

2021



**ikerbasque** Basque Foundation for Science





# ANNUAL REPORT 2021



# AN **EXCELLENT** YEAR

SENENTXU LANCEROS-MENDEZ Ikerbasque Professor / Scientific Director

Science and technology have been evidenced this year as the driving force for hope around the world in the pandemic situation we are still experiencing

Science and technology are also the driving force of BCMaterials, which annual results are presented in this report.

2021 has been and excellent but also a quite special year to stablish BCMaterials as a leading research center for next generation materials development, an increasing demand from society and at the core of the on-going transformations related to sustainable development and energy transition, digitalization of society and novel and more efficient health solutions.

It has been an excellent year in terms of scientific discoveries and applications, research outputs and increasing figures of merit, as indicated by the growing number publications, impact, funded projects, works with industry and technology transfer, national and international collaborations.

It has been an excellent year for the incorporation of researchers and administrative colleagues, for the increasing number of graduate, master and PhD students incorporated and/or obtaining degree in collaboration with BCMaterials.

It has been also an excellent year based on the consolidation of our facilities, with the full occupation of the space and the opening of laboratories in all areas of research of BCMaterials: Energy, Environment, Digitalization and Advanced Technologies and Biomedicine and Biotechnology.

This increasing activity, results and performance have been achieved by the dedication scientist, and our commitment to perform all those and compromise of the BCMaterials community: researchers, administration, associates from the UPV/EHU, and International Advisory Committee, together with the continuous support from the Basque Government, Ikerbasque and the UPV/ EHU. Further, this activity also represents the trust



and confidence from all our collaboration partners, all over the globe.

It has been a special year, on the other hand, as it represents the end of an important phase in the development and consolidation of BCMaterials. The strategic program 2018-2021 came to an end, with the satisfaction to have fulfilled our compromises, leading BCMaterials to the excellence.

It has been a special year because the completion of a specific phase leads to the reflection about BCMaterials: to what it was, to what it is... to what it could have been... to what it still can become...

2022 represents the beginning of a new strategic program full of possibilities and opportunities. The

### It is never too late to be what you might have been.

George Eliot (Mary Ann Evans, 1819-1880)

new strategy, the reformulation of the research lines, the emerging of new research groups, the full implementation of the new facilities and the new research lines will set the guidelines of a path still to be travelled, and empty picture still to be drawn, which beauty, impact and fulfilment just depends on us: on keeping the focus on scientific excellence, on convincingly addressing society challenges, on sharing our passion for science and technology with society, on supporting the next generation of actions with solidarity, compromise, honesty and dedication.

Next generation materials should definitely contribute to a better life; next generation materials must definitely have the seal of this generation BCMaterials!

# CONTENTS

8

10

12

14

18

BCMATERIALS IN NUMBERS BCMATERIALS COMMUNITY **GENEDER EQUIALITY AT BCMATERIALS ADVISORY COMMITTEE** CENTER

**RESEARCH LINES AND AREAS** 

()) RESEARCH ACTIVITY

**N1** 

THE

OUTPUT SAMPLES	20
JOURNAL COVERS	74
SPECIAL ACTION: IKUR ESTRATEGY	76
BOOKS, REVIEWS & PAPERS	78
PRIZES AND ACKNOWLEDGMENTS	80
FOUNDING SOURCES &	
RESEARCH PROJECTS	82
TRAINING ACTIVITIES	94
INNOVATION ACTION:	
BIOENCE SPIN-OFF	98

OUR SERVICES

OUR LABS	102
MATERIAL SYNTHESIS	104
MATERIAL PROCESING	106
CHARACTERIZATION	108
PROTOTYPING	110

04	AT BCMATERIALS	114
04	OUT BCMATERIALS	120
REACH	SCIENCE FOR SOCIETY	122
IVITIES	WOMEN IN SCIENCE DAY	126
	MEDIA IMPACT	128

OUT

ACT

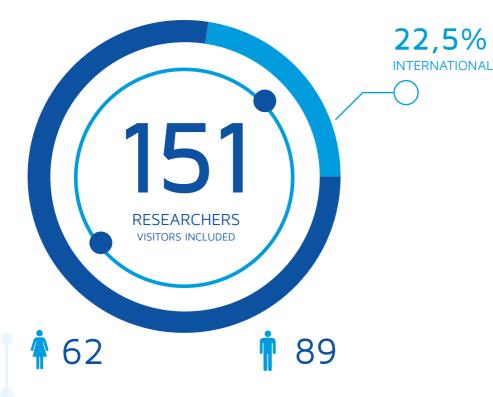
# OOA THE HE HE

BCMaterials, Basque Center on Materials, Applications and Nanostructures, is an autonomous research center launched in June 2012 by Ikerbasque, the Basque Foundation for Science and the University of the Basque Country (UPV/EHU) as a research center for Materials, Applications and Nanostructures. The center is included in the BERC's (Basque Excellence Research Centers) network and its mission is to generate knowledge on next generation materials, turning this knowledge into (multi)functional solutions and devices for the benefit of society.

AFORMA TEKNOLOGIKOA

# **BCMATERIALS IN NUMBERS**

**RESEARCH COMMUNITY** 





RESEARCH OUTPUT

226 50 PUBLICATIONS H INDEX 2

BOOKS

4693 CITATIONS

ISI



83%

**O1 PUBLICATIONS** 

PROJECTS AND FUNDING

3.015.000 € ONGOING FUNDING **PROJECTS** TRAINING

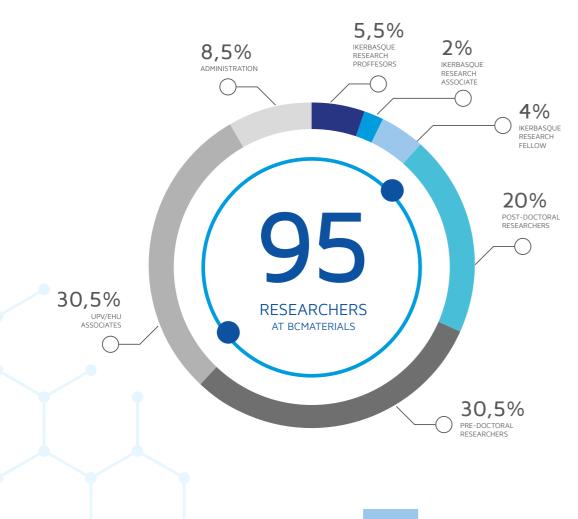
9 PHD THESIS DEFENDED

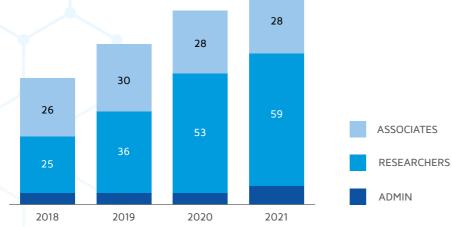
18 MASTER THESIS

**UNDERGRADUTE** PROJECTS



# **BCMATERIALS** COMMUNITY





88888	China
XXXXX	Colom
RESEARCH STAFF	Costa I
	Czech Republ
	Egypt
	France
	Germa
	India
	Italy
	Portug
	Casia

	Colombia	2
	Costa Rica	1
	Czech Republic	1
	Egypt	2
	France	1
	Germany	2
	India	4
	Italy	1
	Portugal	2
≻	Spain	36
LIT LIT	Sri Lanka	1
NATIONALITY	United Kingdom	2
NA	Ukraine	2

2

le		Chile	1
		China	3
		Colombia	2
VISITORS		ltəly	1
64		Poland	1
		Portugal	1
	10	Spain	53
$\sim$	NAT	Turkey	1



# **GENDER** EQUALITY

Science and technology, truly universal, noble and needed human endeavours, can just achieve their full potential in an environment where excellence and equality are unavoidably placed together. BCMaterials continues its effort and commitment with gender equality to achieve materials for a better life ... in a better place.

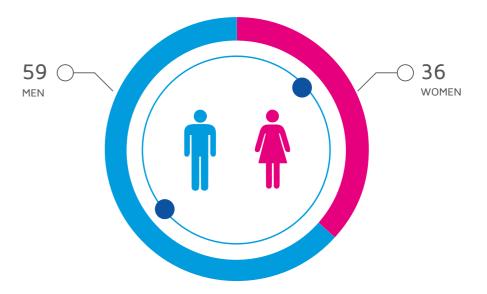
## **EQUALITY PLAN** 2021-2025

BCMaterials, in its commitment to guarantee gender equality in the institution, launched the '2021-2025 Equality Plan'. The Plan provides for specific measures in areas such as personnel selection and hiring processes, training in gender equality and work and family reconciliation..... Each action has compliance indicators that will allow its evaluation in order to comply with the provisions of the Law of Effective Equality between Men and Women.

#### | GOALS

- Ensure compliance with effective gender equality.
- Incorporate equality in the Center's strategy.
- Raise awareness of equality among company personnel.
- Guarantee the principle of equal pay.
- Facilitate the reconciliation of personal, family and work life of the people who make up the company's staff.
- Prevent sexual and gender-based harassment in the workplace.

#### **GENDER** DISTRIBUTION AT BCMATERIALS



# ADVISORY COMMITEE

The International Advisory Committee is made up of internationally recognized experts in the different strategic areas of the center. It is a body in charge of monitoring and supporting the progress of the center, helping to improve its competitiveness to position BCMaterials as a reference center worldwide.

## MEMBERS





#### PROF. MARIA VALLET- REGÍ

Leader of the Smart Biomaterials Research Group Group leader of the Biomedical Research Networking Centre in Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), and of the Research Institute of the Hospital 12 de Octubre, Madrid. Spain

Dept. of Chemistry in Pharmaceutical Sciences Faculty of Pharmacy, Universidad Complutense Madrid (UCM)



#### PROF. MARIA VALLET- REGÍ

Director ARC Centre of Excellence for Electromaterials Science (ACES) Director ANFF (Materials Node) Director Translational Research Initiative for Cellular Engineering and Printing (TRICEP)



#### PROF. CAROLINE A. ROSS

Associate Head of the Department of Materials Science and Engineering Toyota Professor of Materials Science and Engineering Massachusetts Institute of Technology (MIT), USA

PROF. OMAR M. YAGHI

of California, Berkeley

BASE

Co-Director: Kavli Energy

James and Neeltje Tretter Chair Professor of Chemistry University

NanoSciences Institute at Berkeley

California Research Alliance by



#### PROF. SABETH VERPOORTE

Professor of microfluidics and miniaturized "lab-on-a-chip" systems Faculty of Science and Engineering University of Groningen, Netherlands



#### PROF. PHIL WITHERS FRS FRENG

Regius Professor of Materials at the University of Manchester, UK Chief Scientist of the Henry Royce Institute RESEARCH ACTIONS

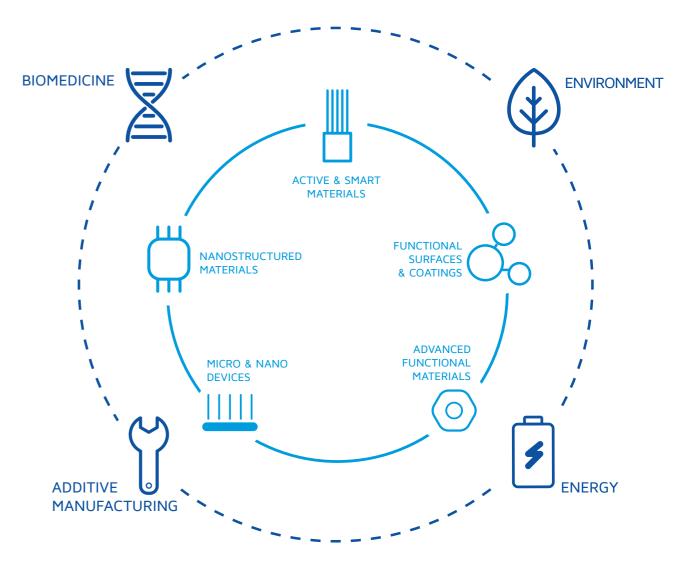
BCMaterials organizes its activities into Research lines and Research areas. Research lines are designed to generate knowledge in the new generation of smart, active and multifunctional materials, to achieve excellence in the next generation of materials, to discover materials and effects and to transfer this knowledge to society. Research areas are designed to take advantage of the generated knowledge in advanced materials and to apply them to tackle the most relevant challenges of modern society, ranging from environmental prevention, monitoring and remediation, energy generation and storage, biomedicine and biotechnology as well as to provide the advanced materials required by the digitalization strategies.

BATIATE

0 --- 0 95 --- 0

# RESEARCH LINES & AREAS

Melt Spinner SC



## AREAS

MATERIALS 2

Research areas are designed to take advantage to the generated knowledge in advanced materials and to apply them to tackle the most relevant challenges of modern society, ranging from environmental prevention, monitoring and remediation, energy generation and storage, biomedicine and biotechnology as well as to provide the advanced materials required by the digitalization strategies.

## LINES

Research lines are designed to generate knowledge in the new generation of smart, active and multifunctional materials, to achieve excellence in the next generation of materials, to discover materials and effects and to transfer this knowledge to society. Within the research áreas, one or more of theses research lines work together in order to give answer to specific technological and society challenges.

BCMATERIALS | ANNUAL REPORT 2021



# RESEARCH AREA 1 BIOMEDICINE

Related to the aging of population and the strong needs on early detection of illnesses, advanced biomedical approaches are definitely needed. Advanced multifunctional materials, advanced manufacturing and nanoscience and nanotechnology are providing new tools in order to tackle those important challenges. In this context, BCMaterials is focusing, among others, on the development of materials and new approaches for nanoparticle based biomedicine, from hyperthermia to point of care devices, as well as on the development of active scaffolds and microenvironments for tissue engineering.

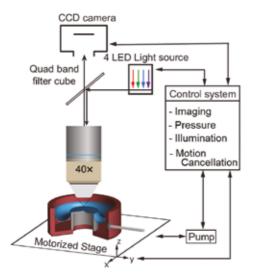
## FOCUS ON TIME: DYNAMIC IMAGING REVEALS STRETCH-DEPENDENT CELL RELAXATION AND NUCLEAR DEFORMATION

Aron N Horvath, Andreas A Ziegler, Stephan Gerhard, Claude N Holenstein, Benjamin Beyeler, Jess G Snedeker and Unai Silvan. Biophysical Journal 120(5), pp. 764-772.

Among the stimuli to which cells are exposed in vivo, tensile deformations have been shown to trigger specific cellular responses in musculoskeletal, cardiovascular, and stromal tissues. However, the early response of cells to sustained substrate-based stretching remains elusive due to the short time span in which it occurs. Here, we present a live tensile force system to measure the tensile properties of cells immediately after mechanical deformation of the surface to which they adhere, and describe cell relaxation and force propagation into the nuclear compartment.

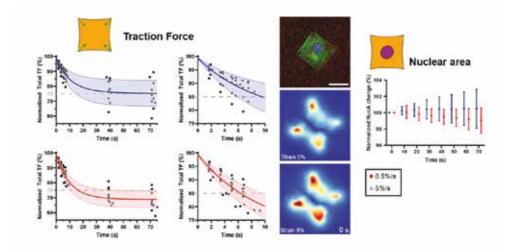
Mechanical coupling between cells and their microenvironment influences tissue homeostasis, with mechanical cues being central for the normal function of tissues. In this context, tissue strain and the derived signalling have been linked to cellular processes such as cell differentiation, immune response, and cancer progression, among others. At the cellular level, tensile deformations are known to drive focal adhesion reinforcement and cytoskeletal remodelling and to cause changes in

traction force generation and in nuclear architecture and function. It has also been shown that although some of these events occur over long periods of time, the initial response is triggered shortly after the application of mechanical stimulation. To elucidate the early response of cells to substrate deformations, we have developed a dynamic tensile force microscopy method that enables subsecond temporal resolution imaging of transient cellular events. The system uses a novel tracking



#### Fig 1 Schematic illustration of the tracking microscope, which consists of a wide

which consists of a widefield fluorescence microscope equipped with a motorized stage, a four-channel LED light source, and a pressurecontrolled, vacuum-actuated equibiaxial stretching device.



approach with minimal computational requirements to compensate in real time for the strain-induced motion of the substrate. Using this tool, we have characterized the transient subcellular forces and nuclear deformations of single cells immediately after the application of equibiaxial stretch and described significant differences in cell relaxation dynamics and intracellular force transmission to the nuclear compartment in cells stretched at different strain rates. Specifically, we observed a faster and more pronounced decay in the force generated by cells exposed to faster strain rates. Cells stretched at 5%/s relaxed their contractility by 15% during the first 6 seconds and by an additional 10% within 16 seconds, compared with those stretched at 0.5%/s, in which the same relaxation was reached after 10 and 70 seconds, respectively. Regarding the nuclear compartment, in cells stretched at slow speed, the nucleus invariably remained flat, whereas in cells stretched at a higher strain rate, the nuclei rounded up immediately after stimulation and continued increasing their height over the next minute.

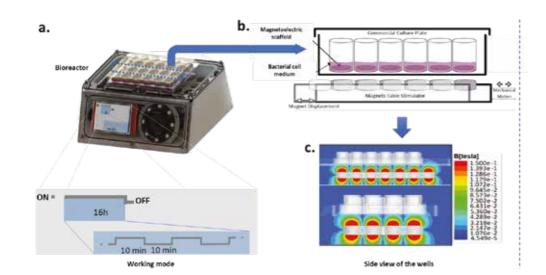
#### Fig 2

Quantification of single cell relaxation after substrate deformation (red 0.5% deformation per second, blue 5% deformation per second) (left panels). Example of a fibroblast adhering to a micropattern (red, fluorescently labeled microspheres; green, actin network; blue, nucleus), and heatmaps of cell tractions before (0% strain) and immediately after the mechanical perturbation (5% strain) (middle panels). Quantification of the nuclear deformation after stretching (right panel).



## MAGNETOELECTRIC POLYMER-BASED NANOCOMPOSITES WITH MAGNETICALLY CONTROLLED ANTIMICROBIAL ACTIVITY

Margarida M. Fernandes, Pedro Martins, Daniela M. Correia, Estela O. Carvalho, Miguel Gama, Manuel Vazquez, Cristina Bran, Senentxu Lanceros-Mendez. ACS Applied Bio Materials, 4(1), pp. 559-570.

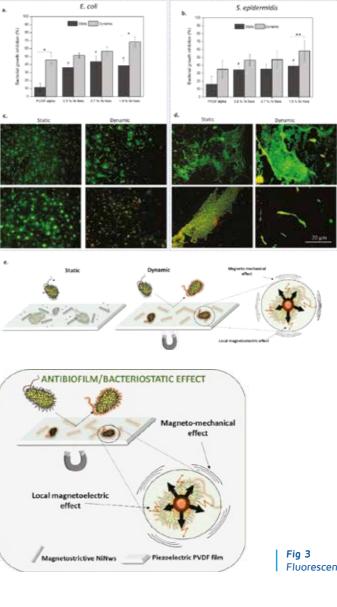


#### Fig 1

Schematic representation of the (a.) magnetic bioreactor used for the bacterial assays and the stimulation profile applied by the bioreactor: the samples were subjected to a magnetic field variation for 16h, which were divided into 10 min of activity and 10 min of resting time; (b.) bioreactor operating principle depicting the 15 mm displacement of the permanent magnets below the culture wells and (c.) magnetic field force lines simulation in frontal and side planes which produce an alternated magnetic field that stimulate the magnetoelectric scaffolds46. The samples were subjected to a magnetic field that vary from 0 Oe to 230 Oe.

"

In the era of global overuse of antibiotics, these are losing efficacy as microorganisms strive to establish special advanced mechanisms of resistance. Advanced antimicrobial strategies via materials able to control microbial infections are urgently needed. In this work, nanocomposite films were developed based on piezoelectric polymers filled with magnetic nanowires, allowing to enhance the antimicrobial activity by applying a magnetic stimulus. More than 55% of bacterial growth inhibition was obtained for representative Gram-positive and Gram-negative bacteria. This work opens the room for applications in medical devices with improved control of healthcare-associated infections.



In the era of global overuse of antibiotics, these are losing efficacy as microorganisms strive to establish special advanced mechanisms of resistance. Advanced antimicrobial strategies via development of alternative drugs and materials able to control microbial infections, especially in clinical settings, are urgently needed. In this work, novel nanocomposite films were developed from the piezoelectric polyvinylidene fluoride (PVDF) polymer filled with nickel nanowires (NiNws), in an attempt to control and enhance the antimicrobial activity on-demand, via applying the magnetic stimulus. The material was achieved via polymer crystallization in the electroactive -phase when anisotropic and negatively charged NiNws were incorporated in the polymeric matrix



#### Fig 2

Bacterial growth inhibition of E. coli (a.) and S. epidermidis (b.) in suspension in the presence of the control film (PVDF-) and the NiNws loaded PVDF films with and without magnetic field application. \*P < 0.01, \*\*P < 0.1 when compared with each other and #P < 0.01 when compared to the control sample PVDF-alpha at static conditions;

Fluorescence Graphical abstract:

at a concentration of 1.5 wt.%. The antimicrobial properties could be further tuned and considerably boosted through the application of an external magnetic field. More than 55% of bacterial growth inhibition was obtained by employing controlled dynamic magnetic conditions for representative Gram-positive and Gram-negative bacteria, compared to only 25 % inhibition obtained under static, i.e without magnetic stimuli, conditions, being the antibiofilm activity clearly improved as well upon dynamic conditions. The herein demonstrated proof-of-concept for materials able to boost on-demand their antimicrobial activity opens the room for applications in novel medical devices with improved control of healthcareassociated infections.



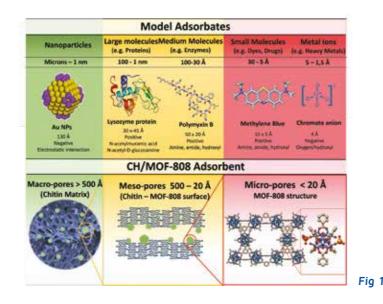
# RESEARCH AREA 2 ENVIRONMENT

The strong technological advances of recent years are leaving important footprints in our environment. In this scope, three main issues must be solved in the near future: environmental friendlier technologies, sensors for environmental monitoring and remediation of contaminated scenarios. In these areas, BCMaterials is strongly focusing on the development of prevention (environmental friendly materials and processes), monitoring (environmental sensing) and remediation strategies for water and air.



## CHITIN/METAL-ORGANIC FRAMEWORK COMPOSITES AS WIDE-RANGE ADSORBENT

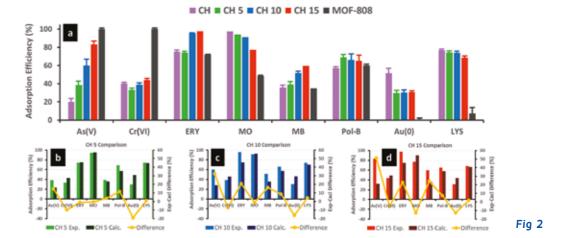
Gabriel I. Tovar Jimenez, Ainara Valverde, Cristian Mendes-Felipe, Stefan Wuttke, Arkaitz Fidalgo-Marijuan, Edurne S. Larrea, Luis Lezama, Fangyuan Zheng, Javier Reguera, Senentxu Lanceros-Méndez, María I. Arriortua, Guillermo Copello, Roberto Fernández de Luis. ChemSusChem 14(14), pp. 2892-2901.



## 66

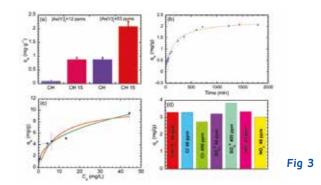
Composites based on chitin (CH) biopolymer and metal-organic framework (MOF) microporous nanoparticles have been developed as broad-scope pollutant absorbent. Detailed characterization of the CH/MOF composites revealed that the MOF nanoparticles interacted through electrostatic forces with the CH matrix, inducing compartmentalization of the CH macropores that led to an overall surface area increase in the composites. This created a micro-, meso-, and microporous structure that efficiently retained pollutants with a broad spectrum of different chemical natures, charges, and sizes.

The challenge of the current water remediation lies in the pollution heterogeneity. The development of efficient and broadly applicable water remediation technologies is an urgent need and must consider the fundamental properties of these hazardous molecules, such as their size, shape, charge, and potential binding groups (Figure 1). Metal-organic framework (MOF-808) nanoparticles incorporation into chitin gel polymeric matrix develops micro-, meso- and macro-porous composites that can be used as broad-scope adsorbents. This is possible because MOF-808 nanoparticles compartmentalize the macro-porous structure of chitin polymeric matrix into mesopores, endow the composite with the inherent micro-porosity of the MOF-808 material itself, and additionally, increase the surface area available for absorption. Due to their micro-, meso-, and macroporous nature, the Chitin/MOF-808 composites are able to work efficiently for the adsorption of a large variety of pollutants ranging from small ions (CrVI and AsV)



and molecules (erythrosine, methylene blue, methyl orange, Polymyxin B) to large proteins (Lysozime) or nanoparticles (Au - 50 nm) (Figure 2). Chitin/ MOF-808 composites exhibit the chemical affinity of their Chitin and MOF-808 separate components; however, in some cases (e.g. AsV, methylene blue, erythrosine, and Polymyxin B), the material benefits from their synergistic interactions, outperforming the averaged sum of both MOF-808 and chitin adsorption capacities and efficiencies Figure 2. This synergetic effect is attributed to (i) the compartmentalization of the chitin macropores when including MOF-808 nanoparticles within its structure, and (ii) the active role of the interface between MOF-808 and chitin during adsorption. CH/MOF-808 composites are also able to work efficiently in terms of capacity and kinetics over AsV capture in solutions mimicking real polluted waters. Considering the performance of the CH/ MOF-808 systems, it can be concluded that we have achieved a broad adsorption technology

able to work in the presence of a complex variety of pollutants that can be found in current water streams. Moreover, the MOF structural diversity and designability at the molecular level, combined with the easy processability and biocompatibility of CH polymers, makes the developed materials suitable for applications where available surface area, pore size, and pore chemistry become relevant issues.





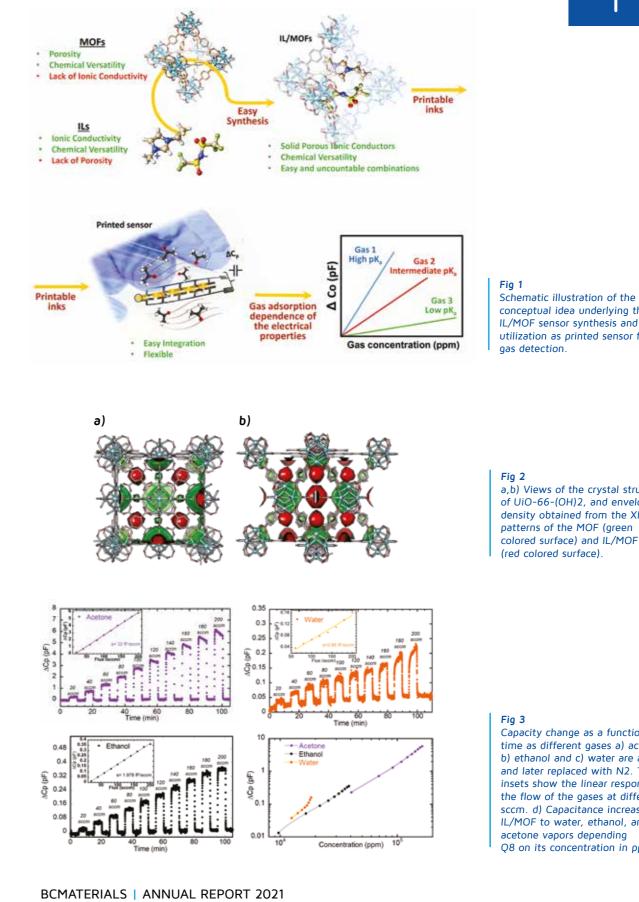
Eduardo Fernández, Paula G. Saiz, Nikola Perinka, Stefan Wuttke, and Roberto Fernández de Luis. Advanced Functional Materials, 31(25),2010703

The paper presents a printable ionic liquid/metal-organic framework (IL/ MOF) active film capacitive sensors. The ionic liquids exhibit appealing electrical properties that are partially maintained even when they are encapsulated within the porous frameworks. As demonstrated, the IL/MOF composites are a tremendously versatile platform of porous materials that exhibit diverse electrical responses upon exposure to different gas molecules. Additionally, the IL/MOFs can easily be made into films by spray printing capacitive transductor platforms, which greatly enhances the sensing kinetics, sensitivity, responsiveness, and reproducibility of the bulk IL/MOF material.

The paper evaluates the potential of 2D printing technologies to create thin film gas sensors from ionic liquid (IL)/metal-organic framework (MOF) composites. To accomplish this, the MOF was synthesized solvothermally then impregnated it with the IL. The structure and basic properties of the IL/ MOF composites were characterized using thermal, spectroscopic and X-ray diffraction techniques, and the resultant sensing capacity of the bulk material was evaluated by impedance spectroscopy. The IL/MOF systems were then integrated into a 2D printed silver capacitive circuit by spray and tested on a custom-made gas flow apparatus. Exposure of the IL/MOF based sensors to water, acetone and ethanol induces a repetitive variation of the capacitance (from 0.05 to 7 pico-Farads) that is dependent on the nature of the gas. IL/MOF based sensors can detect changes in concentrations in the range of 10k-100k ppm in less than a second.

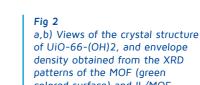
The integration of IL/MOF in 2D printed electronic circuits enhances gas sensing response, kinetics (ultra-fast response within a second), and recovery

of the bulk IL/MOF material. Spray printing has been revealed as an easy method of processing IL/MOF inks without disrupting the ionic liquid encapsulation within the MOF pores. Indeed, the rheological properties of IL/MOF ink have been adjusted to meet the requirements of 2D printing technology, a step forward that will enable 2D printing processing of IL/MOF based sensors in the near future. The encapsulation of ionic liquids into UiO-66-(OH)2 studied in this work enables the transfer of this strategy to endow other electrical insulator MOFs with an electrical response that would likely dependent on gas adsorption. Overall, this paper provides a straightforward protocol to assemble miniaturized 2D sensors based on IL/ MOFs. Although the 2D printing of IL/MOFs to create gas sensors has great potential to be used in a number of applications, there is plenty of room for improvement in the sensitivity, selectivity and minimum detection threshold of IL/MOF sensors.





Schematic illustration of the conceptual idea underlying the IL/MOF sensor synthesis and its utilization as printed sensor for



Capacity change as a function of time as different gases a) acetone. b) ethanol and c) water are added and later replaced with N2. The insets show the linear response to the flow of the gases at different sccm. d) Capacitance increase of IL/MOF to water, ethanol, and acetone vapors depending Q8 on its concentration in ppm

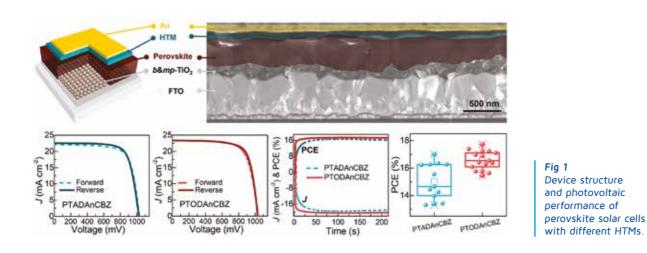
# RESEARCH AREA 3

One of the grand challenges facing humankind is related to energy. Energy generation and storage are among the key issues of modern society, increasingly dependent on mobility. BCMaterials specifically focus on the conversion between solar energy and chemical energy in applications such as perovskite and kesterite based solar cells. We also work on the development of energy harvesting systems, mainly based on mechanoelectric (piezoelectric and triboelectric) and thermo-electric systems for self-powered and wearable sensors. Finally, materials and concepts are being developed for Li and Na batteries, as well as new approaches for solid electrolytes and printable batteries. 4

## TAILORING OF A PHENOTHIAZINE CORE FOR ELECTRICAL CONDUCTIVITY AND THERMAL STABILITY: HOLE-SELECTIVE LAYERS IN PEROVSKITE SOLAR CELLS

5

Peng Huang, Manju, Samrana Kazim, Luis Lezama, Rajneesh Misra, and Shahzada Ahmad. ACS Applied Materials and Interfaces. 13(28), pp. 33311-33320.



# 44

designed We and developed two phenothiazine-based hole transport materials: PTADAnCBZ with an electrondonating sulfur atom and PTODAnCBZ with an electron-withdrawing sulfone group in the core. PTODAnCBZ in contrast to PTADAnCBZ possesses a unique molecular orbital distribution and lower dihedral angles, which endowed it with excellent optoelectrical properties, improved charge transportation, and thermal stability under multi-stress conditions. The solar cells with PTODAnCBZ yielded a higher photovoltaic performance as compared to PTADAnCBZ and were on par with Spiro-OMeTAD.

Spiro-OMeTAD is used as a benchmark HSL for PSC fabrication, but their apparent shortcomings are considered as constraints in the scale-up of the PSCs. Herein, we designed and developed two phenothiazine-based hole transport materials: PTADAnCBZ with an electron-donating sulfur atom and PTODAnCBZ with an electron-withdrawing sulfone group in the core, and decipher the structure-properties-device performance relationship impacted by functional electron groups.

PTODAnCBZ gave a higher transporting ability than PTADAnCBZ and Spiro-OMeTAD owing to the improved ICT affected by the introduction of dioxide. PTODAnCBZ with 52.55 and 49.27° dihedral angles possesses a lower level of planarity as compared to PTADAnCBZ with 52.40 and 73.93°, which reduces the molecular stacking and help in the formation of a uniform film in PTODAnCBZ. Besides, the EHOMO value of PTODAnCBZ obtained by cyclic voltammetry is slightly lower than that of PTADAnCBZ, illustrating favorable hole

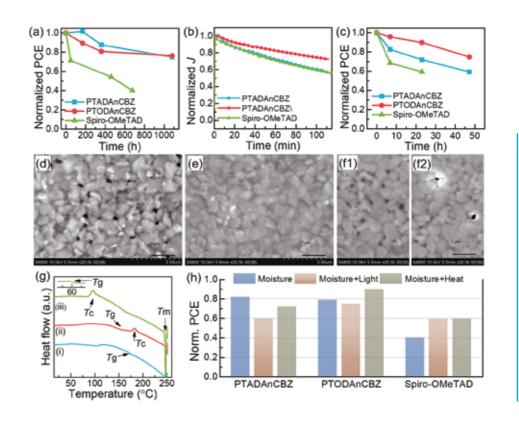


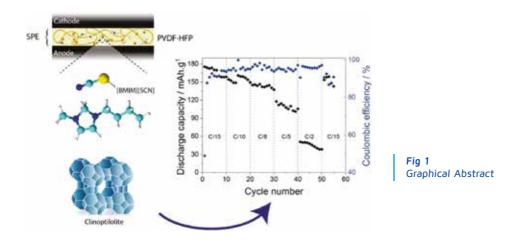
Fig 2 Long-term stability of perovskite devices PCE plots of PSCs aged under (a) ambient conditions, (b) moisture and illumination, (c) moisture and thermal stress. SEM images of perovskite films with (d) PTADAnCBZ (e) PTODAnCBZ, and (f1, f2) Spiro-OMeTAD after thermal aging. (a) DSC curves for doped (i) PTADAnCBZ, (ii) PTODAnCBZ, and (iii) Spiro-OMeTAD. (f) Summary of PCE after aging.

transportation. For the photovoltaic performance of PSCs with different HTMs, the PTODAnCBZbased PSC displayed a PCE of 17.73%, which is comparable with that of Spiro-OMeTAD, while the PTADAnCBZ-based PSC gave a relatively lower PCE of 17.01%.

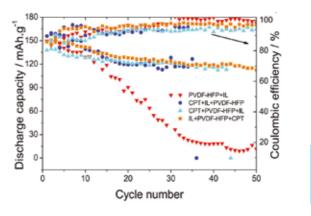
Device stability and performance are crucial aspects in evaluating PV reliability. It is found that PTODAnCBZ presented improved stability under multi-stress including moisture, moisture and light, and moisture and heat conditions, as compared to PTADAnCBZ and Spiro-OMeTAD. The DSC curves analysis was introduced to unravel the thermal stability of doped HTMs. It is known that the deformation of HTMs arises from crystallization treated at a temperature above glass-transition temperature (T<sub>g</sub>). The doped Spiro-OMeTAD displays a low T<sub>g</sub> (62 °C) and the crystallization peak (Tc, 100 °C), leading to the degradation of Spiro-OMeTAD-based PSCs under thermal stress at 85 °C. However, the doped PTADAnCBZ films preserve the amorphous properties within a wide range of temperatures, and doped PTODAnCBZ have Tg and Tc, distinctly higher than the thermal stress. The excellent thermal properties of phenothiazinebased HTMs will induce improved stability in PSCs.

## HIGH-PERFORMANCE ROOM TEMPERATURE LITHIUM-ION BATTERY SOLID POLYMER ELECTROLYTES BASED ON POLY(VINYLIDENE FLUORIDE- CO-HEXAFLUOROPROPYLENE) COMBINING IONIC LIQUID AND ZEOLITE

João C. Barbosa, Daniela M. Correia, Eva M. Fernández, Arkaitz Fidalgo-Marijuan, Gotzone Barandika, Renato Gonçalves, Stanislav Ferdov, Verónica de Zea Bermudez, Carlos M. Costa, and Senentxu Lanceros-Mendez. ACS Appl. Mater. Interfaces 2021, 13, 41, 48889–48900.



The demand for more efficient energy storage devices has led to the exponential growth of lithium-ion batteries. To overcome the limitations of these systems, solid-state technology emerges as a suitable approach. This work reports on a solid polymer electrolyte system based on (PVDF-HFP), the ionic liquid ([BMIM][SCN]), and clinoptilolite zeolite. The preparation method, the electrolyte stability, ionic conductivity, and battery performance were studied. The developed electrolytes show an improved r.t. ionic conductivity  $(1.9 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1})$ , and high thermal and mechanical stability. The batteries exhibit a performance of 160.3 mAh·g<sup>-1</sup> (C/15-rate), with a capacity retention of 76% after 50 cycles.



PVDF-HFP+IL Three-component approach

PVDF-HFP films were prepared and applied as solid polymer electrolytes (SPE) for lithium ion batteries, in a three-component approach, using clinoptilolite zeolite and [BMIM][SCN] ionic liquid as doping agents. Clinoptilolite was used as a stabilizer for the mechanical and thermal properties, while the ionic liquid allowed us to improve the ion conductivity of the SPE. Different preparation methods were used, and their influence on the SPE properties was analyzed. We showed that the order of addition of the components has a significant influence on the film structure and polymer crystallization. The films exhibit a compact nonporous texture, independently of processing conditions and sample composition. Analysis of the SEM images allows concluding that the order of addition of the components affects the spherulite-like structure typical of PVDF-HFP and related polymers. The ATR/FTIR analysis shows differences in the intensity of the absorption band characteristic of the clinoptilolite, indicating that the preparation method influences the strength of the electrostatic interactions that occurs between

**Fig 2** Comparison of the cycling stability of the electrolytes at C/15, together with the corresponding Coulombic efficiency.

Schematic representation of the lithium-ion transport mechanism in the PVDF-HFP + IL and PVDF-HFP with IL and Zeolite.

Fig 3

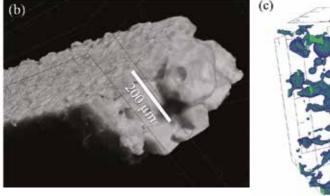
the ionic liquid and the zeolite. Further, the zeolite has a stabilizing effect in the SPE, as proven by the thermal and mechanical properties. The variation of the ionic conductivity over temperature was also affected by the preparation method, with the measured values (up to 1.9×10<sup>-4</sup> S·cm<sup>-1</sup> at 30 °C) being suitable for application in batteries. The different SPEs assembled into the batteries demonstrated an enhancement in the battery stability during 50 cycles when compared with the SPEs devoid of CPT, with an excellent discharge capacity value of 160.3 mAh·q<sup>-1</sup> at a C/15-rate and room temperature for the Ionic Liquid + PVDFHFP + Clinoptilolite sample. The assembled batteries also show a good behaviour in fast charging, being able to deliver 45 mAh $\cdot$ g<sup>-1</sup> at a C/2-rate. The promising results reported in this work represent an interesting option for future generation of safer, more durable, and environmentally friendlier solid-state batteries by overcoming the present limitations at room temperature operation.

# RESEARCH AREA 4 ADDITIVE MANUFACTURING

Technological advances often rely on both new materials and processing/manufacturing technologies. Additive manufacturing is undergoing strong developments allowing customized production. Furthermore, conventional manufacturing technologies are being modified to accommodate the concepts of Industry 4.0 and digitalization, as well as to produce advanced materials and solutions in a more environmental friendly and efficient way. BCMaterials is working on the development of smart and multifunctional materials with improved integration through advanced manufacturing processes. Self-sensing, selfcleaning and self-repairing materials are being developed and integrated into functional prototypes, among others.

## MASTERING A 1.2 K HYSTERESIS FOR MARTENSITIC PARA-FERROMAGNETIC PARTIAL TRANSFORMATION IN NI-MN(CU)-GA MAGNETOCALORIC MATERIAL VIA BINDER JET 3D PRINTING

Erica Stevensa, Katerina Kimesa, Daniel Salazar, Rafael Rodrigueza, Aaron Acierno, Patricia Lázpita, Volodymyr Chernenko, Markus Chmielusa. Additive Manufacturing, 2021, 37, 101560.



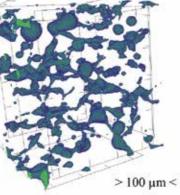
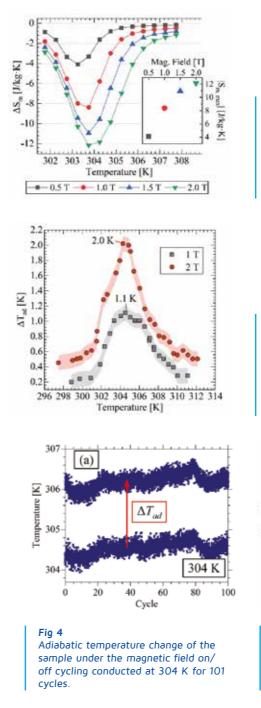


Fig 1 (a) 3D visualizations using data collected by  $\mu$ CT of a single grain on the top of the slice, and (b) porosity only, visualized for a small cube of volume.

Magnetocaloric (MC) materials have gained traction in the research and industry communities for their prospects in solid state magnetic refrigeration. Important to the commercialization of MC materials are: (1) establishment of a fabrication method that can combine high surface area for heat transfer and geometric freedom for designing an efficient heat exchanger which has low pressure drop for the coolant and (2) advancement of low-cost alloys with appropriate MC properties. In this regard, additive manufacturing may provide the geometric freedom necessary for adapting designs to solid state cooling.

The Ni-Mn(Cu)-Ga Heusler ferromagnetic shape memory alloys (FSMAs), exhibiting a martensitic para-ferromagnetic transformation at T\_==304 K, can provide a low-cost MC material, very promising for magnetic cooling. In this study, a Ni<sub>495</sub>Mn<sub>191</sub>Cu<sub>66</sub>Ga<sub>24.8</sub> (at.%) alloy is additively manufactured using powder bed binder jet 3D printing with subsequent sintering. This printed and sintered material enabled a large change of magnetization during partial transformation cycles with the smallest temperature hysteresis recorded for FSMAs, equal to about 1.2 K, regardless the value of magnetic field applied. The maximum of magnetic field-induced entropy change | S\_  $_{21}$  |  $\approx$  12.0 J/kg·K was estimated at 304 K. These results demonstrate the viability of powder bed binder jet 3D printing as an effective fabrication

binder jet 3D printing as an effective fabrication method for functional magnetocalorics, as well as the outstanding MC characteristics of a low-cost Ni-Mn(Cu)-Ga Heusler-type FSMA. Post-processing included sintering in an argon-purged vacuum atmosphere followed by an air cool. Samples showed a  $\Delta T_{ad}$  of 2 K under 2 T at 304 K. The subsequent cycling resulted in a stable  $\Delta T_{ad}$  of approximately



1.65 K. The stable cycling of such a value of  $\Delta T_{ad}$  is achieved owing to a record-breaking for FSMAs low hysteresis, of 1.2 K, accompanying a partial magnetostructural martensitic transformation, with still-high values of  $\Delta M$  and a narrow transformation interval. The possible incorporation of carbon from the binder may cause observed volumetric expansion which might serve as additional factor improving functionality of printed material. Pores

#### Fig 2 Temperature dependencies of the magnetic field induced entropy change, $\Delta S_m$ , at different constant magnetic fields in the range from 0.5 T to 2.0 T. Inset demonstrates the evolution of $\Delta S_{m, max}(H)$ .

Fig 3 Magnetic field induced adiabatic temperature change at 1 T and 2 T measured at different temperatures during step-like cooling. Shaded bands indicate a ±0.1 K of uncertainty in the measurements.

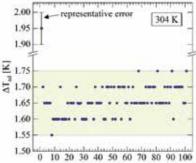
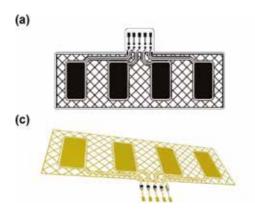


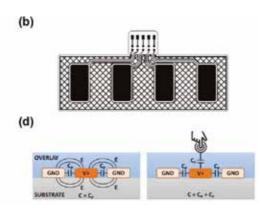
Fig 5 Magnetic field cycling performed at the temperature where  $\Delta T_{max}$  was observed (304 K). The first data point shows a representative ±0.5 K of uncertainty that is assumed to be valid for all other plotted points. The filled area indicates where 97.5% of all points and their error bars fall within, excluding the first data point.

> at grain boundaries allow for better conditions for reversible volumetric expansion necessary for functionality. Powder bed binder jet printing is proved to be a successful processing route for magnetocaloric materials, such as Ni-Mn-Cu-Ga FSMA.

## CAPACITIVE AND ILLUMINATION SYSTEMS BASED ON PRINTED AND HYBRID ELECTRONICS

Nikola Perinka, Borja Pozo, Erlantz Fernández de Gorostiza, Cristian Mendes-Felipe, José Luis Vilas-Vilela and Senentxu Lanceros-Méndez. Flexible and Printed Electronics. 6(1),015004.





#### Fig 1 Capacitive sensors. (a) Design of the capacitive sensor with low-density ground net. (b) Design of the capacitive sensor with high-density ground net. (c) 3D design of the capacitive sensor with attached rigid electronic

sensors

components. (d) Working principle of the mutual capacitive

## "

Functional electronic systems have been screen- or inkjet-printed on different plastic substrates. Mutual capacitive sensors were designed and printed on flexible substrates and the capacitive response and functionality of the printed sensor with integrated passive electronic components was demonstrated. The influence of the substrate, sensor design and the printing technique parameters on both printability and functionality are discussed. Further, a flexible illumination system was developed, where the printed circuit was combined with surface mounted light emitting diodes and integrated circuits.

The field of printed electronics has recently experienced a high demand of implementing the electronics directly on the 3D-shaped plastics. That can be realized by combination of the printed electronics with injection-moulding processes. Therefore, functional electronic systems, such as mutual capacitive sensors and illumination systems with LEDs have been screen- or inkjet-printed on different plastic substrates, including polyethylene terephthalate (PET), polycarbonate (PC) and polycarbonate/acrylonitrile butadiene styrene blends (PC/ABS). The main stress has been put on polycarbonate-based substrates as they represent a significant part of plastic-based industry with integrated electronics. The capacitive sensors were designed in accordance with the desired named applications and subsequently printed on the flexible substrates. The capacitive response and

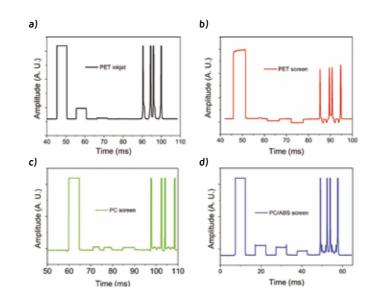
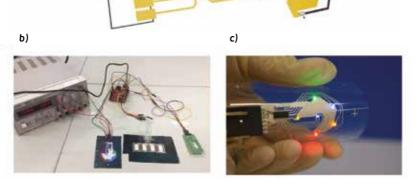




Fig 2

Results of the tactile detection of sensors with the low-density ground net design on various substrates. (a) PET substrate and manufactured by inkjet printing. (b) PET substrate and manufactured by screen printing. (c) P substrate and manufactured with screen printing. (d) PC/ABS substrate and manufactured with screen printing.



Final integration of all printed tested components. (a) 3D design of the printed illumination circuit with integrated rigid components. (b) Working set of capacitive sensors with illumination circuit. (c) Demonstration of flexibility of the printed illumination circuit.

functionality of the printed sensors with integrated passive electronic components was demonstrated and the pros and cons of the both used techniques for the development of such capacitive sensors were evaluated. The plastic substrates were also characterized in terms of their wettability by the contact angle measurement and the printed conductive layer morphology was examined by scanning electron microscopy.

a

The produced capacitive sensors were finally integrated with a printed flexible illumination circuit to control different the LEDs with programmed illumination sequences. The capacity of all tested sensor ranged from 3.5 to 6 pF in touch free state and from 7.5 to 11 pF in touch active state. The capacitive sensors operated in a stable way in the frequency range from 900 Hz to 100 kHz. The inkjet-printed sensor showed generally higher

significantly lower (of the order of tens of  $\Omega$ ) and more homogeneous resistance values. It was also observed that the used silver ink interacted with PC and PC/ABS substrates, which resulted in an increase of the resistance of the printed tracks on PC and on non-continuous printed tracks on PC/ ABS. Therefore, screen printing resulted to be more suitable for PC and PC/ABS substrates, whereas both inkjet and screen printing can be used on PET standard substrate. The reported work opens the way for the development of injection-moulded electronic components and their performance tailoring as a function of varying injection-moulding parameters.

and more dispersed resistance values (up to  $k\Omega$ 

range), whereas the screen-printed ones showed

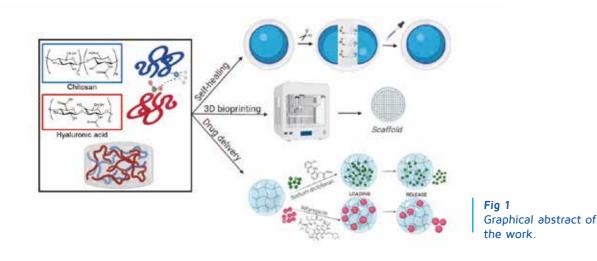
Fig 3

# RESEARCH LINE 1 ACTIVE & SMART MATERIALS

Active and smart materials are at the core of the on-going rapid technological development. Shape memory, magnetocaloric and elastocaloric materials, piezoelectric, magnetoelectric and selfhealing materials, as well as multifunctional hydrogels are being developed. A deep understating on the structural and molecular modifications behind the active responses allows tailoring materials responses.

## **3D PRINTABLE SELF-HEALING HYALURONIC ACID/CHITOSAN POLYCOMPLEX HYDROGELS** WITH DRUG RELEASE CAPABILITY

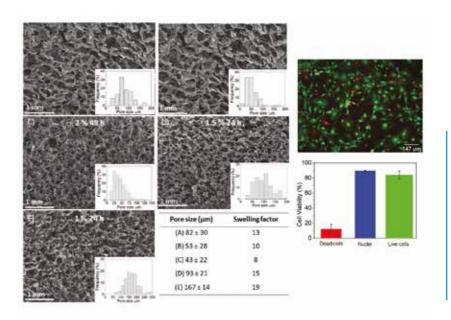
Sheila Maiz-Fernández, Nagore Barroso, Leyre Pérez-Álvarez, Unai Silván, José Luis Vilas-Vilela and Senentxu Lanceros-Mendez. International Journal of Biological Macromolecules, 188, pp 820-832.



Multifunctional printable biomaterials play an essential role in the development of advanced biomedical approaches. Due to the varying requirements in terms of pore size, stiffness and degradation dynamics depending on their specific use, the development of highly versatile and tuneable systems is of utmost interest. Here, we explore the biophysical properties of hydrogels composed of two natural polysaccharides, chitosan and hyaluronic acid, and investigate their mechanical properties, biocompatibility and drug release capability, and their potential for 3D printing.

The unique attributes of hydrogels to mimic electrostatic interactions between polyelectrolytes biological tissues, such as their mechanical properties and high water content, have positioned them as essential elements for the development of personalized tissue engineering devices, scaffolds for regenerative medicine, and for the development of custom implants, which is also driving the increasing interest in hydrogels produced using 3D printing technologies. Hydrogels formed by

are known as polyelectrolyte complex (PEC) hydrogels and are formed by combining polymers with a large number of ionizable groups through electrostatic interchain interactions. Among PEC hydrogels, those prepared using the polymers of natural origin chitosan (CHI) and hyaluronic acid (HA) have shown favourable biocompatibility and great versatility. In this context, in the present



work, we have analyzed the mucoadhesivity, swelling, biodegradability, mechanical stability, and rheological properties of hydrogels composed of these polymers and further optimized their formulation for various applications. To this end, we modified the synthesis parameters, including polysaccharide content and complexation time, according to the electrostatic interactions existing between the two polyelectrolytes. The analysis of their self-healing ability and their application as inks for bioprinting exposed the great potential of HA/CHI hydrogels. Moreover, these hydrogels were used for sustained release of diclofenac and rifampicin, an anionic anti-inflammatory drug and a neutral antibiotic, respectively, proving a non-Fickian transport mechanism. Taken together, the HA/CHI PEC hydrogels developed here have great potential as three-dimensional biodegradable scaffolds and as soft implants for personalized medicine with drug release capability and longer durability against mechanical damage.

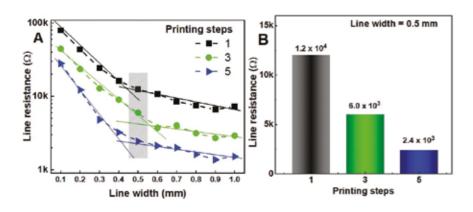
#### Fig 2

Scanning electron images and pore size distribution of the PEC hydrogels analyzed in the study (left panels). Fluorescence microscopy image of the live/dead assay (blue, nuclei; red, dead cells; green, live cells) and quantification of cell viability after 24-hour incubation with CHI/HA hydrogels.

## ENVIRONMENTALLY FRIENDLY GRAPHENE BASED CONDUCTIVE INKS FOR MULTI-TOUCH CAPACITIVE SENSING SURFACES

Miguel Franco, Vitor Correia, Pedro Marques, Fábio Sousa, Rui Silva, Bruno R. Figueiredo, Adriana Bernardes, Rui P. Silva, Senentxu Lanceros-Méndez, Pedro Costa. Advanced Materials Interfaces, 8(18),2100578

Conductive graphene-based inks have been developed for printed electronics. A capacitive multi-touch sensing surface has been developed using conducting graphene nanoparticles based inks with carboxymethyl cellulose as a binder. A touchscreen based on printed conductive lines and columns was developed by screen printing. The screen-printed flexible touchscreen, composed by 40 columns × 28 rows in the form of an 8" touchscreen with integrated electric circuit and a graphic interface, shows with multi-touch capabilities and fast signal processing.



Conductive graphene-based inks can be tailored for functional applications and, in particular, for printed electronics. Transparent, flexible and easy printable materials are nowadays increasingly required for sensing applications. In this context, a capacitive multi-touch sensing surface has been developed using conducting graphene nanoparticles (GNP) based ink with carboxymethyl cellulose (CMC) as a binder. The rheological properties of the ink were tailored to be printed by the screen-printing technique. Fig 1

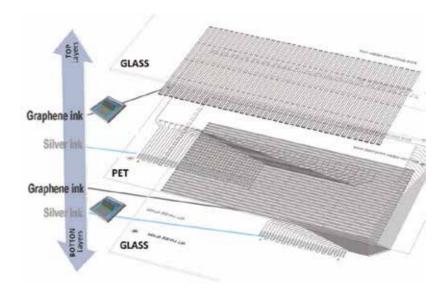
A) Electrical resistance of printed lines with 1, 3 and 5 printing steps as a function of line width from 0.1 mm to 1 mm. B) Line resistance for 1, 3 and 5 printing steps in a printed line of 0.5 mm width. The length of the lines was 50 mm in all cases.

The touchscreen is based on printed conductive lines and columns, and thus the characteristics of the printed lines were optimized based on the line width and number of printing steps. The optimal printed conditions were 0.5 mm of width and 5 printing steps, leading to electrical resistance of 2.4 k $\Omega$ . The screen-printed flexible touchscreen was composed by 40 columns × 28 rows. An electric circuit and a graphic interface were also developed leading to an 8" touchscreen with multi-touch capabilities and fast signal processing.



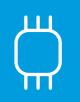
#### Fig 2

Illustration of the device based on a screen-printed flexible matrix using water-based graphene nanoparticles inks with cellulose as polymer binder.



#### Fig 3

Schematic representation of the electrode layers that compose the capacitive touch sensor. The electrodes consist of two layers: sensing lines based on the developed graphene nanoparticles inks and a highly conductive pad based on silverbased inks. The touch sensing device has a bottom and a top electrode.



# RESEARCH LINE 2 NANO-STRUCTURED MATERIALS

Nanostructures are being developed in order to take advantage of their specifically tailored properties and to make use of them in the development of multiresponsive composites. Magnetic, plasmonic and photocatalytic nanoparticles are being developed, among others. Further, novel porous materials, basically MOFS and Zeolites are being investigated based on their tuneability and outstanding intrinsic properties.

## LINKER EXCHANGE VIA MIGRATION ALONG BACKBONE IN METAL-ORGANIC FRAMEWORKS

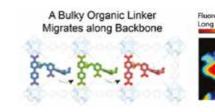
Nader Al Danaf, Waldemar Schrimpf, Patrick Hirschle, Don C. Lamb, Zhe Ji, and Stefan Wuttke. Journal of the American Chemical Society, 143 (28), pp 10541-10546.

#### In metal-organic frameworks (MOFs), organic linkers are subject to post-synthetic exchange (PSE) when new linkers reach sites of PSE by diffusion. Here, we show that during PSE a bulky organic linker is able to penetrate narrow-window MOF crystals. The bulky linker migrates by continuously replacing the linkers gating the otherwise impassable windows and serially occupying an array of backbone sites, a mechanism we term through-backbone diffusion. A necessary consequence of this process is the accumulation of missing-linker defects along the diffusion trajectories. Using fluorescence intensity and lifetime imaging microscopy, we found a gradient of missinglinker defects from crystal surface to interior, consistent with the spatial progression of PSE. Our success in incorporating bulky functional groups via PSE extends the scope of MOFs that can be used to host sizable, sophisticated quest species, including large catalysts or biomolecules, which were previously deemed only incorporable into MOFs of very large windows.

Metal-organic frameworks (MOFs) present an unprecedented scaffold for performing chemical transformations in a single-crystal-to-single-crystal manner. Post-synthetic exchange (PSE) of organic linkers, one of the most practiced transformations, allows incorporation of linkers bearing new functionalities of interest. This can be achieved simply by soaking MOF crystals in a solution of new linker, during which the new linker diffuses through pore window and reaches crystal interior, resulting in linker exchange throughout the whole crystal. To this end, it is widely accepted that the new linker has to be smaller than the MOF window, limiting the scope of linkers and MOFs that can are amenable to PSE.

In this paper we observed that a bulky linker is able to penetrate crystals of a narrow-window MOF and achieves PSE in crystal interior. This observation was surprising because the linker we chose is too large to pass the MOF window (i.e. the conventional through-window diffusion). Instead, we found that the bulky linker can continuously replace the linkers gating the otherwise impassable windows and thereby migrate along consecutive backbone sites, a mechanism we term through-backbone diffusion. Every time the new linker migrates from one pore to the other, it has to first dissociate from the current site of backbone, leaving behind a missing-linker defect. This ultimately results in the accumulation of defects along the diffusion trajectory, a distinctive feature of the throughbackbone diffusion mechanism. We employed fluorescence intensity and lifetime imaging microscopy to track defect formation and map defect distribution accompanying the progression of PSE. By correlating fluorescence lifetime with local defect level, we found high defect level on crystal surface where many diffusion events start from, and low defect level in the core where only a few PSE events reach this depth, a strong evidence supporting the through-backbone diffusion mechanism.

Fundamentally, our discovery of through-backbone diffusion fills the gap where through-window diffusion was believed the only mechanism of PSE in MOFs. Although through-backbone diffusion was found in our studies of a bulky linker, we envision it is a general mechanism that also plays a role in the



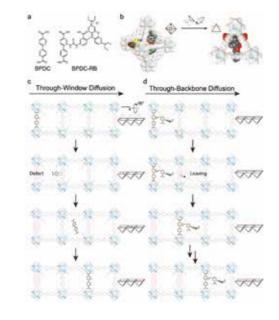


Fig 1 (a) The molecular structures of BPDC and BPDC-RB. (b) The space-filling model of an octahedron unit in UiO-67, which comprises a BPDC-RB linker, and a projection of BPDC-RB beneath a triangular window. (c) Structure illustration of through-window diffusion of a small linker, and (d) through-backbone diffusion of the bulky linker BPDC-RB in UiO-67. Color code for BPDC-RB: C, grey; O, red; S, yellow; N, green. Color code for other UiO-67 components: Zr cluster, blue: C and O. off-white.

surface

Fig 2 (a) A schematic diagram of an octahedral crystal of UiO-67. (b) The crystal is oriented along the [111] direction. (c) Fluorescence and lifetime images were collected both laterally and axially.

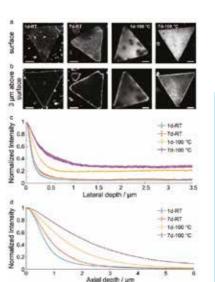


Fig 3 Fluorescence imaging of UiO-67 crystals after PSE in MeOH/DMF. (a) Fluorescence images taken at the surface and (b) 3  $\mu$ m above the surface. The scale bar is 15  $\mu$ m. (c) Fluorescence intensity profile along lateral and (d) axial directions (error bars from measurements on 8-10 UiO-67 crystals per condition). Fig 4 Elugrescence lifetime analysis

Fluorescence lifetime analysis of UiO-67 crystals after PSE in MeOH/DMF. (a) Fluorescence lifetime decay. (b) The phasor plot of lifetime. (c) FLIM images of UiO-67 crystal.

diffusion of linkers smaller than MOF window. Our results also blur the boundary between diffusion in liquid and in solid; while the linker migration along MOF backbone takes place in solvated pore environments, it is analogous to the diffusion of atoms in inorganic lattices.

Our success in incorporating bulky functional groups

extend the scope of MOFs that can be used to host sizable, sophisticated guest species, including large catalysts or biomolecules, which were previously deemed only incorporable into MOFs of very large pore windows. Hence, we believe that our paper is of high interest to the diverse readership.

Ö

## HIGH MAGNETIZATION FeCo NANOPARTICLES FOR MAGNETORHEOLOGICAL FLUIDS WITH ENHANCED RESPONSE

Virginia Vadillo, Ainara Gómez, Joanes Berasategi, Jon Gutiérrez, Maite Insausti, Izaskun Gil de Muro, Joseba S. Garitaonandia, Arantxa Arbe, Amaia Iturrospe, M. Mounir Bou-Ali and Jose Manuel Barandiarán. Soft Matter, 17(4), pp. 840-852

The fabrication of a new magnetorheological fluid with FeCo magnetic nanoparticles (NPs) as magnetic fillers has been performed. These NPs, fabricated by a chemical reduction technique, show a pure crystalline phase with sizes in the 30-50 nm range and high magnetization, 212±2 Am<sup>2</sup>/kg. They agglomerate due to the strong magnetic dipolar interaction among them. The nanoparticles, together with oleic acid as surfactant, mineral oil as carrier liquid and Aerosil 300 as additive, were used to synthesize a magnetorheological fluid which showed a strong magnetorheological response with increasing shear stress values as the magnetic field intensity increased.

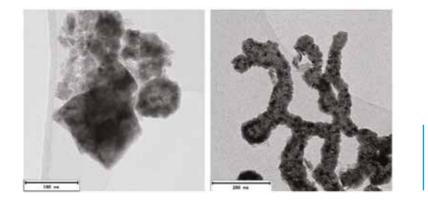
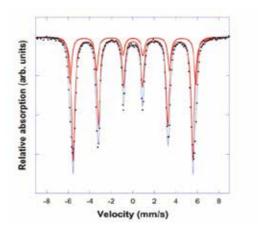


Fig 1 TEM images of the raw powder of FeCo nanoparticles: (a) single NPs and (b) their agglomeration in a dendritic structure.

Magnetorheological (MR) fluids are stable suspensions of magnetic microparticles, that is, magnetic multidomain particles, dispersed in a liquid carrier. One of their most important characteristics still higher saturation magnetization value than is the reversible rheological behaviour they exhibit, that can be modified by application of an external magnetic field. Because of this, they are also called "intelligent" fluids. Bearing in mind that magnetic filler parameters like the particle size distribution or its magnetic saturation value are of critical importance in the rheological behaviour of MR

fluids, the aim of this work has been to improve the behaviour of magnetorheological fluids by using magnetic nanoparticles of FeCo composition with previously studied pure Fe nanoparticles. These FeCo nanoparticles have been synthesized through chemical reduction. Iron(III) chloride hexahydrate and cobalt(II) acetate tetrahydrate precursors in the presence of ammonium fluoride were reduced by aluminium and a black powder was magnetically collected and characterized by X-ray



Shear stress (Pa)

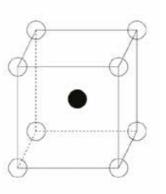


Fig 2 a) Room temperature Mössbauer spectrum and (b) ordered B2 structure of the FeCo NPs.

O kA/m 12.7 kAin 26.1 kAin increasing H 67.9 kAlm 140.1 kA/m 280.9 kA/m
 616.7 kA/m (a) FeCo NPs Pre-yield range Post-vield range 0 kA/m 12.7 kAin A 26.1 kA/m + 67.9 kA/m Increasing H 140.1 kA/m 280.9 kA/m
 616.7 kA/m 0.1 (b) Fe-EEW NPs Pre-vield range Post-vield range 0.1 0.01 10 100 Shear rate (1/s)

> Fig 3 Rheological curves as a function of the applied magnetic field: (a) for the new FeCo-MR fluid studied and (b) the one fabricated with Fe nanoparticles obtained by the EEW technique.

diffraction, Transmission Electron Microscopy and Inductively Coupled Plasma-Mass Spectrometry. FeCo nanoparticles of size ranging among 30-50 nm that easily agglomerate in bigger entities of about 200-500 nm due to the strong magnetic dipolar interactions have been observed (Fig. 1). Magnetic analysis shows a saturation magnetization of 212  $\pm$  2 Am<sup>2</sup>/kg, a value 8% lower than the expected due to nanoscale dimensions. Mössbauer measurements indicate that all the Fe atoms are in the FeCo alloy and no clusters of bcc-Fe are

shown up. The symmetry of the spectrum denotes high symmetrical crystallographic locations for the Fe atoms and confirms therefore a cubic structure of the alloy (Fig. 2). The fully characterized FeCo nanoparticles were dispersed, first by ultrasound stirring and afterwards by mechanical stirring, in mineral oil as carrier liquid and Aerosil 300 as additive. Finally, oleic acid was added as surfactant and different magnetorheological fluids (MRF) were prepared. For comparison, a previously reported Fe (Fe-EEW) nanoparticle containing MRF fluid has also been studied by applying magnetic fields up to 616.7 kA/m.

Both fluids showed a strong magnetorheological response with increasing shear stress values as the magnetic field intensity increased, behaviour that was fitted by using the Herschel-Bulkley model. The Fe-EEW MRF presents a good magnetorheological response for applied magnetic fields up to 140.1 kA/m, with a yield stress value of 1250 Pa. For higher values of the applied magnetic field, there are evidences of Fe nanoparticles agglomerates that perturb the magnetorheological response of this fluid. However, the new FeCo-MR fluid shows superior performance up to 616.7 kA/m, with a yield stress value of 2729 Pa (Fig. 3). This value competes with the best ones reported in the most recent literature. A good reversibility after demagnetization process of the new FeCo-MR fluid has also been observed, a better response than the one measured for the Fe-EEW magnetorheological fluid. Future work points towards the fabrication of a magnetorheological fluid containing magnetic nanoparticles of Fe70Co30 with well defined size distribution and saturation magnetization up to 240  $Am^2/kq$ , prepared by means of a modified chemical route in order to prevent further agglomeration.

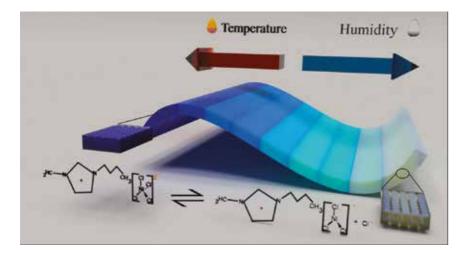


# RESEARCH LINE 3 FUNCTIONAL SURFACES & COATINGS

Surface properties present relevant and specific scientific challenges that must be understood in depth prior to their implementation in coatings and/or devices. Patterning and/ or chemical modification are being used to obtain surfaces with specific and tailored magnetic, optical and mechanical responses upon the application of the pertinent stimulus. In this context, BCMaterials is working on the investigation of patterned surfaces and films as well as on the functional surface modification following a wide variety of methods, including chemical and physical deposition and printing techniques, among others.

## PHOTOCURABLE TEMPERATURE ACTIVATED HUMIDITY HYBRID SENSING MATERIALS FOR MULTIFUNCTIONAL COATINGS

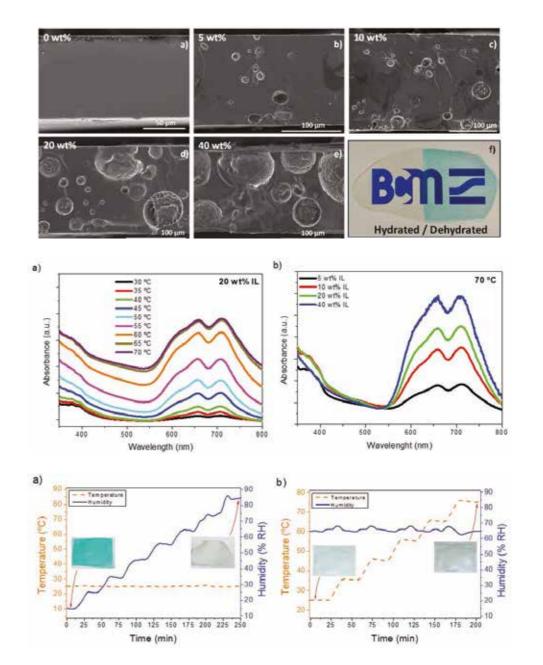
Cristian Mendes-Felipe, Manuel Salado, Liliana C Fernandes, Daniela M Correia, Leire Ruiz-Rubio, Mohammad Tariq, José M SS Esperança, JL Vilas-Vilela, S Lanceros-Mendez. Polymer 221,123635



Photocurable thermochromic and humidity responsive materials based on polyurethane acrylated (PUA) and bis(1-butyl-3-methylimidazolium) tetrachloronickelate ( $[Bmim]_2[NiCl_4]$ ) ionic liquid (IL) have been prepared with varying IL content up to 40 wt% within the polymer matrix. The influence of IL content on the photopolymerization process, morphology, Young modulus and electrical conductivity of the materials was evaluated. As result, the incorporation of the IL entails the appearance of a porous network structure. Further, it was observed a colour variation is thermally activated and humidity governed.

Flexible electronic devices and smart and multifunctional coatings are one of the cornerstones of the current technological advances. Besides the great advantages of multifunctional materials composed by ionic liquids (ILs) and UV curable polymers for additive manufacturing and protective and functional coatings, no studies concerning thermochromic IL-based UV curable hybrid materials able to change the colour with the temperature and to detect relative humidity variations (humidity

sensor) have been reported. Bearing this in mind, in this work, a flexible and cost-effective dual humidity and temperature sensor and/or coating material has been successfully developed. After the incorporation of ionic liquid (bis(1-butyl-3-methylimidazolium) tetrachloronickelate ([Bmim]<sub>2</sub>[NiCl<sub>4</sub>])) into a UV-curable polymer matrix (polyurethane acrylated (PUA)), a porous network structure is obtained without relevant chemical changes neither in the IL or in the polymer matrix.



In addition, the incorporation of the IL slightly influences the UV curing process of the polymer obtaining in all cases a polymer curing conversion of 88% or above. Further, the inclusion of the IL influences the electrical and mechanical properties of the samples for the higher IL contents obtaining an improvement in the electrical conductivity and a decrease on the Young modulus. All composites exhibit humidity dependent thermochromism from colourless to blue, even at low IL loads. Interestingly, humidity has a strong influence in the thermochromic effect up to 55% RH and that this process is thermally influenced. This effect can be ascribed to the water absorption/dehydration

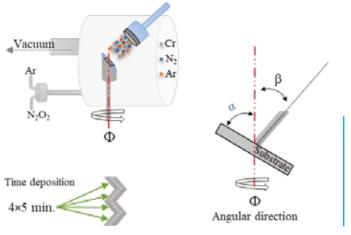
of  $[\text{NiCl}_4]^{2^-}$ , which is related to a variation in the coordination number of the Ni(II) from octahedral to tetrahedral geometries depending on the hydrated  $([\text{NiCl}_2O)_6]^{2^+})$  or dehydrated  $([\text{NiCl}_4]^2)$  state. Thus, the present work demonstrated the suitability of UV curable hybrid materials for smart and multifunctional coatings processable by additive manufacturing technologies, paving the way to cost-effective sensing coatings with a low carbon footprint due to it solvent-less process.

BCMATERIALS | ANNUAL REPORT 2021

## **MULTIFUNCTIONAL HARD COATINGS BASED ON CRNX FOR TEMPERATURE** SENSING APPLICATIONS

Armando Ferreira, Marcio A. Correa, João Paulo Silva, Daniela Correia, Senentxu Lanceros-Mendez and Filipe Vaz. Sensors and Actuators, A: Physical 329,112794

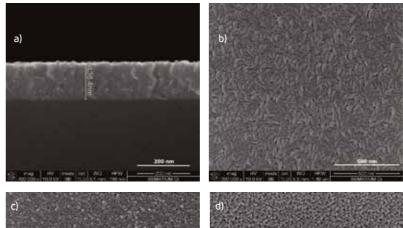
This work presents a multifunctional coating system, CrNx, with temperature sensing capability. A systematic study of the thermo-resistive effect of nanostructured chromium nitride (CrNx) thin films prepared by reactive magnetron sputtering with a negative temperature coefficient of resistance (TCR) has been carried out. The present results open new technological possibilities for the application of CrNx coatings as resistive temperature detection systems.

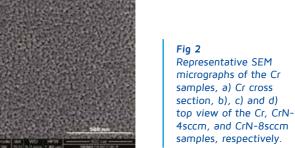


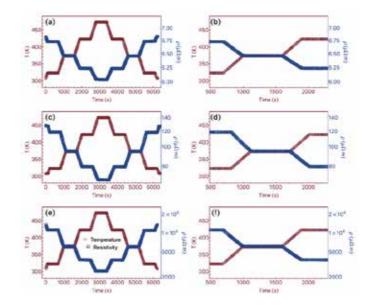
This paper reports on the preparation of a multifunctional coating system, CrNx, with temperature sensing capability. A systematic study of the thermo-resistive effect of chromium nitride (CrNx) thin films with a negative temperature coefficient of resistance (TCR) has been carried out. The CrNx nanostructures were grown by reactive magnetron sputtering under distinct Ar+N2 conditions. To confer a zigzag columnar morphology to the CrNx we explored the oblique angle deposition technique. The structural properties of CrNx coatings for resistive temperature detector have been studied through X-ray diffraction and Scanning Electron Microscopy. The thermo-

Fig 1 Schematic diagram of the Oblique Angle Deposition set-up.  $\alpha$  is the applied angle of the substrate relative to the Cr particle flux,  $\beta$  is the column growth angle, and  $\Omega$  is the angular direction.

resistive response was evaluated by measuring the electrical resistivity as a function of temperature by the two-point method. The results observed for the CrNx films produced with N2 flux between 4 and 8 sccm present a stable and negative TCR. Values of -9.17x10-4, -5.31x10-3, and -1.476x10-2 were observed for the films grown with 4, 6, and 8 sccm, respectively. The grain-boundary was used to theoretically describe our results. The results open new technological possibilities for the application (RTD) systems.







#### Fig 3

Temperature dependent electrical resistivity over time. (a) Results for the N2 flux of 4 sccm. (b) Zoomed range of the sample deposited with a N2 flux of 4 sccm. (c) N2 flux of 6 sccm. (d) Zoomed curves for N2 flux of 6 sccm. (e) Results for the samples deposited with N2 flux of 8 sccm. (f) Zommed curves for N2 flux of 8 sccm



# RESEARCH LINE 4 ADVANCED FUNCTIONAL MATERIALS

This research line is focussed on the development and implementation of advanced functional materials for specific technological needs in order to address relevant society concerns. Functional materials are of critical importance in materials for energy such as electro- and magnetocaloric materials, for energy storage and for solar energy harvesting. In this regard, BCMaterials covers the synthesis, development and scale-up of a wide range of materials for fuel cells and batteries, photovoltaic materials, permanent magnets, sensors and biosensors. Membrane technologies for environmental monitoring and remediation are also being developed.

62

## P-GaN-SUBSTRATE SPROUTED GIANT PURE NEGATIVE ELECTROCALORIC EFFECT IN Mn-DOPED Pb(Zr<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>3</sub> THIN FILM WITH A SUPER-BROAD OPERATIONAL TEMPERATURE

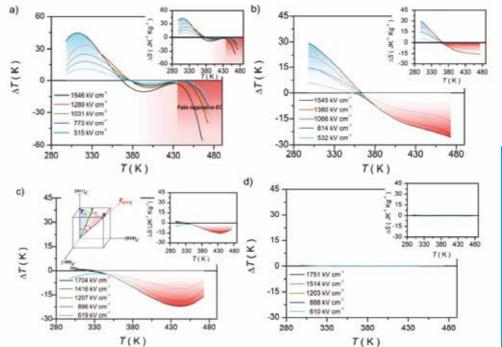
RANGE

Biaolin Peng, Tingting Wang, Laijun Liu, Xue Chen, Jingfeng Li, Qi Zhang, Rusen Yang, Wenhong Sun, Zhong Lin Wang. Nano Energy, 86,106059.

Ferroelectric thin films simultaneously with large positive and negative electrocaloric (EC) effects are attractive to modern electronics, communications, etc. This work demonstrated that a giant positive EC effect of Mndoped Pb(Zr<sub>o</sub>,Ti<sub>o</sub>)O, thin film can be tailored into a pure negative EC effect with a recorded super-broad operational temperature range (~ 150 K). An electric-field induced structural phase transition plays a key role in obtaining the pure negative EC effect. It is concluded that ferroelectric thin film can be used to generate a pure negative EC effect in a broad temperature range.

Destruction of the ozone laver in the Earth's atmosphere caused by the use of refrigerant (such as Freon) has intensified the global warming effect. Emission-free and environmentally friendly solidstate refrigeration devices with a high-coolingperformance via electrocaloric (EC) effect should be very welcomed in many fields, such as modern electronics, communications, medical and military, etc. There are two key challenges for the practical application of the EC refrigeration technology. The first one is to design a more suitable cooling system to ensure a larger temperature span and cooling effect. The second one is to find a more suitable EC material, both to ensure excellent refrigeration effect, and to ensure cheap and easy to obtain. It is recently suggested that combining both positive and negative EC effects in one cooling cycle can complete the cooling process in one step with a sustainably applied electric field in the cooling process, which would exhibit a higher EC effect than the use of a single positive or negative EC effect.

In this work, a giant positive EC effect ( $T_{max} \sim 44.5$  K and max ~ - 42.8 J K<sup>-1</sup> kg<sup>-1</sup>) around room temperature can be easily tailored into a giant negative EC effect ( $T_{max} \sim -23.5$  K and  $S_{max} \sim 16.3$  J K<sup>-1</sup> kg<sup>-1</sup>) with a recorded super-broad operational temperature range (~ 150 K) which is comparable to the best negative EC effects reported so far by directly depositing the Mn-doped Pb(Zr<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>3</sub> (PZT) on the p-GaN substrate rather than on the Pt/TiO<sub>x</sub>/SiO<sub>2</sub>/Si substrate using a sol-gel method. Under the sprouting of the p-GaN-substrate, the electric field-induced structural-phase-transition (nano-scaled tetragonal phase to rhombohedral phase) plays a key role on the recorded pure



b) Calun nanodomians DI LING domians <u>5 mm</u>

negative EC effect with a super-broad operational temperature range. It is proposed that directly depositing thin film on p-GaN-substrate that has a high conductivity can be used as a simpleuniversal strategy to obtain large negative EC effect in a broad operational temperature range. Next-generation refrigeration devices with high cooling performance are hopefully to be realized via the strategy of combining both the negative and positive EC effects.

Fig 1  $\Delta T$  of thin films at selected temperatures. (a), (b), (c) and (d) on the Pt/TiO\_/SiO\_/ Si(100), LaNiÔ\_/n-Si(100), p-GaN (n = 4)× 1017), and n-Si(100) substrates, respectively. Insets in (a), (b), (c) and (d):  $\Delta S$  (right lower corners). Inset (left upper corner) in (c): electric-field induced phase transition model (T to R).

Fig 2 Mechanism of the negative EC effects of thin film deposited on the p-GaN substrate (n = 4 × 1017), (a) Atomscale HRTEM image of the interface between the PZT-Mn and the p-GaN substrate (n = 4 × 1017). (b) Atomscale HRTEM image of the interface between the PZT-Mn and the n-GaN substrate (n = 5 × 1018).

## DENITROGENATION PROCESS IN THMN<sub>12</sub> NITRIDE BY IN SITU NEUTRON POWDER DIFFRACTION

A. Aubert, I. Puente-Orench, J.M. Porro, S. Luca, J.S. Garitaonaindia, J.M. Barandiaran, G.C. Hadjipanayis. Physical Review Materials 5 (1) 014415.

**-**

ThMn<sub>12</sub> nitrides are good candidates for high performance permanent magnets. A key challenge is to transfer the good properties of the powder into a useful bulk magnet. In this study, we investigate the magnetic and structural stability of the  $(Nd_{0.75}, Pr_{0.25})_{1.2}Fe_{10.5}Mo_{1.5}N_x$  compound (x = 0 and 0.85) as function of temperature by means of neutron powder diffraction. A decomposition takes place mainly via the formation of the  $\alpha$ -(Fe,Mo) phase, whereas the nitrogen remains stable in the lattice and the magnetic properties of the nitrides are maintained after the thermal treatments up to 900 K. This study demonstrates that the ThMn<sub>12</sub> nitrides with the Mo stabilizing element offer good prospects for a bulk magnet provided an adequate processing route is found.

The critical and strategic character of rare earth (RE) elements as raw materials has motivated a renewed interest in the search for rare-earth-lean and rare-earth-free hard magnetic materials for permanent magnet applications. In this regard, Nd-based 1:12 structures have a weak net anisotropy field (<1 T) at room temperature as it is predominantly determined by the Fe-sublattice anisotropy. However, adding an interstitial light element (e.g., N or C) modifies the unit cell without changing the symmetry of the parent compound; this changes the Fe-Fe interaction and establishes a strong positive crystal field coefficient  $A_{20}$  at the Nd(2a) site, which is effective to create a large uniaxial magnetic anisotropy. Even though powder nitrides have recently shown success in obtaining hard magnetic properties, one of the remaining challenges is to transfer the good properties of the powder into a useful bulk magnet. One weakness of ThMn<sub>12</sub> nitrides is their tendency to disproportionate or eventually denitrogenate at temperatures required for sintering. After a

certain temperature is reached, one can expect an irreversible decomposition into other stable phases, like -Fe or NdN, which limits the possibility of converting the hard magnetic properties of the nitrogenated powder into a dense permanent magnet. Thus, understanding the thermostability of this phase is of key importance.

In the present study, we investigate the denitrogenation and decomposition process of  $(Nd_{0.75}, Pr_{0.25})_{1.2}Fe_{10.5}Mo_{1.5}N_x$  with a ThMn<sub>12</sub> structure. We first investigate the structural and magnetic properties of the parent compound and its nitride to ensure that appropriate nitrogenation occurred. Then, we employed neutron powder diffraction to study the temperature-induced structural changes up to 1100 K of both compounds. The nitrides show excellent phase stability up to high temperatures (<930 K), which is attributed to an appropriate nitrogenation process and the use of Mo as a stabilizing element. The heating of the nitrides shows that the denitrogenation process is different from the nitrogenation, as the atomic site

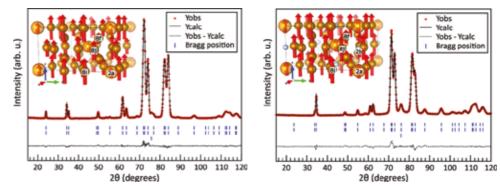


Fig 1 Plot of the Rietveld refinement of the powder neutron diffraction pattern recorded at room temperature for  $(Nd_{0.75'}, Pr_{0.25})_{1.2}Fe_{10.5}Mo_{1.5}(left)$  and the  $(Nd_{0.75'}, Pr_{0.25})_{1.2}Fe_{10.5}Mo_{1.5}N_{0.85}$  (right). The red points are experimental data and the black line corresponds to the Rietveld fit. The first and second blue rows of the Bragg peak positions refer to the nuclear and magnetic contributions of the ThMn<sub>12</sub>, respectively. The third blue row refers to the nuclear contribution of  $\alpha$ -(Fe,Mo) phase. The dashed line is the difference between the observed and calculated patterns. The inset shows the ThMn<sub>12</sub> crystal structure with the atomic magnetic moments.

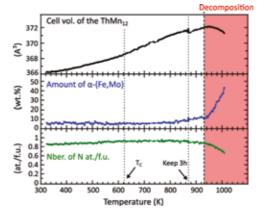


Fig 2 Thermal evolution of the cell volume of the ThMn<sub>12</sub> (top, black line); mass fraction of the secondary phase  $\alpha$ -(Fe,Mo) (center, blue line), and occupancy of nitrogen atoms (bottom, green line) obtained by Rietveld refinements of the (Nd<sub>0.75</sub>, Pr<sub>0.25</sub>)<sub>1.2</sub>Fe<sub>10.5</sub>Mo<sub>1.5</sub>N<sub>x</sub> neutron diffraction data.

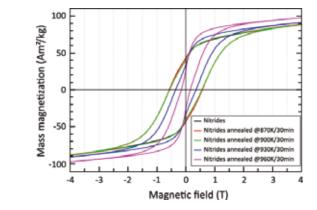


Fig 3 Magnetic hysteresis loops of the nitrides (Nd<sub>0.75'</sub>  $Pr_{0.25}$ )<sub>1.2</sub>Fe<sub>10.5</sub>Mo<sub>1.5</sub>N<sub>x</sub> after being heat treated at different temperatures.

occupancy of the nitrogen in the lattice is stable until approximately 930 K. Above this temperature, the formation of -(Fe,Mo) rapidly increases, which results in the loss of nitrogen. Finally, we show that the magnetic properties of the nitrides are maintained after thermal treatments up to 900 K.

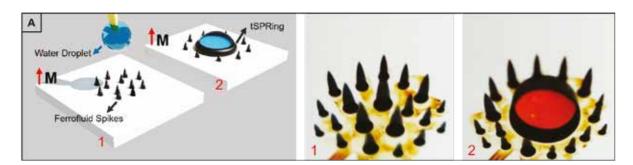
These results offer good prospects for the use of the  $ThMn_{12}$  nitrides as bulk magnets provided an adequate processing route is found.

# RESEARCH LINE 5 MICRO & NANO DEVICES

The multifunctional materials, nanostructures and surfaces being developed are implemented in functional prototypes demonstrating the suitability of the materials for advanced applications. Thus, radiofrequency instrumentation is being implemented for MRI, hyperthermia, and wideband ferromagnetic resonance applications. Force, deformation, magnetic, magnetostrictive and chemical sensors are being produced. In addition, the study and implementation of printed and flexible electronic devices is being used for applications in areas such as wearables, point of care devices, interactive surfaces and structural health monitoring.

## TUNABLE SUPERPARAMAGNETIC **RING (TSPRING) FOR DROPLET MANIPULATION**

Vahid Nasirimarekani, Fernando Benito-Lopez and Lourdes Basabe-Desmonts. Advanced Functional Materials 2021, 31(32), 2100178



#### Fia 1

Cartoon showing the formation of the tSPRING, first a magnetic field over the Ms of the ferrofluid is applied to a layer of ferrofluid deposited over a surface, the instabilities form and then a droplet of water is loaded between the instabilities (Left). Photograph of spike pattern formed by out-of-plane magnetic field induced by a magnet positioned underneath (middle), and photograph of the tSPRing formed around a water droplet, which was pipetted in between the spikes (right)

Droplet manipulation is gaining great interest in various fields, including technological applications and fundamental studies in dynamical systems. The Lab-on-a-chip and microfluidics community is especially interested in the precise handling of small volumes of fluids, droplet microfluidics. An investigation carried out by the Microfluidics Cluster UPV / EHU has found that a superparamagnetic ring forms spontaneously around a drop of water when an oil-based ferrofluid is in contact with the drop under the influence of a magnetic field and varies according to the intensity of the magnetic field that is applied.

A tunable superparamgnetic ring (tSPRing) is spontaneously formed around a water droplet tSPRing and a water droplet, resembles the cupcake when an oil-based ferrofluid is in contact with the droplet under the influence of a magnetic field. The interfacial interaction between both liquids the underside of a substrate. The dimension of the and the soft magnetic characteristics of the ring allows a robust, controllable, and programmable manipulation of the enclosed droplets. The water droplet can be precisely moved by moving the

external magnetic field. The combination of the assembly (Figure 1). This assembly could be formed on top of a substrate, or as a hanging cupcake on ring depends on the volume relationship between the water and the ferrofluid, while its aspect ratio (height to diameter) is related to the magnetic field strength and the field curvature. The ring is a

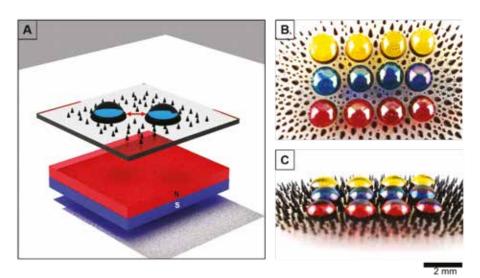


Fig 2 A) Schematic drawing of two drops enclosed in tSPRings. B,C) Photographs of a tSPring enclosed water droplets array on top of a PMMA substrate.

paramagnetic magnet and behaves as an instability staying away from other instabilities at a defined distance. The encloses the water droplets stabilizing them and preventing their mixing (Figure 2). Even when two or more cupcakes are mechanically brought together the water droplets do not mix, because their ferrofluid rings fuse to form a physical isolating barrier. However, the tSPRing is an on-off switchable structure and those droplets can be mixed by turning off the magnetic field. In comparison with other droplet manipulation systems, tSPRing is based on liquid-liquid interfacial interaction. It allows droplet manipulation over wide range of substrates and does not require complex fabrication processes. tSPRing enables a versatile and generic fluidic control platform for droplets

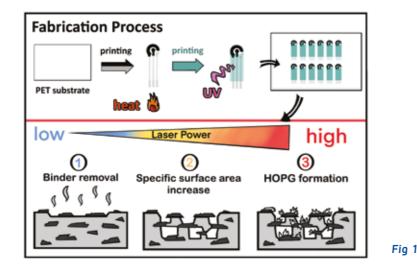
of any size and volume. The fact that both the liquids, the ferrofluid and the water, are immiscible prevents the contamination of the water droplets and allows the easy recovery of its contents. To the best of our knowledge, the use of tSPRing for manipulation of a hanging droplet is the first example of magnetic manipulation of droplets on an upside-down surface, what opens the door to novel applications. Likewise, it provides a new scenario for fundamental studies on oil-water interface since the external magnetic field modifies the natural capillarity wrapping of the water droplet. We conclude that tSPRing constitutes an advantageous new approach for open surface droplet microfluidics.

BCMATERIALS | ANNUAL REPORT 2021

### OUTPUT SAMPLES

## LASER-INDUCED HIGHLY ORIENTED PYROLYTIC GRAPHITE FOR HIGH-PERFORMANCE SCREEN-PRINTED ELECTRODES

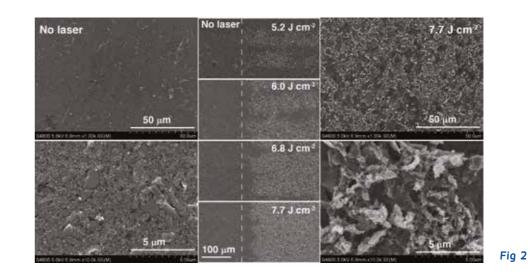
Alejandro .F. Alba, Joseba Totoricaguena-Gorriño, Lía Campos-Arias, Nikola Pe inka, Leire Ruiz-Rubio, José Luis Vilas-Vilela, Senentxu Lanceros-Méndez, F. Javier del Campo. Materials Advances, 2 (18), pp. 5912-5921

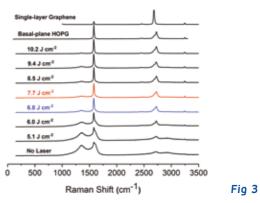


Screen-printed carbon electrodes (SPCEs) are increasing popular in a wide range of applications, from electroanalysis to energy storage and power generation. Highly oriented pyrolytic graphite (HOPG), an ordered form of graphite, displays excellent electrochemical properties, but it has hitherto been unavailable in printable form. In this work, we present a straightforward laser-based process to selectively transform, in ambient conditions, the surface of conventional SPCEs into highly homogeneous HOPG. Mild laser dosing in the range of a few mJ cm<sup>-2</sup> bring three key advantages: surface binder impurities are removed, electron transfer rates are enhanced by orders of magnitude, and electrode surface area is increased up to 5-fold.

The mass fabrication of electrochemical sensors and biosensors, batteries and fuel cells has benefited enormously from screen-printing technologies. Carbon-based materials, particularly graphite, have become dominant due to their excellent balance between suitable electrochemical properties

(chemical inertness, wide accessible potential window and low background currents, among others) and affordable cost. Screen-printed carbon electrodes (SPCE) are mainly based on graphite and amorphous carbon, and one of their main limitations is that, due to their fabrication process,





they display significantly lower electron transfer rates than their counterparts made of bulk carbon material. In addition, the wide variety of commercial pastes available, each with a different composition, results in electrodes of widely different quality and performance. This has led many researchers to investigate various activation protocols covering wet chemistry and dry techniques. Popular examples of these routes are electrochemical methods and oxygen plasma treatments, respectively. However, these methods have limitations in terms of either process throughput or reproducibility, which difficults their up-scaling.

Although laser activation of carbon electrodes has been known for over 20 years, the use of affordable CO<sub>2</sub> laser systems in the activation of carbon electrodes is much more recent, and has led to reports of "laser-induced graphene" and "laser-induced graphitization". In this work, we studied the effect of mild laser irradiation on screen-printed graphite structures and made some exciting discoveries. First, changes in appearance and surface morphology were first observed (Figure

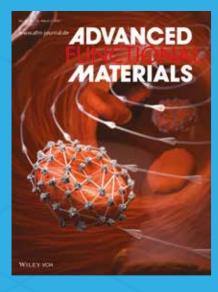
1; sem images). Raman spectroscopy (Figure 2) showed that the resulting surfaces presented a form of highly oriented pyrolytic graphite, and ruled out the formation of graphene. This transformation was then confirmed by cyclic voltammetry of benchmark redox systems (Figure 3), which showed significant increases in electron transfer rates for both inner and outer-sphere systems.

The results are highly significant due to the simplicity, selectivity affordability and scalability of the process, which is extremely energy efficient. Because the transformation only occurs in the irradiated areas and the  $CO_2$  laser spot size is in the order of 100 µm, it is possible to treat only the desired electrode regions, leaving the rest of the device surface untouched. The results demonstrate the selective transformation of conventional screen-printed carbon electrodes into a much more active graphite form, which can be of great interest in electroanalysis and energy storage applications.

# JOURNAL COVERS

Research and innovation performed at BCMaterials has been hinglighted in some of the most prestigious and influential international scientific journlas. This is a selection of some of our journal covers published in 2021.

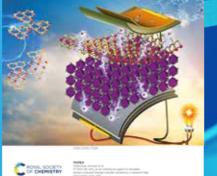




## Advanced Functional Materials

Red Blood Cell Superstructures: Modular Assembly of Red Blood Cell Superstructures from Metal–Organic Framework Nanoparticle-Based Building Blocks Native red blood cells (RBCs) are assembled within and protected by functional exoskeletons of interlinked MOF nanoparticles. The armored RBCs preserve the original properties of RBCs (oxygen storage) and inherit the exogenous properties of functionalizing nanoparticles. Their synthesis is generalizable and creates novel hybrid biomaterials for endogenous in vivo sensing and biorthogonal imaging applications.





## Journal of Materials Chemistry C

1T-Rich 2D-WS 2 as an interfacial agent to escalate photo-induced charge transfer dynamics in dopant-free perovskite solar cells

The deficiency in the photo-induced charge transfer dynamics at the perovskite-charge transport layer interfaces due to depleted energy alignment and surface traps impedes perovskite solar cells performance improvement. Herein, we suggest a simplistic interfacial engineering protocol to overcome current challenges.



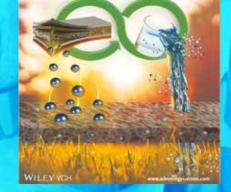


## Materials Advances

Laser-induced highly oriented pyrolytic graphite for high-performance screen-printed electrodes In this work, we present a straightforward laser-

based process to selectively transform, in ambient conditions, the surface of conventional screen-printed carbon electrodes into highly homogeneous highly oriented pyrolytic graphite. Energy densities between 6.8 and 7.7 mJ cm-2 result in a binder-free, highpurityhighly oriented pyrolytic graphite surface with very fast electron transfer rates. Cyclic voltammetry of model systems ferrocyanide, ferrocenecarboxylic acid, dopamine and hydroquinone has been used to determine variations in electrode kinetics. Differential pulse voltammetry has been used to demonstrate the ability of these electrodes to detect dopamine in the presence of an excess amount of ascorbic acid.

#### ADVANCED ENERGY & SUSTAINABILITY RESEARCH



## Advanced Energy & Sustainability Research

Porous Composite Bifunctional Membranes for Lithium-Ion Battery Separator and Photocatalytic Degradation Applications: Toward Multifunctionality for Circular Economy

In the context of circular economy concepts, the use/ re-use of multifunctional materials emerges as a needed approach for a sustainable future. This work reports on the development of hybrid PVDF-TrFE/TiO2 membranes for lithium-ion battery and photocatalytic degradation applications. The membranes are proven to be suitable for both applications and the applicability of the multifunctional membranes in the context of a circular economy and sustainable approaches is also demonstrated.

## SPECIAL ACTION

# **IKUR 2030** ESTRATEGY

IKUR is the Basque strategy promoted by the Education Department of the Basque Government to boost the Scientific Research in specific strategical areas and to position them at international level. BCMaterials is aligned with and committed to contribute to the success of this importat strategic endeavour.

# iXUC estrategia

## STRATEGICAL AREAS

## 

Within this area, BCMaterials will focus on the development of biomimetic active microenviroments based on both multifunctional materials and microfluidic systems.

## QUANTUM TECHNOLOGIES

In this area, BCMaterials will focus its efforts in the areas of single molecular magnets and artificial spin-ice systems.

## **3** | NEUTRIONICS

The strong committment of BCMaterials in the use of neutron sciences for the development of next generation materials will be reflected, within the present framework, in the development of advanced materials for energy storage systems, in improving the understanding of proteinelectroactive scaffolds interactions and in the development of multifunctional hybrid materials.

# 4HIGH PERFORMANCE COMPUTINGAND ARTIFICIAL INTELLIGENCE

High performance computational materials science and artificial intelligence/machine learning approaches will be implemented for the desing of next generation responsive materials and for their implementation into high-end applications.

BCMATERIALS | ANNUAL REPORT 2021

# **BOOKS &** REVIEW PAPERS



Ahmed Esmail Shakan Abdel Salam Hamely Mokhlouf Searathia Lanceron-Mendez fallitori Advances in Nanocomposite

Materials for Environmental and Energy Harvesting Applications

Springer

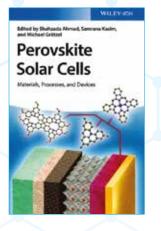
### ADVANCES IN NANOCOMPOSITE MATERIALS FOR ENVIRONMENTAL AND ENERGY HARVESTING APPLICATIONS

Ahmed Ismail Shalan, AbdelSalam Makhlouf, Senentxu Lanceros-Méndez

This book discusses the fundamental properties, synthesis strategies, physical-chemical characterization protocols and applications of recently explored nanocomposite materials in the areas of environmental remediation and energy harvesting.

This book presents a panorama of current research in the field of nanocomposite structures for different applications and assesses the advantages and disadvantages of using different types of nanocomposite in the design of specific products.

The comprehensive chapters explain the relationship between nanocomposite characteristics and the mechanisms related to applications in environmental remediation and harvesting.



#### PEROVSKITE SOLAR CELLS MATERIALS, PROCESSES AND DEVICES

Shahzada Ahmad, Samrana Kazim, Michael Grätzel

This book provides an up-to-date overview of the current state of perovskite solar cell research. Addressing the key areas in the rapidly growing field, this comprehensive volume covers novel materials, advanced theory, modelling and simulation, device physics, new processes, and the critical issue of solar cell stability. Contributions by an international panel of researchers highlight both the opportunities and challenges related to perovskite solar cells while offering detailed insights on topics such as the photon recycling processes, interfacial properties, and charge transfer principles of perovskite-based devices.

#### From Molecules to Frameworks to Superframework Crystals

Zhe Ji, Ralph Freund, Christian S. Diercks, Patrick Hirschle, Omar M. Yaghi, Stefan Wuttke. Advanced Materials 33(42),2103808

## Microfluidics and materials for smart water monitoring: A review

Janire Sáez, Raquel Catalán-Carrio, Róisín M.Owens, Lourdes Basabe-Desmonts, Fernando Benito-Lopez **Analytica Chimica Acta 1186,338392** 

#### Magnetic materials: a journey from finding north to an exciting printed future

K. J. Merazzo, A. C. Lima, M. Rincón-Iglesias, L. C. Fernandes, N. Pereira, S. Lanceros-Mendez and P. Martins
Materials Horizons 8(10), pp. 2654-2684

## Recycling and environmental issues of lithium-ion batteries: Advances, challenges and opportunities

C.M.Costa, J.C.Barbosa, R.Gonçalves. H.Castro. F.J. Del Campo, S.Lanceros-Méndez Energy Storage Materials 37, pp. 433-465

#### Ionic Liquid-Based Materials for Biomedical Applications

Daniela Maria Correia, Liliana Correia Fernandes, Margarida Macedo Fernandes, Bruno Hermenegildo, Rafaela Marques Meira,Clarisse Ribeiro, Sylvie Ribeiro, Javier Reguera, Senentxu Lanceros-Méndez Nanomaterials. 11(9),2401

# **PRIZES** & ACKNOWLEDGEMENTS



## **PRIZE TO THE MOST INNOVATIVE PHD THESIS**

#### Nelson Castro:

"Design, Construction and Validation of a New Generation of Bioreactors for Tissue Engineering Applications"

Zitek Emprendedores Contest



## WORLD'S TOP 2% **MOST INFLUENTIAL SCIENTISTS\***

9 BCMaterials researchers in this annual list published by the Standford University (USA). I attribute my success to this: I never gave or took any excuse.

> Florence Nightingale (1820-1910)





Shahzada Ahmad



Koro de la Caba







Qi Zhang



Erlantz Lizundia



## 3<sup>RD</sup> PRIZE TO THE **BEST POSTERS**

Paula Glez. Saiz: "Desarrollo e impartición de una actividad STEM englobada en el marco de la Agenda 2030"

#### LatinXChem poster contest

DESARROLLO E IMPARTICIÓN DE UNA ACTIVIDAD STEM ENGLOBADA En el harco de la Agenda 2030 Paula G. Saiz 1 DOLATANTE D

**iji** 



Stefan Wuttke





Pedro Guerrero

BCMATERIALS | ANNUAL REPORT 2021

Verónica Palomares

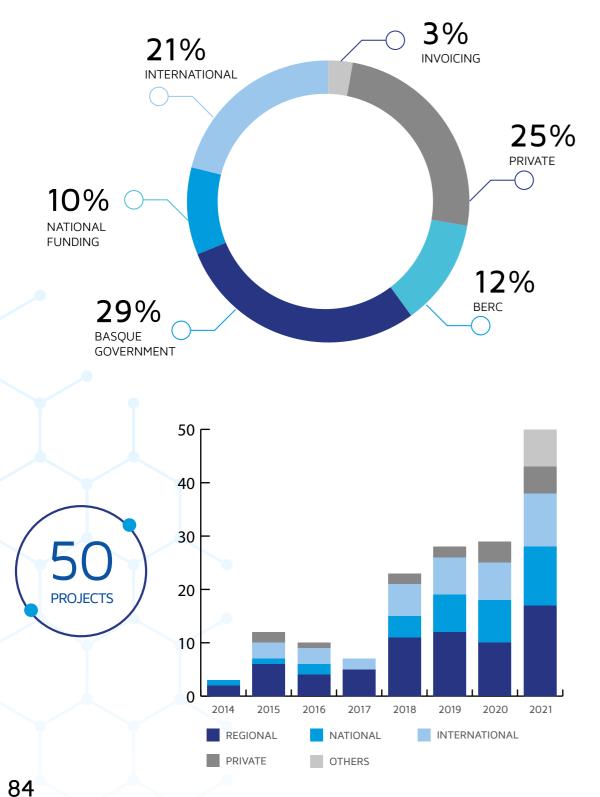


# FOUNDING SOURCES & RESEARCH PROJECTS

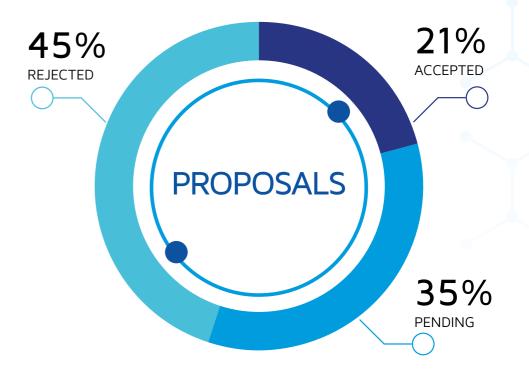
Research projects represent the core of our activities as, most often in collaborative endeavours, set as specific framework for scientific or technological advances. Research projects represent also timely innovations for the generation and knowledge and technology transfer for the benefit of society.



# FOUNDING SOURCES **& RESEARCH PROJECTS**







#### I FINANCIAL BODIES



# **BASQUE** RESEARCH PROJECTS

CARNK Inmunoterapia con CAR-NKs: nuevo tratamiento dirigido contra cáncer hematológico refractario EJ/GV, ELKARTEK Tipo 1 KK-2020/00068 2020-2021

MMMFAVIND Materiales magnetoactivos multifuncionales para fabricación avanzada e industria inteligente EJ/GV, ELKARTEK Tipo 1 KK-2020/00099 2020-2021

ENSOL2 Desarrollo de tecnologías fotovoltaicas avanzadas EJ/GV, ELKARTEK Tipo 1 KK-2020/00077 2020-2021

INTOOL2 Herramientas de corte inteligentes sensorizadas mediante recubrimientos funcionales EJ/GV, ELKARTEK Tipo 1 KK-2020/00103 2020-2021

FRONTIERS 2020 Superficies multifuncionales en la frontera del conocimiento EJ/GV, ELKARTEK Tipo 1 KK-2020/00108 2020-2021

IDEA2 Investigación y Desarrollo en Electrónica Aditiva 3D Impresión e Integración EJ/GV, ELKARTEK Tipo 1 KK-2021/00040 2021-2022

UIIOT Microtecnologías como motor de desarrollo de Microsistemas avanzados integrados EJ/GV, ELKARTEK Tipo 1 KK-2021/00082 2021-2022

BISUM Blo-inspired SUrfaces for Machine elements (BISUM) EJ/GV, ELKARTEK Tipo 1 KK-2021/00089 2021-2022

BIOBASED Investigación en materiales y procesos biobasados para la estrategia de bioeconomía de Euskadi EJ/GV, ELKARTEK Tipo 1 KK-2021/00131 2021-2022

FRONTIERS 2021 Superficies multifuncionales en la frontera del conocimiento EJ/GV, ELKARTEK Tipo 1 KK-2021/00124 2021-2022

MULTIMAG Desarrollo de sensores y actuadores impresos multifuncionales basados en una nueva generación de tintas magneto activas EJ/GV PIBA PI\_2018\_1\_0006 2018-2021

PISCES Printable kesterites solar cells and interface optimization for high performance devices EJ/GV PIBA\_2018\_1\_0087 2018-2021

MAGMETOS Magnetic metamaterials for All Optical Switching phenomena EJ/GV PIBA PI\_2021\_1\_0051 2021-2023

AEROJET AM NEOTECH AM EJ/GV EKIZIEN EC21\_2021\_1\_0016 2021

ALOPRP Creación de apósitos con plasma rico en plaquetas alogénicos para la curación de heridas crónicas EJ/GV Ayudas a Proyectos de Investigación y Desarrollo en Salud Dep. Salud\_2021333057 2021

B&B Bilateral cooperation in advanced materials and applications BCM Bordeaux University Euskampus Cooperacion Bordeaux Euskampus Bordeaux 2021

COVID SARS-CoV-2 prevención, detección y tratamiento. Ikerbasque 2020-2021

# **NATIONAL** PROJECTS

MULTIMART Materiales martensiticos multifuncionales de nueva generación para aplicaciones en energía y actuación RETOS I+D RTI2018-094683-B-C53 2019-2021

MAGTERIA Bacterias magnetotacticas como generadoras de nanoparticulas magneticas modelo y bio-robots para terapias especificas RETOS I+D MAT2017-83631-C3-2-R 2018-2021

BASO Desarrollo de andamiajes biomiméticos activos para el estudio de microentorno de tumor en osteosarcoma PROYECTOS I+D+I PID2019-106099RB-C43 2020-2023

PARASOL Perovskitas libres de plomo que emplean dicalcogenuro de metales de transición como capas de carga selectiva para la tecnología de células solares de perovskita

RETOS I+D RTI2018-102292-B-I00 2019-2021

ARISE All Inorganic Halide Perovskite Nanocrystals for Thin Film Solar Cells PROYECTOS I+D+I PID2019-111774RB-I00 2020-2023

JUAN DE LA CIERVA FORMACIÓN Ahmed Shalan FJC2018-037717-I 2019-2021

EC-SERS2SOERS Desarrollo de dispositivos para EC-SERS/EC-SOERS PROYECTOS I+D+I PID2020-113154RB-C22 2021-2024

HIERACHMOFS Adsorbentes metal organicos jerarquicos para acondicionamiento de combustibles renovables en pilas de óxido sólido PROYECTOS I+D+I PID2020-115935RB-C42 2021-2024

MTBOTS Guiado y control de bacterias magnetotácticas para terapias del cancer PROYECTOS I+D+I PID2020-115704RB-C32 2021-2024 PINCHE Promoting INternational Collaboration for Horizon Europe framework programme Europa Investigacion EIN2020-112406 2020-2022

BIDEKO Biodegradable and compostable batteries for precision agriculture and decentralized energy systems Lineas Estratégicas PLEC2021-007801 2021-2023

SOLARSENIC Planta piloto del sistema de tratamiento de aguas para la remoción de arsénico mediante nanomateriales y energía solar, SolArsenic, validado en condiciones reales Fondo Fomento Chile IT 1910006 2021-2023

# EUROPEAN AND INTERNATIONAL PROJECTS

# **PRIVATE** PROJECTS

WEARPLEX Wearable multiplexed biomedical electrodes H2020-ICT-2018-2 2019-2021

MOLEMAT Molecularly Engineered Materials and process for Perovskite solar cell technology ERC-COG 2017-2022

MULTIFUN Enabling multi-functional performance through multi-material additive manufacturing H2020-NMBP-2018 2020-2023

INDESMOF International Network on Ionic Liquid Deep Eutectic Solvent Based Metal Organic Frameworks Mixed Matrix Membranes. H2020-MSCA-RISE-2017 2018-2021

SMILIES Two-dimensional Transition Metal Dichalcogenides as Charge Transporting Layers for High Efficient Perovskite Solar Cells H2020-MSCA-IF-2019 2020-2023

ANIMOC Directional Assembly of Emergent Luminescent and Anisotropic d10 Coinage Metal Organic Chalcogenolate Nanomaterials for Fabrication of Pressure Sensitive Devices H2020-MSCA-IF-2020 2021-2022

ROCHE Multilayer approach for solid-state batteries H2020-MSCA-GF-2020 2022-2025

4AIRCRAFT Air Carbon Recycling for Aviation Fuel Technology H2020-LC-SC3-2020 2021-2025

SOLARSENIC CHILE "Planta piloto del sistema de tratamiento de aguas para la remoción de arsénico mediante nanomateriales y energía solar, SolArsenic, validado en condiciones reales" Fondo Fomento Chile IT 1910006 2020-2021

UNESCO Mine tailing revalorization IGCP 682: Mine Tailing Revalorization DYNASOL Evaluación de copolímeros basados en estireno y butadieno para aplicaciones avanzadas en sensores y actuadores y baterias recargables ion-litio DYNASOL 2019-2021

E-POLYMER Nuevos grados de abs sus copolímeros y blends termoplasticos con funcionalidades avanzadas para automocion e-mobility ELIX POLYMERS 2020-2023

SERCON Dispositivo de medida y seguridad para sistemas de construcción avanzados ULMA 2020-2021

FLAT-LIT Desarrollo de tinta electroluminiscente imprimible, termoconformable e inyectable WALTER PACK 2019-2021

WIND2GRID Investigación aplicada a subestaciones flotantes para eólica offshore VIUDA DE SAINZ 2020-2021









# RESEARCH NETWORK







ARGELIA • ARGENTINE • AUSTRALIA • AUSTRIA • BELGIUM • BRASIL • CANADA • CHILE • CHINA • COLOMBIA • CZECH REPUBLIC • DENMARK • EGYPTFINLAND • FRANCE • GERMANY • GREECE • INDIA • IRAN • IRELAND • ITALY • JAPAN • MALAYSIA MOROCCO • NORWAY • PAKISTAN • POLAND • PORTUGAL • RUSSIA • SERBIA • SLOVAKIA • SAUDI ARABIA • SWEDEN • SWITZERLAND • THAILAND • TURKEY • UNITED KINGDOM • UKRAINE • USA • VIETNAM

# TRAINING ACTIVITIES

As a research center of excellence, BCMaterials is committed, mostly together with the UPV/EHU but also with other regional, national and international institutions, with the training of the next generation of scientist. This is our duty, but mostly our conviction and pleasure. We offer our expertise, laboratories and human resources to motivate, guide and advise the next generation of scientist in all our areas of expertise. Thus, BCMaterials offers a complete PhD program to graduate students from all around the world who wish to start a research career in a materials science-related field at a top international research institution. BCMaterials collaborate with various official master and graduate programs, and we offer different internship possibilities.

That Spinner St

mant

## 9 PhD Defended

#### 1. ALAZNE GALDAMES

REMEDIACIÓN DE CONTAMINANTES PERSISTENTES MEDIANTE MÉTODOS HÍBRIDOS

#### 2. ENRIQUE AZUAJE

COMBINED MICROPATTERN OF CELLS, BIOSENSORS AND NANOMATERIALS: TOWARDS THE INTEGRATION OF CELL MONITORING MICROSYSTEMS

#### 3. SHEILA MAÍZ FERNÁNDEZ

INJECTABLE 4D HYDROGELS FOR APPLICATION IN REGENERATIVE MEDICINE

#### 4. MAITE GARCÍA

MATERIALS SCIENCE AND MICROFABRICATION: KEY TOOLS TO DEVELOP MICROSYSTEMS FOR CHEMICAL AND CELLULAR MONITORING

5. VAHID NASIRIMAREKANI OPEN SURFACE ACTIVE AND PASIVE MAGNETIC DIGITAL MICROFLUIDICS

#### 6. AITOR SAN FRANCISCO LASA

MARCO PARA EL LCA EN PRODUCTOS REMANUFACTURADOS Y ESTUDIO COMPARATIVO DE IMPACTO AMBIENTAL ENTRE SERVOMOTORES DE NUEVA FABRICACIÓN Y SERVOMOTORES REMANUFACTURADOS

#### 7. JOSE RAMON DIOS

COMPOSITES POLIMÉRICOS CONDUCTORES Y PIEZORRESISTIVOS INTEGRADOS MEDIANTE PROCESOS DE FABRICACIÓN AVANZADA

8. BRUNA F. GONÇALVES NOVEL PRINTABLE PHOTOVOLTAIC SYSTEMS BASED ON CU(IN,GA)SE2 CHALCOPYRITE

#### 9. AJITH KULARATHNA ALULHARE GEDARA

VALIDATION OF INNOVATIVE BINDER SOLUTION FOR WOODEN CIRCULAR DESIGNED PRODUCTS



## 18 Master Theses

## MASTER SCHOLARSHIPS

BCMaterials offers Master Scholarships to perform research in areas as diverse and challenging as materials for sensors and actuators, which are critical for the Internet of Things and Industry 4.0; materials for advanced biological and biomedical applications; materials for energy (both generation and storage) or materials for environmental monitoring and remediation.



## Master in New Materials

Its objective is to provide a solid training in the most current methodologies for the synthesis, characterization, properties and applications of new materials, in fields as diverse as biomaterials, nanomaterials, intelligent materials, materials for energy, electronics, catalysis, etc.





### Master in Environmental Contamination and Toxicology

The master will train the students as a professionals in the biological assessment of the health of ecosystem, both marine and fresh water, and terrestrial.



### Master in Biomedical Research

The master offers updated training on the molecular, cellular and physiological mechanisms involved in the development of the disease, necessary to carry out research that leads to the achievement of valid results and conclusions on topics of biosanitary interest.



## INNOVATION ACTION

# | **BIOENCE** | SPIN-OFF

In 2020 BCMaterials, together with the University of Minho, Portugal, issued a patent for a new modular magnetically driven bioreactor for cellular cultures and biomedical applications.

The year 2021 saw the birth of Bionce,

a spin-off of BCMaterials for the development and commercialization of the bioreactors.

This new device, called BioDyce, strongly differ from the ones in the market as they have been especially designed for smart & active scaffolds for localized dynamic stimuli, where the scaffold itself works not only as the support structure but also as an actuator considering the electroactive nature (e.g., piezoelectricity) of different the natural tissues. Areas of application include:

 Testing implant biomaterials.
 Determine the effect of drugs and molecules in physiologically relevant conditions,

3.Expanding patient-derived cells under conditions that mimic the in-vivo tissue microenvironment, promoting also cell differentiation and proliferation

Karla Merazzo and Nelson Castro, BCMaterials, researchers and founders of Bioence, along with Ricardo Pereira, at the B-Venture event (Bilbao, 19-20 October 2021)





BioDyce provides integrated bioreactor solutions for cell culture integrating magnetic and/or electrical stimuli. Further, the systems can be equipped with peripheral modules, to expand their active performance, designed especially for smart scaffolds as active actuators. Thus, scaffolds may act as static or dynamic supports for the cells allowing to provide a variety of highly controlled dynamic stimulations. With this approach, BioDyce improves cellular proliferation and differentiation by mimicking the human body.



A spin-off by:





Universidade do Minho

Funding programs of:







BCMATERIALS | ANNUAL REPORT 2021

# 03 FACILITIES & SERVICES

As a research center of excellence, BCMaterials runs advanced infrastructures for materials synthesis, processing, characterization and integration into proofof-concepts devices. Those facilities are open to all our collaborators and services are also provided whenever we can be useful to the scientific, technological or industrial sectors.

# | OUR | **LABS**

In 2021 BCMaterials undertook a major expansion of its research facilities.Six new laboratories were implemented that will be fully operational in 2022. This substantial increase is consistent with the growth experienced by the center.

With the implementation of these new laboratories, BCMaterials fulfills two important objectives: on the one hand, to have complete and hing-level facilities to carry out its research and, on the other, to increase its catalog of laboratory services to external agents, offering advanced equipments and high-level support.



1	Optics and Optoelectronics	6	Multifunctional Nanochemistry
2	Additive Manufacturing	7	Electricity and Electronics
3	Biomaterials and Biomedicine	8	Metallurgy and Ceramics
4	Environmental Materials and Processes	9	Materials for Energy
5	Advanced Materials and Thin Films	10	Multifunctional Materials Synthesis

## Materials Synthesis

Synthesis of advanced and multifunctional materials is one of the cornerstones of materials innovations. State of art facilities for chemical and physical synthesis of materials are available at different laboratories of BCMaterials. We design, synthesize and modify organic and inorganic, crystalline and amorphous Mesoporous materials, materials. nanoparticles, metallic, ceramic and polymer materials are synthesized with tailor made properties and functionalities.

#### Methods available

Among many others, our labs offer the possibility to use:

- Hydrothermal synthesis of wide scope of inorganic and hybrid materials and nanoparticles.
- Synthesis of mesoporous materials.
- Synthesis of monocrystalline and amorphous metals, and ceramics. It includes both Synthesis and thermal treatments.
- Synthesis of polymers and hydrogels.
- Floating Zone Optical Furnace.
- Crystal System Corp./ FZ-T-P1200-H-I-S 2013.
- Anton Parr Monowave 400 equipped with autosampler MAS24: High throughput synthesis of nanoparticles.
- Sigma 3-30KS: Centrifuge for isolation of nanoparticles.
- Büchi C-850 FlashPrep: Purification of small molecules.
- Büchi Rotavapor R-300: Distillation of solvents.

#### Some of our **services**

We provide advice and support for the design and synthesis of materials with tailor made properties for specific applications including:

- Tailored physical properties: magnetic, electrical, mechanical or thermal, among others.
- Functional properties: photocatalytic, piezoelectric, magnetostrictive, magnetocaloric, among others.
- Advanced properties: self-healing, electrochromic, thermochromic, among others.



## Materials Procesing

Materials are processed in a variety of shapes and forms either to explore their intrinsic properties, to tune them and/or to make them compatible with a variety of applications. From bulk materials to thin-films, from single phase to hybrid materials and composites, materials are processed in our laboratories.

22922222

#### Methods available

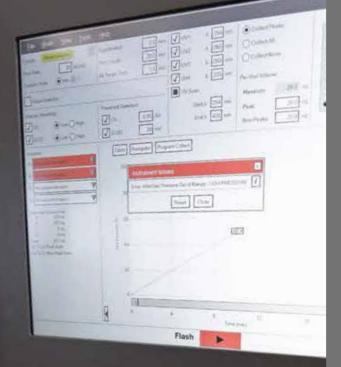
Among many others, our labs offer the possibility to use:

- Design and processing of composite polymer-filler materials.
- Design and processing of inks for screen, ink-jet and direct write printing.
- Processing of thin films by physical and chemical deposition techniques.
- Processing of materials in the form of filament, wires and films.
- Processing of materials in the form of nano- and micro particles.
- Mill Mini Rotary Tube Furnace.
- Melt Spinner.
- Turbomolecular pumped coater.
- A variety of printing and coating techniques.
- Thermal evaporator.

#### Some of our services

We provide advice and support for the design and processing of materials with tailor made properties for specific applications including:

- Tailored physical properties: magnetic, electrical, mechanical or thermal, among others.
- Functional properties: photocatalytic, piezoelectric, magnetostrictive, magnetocaloric, among others.
- Advanced properties: self-healing, electrochromic, thermochormic, among others.



## Characterization

Materials characterization facilities are covering a wide range of techniques, including structural, morphological, thermal, mechanical, electrical, optical, magnetic and functional, including piezoelectric, magnetrostrictive, electrochemical or the sensing/actuation characteristics of materials against physical or chemical solicitations, among others. Some those characterizations are performed at the general facilities of the UPV/EHU – SGiKER.

#### Methods available

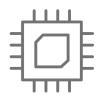
Among many other, our labs offer the possibility to use:

- VSM-Vibrating Sample Magnetometer. Microsense, LLC EZ7-20150305 MicroSense. To measure magnetic moment and coercivity of thin films or studying the magnetic properties of liquids, powders, or bulk samples.
- Perkin Elmer- Diamond DSC N536-0021 (P/N) Melting, Crystallization, Glass Transition, Polymorphism, Purity, Specific Heat, Kinetic Study and Curing Reaction.
- The Ossila Contact Angle Goniometer provides a fast, reliable, and easy method to measure contact angles and surface tensions of liquid droplets.
- Tensile strength tester Shimadzu Instruments AGS-J 500N. High precision and high reliability in material testing Forces are measured with a precision better than ±1% of indicated values, within the range from 1/1 to 1/250 of the rated force.
- Complex impedance equipment Agilent-Keysight E4980. Offering fast measurement speed and outstanding performance at both low and high impedance ranges.
- Custom made photothermal instrument equipped with high power red and near-IR lasers (LUMICS, 672, 784 and 808 nm of 4W of optical power), optical coupling lenses, thermometer based on phototherrmal IR camera (FLIR), thermal based power sensor, and control software.
- The VMP3 is a research-grade multi-channel potentiostat. With its modular chassis design, up to 16 independent potentiostat channels can be installed. The VMP3 can be equipped with additional capabilities, including low current measurement, impedance and high current via plug-in modules.
- Custom made Magnetoelastic measurement system: Automated experimental system for measuring magnetoelastic resonance from 10Hz up to 150 MHz and a field resolution of 8 A/m and maximum magnetic field of 11 kA/m.

#### Some of our services

We provide advice and support for the characterization of a wire variety of materials properties, including the interpretation of the results and the possible ways to tune/ modify those properties. Those characterizations include:

- Structural, morphological, thermal, mechanical, electrical, optical, magnetic, among others.
- Functional, including piezoelectric, magnetrostrictive, electrochemical, among others.





# Prototyping

This facility has been created to strengthen our miniaturisation capabilities. We assess the effect of manufacturing processes on new materials and their properties and to identify the optimum strategies for the design and fabrication of new objects that display the desired functionalities. The goal is to enable the construction of fully-functional demonstrator devices that highlight the value of the new materials.

#### Methods available

Among many others the methods available are:

3D printing (DLP and FDM), CNC milling (Roland MODELA MDX-50), CO2 laser cutting and engraving (Epilog Mini 18 CO2 laser engraver), blade cutting (Roland GS-24 CAMM-1) and thermoforming with suitable CAD/CAM software.

Any combination of processes is possible, including with printing methods such as screen-printing and inkjet-printing.

5 Axes 3D Printed Electronics System. Neotech AMT. PJ15X. Print/Functionalising Tools:

- High Viscosity Print Head Type Piezo Jet
- High viscosity fluid dispense head
- Dual Material (2 Component) Dispense Head
- 3D Printing FDM Module
- Pneumatic Spray Module
- NanoJet (aerosol based print system).

#### Some of our services

Among the services that we can offer we have:

- 3D printing of thermoplastic polymers and functional polymer thermoplastic composites by FDM/FFF.
- 3D printing of functional water- and solvent-based inks by direct ink writing.
- 3D printing of functional UV curable resins by selective laser sintering (SLS).
- 2D printing of functional inks by screen printing and inkjet printing.

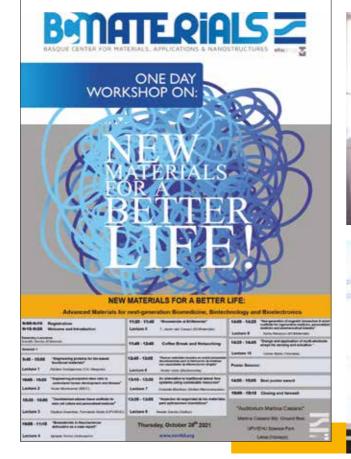
# 04 OUTREACH ACTIVITIES

Working for the benefit of society. Society and fellow scientist must know our motivation, our aims, our way of facing science and technology and our results. Thus, communication activities, from the general to specialized public, represent one of the most rewarding of our activities.



## **9<sup>TH</sup> NM4BL WORKSHOP**

**Advanced Materials** for next-generation Biomedicine, **Biotechnology and Biolectronics** 



BCM

16

UPV

33 OTHERS



SMARTE QIALS 2

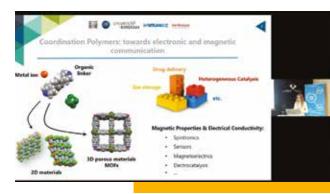


Biomedicine, biotechnology and bioelectronics were the topics of the ninth edition of the 'New Materials for a Better Life' workshop. The program consisted of 10 interesting lectures adressing these challenging and dynamic areas of research that continuously expand knowledge and provide advanced technologies to tackle some of the grand challenges of modern society. NM4BL 2021 allowed to pave the way for collaborative work on the next generation of materials and devices.

83 Achucarro. Basque Center for Neuroscience / 5 Biolan / 4 ATTENDEES CIC Biomagune / 9 ESS Bilbao / 1 Gaiker / 2 IMASMED / 1 IBEC Barcelona / 1 ISS Biodonostia / 2 ISS Biocruces / 1 Mondragon Unibertsitatea / 1 Stanford University 1 Tecnalia / 3 TECNUN Universidad de Ingeniería / 1 Universidade do Minho /1 OTHERS

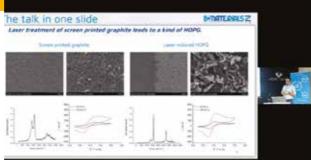


## **B&B2021 SYMPOSYUM**



In a changing world where transformations occur with an unprecented speed, a new generation of materials is playing its part to be a game changer.

Both BCMaterials and the University of Bordeaux pursue similar research goals on understanding and generating knowledge about new materials and applications. This was the starting point of the 'B&B 2021' symposium, a one-day event that consolidated the existing relationships among both institutions and was useful to start new collaborations in key areas of science and technology, in order to join forces in the development of advanced materials and applications.





BCMaterials + University of Bordeaux

**BILATERAL COOPERATION** IN ADVANCED MATERIALS AND APPLICATIONS



#### Prof. S. Lanceros-Mendez

Σ

4

**M** 

U

O

œ Ω

Mr. L. Servant Vice-president for International Networks UBx Introduction – Presentation of participating institutions

#### Dr. R. Fernández de Luis

Mimicking the enzymes to trap metal ions: Encoding the pore space of the MetalOrganic Frameworks with aminoacids

#### Dr. L. Croguennec

A research on materials to meet the increasingly diverse challenges of the electrochemical energy storage.

Prof. F. J. del Campo Laser-induced pyrolytic graphite electrodes for electrochemical sensing and biosensing.

#### Dr. I. Oyarzabal Epelde

High-performance magnetic materials by metal-organic framework engineering

Dr. S. Kazim Emergent semiconducting materials for optoelectronics applications.

Prof. G. Hadziioannou Printed ferrotronics, from materials to devices

ORGANIZERS





SPONSORS



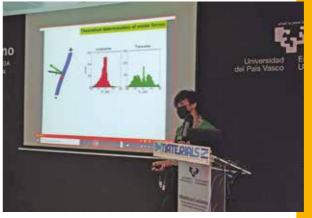




# **SEMINARS** & TALKS

Invited talks and seminars play an essential role in the activity of BCMaterials. Invited talks bring national and international experts to the Center to present and discuss the state of the art of different research areas. Further, our fortnightly seminars are an ideal framework for our researchers to share the progress of their work with their colleagues and develop their communication skills. Communication is essential to share our advances with society through scientific outreach. Because Society needs Science and Science needs Society.









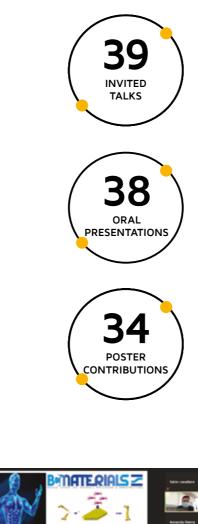


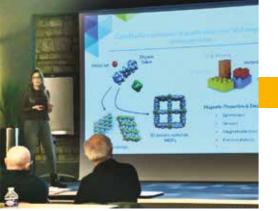




## EXTERNAL DISEMINATION

One of the best indicators of BCMaterials work quality is the number of external disemination activities in which the researchers take part over the year. From poster contributions to oral presentations and talks in meetings, conferences and seminars, all these activities continue shape our international profile and impact.









Remember upon the conduct of each depends the fate of all.

> Alexander the Great (356 BC - 10 June 323 BC)





Virtual Conference on Advances and Challenges in Perovskite and Organic Solar Cells





BCMATERIALS | ANNUAL REPORT 2021

# | SCIENCE | For Society





BCMaterials is an active participatant in the UPV's '**ZIENTZIA ASTEA**' (Science, Technology and Innovation Week), either in on-site or in virtual forms. Videos have been prepared for different experiments aimed for anybody willing to explore the marvels of science with accessible but powerful examples.









As a result of the agreement to promote scientifical outreach with Elhuyar Fundazioa, we participated in the '**ZIENTZIA AZOKA**' initiative evaluating scientific projects of high school students, in live demonstrations of experiments and showing our facilities to the winner projects' authors.



BCMaterials hosts regular SCHOOL VISITS aimed to arise scientifical vocations amon students





#### IKERTZAILEEN EUROPAKO GAUA LA NOCHE EUROPEA INVESTIGADORES E INVESTIGADORAS

The EUROPEAN RESEARCHERS NIGHT, held in Bilbao's city center, is a marvellous opportunity to catch the attention of the youngest, as our researchers could enjoy.

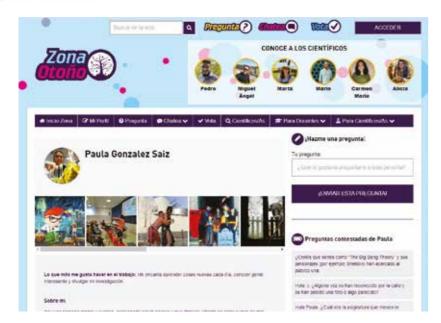








Paula González uploaded her profile at the 'Zona Otoño' section of 'SOMOS CIENTIFICOS Y CIENTÍFICAS. SÁCANOS DE AQUI' website and answered the questions of young students about her research work



# WOMEN IN **SCIENCE** DAY

On the occasion of the celebration of the 'Day of Women and Girls in Science', on February 11th, BCMaterials wanted to show in practice the work of several of its women researchers. How, thanks to their determination, they are contributing to finding scientific solutions that solve challenges in health, energy, environment, industrial production...



BCMaterials @BCMaterials - Feb 11, 2021 Ainara Valverde works with highly porous m Almara Valverde works with highly porous materials able to adsorb multiple kind of compounds. They can be used to adsorb heavy metal ions from wastewater, a growing global concern due to the risk they suppose to the human being. ence #STEM #







The most effective way to do it, is to do it.

> Amelia Earhart (1897 - 1937)







BCMaterials BBCMaterials - Feb 11, 2021 Natalia Rio Is doing her PhD in Magnetic sha Natalia Rio is doing her PhD in Magnetic shape memory alloys. This kind of smart and promising materials are being highly investigated for plenty of applications, among which sensors and accustors outstand.



# **MEDIA IMPACT**



ETB Basque Television unit shooting at BCMaterials headquarters May, 21 2021

> Media are a key player to achieve our goal of transmiting our work at BCMaterials for the benefit of Society. We work for the maximum difusion through both online and offline media. We feel the media as real partners in the challenge to make the public aware of the cutting-edge scientific advances we are working on. like those we take in our Center.



C

0

C

Unibertsitatea

over the borned. We see had to be a subgraph on the first ing the service way in his

00

#### Ander Reizabal: "Gure helburua zetaren multifuntzionaltasuna frogatzea izan da beti"

e patrile ru

latu zen, Pra

and man dut.

iuer masterra eta hurrengo urtean bento, tesia

ieta Taldearekis batera, tesia beraiekin egiteko aukera emas odaterek retat. "Lerear" exirera gauta berruk egiter eta kaster ditut. Batzaetan zerta

Mapping Ignorance Blog

Unibertsitatea.net (UPV-EHU)

OFERTA ESPECIAL: 64

WY multi, Bernelari jamakasko, baosa

July, 20. 2021

July, 19. 2021

mappingignorance

time former -Mimicking nature to face the green environmental

transition F 8+ 1044-100 @ 34/ 16 2021 @ 1 ------

## "Any being if it varies however slightly in any manner prolifable to itself, will have a better

chance of surviving, and thus be naturally selected. From the strong principle of int any selected variety will tend to propagate its new and modified form." - Charles Robert Darwin (1809-1982). The origin of species, 1960

the outset of industrial era, anthropogenic activities have str erre. The heatic pace of technological advances during the XX and XXII centuries and the increa sinar lessa

ESPANHA ONCOLOGIA PANDEMIA CANCRO EUROPA GOVERNO ÚLTIMAS

#### OPINIÃO

P2

#### Veículos elétricos: um desafio e uma oportunidade para Portugal e Europa?

A oportunidade oferecida pela existência de lítio em Portugal apenas poderá ser efetivamente aproveitada fomentando toda a cadeia de valor, desde a extração do minério até à produção de baterias de ião-litio.

IPSHON IMPAR FUGAS PT CINECARTAZ CLUBEP ACADEMIA P



Carlos M. Costa e Senentxu Lanceros-Méndez 17 de Abeil de 2021 5-16.

\*1\_) Dehatisa dis sol ot vehices new tempre vencent a corrida; os usali fortes new tempre



Publico Portuguese Newspaper's digital edition April, 16 2021



Interview Senentxu Lanceros-Mendez Radio Exterior de España





C Receber slertas

Interview Paula González Radio 88 Cantabria





REPORT



www.bcmaterials.net info@bcmaterials.net Bld. Martina Casiano, 3rd. Floor UPV/EHU Science Park Barrio Sarriena s/n 48940 Leioa, Spain