

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 carbonos porosos y su aplicación en el almacenamiento y la conversión de energía. Particularmente, discutiremos la síntesis y aplicaciones de carbonos mesoporosos como recubrimientos funcionales de separadores para baterías de litio-azufre, carbonos nanoestructurados como soportes de catalizador para celdas de combustible y carbonos 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.*

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 (C₆₀),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 conversion¹⁴ 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 $64 \text{ mS} \cdot \text{cm}^{-1}$,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 stability²² and could exhibit high surface area, since the theoretical specific surface area for a single layer graphene sheet is $2630 \text{ m}^2 \cdot \text{g}^{-1}$.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

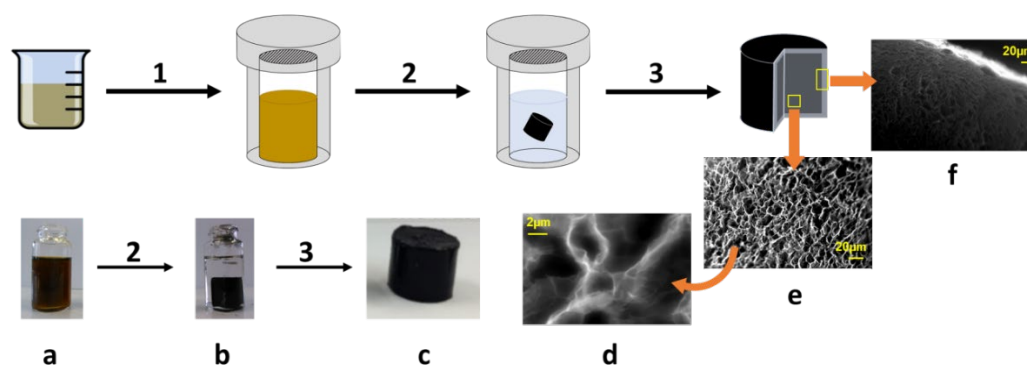


Figure 1. Schematic illustration of the hydrothermal synthesis of rGO aerogel. 1. transfer of the GO aqueous dispersion $\sim 3\text{--}4 \text{ wt } \%$, (photo a) to the autoclave system. 2. Thermal treatment at $180 \text{ }^\circ\text{C}$ during 12h (photo b, hydrogel after the hydrothermal process). 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 pressure²⁵ 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 TiO₂ 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 Fe₂O₃/rGO composites by a solvothermal route using Fe(CH₃COO)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 V₂O₅,³⁰ VO₂,³¹ Co₃O₄,³² ZnO,³³ CoS,³⁴ MoS₂³⁵ have been obtained. For instance, Zensich *et al.* reported a simple but effective strategy to fabricate practical high-loading Li₂S cathodes for high-performance Li-S batteries in carbonate-based electrolyte by the irreversible electrochemical decomposition of a hydrothermally prepared 3D rGO-covered MoS₂ particles composite to a Li₂S@rGO (plus Mo nanoparticles) composite.³⁶ The Li₂S@rGO cathode containing high Li₂S loadings of ≈ 5 mg·cm⁻² showed a high reversibility in capacity and excellent electrochemical performance which was explained by the benefits of the synergistic

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 is turned into carbon by a heat treatment (pyrolysis) at high temperature (above 800 °C) 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.

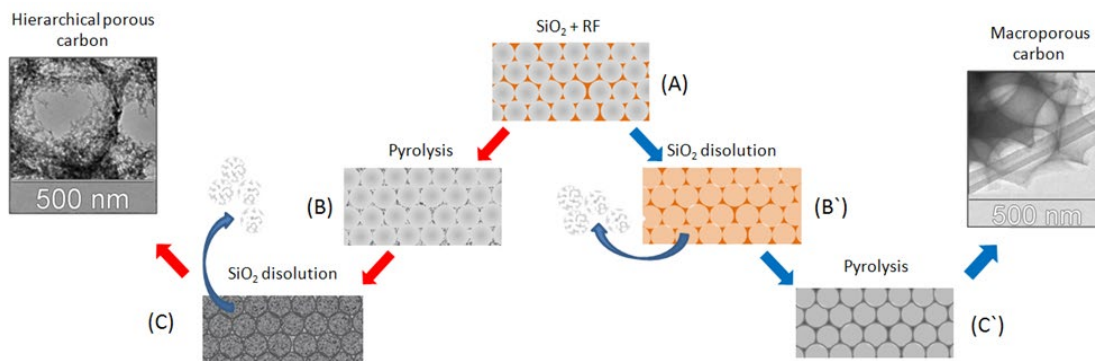


Figure 2. Schematic illustration of the pathways for the carbon synthesis. A-B-C: Synthesis of the mesoporous carbon with hierarchical porous structure (HPC). A-B'-C': Synthesis of macroporous carbon.

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

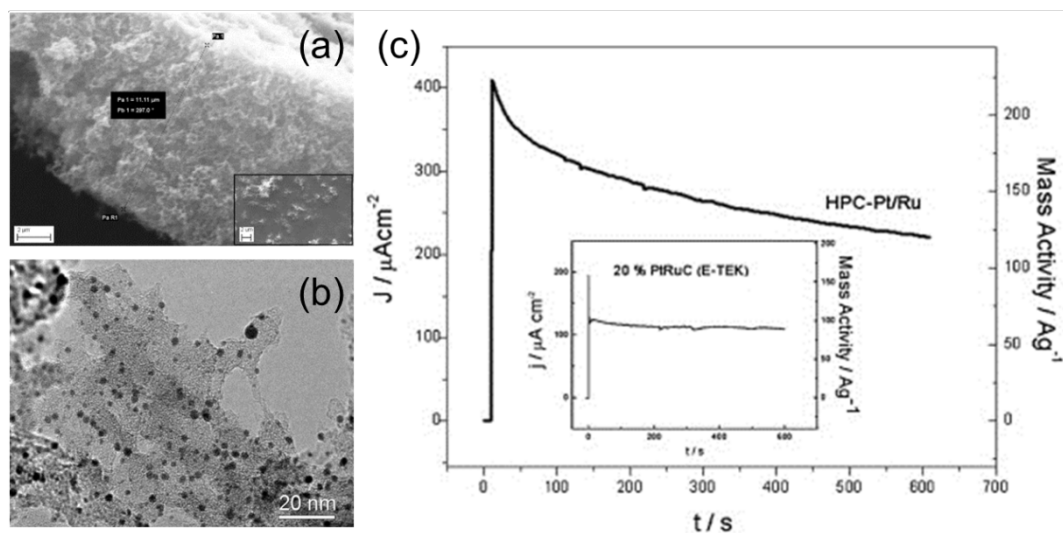


Figure 3. (a) SEM image and (b) HRTEM image of the HPC-Pt/Ru. (c) Current transients for methanol electrooxidation on HPC-Pt/Ru at 0.55 V_{RHE}, 1 M CH₃OH/1 M H₂SO₄. T = 60 °C. *Inset:* current transients for methanol electrooxidation on commercial PtRuC (E-TEK) at 0.55 V_{RHE}, 1 M CH₃OH.

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·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 Li₂S/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 cm³ 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 °C. The mesoporous carbons not only possessed tunable pore volume,⁵⁹ but could also be modified with N-dopants⁶² or N, S co-dopants.⁶³ The authors found that undoped mesoporous carbon with the highest pore volume of 3.23 cm³·g⁻¹ delivered the most important enhancement in the electrochemical performance (initial discharge capacities of 1364 mAh·g⁻¹

and high reversible capacity of $1015 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles at a current rate of 0.2 C; 1 C = $1672 \text{ mA}\cdot\text{g}^{-1}$), 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 $5.4 \text{ mg}\cdot\text{cm}^{-2}$.⁶³ At a current rate of 0.2 and 0.5 C, high areal capacities of 5.9 and $2.9 \text{ mAh}\cdot\text{cm}^{-2}$ were achieved, respectively.

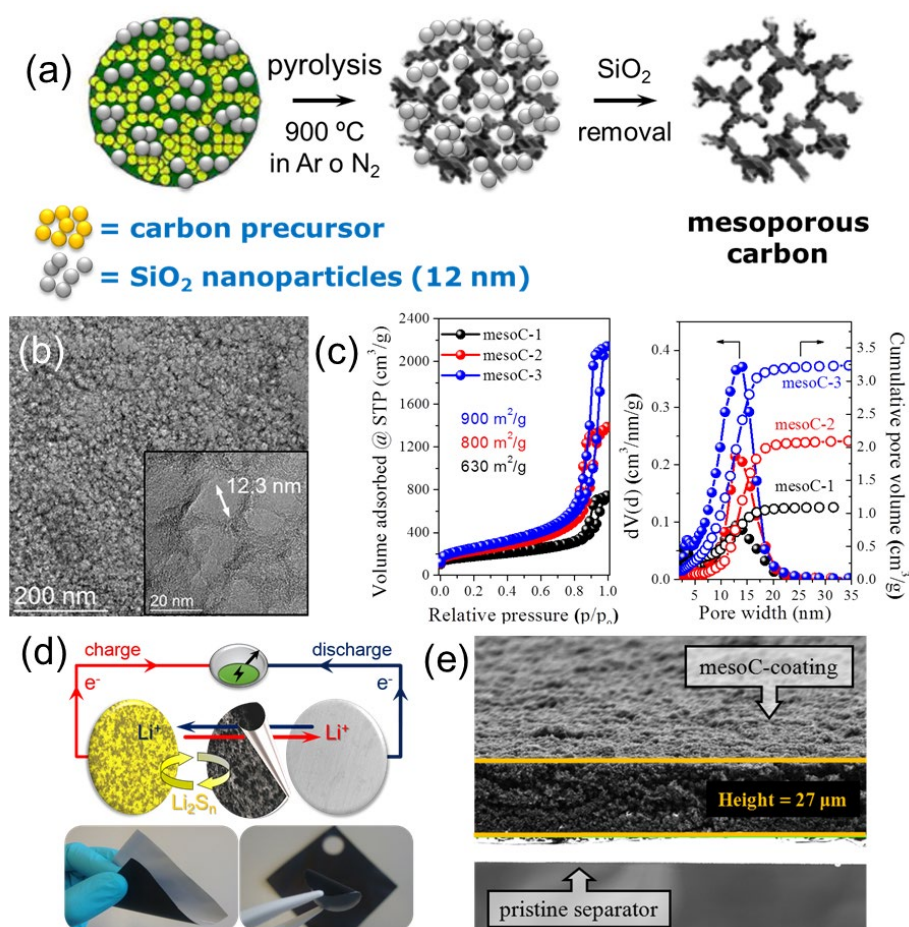


Figure 4. (a) Schematic illustration of the synthesis of mesoporous carbons. (b) Representative TEM images and (c) nitrogen physisorption isotherms and the corresponding pore size distributions of the mesoporous carbons. (d) Schematic configuration of the Li–S batteries with a mesoporous carbon-coated 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 PCS_x, where *x* represents the molar ratio of CTAB to PDAMAC (0.43, 1.28 and 3.85). The CPS_x samples as potential catalysts exhibited good specific surface area (100–400

$\text{m}^2 \cdot \text{g}^{-1}$) 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	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \cdot \text{g}^{-1}$)	V_0^{b} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{t}^{c} ($\text{cm}^3 \cdot \text{g}^{-1}$)	D_{p}^{d} (nm)
CPS _{0,43}	100	0.038	0.570	0.608	34
CPS _{1,28}	95	0.038	0.550	0.589	30
CPS _{3,85}	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 $\text{mmol} \cdot \text{g}^{-1}$, 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 $\text{mmol} \cdot \text{g}^{-1}$ in the first cycle to 0.40 $\text{mmol} \cdot \text{g}^{-1}$ 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.

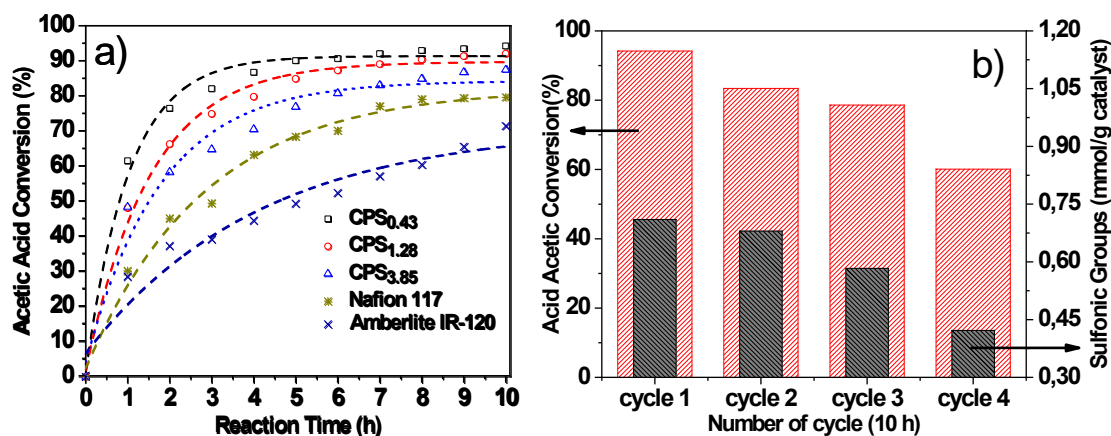


Figure 5. (a) acetic acid-ethanol esterification at 75 °C and (b) reusability of the CPS_{0.43} catalyst.

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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