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EDITORIAL

Estimados Lectores de Anales de la Asociación Química Argentina:

En este nuevo número de nuestra revista les presentamos el segundo número temático editado por la División de Jóvenes Profesionales en Química, de la Asociación Química Argentina (DJPQ-AQA).

El objetivo central de la División DJPQ-AQA es conectar a los jóvenes profesionales de la química que se encuentran ejerciendo su profesión en distintas regiones de nuestro país, catalizando el intercambio de ideas y la cooperación entre ellos.

De ese intenso intercambio y cooperación surge el contenido de este segundo volumen dedicado a Materiales Porosos (Porous Materials) cuya Editora Invitada es la Dra. Paula Angelomé, Investigadora Independiente del CONICET perteneciente al Instituto de Nanociencia y Nanotecnología, CONICET-CNEA, quien recientemente ha sido galardonada con el Premio Estímulo de la Academia Nacional de Ciencias Exactas, Físicas y Naturales (ANCEFN).

Esperamos que este nuevo número de Mini-Reviews entusiasme a otros jóvenes profesionales de la química a conectarse con la DJPQ-AQA a través del email *djpq.aqa@gmail.com*.

Dra. Susana Larrondo
Editora en Jefe

NOTE FROM THE EDITOR

Dear Readers of Anales de la Asociación Química Argentina:

In this new issue of our journal we present the second thematic issue edited by the Division of Young Professionals in Chemistry of the Argentine Chemical Association (DJPQ-AQA).

The main objective of the DJP-AQA Division is to connect young Chemists from different regions of our country, encouraging the exchange of ideas and cooperation among them.

From this intense exchange and cooperation emerges the content of this second issue dedicated to Porous Materials whose Guest Editor is Dr. Paula Angelomé, Independent Researcher of CONICET belonging to the Institute of Nanoscience and Nanotechnology, CONICET-CNEA, who recently received the Stimulus Award from the National Academy of Exact, Physical and Natural Sciences (ANCEFN).

We hope that this new issue of Mini-Reviews will encourage other young chemists to connect with the DJPQ-AQA via email *djpq.aqa@gmail.com.*

Dra. Susana Larrondo
Chief Editor

NOTA DEL EDITOR INVITADO

La necesidad de inmovilizar, concentrar y detectar átomos y moléculas, así como de acelerar reacciones químicas ha promovido, en los últimos años, el desarrollo de una gran variedad de materiales porosos. Estos materiales se caracterizan por presentar una gran superficie específica, usualmente con reactividad diferencial, contenida en un volumen pequeño. Así, pueden ser utilizados como adsorbentes, sensores y catalizadores de alta eficiencia, debido a la maximización de las interacciones superficiales. Además, permiten encapsular y proteger una gran variedad de materiales en el interior de sus poros.

Los materiales porosos se preparan a través de diversas estrategias, muchas de las cuales requieren el uso de moldes moleculares o supramoleculares para dar lugar a una porosidad uniforme y controlada. El tamaño de los poros obtenidos define su clasificación: materiales microporosos (dporo < 2 nm), mesoporosos (dporo entre 2 y 50 nm) y macroporosos (dporo > 50 nm). Con un control adecuado de las condiciones de reacción es posible obtener óxidos, materiales híbridos y carbón con porosidad monomodal o jerárquica. A su vez, la combinación de composición química y tamaño de poro define las propiedades fisicoquímicas de los materiales y, por ende, sus potenciales aplicaciones.

Este número especial abarca las diversas temáticas que son atravesadas por el uso de materiales porosos, presentando un panorama de trabajos realizados en la Argentina. Así, K. Sapag y col. discuten las aplicaciones de diversas clases de materiales porosos en energía y medio ambiente y M. Bruno y col. se centran en el uso de carbones porosos en el área de energía. Por su parte, N. Fellenz y col. describen el uso de organosílica como adsorbente de contaminantes inorgánicos y L. Carlos y col. presentan un estudio sobre materiales magnéticos porosos para el tratamiento de aguas. M. V. Lombardo y col., en tanto, introducen una estrategia novedosa para la obtención de materiales mesoporosos multifuncionales: el método de aerosol y sus recientes avances enmarcados en la química verde. G. Gómez se dedica a la descripción de materiales en la frontera con la materia blanda: materiales poliméricos porosos conocidos como MOFs, en este caso con aplicaciones en sensores luminiscentes. Siguiendo esta misma línea, M. M. Zalduendo y col. presentan sensores construidos a partir de películas delgadas de óxidos mesoporosos. Finalmente, el trabajo de S. Alberti se centra en el uso de películas delgadas híbridas para control de transporte a escala molecular.

Dra. Paula C. Angelomé

Editora Invitada

NOTE FROM THE GUEST EDITOR

The need to immobilize, concentrate and detect atoms and molecules, as well as to accelerate chemical reactions has promoted the development of a wide variety of porous materials in recent years. These materials are characterized by a large specific surface, usually with differential reactivity, contained in a small volume. Thus, they can be used as highly efficient adsorbents, sensors and catalysts, due to surface interactions maximization. In addition, they allow encapsulating and protecting a wide variety of materials inside their pores.

Porous materials can be prepared through various strategies, many of which require the use of molecular or supramolecular templates to give rise to uniform and controlled porosity. The obtained pore diameters define its classification: microporous materials (d_{pore} <2 nm), mesoporous materials (d_{pore} between 2 and 50 nm) and macroporous materials (d_{pore}> 50 nm). With adequate control of the reaction conditions, it is possible to obtain oxides, hybrid materials and carbon with monomodal or hierarchical porosity. Thus, the combination of chemical composition and pore size defines the physicochemical properties of the materials and, therefore, their potential applications.

This special issue covers several themes that are traversed by the use of porous materials, presenting an overview of work performed in Argentina. Thus, K. Sapag et al. discuss the applications of various kinds of porous materials in energy and environment and M. Bruno et al. focus on the use of porous carbons in the energy area. N. Fellenz et al. describe the use of organosilicas as adsorbents of inorganic pollutants and L. Carlos et al. present a study on porous magnetic materials for water treatment. Meanwhile, M. V. Lombardo et al. introduce a novel strategy for obtaining multifunctional mesoporous materials: the aerosol route and the recent advances framed in green chemistry. G. Gómez deals with the description of materials at the border with soft matter: porous polymeric materials known as MOFs, in this case with applications as luminescent sensors. Following this same line, M. M. Zalduendo et al. present sensors builts from mesoporous oxides thin films. Finally, the work of S. Alberti focuses on the use of thin hybrid films for transport control at molecular scale.

Dr. Paula C. Angelomé
Guest Editor

Anales de la Asociación Química Argentina

División Jóvenes Profesionales

Mini-Review

MICRO AND MESOPOROUS MATERIALS IN ENERGY AND ENVIRONMENTAL APPLICATIONS

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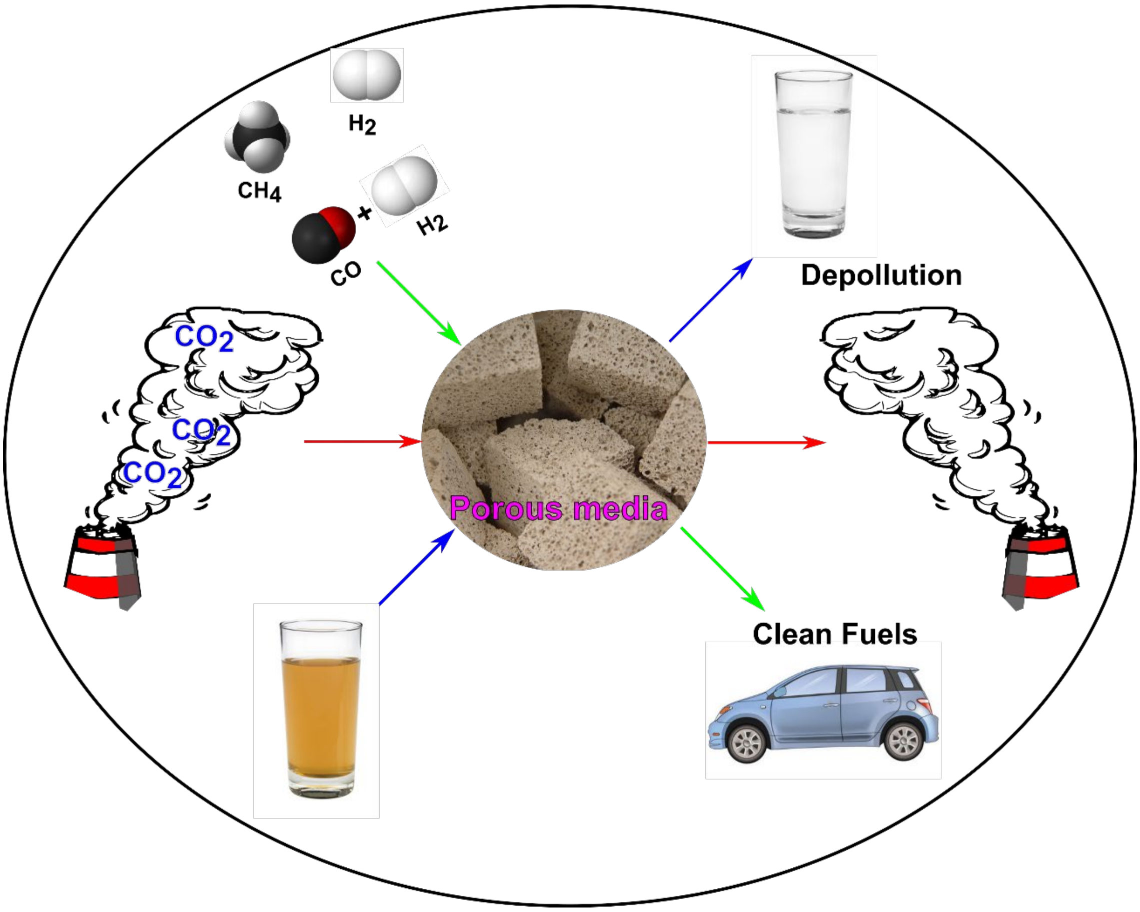
Graphical abstract



Resumen

Los materiales porosos son utilizados en un amplio rango de aplicaciones. En particular, los materiales con tamaño de poro de hasta 100 nm, denominados nanoporosos, son muy interesantes ya que presentan tamaños de poro adecuados para aplicaciones con moléculas involucradas en procesos energéticos y medioambientales. Aquellos materiales con poros menores de 2 nm se denominan microporosos, los que

presentan poros entre 2 y 50 nm, mesoporosos, y los que poseen poros mayores a los 50 nm, macroporosos.
En este trabajo de revisión se presentan algunos materiales estudiados en nuestro laboratorio para aplicaciones en procesos energéticos y medioambientales. El objetivo es mejorar los procesos y encontrar la relación entre las propiedades físicas y químicas con el desempeño en las aplicaciones elegidas. Se reportan resultados acerca de materiales micro-mesoporos, tanto sintéticos como naturales modificados. Estos materiales son utilizados no sólo como adsorbentes en el almacenamiento de H_2, CH_4 y captura de CO_2 a bajas y altas presiones, sino también como soportes de catalizadores en la reacción catalítica de Fischer Tropsch y en procesos de descontaminación de aguas. Los resultados obtenidos muestran que la porosidad juega uno de los roles más significativos, sumado a la morfología y naturaleza química de los materiales. Una de las técnicas más utilizadas para caracterizar materiales porosos, y en la cual nuestro laboratorio es un referente nacional e internacional, es la adsorción de gases, a distintas presiones y temperaturas, por lo que los resultados mostrados tienen como referencia esta técnica, aunque siempre se complementa con otras como XPS, TGA, DTA, TPR, FTIR, RAMAN, NMR, TEM and SEM, entre otras.

Abstract

Porous materials are used in a wide range of applications. Mainly, materials with pore size up to 100 nm, named nanoporous, are interesting because they have suitable pore sizes for applications with molecules involved in energy and environmental processes. Those materials with pores smaller than 2 nm are called microporous, which have pores between 2 and 50 nm, mesoporous and macroporous are those with pores higher than 50 nm. In this review, we present some materials studied in our laboratory in applications in energy and environmental processes. The goal is to improve the processes and find the relationship between the physical and chemical properties with the performance in the chosen applications. Results reported are about synthetic and natural modified materials with pore sizes in the range of micro-mesopores used not only as adsorbents in the storage of H_2, CH_4 and capture of CO_2 at low and high pressures but also as catalyst supports, in the Fischer Tropsch catalytic reaction and aqueous system decontamination. The results obtained show that porosity plays one of the most significant roles, besides the morphology and the chemical nature of the materials. One of the most worldwide used technique to characterize porous materials, and in which our laboratory is a national and international referent, is the adsorption of gases at different pressures and temperatures. Thus, the results have shown this technique as reference, although it is always complemented with other important techniques such as XPS, TGA, DTA, TPR, FTIR, RAMAN, NMR, TEM and SEM among others.

Palabras Clave: *Materiales porosos, adsorción de gases, almacenamiento y captura de gases, adsorción desde solución acuosa, catálisis.*

Keywords: *Porous materials, gas adsorption, storage and capture of gases adsorption from aqueous solution, catalysis.*

Karim Sapag started his teaching career in 1986 as a teaching assistant at Physics Department in the National University of San Luis (UNSL, Argentina). He obtained a Physics Degree (1991) in the UNSL and a PhD (1997) in the Autonomous University of Madrid (Spain). During his doctoral studies, performed under the supervision of Dr. Sagrario Mendioroz at ICP-CSIC, he worked on synthesis and characterization of pillared clays for the Fischer-Tropsch Synthesis. Back in the UNSL, in 1997, he continued with his teaching position and obtained a postdoctoral fellow (1997-1998, CONICET) in the research group of Physical Chemistry of Surfaces (UNSL, San Luis Argentina) under the direction of Prof. Giorgio Zgrablich, working on the development of porous materials to storage natural gas. In 2000 he obtained his first grant and started to develop the Porous Solid Laboratory (LabSoP) that nowadays have theorical, experimental and computational lines of research in the Institute of Applied Physical (INFAP-CONICET). In 2005, he obtained a position as an Adjunct Researcher in the scientific career of CONICET, reaching in 2015 the position of Principal Researcher. In the same year he obtained the position of Full Professor at the UNSL. He has published more than 140 scientific papers, mora than 5 chapters of books, has been in leader position of several national and international research projects and has supervised several postdocs, PhD, MSc and degree students.

Deicy Barrera obtained a Chemical Engineering Degree (2006) from Los Andes University (Colombia). Then, she worked during her Master in Surfaces Sciences and Porous Media in the experimental development of structured porous materials to be used as adsorbents in environmental applications. During her PhD in Physics (2014), under the supervision of Dr. Karim Sapag from National University of San Luis, she developed nanoporous carbons from silica and aluminosilicates templates to be used in the capture and storage of different gases. During this time she realized three internship in Brazilian research groups. In 2014 Dr. Barrera joined the Chemistry Department on Federal University of Minas Gerais (Dr. Rochel Montero Lago, Brasil, 2014) working in applications in antibiotics and hormones adsorption with modified templated carbons. In 2015, she obtained a postdoctoral fellowship from CONICET to work in the Advanced Materials Laboratory of the University of Alicante (Dr. Joaquin Silvestre-Albero, España, 2015) in advanced characterization of porous solids. She came back to the Laboratory of Porous Solids (LabSoP) in the Institute of Applied Physics, National University of San Luis and she holds an assistant researcher from 2017. During 2018 Dr. Barrera obtained a fellowship from Fulbright-CONICET and joined the Dr. Teresa Bandosz research group in the City College of New York, New York. She has published more than 20 scientific papers and has been advisor of thesis of degree, MSc and co-advisor of PhD students.

Anales de la Asociación Química Argentina

División Jóvenes Profesionales

Mini-Review

CARBON NANOMATERIALS: A VERSATILE PLATFORM FOR ENERGY TECHNOLOGIES

Maximiliano Zensich, Angélica M. Baena-Moncada, Luciano Tamborini, Rusbel Coneo Rodríguez, Gabriel A. Planes, Gustavo M. Morales, Diego F. Acevedo, Juan Balach*, Mariano M. Bruno*, Cesar A. Barbero

Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados (IITEMA), Universidad Nacional de Río Cuarto (UNRC)-Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), X5804ZAB, Río Cuarto (Córdoba), Argentina.

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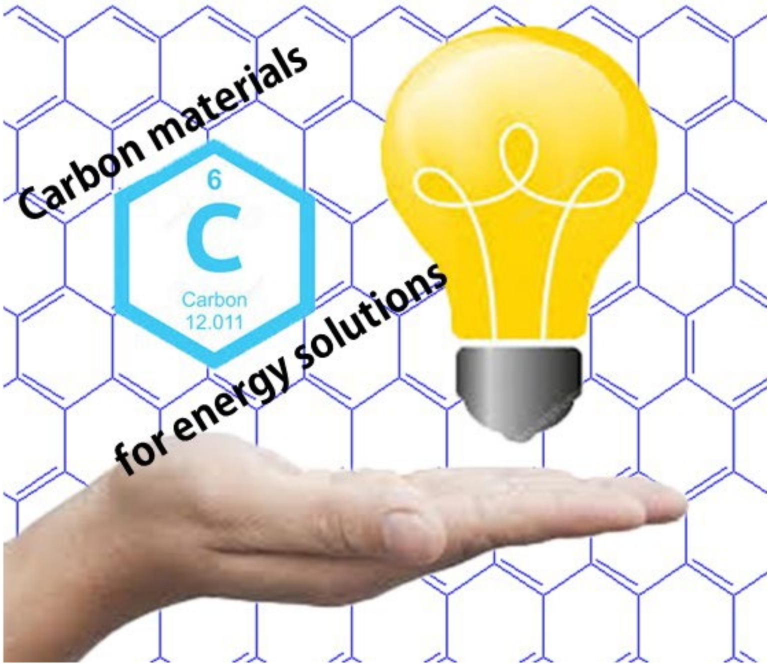
Graphical abstract



Resumen

Los nanomateriales de carbono desempeñan un papel importante en el desarrollo de tecnologías energéticas alternativas limpias y sustentables. Estos materiales son un fascinante tema de estudio, no solo por su buena estabilidad química, mecánica, buena conductividad eléctrica, alta superficie específica y tamaño de poro controlado, sino también porque su estructura porosa puede ser modificada con grupos funcionales para la construcción de sistemas más complejos con un amplio campo de aplicaciones. Además, la química de la superficie, la morfología y las propiedades estructurales de los materiales carbonosos se pueden controlar mediante la elección racional del material precursor de carbón y la metodología de síntesis. Esta revisión destaca el reciente progreso de investigación sobre la síntesis de diferentes carbones porosos y su aplicación en el almacenamiento y la conversión de energía. Particularmente, discutiremos la síntesis y aplicaciones de carbones mesoporosos como recubrimientos funcionales de separadores para baterías de litio-azufre, carbonos nanoestructurados como soportes de catalizador para celdas de combustible y carbones porosos funcionalizados como catalizadores ácidos para la generación de biocombustibles. Concluyendo, se discuten las futuras perspectivas para el desarrollo y aplicación de estos nanomateriales carbonosos.

Abstract

Carbon nanomaterials play an important role in the development of alternative clean and sustainable energy technologies. These materials are a fascinating subject of study themselves, not only for its good chemical and mechanical stability, good electrical conductivity, high specific surface area and controlled pore size, but also because the pore structure can be further modified by active functional groups for the construction of more complex systems with a broad umbrella of applications. Furthermore, the surface chemistry, the morphology and the structural properties of the carbonaceous materials can be controlled by the judicious choice of the carbon precursor material and the route of fabrication. This minireview article spotlights the recent research progress on the synthesis of porous carbon nanomaterials and its application in energy storage and conversion. Particularly, we will discuss the synthesis and applications of mesoporous carbons as functional separator coatings in lithium-sulfur batteries, nanostructured carbons as catalyst supports for fuel cells and functionalized porous carbons as an acid catalyst for biofuel generation. Concluding the minireview, prospects for the future development of practical carbon nanomaterials are discussed.

Palabras Clave: *Carbón, Morfología, Energía, Fabricación, Moldeado.*

Keywords: *Carbon, Morphology, Energy, Fabrication, Template.*

Maximiliano A. Zensich obtained his B.S. in Chemistry in 2014 at the National University of Río Cuarto (UNRC). Currently, he is a Ph.D. student in Chemical Sciences (expected graduation 2019) under the supervision of Prof. G. Morales at the Department of Chemistry, UNRC. He has a financial support from the CONICET Doctoral fellowship program. His research focuses on the development of advanced carbonaceous materials for generation and storage energy applications.

Angélica M. Baena-Moncada has a BSc degree in chemistry from the Universidad del Quíndio, Colombia (2002-2008). She has a PhD in chemical sciences from the Universidad Nacional de Río Cuarto, Argentina (2010-2015). Currently, she works as Full Professor at the Universidad Nacional de Ingeniería. Her research focuses in the structured materials for supercapacitors fuel cells hydrogen production and microbial fuel cells, and the synthesis of nanomaterials for sensors development, green chemistry for gold lixiviation based on electrolytic cells, and the synthesis of hierarchical material.

Luciano H. Tamborini obtained his graduate in Chemical Engineering (2010) and his Ph.D. in Chemistry (2016) at National University of Río Cuarto. He was a CONICET fellow (2011-2016). His research interests focus on the development of advanced catalyst in biodiesel reactions. Dr. Tamborini worked in the area of catalysts for bio-diesel production using porous carbons modified by sulfonic groups as active sites.

Rusbel Coneo Rodríguez was born in Colombia, in 1982. He has a degree in Food Engineering at University of Cartagena (2007). He obtained a M.Sc. in the complex fluid laboratory (University of Huelva – International University of Andalucía). In 2016 he completed his Ph.D. at the National University of Río Cuarto under the supervision of Dr. Gabriel Planes. His Ph.D. thesis was focused in the developed of nano-micro materials for electrochemical sensors. In 2016 he held the position of postdoctoral in the group of Chemistry of Nanomaterials at the CNEA under the supervision of Dr. Paula C. Angelomé, in the study of materials based on mesoporous inorganic oxides and nanoparticles for catalytic applications. Currently, he is permanent researcher of CONICET.

Gabriel Planes is graduated from the National University of Río Cuarto (Argentina) with a Ph.D. (2003). Then, he undertook a postdoctoral fellowship at the University of La Laguna (Tenerife, Spain) in the field of electrocatalysis. Actually, he is Professor at the National University of Río Cuarto and a permanent research of the National Council of Scientific and Technical Research (CONICET). His research focuses on the synthesis of porous carbons and metals and its application for production and storage energy.

Gustavo Marcelo Morales was born in San Basilio, Argentina in 1972. He is Associate Professor of Chemistry at the National University of Río Cuarto (UNRC) and Independent Researcher of the National Research Council of Argentina (CONICET). Gustavo obtained his B.S. in Chemistry in 1997 and then joined to Prof. Cesar Barbero's group where he received his Ph.D. in

Chemical Sciences at the UNRC in 2002. He completed his education as Postdoctoral Research Associate under the supervision of Prof. Luping Yu at the Department of Chemistry, The University of Chicago (2002-2005). His current research interest focus on the study of carbon-based nanomaterials, two-dimensional materials, and the application of scanning probe microscopy techniques to biology.

Diego F. Acevedo obtained his graduate in Chemical Engineering (2000) and his Ph.D. in Chemistry (2006) at National University of Rio Cuarto. He is a Research Professor in the Department of Chemical Engineering at the same university and permanent Research from CONICET. His research interests focus on the development of advanced and functional materials. Dr. Acevedo develops his activities in the field of polymer conductors, studying modifications and applications of them to technological devices. I have also worked with traditional polymers modifying their surface by laser ablation and applying it to the biological and sensor area. He also works in the area of catalysts for both bio diesel (using sulphonated porous carbons) and bioethanol (immobilizing biological catalysts inside hydrogels).

Juan Balach received his bachelors and Ph.D. degrees from National University of Rio Cuarto, Argentina, in 2007 and 2011, respectively. After a postdoctoral research stay (2012) in the Department of Colloid Chemistry at the Max Planck Institute of Colloids and Interfaces, Germany, he joined the Institute for Complex Materials, Leibniz Institute for Solid State and Materials Research (IFW) Dresden, Germany, during 2013–2016. Since 2016, he is a Research Associate of the National Scientific and Technical Research Council (CONICET) at the National University of Rio Cuarto. His interests focus on energy materials, including porous nanocarbons and inorganic nanostructured materials for supercapacitors and next-generation batteries: Li–S batteries, Li-air batteries and aqueous batteries.

Mariano Martin Bruno was born in San Basilio, Argentina, in 1977. He obtained a B.S. in Chemistry (2001) and Ph.D. in Chemistry (2007) at the National University of Río Cuarto (UNRC). He worked (2008-2015) in the Fuel Cell Group at the National Commission of Atomic Energy (CNEA). Currently, he is a researcher of the National Council of Scientific and Technological Research (CONICET) at UNRC. His main research fields involve materials science and electrocatalysis.

Cesar Alfredo Barbero obtained his B.Sc. (1984) and Ph.D. (1988) in Chemistry at National University of Rio Cuarto (UNRC, Argentina). Then, he worked as a postdoc (1988-1991) and Senior Scientist (1991-1994) at the Electrochemistry Section of Paul Scherrer Institute (Switzerland). Presently he is a Researcher of CONICET (Argentina) and Full Professor at UNRC. He has advised 12 Ph.D. and 3 M.Sc. thesis. He has published more than 180 manuscripts on Materials

Chemistry (> 3600 citations, h=34). He received the Tajima Prize of the International Society of Electrochemistry (1997), J.S. Guggenheim Fellowship (2007), Rafael Labriola Prize of AQA (2004) and M.C. Giordano Prize of AAIFQ (2007).

Anales de la Asociación Química Argentina

División Jóvenes Profesionales

Mini-Review

ORDERED MESOPOROUS ORGANOSILICA ADSORBENTS FOR INORGANIC POLLUTANTS REMOVAL FROM WATER

Pedro P. Martin[1], Sergio G. Marchetti[2], Nicolas Fellenz[1,*]

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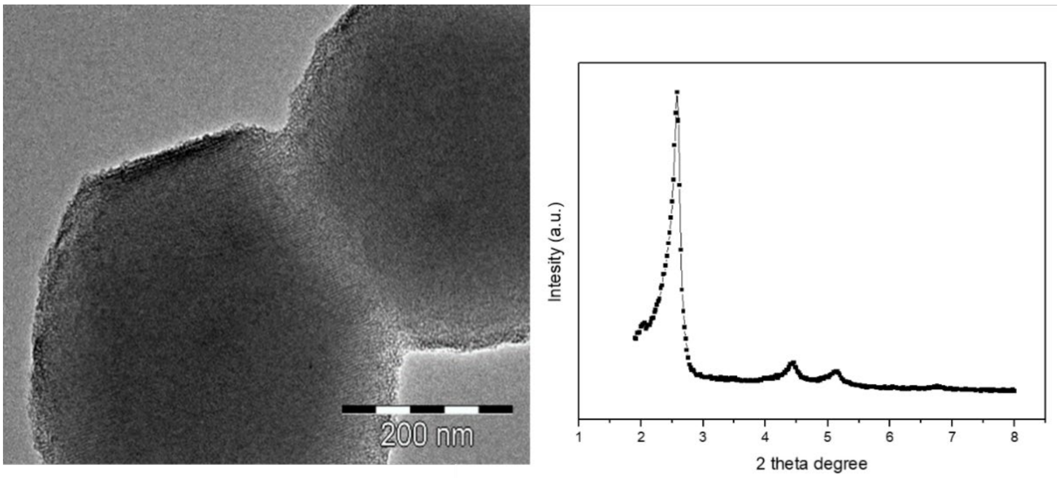
Graphical abstract



TEM image and powder X-ray diffraction profiles at low angles of an MCM-41-NH_2

Resumen

Este manuscrito hace un repaso de las contribuciones más importantes sobre el uso de las sílices mesoporosas ordenadas (SMO) modificadas aplicadas a la remoción de contaminantes inorgánicos de matrices acuosas. En primer lugar, se discute brevemente sobre los diferentes caminos para sintetizar este tipo de materiales mesoporosos nanoestrucurados, mencionando también las características estructurales y químicas principales que se obtienen al utilizar cada uno de ellos. Se hace énfasis en los reportes sobre la aplicación de las SMO como adsorbentes para la remediación ambiental, aunque también se mencionan brevemente otros campos donde se utilizan este tipo de sistemas sólidos nanoestructurados. Finalmente se discute en profundidad sobre la síntesis y aplicación de la SMO denominada MCM-41, su modificación con diferentes grupos orgánicos y su desempeño en la remoción de cromo hexavalente de soluciones acuosas de variada composición química. De esta SMO en particular se discute cómo afectan sobre su desempeño como adsorbente el tamaño de partícula y la cantidad y distribución de grupos orgánicos anclados dentro de la red de mesoporos. Finalmente se mencionan algunas estrategias actualmente en estudio que buscan aumentar la estabilidad de la MCM-41 de manera de conseguir un adsorbente efectivo y de larga vida útil.

Abstract

This article reviews the most important contributions on the use of organically modified ordered mesoporous silicas (OMS) for removal of inorganic pollutants from aqueous matrices. First, we briefly discuss the different preparation methods to synthesize this type of nanostructured mesoporous hybrid materials, mentioning the main structural and chemical features than can be obtained. Emphasis is placed on the application of OMS as adsorbents for environmental remediation purposes, although other fields where this type of nanostructured solid systems are used are also briefly mentioned. Finally, a depth discussion on the synthesis and application of the OMS called MCM-41, its modification with different organic groups, and its performance in the removal of hexavalent chromium from aqueous solutions of varied chemical composition is presented. The MCM-41 mesophase is taken as an example to discuss how the particle size and the amount and distribution of organic groups anchored within the mesoporous network affect the performance of these kind of materials as adsorbents. Finally, some possible strategies that seek to improve the stability of the MCM-41 based sorbents for its use in a wide range of operational conditions are mentioned.

Palabras Clave: *Sílices mesoporosas ordenadas, adsorbentes, remediación, contaminación, cromo.*

Keywords: *Ordered mesoporous silica, sorbents, remediation, pollutants, chromium.*

Pedro Martin is a Postdoctoral fellowship from *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).* His studies were performed at the National University of La Pampa (Argentine), and in 2018 he received his PhD in chemistry from the National University of La Plata (Argentine). He is a member of the Laboratory of Nanostructured Materials since 2015 in National University of Río Negro (Argentine). His research deals with the synthesis and characterization of solid materials with potential applications in water decontamination.

Prof. Sergio G. Marchetti is the head of the Group for research in the Fischer-Tropsch Synthesis, CINDECA, in the Chemistry Department at La Plata University, Argentine. He was appointed as Professor of Transport Phenomena in this University from 1996. His research evolves in nanoscience, nanotechnology, heterogeneous catalysis, and spectroscopies in solids, especially in Mössbauer spectroscopy. His studies were performed at the National University of La Plata (Argentine), where he received his Ph.D. degree in chemistry in 1988. He is the co-author of more than 80 publications, 4 chapter of books and 146 presentations in meetings, symposiums etc., in the field of iron catalysts, iron nanoparticles and Mössbauer spectroscopy.

Nicolás Fellenz is researcher from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and recently he was appointed as associated professor of inorganic chemistry at National Río Negro University, Argentine. His studies were performed at the National University of La Plata (Argentine), where he received his Ph.D. degree in chemistry in 2011. He is the founder of the Laboratory of Nanostructured Materials at National Río Negro University in 2015. His research deals with the synthesis and characterization of nanostructured solid materials with different potential applications, such as: water decontamination, heterogeneous catalysis and drug delivery.

Anales de la Asociación Química Argentina

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Mini-Review

RECENT STUDIES ON MAGNETIC MESOPOROUS NANOMATERIALS FOR WATER TREATMENTS

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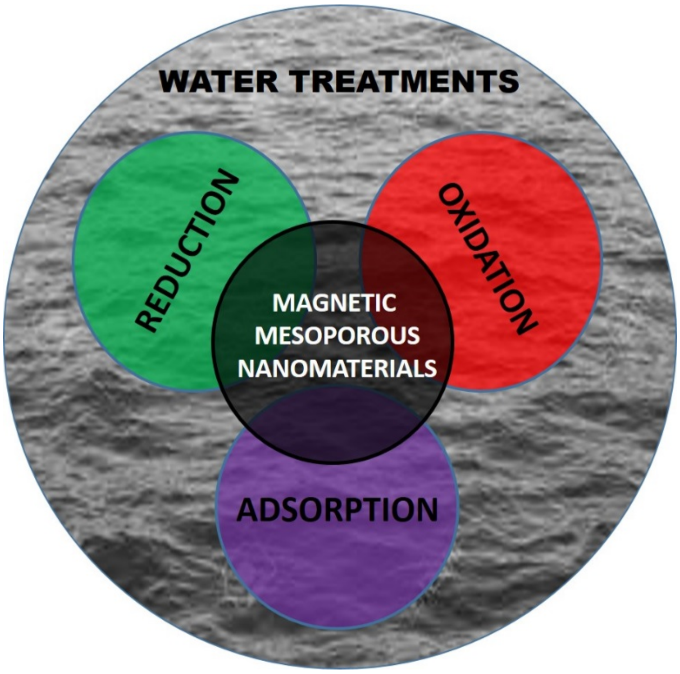
Graphical abstract



Resumen

En el contexto del tratamiento de aguas contaminadas, este trabajo ofrece una visión general y en profundidad de los últimos avances en diseño racional, síntesis y aplicaciones de nanomateriales magnéticos mesoporosos en la adsorción, oxidación química y reacciones de reducción centradas en la eliminación de contaminantes orgánicos. Se presta especial atención a los materiales magnéticos mesoporosos a base de sílice y carbono. Finalmente, se discuten los desafíos que enfrenta la aplicación de estos materiales en sistemas de tratamiento reales.

Abstract

Within the context of wastewater treatments, this review offers a general and in-depth overview of the latest advances in rational design, synthesis and applications of mesoporous magnetic nanomaterials in adsorption, chemical oxidation and reduction reactions focused on the removal of organic pollutants. Special attention is paid to magnetic mesoporous silica- and carbon-based materials. Finally, the challenges facing the application of these materials in real treatment systems are discussed.

Palabras Clave: *magnetita, hierro cero valente, sílice mesoporosa, carbón mesoporoso, nanotecnología*

Keywords: *magnetite, zero valent iron, mesoporous silica, mesoporous carbon, nanotechnology.*

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Marcos Emanuel Peralta obtained his Chemical Engineering degree in 2015 at Universidad Nacional del Comahue (UNCo, Argentina) and got a fellowship from CONICET in 2016. He is currently a PhD student at Universidad Nacional de La Plata (UNLP, Argentina) with Prof. Luciano Carlos and Prof. Daniel Mártire as supervisors and Prof. María Eugenia Parolo as co-supervisor. During 2017, he was staying in Department of Chemistry of University of Torino (UNITO, Italy) and train about magnetic mesoporous silica-based nanoparticles synthesis and characterization techniques under Prof. Giuliana Magnacca advice. Thereafter, he studied surface functionalization of the prepared nanoparticles for pollutant removal from aqueous systems. He came back to UNITO in 2018 and work with Prof. Sushilkumar Jadav (Shivaji University Kolhapur, India) in nanoparticles grafting with thermo-responsive polymer for biomedical applications. He also does teaching activities in Organic Chemistry at Departamento de Química of Facultad de Ingeniería (UNCo).

María Eugenia Parolo received his PhD in Chemistry from Universidad Nacional del Sur (UNS) in 2010 under the supervision of Dr. Marcelo Avena, where she worked on the modification of mineral clays for retention of organic compounds that impact human health and the environment. She obtained the Aaron y Fanny Fideleff de Nijamkin award for the best doctoral thesis in 2010 at the UNS. From 2010 throughout 2014, she joined Clay Minerals Research Center (Universidad Nacional del Comahue) were she was co-director of research focused on Evaluation and optimization of clay minerals from Neuquén. Applications for protection in the environment. She is currently Professor and Researcher (CITAAC-CONICET) at the Department of Chemistry of Universidad Nacional del Comahue (Neuquén), where she is director of a project that combines the synthesis of nanomaterials from clays and iron oxide and their surface modification along with its final application as water treatment, specific adsorption systems. She is currently the technical representative of Chromatography Laboratory (LPC), where it is held research, environmental audits and technology transfer activities. The LPC laboratory integrates the Analytical Network of Latin America and Caribbean.

Luciano Carlos was born in 1978, in Neuquén, Argentina. He received his Chemical degree in 2003 and he got his PhD in Chemistry from the National University of La Plata in 2008. From 2009 to 2010, he got a postdoctoral position at Institute of Theoretical and Applied Research on Physical Chemistry (INIFTA, La Plata, Argentina). From 2011 is a member of the CONICET research career. Currently, he is Independent Researcher and he leads the research group "Advance Oxidation Processes and nanoadsorbentes" at Institute of Research and Development in Process Engineering, Biotechnology and Alternative Energies (PROBIEN, Neuquén, Argentina). His research interests include photochemical processes for pollutant degradation, Advance Oxidation Processes, and development of nanomaterials for the removal of pollutant from waters.

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Mini-Review

TEMPLATED MESOPOROUS NANOMATERIALS BY AEROSOL ROUTE: HISTORY AND NEW INSIGHTS OF GREEN CHEMISTRY APPROACHES

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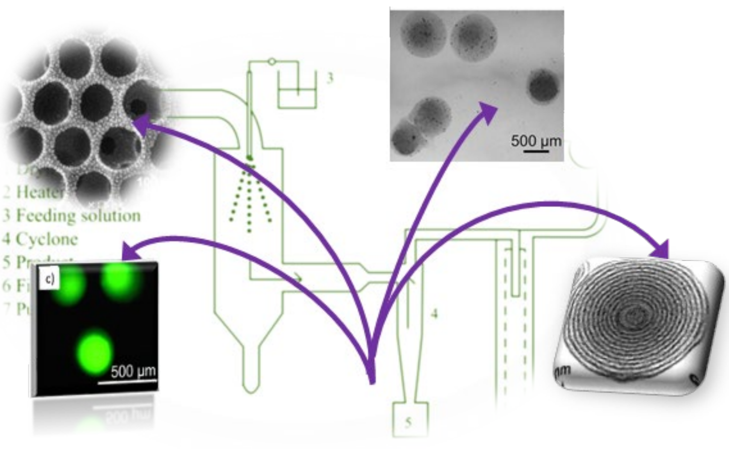
Graphical abstract



Resumen

La combinación de la síntesis por aerosol (o secado por pulverización) con la química Sol-Gel se ha trasformado en las últimas décadas en la más promisoria ruta para la obtención de materiales mesoporosos a escala industrial con variadas aplicaciones como energía, catálisis, purificación de agua, etc.

En el método de secado por pulverización, se atomiza una solución precursora para formar gotas mediante nebulización ultrasónica. Cada gota se puede considerar como un microrreactor individual. Estas gotas resultantes luego son impulsadas mediante un gas portador y pasan a través de un tubo caliente, donde el solvente se evapora rápidamente y las especies precursoras disueltas se ensamblan para generar los productos.

Este método permite la producción continua de una amplia variedad de materiales, minimizando el uso de precursores y reduciendo considerablemente los residuos generados durante la síntesis. También permite obtener partículas con alta pureza, de una manera simple, económica y continua; posibilitando la obtención de partículas esféricas, no aglomeradas y con un tamaño monodisperso.

En este mini-review, presentamos los principios básicos de la síntesis de nanomateriales utilizando el método de secado por pulverización y discutimos la posibilidad de adaptar estos procesos a los principios de la química verde.

Abstract

The combination of aerosol (spray drying process) with sol–gel chemistry has become in, the lasts decades one, of the most promising synthesis routes for the synthesis of industrially scalable mesoporous materials for various applications such as energy, catalysis, water purification, etc.

In the spray drying method a precursor solution is atomized to form droplets by ultrasonic nebulization. Each drop can be considered as an individual microreactor. The resulting droplets are then driven by a carrier gas and pass through a hot tube where the solvent is rapidly evaporated and the dissolved precursor species are assembled to generate the products.

This method allows the continuous production of a wide variety of materials minimizing the use of precursors and considerably reducing the waste generated during the synthesis. The spray drying method permits to obtain particles with a high-purity in a simple, economical and continuous way. This method allows to produce spherical shaped particles that are agglomeration free and have a relatively monodisperse size, which is very useful for material processing.

In this mini-review, we present the basic principles of nanomaterials synthesis using aerosol methods and we discuss the possibility to adapt these processes to the principles of green chemistry.

Palabras Clave: *secado por pulverización, materiales mesoporosos, síntesis de fácil escalado, química verde*

Keywords: *spray drying process, mesoporous materials, easy scalable synthesis, green chemistry.*

MaríaVerónica Lombardo, **PhD.**

She is Licenciate (MSs) in Chemistry (FCEN-UBA, 2007). She worked for 3 years (2006-2009) at Boehringer Ingelheim Argentina in R&D. Then, she obtained a PhD in Science and Technology, Chemistry Mention (3iA, UNSAM, 2013). She made a postdoc (2014-2016) with CONICET scholarship in the Chemistry of Nanomaterials Group. After, she carried out another postdoc (2016-2018) with a CNEA scholarship. Nowadays, she is Assistant Researcher of CONICET in the Chemistry of Nanomaterials Group (CAC-CNEA) and Professor of General Chemistry (ECyT –

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2002: Chemistry degree, Faculty of Exact and Natural Sciences (FCEN), University of Buenos Aires (UBA)

2007: PhD in Chemistry, Inorganic, analitical and Physical Cehmistry Department (DQIAQF)-UBA/INQUIMAE-CONICET. Directors: Dr Fabio D. Cukiernik (FCEN/INQUIMAE), Dr Daniel Guillon (GMO-IPCMS) and Dr Bertrand Donnio (GMO-IPCMS).

2007-2010: Postdoc at the nanoMaterials Chemistry Group, GQ-CAC-CNEA. Supervisors: Dr Galo Soler-Illia and Dr Alejandro Wolosiuk

2011-2014: Researcher at Nanomaterials Chemistry Group, GQ-CAC-CNEA.

Since 2015: Researcher at CIBION. Head of the Hybrid and Structured nanoMaterials Group.

Esteban Franceschini, PhD.

Dr. Esteban Franceschini has a degree in chemistry from the National University of Cordoba and a PhD from the University of Buenos Aires. He worked at the National Atomic Energy Commission (Constituyentes Atomic Center) in the development of nanomaterials for fuel cells and currently is a CONICET associate researcher at Research Institute in Physical Chemistry of Cordoba developing materials for hydrogen generation in alkaline medium

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Mini-Review

LUMINESCENT METAL-ORGANIC FRAMEWORKS (LMOFS) AS MULTIFUNCTIONAL MATERIALS FOR APPLICATIONS IN SOLID-STATE LIGHTING AND SENSING

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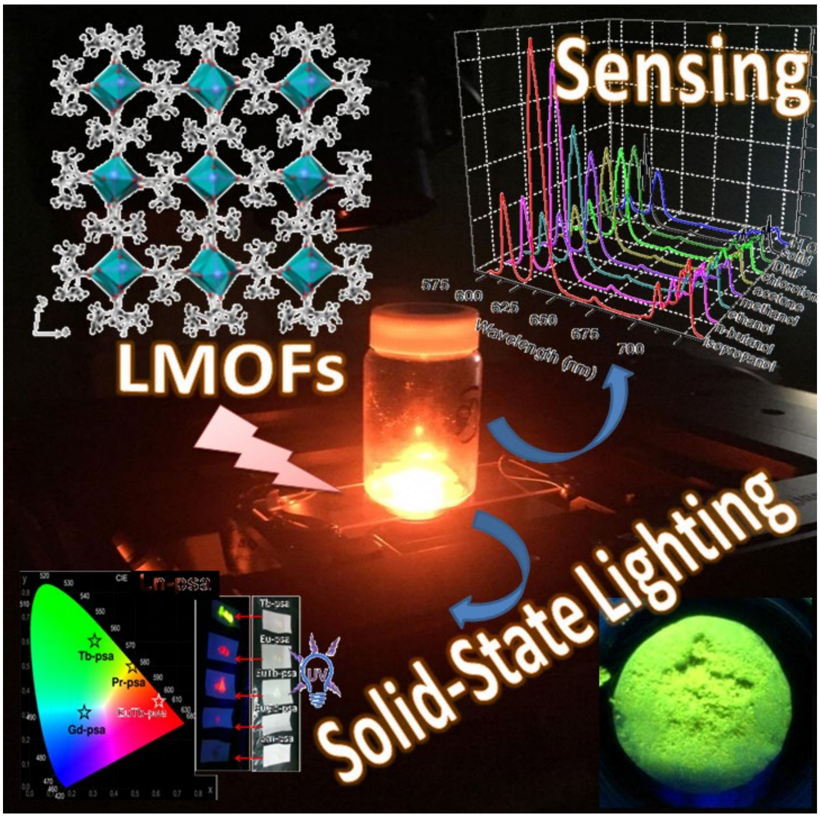
Graphical abstract



Resumen

El intenso estudio acerca de los MOFs (redes orgánicas-inorgánicas) durante los últimos años es un ejemplo del interés despertado por estos compuestos como una nueva generación de materiales multifuncionales para una variedad de aplicaciones emergentes. Inspirados por los trabajos de especialistas reconocidos, la comunidad científica internacional ha explorado distintas condiciones y metodologías de síntesis con el propósito de obtener MOFs con arquitecturas de poro, funcionalidades, texturas y propiedades únicas. En este contexto, la elección de los lantánidos como bloques de construcción, ofrece grandes posibilidades hacia la obtención de MOFs luminiscentes (LMOFs) con potenciales aplicaciones tecnológicas. Con esta motivación, se presentará una revisión y las perspectivas en esta línea de investigación. Además, se llevará a cabo un análisis relacionado al diseño racional de LMOFs considerando la naturaleza del ion lantánido y del ligando y los posibles procesos de transferencia de energía. Finalmente se presentarán algunos de los resultados más relevantes respecto al desarrollo de sensores como así también emisores de luz en estado sólido basados en LMOFs.

Abstract

The intense study of Metal-Organic Frameworks (MOFs) along the last decades, is a clear example of the interest of these materials as a new generation of multifunctional materials for a variety of emerging applications. Inspired by the first works of worldwide known specialists, the international scientific community has been exploring a variety of metal centers and organic ligands under different synthetic conditions and methodologies in order to obtain MOFs with unique pore architectures, functionalities, textures and unique properties. In this context, the choice of lanthanides ions as building blocks offers huge possibilities for the construction of luminescent MOFs (LMOFs) for potential technological applications. With this motivation, a revision on this line of research and perspectives will be presented and discussed. Thus, an analysis concerning to the rational design of LMOFs, considering the nature of the linker, the lanthanide and the possible energy transfer process, will be carried out. Besides, the different type of luminescent performance will be analyzed. Finally, some relevant results towards the development of solid-state lighting and sensors based on LMOFs will be presented.

Palabras Clave: *MOFs, lantánidos, fotoluminiscencia, sensado, emisores*
Keywords: *MOFs, lanthanides, photoluminescence, sensing, lighting.*

Dr. Germán E. Gomez completed his Ph.D in Chemistry at Universidad Nacional de San Luis under the supervision of Profs. G. E. Narda and E. V. Brusau in research topics related to study Lanthanide-Metal Organic Frameworks with luminescent and catalytic properties. After that, he made postdoc stays in Nano-Chemistry group in CAC-CNEA (2015-2017, at the Dr. G. J. A. A. Soler-Illia group), College de France (2016, Dr. Clément Sanchez group) and Ghent University (2016, Dr. R. van Deun group) studying MOFs for chemical and thermal sensing. In 2018 he joined the group of Prof. C. Cahill at George Washington University as a Fulbright postdoctoral fellow, for the development of actinide and lanthanide coordination polymers as solid-state light-emitters. Also, in 2018 he visited the group of Prof. Muralee Murugesu in Ottawa University to work in the project “MOFs and MMPFs for

opto/magnetic applications". Nowadays Gomez is member of CIC-CONICET in INTEQUI for the research of MOFs for sensing, photoluminescence and photocatalysis fields.

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Mini-Review

MESOPOROUS THIN FILMS: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS IN SENSING

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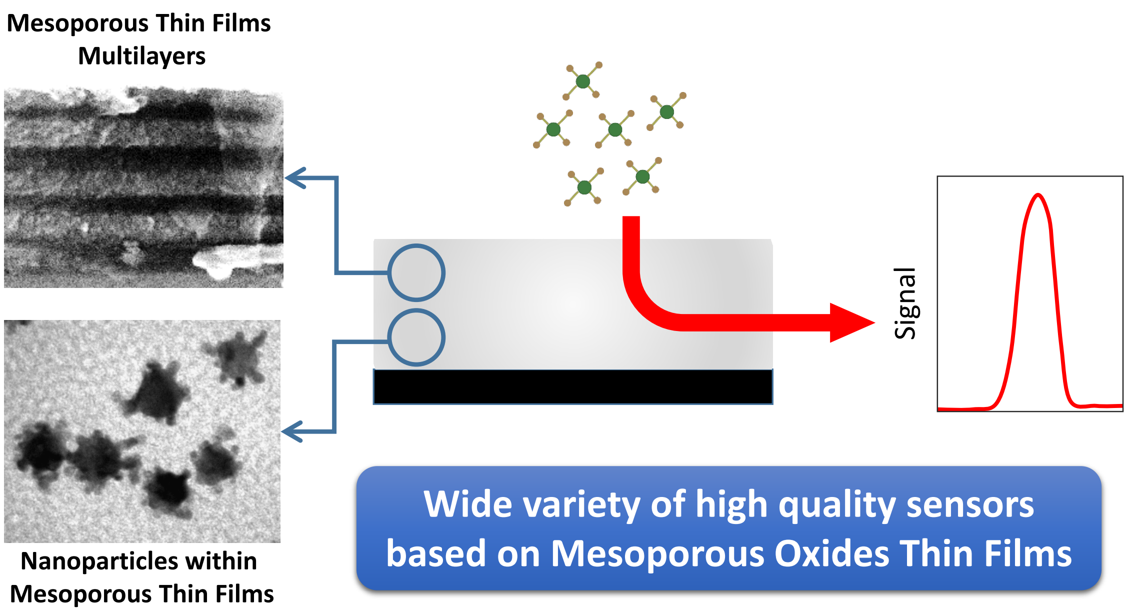

Resumen

Las películas delgadas de óxidos mesoporosos (PDOMPs) han recibido mucha atención en las últimas décadas, principalmente debido a su arreglo controlado de poros con diámetro en el rango 2 - 50 nm y su versatilidad para el desarrollo de dispositivos tecnológicos. Hoy en día, se encuentran disponibles diversos moldes de poros y precursores inorgánicos lo que permite obtener una gran variedad de PDOMPs tanto en términos de composición química (SiO_2, TiO_2, ZrO_2, CeO_2, Al2O_3, HfO_2 y óxidos mixtos) como de tamaños y arreglos de poros. Entre las aplicaciones propuestas para las PDOMPs, una de las más destacadas es su uso como parte constitutiva de sensores. Las principales ventajas de usar

PDOMPs en la construcción de estos dispositivos son: la alta superficie específica, la versatilidad de composición química y la facilidad para depositarlas sobre una gran variedad de sustratos.

En este trabajo de revisión se describen brevemente los métodos de síntesis más usuales para obtener PDOMPs y las técnicas de caracterización más utilizadas para determinar sus propiedades fisicoquímicas. Posteriormente, se analizan dos de las líneas que se están desarrollando en nuestro grupo para obtener sensores específicos y reproducibles basados en PDOMPs: sensores para espectroscopía Raman aumentada por superficies (SERS) obtenidos al combinar las películas con nanopartículas metálicas y sensores ópticos basados en multicapas.

Abstract

Mesoporous oxide thin films (MOTFs) have received much attention in the last decades mainly because of their controlled array of pores with diameter in the 2-50 nm range and their versatility for development of technological devices. Nowadays, a diversity of pore templates as well as inorganic precursors are available, therefore a large variety of MOTFs can be obtained in terms of chemical composition (SiO_2, TiO_2, ZrO_2, CeO_2, Al_2O_3, HfO_2, and mixed oxides) and pore sizes and arrangements. Among all the proposed applications of MOTFs, one of the most prominent is their use as constitutive part of sensors. The main advantages of using MOTFs in the construction of these devices are: high specific surface, chemical composition versatility and the easiness to deposit them onto a wide variety of substrates.

In this minireview, we shortly describe the most common synthesis methods to obtain MOTFs along with the most usual techniques used to characterize their physicochemical properties. Afterwards, we discuss two of the lines that are being developed in our group to obtain specific and reproducible sensors based on MOTFs: Surface Enhanced Raman Spectroscopy (SERS) sensors obtained by combining the films with metallic nanoparticles and optical sensors based on films multilayers.

Palabras Clave: *películas delgadas, óxidos mesoporosos, nanopartículas metálicas, multicapas, sensores*

Keywords: *thin films, mesoporous oxides, metal nanoparticles, multilayers, sensors*

M. Mercedes Zalduendo obtained her degree in Chemistry from Universidad de Buenos Aires in 2014. She joined the Chemistry of Nanomaterials Group and started her PhD in Chemistry in 2015, financed by CONICET, under the supervision of Dr. Paula C. Angelomé. Her thesis is focused on the study of Mesoporous Nanocomposite Thin Films and their applications as optical platforms. She worked for some months in the Bionanoplasmonics Lab (CIC-Biomagune, San Sebastián, Spain) where she studied the SERS sensing capabilities of different platforms.

Josefina Morrone obtained her degree in Chemical Sciences in 2016 at the Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires. In 2017, she started her PhD financed by CONICET at Universidad Nacional de San Martín, under the guide of Dr. María Cecilia Fuertes and Dr. Paula C. Angelomé. Her thesis is focused on the design, construction and characterization of structural and optical properties of sensors based on photonic crystals from ordered mesoporous oxides. During 2018, Josefina stayed for 3 month in the Hybrid materials and Nano-materials Team, in the Sorbonne Université located in Paris (France), under the supervision of Dr. Cédric Boissiere, where she trained about different characterization techniques using ellipsometry.

Paula Y. Steinberg got her degree in chemistry in 2010 and her PhD in chemistry in 2018, both at the Universidad de Buenos Aires, Argentina. Her PhD was developed at the Chemistry of Nanomaterials group (Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Argentina) and financed by CONICET. Dr. Paula C. Angelomé and Dr. Galo J. A. A. Soler-Illia were her advisors. Her PhD thesis concerned the study of the structural control of TiO_2 mesoporous thin films and its effects on the transport and reactivity within confined environments. During 2016, Paula participated in an Elettra synchrotron campaign to study de use of deep X-ray as a novel method to synthesize mesoporous oxides thin films.

M. Cecilia Fuertes obtained a Materials Engineer Degree in 2003, from de University of Mar del Plata, a Master in Material Science (2005) and a PhD in Materials Science and Technology (2009), both from the Sabato Institute-CNEA and the University of San Martín. Her thesis, under direction of Prof. Soler-Illia, was focused on the synthesis and characterization of multiscale materials based on mesoporous oxide thin films. She worked as a postdoctoral fellow at the Solar Energy Division (CNEA), with Dr. Plá (2009-11). From 2011, she is a CONICET staff scientist at CNEA, Buenos Aires, Argentina. Her current main interests include the design, production and characterization of functional nanomaterials and thin films, with applications in optical devices and sensors. She has published 28 scientific papers and a book chapter, has been in charge of national research projects and has supervised PhD, MSc and degree students.

Paula C. Angelomé obtained a Chemistry Degree (2003) and PhD (2008) from University of Buenos Aires (Argentina). During her doctoral thesis, performed under the supervision of Dr. Galo Soler-Illia at CAC-CNEA, she worked on synthesis and characterization of mesoporous metallic, mixed and hybrid oxide thin films. Between 2008 and 2012 she was a postdoctoral fellow in the Colloid Chemistry Group (University of Vigo, Spain) under the direction of Prof. Luiz Liz-Marzán, working on synthesis and applications of metallic nanoparticles and composites. She came back to CNEA in 2012, as a CONICET Researcher and, since 2017, she holds an Independent Research position. She has published more than 35 scientific papers, has been in charge of several national and international research projects and has supervised several postdocs and PhD, MSc and degree students.

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Mini-Review

HYBRID MESOPOROUS SILICA: A PLATFORM FOR GATING CHEMISTRY

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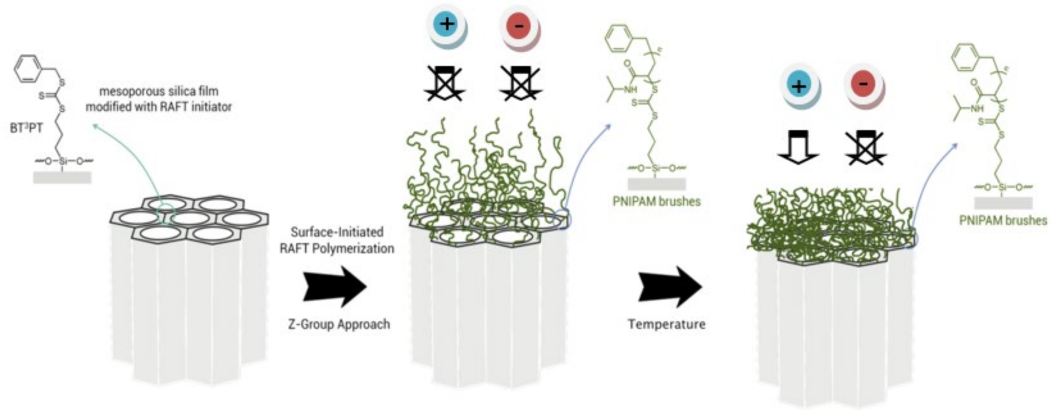
Graphical abstract



Intelligent hybrid systems can be achieved through the integration of element from sol-gel chemistry and polymer science. PNIPAM brushed grafted to mesoporous silica by RAFT polymerization gives birth to a thermoresponsive gate. Above 31 ºC polymer brushes collapse and positive analytes can diffuse through.

Resumen

La combinación de matrices mesoestructuradas de óxidos inorgánicos y su integración con moléculas, polímeros, complejos organometálicos y grupos activos biológicos como bloques de construcción funcionales ha permitido el desarrollo de nuevos materiales híbridos. El control espacial preciso de estos elementos activos en escalas tridimensionales nanométricas representa la clave para el diseño racional de materiales híbridos inteligentes orgánicos-inorgánicos hechos a medida para fines específicos. Estos materiales serían de gran relevancia para un gran número de aplicaciones tecnológicas como optoelectrónicas, catálisis, biosensores, tamices moleculares o liberación controlada de drogas. En particular, estas arquitecturas sólido-blandas nos han permitido crear sofisticados nanosistemas capaces de responder a estímulos externos como pH, potencial redox, concentración de analitos específicos, temperatura o luz, marcando el camino hacia lo que en la actualidad se conoce como "*gating chemistry*". La transducción de dichos estímulos en una respuesta involucra efectos fisicoquímicos como desplazamientos de equilibrio, redistribución de cargas, o limitaciones estéricas provenientes de la reconfiguración de macromoléculas o la degradación de elementos voluminosos. Estos cambios permiten controlar el transporte y la difusión de moléculas huésped o sondas a través de canales o estructuras porosas acercándonos a la posibilidad de mimetizar sistemas biológicos. Este trabajo tiene como objeto mostrar brevemente las diversas estrategias en el diseño de estos sistemas y la motivación detrás de estas complejas nanoarquitecturas.

Abstract

The combination of mesostructured metal oxides as robust platforms and the integration to molecular, polymeric, organometallic or biologically active groups as functional construction blocks has enabled the development of new hybrid materials. The precise localization of this active elements in three-dimensional nanometric scale represents the key for the rational design of intelligent inorganic-organic tailor–made hybrids for specific purposes. Such materials would be of great relevance for a great deal of technological applications as optoelectronics, catalysis, biosensors, molecular sieving or drug delivery. In particular, these hard–soft architectures allowed us to create sophisticated intelligent nanosystems that respond to a variety of external stimuli such as pH, redox potential, molecule concentration, temperature, or light paving the way to what is known as "gating chemistry". Transduction of these stimuli into a predefined response implies exploiting spatial and physicochemical effects such as charge distribution, equilibria displacements, or steric constraints du to degradation of bulky caps or reconfiguration of macromolecules. These changes allow us to control diffusion and transport of probes or host molecules through channels or porous structures diminishing the gap between synthetic and biological systems. This work aims to briefly show a wide variety of strategies for the design of such sophisticated nanoarchitectures and its potential applications.

Palabras Clave: *Materiales híbridos, materiales responsivos, cepillos poliméricos, películas delgadas mesoporosas, liberación controlada de drogas.*

Keywords: *Hybrid materials, Responsive materials, polymeric brushes, mesoporous thin films, drug delivery.*

Sebastián Alberti was in born Bernal (Buenos Aires, Argentina) in 1986. He studied chemistry at the University of Buenos Aires (UBA), receiving his degree in 2012. He has recently obtained his PhD degree at UBA under the joint supervision of Galo Soler-Illia and Omar Azzaroni. His research interest focuses on gated supra- molecular chemistry in mesoporous silica nanoarchitectures.