

# Nano-sized mesoporous carbon particles with bimodal pore system and semi-crystalline porous walls

M. Pérez-Cabero <sup>a,\*</sup>, F.R. García-García <sup>b</sup>, David Vie <sup>a</sup>, I. Rodríguez-Ramos <sup>b</sup>,  
Daniel Beltrán <sup>a</sup>, Pedro Amorós <sup>a,\*</sup>

<sup>a</sup> *Institut de Ciència dels Materials—Universitat de València (ICMUV) P.O. Box 22085, 46071, València, Spain*

<sup>b</sup> *Instituto de Catálisis y Petroleoquímica (CSIC), C/ Marie Curie 2, Cantoblanco, 28049 Madrid, Spain*

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## Abstract

Acetylene CVD carbon replication of a hierarchical pore silica-based material, Fe-UVM-7, is reported. The original template organization, which is based on the aggregation of mesoporous nanoparticles, is accurately replicated in the final carbon material: a bimodal porous carbon combining mesoporous nanoparticles and inter-particle textural-like pores which provide high surface area, a highly accessible pore system and semi-crystalline pore walls in the form of graphitic-like nanodomains is presented.

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## 1. Introduction

Over the last decade, increasing attention has been paid to the study of ordered mesoporous carbons (OMCs), due to their interesting chemical–physical properties and high surface areas. Given their good electrical conductivity, mesoporous carbon materials with high graphitization degree could find many applications in the field of electrochemistry, fuel cells, or biosensors [1,2]. However, it is well known the difficulty of synthesizing mesoporous carbon materials with high surface areas and good graphitic crystallinity, and only few references can be found in the literature, where high pressure or temperature (>1000 °C) conditions are required [3,4]. In some cases, a good selection of the carbon source (i.e. mesophase pitches), allows decreasing the graphitization temperatures [5].

The general OMCs preparation procedure follows the infiltration of a carbon precursor (sucrose, phenol resin, furfuryl alcohol) in the pores of the template (frequently ordered mesoporous silicas), the subsequent carbonization of the

precursor, and finally, the template removal by chemical etching. Usually, OMCs are prepared as micrometric particles, due to the micrometer size of the used silica templates (MCM-48, MCM-41, SBA-15) [6–8]. However, chemical vapour deposition (CVD) method seems to be a better approach than the liquid-phase impregnation method due to an easier control over the amount and quality of the pyrolytic carbon layer deposited in the template pores [1]. Despite this advantage, few references can be found in the literature in which CVD method has been applied to the synthesis of OMCs [9–11], but only using unimodal mesoporous silicas (SBA-15 or MCM-48) as templates. Any well-done replication method keeps the template microstructure and, in general, most of the claimed bimodal OMCs, regardless of the preparative strategy used, present an uncontrolled and accidental microstructure. Although the presence of covering faults in the carbon coating is necessary to allow the silica etching, leading to the final pure carbon material [12], the eventually induced porosity should be considered many times as procedural.

True bimodality has only been observed in materials generated from correct replication procedures of bimodal templates. Thus, bimodal mesoporous carbons have been described as precise replicas of hierarchical templates (bimodal mesoporous silica

\* Corresponding authors. Tel.: +34 96 354 3675; fax: +34 96 354 3633.

E-mail addresses: [Monica.Perez@uv.es](mailto:Monica.Perez@uv.es) (M. Pérez-Cabero),

[Pedro.Amoros@uv.es](mailto:Pedro.Amoros@uv.es) (P. Amorós).

Table 1  
Synthesis conditions for the mesoporous carbon samples and inorganic residue obtained after purification treatments

Sample	Template	Reaction time (h)	C-uptake (wt.%/h)	Inorganic residue (wt.%)
A	UVM-7	2	20	0
B	Fe (2.1%)-UVM-7	1	50	1
C	Fe (2.1%)-UVM-7	2	50	16
D	Fe (4.6%)-UVM-7	2	60	30

[13,14] or mixtures of mesoporous and colloidal silica particles [15,16]). However, their relative low surface area and, specially, their amorphous character, limit their potential applications.

In this paper we present the synthesis of the first nano-sized mesoporous carbon particles (denoted as C-UVM-7), with bimodal pore system and semi-crystalline character, as faithful replicas of bimodal UVM-7 nanometric silica particles, prepared by CVD of acetylene on the template. UVM-7 silicas [17] can be considered as a nanometric version of the well known MCM-41 materials, and the most outstanding feature concerning these materials is their peculiar architecture: a continuous network constructed from aggregated small mesoporous nanoparticles that generates a non-ordered system of large pores (between large-meso and macro). In the case of the UVM-7 pure silicas, the standard dimension of the nanoparticles is very small (12–17 nm); they are slightly larger (30–70 nm) in the case of doped M-UVM-7 materials.

It is well known that iron is an effective catalyst for graphene layer growth [5], then desired graphitization process is expected to be favored on Fe-containing UVM-7 silica. UVM-7

derivatives are synthesized through the Atrane method, a reproducible one-pot surfactant-assisted procedure based on the use of atrane complexes (containing triethanolamine species as ligands) as hydrolytic inorganic precursors [18]. This strategy overcomes any problem associated with reactivity differences of heteroelements, and then is adequate for the Fe incorporation inside the silica network. The use of a silica template containing well dispersed transition metal is a priori, an adequate method to provide a good quality surface covering of the surface through graphene and/or carbon nanostructures formation.

## 2. Experimental

For these experiments, Fe-UVM-7 templates were prepared by simply adding variable amounts of the respective Fe–atrane complex to the silatrane containing solution following the general procedure for M-UVM-7 [17]. Iron contents in the calcined materials (2.1 and 4.6 wt.% respectively) were analyzed through ICP (Perkin-Elmer Mod. 3300 DV). All samples maintained typical UVM-7 features, as it was confirmed by XRD, TEM and porosimetry (SBET=1000 m<sup>2</sup>/g and bimodal pore system: 3 and 25 nm mesopores).

Mesoporous carbons were prepared by CVD of acetylene in a thermobalance (C.I. Electronic) at 700 °C, following the general procedure already described for the catalytic synthesis of carbon nanotubes [19]. The carbon deposition depends on parameters as Fe-content, reaction time and nature of the precursor gas. The resulting as-synthesized carbonaceous samples were submitted to purification in NaOH solution (pH>12), to completely remove the inorganic silica template. All purified carbonaceous samples were characterized by thermogravimetric analysis (TGA) under oxygen atmosphere in a Setaram Setsys 16/18, transmission electron microscopy

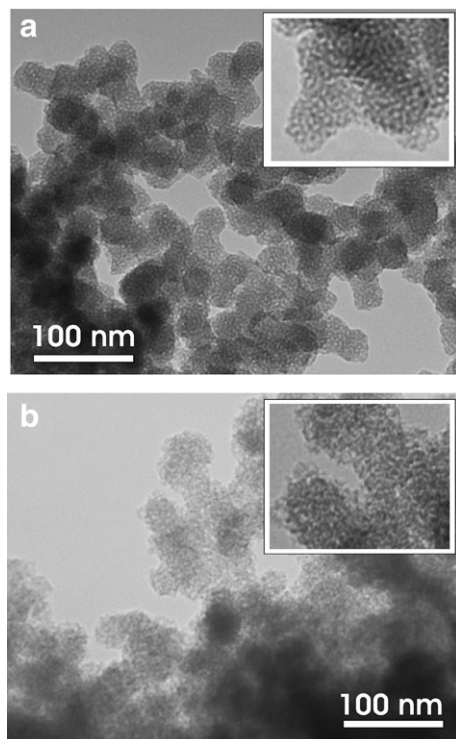


Fig. 1. TEM images of (a) Fe-UVM-7 and (b) C-UVM-7. The insets show enlarged ( $\times 2$ ) images.

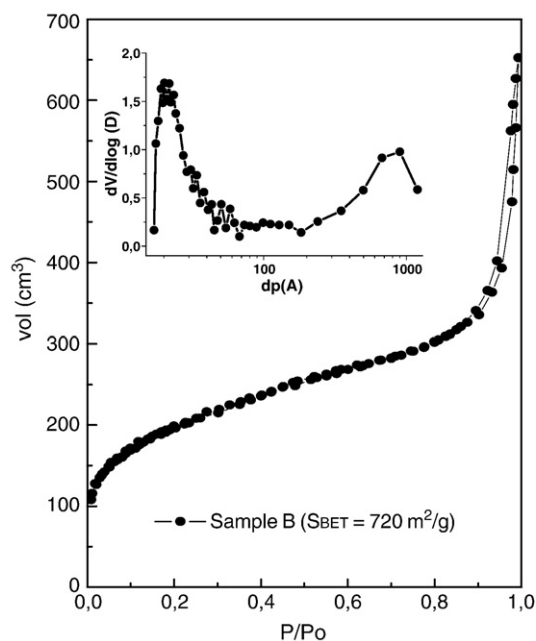


Fig. 2. N<sub>2</sub> adsorption–desorption isotherm and BJH pore distribution (inset) of sample B.

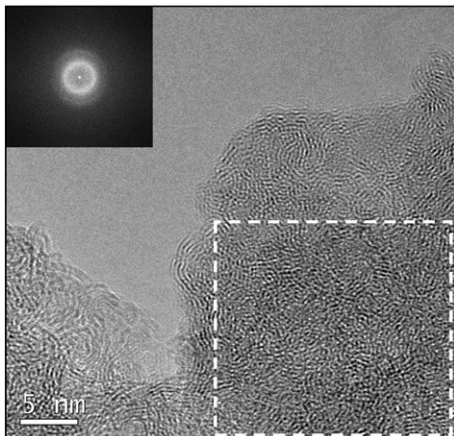


Fig. 3. HRTEM image of sample B.

(TEM and HRTEM) in a JEOL JEM-1010 at 100 kV and in a high resolution TEM Tecnai G<sup>2</sup> at 200 kV and N<sub>2</sub> adsorption–desorption isotherms (Micromeritics ASAP-2010).

### 3. Results and discussion

The absence of Fe in the inorganic template (sample A) led to lower carbon deposits at 700 °C (Table 1), which quickly increased with the template Fe content and/or the reaction time (samples B, C, D). Their general combustion behavior proceeded through two exothermal steps, at temperatures around 410 °C and 470 °C, which indicates heterogeneity in the nature of the carbonaceous material, either structural or textural (Appendix A: Fig. S1). Nevertheless, the presence of growing amounts of inorganic residue after the samples combustion indicates a hindered etching process. The replication quality of UVM-7 depends on the formation of a homogeneous and thick enough carbon coating, but it can eventually be so thick and complete that prevents the complete silica etching.

The conditions leading to sample B seemed to be adequate to achieve a reasonable carbon replica of the template and we have selected this sample for presenting further characterization in this work. By TEM images comparison (Fig. 1) it is revealed a clear microstructural relationship between the iron–silica template and its carbonaceous replica. Thus, Fig. 2(b) shows that sample B is made up of porous carbon nanoparticles (ca. 40–60 nm) which keep the interparticle porous texture characteristic of the template. Similar hierarchical porous carbons have been recently described starting from MSU-1 silicas as templates [20, note added in proof].

The mesoscopic order however, seems to diminish, as it is also evidenced by a peak significant intensity reduction in the low-angle XRD domain (Appendix A: Fig. S2). Despite this loss of order, the high BET surface area (720 m<sup>2</sup>/g) and highly accessible hierarchical pore systems, characteristic of the UVM-7 template, are clearly retained. C-UVM-7 bimodality is further illustrated by the N<sub>2</sub> adsorption–desorption isotherms (Fig. 2). As it occurs for UVM-7 silicas, the curve shows two adsorption steps (at intermediate and high  $P/P_0$  values) related to the nitrogen condensation inside the intrananostructure mesopores and the inter-particle macropores (ca. 100 nm), respectively. The smooth curvature of the first step supports the existence of a broad distribution of intra-particle mesopore sizes, which is also confirmed by the wide BJH pore distribution (with pore sizes centered around 2–3 nm in diameter) (Fig. 2, inset). These data are in good accordance with low-angle XRD and TEM images above commented.

HRTEM on a single carbon nanoparticle (Fig. 3) reveals more details about its nature in the sample: it is built-up by turbostratic, onion-skin and worm-like spiral graphitized nano-layers, a microstructure distribution also observed in carbon nanofibers growth on Fe<sub>2</sub>O<sub>3</sub> nanoparticle doped mesoporous silica [5]. The corresponding Fast Fourier Transform (FFT) process of an image area selection is characteristic of a powder polycrystalline material (Fig. 3, inset) and confirms the nanoparticle graphitized structure, with interlayer distances around 0.34–0.38 nm.

Moreover, broad peaks centered around 26 and 43° in  $2\theta$  are observed in the wide-angle XRD patterns (Appendix A: Fig. S3), which indicate the presence of pseudo-graphitized carbon. Then, HRTEM supports that pseudo-graphite domains are the building-blocks conforming the porous walls and that the growth catalyzed by iron nanoparticles on the template pore walls does not have any preferential direction related with the pore axis. Otherwise, the notably high surface area (720 m<sup>2</sup>/g) of C-UVM-7 materials, when compared with other graphitic carbons (ca. 300 m<sup>2</sup>/g), is probably related to a good dispersion of the catalysts on the template walls preserving in high degree the original surface area.

### 4. Conclusions

In short, acetylene CVD carbon replication of a hierarchical pore silica-based material, Fe-UVM-7, allows to synthesize, as far as we know, the first semi-crystalline nano-sized bimodal porous carbon particles. This C-UVM-7 material combines a high surface area together with a highly accessible pore system and semi-crystalline pore walls in the form of graphitic-like nanodomains. The template organization, based on the aggregation of mesoporous nanoparticles, is accurately replicated in the final carbon material: a bimodal porous carbon combining mesoporous nanoparticles and inter-particle textural-like pores. The spongy character of C-UVM-7 results in an enhanced accessibility to their pore voids, what confers them interest to be proved as catalysts or catalysts support. Moreover the semi-crystalline nanoscale organization may confer to C-UVM-7 interesting electronic properties.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2008.01.079.

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