynamic behaviour.
4. Construct new classes of structure preserving strong linearizations for rational matrices, find a procedure to recover the minimal bases of rational matrices out of their strong linearizations and make a backward error analysis of algorithms based on linearizations for rational eigenvalue problems.
5. Progress on the characterization of the assignment of invariants under state feedback and output injection, for linear control singular systems.
6. Complete the study of the hyperinvariant and characteristic subspace lattices.
7. Generalize Berlekamp-Massey algorithm to obtain matrix generators of minimal length for a given sequence of matrices.
8. Study the regularity of the stratified manifold of controllable and observable linear systems with fixed controllability and observability indices.
9. Obtain a general characterization of the stable (A,B)-invariant subspaces.
10. Analyse the geometry of the connected components of the pseudospectra and compute their derivatives in the sense of the Hausdorff metric.
11. Provide conditions for the reduction of a non-analytic matrix function of real variable to its Jordan form under global similarity.

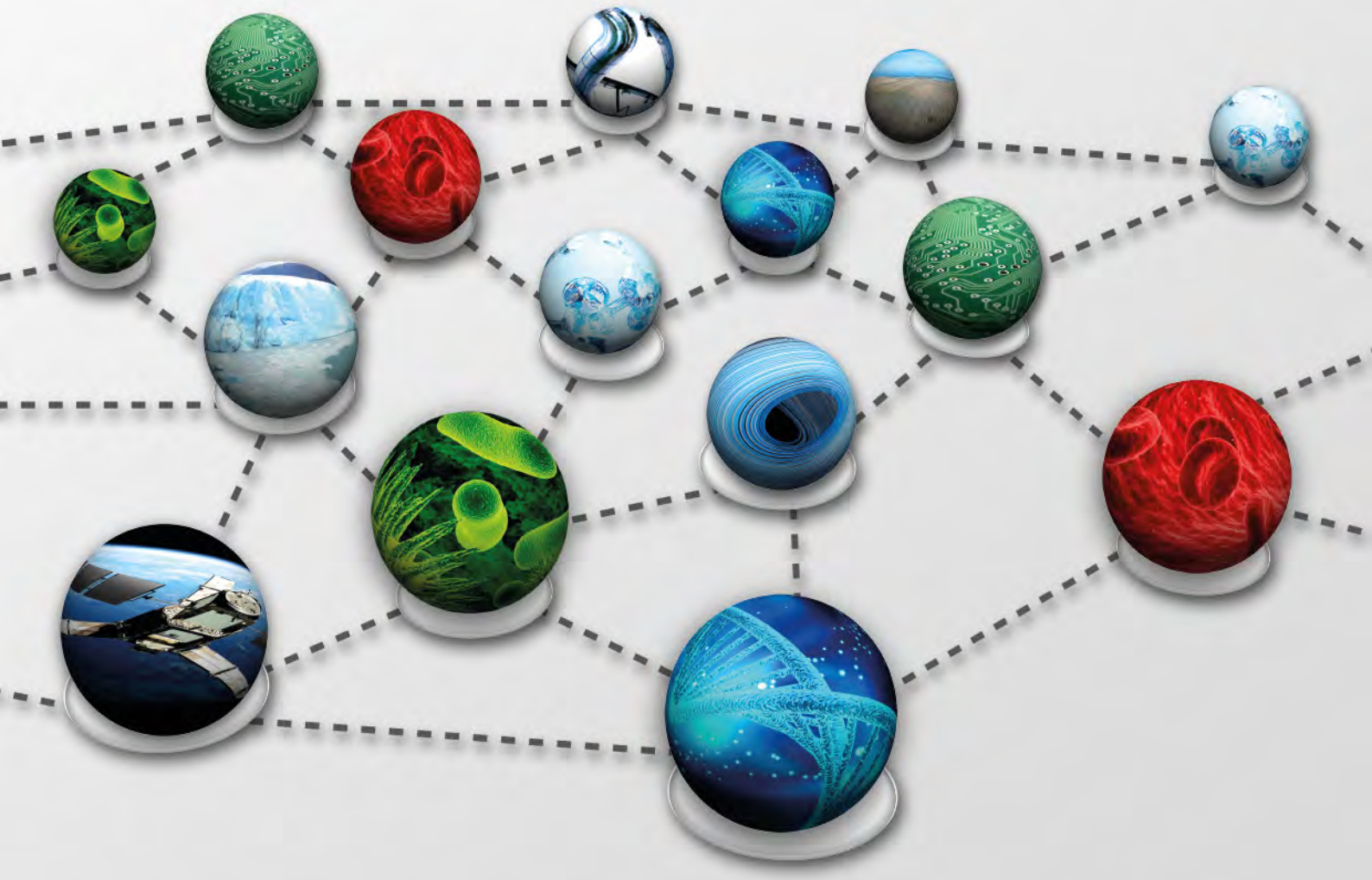
The methods and techniques to be used run over almost all fields of mathematics: from Linear Algebra and Matrix Analysis or Combinatorics to Differential Geometry or Commutative Algebra.

Weekly seminars are kept where the progression of the subgroups' work is shown, the difficulties are discussed and other researchers' work related to our problems is explained. This and the individual study of papers are the main methodological tools. The results are published in the most important specialised journals: Linear Algebra and its Applications, SIAM Journal of Control and Optimization, SIAM Journal on Matrix Analysis and Applications, International Journal of Control, Linear and Multilinear Algebra, Electronic Journal of Linear Algebra, etc.

More information in: http://www.ehu.eus/gama

KIMIKA

QUÍMICA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Natural products in food, beverages and plants

B. Gallo[1], L.A. Berrueta[1], N. Prieto-Perea[1], A. Sasía[1], C. Asensio[1]
R.M. Alonso-Salces[2], Sandra Fuselli[2]
[1] Dpto. Química Analítica, Facultad de Ciencia y Tecnología, Euskal Herriko Unibertsitatea, UPV/EHU, Leioa
[2] Universidad Nacional de Mar del Plata (UNMdP) (Argentina)

KEY WORDS: Polyphenols, anthocyanins, food science, red wine, fruits, vegetables, leaves, beverages, cider, honey, olive oil, agricultural food products, agricultural by-products, antioxidant, antiparasitic, antimicrobial, biotic agents

The chemical analysis of food and beverages has a huge interest in food science in order to develop deep knowledge of natural products, which can lead to an improvement of nutritional quality and manufacturing methods, as well as the detection of geographical origins, bad practices, adulterations and frauds.

Polyphenols are a relevant group of natural products which are widely found in the Plant Kingdom. Due to their antioxidant, antimicrobial and antiparasitic properties these compounds have attracted attention for their many benefits for human health (e.g. cardiovascular diseases, cancer...), and have also been associated with the development of biotic resistance in plants. In addition, they are a key element in explaining some food properties, such as flavour, bitterness, astringency, aroma and colour.

In this regard, and after successful studies in beverages such as ciders and wines, apples, fruit juices, edible oils, coffee, microalga, cyanobacteria and medicinal plants, our research group is currently working in the following projects:

- Anthocyanin and tannin analysis in red wines and in extracts of freeze-dried grape pomace in order to *(i)* evaluate and control vinification procedures; *(ii)* study the influence of microoxygenation and ionic exchange techniques on the vinification procedure; *(iii)* evaluate the influence of enological factors and climatology on different grape varieties and monovarietal wines; and *(iv)* be used as quality parameters related to local Protected Designation of Origin, such as wine colour, which is one of the most important parameters directly related to anthocyanins.

- Characterization of the polyphenolic profiles of agricultural food products determined by HPLC-DAD and UHPLC-DAD-QTOF/MS: Polyphenolic composition together with chemometrics (PCA, LDA, PLS-DA, PLS, neural networks) provides useful tools for quality control, authentication and detection of adulterations of agricultural food products (fruits, vegetables, leaves, fruit derived foods, cider, wine, honey, olive oil); to study the resistance of the tree towards biotic agents; detection of bad practices in food manufacturing (olive oil); optimization of production technologies to obtain foods (lettuce) with high phytochemical quality; and development of novel rapid methods to determine polyphenol composition of agricultural foods (*e.g.* wine) by vibrational spectroscopies and regression models.

- Multivariate data analysis of the polyphenolic profiles of apples, together with quantitative trait locus (QTLs) and molecular markers for the selection of genotypes with high fruit quality (apples) and interesting agro-technological properties such as resistance to biotic agents and regular productivity; with genome-wide association (GWAS) for the detection of important singles nucleotide polymorphism (SNPs) in the formation of phenolic compounds belonging to the leading polyphenol families as a tool for the selection of new varieties with specific phenolic composition in the process of genomic selection in new generation of crossovers improvement; and for the technological characterization of apple varieties.

- Valorization of agricultural food by-products (apple pomace, grape pomace, olive pomace) generated during manufacturing processes by food industry to obtain high value-added bioactive molecules for the food, pharmaceutical and cosmetic industries, as well as for veterinary use, for instance in bee health to control, prevent and fight bee diseases such as American foulbrood or varroasis.

- Natural products in plants, microalgae and cyanobacteria in the search of high value-added bioactive compounds for the food, pharmaceutical and/or cosmetic industries.

Microfluidic Devices as Analytical Miniaturised Platforms for Chemical and Biological Applications

Y. Alvarez-Braña, M. García-Hernando, E. Azuaje-Hualde, A. Calatayud-Sanchez, T. Akyazi, J. Saez, E. Ojeda-Hernandez, J. Barroso-Lazaro, J. Etxebarria-Elezgarai, L. Basabe-Desmonts and F. Benito-Lopez
Microfluidics Cluster UPV/EHU, University of the Basque Country UPV/EHU, Spain

KEY WORDS: microfluidics, Lab-on-a-Chip, integrated microsystems.

Lab on a Chip (LOC) it is a multidisciplinary area of science that covers chemistry, physics, engineering and biotechnology, claiming the miniaturisation of devices for fluidic handling and target detection. The driving force behind this miniaturisation is to enhance the performance gained by downscaling analytical systems and to integrate multiple components into a single device [1]. LOC devices offer many advantages compared to other traditional analytical platforms; for example, the reduced dimensions of microfluidic components allow for the manipulation of small volumes of fluids, which leads to less reagent consumption, reduced costs and less waste generation. The reduced dimensions of these devices allow temperature to be controlled and changed quickly because of the low thermal mass and large surface to volume ratio of microfluidics, which facilitates heat transfer and enables the creation of portable devices for *in situ* testing. Moreover, the ability to couple multiple channels together, facilitates high sample through-put on multicomponent devices and so decreases analysis times. It is this potential of integration of multiple components, which leads to the Micro Total Analysis System concept, where the sampling, fluid handling, detection and report of the results take place in a single run [2].
The integration of chemo/biosensors [3] in the microchannels of a microfluidic device using smart materials has several technological advantages compared to bench based technology, such as reduction of the volume that is needed to monitor certain analytes, minimisation of cross-contamination from the surrounding environment, continuous flow operation and long life storage, among others, Figure 1 (left). Moreover, the incorporation of stimuli responsive materials in microfluidics is enabling new ways of fluidic control and manipulation that overpasses existing technology, opening new avenues for the commercialisation of these devices, Figure 1 (right) [4].
In this contribution, we present the latest advances generated by the Microfluidics Cluster UPV/EHU to provide new functionalities to Point of Care Microfluidic Platforms for applications in chemistry and biology.

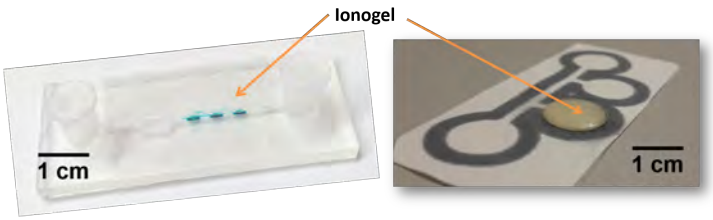


Figure 1: Microfluidic device with integrated pH sensors (left) and paper microfluidic device with integrated passive pump (right) based on ionogel materials.

References:

[1] Review on Microfluidic Paper-based Analytical Devices towards Commercialisation T. Akyazi, L. Basabe-Desmonts, F. Benito-Lopez, *Anal. Chim. Acta*, **2018**, 1001, 1-17.
[2] On-demand Generation and Removal of Alginate Biocompatible Microvalves for Flow Control in Microfluidics, J. Saez, J. Etxebarria, M. Antoñana-Diez, F. Benito-Lopez, *Sens. Actuators B*, **2016**, 234, 1-7.
[3] Ionogel-based Nitrite and Nitrate Sensor for Water Control at the Point-of-Need, J. Saez, G. Arana, L. A. Fernandez-Cuadrado, F. Benito-Lopez, *Procedia Eng.*, **2016**, 168, 518-521.
[4] Light-responsive Materials for Microfluidic Applications, J. ter Schiphorst, J. Saez, D. Diamond, F. Benito Lopez, A. Schenning, *Lab Chip*, **2018**, DOI: 10.1039/C7LC01297G.

Studies in Cultural Heritage and Landscape by means of Analytical Chemistry-IBeA research group

J. M. Madariaga[1], C. Garcia-Florentino[1], E. Estalayo[1], E. Lama[1,2], G. Arana[1], H. Morillas[1], I. Monterrubio-Santin[1], I. Madariaga[1,2], I. Marcaida[1], I. Torre[1], I. Constantini[1], I. Martinez-Arkarazo[1], J. Aramendia[1], K. Castro[1], L. Gomez[1], M. Maguregi[3], M. Veneranda[4], N. Prieto-Taboada[5], M. Olazabal[1], M. D. Rodriguez[2], S. Fdez-Ortiz de Vallejuelo[1], O. Gómez-Laserna[1] and P. Ruiz[1]

[1]Department of Analytical Chemistry, Faculty of Science and Technology, UPV/EHU, Leioa; [2]Department of Painting, Faculty of Fine Arts, UPV/EHU, Leioa; [3]Department of Analytical Chemistry, Faculty of Pharmacy, UPV/EHU, Vitoria-Gasteiz; [4]'ERICA': Advanced Spectroscopy Applied to Earth and Planetary Sciences, Boecillo, Valladolid, Spain; [5]Department of Applied Chemistry, Faculty of Chemistry, UPV/EHU, Donostia

KEY WORDS: Cultural Heritage, Landscape, material decaying, restoration, cleaning solutions, transdisciplinarity

The term cultural heritage encompasses several main categories of heritage but always responds to unique and invaluable spaces (anthropogenic or natural) and artifact deserving to be protected and safeguarded. However, generally this is not an easy goal because many conservation. Taking this into account, IBeA research group has made an important effort in the last years to understand the chemistry behind the decaying processes that affect the cultural heritage and to develop new solutions to revert them. Moreover, the IBeA research group strongly believes that the study of Cultural Heritage is a transdisciplinary commitment where several scientific disciplines converge to achieve the same purpose. In this sense, the main research lines and projects that are currently in progress are:

- **MADyLIN (Innovative diagnostic analytical methodologies and cleaning procedures for inorganic surfaces of the Built Heritage affected by anthropogenic impacts)**: studies degradations processes jeopardizing inorganic materials, and proposes eco-friendly solutions (cleaning by natural products).
- **PHETRUM (Synthesis, characterization and validation of multi-functional nano-reinforced sustainable hybrid products for the recovery and protection of stone surfaces)**: develops new products based on hybrid epoxi-silicon "BPA-free" polymers to serve for the restoration and protection of stone materials.
- **Punta Begoña Galleries**: thanks to the interdisciplinary work and important citizen participation, this project aims to convert the galleries in a "living" resource.
- **APUV (Analytica Pompeiana Universitatis Vasconicae):** analyze the original materials used to build the Pompeian houses and try to provide innovative conservation solutions to the Archaeological Park of Pompeii.
- **Machu Picchu:** a multianalytical methodology is been applied to characterize the composition of the sacred rock of Machu Picchu and the conservation problems triggered by biological factors.
- **Villa Belza:** evaluation of the marine atmosphere impact on the building materials used in Villa Belza building (Biarritz, France).
- **Conservation of paper:** development of new products based on green chemistry for the restoration of paper artifacts.
- **Study and enhancement of the Basque archaeological heritage:** in collaboration with the Archaeological Museum of Biscay analyzing metallic artifacts.
- **Spanish prehistoric paintings in open air-rock or archaeological excavation**: in collaboration with archaeologists to understand the decaying processes threatening their conservation.
- **Development of the Raman instrument for ExoMars2020**: study Martian meteorites, terrestrial analogues and their respective weathering processes to develop the required Raman instrument.
- **Chemical study of degradation processes in underwater metallic materials**: chemical analysis of the raw materials employed and on ascertaining which processes are generating the decaying of them.

In all of these projects/research lines, the development of new analytical techniques is one of the most important challenges. For this purpose, the non-destructive techniques are the most relevant analytical tools to achieve it while avoiding the damage of these important scenarios. Moreover, laboratory equipment (spectrometers, chromatographs and so on) is also useful when sampling is required.

Towards an integrative assessment on global issues in environmental analysis and food safety

N. Arrieta, D. Bilbao, L. Blanco, J.A. Carrero, A. de Diego, B. Duval, N. Etxebarria, L.A. Fernández, A. Gredilla, M. Irazola, L. Kortazar, O. Liñero, J.M. Madariaga, L. Mijangos, M. Olivares, A. Prieto, J. Saez, A. Usobiaga, H. Ziarrusta, O. Zuloaga

Department of Analytical Chemistry, Faculty of Science and Technology, UPV/EHU, P.O. Box 644, 48080 Bilbao, Basque Country (Spain).

KEY WORDS: environment, pollutants, emerging contaminants, contamination, analytical chemistry, food safety, climate change, aquatic environment, beachrock, metabollomics, bioactive compounds, bioaccumulation, toxicity, wastewater.

We live surrounded by chemicals –some of them pollutants- without grasping very well their fate and behaviour in the environment and overlooking their effects on the living organisms and on materials. These issues require a multidisciplinar and an integrative approach to understand the processes that take part in the hazardous effects or in the degradation processes. In IBeA (*Ikerketa eta Berrikuntza Analitikoa*) we lead several research topics in environmental analytical issues and collaborate with many national and European groups.

One of the research lines is focused on the influence of microorganisms and organomineralization processes on the unusual temperate latitude beachrock formations from the Basque Country. For the detection of organic templates different spectroscopic techniques (e.g. SEM-EDX, FE-SEM, Synchrotron XFM Imaging) and other geomicrobiological experiments are being conducted. The project also collaborates in the study of microbialites and beachrock samples from the Great Barrier Reef (GBR). The work aims to develop laboratory-scale models to grow synthetic beachrocks through accelerated microbial carbonate precipitation processes and to verify its bioremediation applicability for the retreating temperate-latitude beachrocks.

Additionally, IBeA participates in the REPLIM network aimed to monitor the dynamics of high mountain lakes and peatbogs and their responses to Climatic Change. REPLIM will reconstruct past changes, characterise present dynamics, and model future impacts, at both territorial and Pyrenean scales. REPLIM will also increase awareness among the stakeholders and the citizens about climate change in high mountains environments and, in definitive, will help to define a strategy of management integrated with the socioeconomic development of the Pyrenees.

In a similar way, estuaries are also studied since they are affected by contamination inputs of different origin. Trace elements are important pollutants that threaten the equilibrium of estuaries due to their toxicity, long persistence and bioaccumulation. Most metal burden entering an estuary is finally stored in sediments. Chemical analysis of sediments have allowed us investigating temporal trends and geographical distribution of metal pollution in Basque estuaries and other estuaries of the world.

Regarding the occurrence of legacy and emergent contaminants, we also lead a multi and inter-disciplinary project aimed at studying in aquatic media the presence of emerging contaminants. The main aim is to study the environmental exposome and the mechanisms of toxic action associated with exposure to emerging contaminants in the aquatic environment by integration of effect directed analysis (EDA), in-vitro cytotoxicity testing, metabolomics and wastewater based epidemiology (WBE) assays.

Finally, food safety is also a new broad research line included among our priorities. In fact, we have studied the speciation of mercury and selenium in tuna fish and importance of measuring carefully species of both metals to address the toxicity attributed to the accumulated fraction of mercury.

For most of these works the development of new and innovative analytical procedures based on cutting edge instrumentation is the key part of our research. In this sense, we can include the use of microfluidic devices or the development of nontarget analytical methods.

The FARMARTEM code

R.M. Alonso[1], M.I. Maguregui[2], M.L. Alonso[1], O. González[1], O.E. Albóniga[1]. B. Uribe[1], L. Ortiz[1], O. de la Hera[1], M. Sanchez[1], M. Ayo[1], M.V. Muñoz[1], M. Dominguez[1]
[1]Analytical Chemistry Department, Faculty of Science and Technology, UPV/EHU
[2]Paint Department, Fine Arts Faculty, UPV/EHU

KEY WORDS: drugs analysis, metabolomics, microencapsulation, food, documents

FARMARTEM research group started up in 1991 with the aim of breaking a science code. FARMARTEM is an analytical chemistry research group working in three different lines: determination of drugs (the oldest line of this group) and metabolomics, environmental and industrial analysis, and forensic studies of documents.

DETERMINATION OF DRUGS AND METABOLOMICS

- Search of the organ maturation biomarkers in the paediatric population by liquid chromatography coupled with mass spectrometry and data processing by XCMS, SIMCA software with Principal Component Analysis (PCA) and Partial Least Square Analysis (PLS-DA). These biomarkers could be used to focus on a personalized medicine and mainly to establish the appropriate drug dosage for neonates and children.
- Research on antifungal resistance by online SPE-HPLC-DAD-FLR method. Invasive candidiasis is becoming a major medical concern. Research in this field, in collaboration with Microbiology department of this Faculty and with Bourdeaux University, is necessary and the ethical limitations of doing studies in human patients require alternatives such as in vitro models. A two-compartment in vitro PK/PD system that simulates human metabolism and exposes microorganisms to changing antifungal drug concentrations will be applied.
- Development of procedures for drug microencapsulation and release studies in controlled delivery systems, such as, contact lenses or tablets.
- Quantification of pharmaceutical drugs impurities by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) required by pharmaceutical industries.

ENVIRONMENTAL AND INDUSTRIAL ANALYSIS

- Development of analytical methods for the quantification of different analytes in various environmental matrixes using analytical techniques such as solid phase extraction (SPE, SPME) and subsequent analysis by GC-MS or HPLC-DAD.
- Characterization of gas sample used in dielectric gas mixture of medium voltage electrical distribution cells. This research is being carried out by using GC/MS-Thermal conductivity detector (TCD) analytical technique in collaboration with Ormazabal (a Velatia Company) and the Engineering department of this Faculty.
- Development of analytical methods for analysis of organic and inorganic ions by ion chromatography and capillary electrophoresis for their application to food safety.

FORENSIC STUDIES OF DOCUMENTS

- Optical analysis of inks: They allow to detect documental manipulations and to identify writing tools (ballpoint pens, felt-tip pens, markers...). The main analytical technique used is infrared microscopy.
- Characterization and dating of inks and paper: It is possible to determine the age of a document by LC-MS and/or MHS-SPME-GC/MS and Py-GC/MS.
- DR-UV-vis-NIR with multivariate chemometrics.

Advanced spectroscopic and magnetic techniques in molecular and nanoscale research

Jone Garate, Iciar Uriarte, Lucía Martínez, Iker Lamas, Ander Camiruaga, Isaac Montoya, Irene Aizpitarte, Roberto Fernández, Camilla Calabrese, Igor Galetich, José Andrés Fernández, Asier Longarte, Carolina Redondo, Rafael Morales, Emilio J. Cocinero, and Francisco J. Basterretxea
Department of Physical Chemistry, UPV/EHU.

KEY WORDS: laser spectroscopy, microwave spectroscopy, ultrafast processes, nanomagnetism, nanostructures, lipidomics, cancer, metabolites, vaccines, nanomedicine, biosensors.

The Spectroscopy Group works in research lines that comprise different subjects, all focusing on a molecular and nanometric scale. It designs and applies state of the art spectroscopic techniques to a variety of problems in chemistry that partly overlap with the fields of biology or physics. The group works in spectroscopic instrumentation to achieve high resolutions, both in time and energy, and high control of physical and chemical properties at the nanoscale. Thus, ultrafast lasers allow detection of phenomena in the timescale of femtoseconds, whereas microwave spectrometers can resolve molecular energy levels that differ only a few kHz. On the other hand, combining nanosecond laser pulses with mass spectrometric detection it is possible to discriminate among different molecular conformers of the same species. Finally, laser lithography techniques, together with magneto-optical spectroscopy, allow fabrication and characterization of singular patterned nanostructures.

The previous techniques are well suited to investigate numerous scientific problems at a molecular and nanometric level. A brief list of the ongoing research lines of the group is given below:

- The study of *ultrafast molecular phenomena* using femtosecond laser pulses, such as dissociative processes, energy transfer among excited electronic states, or between solute and solvent molecules. These phenomena are essential to understand intra- and intermolecular interactions.
- *Design of femtosecond laser pulses* of given time and energy to be used as a spectroscopic excitation source.
- *Microwave spectroscopy* techniques, combined with laser vaporization techniques, allow to obtain molecular structures and gas-phase dynamics of biomolecular building blocks, such as sugars, of which few experimental studies free from the interation with solvent molecules can be found. These studies are also the basis for the detection of prebiotic molecules in the interstellar space.
- *Laser electronic spectroscopy* with pulsed supersonic jets and mass resolution is a powerful tool to characterize electronic transitions of rather big molecules and can further discriminate among a usually numerous family of conformers. This techniques are adequate to study interactions between molecular moieties of interest in the biosciences, such as anesthesic-receptor, or bonding among the nitrogenated bases in DNA and RNA chains.
- More specific mass spectrometric techniques, such as *Matrix Assisted Laser Desorption Ionization* (MALDI), allow the obtention of bidimensional images of biological tissues; in this way the distributions of lipids or other substances can be monitored quickly. This technique has immediate medical applications.
- Nanofabrication and characterization of structures at the nanometer scale allow designing of *magnetic nanostructures* (discs, rods and other geometries) with distinctive properties, different from those of macroscopic elements. These patterned structures have a wide application in fields such as magnetic storage of information or biomedicine, for example, cancer diagnostics.

Design and computationally aided spectroscopic characterization of multifunctional materials

Iñigo López Arbeloa[1], Teresa Arbeloa[1], Jorge Bañuelos[1], Virginia Martinez[1], Hegoi Manzano[2], Leire Gartzia[1], Rebeca Sola[1], Eduardo Duque[1], Ruth Prieto[1], Edurne Avellanal[1], Ainhoa Oliden[1] and Xabier Mendez[2]
[1]Dpto. Química Física; [2]Dpto. Física de la Materia Condesada.

KEY WORDS: dyes, fluorescence, nanomaterials, laser, singlet oxygen, atomistic simulation, biophotonics.

One of the main goals of the Molecular Spectroscopy group is to understand the complex interaction of electromagnetic radiation with matter and to unravel the undergoing induced phenomena, as key processes in many optolectronic devices or in biophotonics. The knowledge of the underlying photophysical processes is essential to understand the workability of such applications and to know how to improve their performance. We focus mainly in the impact of the light spanning the ultraviolet-visible-near infrared region of the electromagnetic spectrum on organic dyes and hybrid systems (i.e. fluorophores combined with different matrices) as photoactive materials. To this aim, our laboratory is equipped with advanced spectroscopic techniques with high temporal resolution and sophisticated fluorescence microscopes. The spectroscopic characterization is supported with quantum mechanics calculations at the molecular level. Moreover, we have implemented the required skills to apply computational tools to simulate the physicochemical and mechanical properties of materials in the solid state.
Overall, our research activity can be divided in four strategic lines closely interconnected between them, in which the experimental spectroscopic work is supplemented with the computational studies:

1. **Multifunctional organic laser dyes.** After a rational design chromophores can be tailored in which the photophysical signatures can be deeply modulated in a controlled way by the substitution pattern. As a result, we are able to attain fluorophores suitable for dye lasers, for sensing applications (i.e. fluorescent probes in bioimaging), multchomophoric dyes as chiral agents or even molecular antennae for light harvesting.

2. **Singlet oxygen photosensitizers for photodynamic therapy.** The aforementioned tunability of the spectroscopic properties of the organic dyes enables the design of biocompatible chromophores able to generate singlet oxygen. This cytotoxic species is able to kill tumoral cells via a non-invasive method promoted by light (called photodynamic therapy). A fine balance between this sensing ability and the therapeutic activity allows the development of dual luminophores able to visualize the tumoral cells and treat them (theragnosis) simultaneously.

3. **Photoactive materials**. To translate the work carried out in the laboratory to the technological scale the aforementioned fluorophores are encapsulated or linked to a wide variety of inorganic (porous aluminosilicates, silicate nanoparticles) or organic (Metal-organic frameworks, polymeric nanoparticles) hosts and carriers. As consequence, versatile fluorescent materials can be customized with applications in non-linear optics as microlasers, antenna materials or while-light emitters or biomedicine, as drug delivery systems.

4. **Atomistic simulation of materials**. A wide range of molecular simulation techniques are applied to study the correlation between structure and properties of materials. Molecular dynamics, as well as more accurate DFT methods, allow the simulation of key structural parameters and electronic structure in crystals, molecular adsorption and diffusion processes in nanopores, elasticity and mechanical properties of complex solids, and chemical reactions in catalytic materials.

The multidisciplinary nature of the above-mentioned milestones requires a multidisciplinary work and a dynamic coordination with research groups specialized in organic and inorganic chemistry, physics, optics, materials science, biochemistry and biomedicine.

Polymers: a new era for materials

N. Barroso, M. Garate, D. Helgera, I. Isusi, M. Parra, A. Regil, A. Vilches, J. Andrade, S. Maiz, J.Sanchez, A. Valverde, M. Azkune[2],A.Burgoa[3], C. Mendes[4], A. Reizabal[4], A. Galdames, J. M. Laza, L. Ruiz, L. Pérez, M. I. Moreno[5], J.L. Vilas
Macromolecular Chemistry Group (LABQUIMAC). Physical Chemistry Dept. FCyT. UPV/EHU
[2]Applied Photonic group. Faculty of Engineering Bilbao UPV/EHU, [3]Leartiker. Markina-Xemein, [4]BCMaterials. Basque Center for Materials, Applications and Nanostructures, UPV/EHU, [5]LABQUIMAC, Organic Chemistry II Dept. FCyT, EHU/EHU

KEY WORDS: biocompatible implants, shape-memory polymers, hydrogels, nanogels, optical fibers, printable smart materials, bioremediation, active packaging materials, silkworm fibroine.

Since polymers were discovered in 1920 by Herman Staudinger, polymer science has grown to become today one of the fundamental scientific areas. Nowadays, the discovery and development of new polymeric materials is essential to continue contributing to the advancement of humanity.

Our research deals with the synthesis and analysis of new materials based on polymers in order to improve fundamental aspects of life. Our efforts are focused on four areas: biomedical devices, environmental improvement, self-healing and shape memory materials and additive manufacturing.

BIOMEDICINE
New materials that reduce the infections caused by the adhesion of bacteria in medical implants. Natural polymers are employed to construct multilayers (inorganic and polymeric) using different strategies such as layer by layer (LbL) or grafting. Besides, the influence of micro- and nano-topography of surfaces on bacterial adhesion to polymers is also investigated. Furthermore, we considered the “click” reaction in polymeric surfaces for the conjugation of complex organic structures on the surface of many materials.
Natural based injectable hydrogels that enhance cell adhesion and lead to the development of a new generation of electroactive hydrogels to be applied in *in vivo* tissue engineering. In addition, biodegradable nanogels are also studied as specific drug carriers for new cancer therapies.
Implementation of hollow-core polymer microstructured optical fibers as sensing platforms to allow the enhancement of various sensing methods such as the Raman Spectroscopy.

SHAPE MEMORY AND SELF-HEALING MATERIALS
Shape memory polymers (SMPs) are capable of fixing temporary shape and recovering to the permanent shape in response to external stimuli. Hydrogels with the ability to repair themselves after damage are another hot pot in our laboratory. These materials present more than one triggering stimulus that can be used to induce the shape memory and self-healing effect. Beyond all these, hybrid organic inorganic interactions represent a highly interesting possibility due to their properties and versatility, allowing the fabrication of multiresponsive systems.

ADDITIVE MANUFACTURING
Additive manufacturing, has developed rapidly in the last 10 years and has demonstrated significant potential in cost reduction of performance-critical components. To follow this road, our group is researching the development of wireless, sustainable and interconnected autonomous smart systems. Despite the large maturity of 2D and 3D printed technologies, the number of materials with suitable properties to be printed is still small. For this deal, we promote the use of polymers as printable smart materials for based the development of more environmental friendly technologies into devices of materials.

ENVIRONMENTAL IMPROVEMENT
Finally, in order to reduce human environmental impact, we are working in new bioremediation techniques and in the substitution of petrochemical compounds by new bio-based polymers in three different ways:

- Using different innovative methods for remediation, as treatments with zero-valent iron nanoparticles (nZVI) as a cost effective and environmentally friendly agent for environmental remediation.
- Promoting the Poly-L-isomer of lactic acid (PLLA) is as functional packaging material due to its good properties: non-toxic, derived from natural sources and biodegradability.
- Working in the long range of morphologies adopted by silkworm fibroin for sensors and actuators.

The Importance of Being Keggin: Polyoxometalate Chemistry in the 85th Anniversary of the Keggin Structure

Juan M. Gutiérrez-Zorrilla, Beñat Artetxe, Leire San Felices, Santiago Reinoso, Pablo Vitoria, Estibaliz Ruiz-Bilbao, Aitor Nunes, Markel Pardo, Leticia Fernández-Navarro, Estíbaliz González-Díez
Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, P. O. Box 644, 48080 Bilbao, Spain

KEY WORDS: Polyoxometalates, Porous materials, Smart polymers.

Polyoxometalates (POMs) are a well-known class of metal–oxo anionic clusters that encompasses species with a large variety of shapes and compositions, as well as applications in fields of current technological, economic, and environmental interest (e.g., catalysis, medicine, energy, materials science). A plethora of POM-based compounds has been described since the first structural report of a polyanion in 1933 by J.F. Keggin. The $[XM_{12}O_{40}]^{n-}$ Keggin-type anion (usually X = Si, Ge, P and M = Mo, W), named after him, represented the origin of a new research field and is currently at the center of the POM community. The beauty of this chemistry lies in its resemblance to the "Lego" game at the microscopic level; that is, the removal of one or more octahedral $\{MO_6\}$ building blocks from the parent plenary structure results in the so-called *lacunary* POM frameworks, which can be used as multidentate O-donor ligands to incorporate additional functionalities (ie. organic moieties, 3d- or 4f-metal centers) into the inorganic skeleton to design novel architectures with remarkable properties. Owing to their interesting features (high solution and thermal stability, high acidity, versatile redox properties), POMs are ideal candidates to be used as active molecular components in the formation of advanced functional materials.

As much as three different research lines focused on the synthesis and structural characterization of POM-based materials are being developed in our group:

ORGANIC DERIVATIZATION OF POMs
The organic derivatization of POMs has been identified as a key factor for the clusters to be suitably incorporated into functional materials. Different synthetic routes have been explored to prepare solution stable hybrid clusters. These include i) the use of organo p-block derivatives (organosilyl, -phosphoryl or –stannyl moieties) in combination with lacunary polyoxotungstates, ii) condensation of tris(alkoxo) ligands to the surface of molybdates and vanadates, and iii) reactions of POMs with exposed 3d- or 4f-metal centers displaying at least two available coordination sites toward organic ligands with chelating ability. Synergistic effects between both organic and inorganic components have resulted in catalytically- and photo-active materials or single-ion magnets among others.

MULTIFUNCTIONAL POM-BASED OPEN FRAMEWORKS
The grafting of discrete coordination complexes with peripheral organic ligands to POM surfaces can result in three-dimensional crystalline frameworks with permanent porosity. The use of first-row transition metal complexes of macrocyclic polyamines in combination with POM clusters has led to covalent open frameworks with interesting functionalities such as selective adsorption of gas molecules (CO_2 over N_2) and remarkable activity as heterogeneous catalyst for the selective oxidation of adamantane among others. This family of compounds have also shown the ability to respond to external stimuli, in such a way that they can undergo thermally triggered single-crystal-to-single-crystal structural transformations promoted by dehydration processes.

SMART POM/POLYMER COMPOSITES
Different families of novel POM/polymer composites with a broad scope of potential applications are being developed:
i) *Biomedicine*: POM-polysaccharide nanogels for breast cancer therapies.
ii) *Thin film technologies:* functional POM-polymer surfaces with catalytic and luminescent properties.
iii) *Materials Science:* modifications in thermal and mechanical properties of cationic polymers through POM-based cross-linking.
iv) *Smart Materials:* POM-based supramolecular shape-memory and self-healing hydrogels.

COLLABORATORS: Dr. J.L. Vilas, Laboratorio de Química Macromolecular (UPV/EHU), Dr. J.A. García (UPV/EHU), Dr. J. Alcañiz-Monge (Universidad de Alicante), Dr. C. Vicent (Universidad Jaume I, Castellón), Dr. M.M. Vivanco (CICBiogune), Dr. U. Kortz (Jacobs University, Bremen), Dr T. Liu (University of Akron, USA).

FUNDING: UPV/EHU (PG17/37, IT1082-16), MINECO (MAT2017-89553-P).

Nanostructured Materials for Energy and Biomedical Applications

T. Rojo[a, b], L. Lezama[a], A. Goñi[a], M. Insausti[a], I. Gil de Muro[a], F. Lopez Arbeloa[d], A. Peña[a], I. Ruiz de Larramendi[a], J. Lago[a], J. M. Rojo[a], V. Palomares[a], E. Goikolea, A. Iturrondobeitia[a], I. Castellanos-Rubio, P. Sánchez[a, c], O. K. Arriortua[a], I. Lozano[a], I. Galarreta[a]

[a] Dpto. Química Inorgánica, [d] Dpto. Química Física, FCT, UPV/EHU, Bº Sarriena, 48940 Leioa, Spain.

[b] CIC ENERGIGUNE, Parque Tecnológico de Álava, Albert Einstein 48, ED. CIC, 01510, Miñano, Spain.

[c] BCMaterials, Parque Científico de UPV/EHU, E-48940, Leioa, Spain

KEY WORDS: Li-ion and Na ion batteries, electrochemistry, spinel, sodium vanadium fluorophosphates, nanoparticles, superparamagnetism, electron magnetic resonance, magnetic hyperthermia

The work developed in this research group can be divided in two main lines: functionalized magnetic nanoparticles for biomedical applications and materials for energy. The first one explores magnetic nanoparticles for their application in the research field of biomedicine. The size confinement to nanometer scale in magnetic materials changes the properties from those of the bulk ferro and ferrimagnetic counterparts. These properties, together with the similarity in size between nanoparticles and biological entities lead to different applications such as drug delivery, MRI contrast or magnetic hyperthermia. For these purposes, the size and characteristics of the nanoparticles, their stabilization and biocompatibility by an adequate surface functionalization are key attributes that must be controlled.

The most usual materials for such applications are the superparamagnetic iron oxides because of their good biocompatibility, low toxicity and suitable magnetic properties. So, our work is focused on optimization of chemical routes to obtain Fe_3O_4 nanoparticles and nickel, manganese or cobalt doped ferrites. These nanostructures functionalized with polymer ligands as PMAO, DMSA, APTES or chitosan render hydrosoluble particles, which have been additionally coated with fluorophores, RGD type peptides or chemotherapy drugs to enhance targetting or delivering. Finally, NPs fluids have been succesfully intrarterial infused to rats with colorectal tumors and exposed to hyperthermia treatment to induce necrosis in tumoral tissues.

The second aspect covered by the group is the search for commercially viable Li-ion and Na-ion batteries, that is, more economic, safer and longer-life batteries. In this sense, new and better-performing cathode materials for lithium ion batteries (LIBs) have been produced by nanosizing, carbon coating, and substitution in the $Li(Mn,M)_2O_4$ (M = Ga^{3+},Si^{4+}) and $Li(Mn_{0.8}Fe_{0.1}M_{0.1})PO_4/C$ (M = Fe, Co, Ni, Cu) compounds. Nanoparticulate NiO and NiO/C composites with different carbon proportions have also been prepared for anode application.

Sodium ion batteries (NIBs) have received increased attention as an alternative to LIBs for stationary storage due to the abundance and low cost of Na. The most important cathodic materials employed in NIBs are the transition metal oxides (Na_xMO_2) and the polyanionic $Na_xM_y(XO_4)_n$ (M= Mn, Fe, Ni, Co; X=Si, P, S) compounds. In this regard, $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ sodium-vanadium fluorophosphates have high reaction voltages (at 3.6 and 4.1 V vs. Na/Na^+) and their good specific capacity values in sodium half-cells (theoretical specific capacity of about 130 mAh/g) leads to high energy density compounds (ca. 500 Wh/kg). The synthesis and exhaustive characterization of advanced cathode composites containing reduced graphene oxide as additive, such as $Na_{2.5}Fe_{1.75}(SO_4)_3$/Ketjen/rGO, provide excellent results, with specific capacities close to the theoretical one at 1C, and a great cycling stability and coulombic efficiency of 96%. Metal-air batteries are also studied due to their high energy density compared to traditional energy storage systems.

Characterization of the different materials comprises powder X-ray diffraction, thermogravimetric analysis, Dynamic Light Scattering (DLS), Scanning and Transmission Electron Microscopy (SEM/TEM), magnetic and hyperthermia measurements and Electron Magnetic Resonance Spectroscopy. The electrochemical measurements are conducted using coin-cell and Swagelok-type cells. In addition, post mortem studies of the cycled electrodes are performed by EPR and XPS techniques in order to further analyze the evolution of the materials.

POROUS METAL-ORGANIC MATERIALS
Designing metal/ligand complexes that self-assemble into open extended 3D architectures

O. Castillo,[1] G. Beobide,[1] J. Pascual-Colino,[1] R. Pérez-Aguirre,[1] S. Pérez-Yañez,[2] M. Perfecto-Irigaray,[1] A. Luque,[1] M. Lanchas,[1] D. Vallejo[1] and P. Román[1]

[1] Inorganic Chemistry Department, Science and Technology Faculty (UPV/EHU); [2] Inorganic Chemistry Department, Pharmacy Faculty (UPV/EHU)

KEY WORDS: MOFs, MOGs, MOAs, Porosity, Solvent-Free Synthesis.

The research group develops a great variety of materials that share a common feature: its porous nature. Below you can find a more detailed description of each family of materials

Metal−organic frameworks (MOFs). Metal–organic frameworks (MOFs) are a class of hybrid materials comprising metal ion-based vertices and organic ligands (linkers) that serve to connect the vertices into two or three-dimensional periodic structures. The structures and properties of MOFs can be carefully tailored by judicious selection of metal ion and organic linker building blocks. They encompass an area of chemistry that has experienced impressive growth during the last decades because of their various potential applications in catalysis, gas storage, chemical separations, sensing, ion exchange, drug delivery, and optics. Regarding the adsorption field, it is worth mentioning that their large surface areas, adjustable pore sizes, and controllable functionalities are key factors that make MOFs promising candidates for adsorptive separations and purification purposes.

Supramolecular Metal-Organic Frameworks (SMOFs). Taking into account the great potential of MOFs, we decided to explore a related type of material, in which the coordination bonds are replaced with hydrogen bonds as connectors, which are also directional and predictable interactions, to sustain the three-dimensional (3D) crystal building containing potentially accessible voids. Although such kinds of alternative materials can arise a similar fascination to that of MOFs, the crystal engineering principles and the synthetic approach are not yet settled, and examples of this kind of material are rather scarce.

Metal-organic gels (MOGs) and Metal-organic aerogels (MOAs). In the last few years, metal-organic gels (MOGs), also called metallogels, have emerged as an alternative material to MOFs. Ideally, during the gel formation, the coordination polymer grows as nanoscopic primary particles that crosslink stochastically into the reaction media, creating a 3D solid network that entraps all synthesis solvent within. Gel drying by evaporation of the solvent induces a severe shrinkage of the microstructure and leads to a material called xerogel (MOX, metal-organic xerogel) with reduced porosity. Contrarily, supercritical drying of MOGs removes the solvent without collapsing their microstructure, and it leads to metal-organic aerogels (MOAs) that are hundreds of times lighter than MOFs. Therefore, porosity in MOGs and MOAs has a microstructural origin and not a strictly crystallographic one like in MOFs. Thus, the gelation approach enables the preparation of porous materials from metal-organic systems that do not necessarily render an open framework. Keeping in mind that the examples of MOGs and MOAs are still relatively rare, there is an exciting chance to prepare metal-organic porous materials from coordination polymers that lack crystalline origin porosity but gather striking electrical, magnetic, and optical properties.

Finally, another objective of the research groupr is to develop synthetic methods that allow obtaining these materials with a low environtmental impact and at reasonable cost. In this sense, we have developed a solvent free technique that provides a more sustainable route as it avoids the use of the usually employed expensive and/or toxic solvents

Organometallics in Synthesis

I. Barbolla,[1] A. Carral-Menoyo,[1] C. Santiago [1] M. Martínez-Nunes,[1] H. Bediaga, M. Gómez-Redondo, [1] P. Gutiérrez,[1] L. Moya,[1] V. Yañez,[1,2] S. Arrasate,[1] H. González-Díaz,[1,3] N. Sotomayor [1] E. Lete[1]
[1]Departamento Química Orgánica II, Facultad de Ciencia y Tecnología, Universidad del País Vasco/Euskal Herriko Unibertsitatea;[2]Universidad Autónoma de Yucatán (México), [3] IKERBASQUE

KEY WORDS: asymmetric synthesis, organometallics, chemoinformatics

Our group works on Organic Synthesis, mainly in asymmetric synthesis and organometallic chemistry. Our projects are focused on the development of new synthetic methods based mainly on lithium and palladium chemistry for the stereocontrolled formation of carbon-carbon bonds. The group has a solid background in Organic Synthesis, which allows us to face the preparation and structural determination of any kind of organic molecules. Our research interests are summarized in the following lines:

Line 1. Metal-catalyzed reactions in the synthesis of heterocycles
The application of palladium-catalyzed C-C bond forming reactions is studied for the synthesis of heterocyclic systems. We have shown that Heck-type reactions, direct C-H arylation and both inter and intramolecular C-H alkenylation reactions are versatile and effective tools for the synthesis of polyfunctionalized medium-size rings. Asymmetric variants and cascade reactions have also been developed. The use of other metals, such as rhodium and ruthenium for these types of reactions is also being studied.

Line 2. Lithiation-cyclization sequence in the stereocontrolled synthesis of nitrogen heterocycles
The Parham-type intramolecular reactions for the construction of fused heterocyclic systems are explored. The synthetic utility of the procedure has been shown by application to the synthesis of a variety of products with relevant biological activities, natural products or analogues.

Line 3. Enantioselective alpha-amidoalkylation reactions
The Parham cyclization–enantioselective intermolecular alpha-amidoalkylation and organolithium addition–enantioselective intramolecular alpha-amidoalkylation sequences provide a novel synthesis of enantioenriched substituted fused isoquinoline systems. The enantioselection is controlled by using sterically demanding Brønsted acids as catalysts.

Line 4. New computational models for the prediction of chemical reactivity, biological activity and toxicity
We are also developing new computational multi-target QSRR methods capable of predicting enantioselectivity levels of a given reaction when structural modifications (on substrates, ligands or catalysts) or experimental conditions are carried out. On the other hand, multi-target QSAR (quantitative structure-activity relationship) or QSTR (structure-toxicity relationship) models are also being carried out.

For reviews on our work, see: *Eur. J. Org. Chem.* **2011**, 3610; *Carbolithiation of carbon-carbon multiple bonds*, en *Science of Synthesis. Knowledge Updates 2011/4,* D. G. Hall, K. Ishihara, J. J. Li, I. Marek, M. North, E. Schaumann, S. M. Weinreb, M. Yus, Eds.; Thieme: Stuttgart, **2012**, p. 191. *Beilstein J. Org. Chem.* **2013**, *9,* 313.
For some selected publications: *Eur. J. Org. Chem.* **2017**, 2462 (highlighted in *SYNFACTS* **2017**, *13*, 0693), *ACS Omega,* **2017**, *2,* 2706; *Mar. Drugs* **2017**, *15, 276; RSC Adv.* **2016**, *6*, 38602; *Eur. J. Org. Chem.* **2016**, 2054; *Chemistry Open* **2016**, *5*, 540; *Adv. Synth. Catal.* **2015**, *357,* 3206; *Adv. Synth. Catal.* **2015**, *357*, 463; *Adv. Synth. Catal.* **2014**, *356*, 1853.
More detailed information can be found in our web page: www.ehu.es/oms

New synthetic methodologies based on sustainable procedures

Esther Domínguez, Raul SanMartin, María Teresa Herrero, Imanol Tellitu, Garazi Urgoitia, Iratxe Astarloa, Aimar García, Galder Llorente, Miriam Feijoo, Aitor Herrán and Maria Obieta
[1] Department of Organic Chemistry II, Faculty of Science and Technology, University of the Basque Country (UPV/EHU). Sarriena auzoa z/g, 48940 Leioa.

KEY WORDS: sustainable chemistry, new catalysts, renewable sources

Our research group works actively on the exploration of methodologies for the preparation of compounds of industrial interest using new catalyst systems in sustainable media. In addition to the synthesis of several metal complexes featuring significantly improved catalytic profiles, new applications for the latter compounds and other catalyst systems are constantly sought so that the access to relevant chemical entities (biologically active compounds, natural products, new materials) is simplified and performed through very short, efficient synthetic sequences where the presence of metal traces in final products is minimized and sustainable reaction media are mainly used. Cascade and multicomponent reactions are explored in order to shorten synthetic sequences and to improve the atom-economy of the whole process. Special attention is paid to environmentally more friendly, safer, and therefore more convenient reagents (molecular oxygen- and hypervalent iodine-based oxidants, carbon dioxide, bioderived chemicals, etc.) and to alternative energy inputs. As part of the so-called chemical recycling and circular economy, catalytic degradation of industrial waste materials is also under research in our laboratories.

Group of Asymmetric Synthesis, Sustainable Chemistry and Biomimetic Processes

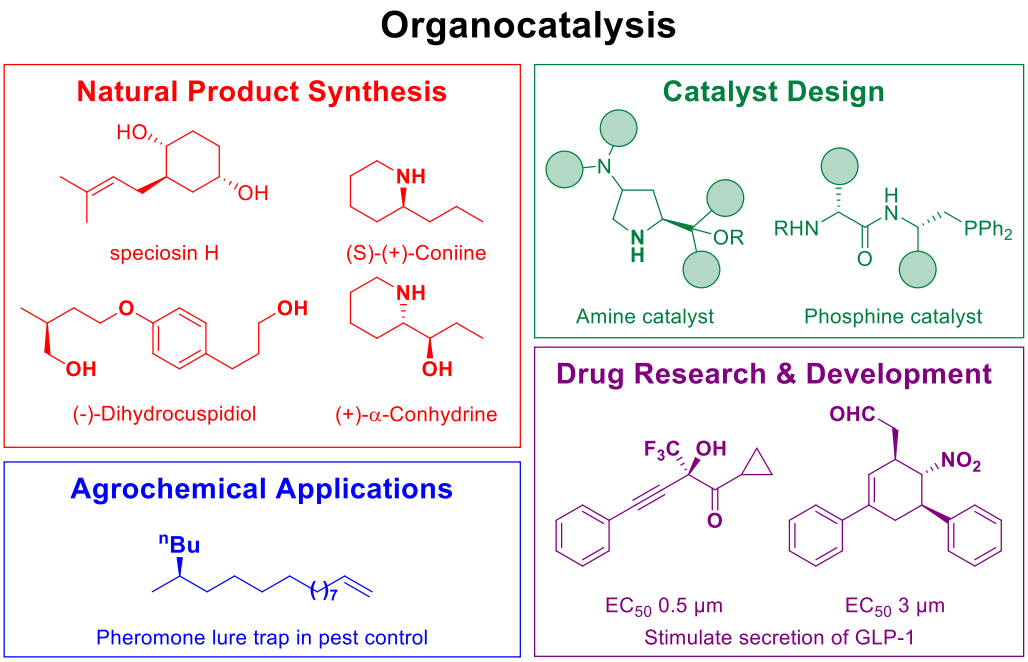
Jose L. Vicario, Luisa Carrillo, Efraím Reyes, Uxue Uria, Rubén Manzano, Raquel Mato, Alesandere Ortega, Estibaliz Diaz, Sandra Rodriguez, Lorena Garcia, Estefanía Capel*
Department of Organic Chemistry II, Faculty of Science and Technology, UPV/EHU.

KEY WORDS: Organocatalysis, Sustainable Chemistry, Green Chemistry, Chiral Drug Synthesis, Biomimetic Processes.

Observing how Mother Nature solves complex problems in an easy way, the human being has been trying to imitate it for many centuries. Thus, the high catalytic efficiency of several enzymes in many natural processes has inspired many researchers to imitate and even improve its action, creating new protein-based biocatalysts, and more recently, using small organic molecules as simple catalysts (organocatalysts).

In asymmetric synthesis, not only should the catalyst accelerate the reaction but it also should be very stereoselective and flexible, in order to allow its use for the synthesis of different target molecules such us natural products or agrochemicals. Additionally, organocatalysts are stable in air, water-compatible most of them commercially available, thus showing a great advantage when employed by pharma-, especially in drug research, due to the fact that the presence of traces of contaminating transition metals is absolutely forbidden by legal regulations.

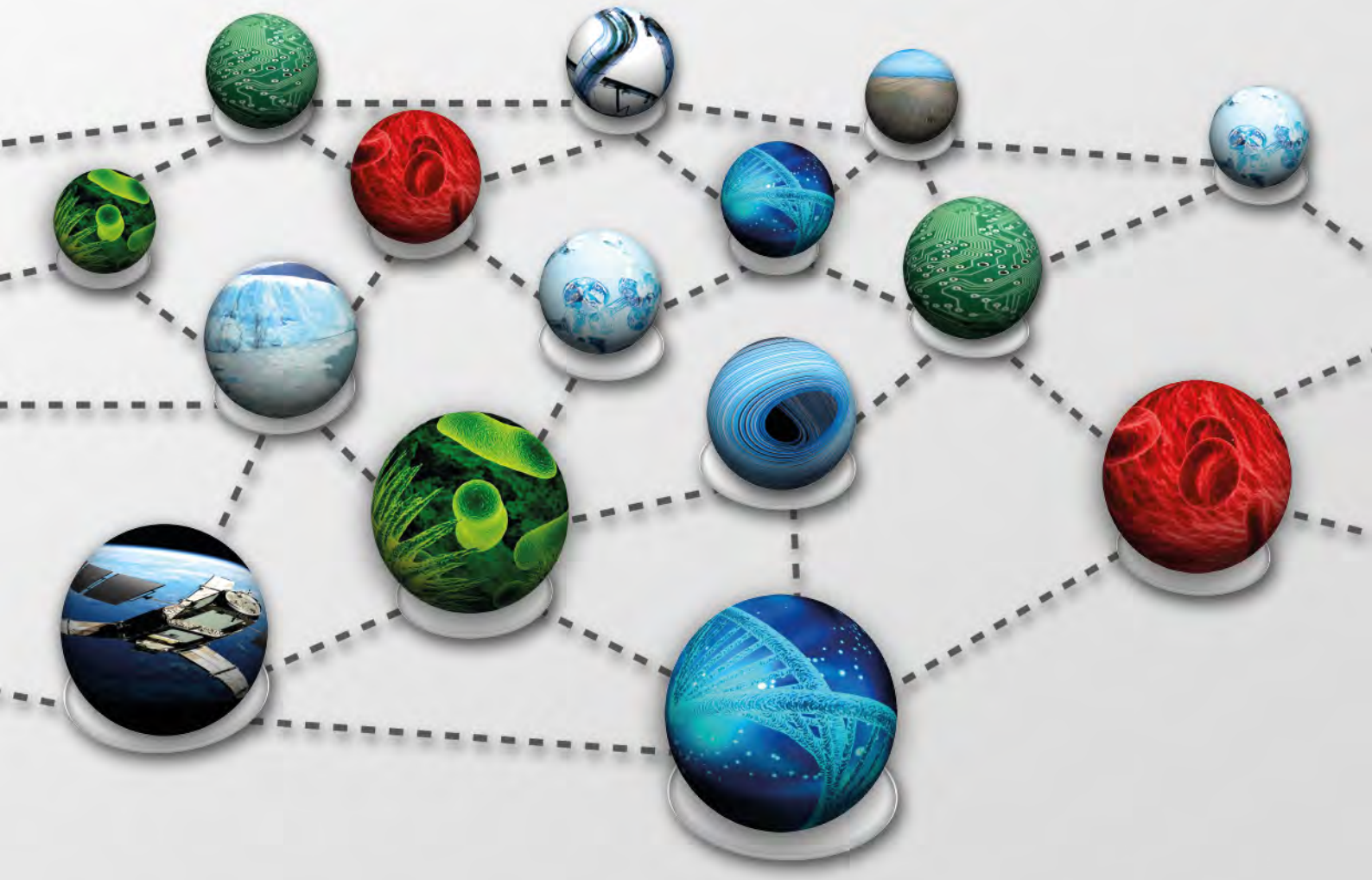
Our research in this field has prompted us to study several organocatalytic methodologies in these research lines and to the design of new catalysts which allow carrying out the reaction in water. These findings, together with the previously described advantages of organocatalysis are in accordance with the principles of Green Chemistry.



Our experience in Asymmetric Synthesis is well known and internationally recognized. Our research group provides laboratory facilities for students in the last year of degree, Master students, PhD. students or post-doctoral researchers. More information can be found in the group web page (http://www.ehu.es/GSA).

INGENIERITZA KIMIKOA

INGENIERÍA QUÍMICA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Enviromental sustainability: technologies for pollutants abatements and power-to-gas CO_2 utilization

A. Aranzabal, J.L. Ayastuy, A. Bermejo, M.J. Cano, Z. Boukha, J.M. Castresana, A. Choya, U. De La Torre, B. De Rivas, M. Gil-Calvo, J.A. González-Marcos, M.P. González-Marcos, J.R. González Velasco, M.A. Gutiérrez-Ortiz, J.I. Gutiérrez-Ortiz, R. López-Fonseca, J.A. Martín, A. Morales-Marín, J.A. Onrubia, B. Pereda-Ayo, A. Quindimil, A. Reynoso, A. Sanz, M. Urrutxua

Goup of Chemical Technologies for Environmental Sustainability, Deptartment of Chemical Engineering, Faculty of Science and Technology, University of The Basque Country, UPV/EHU, Leioa, Bizkaia, Spain

KEY WORDS: environmental catalysis, NSR, SCR, NOx removal, CO_2 methanation, P2G

CATALYTIC TECHNOLOGIES FOR POLLUTANTS ABATEMENT FROM STATIONARY AND MOBILE SOURCES

Mobile sources. TQSA does research on two technologies for NOx removal from diesel engine exhaust gases: NOx storage and reduction (NSR) and selective catalytic reduction (SCR). The NSR technology requires a catalyst combining NOx adsorption sites and metallic sites to enhance oxidation and reduction reactions, what is achieved on a Pt-Ba/Al_2O_3 formulation washcoated over cordierite monolith. On the other hand, the SCR technology feeds continuously a reducing agent (NH_3 or hydrocarbon) which is adsorbed on Cu-zeolite catalyst and subsequently reacts with NOx to selectively form N_2. More recently, we have combined both technologies in two consecutive bed reactors achieving potential zero emission levels of pollutants (CO, HC and NO_x).

Stationary sources. Among the variety of pollutants coming from industrial effluents, we are interested in reduction of methane emissions (energy power plants and natural gas engines), halogenated volatile organic compounds (HVOC in PVC chemical plants, and textile, electronic and metallurgical industries) and dioxins/furanes with NOx (solid wastes incineration plants). Under this frame, TQSA develops:

1. Catalysts for individual pollutant removal, such as chlorinated volatile organic compounds, or methane from its own combustion in small engines.
2. Catalysts for simultaneous elimination of dioxins (PCCD)/furanes(F) together with NOx from municipal waste incineration plants.

POWER-TO-GAS: METHANATION OF CO_2 TO PRODUCE SINTHETIC NATURAL GAS (SNG)

The concept power-to-gas or abbreviated as P2G, is based on the process which is able to produce hydrogen from exceeding electric energy, which is directly introduced into the transport and distribution gas network to be used when demand exists or well is utilized for production of SNG, which is also injected into the mentioned network. Wind, solar or any other renewable energy can be used in the P2G process.

We, at TQSA, are designing catalysts (Ni, Ru) to carry out efficiently the methanation reaction, as well as reactors integrated with heat exchange to allow the capture and valorization of CO_2 generated in industry, by its transformation with renewable H_2 (wind, solar, …) into SGN that can be used again as fuel in the process boilers, e.g. paper manufacturing industries.

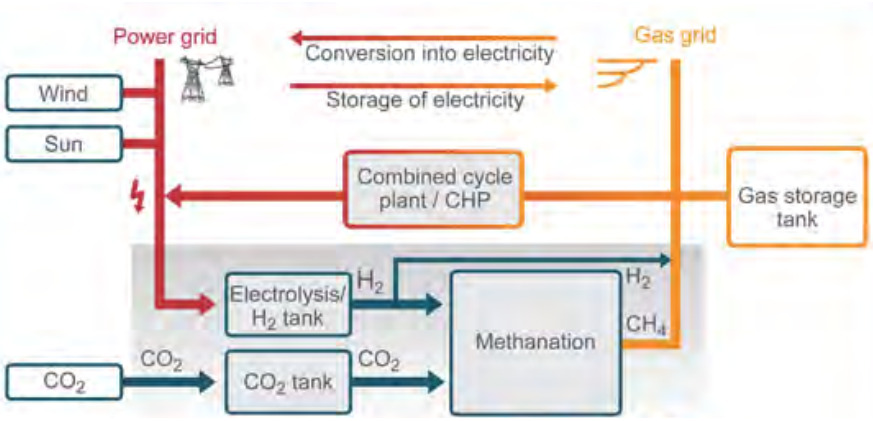


Fig. 1. Schematics of the P2G process.

Challenges in clean and safe energy: technologies for sustainable hydrogen production

J.I. Álvarez, A. Aranzabal, J.L. Ayastuy, A. Bermejo, Z. Boukha, A. Choya, U. De La Torre, B. De Rivas, M. Gil-Calvo, J.A. González-Marcos, M.P. González-Marcos, J.R. González Velasco, M.A. Gutiérrez-Ortiz, J.I. Gutiérrez-Ortiz, U. Iriarte, R. López-Fonseca, J.A. Martín, A. Morales-Marín, J.A. Onrubia, B. Pereda-Ayo, A. Quindimil, A. Reynoso, A. Sanz, M. Urrutxua
Goup of Chemical Technologies for Environmental Sustainability, Deptartment of Chemical Engineering, Faculty of Science and Technology, University of The Basque Country, UPV/EHU, Leioa, Bizkaia, Spain

KEY WORDS: Hydrogen production, SR, APR, biomass, glycerol, CO-PROX, WGS, OWGS.

The increasing economic development in the world has brought an increase in energy consumption, so it is necessary to develop a new energy map where renewable energies would occupy a prominent place to meet the demand and assure the energy supply, protecting the environment. In addition to reducing air pollution and emissions of greenhouse gases, the use of hydrogen as an "energy vector" would reduce the current dependence on fossil fuels, thus promoting the development of fuel cell technology (particularly in the transport sector).

Hydrogen, as new energy vector, will be the main energy supply by means of the fuel cells in the near future. TQSA research group has focused its efforts on the development of catalysts for producing H_2 —rich streams from different types of gas-phase reforming (POX (Partial Oxidation), SR (Steam Reforming), OSR (Oxidative Steam Reforming)— from hydrocarbons of different nature —natural gas (CH_4), petrol (*i*-C_8H1_8), diesel (*n*-$C_{14}H_{30}$)—.

The use of hydrogen, derived from biomass using processes, in the fuel cell technology, allows a net zero emission of CO_2. The production of biodiesel generates an abundant availability of aqueous solition of glycerol. Research efforts to find new application of glycerol as a low cost raw material have introduce the aqueous phase reforming (APR) for converting glycerol into hydrogen. Aqueous streams in the petrochemical industry also contain a large amount of difficult to separate hydrocarbons. The aqueous phase reforming of such streams will allow its valorization through conversion into hydrogen.

Among the catalysts developed for this purpose, NiAl O_4(Al_2O_3), obtained from the nickel aluminate spinel, offers several advantages in reforming processes, such as high catalytic stability and high metal dispersion after reduction at high temperature. These catalysts have been tested in their traditional powder form, but the objective now is to incorporate them in structured metallic wire mesh catalysts, which would allow working at higher space velocity with a minimal pressure drop.

The H_2 produced is then fed to the fuel cell. Since the fuel cell has a low tolerance for CO and its content in the hydrogen stream should be minimized (<1 ppm under stationary conditions and <25 ppm for specific peaks), a prior purification to reduce the content of CO and enrich the H stream is required, first by water gas shift reactions (WGS) and then by CO oxidation (CO-PROX), thus preventing poisoning.

The most viable alternative during the transition to the widespread use of hydrogen in automotive is the on-board production. Therefore, our aim is the *in situ* generation of H_2 and the design of a catalytic converter to perform both the WGS reaction and CO-PROX reaction, i. e. the Oxygen-enhanced WGS (OWGS), in order to purify the hydrogen stream from the hydrocarbon reforming. In this way, the volume of the converter could be reduced, thus making it more viable for its employment in the automotive industry.

Bimetallic Au-Co_3O_4/CeO and Au-CuO/CeO catalysts have been synthesized for this OWGS process, achieving higher conversions than those obtained in the WGS reaction. In order to reduce both the cost and the converter size, the catalysts have been incorporated into monolithic structures, which allow working at higher space velocity, thus getting higher conversions than those obtained with the powder catalysts.

Chemical Engineering in Energy Efficiency and Environment

C. Ferreiro[1], A. Serra[1], J. Pérez-Outeiral[1], A. Menéndez[2], A. de Luis[2], N. Villota[3], J.M. Lomas[3], J.I. Lombraña[1]
[1]Department of Chemical Engineering. University of the Basque Country UPV/EHU. P.O. Box 644. E-48080 Bilbao, Spain;
[2] Department of Chemical Engineering and Environment. University School of Mines and Civil Engineering. University of the Basque Country UPV/EHU. Paseo Rafael Moreno "Pitxitxi", 2. E-48013 Bilbao, Spain;
[3] Department of Environmental and Chemical Engineering. University School of Engineering. Vitoria-Gasteiz. University of the Basque Country UPV/EHU. Nieves Cano, 12. E-01006. Alava, Spain.

KEY WORDS: Advanced oxidation technologies, catalytic ozonation, microwave drying, membrane technologies.

The research group “Chemical Engineering in Energy Efficiency and Environment” conducts its research in the labs of Dept. of Chemical Engineering in the Faculty of Science and Technology. Research work focuses, on the one hand, on the study of different aspects applied to the improvement of the water treatment operations, either by modelling and optimization of operational conditions or through the development of new processes.
Another line of research is dedicated to developing innovative drying processes applied to the food industry and more recently to the probiotic material production. It is remarkable the involvement, in the recent years, in the study and modelling of reaction systems with addition of filtration and membrane technologies applied to wastewater treatment and also to the production of high value-added foods. The excellence of the work carried out is reflected in the recognition of consolidated group A (BOPV 5-12-16) that this research group currently has, and it is integrated into the training units and research (UFI: UFI11/39 UPV/EHU).

Besides the two research lines before mentioned, it should be added recently the research in collaboration with companies and technological centres. A detail of the research lines in which the group works is shown below:
I.-Development of techniques for advanced oxidation (TOAs) for the remediation of contamination of the medium water.
I.a. TOAs in combination with membrane technologies.
I.b. TOAs integrated in multidisciplinary actions for solving the impact of emerging contaminants.
II. Development of efficient drying technologies for the production of dehydrated temperature-sensitive foods.
III- Collaborative projects with enterprise and technology centres.

As projects in the last years, we can mention:

MINI-REACTORES PARA GENERACIÓN DE PRODUCTOS DE ALTO VALOR AÑADIDO. Gobierno Vasco. ELKARTEK17/16.
NUEVOS GASES DIELÉCTRICOS PARA EQUIPOS DE MEDIA TENSIÓN. Gobierno Vasco ELKARTEK17/09
VALORACIÓN DE TECNOLOGÍAS DE OXIDACIÓN AVANZADA PARA LA DESTRUCCIÓN DE CONTAMINANTES EMERGENTES CON ACTIVIDAD DE DISRUPCIÓN ENDOCRINA. Gobierno Vasco, SAI13/249.
APLICACIÓN DE LA TECNOLOGÍA UV/H_2O_2 PARA LA REMEDIACIÓN DE CONTAMINANTES PERSISTENTES EN LA CAPV. Agencia Vasca del Agua, URA12/04.
APLICACIÓN DE NUEVAS TÉCNICAS DE CALENTAMIENTO CON MICROONDAS PARA EL PROCESADO TÉRMICO DE ALIMENTOS CON INGREDIENTES PROBIÓTICOS Y TERMOSENSIBLES. MICINN12/193.

Catalytic processes for obtaining fuels and raw materials

A.T. Aguayo, J.M. Arandes, A. Arandia, A. Ateka, M.J. Azkoiti, J. Bilbao, P. Castaño, T. Cordero-Lanzac, M. Díaz, J. Ereña, N. García-Gómez, A.G. Gayubo, A. Gutiérrez, I. Hita, L. Oar-Arteta, A. Ochoa, R. Palos, A. Remiro, E. Rodríguez, P. Rodríguez-Vega, M. Sánchez-Contador, I. Sierra, J. Valecillos, J. Vela, B. Valle
Department of Chemical Engineering (CPWV Group), University of the Basque Country (UPV/EHU),
P.O. Box 644, 48040, Bilbao, Spain

KEY WORDS: Biorefinery, Waste-refinery, Fuels, Raw materials

The group's work in the Catalytic Processes lines pursues the development of new processes for the sustainable production of fuels and raw materials from non-fossil sources, CO_2, methane and streams of secondary interest in the refinery.

The study of these catalytic processes is part of the Biorefinery and Waste-Refinery R+D+I platforms, and different features are addressed in each process: catalyst design and knowledge of the reaction mechanism, kinetic modelling, proposal and design of new reactors, and simulation and scaling up of the industrial process. These lines are developed in collaboration with the waste valorization lines (of the same group), which study alternative routes and whose derivates (bio-oil, fluids of plastics and tires pyrolysis, syngas) are the raw materials for part of the processes studied. In parallel, progress is made in the methodology of each of these research features. Due to the projection of the recent results in the international scientific and technological community, contributions in the following lines can be highlighted:

Production of hydrogen from Bio-oil. The raw bio-oil is valorized using a two-stage reaction system that allows separating pyrolytic lignin in a primary reactor, easing the reforming in the second (fluidized) reactor. $NiAl_2O_4$ spinel and $Rh/CeO_2/ZrO_2$ catalysts are proposed due to their stability and regenerability. A mechanism that describes the evolution of the individual reaction stages (reforming, water gas shift, thermal-cracking) and a kinetic model that rationally quantifies products production and distribution and their evolution with time have been proposed.

Direct synthesis of dimethyl ether (DME) from CO_2. The most recent results of the group in this field are framed in: i) the study of the thermodynamics, quantifying the advantages of DME synthesis to valorize CO_2 with respect to methanol synthesis; ii) the proposal of original, selective and stable CuO-ZnO-MnO/SAPO-18 and CuO-ZnO-ZrO_2/SAPO-18 hybrid catalysts,; iii) the proposal of core-shell catalysts (CuO-ZnO-ZrO_2/SAPO-11) to enhance the advantages of the bifunctional catalyst; iv) the kinetic modeling of the process with the new catalysts; v) the experimental implantation of an original membrane reactor to take advantage of the thermodynamic benefit of removing the water from the reaction medium.

Cracking, hydrodeoxygenation and hydrocracking of derivates of biomass and wastes of the consumer society. The experimentation under the conditions used in the industrial cracking (FCC) and hydroprocessing units has allowed to explore the capabilities of these units for the valorization of plastics dissolved in refinery streams, of bio-oil (liquid from biomass pyrolysis), and liquid of tires pyrolysis, following in all cases the strategy of co-feeding these new streams together with the usual refinery streams. Likewise, new Pt-Pd/C catalysts have been proposed for adapting bio-oil (by means of hydrodeoxigenation) as fuel or raw material for the units of the current petrochemical industry. Part of this research has been carried out with the collaboration of Petronor S.A.

Sustainable olefins production. Among the routes studied by the group for the production of olefins: i) the conversion of DME and the catalytic cracking of naphtha offer better (technological and environmental) perspectives than the current routes and the recent progress lies in improving the catalysts (HZSM-5 zeolite, SAPOs, hybrids and core-shell structures), kinetic modeling and design of new reactors with catalyst circulation. The results of methane conversion (via chloromethane), which has been proven to take place through mechanisms and with a kinetic scheme similar to that of methanol conversion (MTO process), also offer good prospects. The study of the reaction schemes of these processes and their kinetic modeling, is aimed at the intensification of the selective production of propylene.

Thermochemical processes for waste valorization

A. Atxutegi, R. Aguado. H. Altzibar, J. Alvarez, S. Alvarez, M. Amutio, M.Arabiourrutia, A. Arregi, M. Artetxe, I. Barbarias, J. Bilbao, M. Cortazar, G. Elordi, I. Estiati, E. Fernández, I. García, J. González, J. Izquierdo, G. Lopez, M. Olazar, A. Pablos, M.J. San José, L. Santamaría, M. Tellabide, J. Vegas
Department of Chemical Engineering (CPWV Group), University of the Basque Country (UPV/EHU), P.O. Box 644, 48040, Bilbao, Spain

KEY WORDS: Biorefinery, Waste-refinery, Fuels, Raw materials

The group's work in the waste valorization lines pursues the development of new thermochemical processes (drying, combustion, pyrolysis, gasification, pyrolysis-reforming) for the sustainable production of fuels and raw materials from renewable sources (lignocellulosic biomass) and wastes from the consumer society (plastics, tires, sewage sludge).

The study of these processes is part of the Biorefinery and Waste-Refinery R+D+I platforms, and its implementation requires the design and use of original process equipment. Many of the studied processes use solid-gas contact in spouted bed pilot plant scale original equipments. Recent progress in these lines can be grouped into:

Design of new gas-solid contact equipment. Among the improvements made in the design of the conical spouted bed, with the aim of increasing the stability and establishing a precise gas and solid circulation regime, adequate to the characteristics of different processes and solids (fine, wet), devices for the confinement of the areas of the spout and the source have been proposed. The fluid dynamic studies carried out in pilot plants have allowed establishing optimal dimensions of the devices and establishing fluid dynamic correlations for the design of the equipment. In addition, remarkable improvements are made in the development of original mathematical models for the simulation of gas and solid circulation.

Pyrolysis. The capacity of the conical spouted bed for the pyrolysis of biomass has been extended to a wide variety of these materials, having a great relevance the results obtained with rice husk, due to the characteristics of the bio-oil and the valorization perspectives of the solid waste, obtaining products of high added value. Likewise, the pyrolysis of some plastics (polyolefins, polystyrene, polymetalmethacrylate) allows the recovery of the monomers.

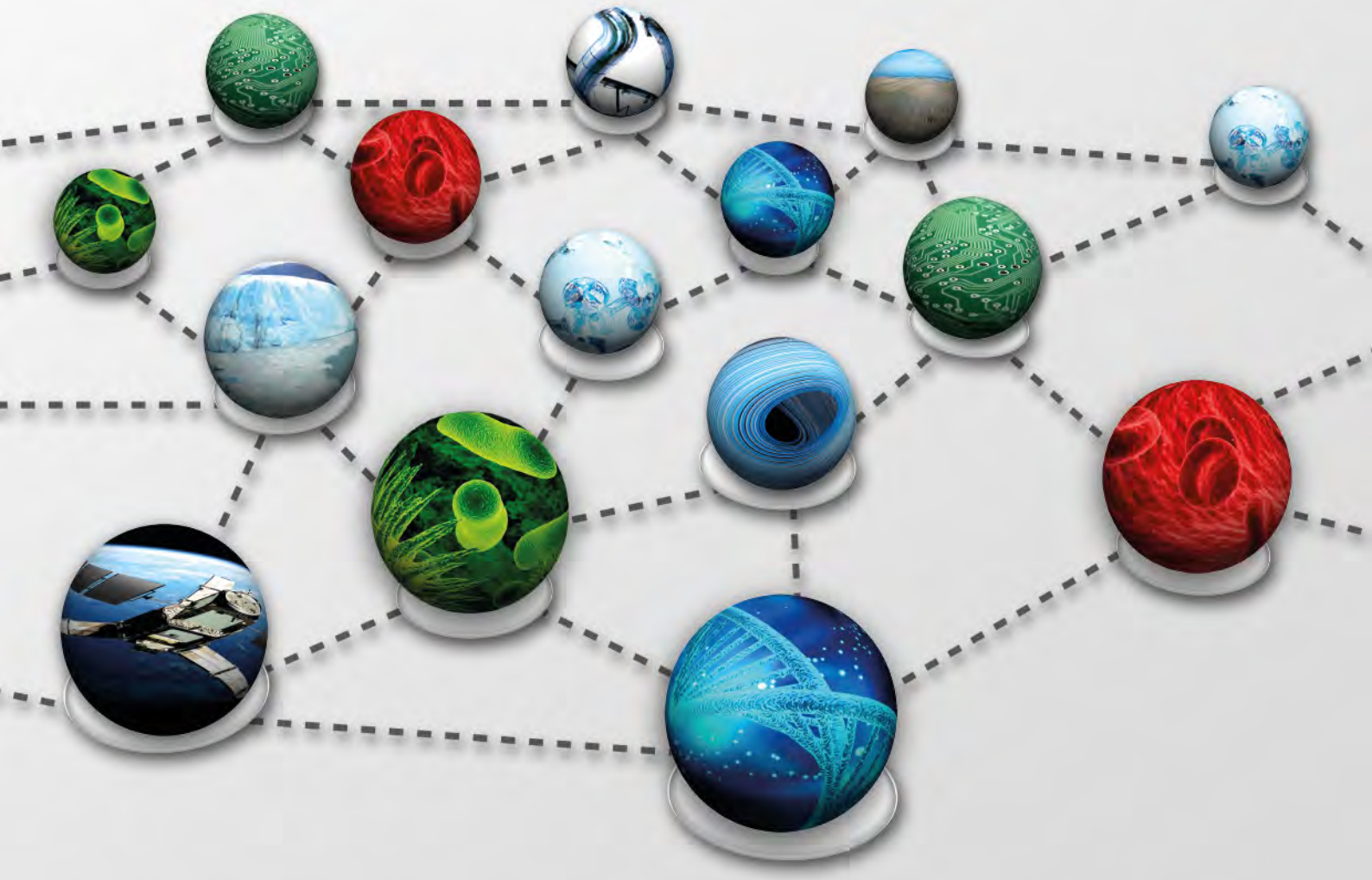
Gasification. The incorporation of the technological improvements of the conical spouted bed (configuration of the spout and the source) has allowed to achieve relevant advantages in the gasification of biomass, by controlling the residence time of the gas, minimizing the formation of tar (problem that conditions the viability of the gasification). This tar formation is almost avoided incorporating primary catalysts in the reactor.

System in two stages (pyrolysis/reforming). The on line pyrolysis/reforming technology is ideal for the production of H_2 from biomass and/or plastics, which are pyrolized in an ideal system to maximize the yield of volatiles (in conical spouted bed), and these volatiles are reformed online in a fluidized bed catalytic reactor. The studies have been carried out with different residues and mixtures, and include catalyst screening (commercial and prepared in the laboratory), the knowledge of reaction and deactivation mechanisms, and the kinetic modelling and simulation of the processes. The development of technology arouses great industrial interest, since it offers good prospects for its large-scale implementation.

In addition to international collaboration in research, the applied approach facilitates the collaboration with the industry, with the spin-off NOVATTIA S.L. as an active partner for the development of some equipment on a larger scale. It is also noteworthy that the work in these research lines is complemented by the other lines of the group, focused on catalytic processes, since they study other routes for the same objectives and develop catalysts, characterization techniques and kinetic models, which can be used in the previously described lines.

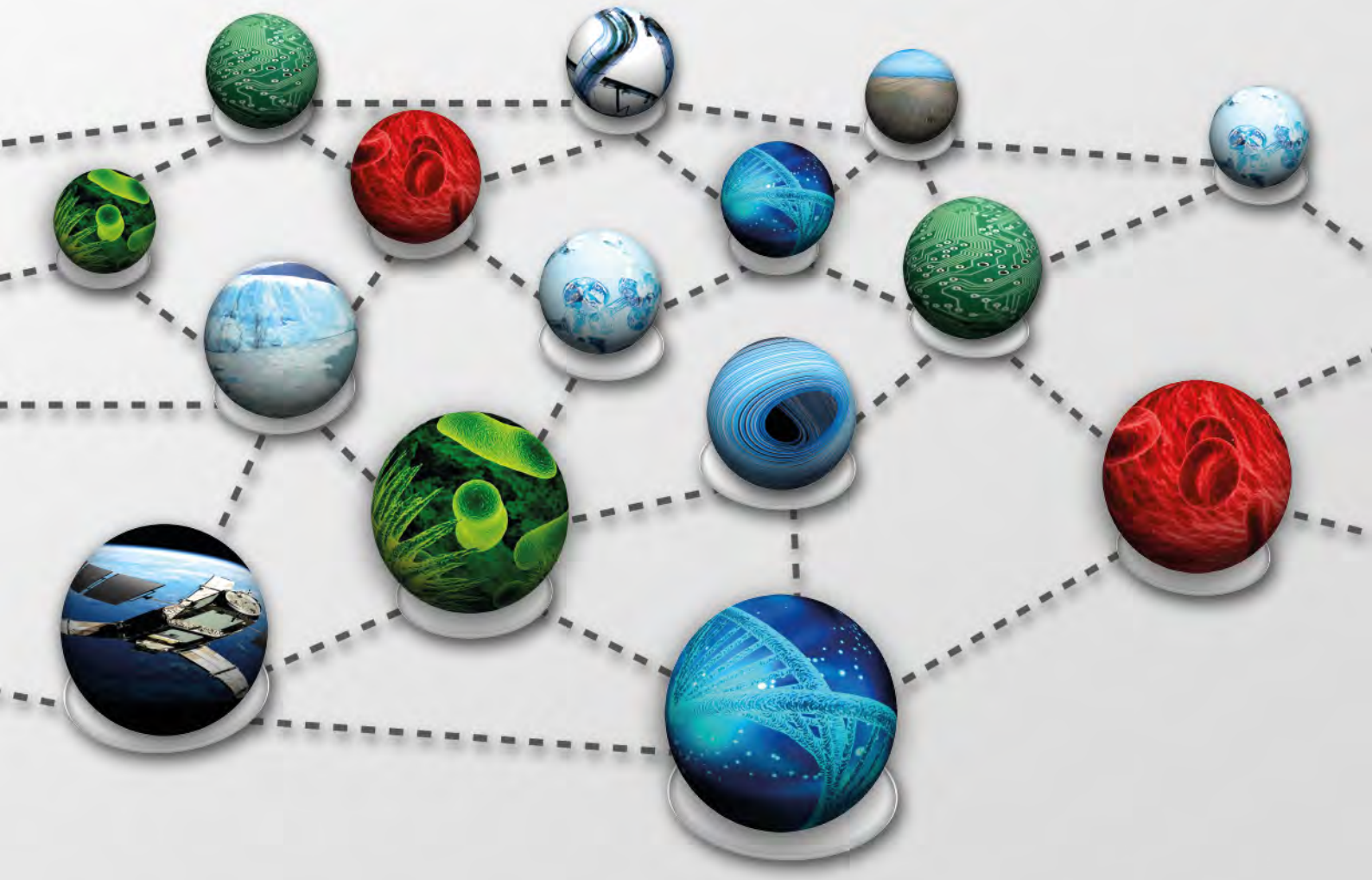
Beste Ikergune Batzuk

Otros Centros de Investigación



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

INSTITUTO BIOFISIKA INSTITUTOA



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

From atomic details of calcium signalling to human brain disorders

Janire Urrutia[1], Arantza Muguruza[1], Eider Nuñez[1], Covadonga Malo[1], Alejandra Aguado[1] and Alvaro Villarroel[1]
[1]Instituto Biofisika Institutoa. UPV/EHU-CSIC. Leioa, Bizkaia.

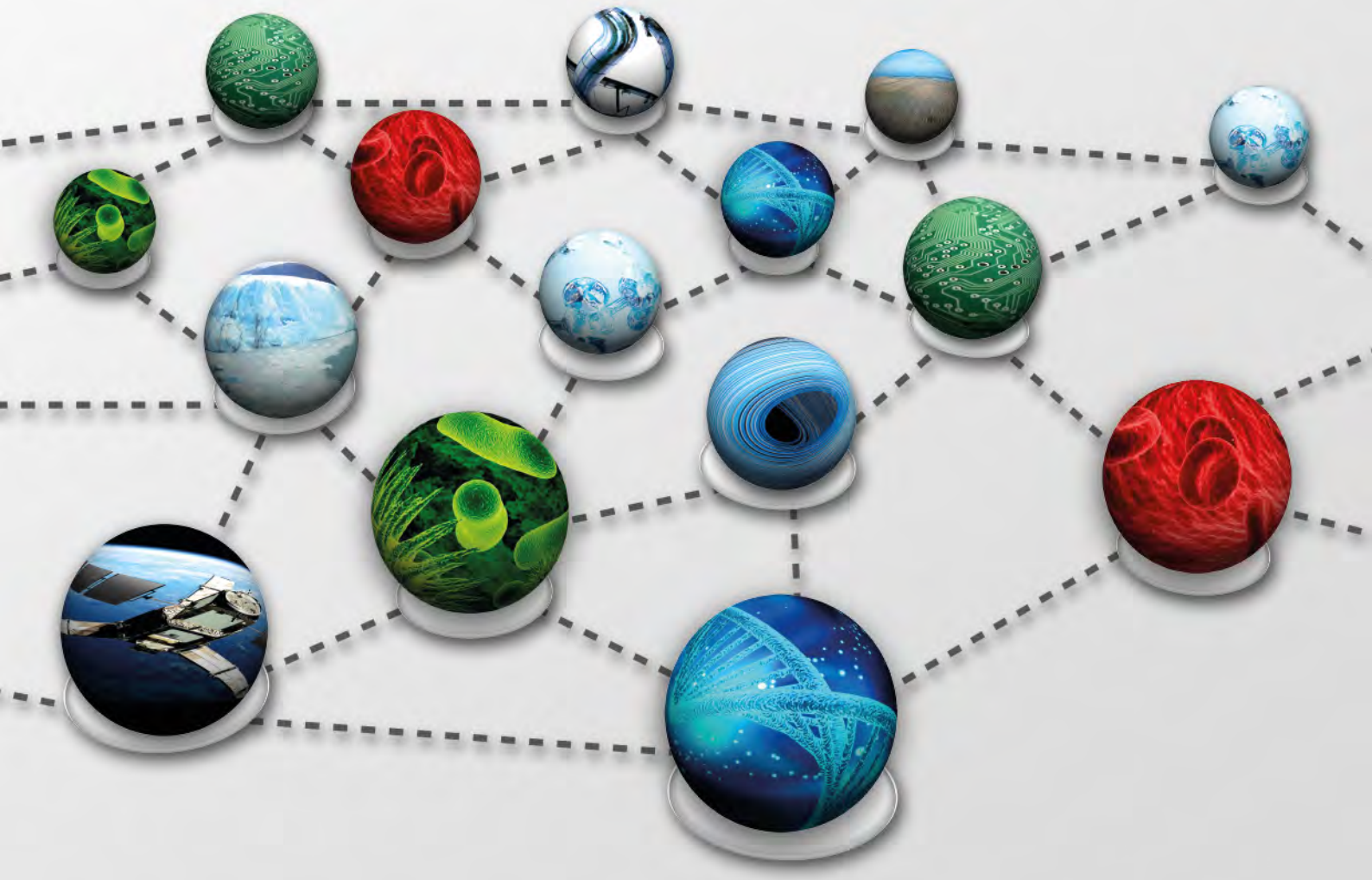
KEY WORDS: Kv7.2, CaM, Ca^{2+}, mutations, encephalopathy.

The KCNQ2 gene encodes the Kv7.2 protein, which is one of the channels that control electrical signaling in the brain. The M-current generated by this channel can be modulated by neurotransmitters and mutations. A small protein that acts as a calcium sensor, named Calmodulin (CaM), controls Kv7.2 channel trafficking to the membrane, gating and regulation. In our laboratory, we are interested on the next two key points for understanding Kv7.2 function:

1. We want to understand from basic principles how the atomic movements within a protein lead to higher functions, such as neuronal communication, learning and memory. As such, knowledge of the **structure-function relationship of the Kv7.2** is pivotal for understanding how a chemical signal affects the electrical signals of neurons. We have discovered that the interaction CaM plays a key role in this signal transduction event, therefore we have solved the atomic structure and we are now deciphering how calcium regulates function.
2. Mutations in this gene cause Early Infantile Epileptic Encephalopathy-7 (EIEE7) and Benign Familial Neonatal Seizures-1 (BFNS1). Patients show delayed neurologic development years after the remission of seizures. We study how **mutations in this gene affect the protein function to understand how these atomic movements within the protein lead to neuronal disease**.

Different techniques are use in our laboratory to carry out our investigation. In order to obtain the required constructions for expression in both bacterial cells and HEK293T cell line, genetic engineering techniques are used. Once we have the constructs, we analyze them by *in vitro* Förster Resonance Energy Transfer (FRET), *in cellulo* FRET, whole-cell patch-clamp to see the channels in action, western blotting and immunoprecipitation techniques.

CIC ENERGIGUNE



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

Solid polymer electrolytes for safe and high energy density lithium batteries

Xabier Judez, Maria Martinez-Ibañez, Eduardo Sánchez-Díez, Ismael Gracia, Heng Zhang, Gebrekidan Gebresilassie Eshetu, Chunmei Li, Itziar Aldalur, Uxue Oteo, Devaraj Shanmukaraj, Lide M. Martinez-Rodriguez, Michel Armand
CIC Energigune. Parque Tecnológico de Álava, Albert Einstein 48, 01510 Miñano, Álava, Spain

KEY WORDS: Lithium batteries, Solid polymer electrolytes, Lithium-sulfur batteries.

As a result of the growing demand in energy and the exhaustion of conventional sources, electrochemical energy storage has key role when trying to overcome this challenge. In recent years, classical Li-ion batteries (LIB) have experienced a significant development and have become components in most portable electronic devices. Despite those advances, the energy density of the state-of-art cannot satisfy the actual practical requirements. Moreover, the potential security risks such as volatilization, flammability and explosion, intrinsic to the use of non-aqueous liquid electrolytes have to be overcome.

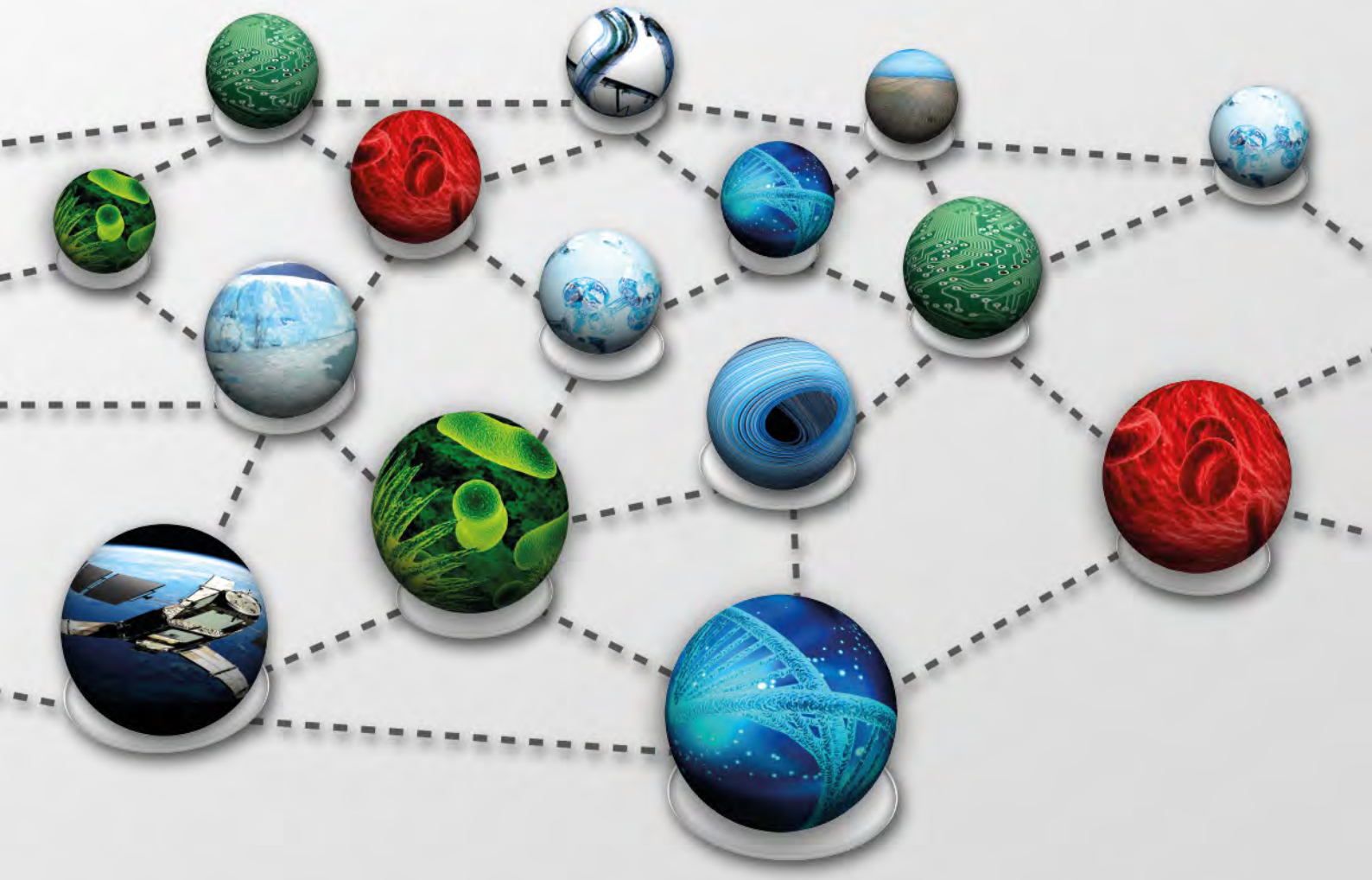
Solid polymer electrolytes (SPEs) offer a perfect solution to these safety concerns whilst have the capacity to inhibit difficulties associated with the use of a lithium metal anode, e.g. dendrite growth. In addition to their outstanding thermal and electrochemical stability, SPEs offer excellent flexibility and low cost in design. Having attracted the interest of both academia and industry, their application in a lithium metal battery (LMB) for an electric car, Autolib®, in France and USA[1] is a clear prove of success of this new technology and the goals that it can fulfill. In addition, the low density of SPEs, compared to other solid electrolyte like inorganic-ceramic materials, allows a high gravimetric energy density to be readily achieved.[2]

This strategy has been also successfully applied to an emerging field as it is the case of lithium-sulfur (Li-S) batteries of particular interest in view of their low-cost and high gravimetric energy density. SPEs seem to be key in the suppression of undesired diffusion of reaction intermediates in addition to the already mentioned excellent compatibility with Li metal anode, which have restricted the deployment of Li-S batteries into commercial market.[3] An overview of recent results enlisting highly conductive SPEs and highly performing SPE-based Li-S batteries will be presented.[4,5]

References

[1] H. Zhang, C. Li, M. Piszcz, E. Coya, T. Rojo, L. M. Rodriguez-Martinez, M. Armand, Z. Zhou, Chem. Soc. Rev., 46 (2017) 797–815.
[2] C. Li, H. Zhang, L. Otaegui, G. Singh, M. Armand, L. M. Rodriguez-Martinez, J. Power Sources, 326 (2016) 1–5.
[3] X. Judez, H. Zhang, C. Li, G. G. Eshetu, J. A. González-Marcos, M. Armand, L. M. Rodriguez-Martinez, J. Electrochem. Soc., 165 (2018) A6008–A6016.
[4] X. Judez, H. Zhang, C. Li, G. G. Eshetu, Y. Zhang, J. A. González-Marcos, M. Armand, L. M. Rodriguez-Martinez, J. Phys. Chem. Lett., 8 (2017) 3473–3477.
[5] G. G. Eshetu, X. Judez, C. Li, O. Bondarchuk, L. M. Rodriguez-Martinez, H. Zhang, M. Armand, Angew. Chem., 129 (2017) 1–6.

SGIKER



Diziplina Anitzeko Sareak Ehunduz
Tejiendo Redes Multidisciplinares

The SGIker Platforms aligned with the strategic lines of the Horizon 2020 Program

Advanced Research Facilities of University of the Basque Country (UPV/EHU) (SGIker)

KEY WORDS: SGIker, Horizon 2020 Program, PCTI Euskadi 2020

The Platforms of the Advanced Research Facilities, SGIker, have been developing since 2004 an essential support to the investigation in the areas of Advanced Manufacturing, Energy and Sustainability and Biosciences and Health, considered all of them as strategic lines in the European Horizon 2020 Program, in Science, Technology and Innovation Plan Euskadi 2020 and world research, inside and outside the UPV/EHU.
A highly qualified staff and infrastructure, present in the three campuses of the UPV / EHU, accompany the research staff in all phases of knowledge generation. As a result of this team work, an analysis of the publications generated by the users of the SGIker Platforms reveals the multidisciplinary relationship of the works, as well as the pre-eminence of those topics that most concern society.

In a graphic view it will be shown the existence of multiple intangible research networks in which the different knowledge and techniques necessary to face the challenges of current Science are crossed.