



Aqueous synthesis of bimodal mesoporous carbons and carbon-silica mesostructures under basic conditions



Felipe Rodríguez ^{a, b, *}, Mietek Jaroniec ^b, Betty L. López ^a, Nilantha P. Wickramaratne ^b

^a Grupo Ciencia de los Materiales, Universidad de Antioquia, Calle 62 52 59, Medellín, Antioquia, Colombia

^b Department of Chemistry and Biochemistry, Kent State University, Kent, OH 44242, USA

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ABSTRACT

Carbonization of the composite materials obtained by co-condensation of phenol-formaldehyde resin and tetraethyl orthosilicate (TEOS) in a basic aqueous solution in the presence of Pluronic F127 block copolymer template yields mesoporous carbon/silica composite materials (CSX). These materials have mesopore volumes of about 0.4 cm³/g and pore sizes between 6 and 8 nm (at the maximum of the pore size distribution) that are larger than those of the ordered mesoporous carbons (OMC) synthesized by the same procedure but without TEOS. Calcination of CSX in air yields mesoporous silicas (SX) with pore sizes around 11 nm and pore volumes of about 1 cm³/g. Dissolution of the silica domains in CSX yields carbons (CX) with pore volumes and surface areas as high as 1.84 cm³/g and 1500 m²/g, respectively. These carbons feature bimodal structures with larger mesopores of about 7–8 nm (porosity of CSX) and smaller mesopores with sizes closer to 5 nm, which are created by silica dissolution. The mesopore volume of CX after silica dissolution can be tuned by varying carbonization temperature (between 500 and 850 °C) to modify the concentration of silica nanodomains in CSX without significant change in the size of mesopores in CSX. Regardless of the phenol/TEOS ratio used (between 2 and 7) all the materials have similar composition, pore size distribution and pore volumes; however, the synthesis yield decreases with decreasing amount of TEOS. The final SiO₂ content in CSX does not increase with the amount of TEOS added like in the synthesis of OMC by evaporation induced self-assembly or self-assembly in acidic solutions.

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1. Introduction

There is a great interest in the development of ordered mesostructures since discovery of the surfactant-templated synthesis of ordered mesoporous silicas. This discovery showed that the self-assembly of surfactants and inorganic and/or organic species is a powerful strategy for the synthesis of mesostructured composites, which after removal (calcination or extraction) of the surfactant templates can be transformed into materials with ordered porosity.

Among nanostructured materials, mesoporous carbons have attracted a lot of attention in many fields such as electrochemistry, energy storage, separation and chromatography, mainly due to some of their properties like high thermal and chemical stabilities. Ordered mesoporous carbon (OMC) materials with various types of

mesostructures have been successfully synthesized using phenolic resins as carbon precursors and Pluronic block copolymers as soft templates by evaporation induced self-assembly (EISA) [1–4] or by conventional self-assembly, which are carried out in a solution without the need to evaporate solvents [5–8].

Among synthesis routes, which do not involve evaporation of solvents, the method proposed by Liang and Dai [5] is widely used [8–11]. In this synthesis phloroglucinol (or resorcinol) and formaldehyde polymerize in an acidic ethanol-water solution containing Pluronic block copolymer (structure-directing agent), which results in the formation of two separate phases, polymeric and aqueous ones. The polymer-rich phase is subjected to the removal of polymeric template by thermal treatment or extraction, yielding mesoporous phenolic resin, which after further heating in inert atmosphere can be converted to mesoporous carbon with monolithic, fiber- or film-type morphology.

In the aqueous-phase synthesis developed by Zhao's group [6] a resol obtained by base-catalyzed polymerization of phenol and formaldehyde in an aqueous solution at pH between 8.5 and 9 and

* Corresponding author. Grupo Ciencia de los Materiales, Universidad de Antioquia, Calle 62 52 59, Medellín, Antioquia, Colombia. Tel.: +57 (4) 2505234.

E-mail address: frxyz@gmail.com (F. Rodríguez).

triblock copolymer aqueous solution are mixed. Self-assembly, formation and solidification of the mesostructure in this basic aqueous solution, followed by template removal, gives a mesoporous carbon. This procedure, depending on the experimental conditions, can be used to synthesize particles with sizes ranging from micrometers to millimeters [12–14], monoliths with hierarchical porosity [15] or nanosized particles [16]. However in all these materials the size and volume of the mesopores generated by block copolymers are relatively small as compared to other OMC materials.

Based on the HRSEM, STEM, cryo-SEM imaging, involving slicing of single crystals of FDU-16 OMC, Zhao and his coworkers [14] proposed that the resol precursors interact with poly(ethylene oxide) segments of the amphiphilic triblock copolymer Pluronic F127 through hydrogen bonds, which results in the formation of spherical composite micelles that after further cross-linking connect with each other through carbon–carbon bonds to form micelle aggregates; the latter act as nuclei for the single-crystal growth. Then, more micelles are transferred to the nuclei surface to form via layer-by-layer mechanism a body-centered cubic F127/resol composite single crystal. The FDU-16 particles can reach the final size (2–4 μm) after 2 days, but during thermal treatment the order of porous structure increases through some rearrangement of these micelles within particles [14].

Beside formation of the micellar block copolymer mesophase the synthesis process of mesoporous materials may involve the displacement of solvent molecules in hydrophilic domains of the micelles by the material precursors. This process can take place due to strong interactions between hydrophilic segments of block copolymer and the material precursors. In many cases the self-assembly of the composite material is induced by gradual condensation/polymerization of the material precursors followed by additional cross linking that increases the stability of the formed mesostructure.

The formation mechanism of the OMC in basic aqueous solutions is similar to that proposed for the aqueous synthesis of ordered mesoporous silicas using tetraethyl orthosilicate (TEOS) as silica source and Pluronic P123 or F127 block copolymer as a soft template in acidic aqueous phase [17]. First, the composite SiO_2 /surfactant micelles are stable, but the zeta potential of the particles decreases during polymerization of siliceous species. When this colloidal system becomes unstable the composite micelles aggregate into micron-sized particles. These particles can be deformed under pressure after phase separation, but the formation of siloxane bonds increase the stability of the structure and finally transform the particles into a solid material. During thermal treatment there is a further rearrangement of the structure that increases the mesostructural order of the resulting silica [17].

Considering all this, it is possible that in the synthesis of OMC in aqueous basic solution the colloidal system might become unstable due to the polymerization of resol, which can make the phenolic resin more hydrophobic. The small pore size and volume of these OMC might be related to the larger contraction of the structure during carbonization process.

Zhao and coworkers [18] performed also the self-assembly synthesis of OMC in acid media by EISA using phenol/formaldehyde resol (carbon precursor), Pluronic block copolymer (soft template) and TEOS; the latter was used as the reinforcing agent to incorporate a rigid silica framework into carbon mesostructure to reduce its contraction during carbonization and preserve larger pore size and volume. After removal of silica from the carbon/silica composite there is an increase in the pore volume of the resulting OMC. Some of carbon samples showed bimodal pore size distributions because the dissolution of silica domains in the walls of mesoporous carbons generates pores with sizes of about 2.5 nm. It

is also possible to get ordered mesoporous silicas by calcination in air of the composite materials if the silica content is high enough [18].

TEOS has also been used in other synthesis procedures of OMC. In the synthesis involving polymerization of resorcinol and formaldehyde in the presence of Pluronic triblock copolymer and TEOS under acidic conditions [19], the size of mesopores of the composite material increases with increasing TEOS content (up to 60%). After silica dissolution there is an increase in the pore volume. When the TEOS content is higher than 50% there is also a considerable increase in the pore size between 1 and 4 nm. In these composite materials TEOS is converted to very small silica domains uniformly embedded in the carbon framework that turn into micropores and small mesopores after silica dissolution. It is also possible to get mesoporous silicas by calcination in air of the composite materials when the silica content is high enough [19].

The characteristics of the materials prepared by EISA and by self-assembly in acidic solution show that phenolic resin and TEOS can form a hybrid framework with small (less than 4 nm) silica domains. According to these synthesis routes it is possible to obtain mesoporous carbon or mesoporous silica from the same composite material; which suggests that the SiO_2 and phenolic resin domains in the hybrid framework are bicontinuous as it is proposed in Ref. [18]. The SiO_2 domains might be a network of silica particles (formed during synthesis) occluded within phenolic resin/block copolymer framework (the composite material) or a nanostructure formed as a result of the phase separation of phenolic resin and silica blend inside hydrophilic domains of the block copolymer micelles.

Morphological investigations of the hybrid materials composed of phenolic resin and silica (prepared by in situ hydrolysis and condensation of tetramethoxy orthosilicate) (TMOS) via casting method [20] show that the silica-rich domains (having sizes in micrometers or nanometers) are made of smaller irregularly shaped silica particles (having sizes below 5 nm; most likely the primary particles formed during the early stage of the sol–gel process) or aggregates of these primary particles homogeneously dispersed in the hybrid in the form of a partially or fully continuous siliceous network. As the phase separation progresses the transparency of the sample decreases gradually as the average size of the silica aggregates increases.

The phase separation is induced by an increase in the molecular weight of the siliceous species in the hybrid system. An early immobilization of the system by reducing its mobility (due to the solvent evaporation or formation of a silica network) can stop the phase separation in an early stage, where there is a homogeneous dispersion of small (less than 5 nm) particles of silica. If the reduction in the mobility of the system is slow the size of silica aggregates (they interact well with phenolic resin species) increases (in some opaque samples the aggregates seem to be spherical particles with sizes in the micrometer range); however, they are still composed of smaller (below 5 nm) silica particles and larger phenolic resin domains surrounding them. The phenolic resin-rich regions surrounding silica aggregates do not seem to have any SiO_2 [20].

The preparation of OMC by EISA is somewhat similar to the solvent casting used to prepare the TMOS/phenolic resin composite materials, which suggest that in both types of the TEOS-assisted synthesis of OMC [18,19] the small (less than 5 nm) silica domains can be formed because of the phase separation within the hydrophilic domains of the block copolymer mesophase.

The use of phase separation to produce porous materials has been extensively explored in different systems, including synthesis of hierarchical (meso/macro) porous carbons by soft templating [21]. Considering that TEOS and phenolic resins co-assemble well, it

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