

Synthesis of ordered mesoporous carbon monoliths with bicontinuous cubic pore structure of *Ia3d* symmetry†

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Received (in Cambridge, UK) 23rd September 2002, Accepted 15th October 2002

First published as an Advance Article on the web 28th October 2002

Large-diameter-sized mesoporous carbon monoliths with bicontinuous cubic structure of *Ia3d* symmetry have been synthesized by using mesoporous silica monoliths as hard templates; such carbon monoliths show potential application of advanced electrodes and electrochemical double layer capacitors.

Ordered non-siliceous mesostructured materials are of great interest because of their diversities in composites that lead to potential applications in catalysis, optics, electronics, magnetics and so on.^{1–3} Since the first report of non-siliceous mesostructure in 1994,⁴ four strategies, including surfactant (ligand)/inorganic self-assembly, true liquid crystal templating, nanocasting and nanocrystal templating, have been established for synthesizing these kinds of materials based on their chemical compositions and properties.⁵ Among all these strategies, nanocasting by using three-dimensional (3D) structured mesoporous silica as a hard template has attracted much attention, and a case in point is the successful synthesis of ordered mesoporous carbons, namely the CMK family, reported by Ryoo and co-workers.^{6–10} They have demonstrated that carbonization of sucrose, furfuryl alcohol, and acetylene can be performed inside the mesopores of MCM-48 (CMK-1, CMK-4),^{6,7} SBA-1 (CMK-2)⁸ and SBA-15 (CMK-3, CMK-5)^{9,10} so that well-ordered mesoporous carbons can be obtained after the template is completely removed. The carbon materials with high surface area and ordered pore structure possess great technological interests for the development of catalysts, electrodes, sensors, and hydrogen storage systems.¹⁰ Furthermore, different macroscopic morphologies are expected for advanced property research. Mesoporous carbon monolith is an especially ideal material for the electrochemical doubly-layered capacitor (EDLC) that has been considered as a promising high power energy source.^{11–13} However, so far, mesoporous carbon monoliths have not been reported.

In this paper, we report the synthesis of large-diameter-sized mesoporous carbon monoliths with a bicontinuous cubic structure of *Ia3d* symmetry by using mesoporous silica monoliths as hard templates. The preliminary electrochemical experiments show their potential application in advanced electrodes and EDLC. To the best of our knowledge, this is the first report of a mesoporous carbon monolith with a bicontinuous cubic structure of *Ia3d* symmetry synthesized by a simple carbonization process of sucrose.

As hard templates, large-sized mesoporous silica monoliths were synthesized through a templated sol-gel process. The residue solvents in the silica gel were evaporated at 363 K by covering with a layer of inert medium liquid paraffin, and then the monolith was calcined at 823 K in air to remove the templates. For the synthesis of mesoporous carbon monoliths, mesoporous silica monoliths were impregnated with sucrose solution in the presence of sulfuric acid and dried at 323 K and subsequently at 433 K. Then the impregnation/drying step was repeated once. The obtained sample was carbonized under N₂

atmosphere at 1223 K, and finally, the silica template was dissolved with an aqueous solution of HF acid (10%). Mesoporous carbon monoliths are black in color and maintain the shape of the silica templates, but obvious volume shrinkage was also observed (Fig. 1). Energy-dispersion X-ray spectra (EDX) at all areas show that the product is constructed by pure carbon without any detectable Si element.

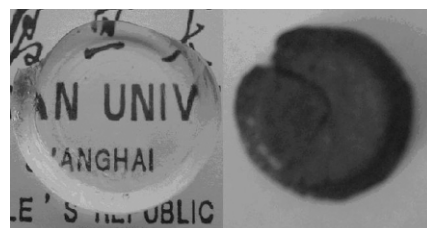


Fig. 1 Photographic images of mesoporous carbon monolith prepared by using mesoporous silica monolith as a template after removal of silica. The left image is the mesostructured silica monolith used as template, which is about 2.1 cm in diameter and 0.3 cm in thickness; whereas the right image is the mesoporous carbon monolith of about 1.7 cm in diameter and 0.2 cm in thickness.

XRD patterns (Fig. 2) of mesoporous silica monoliths show two peaks at $2\theta = 1.13^\circ$ and 1.31° with a d spacing ratio of 0.863, implying the indexation of (211) and (220) diffraction peaks for bicontinuous cubic space group (*Ia3d*). Another broad diffraction peak in the range of $2\theta = 1.6$ – 2.5 may be attributed to the overlapping of (321), (400), (420) and (332) diffraction peaks of the *Ia3d* space group. TEM images of the silica templates show large ordered domains with ordered 3D bicontinuous mesostructure (see ESI†), and the cell parameter (a) is calculated to be 19.0 nm, in good agreement with the value estimated from XRD data, further suggesting the *Ia3d* symmetry of the silica templates synthesized at a high evaporation temperature (363 K).^{14,15}

The small angle XRD pattern (Fig. 2) of the carbon monolith prepared by mesoporous silica monolith as a hard template

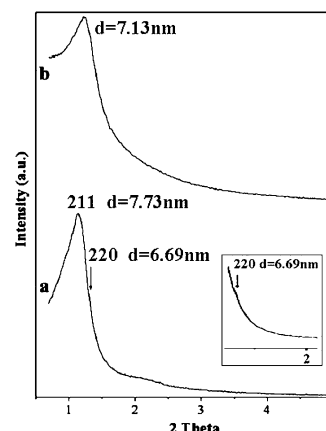


Fig. 2 XRD patterns of (a) mesoporous silica monolith, (b) mesoporous carbon monolith with cubic mesostructure of *Ia3d* symmetry.

† Electronic supplementary information (ESI) available: experimental section and further characterisation data (Fig. S1–4). See <http://www.rsc.org/suppdata/cc/b2/b209233f>

shows one broad diffraction peak at $2\theta = 1.23^\circ$, revealing that long-range ordered mesostructure is partly maintained even after complete removal of the silica template. TEM images and corresponding Fourier diffractograms recorded along [111], [110] and [311] directions of the mesoporous carbon monoliths clearly show ordered 3D bicontinuous mesostructure (Fig. 3).^{7,16,18} The unit cell parameter (a) of the sample is calculated to be 17.5 nm, which is in good agreement with that determined from the XRD data. The nitrogen adsorption isotherm (see ESI†) of the mesoporous carbon monolith yields a type IV isotherm with a H_1 hysteresis loop. A narrow pore-size distribution indicates that the monolith has well uniform pore structure. The mean pore diameter is calculated to be 4.58 nm. The BET surface area and the total pore volume are $1530 \text{ m}^2 \text{ g}^{-1}$ and $1.93 \text{ cm}^3 \text{ g}^{-1}$, respectively.

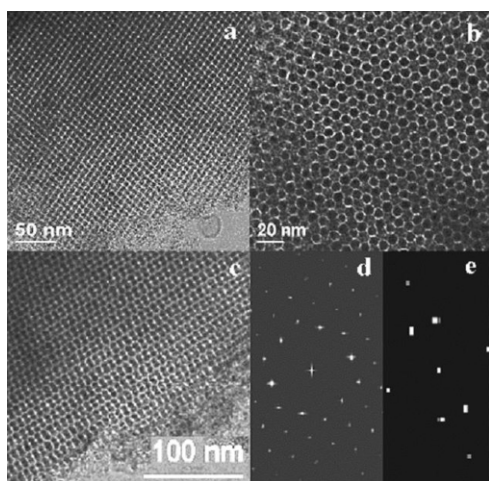


Fig. 3 TEM images of mesoporous carbon monolith with bicontinuous cubic mesostructure of $Ia3d$ symmetry: along the (a) [110], (b) [111], (c) [311] direction and Fourier diffractogram of (d) [111] and (e) [311] direction.

As Ryoo *et al.* reported,^{6–8} when using MCM-48 ($Ia3d$) as a hard template, the symmetry of the derived carbon network changes from cubic $Ia3d$ to either cubic $I4_132$ or lower (CMK-1). Mesoporous carbon with $Ia3d$ symmetry (CMK-4) can only be obtained by using partially disordered AIMCM-48 as a hard template and employing acetylene as carbon precursor.^{7,16} Our mesoporous silica monoliths used as templates here are synthesized by triblock copolymer P123, possessing larger pore size than MCM-48 from cationic surfactants. Due to this fact, carbons tend to be fully incorporated into the channels of the silica template to form a more rigid carbon framework which prevents the symmetry change as described above, and therefore makes the mesoporous carbon framework reported here truly a replica structure of $Ia3d$ symmetry.

Pure carbon monoliths were put to preliminary electrochemical research without macromolecule binder or substrate to increase electrode conductivity. The conductivity of mesoporous carbon monolith electrode derived from the volt-ampere characteristic profile (see ESI†) is 43 S m^{-1} . The cyclic voltammogram¹⁹ (Fig. 4) obtained by using the mesoporous carbon monolith as a working electrode demonstrates the obvious charge/discharge process and the charge/discharge current is high up to 0.04 A, showing potential applications in EDLC. This high conductivity and excellent EDLC performance may be attributed to the high porosity (up to 80%), high surface area and ordered 3D interconnected pure carbon framework of the mesoporous carbon monoliths.

In conclusion, bicontinuous cubic mesoporous carbons of $Ia3d$ symmetry with monolithic morphology have been first synthesized by using mesoporous silica monolith as a hard template. Such carbon monoliths show potential applications of advanced electrodes and EDLC due to their large-sized

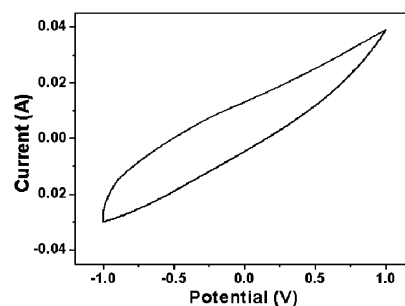


Fig. 4 Cyclic voltammogram curve of the mesoporous carbon monolith with bicontinuous cubic mesostructure of $Ia3d$ symmetry.

continuous carbon framework, high surface area and 3D interconnected mesoporous structure.

We thank Professor J. Kong for electrochemical experiments, H. Jiang for adsorption measurements and gratefully acknowledge the support of this research by the NSFC (9925309, 20173012), National Education Ministry, State Key Basic Research Program of PRC (G2000048001), Shanghai Nanotech. Center (0152nm029), Fudan Graduate Innovation Funds.

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- Experiments were performed using an CHV1610 electrochemical workstation in the potential form -1.0 to 1.0 V (vs. SCE) with a scan rate 10 mV s^{-1} . The working electrode was a carbon monolith with dimensions of $1.5 \times 5.0 \times 8.0 \text{ mm}$ and a mass of 0.026 g . The electrolyte was aqueous $1.0 \text{ M H}_2\text{SO}_4$. A Pt flag and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively.