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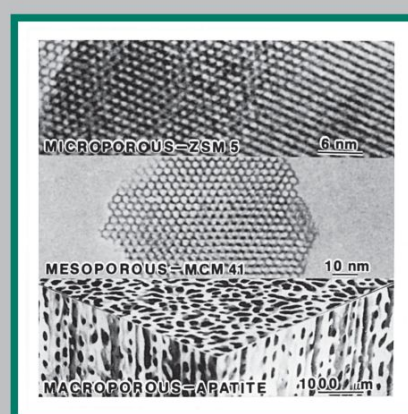
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Direct synthesis of ordered mesoporous carbon applied in hydrogen storage

Juliana M. Juárez¹ · Marcos Gómez Costa¹ · Oscar A. Anunziata¹

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Abstract

In this work, we present a direct, novel and low cost method for the preparation of an ordered mesoporous carbon (OMC). OMC was successfully synthesized by the carbonization of the silica/triblock copolymer/sucrose composite in the presence of sulfuric acid. The resulting material was characterized by XRD, N₂ sorption analysis and TEM techniques. The novel synthesis technique improved significantly the H₂ storage properties (3.78 wt%) compared with that of CMK-3 synthesized using the nanocasting strategy (2.2 wt%) at 77 K and 10 bar.

Keywords Carbon materials · Hydrogen storage · OMC · Nanomaterials

1 Introduction

Ordered mesoporous carbon materials have attracted much attention due to their high specific surface area, interesting pore volume and large pore diameter. These kind of materials have different applications such as adsorption, catalysis, gas separation, energy storage and fuel cells [1–6].

The ordered mesoporous carbon (OMC) materials are synthesized by nanocasting strategy using various inorganic template such as zeolites [7], alumina membranes [8], and mesoporous silica materials [9] among others. Usually it involves complicated multistep synthetic procedure, where the mesoporous silica material called the hard template, is impregnated with a suitable carbon precursor such as sucrose. After the carbonization of the composite material, the carbon replica is obtained by extracting the silica template [9].

For instance, SBA-15, mesoporous silica material synthesized using triblock copolymer Pluronic P123 and Tetraethyl orthosilicate (TEOS) is used as hard template and sucrose as carbon source in order to obtain the hexagonal ordered

mesoporous carbon CMK-3 [9]. Then, we have developed a novel method of direct synthesis of OMC materials.

Several works have been done efforts in order to obtain a direct synthesis of OMC. Liu et al. used a soluble resol polymer as an organic precursor; prehydrolyzed TEOS is used as an inorganic precursor, and triblock copolymer F127 is used as a template. With this kind of synthesis ordered mesoporous carbons were obtained with pore sizes of ≈ 6.7 nm and pore volumes of ≈ 2.0 cm³/g and high surface areas up to ≈ 2470 m²/g [10]. CMK-8 have been synthesized using Pluronic P123 as structure directing agent, sucrose as carbon precursor and *n*-butanol under acidic condition [11].

On the other hand, hydrogen is an environmentally friendly fuel and a substitute energy source for many uses. Some advantages to use hydrogen, as fuel is it is simple adsorption–desorption kinetics, lightweight and low cost. Nanostructured carbon are good candidates as hydrogen storage materials [9, 12].

In this work, we present a novel and direct synthesis of an ordered mesoporous carbon (OMC), which has been characterized and applied in hydrogen uptake and storage.

2 Materials and methods

2.1 Materials

Tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich), Poly(ethylene glycol)-block-poly(propylene

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glycol)-block-poly (ethylene glycol), (EO₂₀PO₇₀EO₂₀; P123-Sigma-Aldrich), Sucrose ($\geq 99.0\%$, FLUKA).

2.2 Synthesis of mesoporous carbon material

The novel mesoporous carbon was synthesized by self-assembly method, using copolymer P123 as the directing agent, Sucrose as carbon precursor and TEOS under acid conditions. Briefly, 4 g of triblock copolymer P123 and 1 g of sucrose were dissolved at 40 °C in an HCl solution (2 M). After 2 h, the silica precursor TEOS (9.2 ml) was added and kept under vigorous stirring for 15 min. The resulting mixture was transferred into Polypropylene bottle and kept at 100 °C for 24 h. The molar composition was 1 SiO₂:0.017:EO₂₀PO₇₀EO₂₀:7.7 HCl:212 H₂O:0.071 C₁₂H₂₂O₁₁. The solid was filtered and washed with deionized water until pH ~ 6. After complete drying (48 h at 50 °C), 1 g of the composite silica/P123/sucrose was added to a solution of 1 ml of H₂SO₄ (98 wt%) and 10 ml of deionized H₂O. The resulting mixture was stirred at ambient temperature for 18 h and then dried at 160 °C for 6 h. This dark brown powder was then heated to 900 °C under nitrogen flow (20 mL/min) in order to complete the carbonization of the sucrose. To remove the silica, the composite was treated with an HF solution (5 wt%) at room temperature. To ensure the complete removal of the silica this procedure was performed twice. The carbon without silica was filtered, washed with ethanol solution and dried at 50 °C.

The possible mechanism that takes place in synthesis of OMC obtained by procedure described above should be:

Bonds are formed between the hydrolyzed TEOS and the OH groups of sucrose (it is well known that TEOS or oligomer silicate species can react with the hydroxyl group). The interaction of C–Si would not be possible. When P123 micelles are molded, the structure begins to form by the composite TEOS/Sucrose around them. The bonds that join the organic/inorganic framework are weak. When performing the heat treatment at 900 °C in an inert atmosphere, the organic portion of the sucrose is carbonized, while the

template was volatilized and extracted through the N₂ current as temperature increase (around 450 °C). Then, the inorganic silica matrix is removed with HF leaving the mesoporous carbonaceous structure with micropores caused by the leaching of the inorganic Si–O framework.

2.3 Characterizations

X-ray diffraction analyses were obtained with a PANALYTICAL Phillips X'pert XDS diffractometer with a diffractometer beam monochromator and CuK α radiation source. N₂ adsorption/desorption isotherms at 77 K were measured on ASAP 2020 equipment after degassing the samples at 400 °C, determining textural properties such as surface area and pore volume. Pore size distribution was estimated using Barrett, Joyner, and Halenda algorithm. TEM micrographs were obtained on a JEOL model JEM-1200 EX II microscope. H₂ chemisorption was performed using a Micromeritics Chemisorb 2720, with a flow of 14 mL/min of 98% N₂/He.

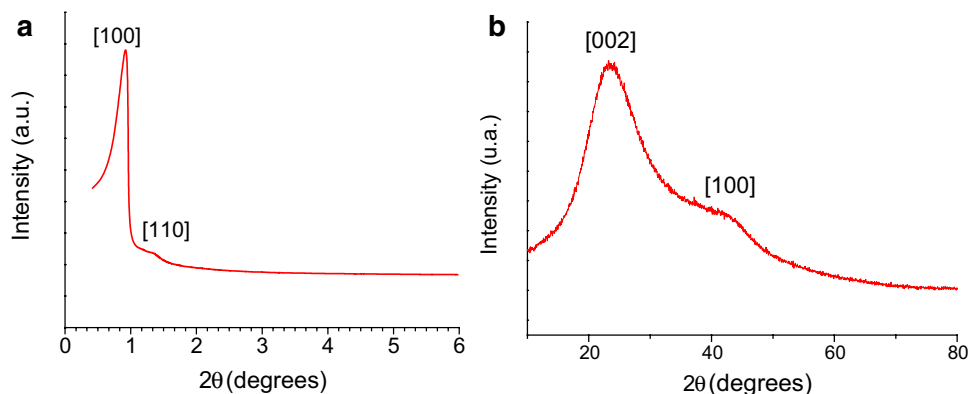
3 Results and discussion

3.1 XRD studies and textural properties

Low-angle XRD patterns of the novel OMC were recorded to determine the degree of structural order. Figure 1a shows the powder low X-ray diffraction pattern, which presents a very intense peak at $2\theta \approx 0.9^\circ$ that can be indexed as the (1 0 0) reflection and another peak $2\theta \approx 1.4^\circ$ that can be indexed as the (1 0 0) and (1 1 0) reflections respectively. Both reflections peaks can be associated with the p6mm hexagonal symmetry [13].

The wide-angle XRD pattern of the OMC synthesized in the Fig. 1b presents two broad diffraction peaks that can be indexed to (0 0 2) and (1 0 0) planes for typical graphite carbons [14].

Fig. 1 XRD patterns of OMC **a** Small-Angle and **b** Wide-Angle



The N₂ adsorption–desorption isotherms and pore size distribution for the novel OMC are shown in Fig. 2. Both curves are clearly type IV, with a clear desorption hysteresis loop, typical characteristic of mesoporous materials with a marked loop in the adsorption at an approximately relative pressure P/P_0 of 0.6. In addition, the sample show high specific surface area, pore volume and narrow mesopore and micropore size distribution. The BET surface area for the sample is 415 m²/g, the mesopore volume is 0.60 cm³/g and micropore volume is 0.12 cm³/g. Average mesopore and micropore diameter is 3.50 and 1.14 nm, respectively (Table 1).

3.2 TEM studies

TEM image (Fig. 3a) shows OMC particles consisting in curved rod-like particles formed by a mesochannels array

with quite uniform sizes of about (0.8 μm long and 0.18 μm wide). In Fig. 3b can be observed that nanochannels consisting of an alternating carbon rod array of about 8 nm forming a channel array close 3.5 nm diameter.

3.3 Hydrogen uptake measurements

Hydrogen adsorption was valued at different pressures and cryogenic temperature (77 K) (Fig. 4).

Freundlich isotherm [15] was selected to fit experimental data, which is a purely empirical formula for gaseous adsorbates. Nonlinear least-square regression for arbitrary fit functions was applied to fit the experimental data and Levenberg–Marquardt method to minimizing the objective function. The fitting accuracy was $R^2 = 0.97$.

The hydrogen storage is defined as “uptake,” because the carbon material behaves as a sponge, because the process

Fig. 2 Nitrogen adsorption–desorption isotherm at 77 K and pore size distribution of OMC

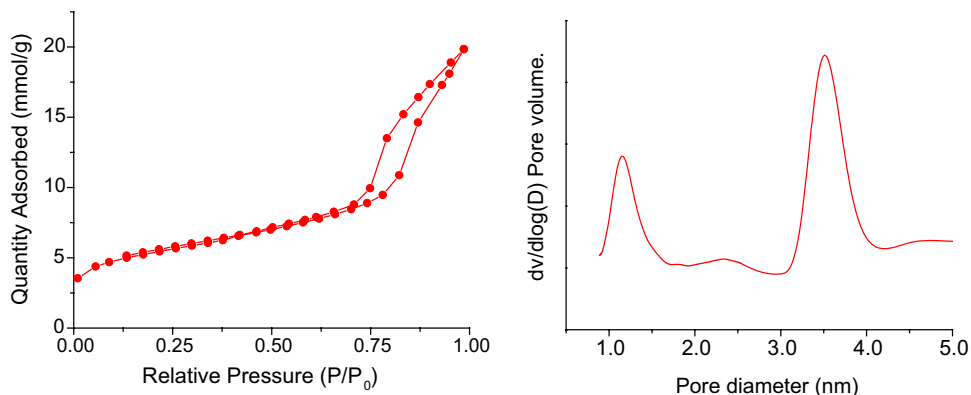


Table 1 Textural properties of the material

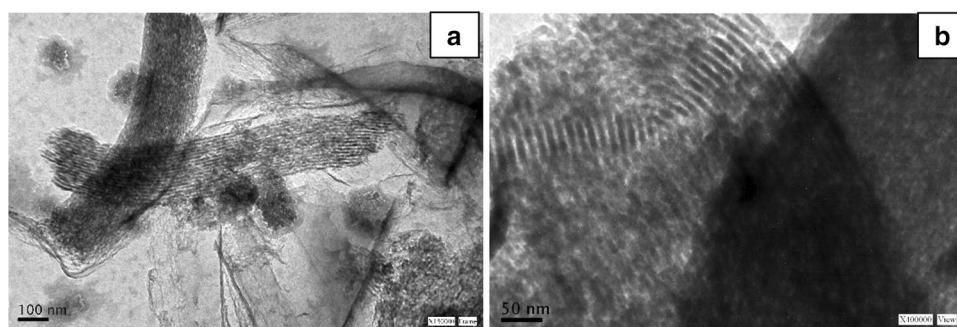
Material	S_{BET} (m ² g ⁻¹) ^a	Pore volume (cm ³ g ⁻¹) ^b		Pore diameter (nm) ^b		Hydrogen uptake (wt %) ^c
		$V_{\mu p}$	V_{TP}	Micropore	Mesopore	
OMC	415	0.12	0.60	1.14	3.50	3.78

^aDetermined by BET specific surface area ($\pm 2\%$)

^bCalculated by BJH method from the adsorption branch

^cH₂ sorption at 10 bars and 77 K

Fig. 3 TEM images of OMC produced by direct synthesis



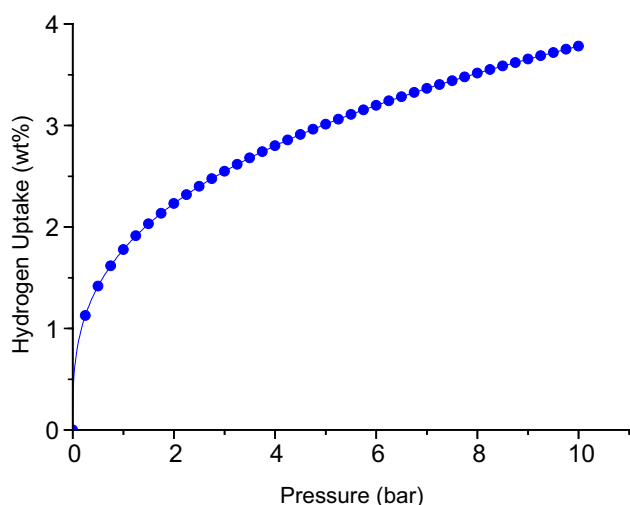


Fig. 4 Hydrogen adsorption–desorption isotherms of the novel OMC

is completely reversible and the curve remains in the same place as each point returned to baseline when measurements were carried out without the bath of liquid N_2 .

In commercial activated carbons and carbon fibers hydrogen storage measurements cannot be greater than 2.0 wt% according to a number of reports [16]. The hydrogen adsorbed on single-wall nanotubes at atmospheric pressure range approximately 0.01 wt% at 298 K and 1 wt% at 77 K [17], and H_2 sorption on carbon nanofibers activated is between 0.05 and 0.35 wt% [18]. CO_2 activation influence in ordered porous carbon CMK-3 was studied by Xia et al. [19]. The H_2 uptake in CMK-3 is around 1.2 wt% at 1 bar and on activated CMK-3 around 2% [19].

Hybrid materials and Composites designed by metal/carbon have been calculated at more than 3.0 wt% [20]. CMK-3 and Pt-CMK-3 synthesized by us using the nanocasting strategy reached 2.2 and 3.3 wt% at 77 K and 10 bar, respectively [9]. This OMC improve the hydrogen uptake at 10 bar (3.78 wt%).

In these nanostructured carbons, exist a microporosity in the walls. As carbon nanorods (walls) measure 8 nm wide, there is enough microporosity. The nanochannels help to give better access of the hydrogen to the micropores of the walls.

Carbon materials with large surface areas, like the OMC, consist of sheets of small hexagonal carbon rings, called “graphene sheets”. Orientation of the graphene sheets may also play an important role in the hydrogen uptake.

Since the graphene sheets offer defects, the size and orientation of the defective micrograph sheets could influence the adsorption process by altering the dispersion forces of London between the hydrogen molecules and the surface. The surface presents porosity in relation to the micrographene domains, particularly that of the defective layers. In this way, more favorable sites for H_2 adsorption, are

generated, although in general the interaction between the hydrogen molecule and the carbon surface is a van der Waals force [21].

In addition, micropores can provide carbon materials (CMK-3 for example), including the OMC material a greater van der Waals interaction with hydrogen molecules increasing their adsorption capacity [22].

Higher edge exposure on the carbon surface results in increased physical H_2 adsorption per square meter of surface area. The large surface area created by the mesoporous channels of OMC should be result in a high amount of hydrogen molecules can access the micropores that contain favorable sites to hydrogen sorption.

The nanochannels relate to the space between the carbon nanorods and the micropores could be attributed to small holes inside the carbon rods. The micropores origin is not also clear and has not been extensively studied [23].

4 Conclusions

A novel ordered mesoporous carbon was successfully synthesized, eliminating the multistep procedures. In the synthesis we used Pluronic P123, TEOS, H_2SO_4 and sucrose. The new material has high specific surface area, pore volume and narrow mesopore size distribution. The novel synthesis technique improved significantly the H_2 storage properties (3.78 wt%).

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