

ORDERED NANOPOROUS CARBON STRUCTURES SYNTHESIZED USING LARGE-PORE MESOPOROUS SILICA TEMPLATES

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Introduction

Poly(alkylene oxide)-type block copolymers have been recently shown to be particularly versatile as structure-directing agents for the preparation of ordered large-pore mesoporous silica materials. In principle, the structure direction is achieved through the formation of periodic supramolecular self-assemblies between the polymeric surfactants and a silica source in the aqueous solution. The organic polymers in the periodic nanocomposite materials are easily removed by calcination in air or extraction with solvents, to produce large-pore mesoporous silicas. Exceptional control of the phase behavior has been achieved using the triblock copolymers with butanol at low acid concentrations. This allows the phase control with various structures such as two-dimensional hexagonal (2D-hex) $p6mm$ (honeycomb-like structure, known as SBA-15), cubic $Im3m$ (*bcc* packing of spherical nanopores), cubic $Fm3m$ (*fcc* packing of nanopores) and cubic $Ia3d$ (gyroid structure with bicontinuous mesoporosity) [1-4]. The pore topology and pore connectivity can be tailored as a function of the copolymer concentration, synthesis temperature, or volume fraction of the different copolymer blocks. The pore diameters are tunable, typically, in the range of 5 – 15 nm. Extensive researches on such structural and textural control have been recently reported, aiming at the design of functional nanoporous solids with various structures. Most notably, such mesoporous silicas turned out to be versatile templates for the synthesis of carbon materials with highly ordered nanoporous architectures.

In the present work, ordered mesoporous carbons with various structures have been obtained via the template-directed synthesis route using large-pore mesoporous silicas. The various nanoporous structures of the carbons correspond to the faithful replication of the silica templates. Here, we present our recent progresses related to the synthesis and characterization of ordered mesoporous carbons using the large-pore ordered mesoporous silicas as templates.

Experimental

The preparation of large-pore mesoporous silicas was accomplished with two poly(alkylene oxide)-type triblock copolymers, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, BASF) and $EO_{106}PO_{70}EO_{106}$ (Pluronic F127, BASF), as the structure-directing agent and tetraethyl orthosilicate as the silica source under low concentration of HCl condition.

Butanol was added as a co-surfactant. The formation of mesoporous silicas took place at a temperature in the range of 308 - 318 K. The products were hydrothermally aged at 373 K. The details of the synthesis conditions were selected for each desired material with different pore structure, pore size and connectivity, as reported elsewhere [1-4]. The synthesis of the nanoporous carbons was carried out using the large-pore mesoporous silicas as the templates. Sucrose, furfuryl alcohol, or acenaphthene was used as the carbon precursor [5-8]. The carbon precursors were impregnated or adsorbed inside the pores of mesoporous silicas or aluminosilicates. Subsequent pyrolysis converted the carbon precursors into rigid carbon structures. The mesoporous silica templates were then removed using ethanol-water solution of HF or NaOH.

Results and Discussion

Figure 1 shows the powder X-ray diffraction (XRD) patterns for the large-pore mesoporous silica templates synthesized using $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ and $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, their carbon replicas and 3D structural modeling of the carbons. The structural symmetry of the mesoporous materials was analyzed using transmission electron microscopy (TEM) in addition to the XRD investigation. The result from XRD patterns of the mesoporous silicas in low-angle area shows several distinct Bragg diffraction lines below $2\theta = 2^\circ$, which indicates that large-pore ordered mesoporous silicas were successfully synthesized using the poly(alkylene oxide)-type triblock copolymers. The mesoporous silicas are characterized with structures belonging to the 2D-hex $p6mm$, cubic $Im3m$, cubic $Fm3m$ and cubic $Ia3d$ space group with the lattice parameters, 9.50, 17.1, 19.0 and 22.9 nm, respectively. The structures of carbons are assigned to the same symmetries of the silica template with the lattice parameters, 8.55, 15.3, 17.1 and 20.6 nm, respectively. Thus, the XRD patterns show no apparent differences between silica templates and carbon replicas, except for the intensity change and lattice contraction. Such a lattice contraction occurs typically during the high-temperature pyrolysis process.

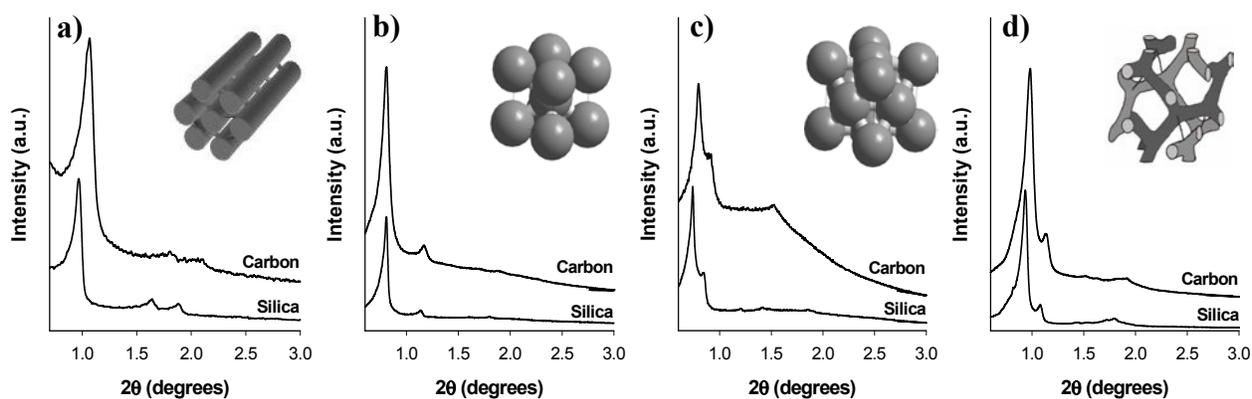


Figure 1. XRD patterns of large pore mesoporous silicas and their carbon replicas, and 3D structural models: a) 2D hexagonal $p6mm$, b) cubic $Im3m$, c) cubic $Fm3m$, and d) bicontinuous cubic $Ia3d$ structures.

The faithful replication of the silica structures allows us to construct the structure models for carbon shown in Figure 1, based on the known structure of the mesoporous silica template. From the structure models, it is reasonable that a 3D connectivity between adjacent pores in silica is necessary for the symmetry retention during the replication process [9].

We have analyzed pore structure of the carbon products using nitrogen adsorption isotherms. Figure 2 shows the adsorption-desorption isotherms for the 2D-hex mesoporous carbon. The BJH analysis of the N_2 adsorption data indicates that the carbon has uniform nanopores around 3.5 nm in diameter. The BET surface area of this carbon is $1300 \text{ m}^2\text{g}^{-1}$, and the mesopore volume is $1.2 \text{ cm}^3\text{g}^{-1}$. The same analysis for other carbon products indicates that mesoporous carbons synthesized with the large-pore mesoporous silicas have very large specific surface areas ranging from 1000 to $2300 \text{ m}^2\text{g}^{-1}$ and large-pore volumes 1.0 to $2.0 \text{ cm}^3\text{g}^{-1}$, with a narrow distribution of mesopore diameters centered in the range of 3 to 5 nm. A

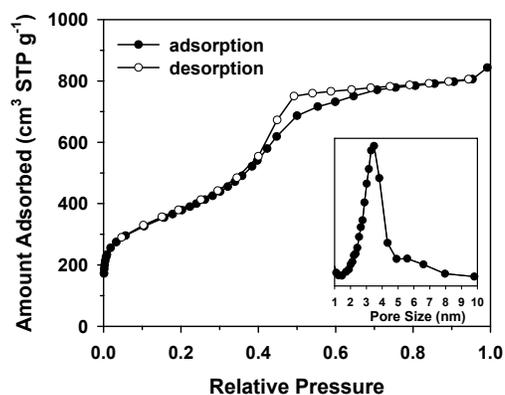


Figure 2. N_2 isotherm and BJH pore size distribution of 2D hexagonal mesoporous carbon

recent study on ordered mesoporous carbons showed that the pore diameters could be changed with mesoporous silica materials with different pore-wall thickness [10].

The ordered nature of mesoporous structures, with uniform pores, controllable pore diameters, high specific surface areas and large pore volumes, imparts the mesoporous carbons with a unique opportunity for the application as a standard or reference material in the studies of adsorption, catalysis and other numerous fundamental properties of mesoporous and microporous carbons. Owing to the recent development of the electron single crystallography for mesostructured materials [11], it is now possible to determine the pore structures absolutely at least for 3-D ordered CMK-*n* carbons. The pore shapes and diameters, solved by the electron crystallography, can be compared with the pore structural data obtained from other analysis techniques such as the BJH method, density functional theory and Kelvin equation. Even without the rigorous structural analysis, the presence of well-defined Bragg XRD lines of the CMK-*n* carbons offers many advantages for characterization. The XRD lines can be used for identification of the structures. The XRD lines increase in intensity with the addition of guest species inside mesopores, which can be used to monitor the adsorption. As seen in the case of the synthesis of polymer composite materials, the XRD intensity can also increase depending on the location of the guest species. Thus, the presence of the distinct XRD patterns in mesoporous carbons provides new opportunities for precisely monitoring various physico-chemical phenomena that take place inside the well-defined carbon pores or at the pore walls such as adsorption, impregnation, framework changes, formation of metal clusters and grafted functional groups. Accompanying with the opportunities for fundamental studies, the mesoporous carbon materials promise to be a suitable alternate for adsorbents, catalyst supports, energy storage media, and materials for advanced electronic applications.

Conclusions

In this study, large-pore mesoporous silica materials with various pore structures were successfully synthesized using the poly(alkylene oxide)-type triblock copolymers as the structure-directing agent. The large-pore mesoporous silicas were faithfully replicated to highly ordered nanoporous carbon materials through the 'nano-templating' route. The ordered mesoporous carbons thus obtained are characterized with uniform pore structures with 3D pore connectivity, controllable pore diameters, high specific surface areas and large pore volumes. The carbon materials provide new opportunities as a standard material for pore size analyses, in addition to their applicability as new adsorbents, catalysts and electrode materials.

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