

# TEN YEARS OF RESEARCH ON ORDERED MESOPOROUS CARBONS: MAJOR ADVANCES IN SYNTHESIS, PROPERTIES AND POTENTIAL APPLICATIONS

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About ten years ago Ryoo and co-workers [1,2] reported the hard-templating (HT) synthesis of ordered mesoporous carbons (OMCs) by using ordered mesoporous silicas (OMSs) as hard templates. Five years afterward the soft-templating (ST) synthesis of OMCs has been discovered [3-6]. Significant progress has been made in both hard- and soft-templating synthesis of OMCs [7-10]. Major advances in the synthesis of these fascinating materials, their properties and potential applications are briefly presented. The current efforts are focused on the development of carbons with hierarchical porous structures as well as carbon-based hybrid materials with incorporated inorganic and organic species for adsorption, catalytic, environmental and energy-related applications.

The HT synthesis (see Fig. 1) includes infiltration of pores of a hard template (usually OMS or colloidal silica) with carbon precursors (e.g., sucrose, polymers) followed by carbonization and template removal with HF or NaOH solutions [2,11-13]. Depending on the template used the resulting inverse carbon replicas possess disordered or ordered porosity. OMCs are obtained by using OMSs or colloidal silica crystals as hard templates. The use of colloidal silica in the HT synthesis affords disordered carbons with uniform spherical mesopores.

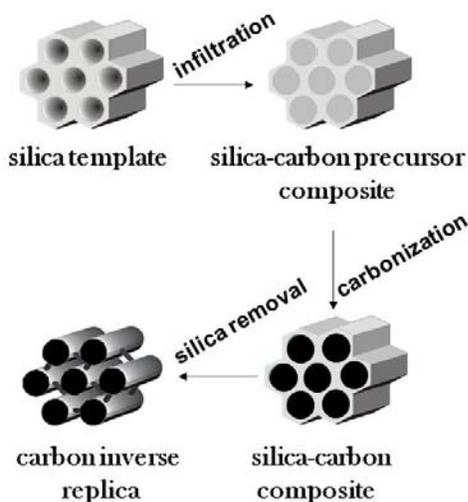


Fig. 1. Illustration of hard-templating synthesis of OMCs.

In contrast to HT, the ST synthesis involves ordered mesophases of block copolymers such as poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) triblock

copolymers (PEO-PPO-PEO) as soft templates [5,6]. A typical ST synthesis (see Fig. 2) includes polymerization of formaldehyde and phenol (or its derivatives such as resorcinol and phloroglucinol) in hydrophilic domains of PEO-PPO-PEO (soft template) giving a polymeric nanocomposite, which can be converted to ordered mesoporous phenolic resin and OMC by controlled thermal treatment in neutral atmosphere. Depending on the soft template and the synthesis conditions used, different OMC structures can be obtained.

Both HT and ST routes provide carbons with ordered and uniform mesopores, while some important applications such as gas storage, removal of pollutants of different sizes, heterogeneous catalysis, energy storage and conversion, require carbons with hierarchical structures that contain micropores, mesopores and even macropores. Therefore, the development of hierarchically porous carbons is currently an important issue.

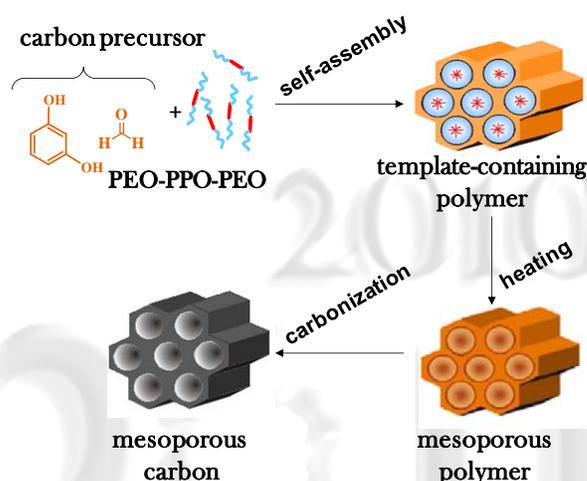
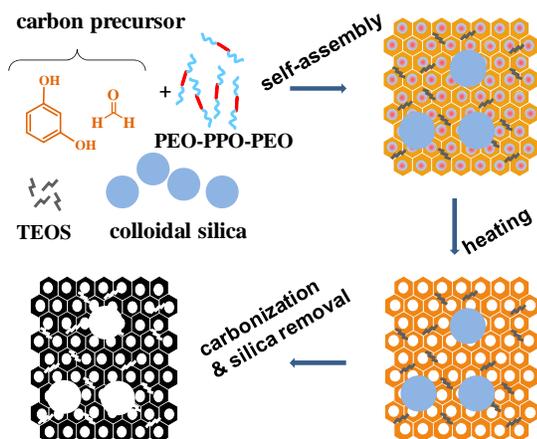


Fig. 2. Illustration of soft-templating synthesis of OMCs.

An effective way of creating hierarchically porous carbons is to carry out the ST synthesis in the presence of tetraethyl orthosilicate (TEOS) and/or colloidal silica followed by dissolution of TEOS-generated silica and/or colloidal silica. It was shown elsewhere [14] that the silica-rich mesoporous carbons with a uniform distribution of silica can be obtained by soft templating synthesis in the presence of TEOS. Removal of silica from these silica-carbon nanocomposites afforded high surface area carbons, which besides soft-templated ordered mesopores contain substantial amount of fine pores created by removal of the TEOS-generated silica [14]. Also, bimodal mesoporous carbons were prepared by soft-templating in the presence of significant amount of colloidal silica [15]. A combination of the ST synthesis in the presence of TEOS with colloidal (hard) templating, as shown in Fig. 3, resulted in truly hierarchical carbon structures that in addition to the aforementioned fine pores (created by dissolution of the TEOS-generated silica) and primary mesopores (formed during ST self-assembly) contain extra large spherical mesopores or macropores obtained by dissolution of the colloidal silica used [16]. Thus, the resulting hierarchical structures possessed at least three types of pores, the fraction of which can be tuned by

varying the amount of TEOS and colloidal silica used. Also, the size of spherical pores can be easily tailored by using silica colloids of different diameters.



**Fig. 3.** Illustration of the soft-templating synthesis of hierarchical porous carbons in the presence of TEOS and colloidal silica. In this one-pot synthesis a mixture of resorcinol and formaldehyde (carbon precursors) polymerize in the ordered mesodomains of block copolymer (soft template) giving self-assembled polymer-silica composite, which during thermal treatment is converted to phenolic resin-silica composite, and its subsequent carbonization and silica dissolution gives hierarchical porous carbon. This scheme was made on the basis of illustrations shown in [16].

The recent work [16] shows that a combination of the soft templating and hard templating strategies creates new opportunities for the development of hierarchical porous carbons with high surface area, large pore volume and tunable pore size distribution. Note that a further enlargement of the surface area and microporosity of these hierarchical carbons can be achieved without significant alteration of their mesoporous structure by post-synthesis activation either with KOH [17], carbon dioxide and water vapor [18]. In addition, their surface properties can be tailored by performing synthesis in the presence of suitable organosilanes, which can act as the source of dopants and as the pore-generating agents [19]. The latter study shows a great potential of the organosilane-assisted synthesis for the development of hierarchically porous carbon structures with high surface area, large pore volume and desired surface and framework properties.

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