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# ANALES DE LA ASOCIACIÓN QUÍMICA ARGENTINA

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# Anales de la Asociación Química Argentina

## Volumen Especial: Materiales Porosos

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# Contenido

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### Mini-Reviews

# 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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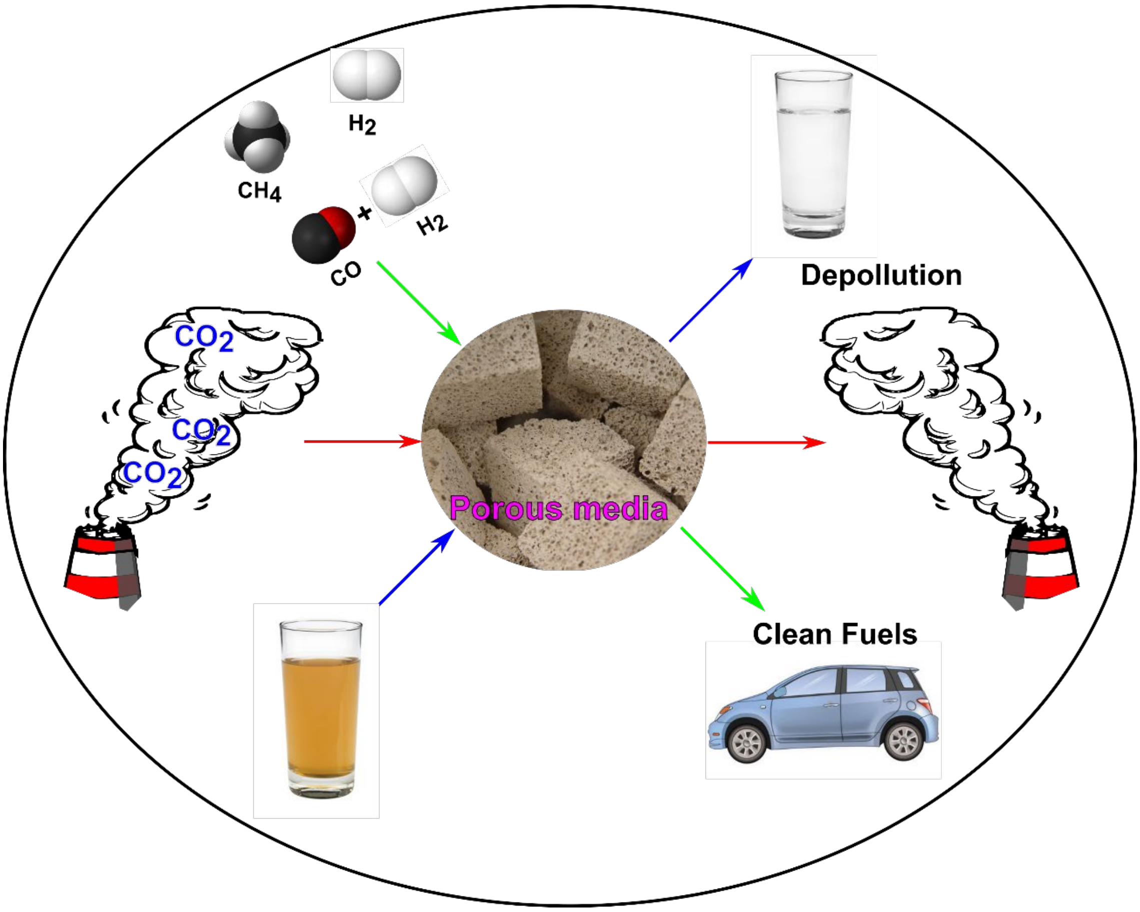
## Graphical abstract



## 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.*

## 1. Introduction

The development of novel porous materials to be used in energy and environmental applications is a subject in continuous expansion. The energy and environmental problems have arisen because of the expansion and growth of the world, and mainly due to the establishment of different industries and, in many cases, the waste generation. Currently, these problems have been accentuated generating strong interest from the scientific field, seeking to innovate not only for generating cleaner/greener processes but also in the way to remove the pollutants that cause different environmental damages.

Regarding the energy applications, the storage of different gases as hydrogen and methane in porous materials has been widely studied [1] [2] [3] [4]. However, many challenges concerning this topic are still under research to obtain technological applications. Another interesting energetic application is the obtaining of synthetic hydrocarbons, where the porous materials can be used as a catalyst to control the selectivity of the process [5] [6]. As regard as the environmental pollutants, the $CO_2$ emissions to the atmosphere has contributed significantly to the global warming of the planet and the difficult to reduce these gas emissions have generated great interest and effort to develop new technologies to capture and storage this greenhouse gas [7] [8]. Besides of CO2 emissions, many other pollutants from different chemical, pharmaceutical and agrochemical industries are a relevant topic in environmental remediation. In the last years, different antibiotics and hormones have been considered emerging pollutants of the aquatic ecosystem, even at low concentrations [9] [10]. Additionally, other contaminants as fungicides and pesticides are also the cause of environmental problems [11] [12]. In all the cases, an appropriate adsorbent can be used to reduce or remove these contaminants, where the nanoporous materials play an essential role.

In the last years, the synthesis of porous materials has been focused on the control of microporosity, mesoporosity and even macroporosity, including synthetic methods, design concepts, and fundamental principles for obtaining novel materials. The development of these materials led to challenges in the field of characterization and comprehensive textural, structural, morphological and surface, among others. Different characterization techniques, such as X-ray diffraction, gas adsorption, mercury porosimetry, thermal analysis, electron microscopy (scanning and transmission) are widely used to study porous materials [13]. Regarding the texture, gas adsorption is a well-established technique to determine the surface area and porosity [14], recommended for physisorption characterization (IUPAC) and the most used in our laboratory.

The study of the influence of the textural, structural, surface and morphological properties of the porous materials in different applications aims to facilitate the design of new materials and the adjustment or improvement of old/traditional syntheses.

Based on the experience of our research group, Laboratory of Porous Solids (LabSoP), the aim of this review is present several examples regarding the synthesis, characterization and applications in different environment and energy fields where these materials could be used.

## 2. Materials

### 2.1. Synthesized in the LabSoP

#### *2.1.1. Pillared Clays*

Pillared clays (PILCs) are micro-mesoporous materials obtained from clays type smectites by the intercalation between its laminar structures of big metallic oligocations by cationic interchange [15]. The final material ha a more stable porous structure (calcined up to 500-600 °C) than the raw materials. Several metallic oligocations can be incorporated, like Al, Si, Zr and Fe. The final materials can be used as support of catalysts or as adsorbents in different applications. The final porous structure of the PILCs depends on different conditions such as oligocations and synthesis method. Scheme of the possible scenarios of the final material after a pillaring process is shown in Figure 1 [16].

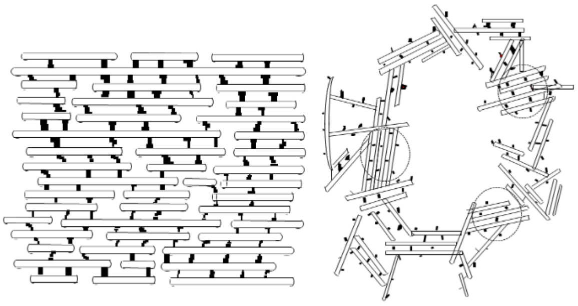


**Figure 1.** Scheme of the structural arrangement of pillared clays: (left) ordered, (right) turbostratic. Metal oxides form pillars in the interlayer region of the clays giving as result the microporosity of the PILCs.

### *2.1.2 Activated Carbons*

The activated carbon (AC) is considered the universal adsorbent. Activated carbon is processed coal with a highly developed pore structure and a large internal surface area. The AC is obtained by a "carbonization" process, followed by an activation step of the carbonaceous material. The activation is necessary to convert the pyrolyzed material into a high porosity adsorbent with an important surface development. In the process of activation, carbonaceous materials are subjected to selective thermal treatments, under conditions in which occur the formation of innumerable pores, cracks and breaks. The surface area occupied by pores is significantly increased. The physical activation could be carried out with CO, air or water, while the chemical process use KOH, $K_2CO_3$, $ZnCl_2$ or $H_3PO_4$, among others, as activating agents. Currently, the activated carbons present not only micropores in its structure but also mesopores and even macropores. Activated carbons have a slit porous structure, and it is composed of disordered graphene sheets. In Figure 2, schematic representation of said material is shown.

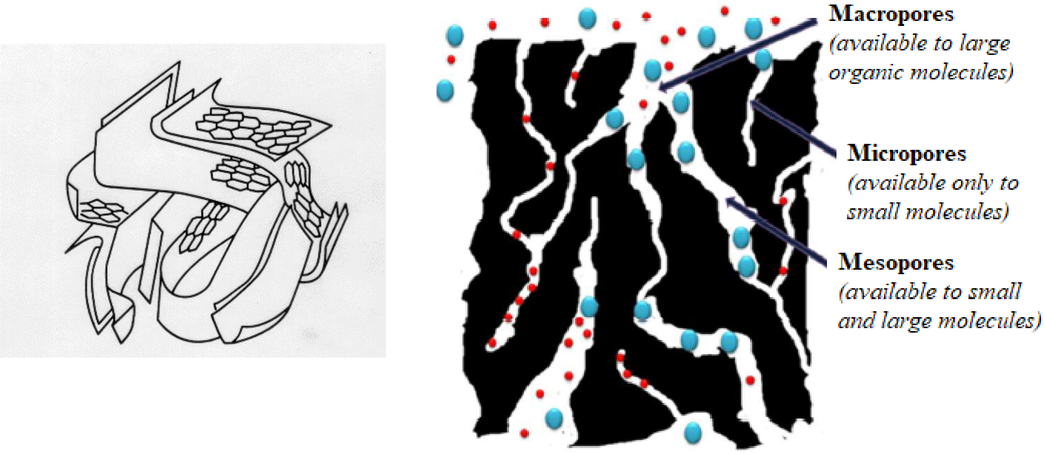


**Figure 2.** Scheme of the pore structure of activated carbons. (Left) Reproduced from [17] and (right) adapted from [18], with permission from The Royal Society of Chemistry.

### *2.1.3 Silica ordered mesoporous materials*

The ordered mesoporous materials of silica (Si-OMM) were developed in the 90s, where one of the first reported is the so-called MCM-41 (Mobil Crystalline Material). MCM-41 and SBA-15 have been the Si-OMM most widely studied not only due to their highly ordered structure but also because diverse pore sizes and wall thickness can be designed employing suitable synthesis conditions [19]. These materials are constituted by a set of cylindrical pores of uniform diameters, open at both ends and forming an hexagonal arrangement, similar to the macroscopic structures of honeycombs. The synthesis pathway for obtaining these materials is by using a surfactant. A non-ionic triblock copolymer (Pluronic P123) is used for SBA-15, which is placed in a basic or acid medium to form micelles. After, a source of Si such as TEOS (tetraethylorthosilicate) is added forming cylinders that are arranged in a hexagonal structure. Calcination step is carried out to remove the surfactant and finally, the mesopores structure is formed. In Figure 3, a synthesis scheme to obtain SBA-15 is shown.

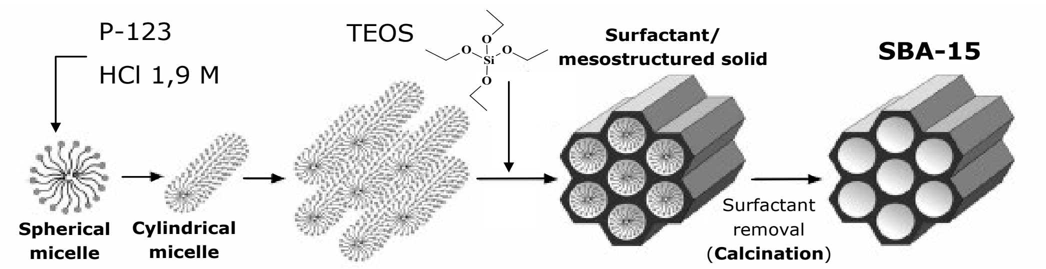


**Figure 3.** Scheme of the synthesis process to obtain SBA-15. Adapted with permission from reference [20].

### *2.1.4 Ordered nanostructured carbons*

The synthesis of the ordered nanostructured carbons (ONC) is based on the nanocasting technique [21]. A porous inorganic material used as a template, e.g. Si-OMM, pillared clays, zeolites, among others, is impregnated with a carbon source as sucrose, furfuryl alcohol, glycerol or another suitable carbon precursor. Next controlled polymerization and carbonization steps are carried out, forming the microporosity of the final material. The mesoporosity is obtained after the removal of the template with an acid or basic treatment, resulting in an inverse/negative replica of the inorganic material [8] [22]. In Figure 4, the porous structure of some of these novel structures is shown, where depending on the amount of carbon and the carbon source incorporated in the pores, structures like "rod-like" as CMK-3 or "tube-like" as CMK-5 are obtained.

**Figure 4.** Scheme of some porous structures of ONC from SBA-15.* Reproduced with permission from reference [23].

### *2.1.5 Metal-Organic Framework*

The metal-organic frameworks (MOFs), are considered as the porous materials of the new generation in the materials science. MOFs are organic-inorganic materials which can be synthesized using metallic ions and multi-functional organic ligands. Variation in these building blocks let us design porous crystalline structures with different properties. Figure 5 displays the formation of this kind of materials. The textural properties, as well as the chemical nature, can be accurately designed by varying the organic ligand or the metal centers. Some of the MOFs studied in different applications at our laboratory were synthesized, and others were commercial materials.

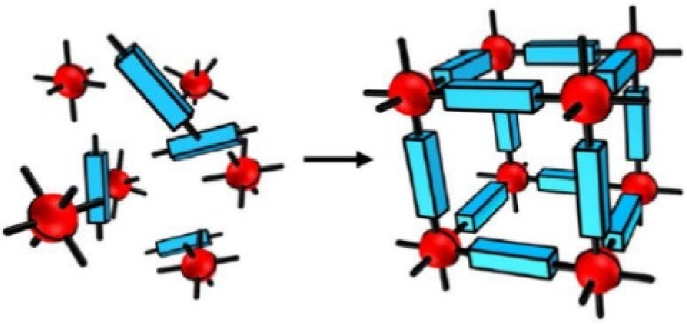


**Figure 5.** Scheme of formation of MOFs (red: metal sites; light blue: organic links).

## 2.2. Commercials porous materials

### *2.2.1 Zeolites*

The zeolites are crystalline aluminosilicates where their structure consists of a three-dimensional network of $SiO_4$ and $AlO^-_4$ tetrahedra linked by their oxygen atoms, originating more or less complex polyhedral structures. Thus, cavities or channels of different dimensions are formed, which constitute the pores, with different pore diameters and different Si/Al ratio. These compounds are very stable chemically and thermally. These molecular sieves are used in both physical separation and purification processes as well as chemical refining and petrochemical applications. Zeolites have attracted considerable attention in catalytic processes such as hydrocarbon conversion reactions [24], as well as in adsorption processes where different results about their adsorptive properties have been reported [25]. Figure 6 shows some of the many reported zeolites.

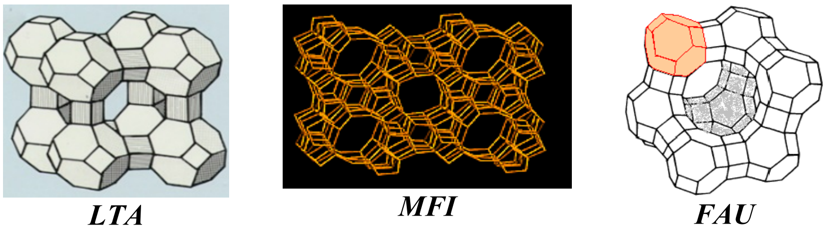


**Figure 6.** Scheme of some typical zeolites.

## 3. Applications

### 3.1. Energetic Applications

#### *3.1.1 Production of gasoline*

Catalytic synthesis made from syngas (CO and $H_2$) yield a great variety of hydrocarbons like paraffin, olefins, alcohols, among others, depending on the catalysts used and on the reaction conditions. The process denominated Fischer–Tropsch synthesis (FTS), is known for producing hydrocarbons nitrogen, sulfur and other heteroatoms free. This is one of the main advantages compared with conventional crude oil-derived liquid products such as diesel and gas oils. The accepted reaction mechanism consists of a polymerization that leads to a distribution of products with different molecular weights. To optimize the production of liquid hydrocarbons, like gasolines, it is necessary to modify the selectivity, for example, by reducing the production of heavy hydrocarbons trough geometric impediments in the catalysts, avoiding the carbon chain growth. This is possible by the use of catalysts with adequate pore size. Different porous materials like ordered mesoporous silicas or carbons, pillared clays, among others, have been used as catalyst support in the FTS. Regarding the active phase, although ruthenium exhibits the highest hydrogenation activity compared with the other three metals (nickel, cobalt and iron), its high price and low availability render it inviable for large-scale production. Meanwhile, nickel is basically a methanation catalyst, and an undesirable production of large amounts of methane is obtained. Thus, cobalt and iron are the more investigated active phases, due to its performance and cost.

For instance, aluminium pillared clays impregnated with Co have shown good performance in the FTS, obtaining a change in the selectivity of heavy hydrocarbons. Figure 7 shows the nitrogen adsorption-desorption isotherms at 77 K (left side) from the catalysts and from the supports (aluminium pillared clays). The incorporation of the active phase modifies the texture of the PILCs. In both catalysts, a diminution in the micropore volume is observed, likely due to the incorporation of the active phase. The mesoporous zone is lightly affected by cobalt. As regard as the selectivity (%) of detected compounds versus the number of carbons is shown, where neither methane nor $CO_2$ has been taken into account [6].

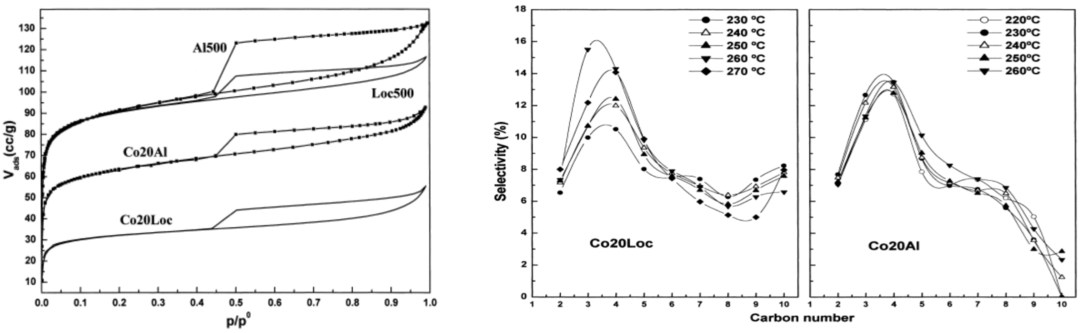


**Figure 7.** $N_2$ adsorption-desorption isotherms at 77 K of both PILCs and prepared catalysts (left) and distribution of products vs. the chain carbon number, using Co20Al and Co20Loc in FTS at different temperatures (right) [6].

From Figure 7, at right, is clear an important cut in the increase of the products with higher carbon number for the sample Co20Al, associated to the its porous structure, principally its micropores.

### *3.1.2 Hydrogen storage*

A comparative study of various porous materials to be used as an alternative to store hydrogen by a physical adsorption process was performed. There was selected, among those commercially available, a set of the most recognized microporous materials namely: zeolites (MS-5A, MS-13X), activated carbon (Maxsorb) and metal-organic frameworks (Cu-BTC, ZIF-8, MIL-53).

The high-pressure adsorption excess isotherms of these materials are shown in Figure 8. It is important to highlight that, at high pressures, the difference between excess adsorption and absolute adsorption must be considered. They are related by equation 1:

$$N_{exc} = N_{ads} - \rho_{bulk} \cdot V_{ads} \tag{1}$$

where $\rho_{bulk}$ is the density of the gas phase, $N_{ads}$ the absolute adsorption isotherm and $V_{ads}$ the volume of the adsorbed phase.

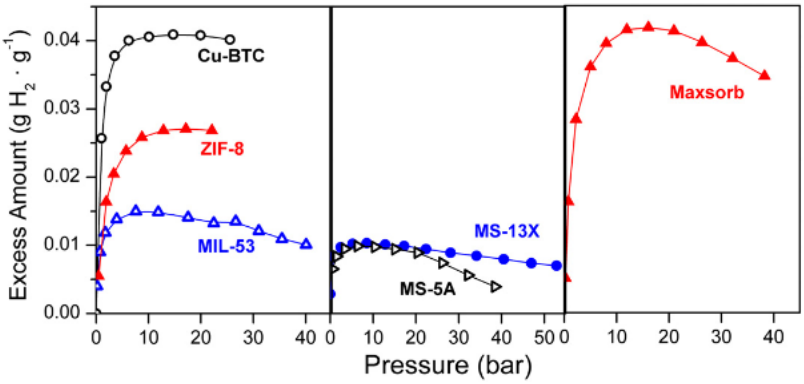


**Figure 8.** High pressure hydrogen adsorption isotherms at 77 K [28]

Different hydrogen adsorption capacities are observed in Figure 9. The differences among these samples are related to the textural properties as specific surface area, $S_{BET}$, and micropore volumes, $V_o$, as is shown in Figure 9.

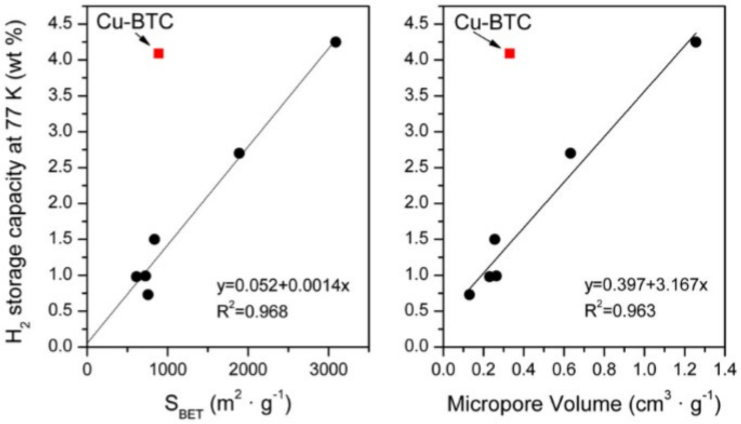


**Figure 9.** Hydrogen storage capacity vs Textural properties [28].

The volume of micropores, related to the surface area in microporous materials, is proportional to the storage of hydrogen at 77 K in materials such as activated carbon, single-walled carbon nanotubes, zeolites and MOFs. However, at low pressure, in the isotherms of the Cu-BTC, a strong adsorbate adsorbent interaction is evidenced, with a positive effect in the increase of the storage capacity.

### *3.1.3 Methane storage*

The use of porous materials to store methane by adsorption, consider materials with elevated surface areas to store high amounts of gas at lower pressures than the conventional compressed natural gas technology (CNG). Methane adsorption was studied in microporous materials with differences in their pore geometry and surface chemistry in order to evaluate the characteristics that enhance methane storage in porous materials.

Figure 10 shows the methane adsorption isotherms at high pressure of different microporous materials including metal-organic frameworks (Cu-BTC, MIL-53 and ZIF-8), zeolites (5A and 13X) and an activated carbon (Maxsorb).

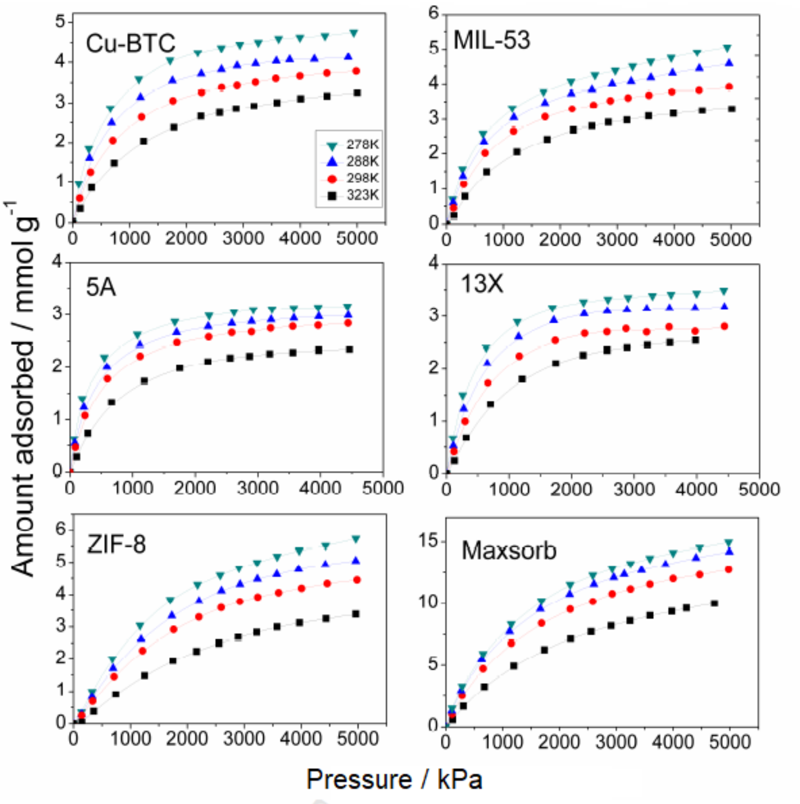


**Figure 10.** High pressure adsorption isotherms of methane at various temperatures [3].

The sample with higher specific surface area is the activated carbon, which shows a higher adsorption capacity. In Figure 11, a relationship between textural properties and the methane adsorption capacity is observed, and a linear tendency is found with the $S_{BET}$ and $V_o$. ZIF-8 presents a deviation indicating that, under the study conditions, the textural and surface properties of this sample, *i.e.*, geometry and pore size, and the affinity towards methane molecules, might not be favorable for the storage of methane at that pressure and temperature.

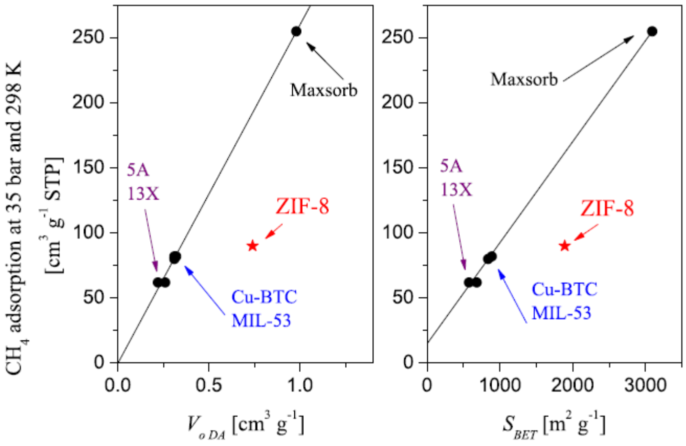


**Figure 11.** Correlation between micropore volume and specific surface area with the methane storage capacity of microporous materials [3].

## 3.2 Environmental applications

### *3.2.1 Carbon dioxide capture*

The difficulty in reducing the $CO_2$ emissions has led to much effort, and resources have been dedicated to the development of new technologies or processes to capture or storage this gas. One of the possible alternatives is based on the adsorption process using different porous materials. Microporous carbons such as activated carbons have been widely used in the $CO_2$ capture since they require simple synthesis processes and due to its physicochemical properties. Nevertheless, at higher pressures, some mesoporous carbons have shown higher $CO_2$ adsorption capacity than microporous activated carbon. The thermodynamic measurements indicate that $CO_2$ is captured by a physisorption mechanism involving direct access (through mesopores) to the micropores within the material [29]. Hierarchical porous materials like CMK-n with an ordered mesoporosity have been studied considering that both the gas adsorption and regeneration processes become less complex than in other materials such as activated carbons. A deep study about the synthesis of CMK-5 and its use as $CO_2$ adsorbent at high pressure (up to 10 bar) and 308 K was carried out, finding the effect of the micropores and mesopores in the $CO_2$ uptake. Figure 12 shows the isotherms, pore size distribution and TEM micrographs of several CMK-5 materials, and it can be observed that the obtained materials are micro-mesoporous materials with high ordered porous structure and defined pore sizes.

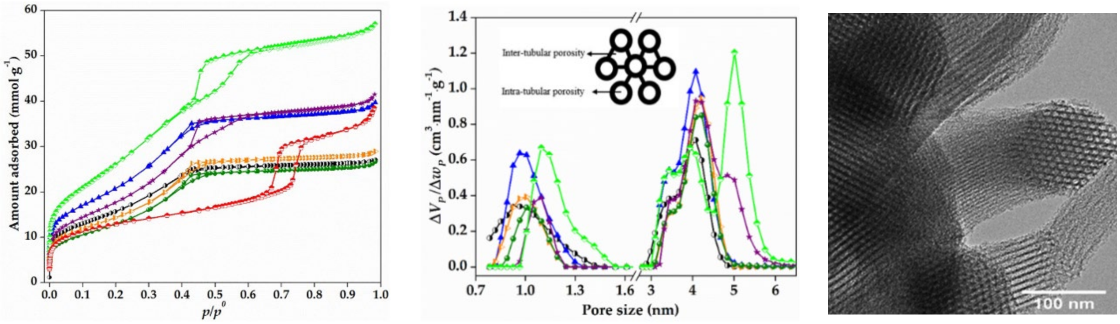


**Figure 12.** $N_2$ adsorption-desorption isotherms at 77 K; Pore size distribution; TEM Micrograph of CMK-5 materials [8].

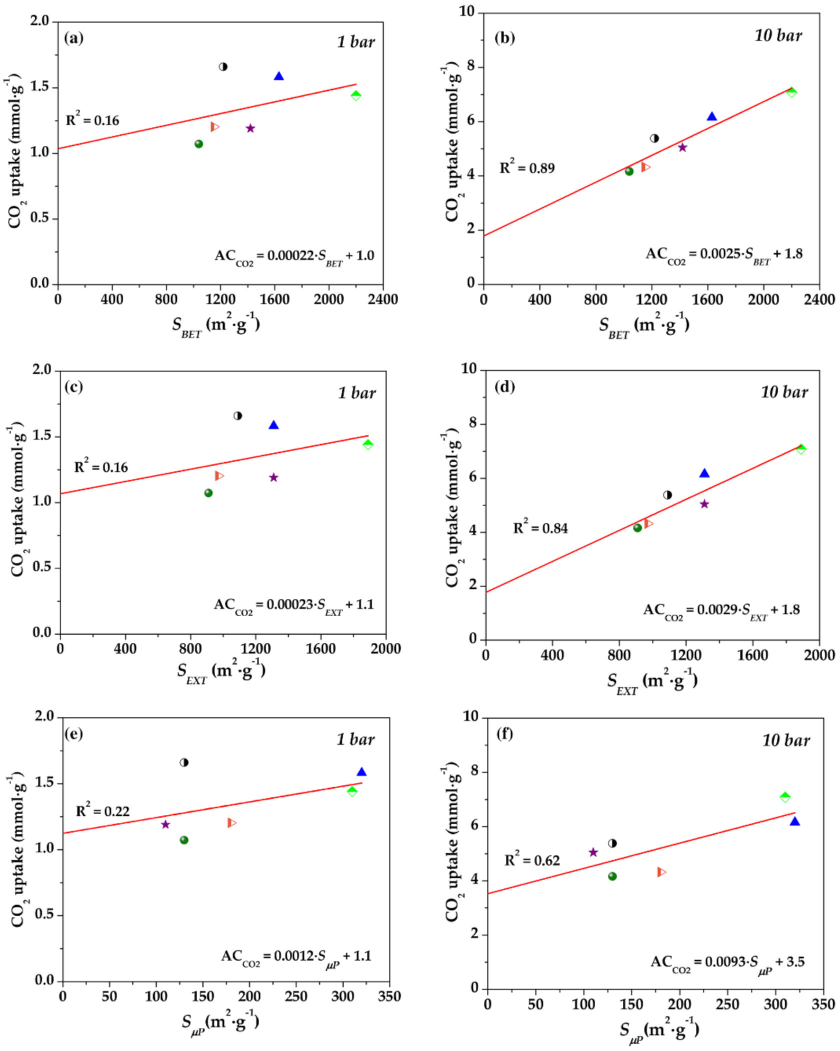


**Figure 13.** Correlation between the textural properties ($S_{\mathrm{BET}}$ and $S_{\mathrm{EXT}}$) and the $CO_2$ adsorption capacities at 1 bar and 10 bar, and 308 K [8].

In Figure 13 can be seen a good correlation (0.89 – 0.84) with $CO_2$ adsorption capacity at 10 bar with the specific surface area ($S_{\mathrm{BET}}$) and the external surface ($S_{\mathrm{EXT}}$). In contrast, a weaker correlation (0.16) is found at 1 bar. These results indicate that $CO_2$ adsorption at low pressure does not use all the specific surface area available (micropores and mesopores) as it is used at high pressure (i.e. 10 bar). Thus, likely the micropore volumes are the main responsible for the $CO_2$ adsorption at low pressure, however, at higher pressures, the mesopores play an essential role.

### *3.2.2 Adsorption*

Many chemical products like fungicides are used in agricultural activities to improve the quality and quantity of food production. Nevertheless, these agrochemical products pollute the natural resources with serious consequences to human health and the environment. For example, the removal of thiabendazole (fungicide widely used in the Alto Valle de Rio Negro-Neuquén, Argentina) using aluminum pillared clays as adsorbents, in comparison with their starting material (a natural clay mineral) was studied.

As is observed in Figure 14, when the amount of adsorbent increases the adsorption capacity abruptly decreases for the natural clay mineral and slightly increases for the Al-PILC. In the natural clay mineral, the low adsorbent concentration could produce an aperture of the clay mineral layers, increasing its exposed surface which favors the ionic exchange and therefore its adsorption capacity. An increase in the natural clay mineral concentration could generate different particle associations in dispersion, decreasing its exposed surface and then its adsorption capacity. Conversely, the PILC do not present this behavior in aqueous dispersion, and consequently, its adsorption capacity increases as the amount of PILC increases. The picture (Figure 14, right side) shows this effect and gives us an idea of the facility to remove the adsorbent from the dispersion.

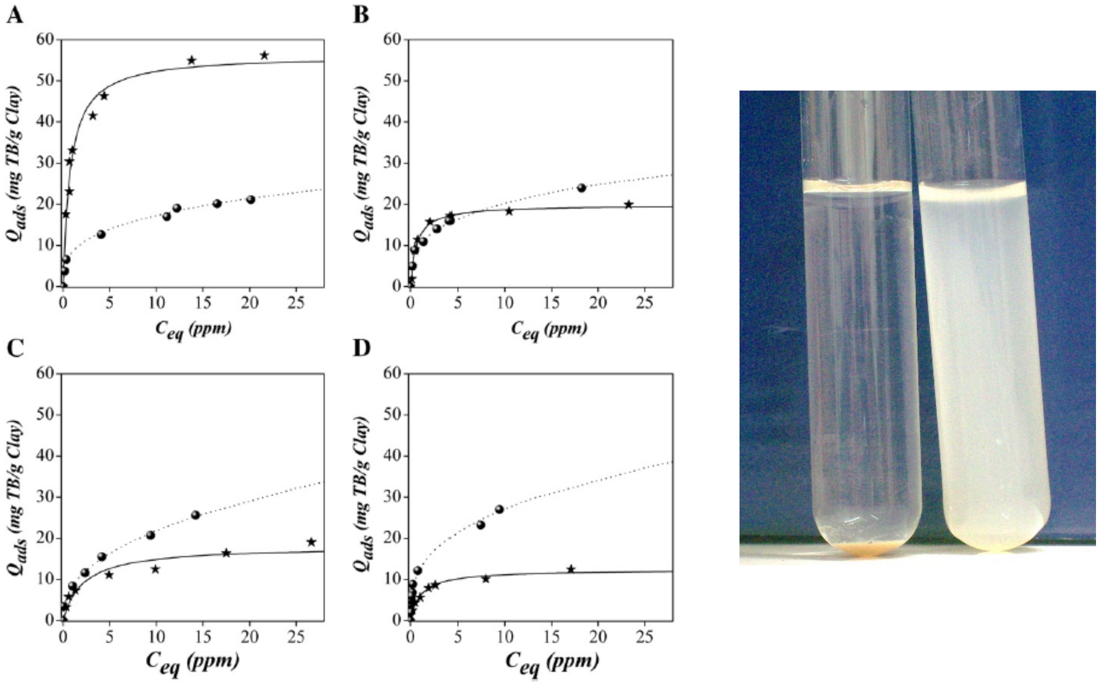


**Figure 14.** TB adsorption isotherms on natural clay mineral (with Langmuir fit) and Al-PIL (with Freundlich fit) for different adsorbent concentrations: A) 0.6 g/L, B) 1.2 g/L, C) 1.8 g/L and D) 2.5 g/L. In the right side: natural clay mineral (right) and the Al-PILC (left) in water dispersion [11].

## 3. Conclusions

Highly porous materials with different textural properties have been obtained and studied (silicas, carbons, MOFs, zeolites, pillared clays, among others).

Modifications in the synthesis processes of these porous materials let us the possibility of tuning their textural properties for applications in energy and environment.

A linear relationship was found between the textural properties such as specific surface area and micropore volume, and the adsorption capacity of the gases. However, it was found that also the mesopores play an important role in the adsorption, mainly at higher pressures.

Textural properties like geometry and pore size play a relevant role in the adsorption process, however the affinity towards gas molecules also must be studied and take into account. Both, texture and surface chemistry could enhance or worsen the adsorption capacity.

**Acknowledgments:**

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**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

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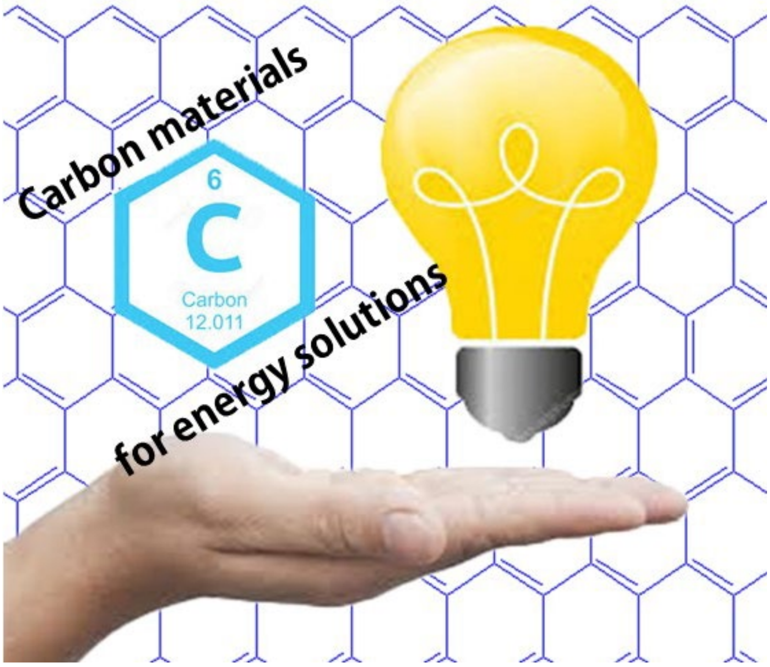
## Graphical abstract



## 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.*

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## 1. Introduction

Over the past decades, carbon nanomaterials in various allotropic forms (e.g., fullerenes, nanotubes, graphene, and diamonds) have received wide attention owing to their unique physical and chemical properties tunable in a wide range, such as large specific surface area, narrow pore size, large pore volume, low density, high thermal and mechanical stability and excellent electronic conductivity. Considering such features, different carbon nanomaterials have been developed: fullerenes ($C_{60}$),[1] carbon nanotubes (CNTs),[2] graphitic carbon nanoonions, graphene,[3] graphene oxide (GO),[4] carbon nanofibers (CNFs),[5] microporous carbons (MPCs),[6] ordered mesoporous carbons (OMCs),[7] porous carbon spheres (CSs),[8] hollow carbon spheres (HCSs),[9] etc. To date, it is reasonable to say that the research on structured carbon materials is facing the most rapid development period ever. Carbon nanomaterials are versatile platforms for a wide number of applications, including sensing,[10] adsorption,[11] electronics,[12] nanomedicine,[13] energy harvesting, storage and conversion[14] and catalysis.[15] These applications depend to a great extent on the features of the carbon structure, surface chemistry, crystallinity, and morphology which, in turn, are determined by the chosen chemical synthesis methodology. The rational and controlled synthesis on carbon nanomaterials will offer a promising opportunity to accurately understand their (desired) physical and chemical properties from the molecular level point of view and, thereby, provide valuable guidelines for practical applications. This minireview spotlights our recent research progress on the synthesis of porous carbon nanomaterials for energy storage and conversion applications.

## 2. Results and discussion

### 2.1. Porous assemblies derived from graphene-based materials: Solvothermal synthesis.

Graphene-based materials have been one of the most extensively explored materials for energy applications during the last ten years. Graphene and graphene-based materials have been used as electrodes for dye-sensitized solar cells, photo-catalysts for water splitting, electrocatalysts for oxygen reduction/hydrogen evolution in fuel cells, high–performance electrodes in supercapacitors, ion ($Li^+$, $Na^+$, $Al^{3+}$, etc.) batteries, lithium-sulfur batteries and lithium–air batteries.[16-20] Graphene-based materials present good solubility and processability in water and several organic solvents. The electrical conductivity reported for pristine graphene is 64 $mS\cdot cm^{-1}$,[21] and the electrical conductivity of graphene-based materials can be broadly adjusted by controlling structural parameters such as the oxidation degree (a measurement of the C/O ratio), sheet size, interlayer distance (and interaction) and dopants. Furthermore, graphene-based materials present high heterogeneous electron transfer activity toward redox-active molecules, good electrochemical stability[22] and could exhibit high surface area, since the theoretical specific surface area for a single layer graphene sheet is 2630 $m^2 \cdot g^{-1}$.[23]

One of the main challenges to overcome when it comes to producing an energy storage device—probably the most explored application so far—containing graphene-based materials as an active or passive element, is the loss of specific surface area compared with the theoretical one. The main reason for such loss is the lack of exposure of the whole graphene area to the electrolyte, which affects the double layer charging. The envisioned solution to this problem is to synthesize three-dimensional (3D) structures. There are different synthetic approaches; the template methods, which can be classified in hard-templates (e.g. silica or polystyrene spheres, metal foams, and ice crystals) and soft-templates (polymeric or amphiphilic compounds); and the template-free methods. The easiest and more straightforward synthetic route is the self-assembly of two-dimensional (2D) GO (or modified GOs) dispersed in water by using a one-step hydrothermal method.[24]

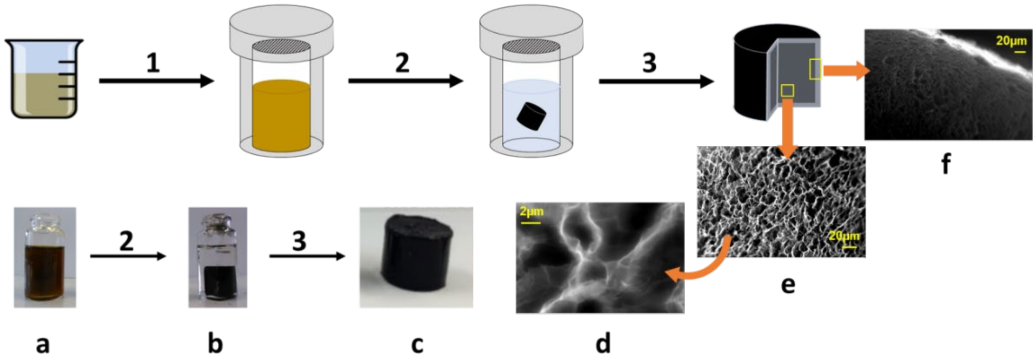

**Figure 1.** Schematic illustration of the hydrothermal synthesis of rGO aerogel. 1. transfer of the GO aqueous dispersion ~ 3–4 wt %, (photo a) to the autoclave system. 2. Thermal treatment at 180 ºC during 12h (photo b, hydrogel after the hydrothermal process). 3. Hydrogel after the freeze-drying procedure (photo c). SEM images of the aerogel core (photos d–e) and wall (photo f).

One alternative is the preparation of hydrogels by chemical reduction of GO with different reducing agents under atmospheric pressure[25] or using crosslinkers such as molecular species capable to interact with GO by non-covalent (e.g. hydrogen bonding, hydrophobic interactions) or covalent bonding.Although the mechanism involved in the hydrothermal formation of 3D structures is not well known,[26] it is accepted that the interaction between graphene-based layers is triggered by a hydrothermal-assisted concurrent reduction of the GO (Figure 1).

In addition, some applications in energy require the presence of a second material (e.g. metal or oxide nanocrystals, other 2D materials, carbon nanoparticles or nanotubes) to enhance the catalytic activity, capacity, conductivity, etc.

In order to be effective and efficient, this second material has to be homogeneously distributed on the entire 3D structure, and because of its size, usually cannot be incorporated to the monolithic structure after the synthesis. Qiu *et al.* reported a one-step hydrothermal method to the growth of ultradispersed mesoporous $TiO_2$ nanocrystals with (001) facets on GO aerogel.[27] In another strategy, Wang *et al.* used a colloid sol as a precursor to produce monolithic 3D metal oxide/rGO aerogels by a solvothermal-induced self-assembly approach.[28] Also, it has been reported the formation of 3D $Fe_2O_3$/rGO composites by a solvothermal route using $Fe(CH_3COO)_2$ as a precursor in water and ethanol.[29] Using a similar approach, the one-pot solvothermal treatment of dispersions containing GO and the precursor, composites of rGO and $V_2O5$,[30] $VO_2$,[31] $Co_3O_4$,[32] ZnO,[33] CoS,[34] $MoS_2$[35] have been obtained. For instance, Zensich *et al.* reported a simple but effective strategy to fabricate practical high-loading $Li_2S$ cathodes for high-performance Li–S batteries in carbonate-based electrolyte by the irreversible electrochemical decomposition of a hydrothermally prepared 3D rGO-covered $MoS_2$ particles composite to a $Li_2S$@rGO (plus Mo nanoparticles) composite.[36] The $Li_2S$@rGO cathode containing high $Li_2S$ loadings of $\approx 5$ $mg \cdot cm^{-2}$ showed a high reversibility in capacity and excellent electrochemical performance which was explained by the benefits of the synergetic effect between the formed $Li_2S$ particles and the rGO substrate which provide superior charge transfer kinetics and ionic pathways in the composite.

Graphene and GO materials provide great potential for commercial application and it is expected a strong development of 2D and 3D heterostructured graphene-based materials in the next years.

### 2.2. Hierarchical porous carbons for fuel cell anodes

Hierarchical porous carbons (HPC) are very interesting carbon-based porous materials. Anodes for fuel cell application require a high dispersion of the catalyst (small metal nanoparticles) over the surface of a conductive material. This situation results in a highly porous matrix composed by the supporting (conductive) material and the catalyst. It is known that the structure of the support material affects severely the mass transfer, in detriment of the fuel cell performance. In addition, with increasing thickness of the catalyst layer, the probability for re-adsorption and further reaction of these intermediates increases, resulting in a structure-depending reaction mechanism.[37-39] Two possible approaches can be considered for the mass transport improvement: (i) short diffusion lengths or (ii) improved diffusion using thicker materials with hierarchical pore design.[40-41] Considering the second approach, the use of a high surface monolithic carbon (a piece of carbon with dimensions on the scale of microns) allows a decrease of the ohmic drop originated in the interparticle contact.[42] On the other hand, the use of new synthetic routes let stay the surface area high enough, beside to the improvement of the mass transport by the *ad-hoc* pore design in hierarchical levels. The most used synthetic routes imply the combination of different templates and there are many interesting reviews discussing these methods.[43-46] Regardless of the approach used, after impregnation of the template with a carbon source (precursor) via polymerization or surface-grafting methods,[47] the precursor it turned into carbon by a heat treatment (pyrolysis) at high temperature (above 800 ºC) in an inert atmosphere (i.e.: argon or nitrogen). Hard templates, like silica and metal oxides, survive to pyrolysis and must be removed before (or after) pyrolysis by chemical etching. If the template is removed before pyrolysis (route A→B'→C' in Figure 2), the whole process results in an inverse replica of the template without additional porosity. If the template is removed after pyrolysis (route A→B→C in Figure 2), a second level of porosity emerges.

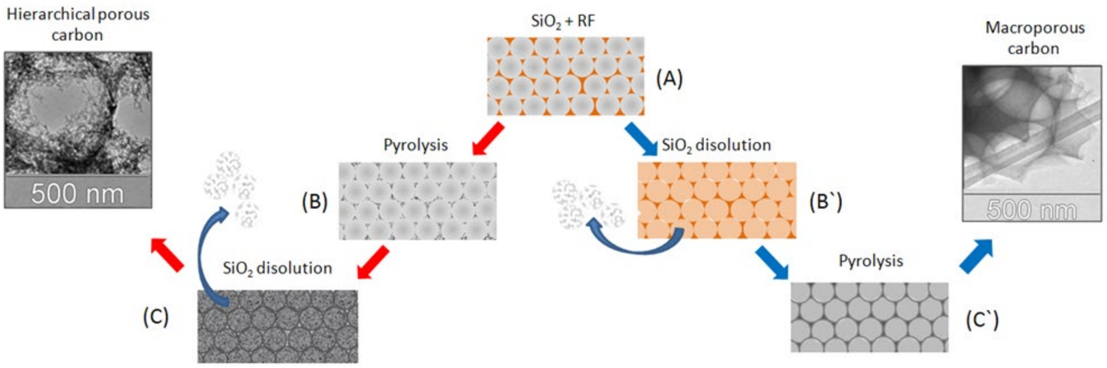

**Figure 2**. Schematic illustration of the pathways for the carbon synthesis. A-B-C: Synthesis of the mesoporous carbon with hierarchical porous structure (HPC). A-B'-C': Synthesis of macroporous carbon.

Baena-Moncada *et al*. reported a HPC supported Pt/Ru for methanol electrooxidation (Figure 3). Compared with the supported commercial PtRuC (E-TEK) catalyst, the HPC-Pt/Ru catalyst exhibited improved electrooxidation activity due to the enhanced mass transport through the porous matrix of the HPC-based support.[41] In addition, the porous structure affected not only the fuel feeding and current density but also the expulsion of reaction sub-products. The conversion efficiency from methanol to $CO_2$ analyzed by calibrated differential electrochemical mass spectrometry (DEMS) showed that the HPC-Pt/Ru has higher current density than the conventional PtRuC E-TEK catalyst even with almost the same $CO_2$ conversion efficiency.[48] Baena-Moncada *et al*. also obtained similar results for formic acid electrooxidation with PtPd supported on HPC.[49] The observed high surface activity towards methanol and formic acid electrooxidation was mainly explained by the authors in terms of the reactant accessibility to the active sites.[42]

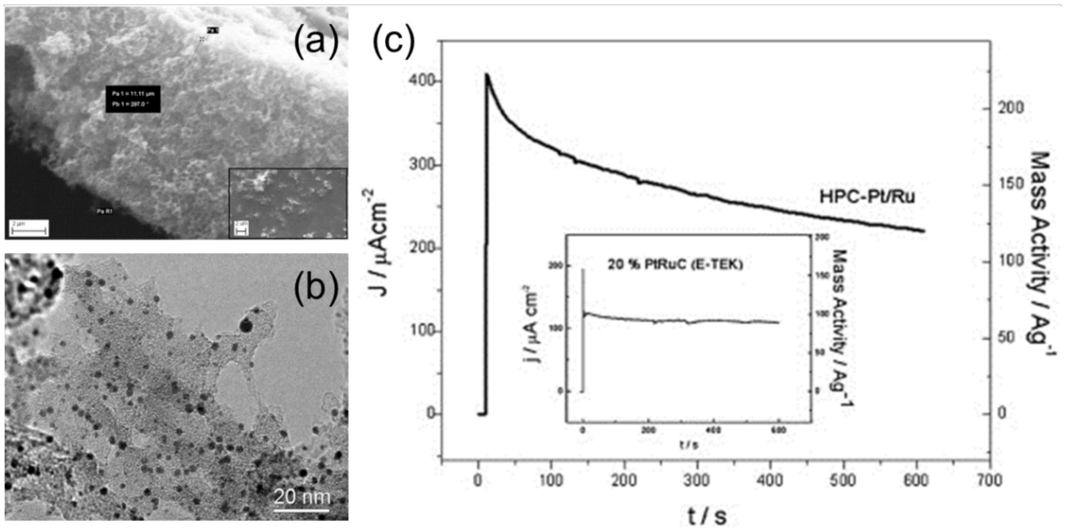

**Figure 3**. (a) SEM image and (b) HRTEM image of the HPC-Pt/Ru. (c) Current transients for methanol electrooxidation on HPC-Pt/Ru at 0.55 $V_{RHE}$, 1 M $CH_3OH$/1 M $H_2SO_4$. T = 60 ºC. *Inset*: current transients for methanol electrooxidation on commercial PtRuC (E-TEK) at 0.55 $V_{RHE}$, 1 M $CH_3OH$.

## 2.3. High-stable Li–S batteries with functional interlayers/hybrid separators.

The lithium-sulfur (Li–S) battery is considered one of the most promising rechargeable energy storage technologies to meet the increasing demand for clean energy transportation systems owing to its notable high theoretical energy density of 2600 $Wh \cdot kg^{-1}$, nearly five-fold greater than state-of-the-art lithium-ion batteries.[50] In addition, the use of elemental sulfur as active cathode material has the advantages of being naturally abundant, inexpensive and environmentally friendly. However, the commercialization of Li–S batteries is challenged by several hurdles, including the insulating nature of sulfur, the large volume changes of sulfur during cycling and, principally, the shuttling of soluble lithium polysulfide (LiPS) intermediates between electrodes, resulting in a fast capacity fading and poor cycling life.[51-53]

The first Li–S battery was described in the 1960s.[54] However, the advances on Li–S batteries reported cells with low capacity and fast capacity fading during the next decades. In 2009, Nazar's group developed an innovative approach to physically encapsulate sulfur, boost its redox kinetics and accommodate the volumetric enlargement of sulfur during lithiation by infiltrating molten sulfur into a highly ordered, nanostructured mesoporous carbon host.[55] This approach has triggered an exhaustive research on using diverse porous, conductive, nanostructured carbon matrices as host cathodes.[56-57] However, the morphology change of solid sulfur to liquid LiPS intermediates during cell operation and the weak interaction of non-polar carbons with polar LiPSs often result in the inevitable escape of soluble LiPS out of the cathode framework. This produces the misplacing of the initial contact with the carbon substrate and lead to the formation of $Li_2S$/sulfur agglomeration/clusters on both the cathode/separator interface and the lithium anode surface, ending up with the sulfur activity and causing the degradation of the battery lifespan.

Beyond conventional encapsulation of the elemental sulfur into porous carbonaceous host matrices, in the last few years, major progress has been made to address the challenges aforementioned by using conductive porous carbon interlayers (located between the separator and the cathode) and functional hybrid separators with a carbon coating layer which further face to the sulfur cathode.[58] The ability of functional hybrid separators and interlayers to capture/retain migrating LiPS intermediates significantly reduces the parasitic reactions, as well as their capability to reactive “numb” sulfur-based species, also enhances the electrochemical performance and lifespan of Li–S cells.

Balach *et al.* comprehensively investigated different mesoporous carbons derived from phenolic resins. Mesoporous carbons with a pore size around 12 nm and tuned pore volume from 1.1 to 3.2 $cm^3\ g^{-1}$ were produced by a facile silica-templated casting process to further fabricate bifunctional interlayers and mesoporous carbon-coated separators for Li–S batteries with high areal sulfur loadings (Figure 4).[59-63] All the cathodes were prepared by using a simple and scalable carbon black/elemental sulfur mixture without any further typical melt diffusion process, at 155 ºC. The mesoporous carbons not only possessed tunable pore volume,[59] but could also be modified with N-dopants[62] or N, S co-dopants.[63] The authors found that undoped mesoporous carbon with the highest pore volume of 3.23 $cm^3\cdot g^{-1}$ delivered the most important enhancement in the electrochemical performance (initial discharge capacities of 1364 $mAh\cdot g^{-1}$

and high reversible capacity of 1015 mAh·g$^{-1}$ after 200 cycles at a current rate of 0.2 C; 1 C = 1672 mA·g$^{-1}$), highlighting the role of the pore volume rather than the specific surface area.[59] While for the heteroatom-doped mesoporous carbon with a comparable pore volume, N, S dual-doped mesoporous carbon-coated separators enabled the best battery performance even when the sulfur loading was as high as 5.4 mg·cm$^{-2}$.[63] At a current rate of 0.2 and 0.5 C, high areal capacities of 5.9 and 2.9 mAh·cm$^{-2}$ were achieved, respectively.

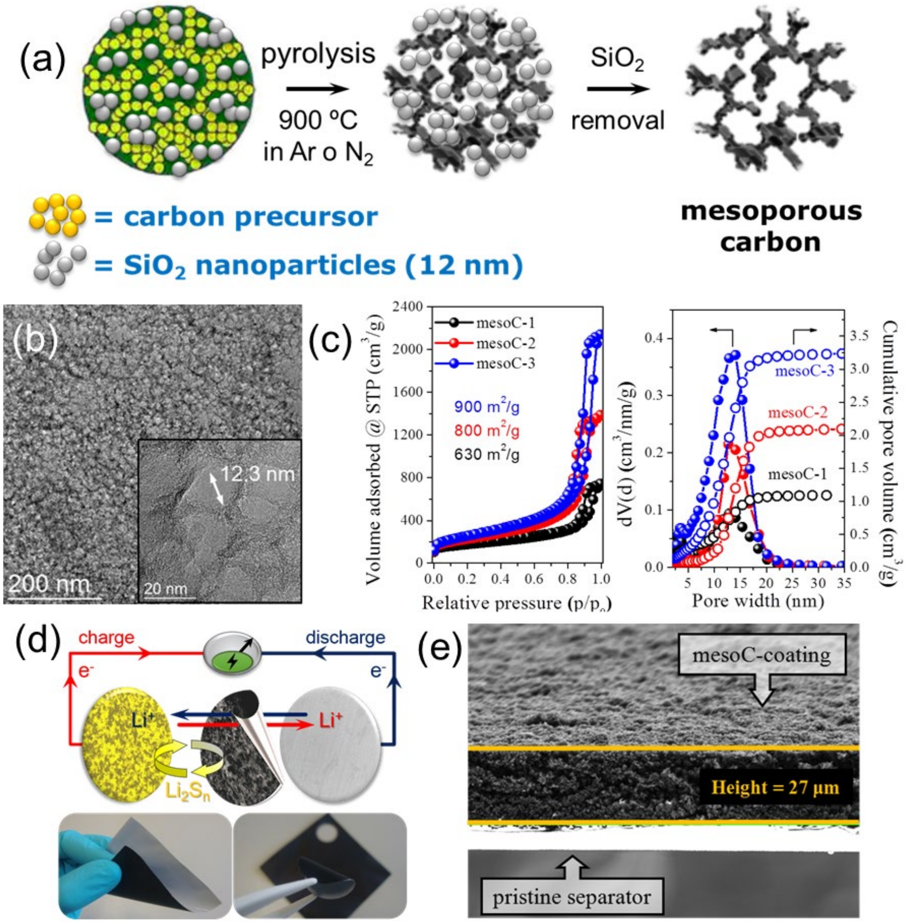

**Figure 4**. (a) Schematic illustration of the synthesis of mesoporous carbons. (b) Representative TEM images and (c) nitrogen physisorption isotherms and the corresponding pore size distributions of the mesoporous carbons. (d) Schematic configuration of the Li–S batteries with a mesoporous carbon-coated separator and digital images of the mesoporous carbon-coated separator. (e) Cross-sectional SEM image of the mesoporous carbon-coated separator.

Although heteroatom doping significantly promotes the chemisorptivity of carbon materials, a multi-functional RuO$_2$ nanoparticle-anchored mesoporous carbon-coated separator could also be used as an electrocatalytic and adsorbing LiPS-net to enhance the redox reaction of migrating LiPS species, to improve active material utilization and boost the electrochemical performance of Li–S batteries.[64]

## 2.4. Sulfonated carbonaceous materials as a heterogeneous catalyst to biodiesel production

There is an increasing interest in improving the environmental conditions claiming of alternative sources of fuel.[65] The biodiesel is one of the best candidates to replace the diesel fuel. Biodiesel—a mixture of methyl esters of long-chain fatty acids—is renewable, clean, and it can be used without modifications in the engines.[66] The biodiesel is usually synthesized by using three kinds of catalysts (either homogeneous or heterogeneous ones): alkalis, acids and enzymes.[66] The homogeneous alkaline catalysts (e.g. sodium hydroxide) are highly hygroscopic and absorb water from the air during storage, affecting their performance.[67] The homogeneous acid catalyst (e.g. sulfuric acid) present the same drawbacks, with the additional problems related to its high corrosive characteristic that obligate to take extra cautions during its handling and storage.[68] Moreover, heterogeneous catalysts are solid and could be quickly separated from the product by filtration and they are also capable to catalyze both the esterification and transesterification reactions in one step.[69] In this regards, Tamborini *et al.* reported a heterogeneous acid catalyst based on a resorcinol-formaldehyde (RF)-based porous carbon functionalized with sulfonic groups.[70] The RF resins used as carbon precursor were synthesized by the polycondensation of resorcinol and formaldehyde using both polydiallyldimethylammonium chloride (PDADMAC) and cetyltrimethylammonium bromide (CTAB) as porous stabilizers and sodium carbonate as the basic catalyst for the reaction.[71-74] Subsequently, the carbons were sulfonated by reacting with concentrated sulfuric acid.[75] Textural properties of the sulfonated porous carbons are summarized in Table 1. These carbons were denoted as PCSx, where *x* represents the molar ratio of CTAB to PDAMAC (0.43, 1.28 and 3.85). The CPSx samples as potential catalysts exhibited good specific surface area (100–400

$m^2 \cdot g^{-1}$) and a large mesopore size around 30 nm (Table 1). These physical properties are of great interest since a large pore size could allow an easy diffusion of the reagents and the products during the catalytic reaction.

**Table 1**. Textural characteristic of CPSx

| Material | $S_{BET}$[a] ($m^2 \cdot g^{-1}$) | $V_0$[b] ($cm^3 \cdot g^{-1}$) | Vmeso ($cm^3 \cdot g^{-1}$) | Vt[c] ($cm^3 \cdot g^{-1}$) | Dp[d] (nm) |
|---|---|---|---|---|---|
| CPS0,43 | 100 | 0.038 | 0.570 | 0.608 | 34 |
| CPS1.28 | 95 | 0.038 | 0.550 | 0.589 | 30 |
| CPS3.85 | 405 | 0.190 | 0.550 | 0.740 | 30 |

[a] Determined from BET theory. [b] Determined from Dubini-Radushkevich. [c] Volume adsorbed at $P/P_0=0.984$. [d] Determined from the BJH desorption method.

Furthermore, the sulfonation process employed to generate the catalytic active sites effectively produces the incorporation of the sulfonic group on the materials surface. The samples $CPS_{0.43}$ $CPS_{1.28}$ and $CPS_{3.85}$ revealed high content of sulfonic groups with 0.71, 1.31 and 0.60 $mmol \cdot g^{-1}$, respectively.

The catalytic activity of the CPSs for the Fischer esterification of acetic acid in ethanol showed that the $CPS_{0.43}$ achieved the highest conversion with 90% after 10 h (Figure 5a). Moreover, the $CPS_{1.28}$ and $CPS_{3.85}$ catalysts also achieved higher conversions (85% and 89%, respectively) than the commercial sulfonated catalysts Nafion® 117 (75%) and Amberlite IR-120 (65%) used as reference materials. After re-utilization of the $CPS_{1.28}$ catalyst, the percentage of acetic acid conversion decreased after each esterification process, reaching conversions of 93%, 85%, 80% and 60% after the first, second, third and fourth cycles, respectively (Figure 5b). This decrease in the percentage of conversion was in agreement with the decrease in the content of sulfonic groups, which changed from 0.71 $mmol \cdot g^{-1}$ in the first cycle to 0.40 $mmol \cdot g^{-1}$ in the fourth cycle, due to the groups leaching and to the deactivation of active sites.

All in all, sulfonated porous carbons could be used as potential catalysts in the acetic acid-ethanol Fischer esterification and they could be reused several times.

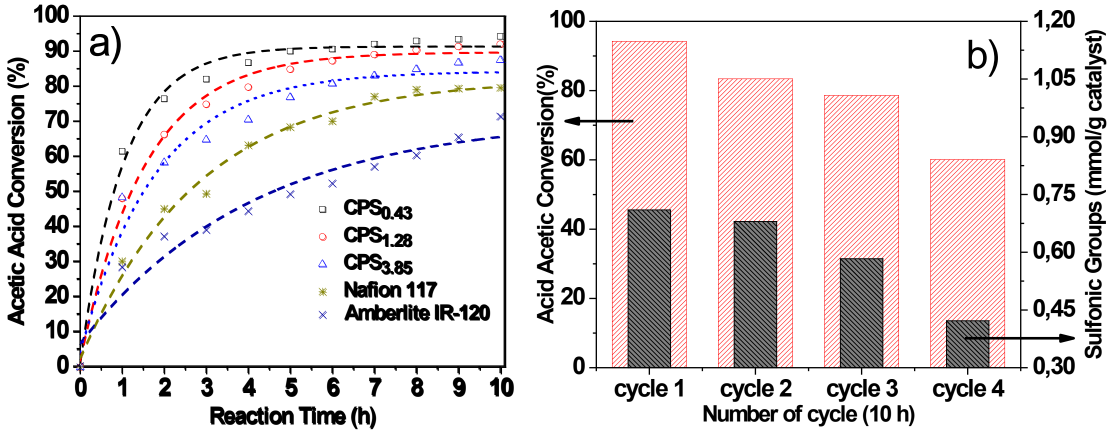

**Figure 5**. (a) acetic acid-ethanol esterification at 75 °C and (b) reusability of the $CPS_{0.43}$ catalyst.

## 3. Conclusions

Through this minireview, we have provided an overview of the fabrication and application of nanostructured carbon materials for storage and conversion of energy. We have also reviewed our recent approaches for the rational synthesis of carbon nanomaterials with tuned properties for these applications. Beyond energy field, nanostructured carbons are highly versatile materials with the possibility to control their properties and they have proven to satisfy the requirements of other application fields.

Several approaches can be considered for the designed carbon materials. They can be prepared from a polymer precursor and the final structural properties can be adjusted by using soft or hard template strategies. Even dual pore forming can be used to obtain hierarchical porous structures. Moreover, the properties of the carbon nanomaterials can be finely-tuned after manufacturing by chemically modifying both its structure and surface features.

We believe that, based on the interdisciplinary knowledge of carbon nanomaterials, the innovation in nanotechnology could be promoted by integrating several areas of expertise, such as electrochemistry, materials science, physics and organic chemistry. The obtained knowledge allows the understanding on the structure and texture control of the designed materials and thus, how they influence on the system's performance. However, most of the materials made use non-renewable resources, arising environmental concerns. The use of the synthetic methods with renewable feedstocks is a current challenge to decrease the carbon footprint of the materials and devices.

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**Anales de la Asociación Química Argentina**

**División Jóvenes Profesionales**

Mini-Review

# ORDERED MESOPOROUS ORGANOSILICA ADSORBENTS FOR INORGANIC POLLUTANTS REMOVAL FROM WATER

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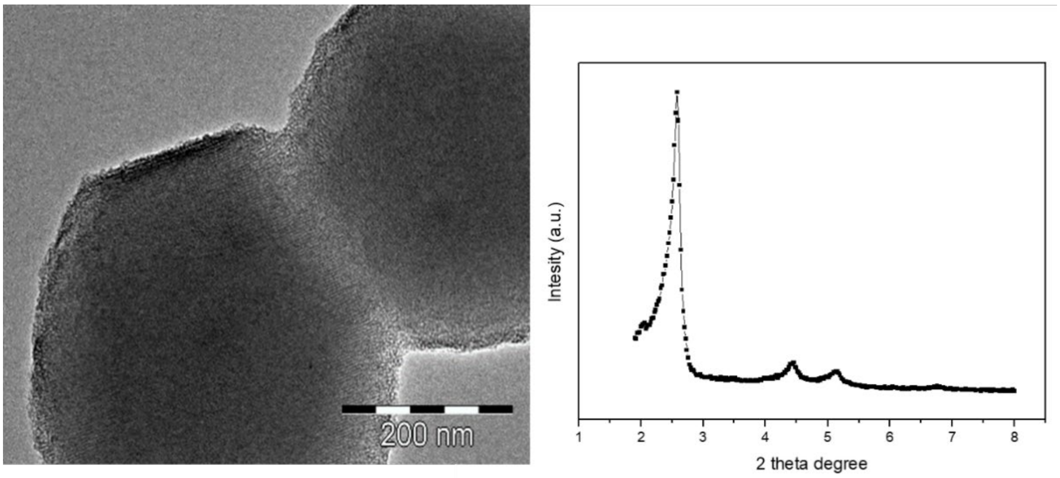
## Graphical abstract



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.*

## 1. Introduction

The availability of potable water is a key factor for human health and development. However, fresh water systems are being modified by several anthropogenic activities, which generate and discharge a wide variety of effluents into lakes, rivers, lagoons and soils containing organic and inorganic pollutants. Therefore, the treatment of aqueous effluents to ensure the conservation, recovery (if needed) and sustainable use of terrestrial and inland fresh water is mandatory for our survival as a species.

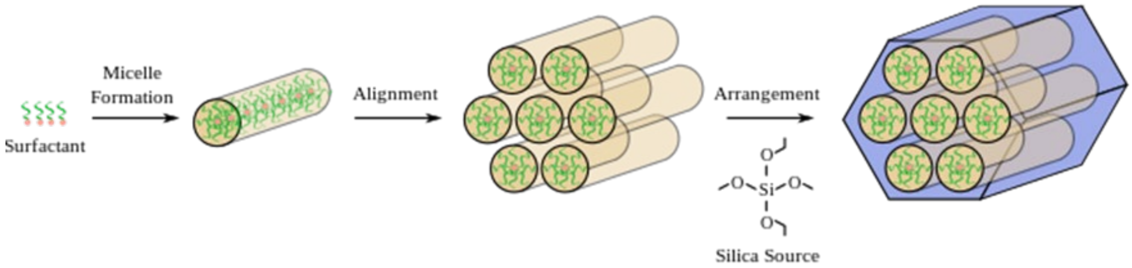
Inorganic compounds are related to several industrial processes, agricultural practice, as well as mining activities, and their existence in natural water courses is one of the most serious environmental problems today. Alloys and steel manufacturing, metal finishing, electroplating, leather tanning process, pigments synthesis and dyeing, use of fertilizers and pesticides, extraction of precious metals, all these processes give rise to aqueous effluents with varying concentrations of a wide variety of inorganic-based compounds. Currently, several methods are being used to treat these effluents looking for minimizing the negative impact to the surrounding aqueous environment: chemical extraction, precipitation, reverse osmosis, remediation by electrodeposition, bioleaching process, ion exchange, cross flow ultrafiltration [1, 2]. Nonetheless, these methods have their own restrictions such as low efficiency, low selectivity towards specific target, high operational costs and production of large quantities of toxic slurry. In this way, adsorption-based technologies emerge as the most effective, economic and selective method for water treatment and preservation. Besides, it can be applied in remote areas on the small scale without electricity requirements. Adsorption is defined by IUPAC as an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Therefore, the surface, i.e. the adsorbent, is the key in these processes. As a consequence, in the last years considerable efforts are being devoted to the development of new adsorbents[3]. The ultimate purpose of these studies is to develop an adsorbent, the ideal one, which fulfilling all optimal features: very high adsorption capacity, perfect selectivity, long-term durability, good mechanical stability, fast uptake processes, easy regeneration consistent with a negligible loss of adsorption capacity on multiple adsorption-desorption cycles, low cost and low toxicity to living species.

In this review, we will discuss the most relevant advances in the development of ordered mesoporous silicas and its application as sorbents to remove inorganic pollutants from water matrices, analysing to what extent these solids are close to the ideal adsorbent. Different preparation methods to synthesize this type of nanostructured mesoporous solid phases are mentioned, highlighting the main features that can be obtained. Special attention is focused in the case of hexavalent chromium removal from water matrices using MCM-41 functionalized with different agents.

## 2. Preparation and characterization methods of ordered mesoporous silicas

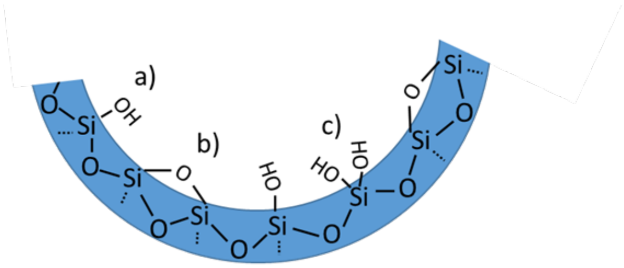
Ordered mesoporous silicas (OMS) are solids structures with a periodic and regular arrangement of well-defined pores, whose walls are constituted by an amorphous inorganic skeleton of $SiO_2$. The pore diameters can be regulated between 2 and 30 nm with a very narrow pore size distribution. The most known and studied mesophases belonging to this group are the hexagonal MCM-41 and cubic MCM-48 (MCM: Mobil Composition of Matter), the hexagonal SBA-15 and cubic SBA-16 (SBA: Santa Barbara Amorphous) [4, 5]. They can be synthetized by the sol–gel route using different silica sources, although the most commonly used is based on alkoxysilanes (e.g. tetraethoxysilane –TEOS–), and a template agent. In a general way, the synthesis can be described as a polymerization reaction, where a monomer containing a silicon atom polymerizes around of structure generated by the template agent. The final mesophase obtained depend markedly of the careful control of the synthesis parameters. Thus, choosing different template agents, by controlling the pH of the synthesis media, and by using or not, co-solvents or additives, mesophases with different pore arrangements, pore diameters, particle sizes, morphologies and topologies can be obtained [4-6].

A typical synthesis procedure of the hexagonal MCM-41 mesophase, with a pore diameter of ≈ 3.0 nm, is represented in Scheme 1. This synthesis is carried out by mixing an aqueous ammonia solution containing the template agent named hexadecytrimethyl-ammonium bromide (CTMA-Br) with TEOS as silica source. The final obtained solid phase was an MCM-41 structure without specific particle morphology [4]. However, using an ethanolic solution of ammonia instead of an aqueous solution, Grün and co-workers were able to prepare submicron sized mesoporous silica spheres (particles sizes of around 500 nm) [7]. This last procedure is in fact a modification of the well-known Stöber process used for the synthesis of non-porous silica spheres [8]. Besides, by changing the number of carbon atoms of the template agent that produces the micelles, as it can see in Scheme 1, the same hexagonal pore ordering can be obtained, but with different pore diameters values, *e.g.*: 1.8 and 2.0 nm using templates agents with 8 and 10 carbon atoms respectively [4, 9].



**Scheme 1.** Sol-gel synthesis pathway of a hexagonal ordered mesoporous silica (surfactant extraction by solvent treatment or calcination is done later, as the last step).

On the other hand, modifying the ratio TEOS/CTMA-Br, the MCM-48 cubic mesophase is obtained instead of the hexagonal structure [10]. If a hydrothermal post-synthesis treatment is incorporated before the surfactant removal, an increasing of the pore diameter and the pore walls thickness via an increase of the crosslinking within the silicate framework occurs [11]. Other possible change in the synthesis route consists in the introduction into the reaction media of a second template agent, which has different affinity for silica. This last modification produces the generation of a layer that surrounds the particles, limiting thus their growth to sizes as small as 20 nm [12]. Besides, different particles morphologies (spheres, shell-like, rugby-like, hexagonal) can be achieved throughout the incorporation, in the synthesis media, of co-solvents and/or a second template agent such as Pluronic F127, ethanol, methanol, ethylene glycol, etc [7, 13]. A characteristic feature of all OMS materials is its very high specific surface area, independently of the synthesis pathway chosen and the final mesophase.



**Scheme 2**. Schematic view of possible groups on the inner surface of an OMS: (a) Si-OH: free silanol, (b) Si-O-Si: siloxane brigde (c) HO-Si-OH: geminal silanol.

In this way, after surfactant removal, values as high as 1500 $m^2$ per gram of solid can be obtained [4,5,7,13,14]. In terms of chemical surface composition of the as-synthesized OMS, different type of silicon atoms can be found: free silanols, germinal silanols and siloxane bridges. These last are produced as a result of two free neighbouring silanols condensation [15]. The Scheme 2 depicts a typical surface of an OMS as-synthesized. Finally, the synthesis is completed after removal of the template agent. This can be done either by calcination or by solvent extraction. The use of one or other method will lead to the same pores arrangement but different chemical surface composition. In a general way, the calcination produces a more hydrophobic pore's surface with a minor Si-OH content due to the appearance of more quantities of siloxane bridges [16]. While the solvent extraction procedure -in which a hydrochloric acid or ethanol solution under reflux is generally used- generates pores with high silanols density. About this, Wang and co-workers reported that the silanol density was increased from 3.4 Si-OH/$nm^2$ for a calcined SBA-15 to 8.5 Si-OH/$nm^2$ for the same solid but where the template was removed by solvent extraction [17].

Due to the chemical reactivity of OMS is essentially governed by their surface properties and composition, their careful characterization is a fundamental issue. A deep surface understanding can be carried out using a set of techniques. X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), $^{29}Si$ and $^{1}H$ nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) give useful information about the surface composition, denoting the potential applications of the synthesized OMS [14, 15].

In Figure 1, a typical X-ray diffraction (XRD) pattern of the ordered hexagonal MCM-41 mesophase and its transmission electronic microscopy image (TEM), are depicted. This sample was synthesized using the procedure described by Cai and co-workers[18]. The solid is composed by faceted particles (≈ 1 μm of size), with linear and parallel channels inside them, with diameter in the mesopore range (≈ 2.8 nm). The XRD pattern has an intense peak at $2\theta = 2.6^\circ$ and two broad and less intense peaks between $2\theta = 4 - 6^\circ$ This diffractogram is characteristic of the hexagonal ordered mesoporous arrangement of the MCM-41 structure.

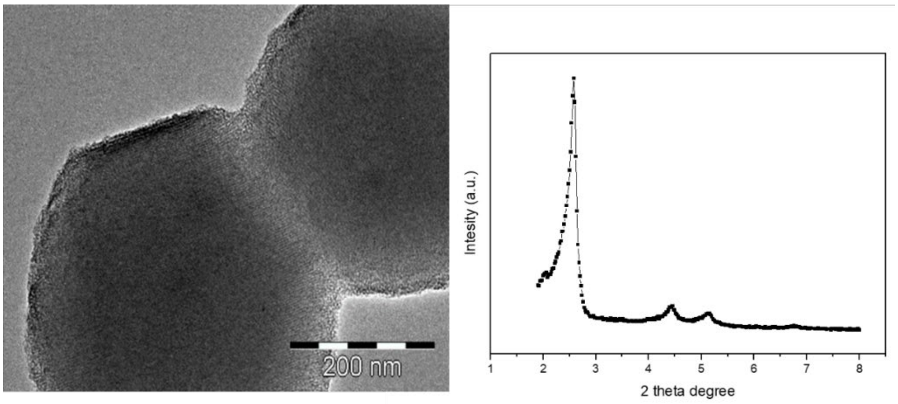
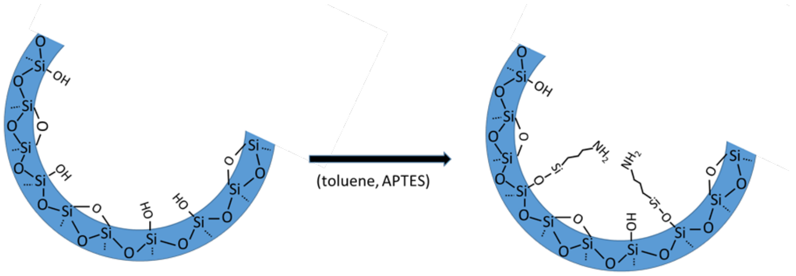


**Figure 1.** TEM image and powder XRD profiles at low angles of an MCM-41-$NH_2$ sample.

All the aforementioned demonstrate the enormous possibilities of OMS nanostructures synthesis, with a wide range of chemical and structural properties. Due to that, this kind of materials have been applied in many fields such as catalysis[19], drug delivery[20], bones regeneration[21], separations[22], optoelectronics and sensing[23].

## 3. Preparation of OMS-based sorbents: surface modification by organics groups incorporation

As it was already mentioned, the surface chemistry of as-synthesized OMS is governed by the presence of silanol species. The acidity of silanol groups, pKa ≈ 3-4, offers the possibility to attach by a post-synthesis treatment a wide variety of organic functions over the OMS surface[24]. The final composite material consist in an organic-inorganic hybrid ordered mesoporous silica which combines in a single solid phase both, the properties of a rigid ordered three-dimensional silica network and the particular chemical reactivity of the organic functionalizing agent[23-24]. A typical functionalization reaction takes place between an organoalkoxysilane with silanols onto the OMS surface (Scheme 3).



**Scheme 3.** Post-synthesis reaction between OMS surface silanols with 3-amipropyltrimetoxysilane (APTES). Notice that not all silanols are replaced by aminopropyl groups.

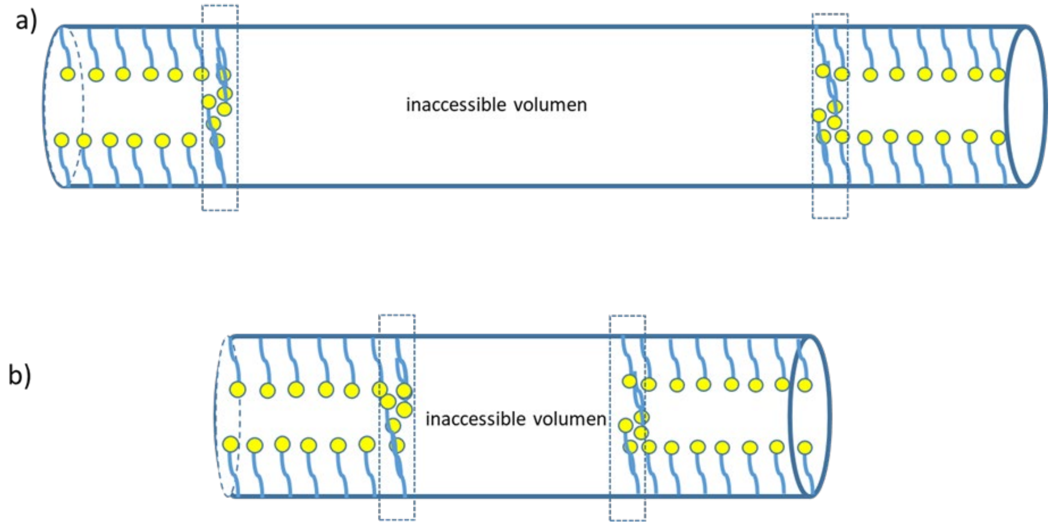
Such grafting is often made in an organic solvent (e.g. toluene, hexane) in which alkoxysilanes or chlorosilanes are soluble. The most common anchored terminal groups are $NH_2$, COOH, SH and $SO_3H$ [9, 17, 20]. Exists a second way to synthetize hybrid organic-inorganic OMS materials, this is named co-condensation or direct method. In this one the organic function, *i.e.* the selected organosilane, is introduced in the synthesis mixture jointly with the TEOS. This step is followed by the hydrothermal synthesis and, finally, the chemical removal of the surfactant is performed (in this method only solvent extraction can be used). The organic functions are distributed homogeneously by this way, unlike the post-synthesis surface modification, avoiding any pores blockage. However, two main disadvantages appear with this synthesis procedure: (a) the formation of the periodic mesoporous structure is often disturbed by the presence of the organosilane in the synthesis mixture, giving rise to solids with low chemical and thermal stability and (b) a fraction of the organic functions are unexposed to the surrounding because they remain inside the pore walls, so they cannot interact with other species[25].

The first examples of adsorbents based on hybrid mesoporous silica have been disclosed in 1997[26, 27]. The most important finding of these works was to demonstrate that the ability of the functionalized adsorbents to bind mercury ions to each active site (thiol ligand) in the material is directly related with the homogeneity and the large framework structural of these type of solids. This advantage was observed in the OMS mesostructures but not when non-ordered silica gel-based adsorbents functionalized with the same thiol ligands were used. This result was attributed to pores blocking effects when the grafting is performed in these disordered porous frameworks. Although disordered silicas, such as silica gel, can exhibit surface areas and average pore diameters comparable to OMS, their broad pore size distributions leads to a significant blockage after functionalization treatment[26, 27]. Thus, high sorption rates in OMS, such as MCM-41, MCM-48, SBA-15 and SBA-16, can be attributed exclusively to the uniform porous structure made of regular and linear mesochannels with monodisperse sizes, where diffusional hindrance is avoided or minimized. The absence of diffusional impediments can be quantified by the Thiele modulus (h) applied to a diffusional/adsorption process[28]. For example, for an MCM-41-$NH_2$ composed by spherical particles (mean particle diameter of 480 nm) with average pore size of 2.5 nm and specific surface area equal to 834 $m^2/g$, a Thiele modulus value of $h^2 = 10^{-7}$ was obtained, expressing that the intraparticle diffusion rate exceeds the adsorption rate by about seven orders of magnitude[28].

After those pioneering works, huge amounts of reports appeared deepening the studies on hybrid OMS-based sorbents, with new synthesis pathways looking for the improvement on pollutant removal performance. All the reported data indicate high separation capacities for these adsorbents jointly with the possibility of regeneration and reuse with low or medium sorption capacity loss. Most of these works investigate the OMS performance as sorbents in batch assays. Instead, very few of them use continuous flow systems. The effects of different operating conditions such as temperature, adsorbent loading, initial ion concentrations, pH and presence of competitive ions have been described. Saad *et al.* demonstrated that phosphate removal was maximized at pH = 5 and it was almost unaffected by the presence of competitive ions when an ammonium-functionalized MCM-48 was used as sorbent[29].

It is already widely demonstrated that pH of the aqueous solution to be treated is a key point to keep in mind when OMS-based sorbents are used, due to the dependence of the OMS surface chemical composition with the pH, especially after organic groups incorporation. For example, the surface of an MCM-41-$NH_2$ when the working pH is fixed at 2 is composed mainly of ammonium ($–NH_3^+$) and silanols (Si-OH) entities, leading to the preferential adsorption of anions on the positively charged sites on the adsorbent surface[30]. At a pH value of 7, the MCM-41-$NH_2$ presents a more complex pore surface composition. Silanols are partially deprotonated creating silanol/silanolate entities which provide negative charges. Meanwhile, with a pKa of ≈ 9–10 (depending the organic tail formulae), the N-containing groups are as ammonium and amino. Therefore, the surface at neutral pH presents negative, neutral and positive sites[30, 31].

The concentration and speciation of the anchored organics groups at the OMS surface is other parameter that affects the performance of this hybrid sorbents. For example, Gartmann *et al.* demonstrated, using MCM-41 and APTES, that increasing the amount of water in the silane solution leads to a non-uniform distribution of the grafted amino groups onto the MCM-41 surface[32]. In the same way, increasing the mass ratio silane/OMS during the functionalization step, the probability of a fast clogging pores -which induces a dramatic fall in the specific surface area and low organic groups loading- is increased. Both phenomena will generate an adsorbent with low removal capacity. By reducing the size of the particles to be functionalized, it is possible to achieve greater load of organic groups, avoiding or minimizing the pores blockage due to clustering of silanes molecules[33]. We have demonstrated this using two different MCM-41 systems, one of them with an average particle diameter of 500 nm and the other one with 1000 nm. A decreasing in the specific surface area from 1032 to 727 $m^2/g$, after APTES post-synthesis functionalization, was registered for the small MCM-41 particles, while a change from 1055 to 517 $m^2/g$ in was observed for the biggest ones[33]. Scheme 4 represents and clarifies this concept showing how an early blockage of pores give rise to a hybrid OMS sorbent with low surface area and low organic groups loading per gram of sample.



**Scheme 4.** Pores blockage representation due to postsynthesis surface treatment with a silane agent. a) and b) represent two cylindrical pores with the same diameter but different length, the largest (a) give rise to an inaccessible area bigger than the shortest (b).

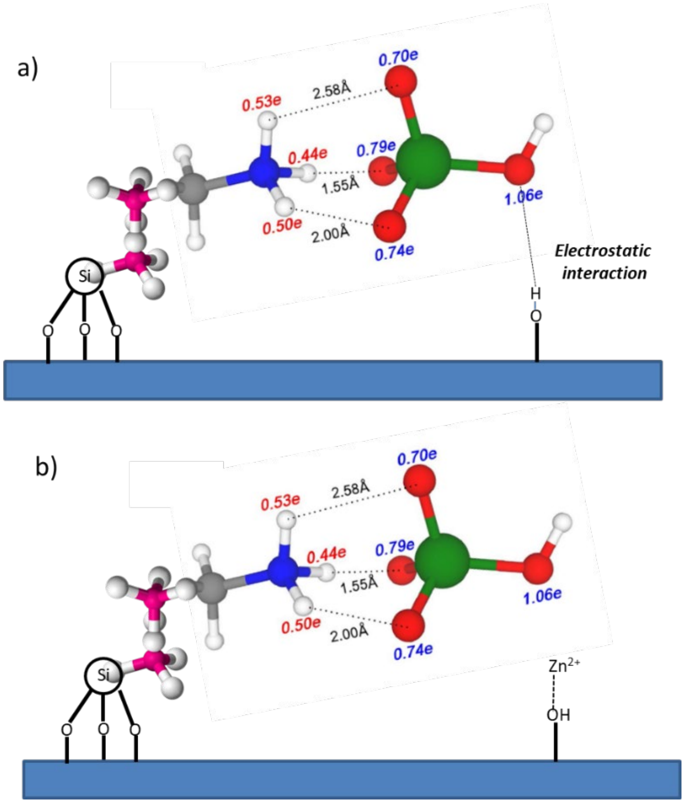
Therefore, being able to control both the load and the distribution of the chemical functions anchored onto the surface is a crucial issue that should be addressed in the OMS-based sorbents development.

## 4. Study case: hexavalent chromium elimination using modified MCM-41-based materials.

Chromium is at the top-priority list of toxic inorganic pollutants defined by the US Environmental Protection Agency due to its mutagenic and carcinogenic properties against biological species[30, 33]. Many industrial activities are associated with hazardous liquid wastes with high contents of chromium compounds: alloys and steel manufacturing, metal finishing, cement production, leather tanning and pigments synthesis and dyeing, among others[30, 33]. Chromium in water matrices, discharged from industries, is commonly trivalent (Cr(III)) or hexavalent (Cr(VI)). However, the hexavalent specie is many times more toxic than the trivalent one because it is highly water soluble and carcinogenic [30, 33]. Therefore, in order to minimize industrial sludges, strategies for remediation of aqueous effluents with high levels of Cr(VI) involving a mechanism of adsorption and reduction to the less toxic trivalent state, present a clear advantage versus those that only achieve separation of Cr(VI) without chemical transformation.

Most of the works describing concomitant adsorption-reduction of hexavalent chromium deal with bio-sorbents or carbon-based systems[34, 35]. Bio-sorbents, especially those with high contents of amino groups, are able to promote this mixed mechanism to eliminate Cr(VI) from water[34]. Surprisingly, in the field of hybrid OMS-based sorbent there are very few articles reporting Cr(VI) reduction. Walcarius *et al.* reported the synthesis of a bi-functionalized MCM-41 containing thiol and sulfonic acid moieties (MCM-41-SH/$SO_3H$). The final hybrid material was applied to the removal of Cr(VI). The obtained results can be explained as a sorption-reduction mechanism involving reduction of Cr(VI) by thiol groups and immobilization of Cr(III) onto sulfonic acid moieties[36]. Besides, the generated Cr(III) species remained adsorbed in the material in a proportion that reached about of 35% of the total Cr(III) produced. On the other hand, metallic iron nanoparticles were immobilized on OMS surface to reduce Cr(VI). This composite material has proved higher removal capacity than the unsupported $Fe^0$ nanoparticles, showing again the advantages of introducing OMS structures as adsorbents [37].

Recently, we have demonstrated that MCM-41-$NH_2$ sorbents have high efficiency for aqueous Cr(VI) elimination at pH = 2[28]. Besides, the selectivity towards to chromium oxyanions could be modulated by changing the pH of the aqueous solution to be treated, adsorbing (or desorbing) preferentially chromium compounds instead of other ions, such as $Zn^{2+}$ [30]. An important finding was that the final Cr(VI) concentration decreases dramatically after batch assays in acidic conditions throughout a combined adsorption-reduction process. The chromium sorption by MCM-41-$NH_2$ can be described as follows: the adsorption of hexavalent chromium starts with the electrostatic interaction between $HCrO_4^-$ and the positive ammonium surface species. After, a partial reduction to Cr(III) occurs [33]. The Cr(III) is partially retained on the surface of the sample, as it was also described by Walcarius[36]. Besides, about of 50% of Cr(III) is kept on the MCM-41-$NH_2$ surface. The experimental adsorption data were well fitted using the Langmuir model, obtaining a total chromium elimination capacity ($q_m$) of 86.4 mg per gram of MCM-41-$NH_2$. However, when zinc was introduced into the water matrix, the reduction capacity was totally suppressed and $q_m$ fall to 30.3 mg per gram of amino-MCM-41[30, 33]. Taking into account that cations such as Zn(II) in aqueous solution interact preferentially with the silanol surface species, this result would indicate that the combined mechanism of adsorption-reduction of hexavalent chromium would be related to the existence of free surface silanols and aminopropyl groups simultaneously. The Scheme 5 shows the interaction between chromium and the MCM-41-$NH_2$ surface, with and without zinc, using the results of first principles calculations reported by Choi *et al.*[38]. When protonated amino functions have a neighbour free silanol, the adsorbed $HCrO_4^-$ can interact with this entity at the same time (Scheme 5-a). Thus, the silanol group would produce an electrostatic attraction on the oxygen atom of –OH that belongs to $HCrO_4^-$. Therefore, the bond between Cr and OH is weakened and the Cr(VI) reduction could occur. On the contrary, if cations are present in the water solution they block the silanols sites, and the interaction $HCrO_4^-$-HO-Si does not occur (Scheme 5-b). The availability of free silanols to interact with Cr species adsorbed on ammonium functionalities and the occurrence of the reduction step can be understand considering the well-known mechanism of Jones Oxidation Reaction (JOR)[39].



**Scheme 5**. Cr (VI) is adsorbed on protonated primary amine by hydrogen bonding. If a free silanol neighbour group is present a second interaction can occurs giving rise to the mixed sorption-reduction mechanism (a). If there are not free silanols or if they are blocked by other species, the second interaction is not possible and only Cr(VI) sorption is observed (b).

## 5. Summary and Outlook.

In this brief review we have described diverse synthesis methods and structural characteristics of ordered mesoporous silica (OMS). Besides, we have mentioned applications in different fields, focusing in their use as sorbent of hexavalent chromium from water. In order to get the highest capacity and selectivity of adsorption, OMS must be functionalized with very diverse type of organic groups. The resulting organic-inorganic OMS hybrids have high removal capacities and selectivities towards to Cr, Cu, Zn, As, P, Hg, etc. in aqueous matrices. Although important advances in the "tailored" structural design of these adsorbents have been made, a lot of disadvantages have yet to be overcome. For example, OMS more "robust", able to be unalterable to many adsorption-desorption cycles are necessaries. In the same way, these organic-inorganic

OMS hybrids must be resistant to the leaching of the functionalizing agent during these cycles. Bearing in mind that the ordered mesochannels structure is essential with the aim to use the solid as sorbent and that an OMS is strongest when its wall has more thickness, the functionalization of nanospheres of the SBA family could allow to achieve these goals. Finally, there is an operative system different from batch reactors that has practically not been studied and that can have a marked influence on the performance and economy of the process. This is the use of a continuous flow adsorption reactor. Therefore, the exploration of this type of systems is extremely important in the immediate future.

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**Anales de la Asociación Química Argentina**

**División Jóvenes Profesionales**

Mini-Review

# RECENT STUDIES ON MAGNETIC MESOPOROUS NANOMATERIALS FOR WATER TREATMENTS

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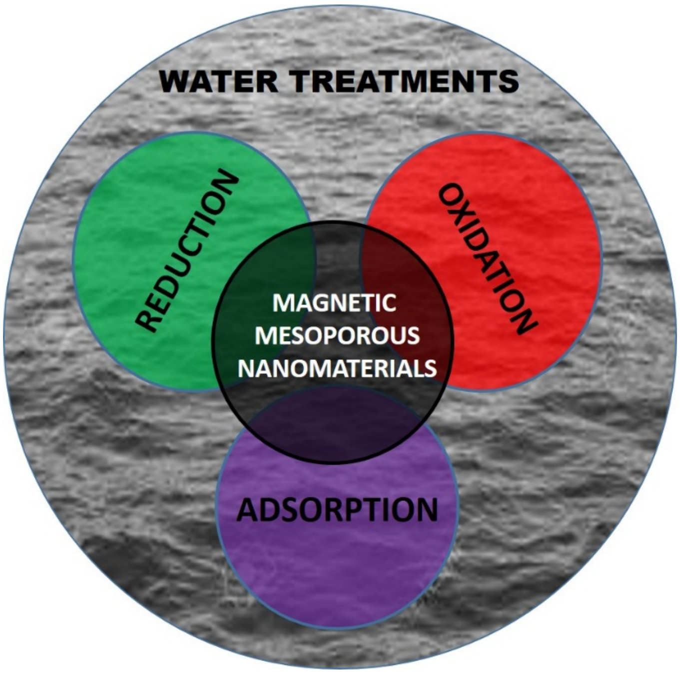
## Graphical abstract



## 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.*

## 1. Introduction

The involvement of nanotechnology in environmental applications is an important topic of current research.[1–3] In particular, nanotechnology-mediated processes can provide water treatment solutions and new treatment capabilities, expanding the water supply from unconventional water sources.[4–6] The unique properties of nanomaterials (NMs), including large surface area, catalytic activity, and magnetic properties, are all promising features for water treatment.[7] Among the NMs with potential application in wastewater treatments, mesoporous materials are propitious as adsorbents and catalyst supports due to its regularly ordered mesoscale channels, high specific surface areas and fast mass transfer kinetics.[8] Mesoporous silica- and carbon-based NMs are the most frequently mesoporous NMs studied for removal of organic contaminants by means of adsorption, and oxidation or reduction reactions. One critical point of the application of NMs in a water remediation process is their separation from treated water for further regeneration and reuse. It is important to note that the special properties that make the NMs unique and useful could adversely affect organisms and ecosystems.[9,10] Thus, avoiding its release to the environment by an efficient separation process minimizes risks to public and environmental health. This issue can be overcomed providing magnetic properties to the NMs allowing an efficient separation with an external magnetic field. Magnetic separation has emerged as a highly efficient, simple and cost-effective method compared to conventional separation processes as filtration or centrifugation.[11] Although there are many magnetic materials, the most used in water treatment are NMs based on nanoscale zero-valent iron (nZVI), magnetite ($Fe_3O_4$) and maghemite ($\gamma$-$Fe_2O_3$).[12] They possess diverse physicochemical and magnetic properties originated from the difference in their iron oxidation state and structure. Therefore, NMs with magnetic properties and mesoporous structures are very promising for efficient applications in water treatments. Recently, different strategies have been developed for the synthesis of magnetic mesoporous NMs with different morphologies and several studies related to its applications in water treatments have been performed.[13–15]

This review gives an overview of the application of magnetic mesoporous NMs in adsorption, reduction and oxidation processes for the removal of organic pollutants in water. Special emphasis will be made on mesoporous silica- and carbon-based materials. In particular, the synthesis and features of these NMs will be summarized, and the performance on the organic pollutant removal by these NMs will be addressed.

## 2. Magnetic mesoporous materials.

### 2.1. Silica based materials

Mesoporous silica-based materials are inorganic solids with a three-dimensional structure made of interconnected $SiO_4$ tetrahedra via siloxane bonds. Due to their outstanding properties, these materials have attracted an exceptional attention in water remediation. These properties include large specific surface area (200–1500 $m^2\ g^{-1}$), high pore volume (up to 1 $cm^3\ g^{-1}$), very adjustable structure and surface chemistry (*i.e.* pore size, surface functionalization, etc.), low toxicity, chemical stability and low production cost.

Since the first report of Mobile Composite of Matter family (MCM-41, MCM-48, and MCM-50 with pore sizes between 2–8 nm) in early 1992,[16,17] many other mesoporous silica-based materials were developed. KIT-5 and KIT-6, similar to MCM-41 in high specific surface area and uniform pore size but with enhanced thermal stability, were produced in 1997.[18] In 1998, researchers of the University of California developed the Santa Barbara Amorphous (SBA) family (SBA-1, SBA-2, SBA-6, SBA-8, SBA-11, SBA-12, SBA-15, and SBA-16) with larger pore diameters (7.5-32.0 nm) and thicker walls.[19,20]

The most common synthesis procedure of mesoporous silica involves a templating agent, typically a surfactant, in aqueous solution that directs the polymerization of a silica precursor, usually a silicon alkoxide like tetraethoxysilane (TEOS) (Figure 1).

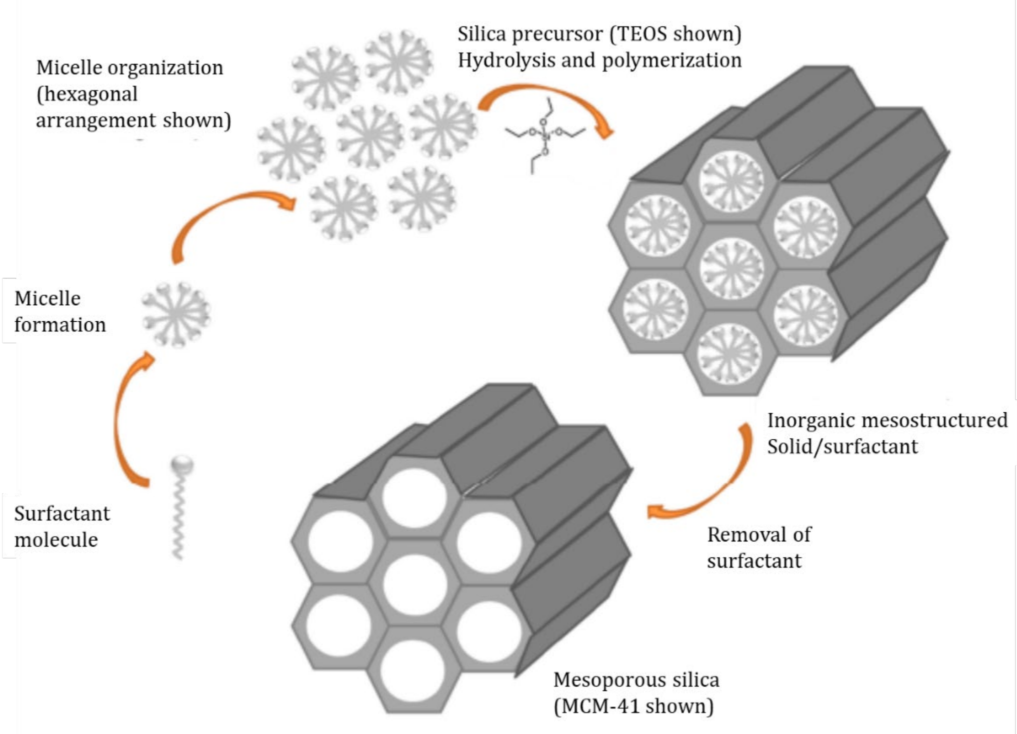


**Figure 1.** Synthesis procedure of mesoporous silica. Adapted from reference 21.

The pore size, particle size and morphology of mesoporous silica can be adjusted by selecting different surfactants, by controlling pH and by using additives.[22] For instance, the synthesis of MCM-41 typically involves the cationic surfactant cetyltrimethylammonium bromide (CTAB) obtaining a pore size between 2-3 nm; meanwhile the neutral co-polymer with larger molecular weight Pluronic P123, leads to around 9 nm pore width in the preparation of SBA-15.[3] Adding a co-solvent, like trimethylbenzene, to expand the micelle formed by the templating agent is another way to obtain wider pores.[23] It is also possible to increase the pore size by post-synthesis hydrothermal treatment.[24–26] The pore structure mainly depends on the relative amounts of template and silica precursor and the packing ability of the surfactant.[27] For silica with pore sizes among 2-5 nm the most usual structures are the hexagonal (MCM-41), 3D cubic (MCM-48) and lamellar (MCM-50), while for larger pore sizes, between 6 and 20 nm, the most common structure is 2D hexagonal (SBA-15).[28] On the other hand, mesoporous silica-based materials can be prepared in neutral, basic or acid media. Highly basic conditions ($pH > 12$) generate fast condensations inducing lamellar mesophases (MCM-50), while moderate alkaline ones ($10 < pH < 12$) preferentially produce hexagonal structures (MCM-48). SBA-15, KIT-5 and KIT-6 are prepared in acid media[29] whereas HMS (hexagonal mesoporous silica)[30] and MSU mesoporous materials[31] are synthetized at neutral pH.

Bare mesoporous silica is rarely reported as a candidate material for water remediation. Usually, a surface functionalization is needed to obtain a material with specific properties regarding of the water remediation method. For instance, functional groups (*i.e.* amino, thiol, aromatic, etc.) that can interact with pollutants (*i.e.* heavy metals, organic molecules) are usually bonded to the silica for adsorption process. Organo-substituted trialkoxysilanes are the most typical molecules applied to functionalize the silica surface.[28] This procedure can be done both post-synthesis or during the synthesis. In post-synthesis methods the alkoxysilane is added to bare silica, their alkoxy groups are hydrolysed and a covalent bond with the silanol groups of the silica surface is formed by condensation.[32] Moreover, it is possible to perform a further reaction of a previously grafted functional group, for example a polymerization of a vinyl alkoxysilane bonded to a mesoporous silica resulting in a polymer functionality.[33,34] Functionalization in the synthesis can be achieved by a co-condensation reaction adding an alkoxysilane, like (3-aminopropyl)triethoxysilane, along with the primary silica precursor in the presence of a surfactant.[35–37]

In order to provide magnetic properties to mesoporous silica-based materials, the integration of iron and iron oxides, such as magnetite or maghemite, to the mesopores structure is commonly carried out. To this end, two approaches are commonly used to prepare materials for environmental applications: **1)** nano- and micro-spheres encapsulating magnetic cores into perpendicularly aligned mesoporous shells. This approach consists in covering a core of iron oxide nanoparticles with a shell of mesoporous silica to produce hierarchical structures known as "core-shell" nanoparticles.[38] These structures have the additional advantage of protecting the iron oxide core from leaching and oxidation in water and, at the same time, reducing the tendency of aggregation of the particles. Recently, Zhang et al.[39] developed core-shell magnetic silica microspheres ($Fe_3O_4@mSiO_2$) using the amphiphilic co-polymer polystyrene-block-poly (4-vinylpyridine) as a templating agent. The obtained material showed large mesopores (10 nm), high specific surface area (244 $m^2$ $g^{-1}$) homogenous core-shell morphology and good adsorption performance of organophosphorus pesticide fenthion (Figure 2A and 2B). **2)** Ordered mesoporous materials loaded with magnetic NPs inside the porous channels. This approach consists in inserting iron oxide nanoparticles into a mesoporous silica matrix. For instance, monodisperse and hierarchically mesoporous silica microspheres embedded with maghemite nanoparticles (Figure 2C).[40] More recently, Fuentes-García and co-workers[41] dispersed magnetite nanoparticles in a silica matrix to study their magnetic properties (Figure 2D).

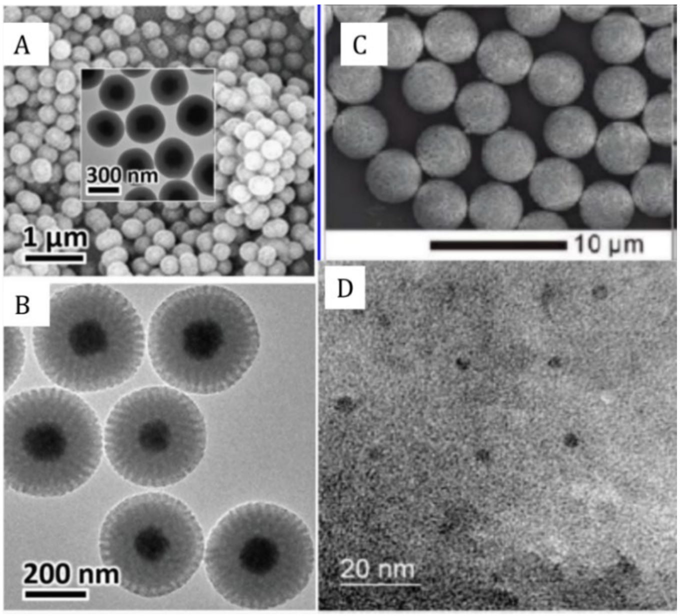


**Figure 2.** SEM (A) and TEM (B) images of core-shell magnetic silica microspheres. Adapted from reference 39. SEM image (C) of maghemite embedded mesoporous silica. Adapted from reference 40. TEM image (D) of magnetite dispersed in a silica matrix, adapted from reference 41.

nZVI can also provide magnetic properties to mesoporous silica materials.[42] However, it is more common to use nZVI as a catalyst because of its strong reduction capability against heavy metals, organochlorine compounds and nitroaromatic compounds.[43,44] In order to maximize the reactive surface area and reduce particle aggregation, nZVI can be embedded in porous materials. The most reported procedure consists in adding an iron source, like iron salts, which diffuse inside the pores, followed by reduction under hydrogen atmosphere or chemical reduction with sodium borohydride. Tang et al.[45] immobilized nZVI on SBA-15 surface. Also, nZVI was successfully loaded inside the channels of mesoporous silica nanoparticles by means of iron impregnation using hexane as a solvent followed by chemical reduction with $NaBH_4$.[46]

## 2.2. Carbon based materials

Mesoporous carbons are other key mesoporous materials for the removal of organic contaminants from water. Activated carbon (AC) is one of the most used supporting materials and one of the most ancient and studied adsorbents. It exhibits specific areas of 500 - 2000 $m^2/g$ and pore diameters generally in the micro- and meso-pore region.[47] AC is obtained from vegetable carbon sources submitted to an activation process (Figure 3). This process consists of a two-step calcination, where the raw material is carbonized at 500-800°C under inert atmosphere followed by activation at 700-1100 °C under $CO_2$ or $H_2O$ steam. Another way to achieve activation is through the use of dehydrating and oxidizing agents such as $ZnCl_2$, $CaCl_2$, KOH, NaOH, $H_2PO_4$ and simultaneous calcination at 400-900 °C.[47–51] The degree of mesoporous content depends on the type of activation and the nature of the chemical agent.[52] For instance, Hu and Srinivasan[52] reported the preparation of mesoporous activated carbons with mesopore contents above 70% by means of a simultaneous physical and chemical activation technique that utilize $CO_2$ and $ZnCl_2$. Ordered mesoporous carbons (OMC) are another family of adsorbents and supporting materials. The first OMC were obtained by Ryoo et al.[53] in 1999. This gave rise to a series of synthesis process called "*hard template*" methods, where a carbon precursor solution is impregnated in the insides of a rigid silica template (Figure 4A). After this impregnation, carbonization creates the carbon structure inside the template, and the desired product is obtained when the silica is removed via acid dissolution.[54–56] Another approach to obtain OMC are the "*soft template*" methods. In this case, a phenol/formaldehyde resin is mixed with a try-block copolymer like Pluronic P123 or F127 and polymerized at temperatures close to 100-150°C to form a solid ordered structure, then this solid is carbonized to obtain the final OMC (Figure 4B).

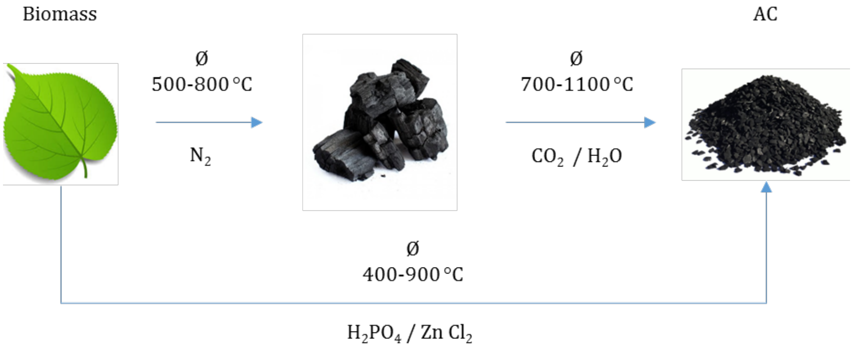


**Figure 3.** Schematic route for activated carbon synthesis.

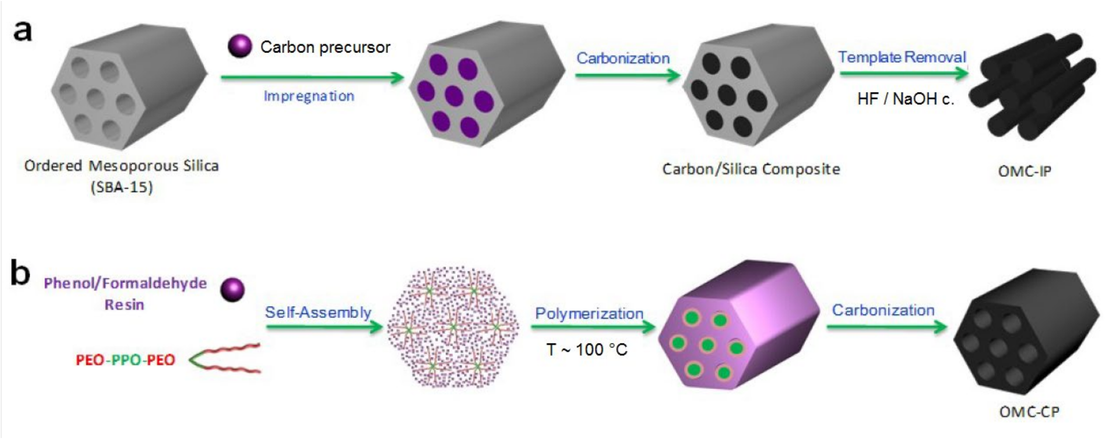


**Figure 4.** OMC synthesis routes: (A) Hard template and (B) Soft template. Adapted from reference 57.

The typical magnetic mesoporous carbon-based MNs for environmental application consist of nZVI supported on the mesoporous carbon matrix and rattle-type magnetic mesoporous hollow carbon materials. These magnetically separable materials show improved adsorption capacities,[45,58,59] can be used as chemical reductors and can serve as catalyst for Fenton like reactions.[60–63] nZVI supported on mesoporous carbon can be broadly classified into three groups: 1) iron supported on unordered mesoporous carbon (UMC), as activated carbon, biochar, etc.;[58,64] 2) iron supported on ordered mesoporous carbon, as CMK and FDU types; 3) other materials that fall out of these two categories, as "core-shell" materials and others.[65–67] The synthesis procedure of the first two mesoporous materials consists of two steps: first mesoporous carbon is subjected to a wet impregnation with iron salts. In this way, the iron precursors are incorporated into the mesopores of the material. The second step involves the reduction of the iron precursors to $Fe^0$ by means of a chemical agent, such as $NaBH_4$, or by calcination at temperatures between 500 and 1000 °C under $N_2$ or $H_2$ atmospheres (Figure 5).[68,69]

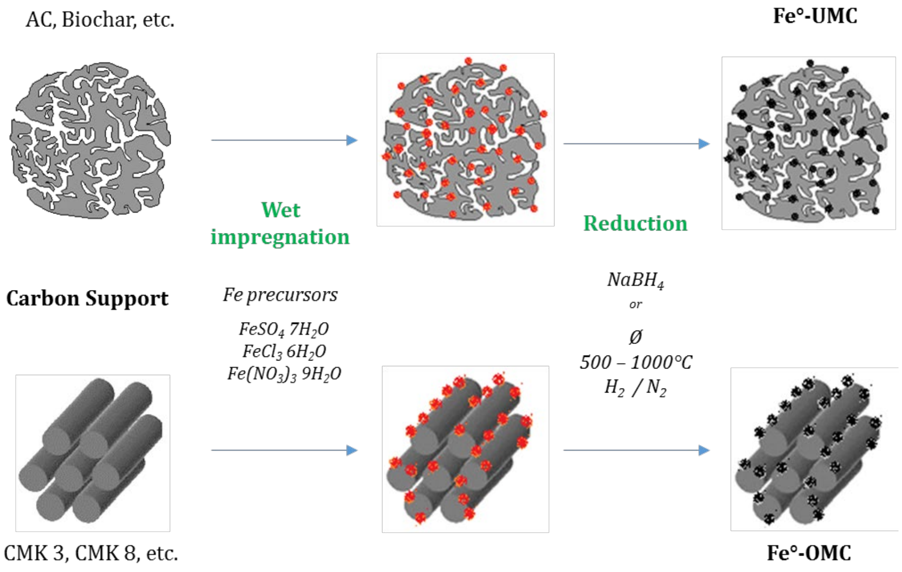


**Figure 5.** Iron loading on carbon matrix through wetness impregnation.

Core-shell materials are obtained in a process that combines carbon precursors such as glucose with iron salts, typically $Fe(NO_3)_3$. These species are dissolved and brought into contact by agitation for a certain period of time and then subjected to hydrothermal treatment at temperatures between 150 and 300 °C for times ranging from 1 to 18 h. Finally, the obtained solid is subjected to a final calcination step at temperatures between 300 and 800 °C in an inert atmosphere. Examples of this process can be found in the literature, where glucose and olive mill wastes were used as carbon sources.[65,66] On the other hand, rattle-type magnetic mesoporous hollow carbon materials have shown great promise as adsorbents for water treatment.[67] This kind of materials are prepared through a hard template approach, which involves encapsulation of phenol-formaldehyde resin in the mesopores of preformed hard template of $Fe_3O_4@SiO_2@mSiO_2$, followed by carbonization and silica removal.[70,71]

## 3. Application of magnetic mesoporous NMs in remediation processes.

### 3.1. Adsorption.

Adsorption is one of the most promising techniques to be applied in water remediation because of its low cost, ease procedure, possibility of regeneration and highly efficient removal of target pollutants. Different steps must be considered in the adsorption process: a) adsorption of the pollutant b) recovery of the adsorbent for further reuse c) adsorbent regeneration, and d) management of both the regeneration solution and the saturated adsorbent. The great challenge is developing highly efficient and reusable adsorbents.

Due to their high specific surface area, pore volume, adaptable structure, functionalizable surface and ease separation, magnetic mesoporous NMs have attracted great attention for adsorption applications. In this section, we summarized recent advances on the application of mesoporous silica- and carbon-based materials for the adsorption of different families of organic pollutants (Table 1). Among organic pollutants, cationic dyes (such as methylene blue or crystal violet) and anionic dyes (like acid orange 10 or methyl orange) are the most frequently reported in adsorption assays. Liu et al.[72] prepared a magnetic bimodal mesoporous carbon via hard-template method with Fe and Ni (Fe/Ni-OMC) as magnetic precursors and tested this NMs for the adsorption of dyes. As expected, alkaline pH was favourable for cationic dye methylene blue adsorption and acid pH was better for anionic dye methyl orange. The maximum adsorption capacities were 959.5 mg $g^{-1}$ and 849.3 mg $g^{-1}$, respectively. The adsorbent was able to be used up to 7 cycles using ethanol as the regeneration solvent. As was stated before, adsorbent regeneration is a significant step for adsorption process cost as well as the final disposition of pollutant. The most common way for regeneration is by using an eluent (e.g. ethanol, acid or basic aqueous solution, acid or basic organic solution) to desorb the adsorbate. Then, if the adsorbate has no commercial value, a degradation process (like oxidation, reduction or calcination) can be performed. Mesoporous silica-based materials were also tested for dyes adsorption. In the study performed by Brigante *et al.*[73], cationic dye malachite green and humic acids were adsorbed onto core-shell magnetic mesoporous silica ($Fe_3O_4$@$mSiO_2$) with different magnetite and silica ratio. For both species, adsorption showed a dependence with pH. They proposed that the adsorption of HA takes place by hydrogen bonds between their functional groups and the active sites of the magnetite. For malachite green, the most relevant interaction proposed were electrostatics among dye positive charge and negative-charged silanol groups.

Mesoporous carbon and organo-functionalized silica were studied as adsorbents of PAHs from aqueous media. Sharma *et al.*[74] tested the removal of 2-naphthol and naphthalene from water with mesoporous carbon coated superparamagnetic $ZnFe_2O_4$ nanoparticles (UMC-$ZnFe_2O_4$). The results revealed higher adsorption capacity ($q_{max}$ = 40.27 mg $g^{-1}$) of polar 2-naphthol than non-polar naphthalene ($q_{max}$ = 24.44 mg $g^{-1}$). The adsorbent was able to be used after 4 washing cycles with alkaline ethanol solution. Furthermore, the mesoporous carbon was prepared from date palm seed waste, which contributes for the adsorbent low-cost.

Tang et al. [45] reported the removal of 2,4-dicholorophenoxyacetic acid (2,4-D), a widely used herbicide, by ordered mesoporous carbon prepared via hard-template method, functionalized with carboxyl groups and magnetized with the deposition of iron oxide nanoparticles inside the pores (OMC-IONPs). The adsorption of 2,4-D on OMC-IONPs resulted in a fast pseudo-second order kinetics, a Langmuir-type isotherm ($q_{max}$ = 310.78 mg $g^{-1}$) and a decrease of the adsorption capacity with temperature and pH. The adsorbent was regenerated with ethanol, retaining percentage of removal up to 50% after 6 cycles of reuse. Recently, the performance of biochar supported nZVI (Biochar-nZVI) in the removal of glyphosate was studied for the first time.[58] Biochar was prepared from palm by calcination and then was used in a liquid-phase reduction process to obtain the absorbent. The adsorption process showed a pseudo second order kinetics, pH dependence and a Langmuir model behaviour. The authors proposed various mechanisms involving the removal process: pore-filling, hydrogen bonding, complexation, and electrostatic interactions. The low-cost adsorbent presented a high adsorption capacity (80 mg $g^{-1}$ at pH 4), however no reuse experiments were performed.

Huang et al.[75] prepared a particular permanently confined micelle array core-shell nanoparticles to use as adsorbent. Maghemite cores were surrounded by 3-(trimethoxysilyl)propyl-octadecyldimethyl-ammonium chloride (TPODAC) surfactant with 1,3,5-trimethyl benzene (TMB) as micelle swelling agent, then TEOS was added to covalently bind the surfactant (which has reactive methoxy group) onto the magnetic cores. Three different TMB:TPODAC weight ratio were used to prepare the adsorbent nanoparticles. In this work, the authors studied the adsorption performance of the as prepared nanoparticles ($\gamma$-$Fe_2O_3$@$SiO_2$-TPODAC) on methyl orange, sulfamethoxazole, gemfibrozil, acenaphthene and phenanthrene. It was found that larger amounts of TMB results in noteworthy higher sorption kinetic rate as well as slightly higher sorption capacity to ECs and PAHs. In addition, the core-shell nanoparticles showed good adsorption capacity after 5 regeneration cycles employing methanol as regeneration solvent.

**Table 1.** Application of magnetic mesoporous nanomaterials as adsorbents for pollutants removal from water.

| Material | Pollutant | Adsorption capacity (mg $g^{-1}$) | Regeneration solvent and reuse cycles | Ref. |
|---|---|---|---|---|
| Fe/Ni-OMC | methylene blue<br>methyl orange | 959<br>849 | EtOH<br>7 cycles | 72 |
| $Fe_3O_4$@$mSiO_2$ | malachite green | - | HCl<br>3 cycles | 73 |
| UMC-$ZnFe_2O_4$ | 2-naphthol<br>naphtalene | 40<br>24 | NaOH-EtOH<br>4 cycles | 74 |
| OMC-IONPs | 2,4-D | 310 | EtOH<br>6 cycles | 45 |
| Biochar-nZVI | glyphosate | 80 | - | 58 |
| $Fe_3O_4$@$mSiO_2$ | Fenthion | 440 | - | 39 |
| $\gamma$-$Fe_2O_3$@$SiO_2$-TPODAC | Methyl orange<br>Sulfamethoxazole<br>Phenanthrene | 104<br>50<br>0.95 | MeOH<br>5 cycles | 75 |

## 3.2. Reduction.

Magnetic mesoporous NMs frequently used in reductive treatments to degrade organic pollutants are mainly made up of nZVI nanoparticles embedded into de mesopores of a solid matrix. It has been proven that nZVI is very effective for the removal and degradation by reductive pathways of a wide variety of chemicals, including nitrated organic compounds, chlorinated organic compounds, organophosphates, nitro amines, PCBs, and organic dyes.[76] The chemical reduction of the pollutant induced by $Fe^0$ typically requires the contaminant to be adsorbed on or near to the surface of the solid.[77] The mesoporous nanocomposites described in this section seek to combine the adsorbent capacities of the mesoporous structure with the reactive characteristics of nZVI. In this section we will describe recent literature results of magnetic mesoporous NMs applied for the removal of organic pollutant from waters by reductive pathways (Table 2).

Tang et al.[78] obtained nZVI dispersed on SBA-15 nanoparticles (Fe-SBA15-WI) by wet impregnation of SBA-15 mesoporous silica and studied the reduction of p-nitrophenol (PNP). They observed a significant dependence of the PNP degradation with the pH, achieving 96% and 16% removal at pH 3 and 9, respectively, by using 400 mg/L solutions of PNP and 5 g/L solid dose. They also found almost no iron leaching from the remaining supernatants. Zhang et al.[79] developed a nanocomposite where nZVI was dispersed inside the SBA-15 mesopores (Fe-SBA15-IWI) using two different types of SBA-15 through incipient wetness impregnation of iron precursors and $H_2$ reduction. Reduction capacity was studied on 20 mg/L solutions of nitrobenzene (NB) achieving 94% and 84% removal for the two different composites and 57% for unsupported bare nZVI. Similarly, Lu et al.[46] studied NB reduction by nZVI incorporated inside the channels of monodisperse mesoporous silica nanospheres (nZVI-MSN) under different experimental conditions such as pH, presence of typical anions, solid dose, etc. and evaluated reusability and stability in successive removal experiments. They obtained a 99 to 74% removal from pH 3 up to 11. Ions including $Na^+$, $K^+$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ showed no effect on NB degradation, while $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$ showed a slight inhibitory effect. Moreover, after seven cycles of reduction the removal efficiency of NB remained higher than 86%. On the other hand, nZVI supported on ordered mesoporous silica (Fe-MCM41) was evaluated for n-dimethylnitrosamine removal from water.[80] Unlike other studies, these authors found a maximum removal around neutral pH, in particular they reached 70%, 90% and 80% removal at pH 4, 7 and 9 respectively. Chen et al.[81] prepared core-shell nanoparticles of nZVI core with a mesoporours silica shell (Fe@m$SiO_2$) by the synthesis of bare nZVI directly followed by mesoporous silica condensation using CTAB and TEOS. Surface charge, dispersion stability and mobility in sand columns were studied. The Fe@m$SiO_2$ nanoparticles were used for treatment of 1,1,1-trichloroethane in water and real groundwater samples obtained from a pesticide factory site. Among nZVI-UMC composites, Choi et al.[82] synthesised granular activated carbon impregnated with reactive iron/palladium bimetallic nanoparticles (Fe/Pd-AC) through traditional wetness impregnation method with $NaBH_4$ reduction, coupled to an additional step of Pd doping. They tested this material against 2-chlorobiphenyl and obtained almost complete dechlorination of 4 mg/L solutions within 1 day at 20 g/L of Fe/Pd-AC. Wang et al.[83] obtained nZVI supported on granular AC (Fe-AC) to reduce various nitrosamines to their corresponding amines, nitrate and nitrite. They also studied the influence of various anions, cations and humic acids (HA), and found that all of this coexisting species had a negative effect on the total reduction obtained. Similarly, Zhang et al.[84] used a traditional wet impregnation method followed by a post annealing treatment (T~ 105-700°C under $N_2$ for 2 h) in order to increase crystallinity and improve electron mobility inside the iron phase of Fe-AC nanocomposites. Dechlorination of trichloroethane, trichloroethylene and tetrachloroethene by Fe-AC reached 95% after 300 min of treatment. They found a negative effect of $Na^+$, $Ca^{2+}$, $SO_4^{2-}$ , $NO_3^-$ and HA, on the substrates dechlorination rate, but no effect on the final dechlorination degree. Wang et al.[85] studied Metronidazole degradation using nZVI supported on non-porous carbon spheres (Fe-CSS). With 1 g/L dose of Fe-CSS under aerobic conditions they observed 94% degradation in 6 min, compared with 36% for bare nZVI in the same time. On the other hand, Ling et al.[86] studied the reduction of nitrobenzene using a nZVI supported on ordered mesoporous carbon (Fe-OMC) prepared from a soft template route and wet impregnation. They observed a 92 % removal of 80 mg/L solutions of NB using a 0.5 g/L of Fe-OMC, compared with a 49% removal for unsupported nZVI under the same conditions.

**Table 2.** Application of magnetic mesoporous nanomaterials in reductive treatments.

| Material | Load | Pollutant | Conc. | %Removal | Ref. |
|---|---|---|---|---|---|
| Pd/Fe-AC | 20 g $L^{-1}$ | 2-chlorobiphenyl | 4 mg $L^{-1}$ | 100 | 82 |
| Fe-AC | 2 g $L^{-1}$ | Nitrosamines | 0.2 mg $L^{-1}$ | 80-100 | 83 |
| Fe-AC | 7 g $L^{-1}$ | Trichloroethylene<br>Tetrachloroethylene | 80 mg $L^{-1}$ | 95 | 84 |
| Fe-CSS | 0.8 g $L^{-1}$ | Metronidazole | 60 mg $L^{-1}$ | 90 | 85 |
| Fe-OMC | 0.5 g $L^{-1}$ | Nitrobenzene | 80 mg $L^{-1}$ | 90 | 86 |
| Fe-SBA15-WI | 5 g $L^{-1}$ | p-nitrophenol | 400 mg $L^{-1}$ | 96 | 78 |
| Fe-SBA15-IWI | 1 g $L^{-1}$ | Nitrobenzene | 20 mg $L^{-1}$ | 94 | 79 |
| Fe-MSN | 2.3 g $L^{-1}$ | Nitrobenzene | 20 mg $L^{-1}$ | 100 | 46 |
| Fe-MCM41 | 0.02 g $L^{-1}$ | N-dimethylnitrosamide | 1 ug $L^{-1}$ | 90 | 80 |
| Fe@m$SiO_2$ | 3.9 g $L^{-1}$ | 1,1,1-trichloroethane | 4.5 mM | 77 | 81 |

### 3.3. Oxidation.

Magnetic mesoporous NMs have recently attracted attention in oxidation processes, such as Fenton processes, for the removal of organic pollutants. The Fenton processes is an Advanced Oxidation Process (AOP) that has gained vast acceptance for its high removal efficiency of organic pollutants. In the Fenton reaction, $H_2O_2$ oxidizes $Fe^{2+}$ to $Fe^{3+}$ producing hydroxyl radical ($HO^{\bullet}$), which is the key reactive specie involved in the degradation of the pollutants.[87] In particular, when ZVI is used in the treatment, ZVI naturally oxidizes upon reaction with $H_2O$ and $O_2$, leading to the formation of oxidation products such as $HO^{\bullet}$ radicals, superoxide radical, ferryl ion species and $H_2O_2$.[88] These reaction products can subsequently degrade organic contaminants through oxidative reactions. Moreover, external addition of $H_2O_2$ cause an efficient pollutant degradation treatment commonly named ZVI-assisted Fenton systems.[89] Immobilizing the nZVI on mesoporous NMs can effectively increase the contact area with pollutants, and prevent the agglomeration of nZVI. Duan et al.[60] investigated ordered mesoporous carbon supported nZVI catalysts (Fe/OMC-300) in Fenton-like degradation of 4-chlorophenol. Under optimal conditions, the authors found 96.1% of 4-chlorophenol and 47.4% of total organic carbon (TOC) removal after 270 min of treatment (at 30°C, initial pH of 3 and 6.6 mmol/L

$H_2O_2$). Shao et al.[90] obtained a complete phenol degradation (>99%) with remarkable low iron leaching by using nZVI embedded within ordered mesoporous carbon (Fe-OMC) as heterogeneous Fenton catalysts in a fixed-bed reactor operated under continuous-flow condition. On the other hand, Zheng et al.[63] demonstrate that surface hydrophilic modification of OMC with uniform dispersed $\gamma$-$Fe_2O_3$ nanoparticles (H-$Fe_2O_3$/OMC) showed enhanced adsorption and degradation performance of methylene blue (MB) in heterogeneous Fenton treatment. Wang et al.[61] found that Fe-$Fe_2O_3$ nanoparticles supported on ordered mesoporous carbon (Fe-$Fe_2O_3$/OMC) degrade 98.1% of 100 mg $L^{-1}$ of Acid Orange II in the presence of $H_2O_2$ (0.5 g $L^{-1}$) at neutral pH and nearly room temperature. They also found an improved catalytic activity for Fe-$Fe_2O_3$/OMC over Fe/OMC and $\gamma$-$Fe_2O_3$/OMC; this effect is explained by an efficient electron transfer between the iron and the iron oxide, which leads to an acceleration of the $Fe^{3+}/Fe^{2+}$ cycle.

## 4. Conclusions and future prospect

In this review, we have outlined various methodologies for the synthesis of magnetic mesoporous nanomaterials, especially silica- and carbon-based materials, with applications in water treatment. We have provided updated examples of their applications in adsorption, reduction and oxidation processes for organic pollutant removal. It was shown that the resulting nanomaterials from magnetic iron and iron oxides encapsulated within or supported on the mesoporous matrices have excellent properties to be used in different water treatments. In particular, magnetic mesoporous nanomaterials are versatile frameworks that can be functionalized with various active compounds to create multifunctional materials. Also, magnetic separation is an environmentally friendly alternative for the separation and recovery of nanomaterials, since it minimizes the use of solvents and auxiliaries, reduces the operation time, and is a cost-effective method compared to conventional separation processes as filtration or centrifugation. However, there are still several issues and challenges to achieve highly efficient magnetic separation designs that avoid the loss of nanomaterials in the separation step with possible release to the environment.

Finally, it is necessary the development of simple and low-cost synthesis methods. Further research should be devoted to designing cost-effective and highly efficient nanomaterials. The use of green synthesis routes for nanomaterials, such as the use of waste materials as precursors, and the application of these eco-friendly nanomaterials will reduce the overall production cost and help reducing the environmental impact.

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**Anales de la Asociación Química Argentina**

**División Jóvenes Profesionales**

Mini-Review

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

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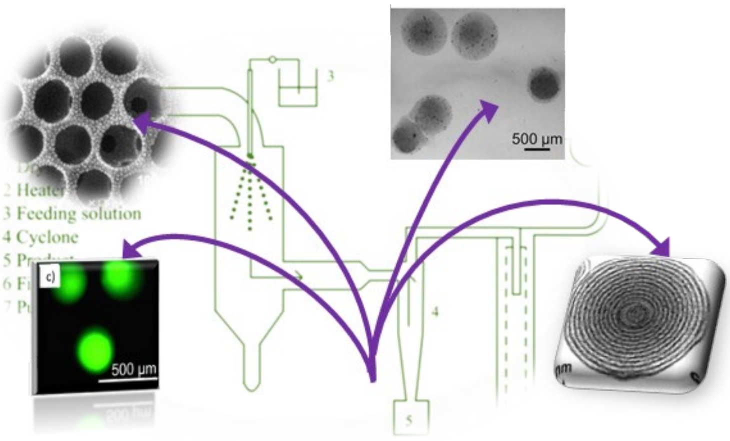
## Graphical abstract



## 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.*

## 1. Introduction

An aerosol, system belonging to the family of colloids, consists of a relatively stable suspension of solid or liquid droplets in a gas or vapour. The term 'aerosol' originates in military research during the First World War.[1, 2] In the 19th century, aerosol particles represented the smallest known division of matter and the fundamental properties of aerosols have been studied for more than 100 years.

Aerosol technology is of great interest in numerous applications. Its use is well established in the food industry[3-11], chemical industry[12, 13], pharmaceutics production[14-18], energy applications [19], just to name a few of its many applications.

The size of the particles is of enormous interest in the establishment of the behavior of the aerosols. The sizes can vary from structures of about 0.001 microns to fog droplets and dust up to 100 microns, which significantly affects the behavior of suspended particles. That is why there are several types of aerosols that are classified according to the physical form and the generation method. The terms commonly used are:[20]

- *Dust:* a solid particle formed by the mechanical disintegration of a material.
- *Fume:* solids produced by physicochemical reactions such as combustion, sublimation or distillation.
- *Smoke:* a visible aerosol produced by the disintegration of the liquid or the condensation of the vapor.

### 1.1. Drying spray devices

In this review we will focus on the aerosols produced by spray drying techniques. Spray drying is a simple, rapid, reproducible and scalable drying technology,[21] which allows mild temperature conditions suitable for biopharmaceuticals sensitive to heat. Compared to other drying technologies used in drug delivery applications, spray drying is a continuous process for directly transforming various liquids (e.g., solutions, emulsions, dispersions, slurries, pastes or even melts) into solid particles with adjustable size, distribution, shape, porosity density and chemical composition.

A wide variety of instruments for the production of aerosols have been described in the literature[22-24] and the techniques used are basically similar to the mechanisms of formation of natural aerosols.

The steps of the spray drying process are basically: (1) heating the drying gas, (2) generating droplets, (3) drying the droplets and (4) collecting the particles.

Figure 1 illustrates a principle flow diagram of a spray dryer. First, the liquid feed is atomized in a nozzle. The reduction in the size of the drop leads to a large increase in the surface area. In the drying chamber, the solvent in the sprayed drops is quickly removed by the continuous flow of a hot drying gas. The dried particles are formed, separated from the gas stream and collected in a collection vessel.

A great deal of time and effort has been devoted to the research and development of aerosol generation devices. This research is usually carried out with the objective of having control of the particle size distributions. Spray drying equipment is commercially available and the production cost is generally lower compared to other drying technologies.[4, 6, 25]

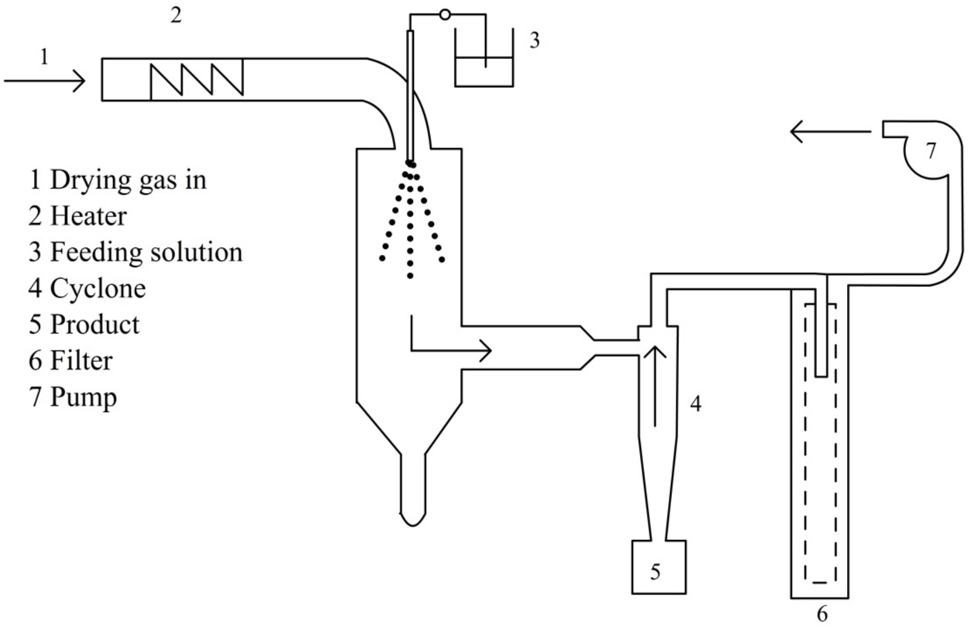


**Figure 1.** Principle flow diagram of a traditional spray dryer.

Polydispersed aerosols have many industrial applications (for example, agricultural spraying), making the applications cheaper because most of the environmental sprays are polydispersed.

Aerosols of very narrow (monodisperse) distributions have many applications in aerosol engineering, for example, for size measurement, equipment calibration, filtration efficiency tests, lung inhalation studies and, ultimately, in the production of ceramic powders. To achieve practical monodispersity, the standard geometric deviation must be less than 1.2.

Atomization generally produces a broad distribution of relatively thick droplets, with the minimum particle size determined by an equilibrium between surface tension forces that resist droplet formation at pressure or other forces that attempt to disrupt the fluid surface. Common methods used to mechanically disperse liquids to form aerosols include air nebulizers,[26,27] rotating discs,[28, 29] ultrasonic nebulizers,[30-32] and vibrating orifice generators.[33] The last three techniques are not strictly based on atomization and are capable of producing monodisperse aerosols.[24, 34]

Another important factor to consider is the concentration of the precursors. The high initial concentrations result in rapid agglomeration and a highly polydispersed aerosols. In addition, smaller primary particles are produced when the temperature increases,[35] although the same increase can cause the decomposition of aerosol precursors.

The aerosol particles generated by the direct sol-gel feeding spray dry method are quite monodisperse for particles in the submicron range,[36-39] although in the case of core-shell particles, dispersion often depends on the initial size of the nuclei core.

Japuntich et al.[40] found that monodispersity depends on a balance between free and forced convection in the condenser tube. Furthermore, they found that the most successful condensates are those with low diffusion coefficients. Thus, a linear correlation between the Reynolds number (Re) or the flux in the capacitor and the Rayleigh number was found. Therefore, for a chosen Re, the Rayleigh number can be found and for a chosen temperature, parameters of the tube radius can be calculated.

## 2. Synthesis methods

The combination of spray drying with the sol-gel technique allows to obtain porous particles in a simple, fast and cheap way, with the possibility of industrial scaling; although the obtaining of mesoporous spherical particles ordered and monodispersed pores is not trivial. The process is usually optimized to produce particles with the desired size, although in general the size distribution is relatively broad. The properties of the sol (concentration and rheology) are important, as are the operating conditions of the dryer (rotor speed, nozzle characteristics, temperature, humidity, etc.).

Most commonly used methods for obtaining porous particles are:

a) Using a surfactant or a block copolymer as template agent. In general, the synthesis involves Evaporation Induced Self-Assembly (EISA)[41], this method consist in solvent evaporation, allowing templated agent to reach the critical micellar concentration (c.m.c.), which induces the formation of the desired mesoporous structure.
b) Using a polymeric hard template agent. In this case the templates are polymeric nanoparticles which are eliminated after synthesis.[42]
c) Using previously synthesized nanoparticles as precursors. These particles can be well dispersed or aggregated.[43]

Lu and co-workers[44] reported a method of spherical silica mesoporous particles synthesis. They started from an acid solution of silica in ethanol/water, where the different surfactants (CTAB, Brij-58, Brij-56 or P123) were far below their c.m.c. By incorporating metal complexes or organic dyes they were also able to obtain nanostructured hybrid mesoporous particles. Although the obtained particles were spherical, they did not achieve monodisperse sizes (see Figure 2). Alonso and co-workers[45] also used EISA and spray-drying to obtain mesoporous silica particles. They used iPrOH as solvent in most cases, but they also tested the use of water. A Büchi Mini-Spray 190 apparatus was employed and cetyl-trimethyl-ammonium bromide (CTAB) was the mesoporous template. They varied the composition of the sols (solvent and siloxane oligomers) but did not varied operating conditions. When the solvent used was iPrOH, some degree of pore order was obtained, but not for the case where the solvent was water. The shape of the particles obtained was spherical in most of the samples with iPrOH as solvent, in case of water they obtained particles inside particles with a broad size distribution.

In addition to silica, there are also reported syntheses of other porous particles such as $TiO_2$[46-48], $ZrO_2$[48], $CeO_2$[48] and $Al_2O_3$[49].

The most common hard templated agent are polystyrene latex (PSL) colloidal suspensions. Precursor of matrix particles can be either nanoparticles[42, 50, 51] or molecular precursors.[52] Then, the polymers are removed by calcination, obtaining structures similar to the ones presented in Figure 3. As expected, the pore sizes increased with PSL particle size. Interestingly, with this approach it is possible to obtain macropores, something that is difficult when the pore size is determined by the size of the micelles, as discussed earlier.

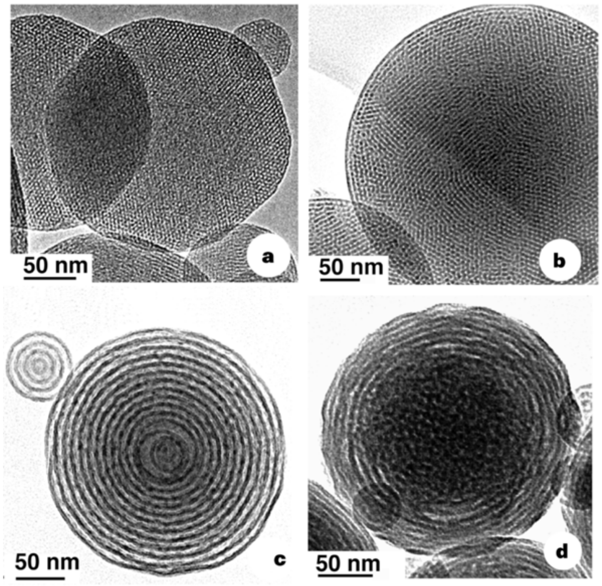


**Figure 2** **(a)** Faceted calcined particles with a hexagonal mesophase ($d_{100}$ = 32.5 Å). The sol was prepared using 5 wt% CTAB as template. **(b)** Calcined particles showing cubic mesostructure. The sol was prepared using 4.2 wt% Brij-58 as template. **(c)** Calcined particles showing a vesicular mesophase ($d_{100}$ = 92 Å). The sol was prepared using 5% P123 as the triblock copolymer template. **(d)** Uncalcined silica particles showing ‘growth’ of ordered vesicular domains from the liquid–vapour interface. The sol was prepared using 2.5% Brij-56 as the template. Reprinted with permission of Springer Nature from reference 44.

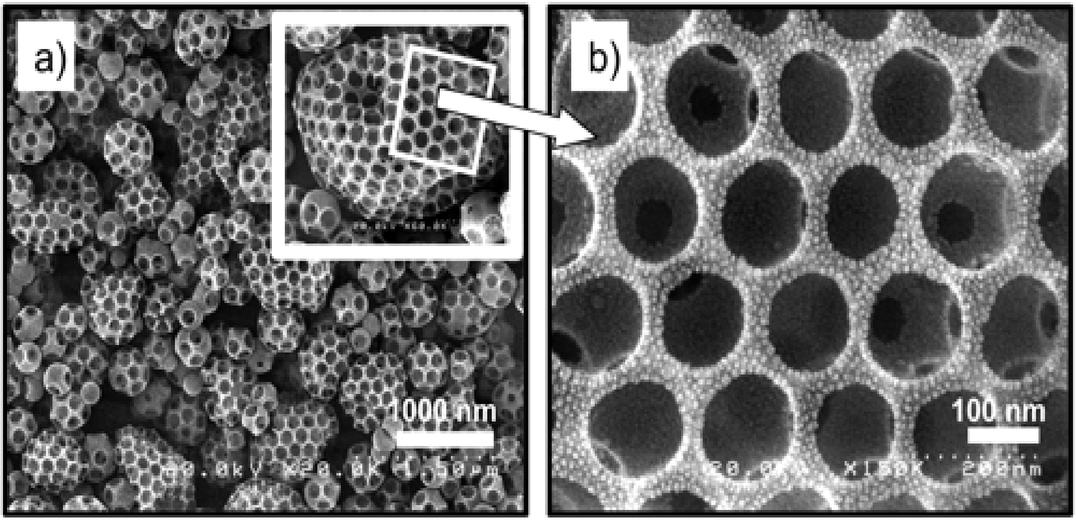


**Figure 3.** SEM images of silica powders prepared using 5 nm of silica particle size and 178 nm PSL particle size: (a) low magnification and (b) high magnification of surface particles. Reprinted with permission from Nano Letters 2002, 2, 4, 389-392. Copyright 2002 American Chemical Society.

The third mentioned synthesis method consists in the coalescence of previously synthesized nanoparticles that can be well dispersed or forming small aggregates. These particles coalesce when the drop dries, giving rise to new particles bigger than the ones used as precursors and leaving small cavities between them that form to the porosity.[42, 50, 51]

Another interesting application involves the formation of core-shell films that can be produced by the condensation of vapours in already existing cores (heterogeneous condensation) or in higher supersaturations, by instantaneous formation of vapour particles, which are grouped and converted into particles when their size exceeds a critical value (homogeneous condensation). Heterogeneous condensation is typically used. In such generators four processes, not necessarily separated, are common: (1) Production of cores, (2) steam generation, (3) mixing of steam cores and (4) condensation through controlled cooling of the carrier gas. Even though, there is great interest in the development of core-shell particles obtained by processing by spray drying in a single step.[53]

The spray drying method has also been adapted to produce thin fibbers (approximately 10 microns). High-viscosity sols and low viscoelastic characteristics are required for this purpose.

Gel particles were also formed using emulsion drying techniques; here droplets of aqueous sol are formed in a partially miscible solvent (for example, trichlorethylene). The water is progressively removed from the sol by transfer to the organic phase, and eventually rigid gel particles are formed. The size of the emulsion droplets can be controlled by adding an appropriate surfactant to the sol and by controlling the stirring conditions used to disperse the aqueous phase in the organic solvent. This method generally produces highly uniform particles that can have a size in the range > 1 µm to about 30 µm. In the two previous methods, narrower size distributions can be achieved by a subsequent centrifugal classification.

## 3. Applications

### 3.1. Pharmaceutical applications

By spray-drying encapsulation, various particle designs can be prepared depending on the required functionality. In the case of pharmaceutical applications, core-shell particles, multi-wall particles, and multi-core or composite particles are commonly used (Figure 4). Spray drying allows the generation of smaller particle sizes than conventional aerosol synthesis methods, which improves the bioavailability and the release of bioactive components and drugs, because they have a higher surface to volume ratio, a higher penetration rate in the cells, stability, and possibility of directed release through the decoration of the surface.[54] Also, a change of crystalline drugs to more amorphous structures provides a faster drug release kinetics. Micro and nanonization is used to change the morphology of the particles from a coarse grain to a very fine powder. This improves the solubility of the final pharmacological product due to the higher surface-to-volume ratio of nanoparticles and due to the more amorphous structures, in which the solvent (e.g., water) can penetrate more efficiently.

Practical applications include, for example, polymeric wall materials, such as gum arabic, serum protein, polyvinyl alcohol, modified starch or maltodextrin[55, 56]. Typical examples are drugs with poor water solubility[57, 58] and salts.[59]

In nanoencapsulation, typically a liquid product is embedded within a solid matrix. The encapsulated oil-in-water nanoemulsion is a common example, in which the oil droplets serve as a reservoir for a lipophilic pharmacological product.

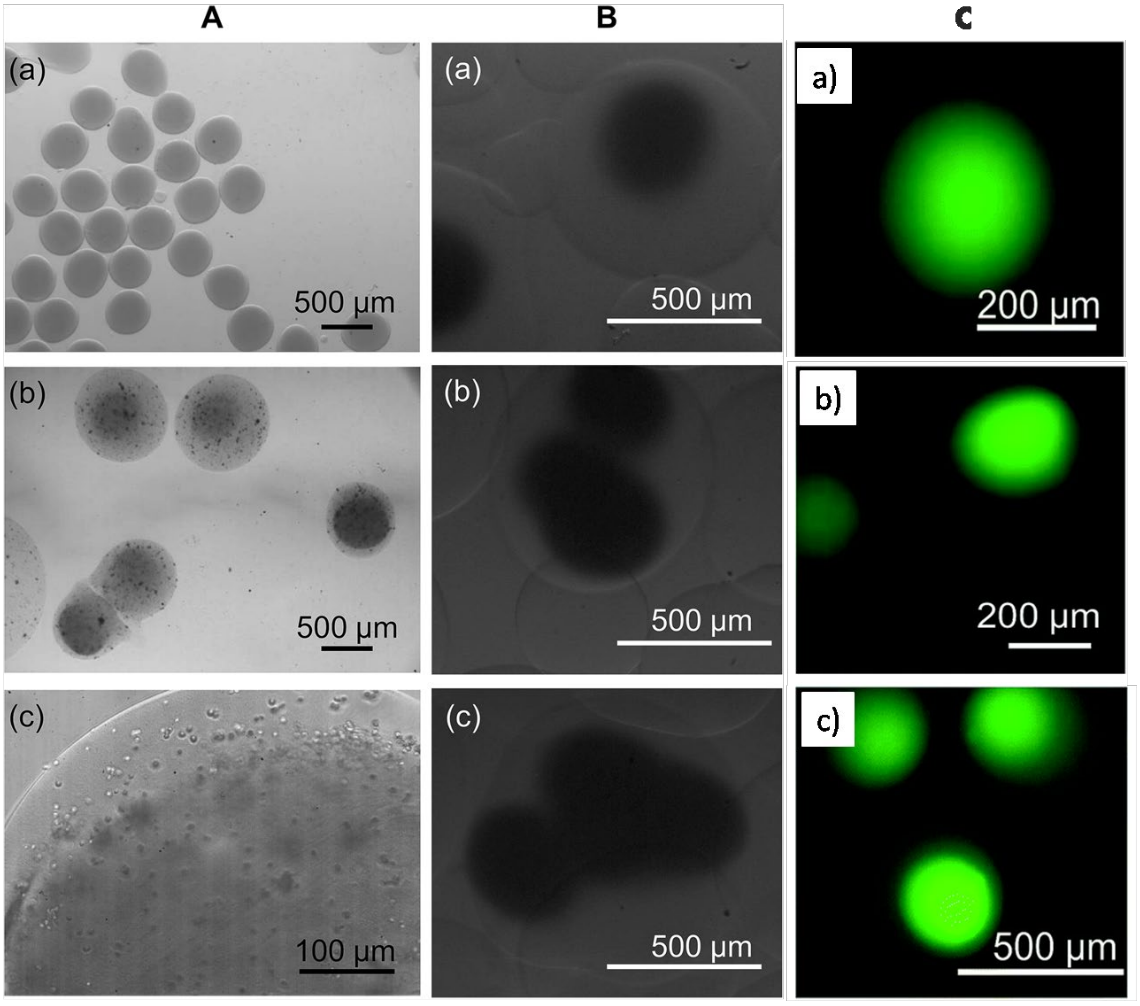


**Figure 4** (A) Optical images of C/C hydrogel microspheres: (a) CMC-based microgels, (b) C/C core–shell hydrogel microspheres, and (c) a magnified view of the edge of a C/C microsphere. (B) Optical images of the C/A hydrogel microspheres, containing (a) one, (b) two and (c) three CMC-based microgel cores. (C) (a-c) fluorescence images of A/A microspheres encapsulating CdTe QDs.W. Lai, A. S. Susha, A. L. Rogach, G. Wang, M. Huang, W. Hu and W. Wong, RSC Adv., 2017, 7, 44482 - Published by The Royal Society of Chemistry.

Depending on the application, there is an optimized set of process parameters. The optimization of process parameters is usually done by trial and error. However, experimental design studies (DOE) help to optimize the nano spray drying process, as shown by several authors.[14, 25, 55, 60-67] The DOE studies allow determining the optimal conditions of the process with fewer experiments, which reduces the cost of the experiments and the materials use, which constitute determining factors for pharmaceutical applications.

### 3.2. Energy applications

The large-scale development and generalized use of materials for energy applications, such as catalysts for water electrolysis, nanomaterials for hydrogen storage or electrodes for lithium batteries, is significantly hampered by the high cost of materials and the low reproducibility. Thus, it is highly desirable to develop cost effective but efficient alternative materials for different energy applications.[68-70]

The implementation of mesoporous materials in electrocatalysis has allowed in recent years to considerably increase the real surface area of the used materials and, therefore, its effective activity.[71, 72]. In particular, mesoporous $TiO_2$ materials are of great interest for different energy applications, due to their intrinsic properties and because these materials can be obtained in the form of mesoporous particles by methods that allow the continuous particles synthesis.[73]

Additionally, the spray dry technique allows the encapsulation of nanomaterials. This core-shell type of structures can be advantageous due to the individual properties of each component material as well as the synergetic properties generated when the used layers are rationally chosen. For example, the use of a mesoporous $Co_3O_4$ core with a mesoporous $TiO_2$ shell forming an hybrid electrode with nickel (or nickel alloys) can increase the activity due to the modification of the Fermi level of Ni while the $TiO_2$ can protect the $Co_3O_4$ from the corrosive environment found in a conventional alkaline electrolyzer.[74]

### 3.3. Environmental applications

Heavy metals are especially toxic to humans because they can be bioaccumulated. There are also law regulations on other pollutants such as pesticides and other organic molecules that come from wastewater from a variety of industries. In this context, mesoporous materials and nanotechnology represent one of the areas of greatest development of the last twenty years and with excellent environmental application perspectives.[75-77] Combination of this kind of materials with synthesis by spray drying makes these materials have better perspectives for their use at industrial scale. In fact, spray drying has been developed for many industrial applications due to its capacity to produce high volumes of particles.[78]

There is a wide variety of materials synthesized for environmental applications such as modified carrageenan microparticles for adsorption of pharmaceutical compounds[79], magnetic chitosan microparticles grafted with methyl acrylate and tetraethylenepentamine for Cd (II) removal[80], lanthanum oxide functionalised silica microspheres for phosphate adsorption[81], graphene-$Fe_3O_4$ hollow hybrid microspheres for heterogeneous Fenton and electro-Fenton reaction[82] (Fenton reaction has been widely used to treat wastewater containing dyes, herbicides, antibiotics, etc), and many other materials.[47, 83, 84]

Previously, these of kind materials for environmental applications were obtained by other synthesis routes; nowadays they can be produced by aerosol, significantly reducing the costs and production times.

## 4. Perspectives and Green chemistry approaches

As shown throughout this work, there are a variety of methods for the production of materials by spray drying. For example, mesoporous powders spray drying production methods using EISA procedure have been recently patented. These methods use volatile and flammable solvents in high proportion which makes their synthesis more expensive, because closed circuits must be used to avoid the ignition of solvents at high drying temperatures. In summary, these synthesis methods have the following limitations:

a) high concentration of volatile organic compounds represent environmental risk,

b) flammable components present risk of ignition and

c) to control the hydrolysis-condensation processes of the inorganic precursors mineral acids in high concentration (pH < 0) are used, which also represent an environmental risk and require special materials for their processing.

These limitations make necessary the development of new synthesis methods to obtain mesoporous materials by spray drying.

In this direction, our working groups have developed and patented a synthesis method for obtaining spherical particles of mesoporous metal oxides having composition, surface area, porosity and size controlled.[85] In this method, the solvent can have a low proportion of organic solvents (less than 25% by mass) or can even be pure water. Thus, risk of ignition is eliminated. This allows to work under an air atmosphere, resulting in a safe and low cost method. The amount of volatile organic compounds is low, which reduces the environmental risk and the precursor solutions are less acidic than in other reported methods.[86]

This new method, friendly to the environment, generates high expectations for obtaining and using large-scale mesoporous materials obtained by spray drying, which have a wide spectrum of applications, some of which were described in this review, but are not only limited to them.

## 5. Conclusions

In this review we have covered some of the basic principles in the synthesis of aerosols, particularly nanostructured aerosols in different ways, including both hard template, and different types of soft template and sol-gel method. We have also explored some of the many facets of the multifunctionality of these materials, considering the possibility of using both organic and inorganic precursors. These materials present an enormous potential for industrial applications due to the fact that the aerosol synthesis methods are easily scalable, in comparison with other nanomaterials synthesis methods. Finally, there is a great interest in developing methods for the synthesis of nanostructured aerosols using environmentally friendly methods that allow the synthesis of multifunctional nanomaterials with a minimum impact on the environment. In this sense, nanostructured aerosols appear as highly promising materials for many applications.

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**Anales de la Asociación Química Argentina**

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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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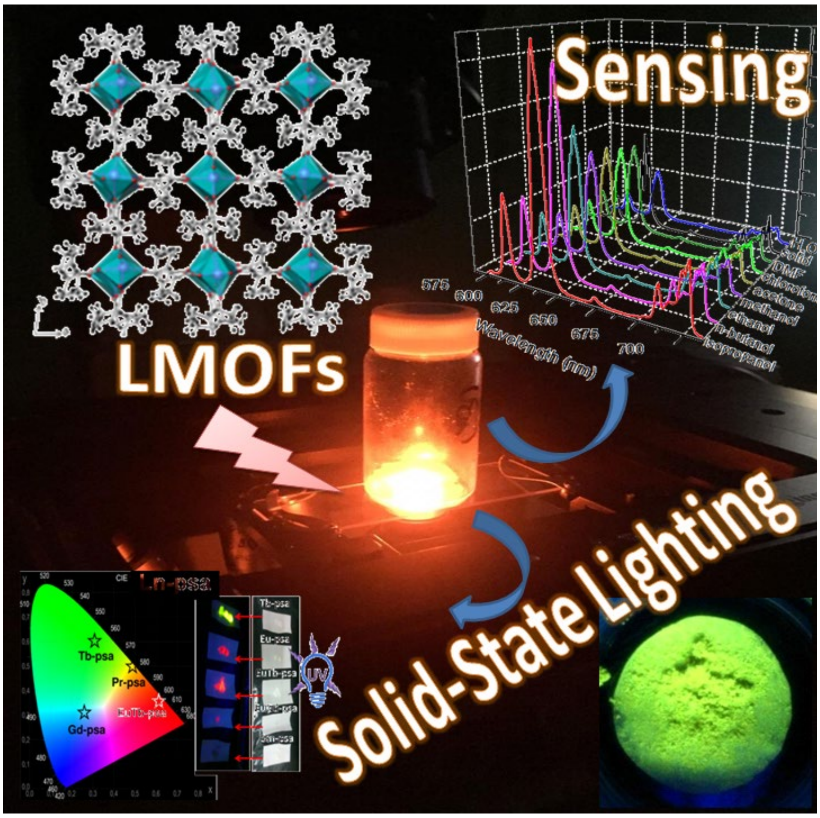
## Graphical abstract



## 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.*

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## 1. Introduction

The field of *Metal-Organic Frameworks* (MOFs) represents an evolution of traditional disciplines such as supramolecular chemistry and solid-state sciences. The coordination chemistry has a huge history devoted to explore structure-properties relationships in coordination polymers (CPs)[1]. CPs can be formed by a *self-assembly process* between metallic ions (nodes) and organic ligands (Figure 1) under different conditions of pH, solvent, temperature and time. The most popular methodologies to synthesize MOFs are the hydro/solvothermal routes;

nevertheless there are plenty of different approaches depending on the textural and crystalline properties required for a desired purpose.

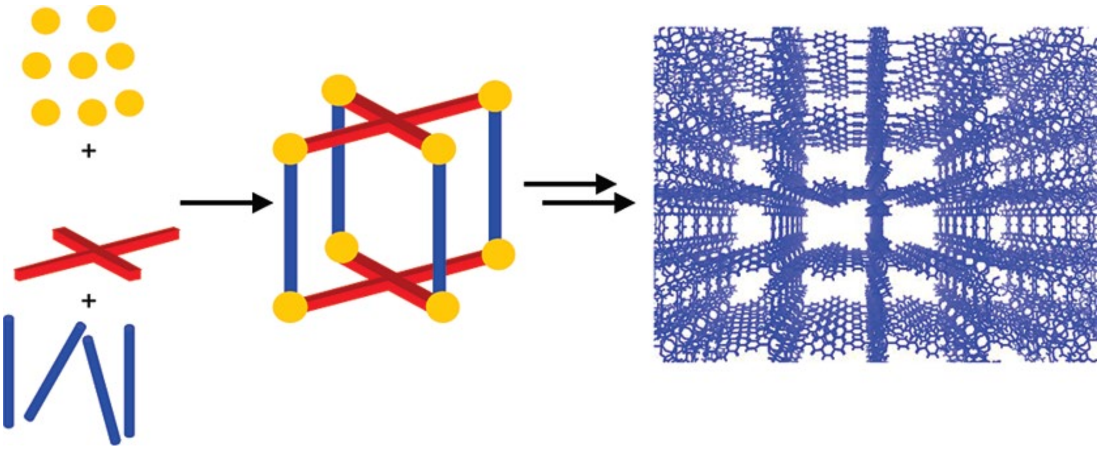

**Figure 1.** Scheme of MOFs synthesis. The red and blue bars represent organic ligands meanwhile yellow circles represent metallic nodes.

With this simple approach, it is possible to synthesize MOFs with specific *on demand* functionalities and porosities. This is the spirit of the quote of the Irish playwright George Bernard Shaw: *"Some people see things as they are and say, why? I dream things that never were and say, why not?"*. This phrase describes the objective of the approach with which MOFs were first made as robust frameworks with permanent porosity in the mid-90's and later scaled up by BASF Company who collaborated with academia on developing the industry of MOFs.[2]

Besides, the "MOF" term was popularized by Prof. O. Yaghi reporting a laminar cobalt trimesate with adsorptive properties[3]. After this pioneer work, Yaghi and many other groups around the world obtained MOFs with particular crystalline open architectures such as IRMOF-n (isoreticular MOFs, n=0-16)[4], HKUST-1[5], MIL-47[6], MIL-53/MIL-88[7] (MIL=Materials Institute Lavoisier), ZIFs (Zeolitic Iminadol Frameworks)[8] among others. A set of most common MOFs are shown in Figure 2.

Some MOF materials present a porous nature and thus, they have been the focus of a mature field with intense development due to their potential applications in catalysis[9], ion exchange and gas separation[10]. Moreover, the possibility of employing a diversity of *building blocks*, allows synthetic chemists to exploit specific and even tuneable properties. Some MOFs have been reported exhibiting more than one property, becoming them real *multifunctional platforms* for many applications (Figure 3).[11]

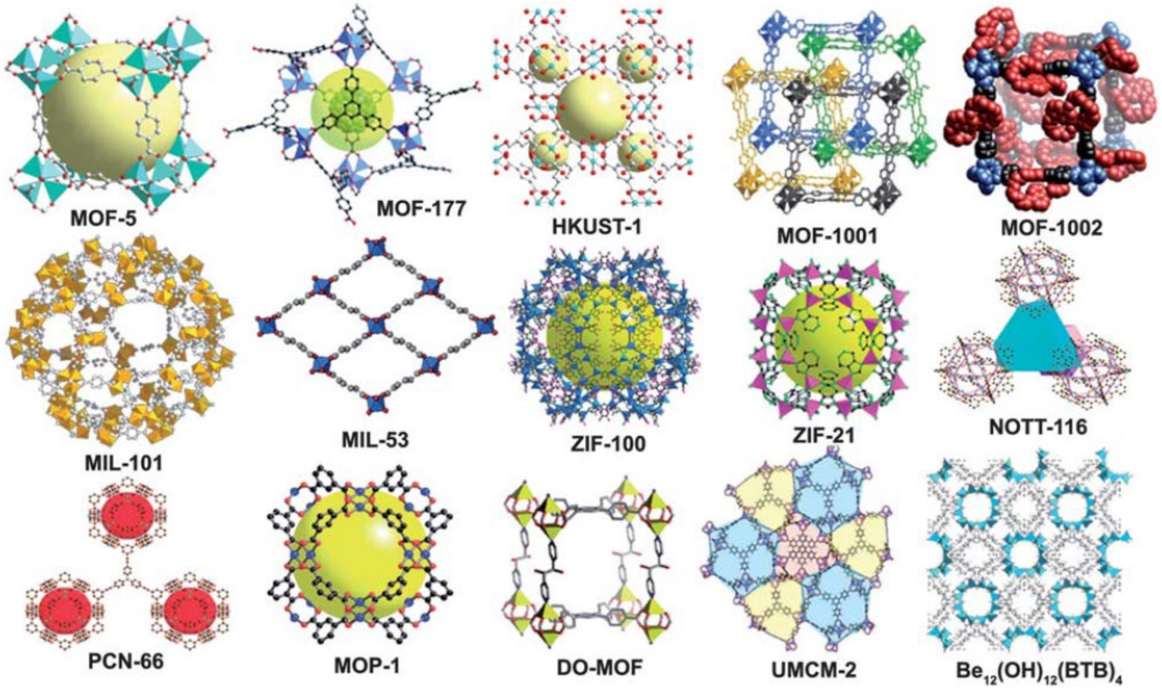

**Figure 2.** Representations of the most common studied porous MOFs in the literature. The colored space represents the potential cavities.

As an example, lanthanide ions are of special interest in photonics and magnetism because of their unique properties which include characteristic narrow 4f-4f transitions, a wide range of lifetime values and high quantum yields (QYs).[12] These features are important qualities in the design of phosphors for *solid-state lighting* (SSL).[13] In this field, Luminescent-MOFs (LMOFs) have been studied not only for SSL but also for the chemical or physical sensing fields. The present short-revision deals with this exciting and growing field, highlighting specific structures as LMOFs examples.

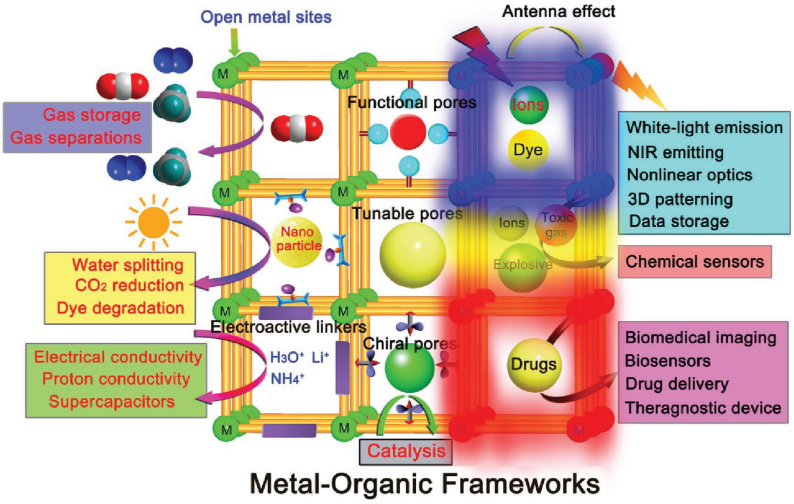

**Figure 3.** Illustration of multifunctional properties studied in MOF literature.

## 2. Luminescence properties

In general, *Luminescence* or *Photoluminescence* (PL) is the term used to describe the process in which light is produced by the absorption of energy. Depending on multiple spin state during the radiative relaxation process, PL contains two basic forms: *fluorescence* (F) and *phosphorescence* (P). The former refers to the emission of light between energy states of the same spin multiplicity and the process generally lasts no more than about 10 nanoseconds. The later, on the other hand, refers to the emission of light between states with difference spin multiplicity and the process lasts from a microsecond to seconds. PL can arise from direct organic ligands excitation, metal-centered emission (widely observed in lanthanide-MOFs through the so-called *antenna effect* or by direct excitation into the 4f levels[13]), or energy migration such as ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT). Besides, guest molecules can also result in PL in MOFs[14] (Figure 4).

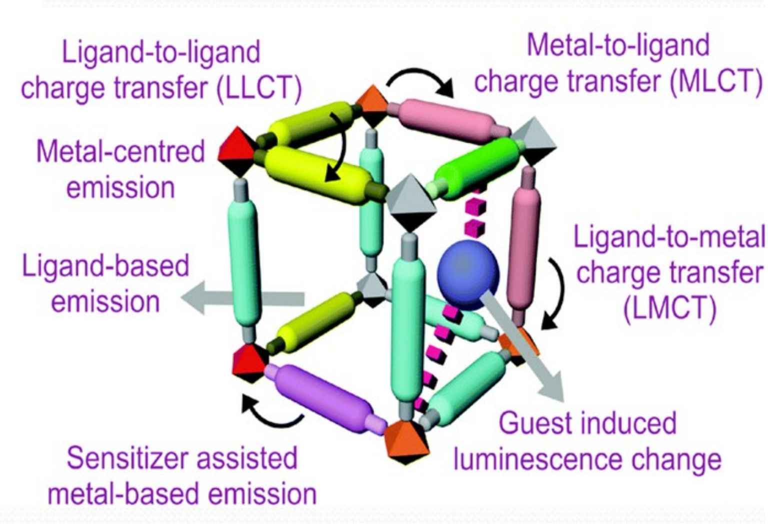

**Figure 4.** Scheme of the diverse PL mechanisms presented in LMOFs.

According to specialized articles,[13] the PL properties of optical materials can be characterized by the following measurements: (1) luminescence spectra, (2) quantum yield (which gives the efficiency of the luminescence process, defined as the ratio of the number of emitted photons released in the process of luminescence to the number of absorbed photons), and (3) the observed lifetime ($\tau_{obs}$). The $\tau_{obs}$ refers to the average time the molecule stays in its excited state before emitting a photon and is determined to be inversely proportional to the sum of the rate constants of the radiative ($k^{rad}$) and the non-radiative ($k^{nr}$) processes, as shown in equation (1).

$$\tau_{obs} = \frac{1}{k^{rad} + \sum_n k_n^{nr}} \qquad (3)$$

## 3. LMOFs for Solid-State lighting

When luminescent components are incorporated into MOFs, the obtained organic-inorganic hybrid materials are very promising as luminescent solid materials.[13,15] The richness of metal ions/clusters and the large number of available organic linkers, represent a great promise to explore sophisticated compounds with tunable PL properties.[15] Taking advantages of their high porosities, the MOFs also have unique properties to serve as rigid/flexible hosts for the encapsulation of guest optical species such as dyes[16], lanthanide ions[17] and quantum dots[18] among others. As a consequence, hundreds of LMOFs have been synthesized and widely explored in recent years, for their potential applications as Solid-state light-emitting devices for white light and NIR light emission, nonlinear optics and 3D patterning and data storage.

From the *material design* point of view, lanthanides are exceptional candidates to obtain LMOFs, due to their electronic properties derived from their electronic levels (see Figure 5), resulting in interesting optical properties[19].

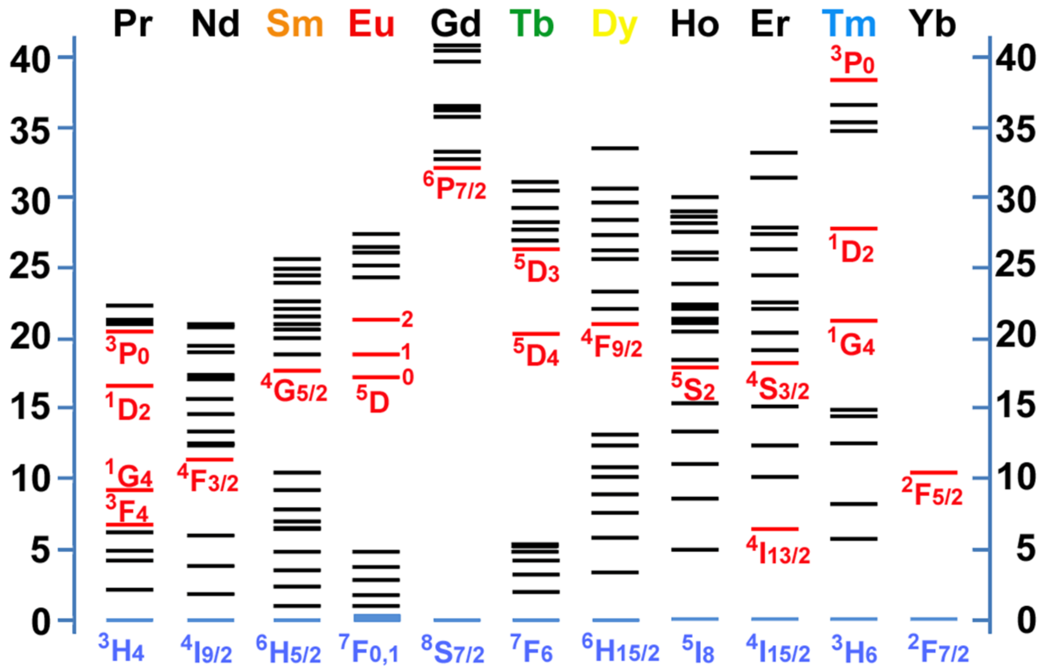

**Figure 5.** Energy diagrams for the lanthanide ions; the values of the energy levels are given as 1000 $cm^{-1}$. The red and blue lines indicated the main luminescent and the fundamental levels, respectively.

"*Lanthanons-these elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us; mocking, mystifying and murmuring strange revelations and possibilities*." Sir William Crookes spoke these well-quoted words in an address to the Royal Society (February 1887) when all but three of the lanthanide elements had been isolated.[20]

Among lanthanides ions, $Sm^{3+}$, $Eu^{3+}$, $Tb^{3+}$ and $Dy^{3+}$ are preferred for optical/optoelectronic device implementation due to their intense, frequently long-lived, and line-like emissions in the visible (orange, red, green and yellow respectively) (Figure 6).[21]

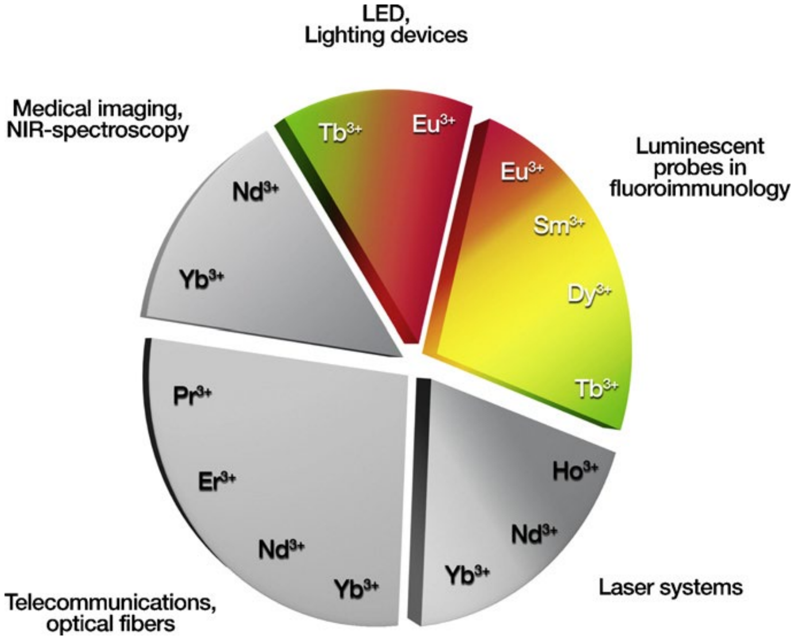

**Figure 6.** Emission type and related applications of lanthanides ions. Adapted with permission from reference 21.

Regarding these features, we have reported luminescent LMOFs constructed by aliphatic ligands confirming that those containing Eu and Tb ions exhibit strong red and green emissions, respectively[22]. The aliphatic nature of ligands such us methyl succinates, prevent for emission by ligand excitation. Thus, the emission spectra are obtained by direct excitation into the $^{2S+1}L_J$ electronic energy levels, yielding lanthanide centered luminescence. Some examples can be found in a set of LMOFs obtained in our research group, as can be seen in Figure 7: **Ln-2,3-dms** (Ln=Sm, Eu, Tb)[22] and some **Ln-psa**[23,24] (Ln=Nd, Sm, Eu, Eu/Gd, Eu/Tb), **Ln-msucc**[25] (Ln= Nd, Sm, Eu, Tb), **Ln-succ-slc**[26] (Tb) and **Ln-3-OHNDS-1**[27a] and **2**[27b] (Sm, Tb) (being **2,3-dms**, **psa**, **msucc**, **succ-slc** and **3-OHNDS** and 2,3-dimethylsuccinate, 2-phenylsuccinate, 2-ethylsuccinate, succinate-salicylate and 3-hidroxi-naphtalenedisulfonate respectively).

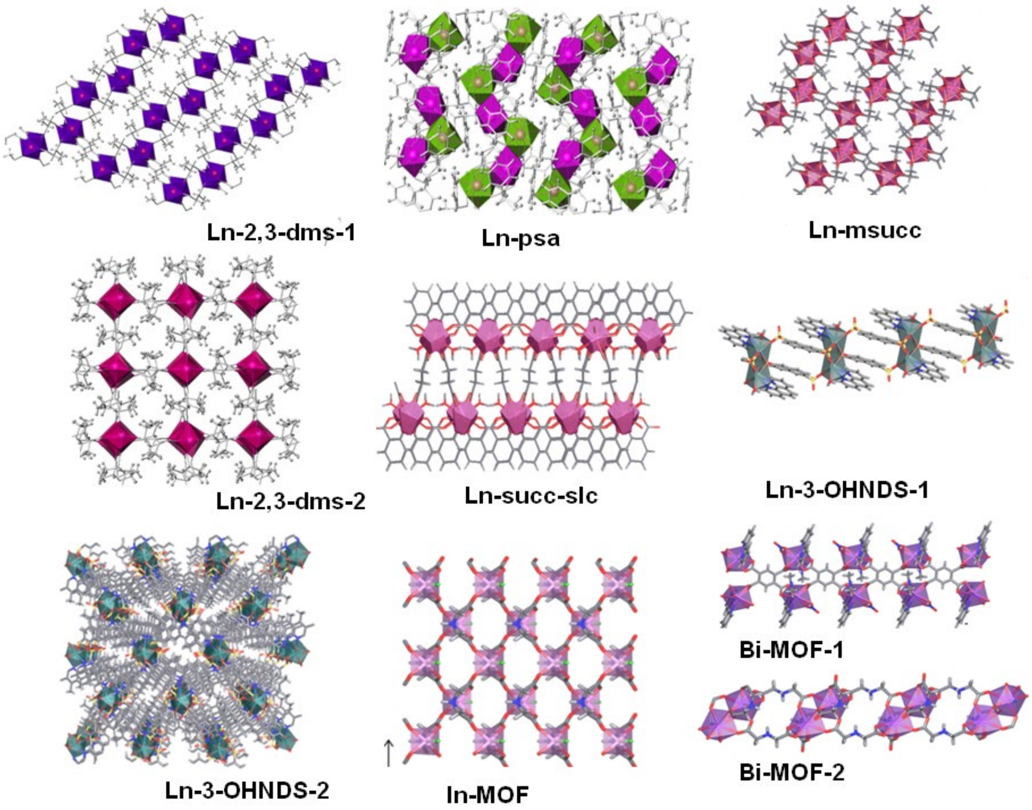

**Figure 7.** Crystalline structures of selected LMOFs discussed in the review, according with References 22-28. The colored polyhedra represent the metallic center in each net.

Also, there are some LMOFs that exhibit ligand centered emission, characterized by blue-green lights. This is the case for some d-block or main-group elements based MOFs/CPs (**Bi-MOF-1**[28] and **2**, **Zn-MOF**[28]) or Ce/Gd/Y/La-MOFs (**Gd-msucc**[25], **Gd-psa**[24], **Y-succ-slc**[26], **La-3-OHNDS**[27]). Figure 8 shows the light type emission in the corresponding CIE x,y diagrams for the selected LMOFs. The evaluation of the PL performance based on the length of $\tau_{obs}$ values set the Tb- and Eu-MOFs as promising materials for devices manufacture.

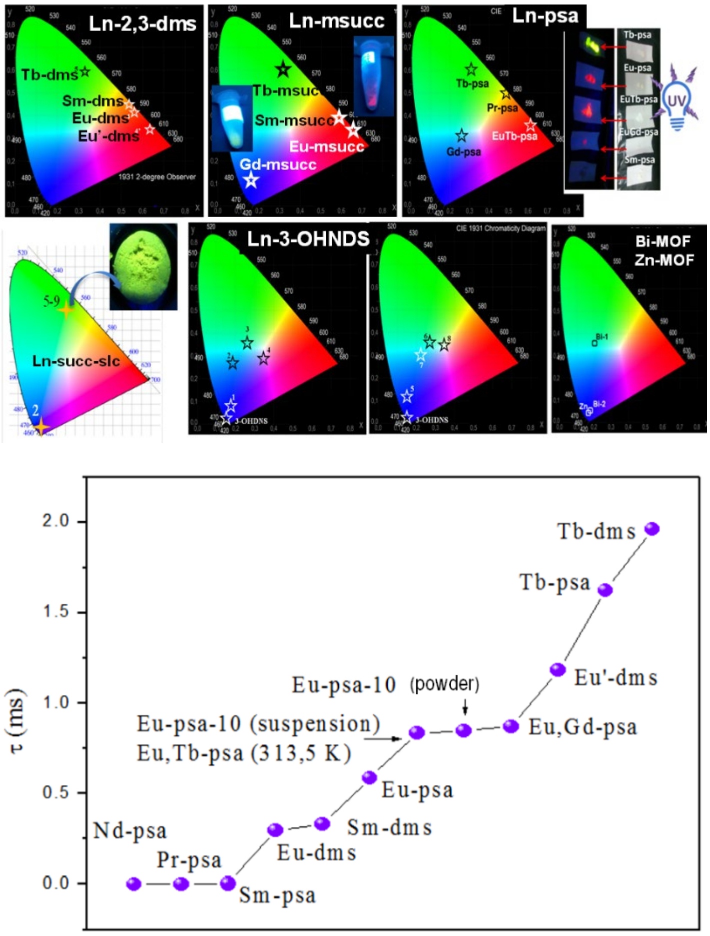

**Figure 8.** CIE x,y diagrams for **Ln-2,3-dms**, **Ln-psa**, **Ln-msucc** and **Ln-succ-slc**, **Ln-3-OHNDS**, **Bi-MOF** and **Zn-MOF** according with references 22-28 respectively (up). $\tau_{obs}$ values of selected LMOFs (bottom).

Moreover, there is an increased interest in exploring new LMOFs based on actinides such us U and Th from depleted minerals. In this sense, the group of Christopher Cahill (GWU, USA) has obtained many MOFs structures based on $[UO_2]^{2+}$ with interesting optical properties[29]. During a recent research stay in this group, we could obtain new open structures with bright green light emission (ascribed to 5f transitions), as can be seen in Figure 9.

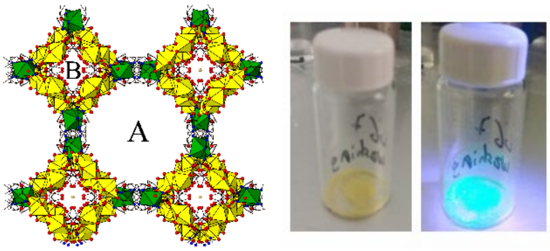

**Figure 9.** Crystalline structure and solid-state luminescence of a novel $UO_2$-MOF under UV excitation.

Besides, the interest in white light-emitting devices stems from their broad applications in displays and lighting, the most addressed topics in the literature. White light-emission can be achieved in LMOFs by modulating factors such as lanthanide concentration, guest species, ligand structure or physical parameters (excitation wavelength and temperature).[30] A combinatorial approach is an effective strategy not only to achieve white light but also to tune the characteristics emissions over a broad landscape of mixed lanthanide combinations in ternary lanthanide LMOFs. The efficacy of this approach is exemplified by the great variety of emission colors present in an extended family of isostructural LMOFs with the general formula, $[(Ce_{2-x-y}Eu_xTb_y(bdc)_3(H_2O)_4]\infty$ (bdc = 1,4-benzene dicarboxylate) (Figure 10).[31]

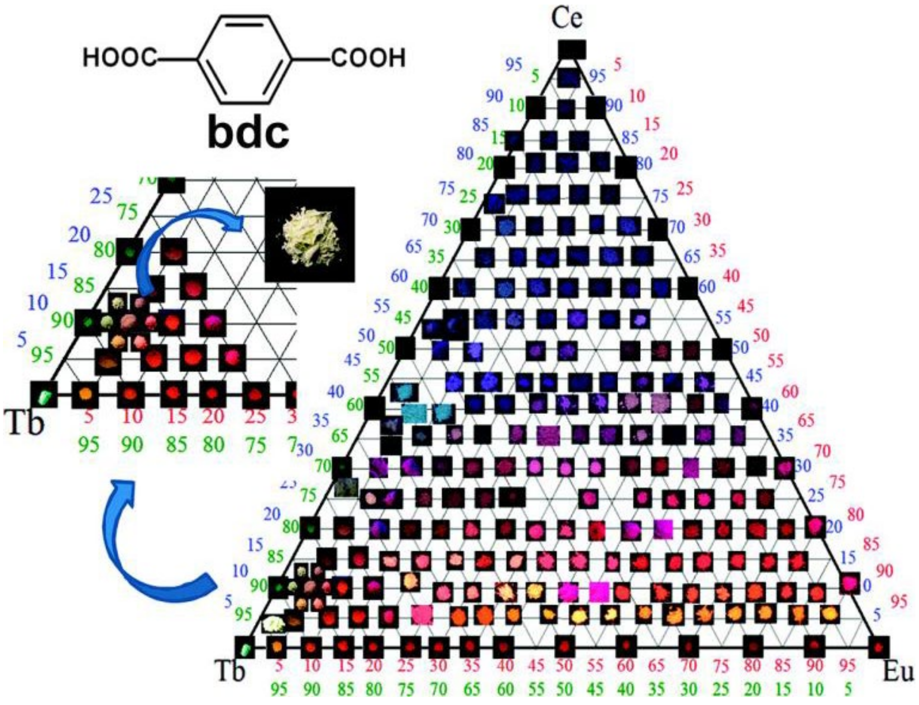

**Figure 10.** The luminescence in the ternary lanthanide LMOFs obtained by the combinatorial mixed metal combinations. Reproduced with permission from reference 31.

## 3. LMOFs for Sensing

Mapping and thermal sensing in an accurate and non-invasive way are important features for the development of devices with applications in nanoscience,[32] especially in the optimization of photodynamic therapy. In this context, lanthanide-LMOFs have attracted particular interest, mainly for the possibility of tuning the colour by controlling the lanthanide doping, this being a key factor for thermo-sensor designing. In this sense, $Eu^{3+}$ and $Tb^{3+}$ ions[33] are useful for the development of physical and chemical heterometallic sensors based on fluorescence intensity ratio (FIR) dependence along a temperature range. In the beginning of 2010 decade, the pioneer work of Cui et al.[34] was the first to report thermometry studies employing Eu/Tb-MOFs platforms (Figure 11). In our context, regarding the **Y-succ-slc** compounds[26], the PL activity from cryogenic to room temperature was explored for Eu/Tb doped phases compounds in terms of FIR, considering the $^5D_4 \rightarrow {}^7F_5$ $Tb^{3+}$ hypersensitive transition that gives rise to linear or exponential decay behaviours. Thermal sensitivity (S%) calculated in the 10–110 K range reached a maximum value of $0.43\%\cdot K^{-1}$ for one of the compounds (Figure 11). A similar value ($0.366\%\ K^{-1}$) was found for **EuTb-psa**[24], whose FIR exhibits an exponential decay in the 13.5–313.5 K range; in this case, for the $^5D_0 \rightarrow {}^7F_2$ $Eu^{3+}$ hypersensitive transition.

Since the first work of chemical sensing using an open LMOF (**Tb-BTC**) based on the hypersensitive lanthanide transition towards fluoride detection (Figure 12a),[35] several Eu and Tb-MOFs have been extensively employed as unique platforms for sensing humidity[36], ions[37] and organics[38] as well as for detecting explosives as hazardous molecules.[39] Motivated by these attractive applications, our group has studied some LMOFs for chemical sensing. Firstly, **Eu-msucc** was tested for sensing protic and aprotic solvents, due to its strong luminescence based on the $^5D_0 \rightarrow {}^7F_2$ transition.[25] A dependence of the FIR values with the nature of the solvent was observed in the emission spectra; being particularly marked in the case of water exposition, producing a significant quenching effect (Figure 12b). A size-solvent dependence of the quenching process was observed, since the feasibility of solvents to interact with the lanthanide centers is conditioned by the accessible volume of the 1D-channels.

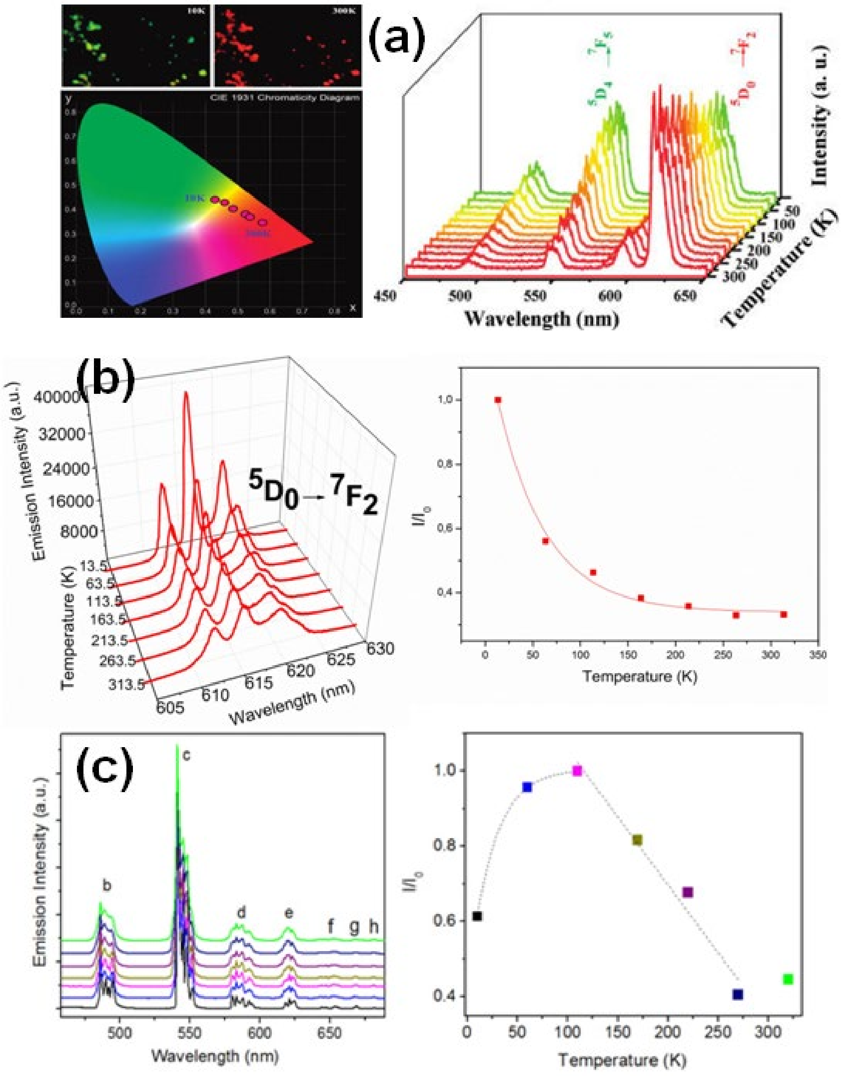

**Figure 11.** Spectroscopy response of a Eu/Tb-MOF along with the temperature according to Reference 26 (a). Thermosensing performance and FIR trends of **Eu/Tb-psa** and **Eu/Tb/Y-succ-slc** platforms. Reproduced with permission from references 24 and 26.

Moreover, the chemo-sensing performance of the **Tb/Y-succ-slc** was tested employing protic and aprotic solvents (see Figure 12c), the FIR and lifetimes being the sensing parameters. The emissions suffered a decrease when the material is suspended into acetone, n-hexane and toluene. In this case, acetone behaves as the most efficient quencher from the employed aprotic solvents (Quenching Efficiency, QE, of 98%). As it is expected, regarding protic solvents, water demonstrated to be the most efficient quencher (QE of 50%). The decrease in $\tau_{obs}$ is consistent with the increase of the QE% values, where the sensor experiments a prominent quenching effect in solvents containing C─H and C=O groups compared with those containing O─H groups.

These preliminary results set the basis for the elaboration of solvato-sensors containing lanthanide LMOFs devices.

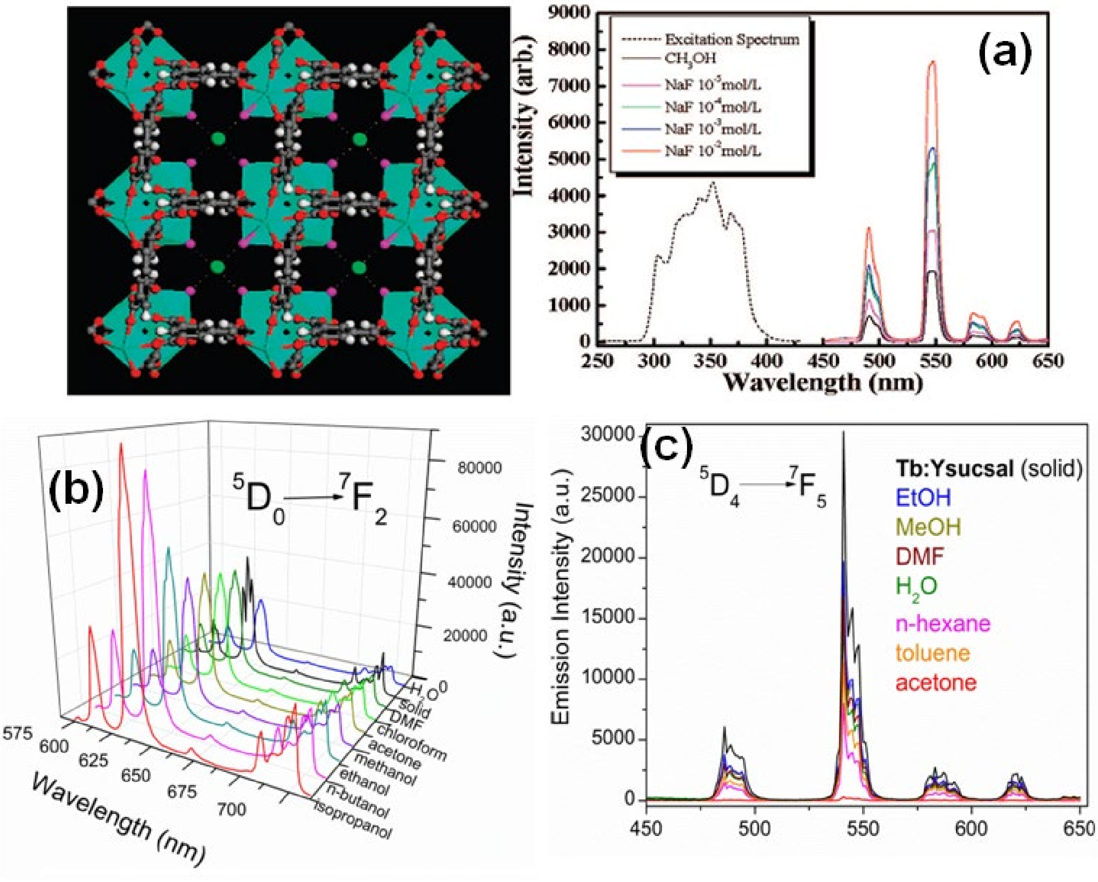

**Figure 12.** Crystalline structure of anion incorporated **Tb-BTC** activated in NaF with the model of fluoride (green) at the center of the channel. PL spectra (solid) of anion incorporated **Tb-BTC** in different concentrations of NaF methanol solution, reproduced with permission from reference 35 (a). Emission spectra of **Eu-msucc** in different solvents, reproduced with permission from reference 25. Emission spectra of **Tb/Y-succ-slc** in different solvents, reproduced with permission from reference 26.

## 4. Conclusions

As was shown in the present revision, the Metal-Organic Frameworks (MOFs) have been studied along the last decades as a type of new emerging multifunctional materials. With this aim, many groups around the world explored a variety of metal centers and organic linkers under different synthetic conditions and methodologies with the purpose of obtaining MOFs with unique functionalities and pore architectures. In this sense, lanthanides offer advantages and possibilities for the elaboration of luminescent MOFs (LMOFs) with optical applications. During the revision, some LMOFs platforms were analyzed in the context of solid-state lighting and sensing field. Finally, according with the literature of LMOFs there is an increased interest in studying these materials for real applications such as the manufacture of lighting devices and the detection of toxics or molecules of biological interest, opening up huge possibilities in materials science.

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**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.

**Anales de la Asociación Química Argentina**

**División Jóvenes Profesionales**

Mini-Review

# MESOPOROUS THIN FILMS: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS IN SENSING

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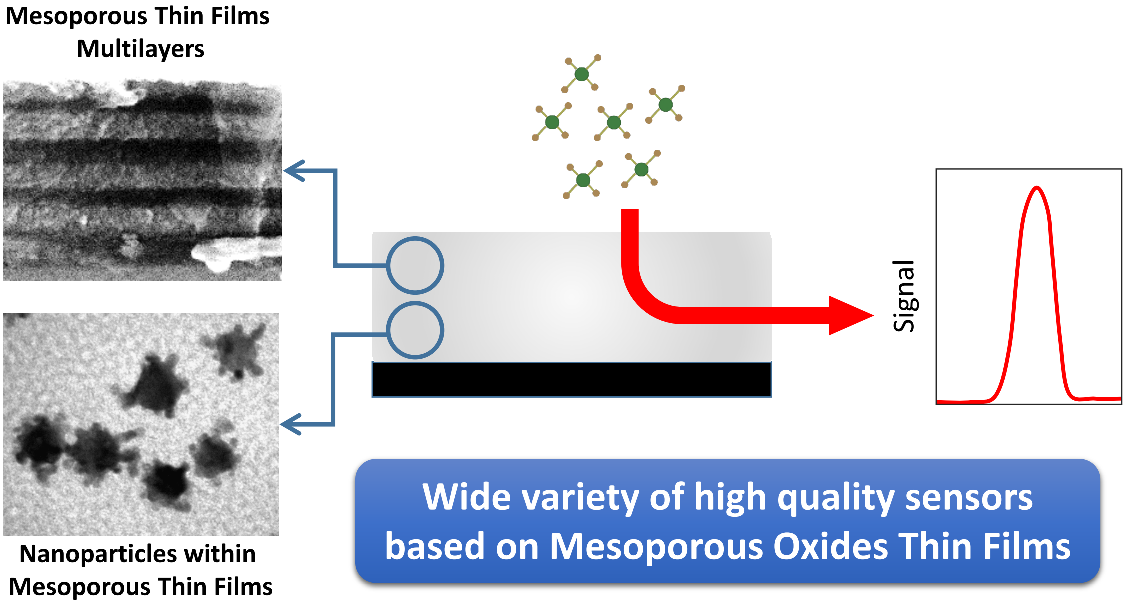
## Graphical abstract



## 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*

## 1. Introduction

Mesoporous oxide thin films (MOTFs) have received much attention in the last decades mainly due to their high surface area and versatility for development of technological devices.[1-2] Mesopores dimensions (2-50 nm diameter)[3] give place to confinement effects which are crucial in catalysis, nanoreactors, nanofluidics and diffusion.[4-8] At the same time, these materials are able to interact with larger molecules than in the case of other (micro)porous materials, such as proteins, polymers and nanoparticles.[9-12]

Typical ways to obtain thin films are by dip-coating or spin-coating a precursor solution onto different substrates such as glass, silicon, gold, quartz or conductive glass (ITO, FTO). Some parameters as withdrawal or spin speed and solution viscosity allow tuning films thickness; and other parameters as ambient humidity and temperature have critical effect on pores spatial organization and films optical quality.[13-14] Although less utilized, other deposition methods are also applied: spray-coating, casting, convective self-assembly and electrochemical assisted deposition.[1] During and after deposition, two processes take place: evaporation induced self-assembly of amphiphilic molecules that form micelles, which work as pores template, and sol-gel reactions, that form the oxide around the micelles.[15-18] Afterwards, samples are treated at moderate or high temperature (200-700°C)[1-2] or with X-rays (2.5-12 keV)[19] to eliminate the pore template and to yield oxide consolidation and even its crystallization. Furthermore, this synthetic methodology permits the addition of other chemical moieties by co-condensation or post-grafting[11, 20-21], and/or the incorporation of metal or semiconducting nanoparticles.[10, 22-23] Thus, a large variety of designs can be achieved.

The resulting MOTFs are defined by their thickness, refractive index, pore size, pore spatial distribution, pore accessibility, wall crystallinity and mechanical properties. All these features can be fully characterized by using several complementary techniques.[1-2, 14] In general pore size and its spatial distribution are obtained by means of scanning and transmission electron microscopy (Figure 1A-C), and grazing incident small angle X-ray scattering (Figure 1D). Inorganic or organic chemical composition is determined with optical spectroscopies such as UV-visible, FTIR and Raman.[14, 24] Wall crystallinity can be verified by X-ray diffraction, selected area electron diffraction, Raman spectroscopy and even X-ray absorption methods[14, 24-26] To obtain information about porosity, thickness and refractive index, X-ray reflectometry (Figure 1E) and environmental ellipsometric porosimetry (EEP, Figure 1F) are carried out.[27-28] Either

EEP or nanoindentation provide MOTFs mechanical properties.[24] In some cases, *in situ* studies are possible and permit to follow films evolution throughout the thermal treatment.[14, 29-32]

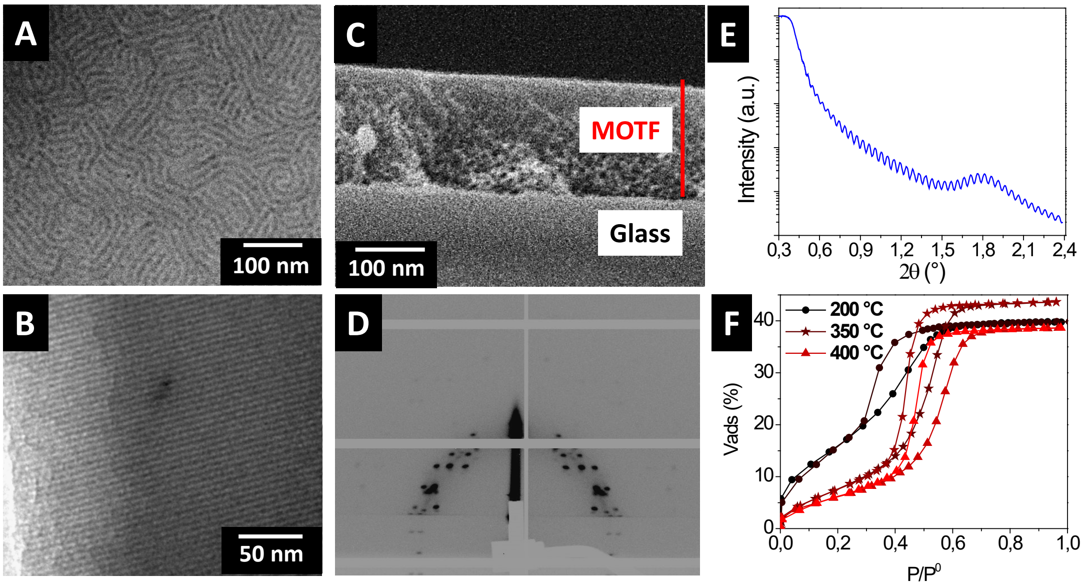


**Figure 1**. (A) SEM image of a mesoporous $SiO_2$ thin film templated with Pluronic F127 and treated at 350°C. (B) TEM image of a mesoporous $SiO_2$ thin film templated with Brij 58 and treated with X-rays. (C) SEM side view of a mesoporous $TiO_2$ thin film templated with Pluronic P123 and treated at 350°C. (D) GISAXS pattern of a $SiO_2$ thin film templated with CTAB deposited on silicon and treated with X-rays. (E) X-ray reflectogram of a $TiO_2$ thin film templated with Pluronic F127 deposited on glass and treated at 350°C. (F) Water adsorption-desorption isotherms of $TiO_2$ thin films templated with Brij 58 deposited on ITO and treated at 200, 350 and 400°C.

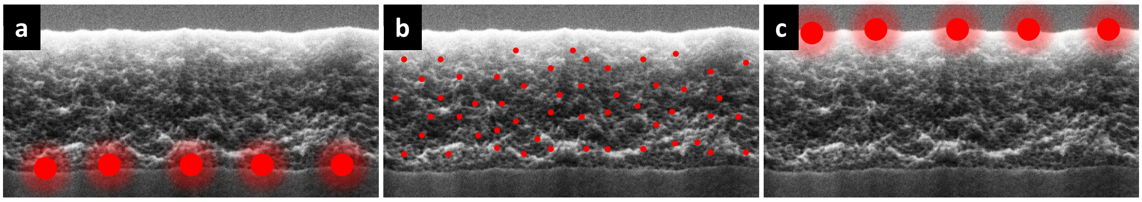
The development of MOTFs was possible thanks to the detailed characterization of each synthesis step and the complete description of the final material´s properties. Nowadays, a diversity of pore templates as well as inorganic precursors are available, therefore a large variety of MOTFs can be obtained 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 distribution (*Pm3n* as in Figure 1D, *Im3m* as in Figure 1A-B, *Fm3m* as in Figure 1C, 2D-hexagonal, 3D-hexagonal).[14, 30, 33-36] The possibility of combining the MOTF with NPs and/or inorganic/organic/biological compounds opens endless potential applications.[1]

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 their high specific surface, their chemical composition versatility and the easiness to deposit them onto a wide variety of substrates. Several examples were presented regarding the applications of MOTFs: single layers of hybrid MOTFs were tested as optical sensors, [37-39] while silica mesoporous films were applied for humidity and vapor sensing.[40-47] Moreover, improvement on specificity and selective sensing can be envisioned when increasing the complexity of the devices, either by combining several MOTFs or by adding other nanomaterials or functions in their structure. In the following sections, we will discuss two of the lines that are being developed in our group to obtain specific and reproducible high complexity sensors based on MOTFs: Surface Enhanced Raman Spectroscopy (SERS) sensors obtained by combining films with metallic nanoparticles and optical sensors based on films' multilayers.

## 2. SERS based sensors

MOTFs can be combined with metal nanoparticles to build a new material with distinctive optical properties.[10, 22-23] MOTFs represent a good alternative for nanoparticles (NPs) support and stabilization, where the large surface area ensures direct contact between the NPs and the environment. Consequently, these platforms had found applications as optical sensors. In particular as SERS based sensors,[48-52] where the MOTFs plays an active role not only generating the enhancement platform but also providing specificity to the detection.[53-58] In this line, the sensor´s performance, affinity and selectivity can be tuned modifying the MOTF pore size, charge and/or functionalization.

Diverse soft chemistry and/or lithography techniques approaches can be used to join MOTFs and metal NPs in a new material.[10, 22-23] The different synthetic pathways will define the material´s final configuration. Some of the proposed architectures are presented in Scheme 1: (a) metal NPs can be placed between the substrate and the film (Architecture 1) or (c) above the film in the air-MOTF interface (Architecture 3). Other possibility is the synthesis of the metal NPs inside the pores or at the walls of the porous film (Architecture 2, Scheme 1b). In all cases, the main features of the MOTF are not altered by the incorporation of the metal NPs.



**Scheme 1.** Schematic representation of possible architectures built by combining metal NPs and MOTF: (a) MOTF deposited on a substrate with immobilized metal NPs; (b) metal NPs synthesized in the pores or at the walls of the MOTF; and (c) metal NPs deposited above the MOTF.

Figure 2 displays electronic microscopy images of different samples with the already described architectures. Figures 2a, b and c represent examples of Architecture 1. NPs of different morphologies (triangles, rods and spheres) were immobilized and coated with a MOTF (Figures 2a, b and c, respectively).[53, 56, 59] More anisotropic shapes can be obtained by NPs overgrowth through the pores of the film that covers them (Figure 2d).[56, 60] In fact, this last feature demonstrates, in a simple way, the accessibility of the MOTF since molecules (in this case, reaction precursors) can diffuse from solution to the bottom of the film, where the NPs are placed. On the other hand, Figures 2e and f are examples of Architecture 2. Gold NPs were synthesized inside the pores of the MOTF and are evenly distributed through the film´s thickness, as can be seen from the SEM cross-section image in Figure 2f.[56, 61]

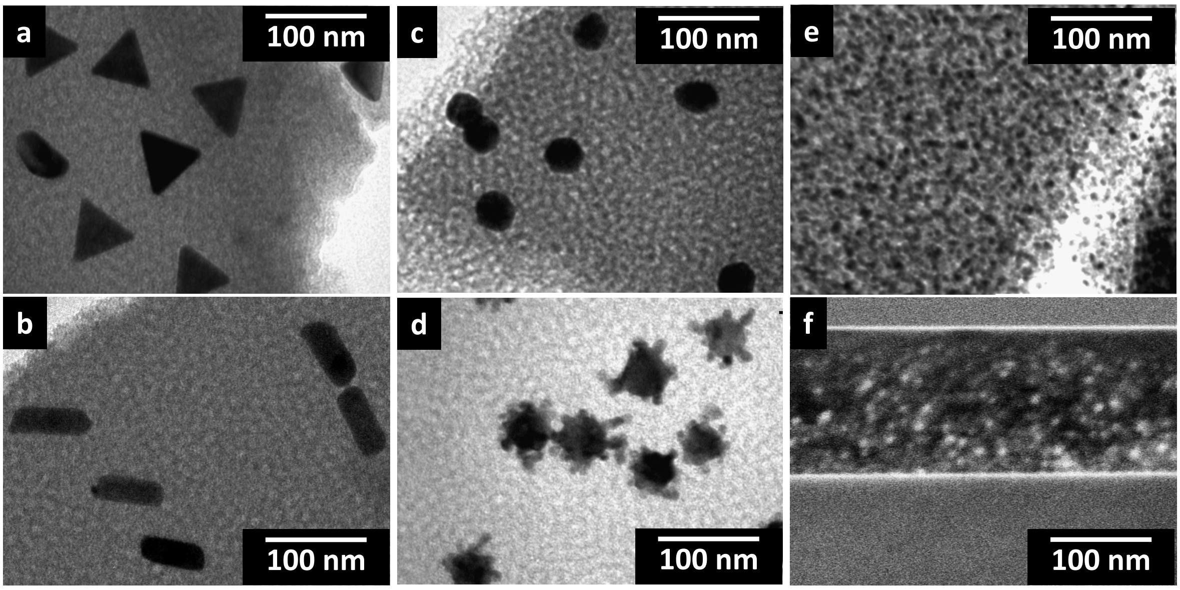


**Figure 2.** TEM images of: (a) Au nanotriangles, (b) Au nanorod, and (c) Au spherical NPs of 35nm diameter covered with mesoporous $TiO_2$. (d) TEM image of overgrown Au 35nm diameter spherical NPs. (e) TEM image and (f) SEM cross-section image of Au NPs synthesized inside a $TiO_2$ mesoporous film.

The final material´s optical properties and sensing capabilities are intrinsically related to its architecture. As an example, Figure 3 shows the SERS intensity of a probe molecule as a function of spatial coordinates, for three different platforms. Panels (a) and (b) correspond to an Architecture 1 type: aggregated 66 nm diameter Au NPs and overgrown isolated Au 66 nm NPs coated with MOTF, respectively. In both cases, a large number of hot spots are formed, given by NPs proximity and the presence of tips in the overgrown NPs.[62-63] Therefore, high SERS intensity is detected. On the other hand, Figure 3c exhibits the SERS performance of a type 2 architecture: Au NPs were synthesized in the pores of a MOTF. Low intensity signal is observed due to the small size of the NPs, limited by pore diameter.[56] However, since NPs are evenly distributed in the three directions of the ordered MOTF, a high signal spatial distribution (usually difficult to obtain through other soft chemistry techniques) is identified. As a general result, high SERS signals are obtained with Architecture 1 sensors while high spatial homogeneity is obtained with architecture 2 devices.[54, 56] Therefore, the choice of one sensing platform over another will depend on the envisioned application. In particular, highly homogeneous type 2 architectures are ideal for routine determination of analytes that are present in µM concentrations. Highly sensitive type 1 architectures, on the other hand, are ideal in case filtering or high sensitivity are needed.[53, 64]

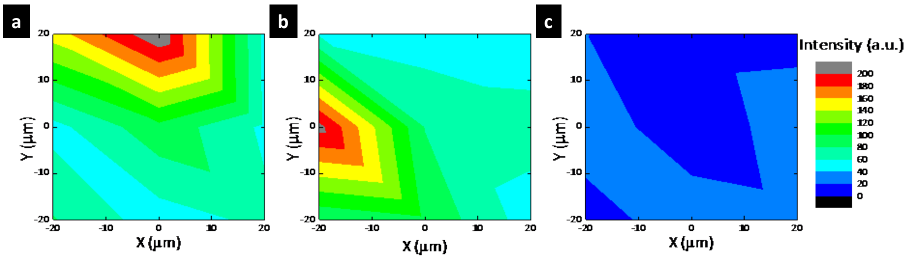


**Figure 3.** SERS maps of p-nitrothiophenol 1340 cm$^{-1}$ band intensity for different samples: (a) aggregated Au 66nm NPs coated with mesoporous TiO$_2$, (b) overgrown isolated Au 66nm NPs covered with mesoporous TiO$_2$, and (c) Au NPs synthesized inside the pores of mesoporous TiO$_2$.

In summary, a great variety of architectures can be obtained combining metal NPs and MOTFs. The features of each component remain in the new material while additional properties arise from their association. Each architecture presents different optical properties, therefore, distinctive sensing capabilities.

## 3. Optical sensors based on multilayered structures

Thin films alternated layers of low/high refractive index lead to obtain one dimension photonic crystals (PC), commonly known as Distributed Bragg Reflector (DBR).[65] If these arrangements are porous, they can be used as optical sensors in both liquid and vapour phase. PC based sensors respond to changes in the medium's refractive index by a shift in the photonic band gap; therefore, it is possible to evidence changes in the environment by a colour variation.[66-70] In a further step, the sensitivity of the sensor can be increased by depositing a noble metal thin film next to the higher refractive index layer; generating the recently experimentally developed Tamm mode.[71-75] Such feature is expected to enhance the sensitivity due to the thinner spectral band that these optical modes present, when compared to the DBR ones.[75]

Mesoporous PC based sensors are mainly obtained by soft chemistry methods using as precursors oxides nanoparticles suspensions[76-80] or sol-gel solutions[75, 81-89] to prepare each MOTF layer. If a Tamm mode based sensor is desired, the thin layer of the noble metal can be either sputtered on top of the multi-layered structure or can be deposited onto the substrate and covered by the DBR. These two possible architectures are depicted in Figure 4, together with a detailed image of the porous multilayer and an optical image of one device.

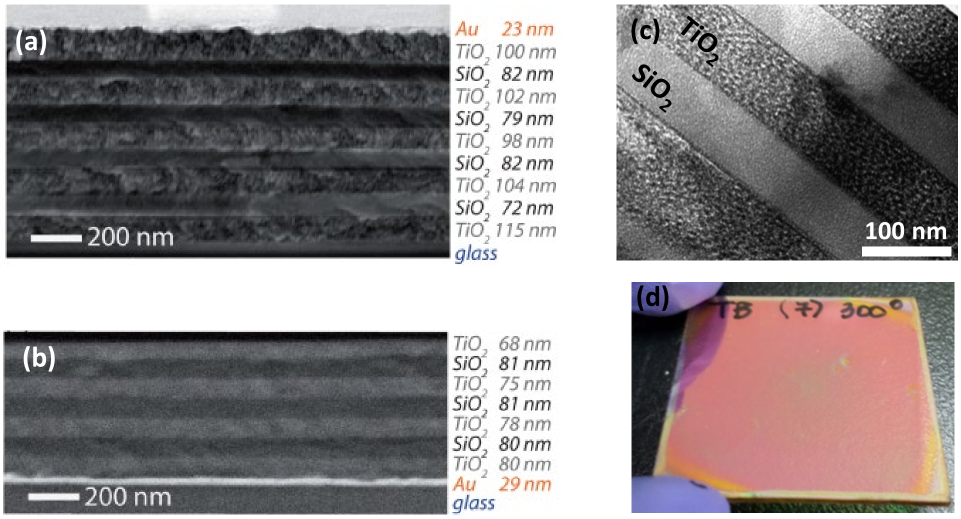


**Figure 4**. SEM images and the corresponding schemes of two possible architectures for a Tamm device: (a) DBR deposited on a glass substrate with a gold layer on top; (b) DBR deposited on a gold coated glass substrate. Reprinted with permission from [75]. Copyright 2014 American Chemical Society. (c) TEM image showing the porous structure of the mesoporous layers and (d) optical image of a Tamm device prepared on glass.

The performance of these sensors is evaluated measuring the variation of the minimum (for the Tamm device[75]) or the maximum (for the PCs based sensors[76-77, 81-82]) of the photonic band gap as a function of the stimulus (*i.e.* vapor concentration, liquid refractive index, etc). The sensitivity and selectivity of the multi-layered materials can be tailored by modifying the physicochemical nature of the MOTFs that forms the device. The chemical modification can be achieved by one-pot co-condensation during the synthesis of the layers, or by post-grafting, either by complexing or forming covalent bonds.[20] An example of the versatility of such chemical modification has been present by Ghazzal *et al.* These authors studied the selectivity of

PCs based on alternated titania and silica mesoporous films by changing the ratio of hydrophobic function of the silica layers by one-pot co-condensation.[85] To evaluate the performance, they exposed the devices to solvents with different hydrophilic behaviour (water or hexane). Figure 5a shows the spectral response of the PC when it is exposed to the solvents, meanwhile the Figure 5b shows the variation of the band gap position as function of the hydrophobic component ratio. It can be observed that as the hydrophobic function content increases, the diffusion of water inside the layers becomes more difficult due to the surface affinity.

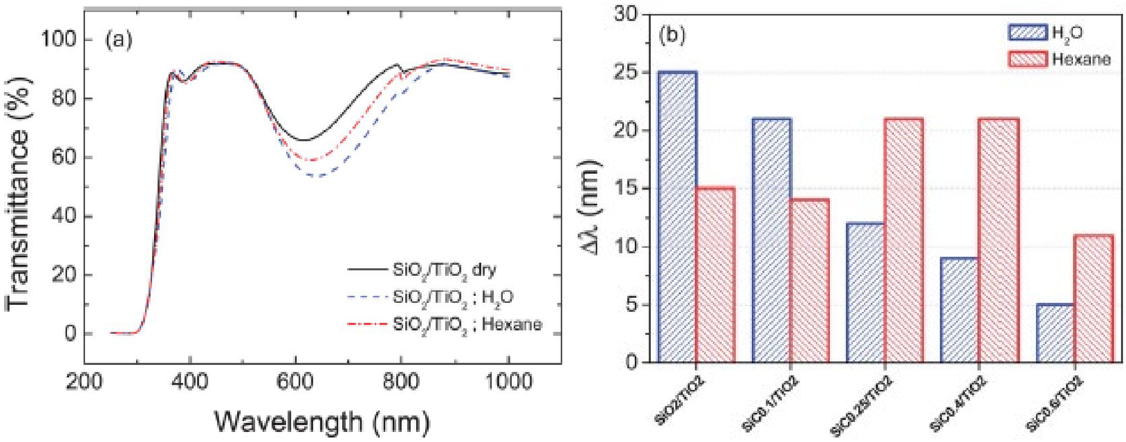


**Figure 5**. (a) Spectral response of a dry PC (black), and when it is exposed to water (blue) and hexane (red). (b) Band gap shift of the photonic crystal as function of the hydrophobic function and the solvent. Reproduced from Ref. [85] with permission from The Royal Society of Chemistry.

Our group has already tested the Tamm devices as optical sensors, proving the response from changes in the environment and opening the path to develop this type of devices.[75] As an example, in Figure 6 the response of two different Tamm devices as toluene detectors is shown, in both liquid (Figure 6a) and vapour (Figure 6b) phases. In a continuation of this work, we have demonstrated the higher sensitivity of these sensors versus those based on PCs. It was also shown that the response of this sensors not only depends on the nature of the device, but also on the physicochemical properties of the solvents, such as polarity or vapour pressure.[90]

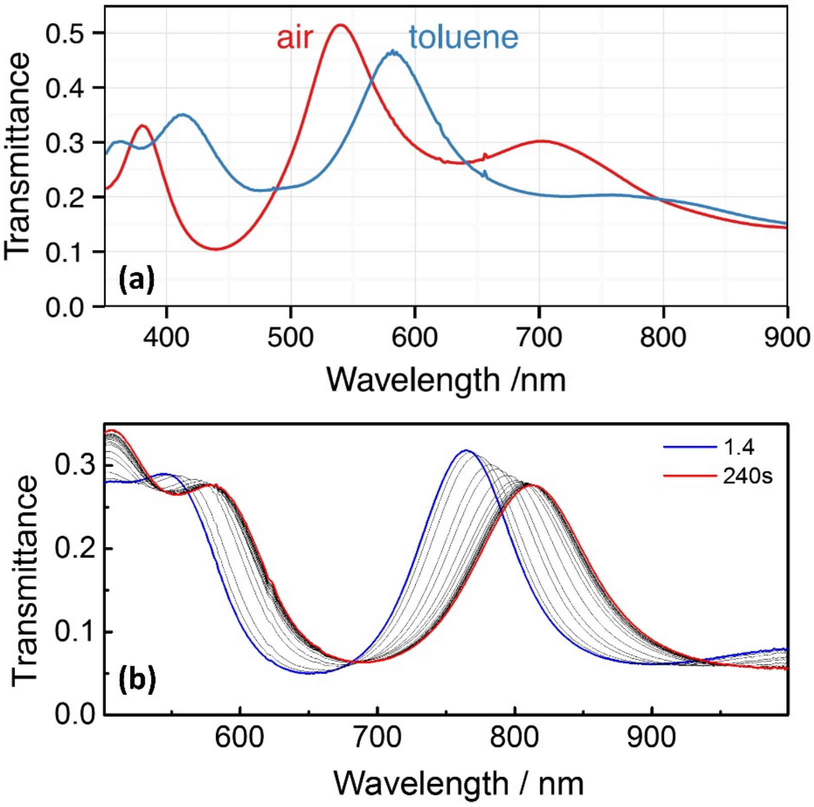


**Figure 6**. (a) Experimental transmittance spectra of a Tamm device exposed to air (red line) and after immersion in liquid toluene (blue line). Reprinted with permission from [75]. Copyright 2014 American Chemical Society. (b) Spectral response of a dry Tamm device (blue) when it is exposed to toluene vapors, until the condensation of liquid toluene inside the pores is reached at 240 s (red).

In summary, mesoporous PC based sensors, both DBR and Tamm devices, were proved to be good as vapour and liquid detectors. It has also been shown that the features of the materials can be modified with accessible reactions, which do not require a difficult work-up. Therefore, the simple design and construction method allows producing sensors on demand, and the combination of them makes possible obtaining photonic noses arrays.[91-92]

## 4. Conclusions

MOFTs are very versatile materials, whose physicochemical and structural characteristics can be designed and tuned from synthesis. Thus, their use as constitutive part of sensors is straightforward. Moreover, if the films are stacked or combined with other nanomaterials, multiple variety of architectures can be obtained, with new properties that depend on the components' physicochemical features and position. Consequently, more complex and specific sensors are expected to be built in such approach. In this minireview, we have demonstrated that MOTFs can be combined with metallic nanoparticles to obtain highly sensitive SERS based sensors with architecture dependent performance. In the same way, we have shown that DBRs based optical sensors can be prepared by stacking MOTFs and the sensitivity of the device can be tuned by taking advantage of the films' functionalization. The selected cases are just a small sample of MOTF based sensing possibilities. Other applications are currently under development worldwide, and much more examples are expected to be available in the near future.

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**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.

**Anales de la Asociación Química Argentina**

**División Jóvenes Profesionales**

Mini-Review

# HYBRID MESOPOROUS SILICA: A PLATFORM FOR GATING CHEMISTRY

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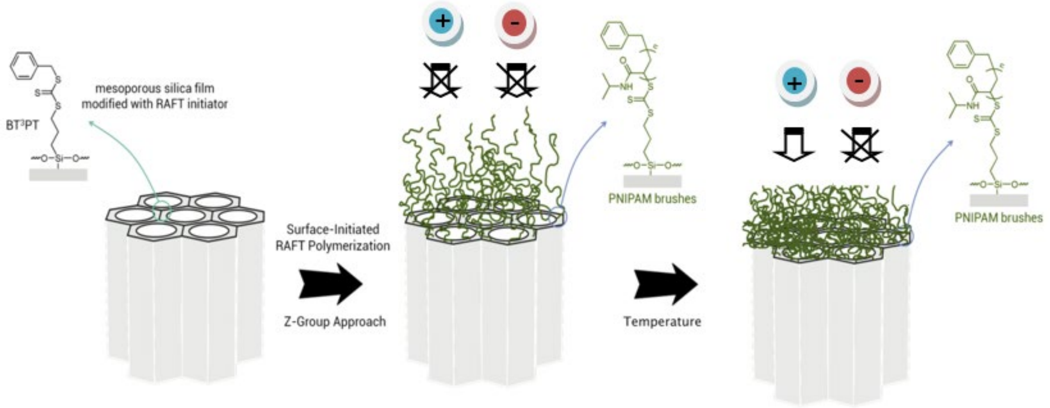
## Graphical abstract



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.*

## 1. Introduction

According to IUPAC, porous materials can be divided in three categories: microporous (pores diameter < 2 nm); mesoporous (2 nm < pore diameter < 50 nm); and macroporous (pore diameter

> 50 nm). Porous materials, either as particles or thin films, presents two level nanostructured features: on one side the diameter of the particles or the thickness of the films and, on the other, the pore size.

Mesoporous oxides display highly ordered monodisperse pores distribution with sizes between 2-50 nm, and high specific surface, ranging from 100 to 1000 $m^2/g$. They are synthesized through the combination of two processes: sol-gel reactions and self-assembly of amphiphilic molecules, as templates. The chemistry of the inorganic matrices can be cleverly tailored by the correct choice of precursors, as mesoporous silicon dioxide, titanium dioxide, zirconium dioxide or mixed oxides may differ significantly in surface charge density, solubility, and electric properties. Mesostructure (porous volume, pore size, and neck side pore distributions) as well as crystallinity of the inorganic walls are crucial features and could be carefully designed according to the searched applications (drug delivery, fuel cells, photovoltaic applications, etc).

Until early 90´s, the most spread porous materials under studies were aluminosilicates known as zeolites.[1] By that time, the potential applications for such materials were limited due to the small pore size (bellow 3 nm). In 1992 *Mobil Oil Corporation* reported the first mesoporous ordered material: A new family was born, M41S (MCM-41, MCM-48, etc) silicas.[2–4] Years later, examples of mesoporous oxides other tan silica appeared.[5–7] Since then, a wide variety of mesoporous inorganic oxide and mixed oxides with pore size raging between 3 to 50 nm were designed. Within this new context, the orchestration of chemical and physical process in confined geometries has begun to be used by the scientific community as a strategy to develop new materials. These new materials embrace both, organic and inorganic materials, towards the design of hybrids material with specific responsive features and with potential applications in sensing, drug delivery, imaging and tissue regeneration.[8]

Confinement within a nano-mesoporous structure changes significantly the interaction between molecules and their surroundings. If molecule size is comparable to pores diameter, the interaction with the walls defines its chemical and physical properties and its dynamic and structural characteristics, which may differ from bulk ones. These features increase in magnitude as the pores become thinner and the interaction between molecules and pore walls become predominant. These properties have awaken the creativity of chemists and materials engineers in the last two decades in the design of new hybrid materials based on porous ceramics with characteristic sizes bellow 50 nm.

Mesoporous silica (Fig. 1) was taken as a starting point to design and synthesize inorganic - polymer hybrids materials with controllable functional properties. Space distribution and the careful choice of molecules will tailor the systems with unique features in a synergistic interplay where both, localization and nature of the functionalization, defines its final behaviour. In this manner, multiresponsive, permselective or selective and responsive membranes capable to modulate the intensity of species transport under different physical, chemical or biological stimuli were synthesized. The design of responsive materials has taken elements arising from different chemical branches such as supramolecular chemistry or macromolecular chemistry, paving the way to what is known as “gating chemistry”.[10] Based on changes on hydrophobicity, charge, specific recognitions or polymer reconfiguration, these materials have obtained great importance as delivery platforms. Sun *et al.* demonstrated the pH responsiveness of poly-(2-(diethylamino)ethyl methacrylate) (PDEAEMA) brush behavior when grafted to a mesoporous silica matrix. This polymer works as a door, opening or closing the pores on demand.[11] Martínez-Mañez and collaborators recently showed the possibility to control transport in MCM41 matrices with pH changes or with different anions concentration. Polyamines grafted to the pore entrance may be reconfigured upon the presence of anions of different size and charges (such as sulfates, chloride, phosphates or ATP).[12]

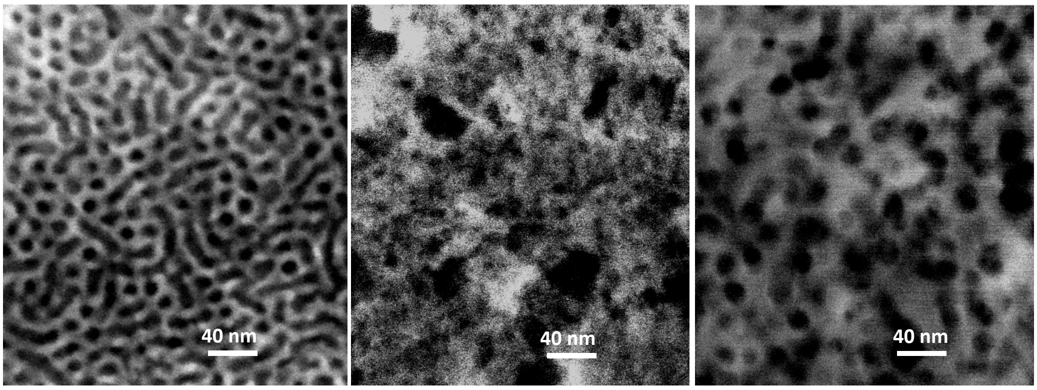


**Figure 1.** SEM images for different silica porous structure achieved through sol gel chemistry using different templates: (a) Pluronic F127, (b) poly-terbutylacrylate-poly styrene triblock copolymers and (c) poly-terbutylacrylate-poly-isopropylacrilamide.[9]

Deep knowledge on silica functionalization and its biocompatibility has taken this material to be one of the best choices for drug delivery applications under specific stimulus.[13,14] Mesoporous silica responsive system for drug delivery purposes have been widely exploited taking advantage of distinct features arising from acid–base behavior, coordination chemistry,[15] auto-tunable systems,[16] or specific irreversible reactions, such as the degradation or cleavage of caps or bulky groups.[17,18] Recently its has been proved that control over delivery can be achieved through hydrolysis of peptide brushes by specific enzymes (Fig. 2).[19]

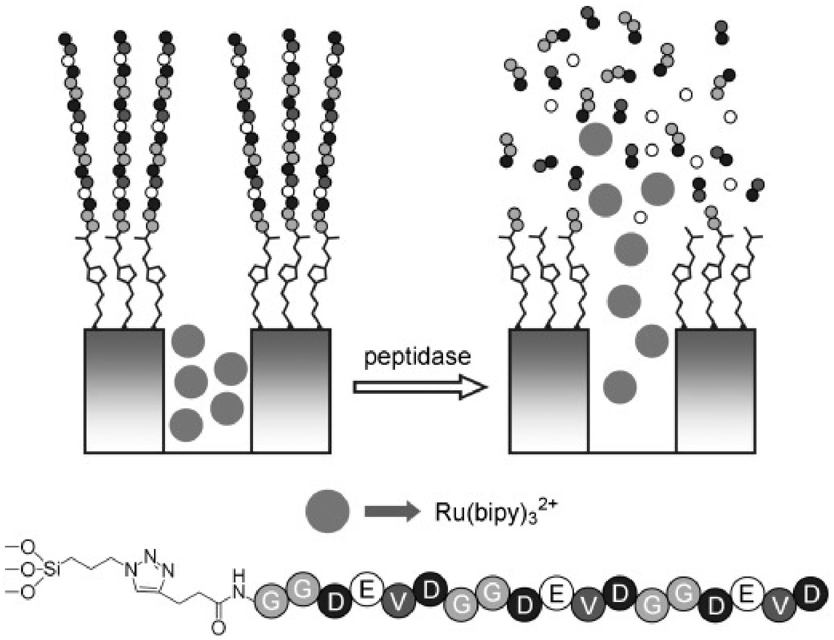


**Figure 2.** Representation and principle of operation of the mesoporous silica functionalized with 3-(azidopropyl) triethoxysilane and capped with the peptide. The C-terminus amide bonds of the negatively charged amino acids contained in the peptide are cleaved in the presence of the enzyme peptidase. Reproduced with permission from Coll *et al*., *Angew. Chem., Int. Ed*., **2011**, 50, 2138–2140. Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA.

Mobile photoactive molecules such as azobencene, grafted to mesoporous substrates were able to increase delivery of drugs as a consequence to light irradiation.[20,21] In similar manner spiropyran-merocyanine[22] or gold nanoparticles were used as caps, able to release the pore cargo under irradiation.[23] The use of redox reactions has also been a widely used stimulus to control molecular gates at the pore entrance. Lin and collaborators took advantage of CdS, $Fe_3O_4$, or Au nanoparticles as caps able to be cleaved under the presence of redox agents as disulfide groups.[13,24–27] Fujiwara *et al.* grafted 3-(trietoxysilyl)propyl isocyanate and 6-hidroxy-2-naftyl disulfide on silica mesoporous surface; the simple addition of ditiotreitol (DTT) opened the pores.[28] With a similar idea Liu *et al.* cross-linked a polymeric network on the surface of mesoporous silica able to work as an on/off switch in response to redox signals.[29] In this work, the polymeric network, crosslinked through disulfide bridges, could be opened with the use of reducing agents (Fig. 3).

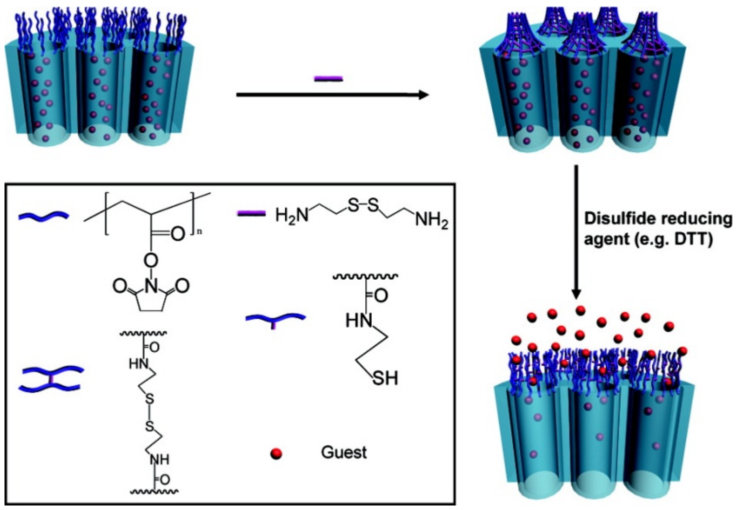


**Figure 3.** Redox-responsive nanogated ensemble. Mesoporous silica capped with redox-active cross-linked polymeric networks. Reproduced with permission from Liu *et al*., *J. Am. Chem. Soc*., 130, 14418–14419. Copyright 2008 American Chemical Society.

The use of caps as gates for pore closure/opening has been a common strategy in the design of delivery particles, from the simple approaches as second generation PANAM dendrimers anchored to the surface of MCM41 to highly sophisticates strategies, as rotaxanes and psedorotoxanes.[13] Zink *et al.* generated pH responsive nanopistons able to shift to an open state with irradiation or changes in redox potential or pH.[30–35] With a similar line of thoughts, Park *et al*. joined polyethylenimine (PEI) and cyclodextrin (CD) to design new pseudorotaxanes over porous surfaces;[36] cyclodextrin works as a valve able to shifts its position according to pH. Kim *et al.* demonstrated the use of a similar cyclodextrin/polyamine pseudorotaxane on the controlled release of a specific drug hosted inside the porous material.[36,37] Other authors have provided further examples of such sophisticated structures with reversible or irreversible features.[38–42] Figure 4 shows two approaches were bulky organic groups such as cucurbit[6]uril (Fig. 4a) or alpha-cyclodextrine (Fig. 4b) were detached from the pore entrance reversibly or irreversibly to release the mesoporous particles cargo.

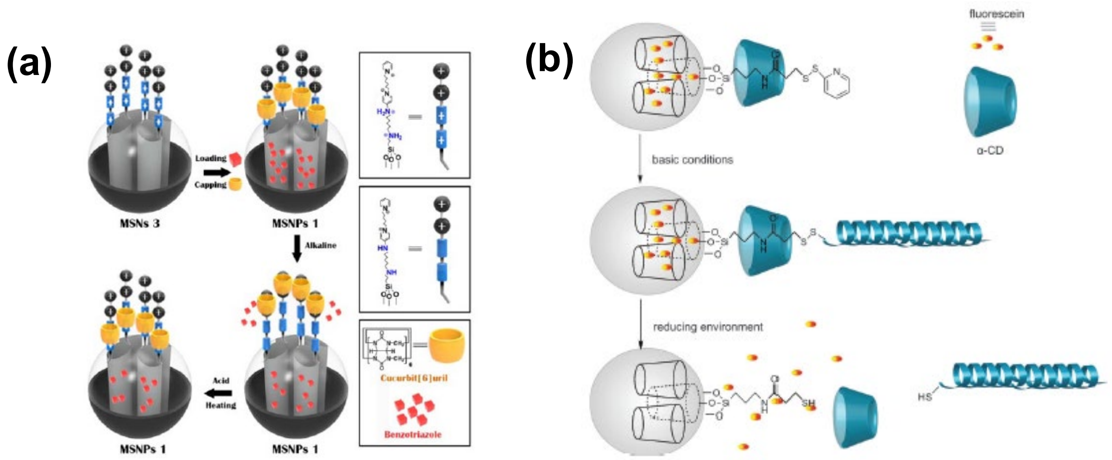


**Figure 4.** a) Schematic representation of MCM-41 grafted with bistable [2]pseudorotaxane, which contains 1,6- hexanediammonium (HDA) and 1,6-bis(pyridinium)hexane (BPH) as two recognition sites, as well as cucurbit[6]uril (CB[6]) as macro-cycles. Reproduced from Wang *et al. Chem. Commun.* **50,** 5068–5071 with permission from The Royal Society of Chemistry. b) Redox-triggered release systems based on peptide modified mesoporous silica. The release of the drugs takes place when the disulfide bridge linking the mesopore outlet and the peptide is cleaved in the presence of dithiothreitol. Reproduced with permission from Porta *et al Phys. Chem. Chem. Phys.* **13,** 9982–9985 with permission from the PCCP Owner Societies.

## 2. Our research: PNIPAM as thermoresponsive gating system

We propose, as the axis of our research, the merging of elements and tools deriving from sol-gel, supramolecular and macromolecular chemistries, to study new alternatives for advanced mesoporous materials development with a precise control over density and spatial localization of functional groups. Such systems have potential applications as permselective membranes, responsive membranes, catalysts and for clinical (biosensors, prosthesis and drug delivery). In this regard, the integration of mesoporous ceramics to macromolecules gives a wide variety of possibilities. We have demonstrated the irreversible permselective changes upon pore walls surface charges modification through polyelectrolytes brushes grafting, due to its high charge density. From another perspective, we have taken advantage from supramolecular specific interaction to change permselectivity in a reversible fashion upon concentration of specific analytes.

In this section we will describe the synthesis and the motivation for the synthesis of thermoresponsive poly-(*N*-isopropylacrylamide) (PNIPAM) over mesoporous silica scaffold as an interesting approach to search for nature mimicking. The integration of PNIPAM in mesoporous matrices has been the subject of study of different groups.[43–47] PNIPAM is a widely studied water-soluble polymer, mainly because of its lower critical solution temperature (LCST) behavior in water, as it precipitates out from water upon heating above $T \approx 31$ °C.[48,49] This temperature-induced phase separation has been exploited for the construction of thermo-associative polymeric systems, that is, polymers that tend to associate in aqueous solution upon heating. The first example of mesoporous materials integrating thermo-active gating properties was reported by Lopez and collaborators in 2003.[50,51] Through Si-ATRP of PNIPAM brushes grafted from mesoporous silica particles this authors demonstrated that these macromolecular entities controlled the uptake and release of rhodamine 6G from the mesoporous particles. Later on, Oupicky *et al.* showed that densely grafted PNIPAM-modified mesoporous silica nanoparticles exhibit good uptake and release properties of fluorescein at room temperature below LCST and a low level of leakage above LCST.[52] Since then, different groups explored similar concepts to thermally control the transport of chemical species through mesoporous matrices.

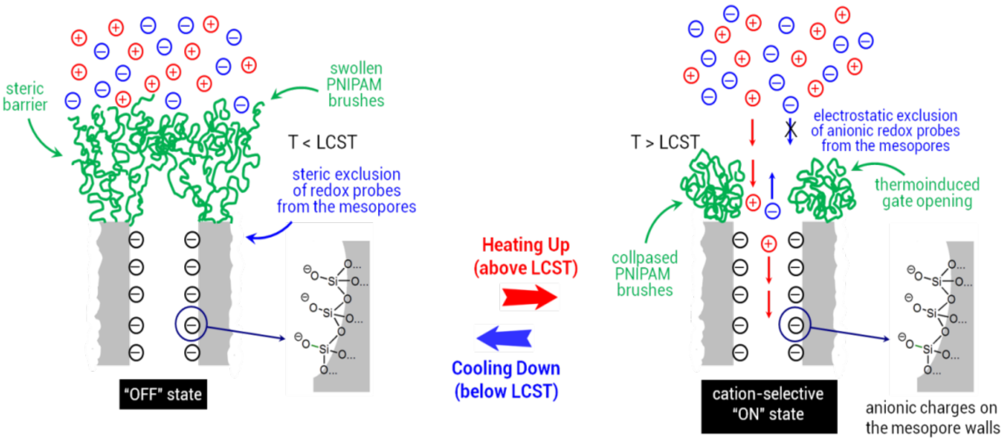


**Figure 5.** Schematic depiction of the ionic transport processes taking place in the hybrid polymer-inorganic interfacial assembly at temperatures below and above LCST. Adapted with permission from *Chem. - A Eur. J.* **2017**, *23* (58), 14500–14506.

In our work,[53] we described the synthesis of an hybrid organic-inorganic assembly displaying thermo-dependent ionic transport properties that, until now, were not observed in nanoporous permselective membranes (Fig. 5). For that purpose RAFT polymerization through a Z-Approach technique was followed. This polymerization technique allows to control growth over mesoporous matrix, guaranteeing a dense polymer layer. The presence of the polymer brush was confirmed through XPS, AFM and ellipsometry measurements (Fig. 6). This last technique allowed to discriminate the location of such functionalization (over or inside the porous structure) and confirmed a 9 nm polymer layer on top the porous matrix and an accessible porous structure. This space distribution is of crucial importance for the understanding of the material's final properties.

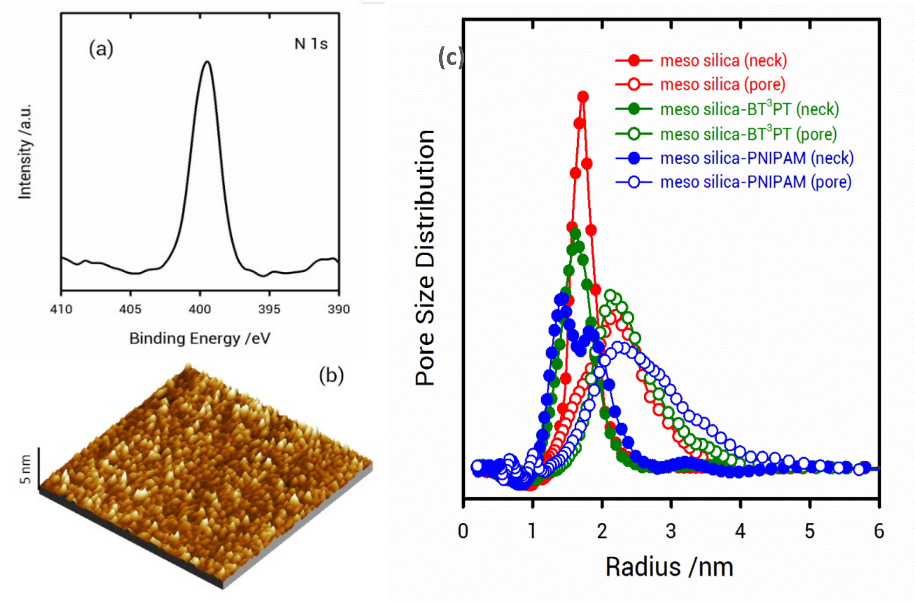


**Figure 6.** (a) N1s XPS spectra corresponding to the mesoporous silica film after PNIPAM polymerization. (b) AFM three-dimensional topography image of PNIPAM-modified mesoporous thin film (PeakForce Tapping mode; maximum z-scale: 5 nm; scan size: 1.5x1.5µm). (c) Pore size distribution of unmodified mesoporous silica films, mesoporous films modified with the RAFT agent (BT3PT), and PNIPAM-modified mesoporous silica films, as determined by ellipsoporosimetry. Adapted with permission from Schmidt *et al, Chem. - A Eur. J.* **2017**, *23* (58), 14500–14506.

The responsive behavior towards the diffusion of different charged probes was followed by cyclic voltammetry in a thermostatized electrochemical chamber. This experiment allowed us to study the influence of temperature and charges in the transport of specific species through the membrane. The experiment was done at 25 and 50 ºC and repeated 4 times. Reversibility to temperature was proved for each cycle (Fig. 7).

In close resemblance to TRPs (Transient Receptor Potential channels),[54] this functional hybrids constituted of PNIPAM-capped mesoporous silica-based thin films are able to discriminate and modulate the transport of cations while inhibiting the passage of anions in the presence of temperature variations. Being able to design multicomponent mesoarchitectures at interfaces with functions similar to thermosensitive biological channels would be of great importance for further expanding the scope of applications of these designed nanoarchitectures.

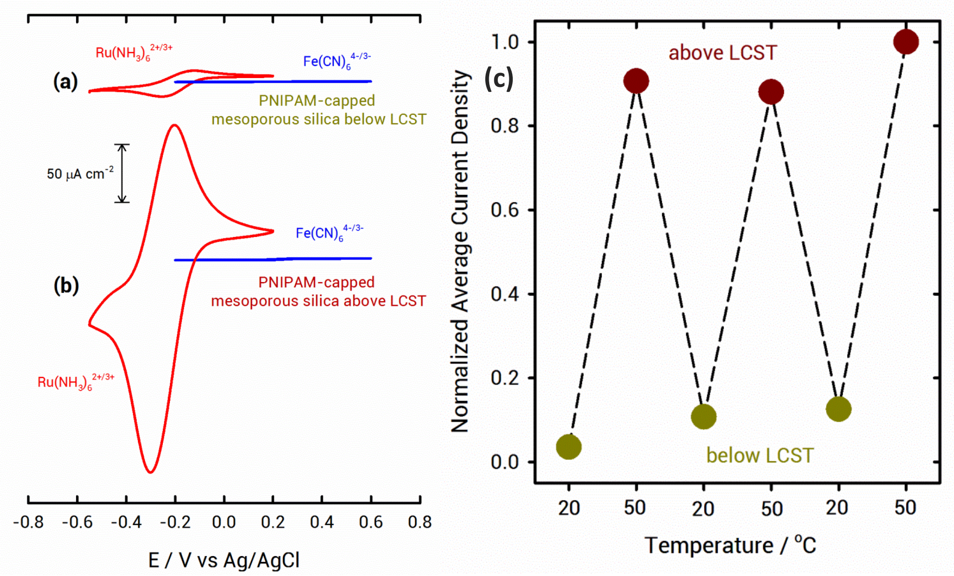


**Figure 7.** Cyclic voltammograms corresponding to: (a) PNIPAM-modified mesoporous silica thin film at 20 ºC (below LCST), (b) PNIPAM-modified mesoporous silica thin film at 50 ºC (above LCST), in the presence of 1 mM $Ru(NH_3)_6^{3+}$ (red trace) and 1 mM $Fe(CN)_6^{3-}$ (blue trace), respectively. Scan rate: 100 mV $s^{-1}$. Supporting electrolyte: 0.1 M KCl.(c) Reversible variation of the normalized electrochemical current of cationic $Ru(NH3)_6^{3+}$ redox probes diffusing through PNIPAM-modified mesoporous silica films upon alternating the solution temperature between 50 ºC (dark red, "ON" state: above LCST) and 20 ºC (dark yellow circles, "OFF" state: below LCST). Supporting electrolyte: 0.1 M KCl. Adapted with permission from Schmidt *et al, Chem. - A Eur. J.* **2017**, *23* (58), 14500–14506.

## 3. Conclusions

Ideal delivery and responsive systems should control transport on time and space. Additionally, it would be desirable for these systems to be reversible and tunable according to the intensity of the stimulus. If those characteristics are reached, then pulse delivery of drugs as it happens for endogenous compounds (*i.e.* insulin, growth hormone, estrogen, etc) could be attained. This would result in an improvement in treatments, and would avoid tolerance or auto-regulation of receptors. For such purposes gating systems and its development appear crucial.

In this context the clever distribution of functionalities within the mesoporous structure, the location of charges, and its density as well as the volume of the molecules attached and its conformation can be manipulated in search of the desired response to a defined stimulus. In the last years in has been proved that functional groups location can be achieved through a wide palette of strategies where the concerted used of confinement properties, charge and steric effects should be taken into account. Each modification would change the materials' properties and those properties will constrain any further modification.

The fusion of different building blocks arising from different branches of chemistry as sol-gel, supramolecular and polymer sciences allows the creation of new materials able to switch between on/off states to deliver their cargo following and environment changes or by an external stimulus, as light or magnetic fields. The design of hybrid materials with gating features, recently defined as "gated chemistry", not only shows the wide palette of materials that can be reached, but gives the reader a new perspective of the promising future of these materials for specific applications as health, environment and energy.

We have exploited a wide variety of strategies for the tailorable design and location of building blocks to mesoporous scaffolds. These strategies include surface-controlled polymerization, layer by layer assembly or electro polymerization. Furthermore, we have described the synergistic behavior of both polymer and inorganic scaffolds, normally neglected in literature, to reach the desired properties. In our group we have proved that both charge and steric hindrance may be adequately tuned for gating purposes exploiting the nature of the inorganic matrix (*i.e.* isoelectric point), polymer response to stimuli and supramolecular chemistry for response to specific analytes.

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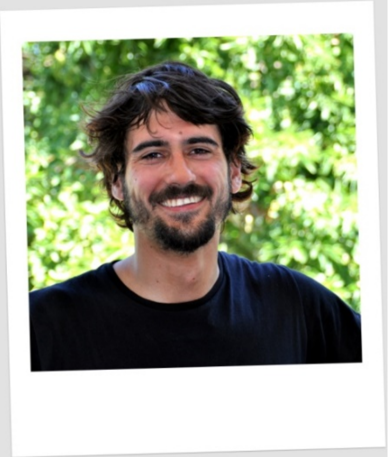

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