

# Highly ordered large caged cubic mesoporous silica structures templated by triblock PEO–PBO–PEO copolymer

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Received (in Cambridge, UK) 21st January 2000, Accepted 1st March 2000

Published on the Web 17th March 2000

Highly ordered, hydrothermally stable, caged cubic mesoporous silica structures ( $Im\bar{3}m$ ) with unusually large pore size (120 Å) have been synthesized by using hydrophobic poly(butylene oxide) containing triblock PEO–PBO–PEO copolymer as a structure-directing agent.

Ordered large pore materials are in great demand because of their potential applications for catalysis, separation of large molecules, medical implants, semiconductors, magnetoelectric devices, etc.<sup>1–8</sup> Using triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) copolymers as structure-directing agents, we have previously reported the synthesis of highly ordered hexagonal mesoporous silica structures (SBA-15) with large pore sizes of 50–300 Å.<sup>2</sup> Three-dimensional cubic mesoporous structures, such as MCM-48 ( $Ia\bar{3}d$ ),<sup>1</sup> SBA-1 ( $Pm\bar{3}n$ )<sup>7</sup> and SBA-16 ( $Im\bar{3}m$ ),<sup>2</sup> show advantages compared to hexagonal mesoporous structures with one-dimensional channels. However, such cubic structures could be synthesized only under strict conditions. Calcined SBA-16 synthesized with PEO–PPO–PEO triblock copolymers has the largest pore size (54 Å) among these cubic silica structures, but can only be synthesized with large PEO segment amphiphilic PEO–PPO–PEO block copolymers, such as F127 ( $EO_{106}PO_{70}EO_{106}$ ) in a narrow range of reaction compositions at room temperature.<sup>2b</sup> The small differences of hydrophilicity/hydrophobicity between PEO and PPO chains at room temperature might be one of the reasons leading to such a small pore size.

Here, we report the synthesis of a highly ordered, ultra hydrothermally stable caged cubic mesoporous silica structure (FDU-1,  $Im\bar{3}m$ ) with large, uniform pore size (120 Å) by using the more hydrophobic poly(butylene oxide) containing triblock copolymer PEO–PBO–PEO as the structure-directing agent.

Cubic mesoporous silica FDU-1 samples were synthesized by using the triblock copolymer  $EO_{39}BO_{47}EO_{39}$  [B50-6600 (Dow)  $\bar{M}_n = 6800$ ] as the structure-directing agent under acidic conditions. In a typical experiment, 0.5 g of B50-6600 was dissolved in 30 g of 2 M HCl. To this homogeneous solution, 2.08 g (0.01 mol) of tetraethylorthosilicate (TEOS) was added with vigorous stirring for 24 h. The resulting solid was then aged at 100 °C for a further 24 h. The solid product was filtered off, washed, and dried *in vacuo* at room temperature. Calcination was carried out in an oven at 550 °C for 6 h in air.

Small angle X-ray diffraction (XRD) patterns of as-synthesized and calcined FDU-1 are shown in Fig. 1. As-synthesized FDU-1 shows a well resolved XRD pattern and the first diffraction peak appears at a low angle ( $2\theta = 0.68$ ). After calcination the first diffraction peak is shifted slightly ( $2\theta = 0.73$ ) due to shrinkage. Calcined FDU-1 shows nine well resolved Bragg peaks. Combined with TEM analysis (see below) we can index the diffraction peaks to 110, 200, 211, 220, 310, 222, 400, 411 and 420 reflections for space group  $Im\bar{3}m$  ( $Q^{229}$ ), respectively. The relative intensity of these observed peaks follows the trend reported in previous literature reports for surfactant–water systems.<sup>9,10</sup> The values of the cubic cell lattice parameter,  $a$ , are calculated to be 183 and 171 Å for as-synthesized and calcined FDU-1, respectively.

Transmission electron micrographs (TEM) of calcined FDU-1 are shown in Fig. 2. Although both simple (P) and centered (I) cubic structures show a square lattice along the [100] direction and a hexagonal lattice along the [111] direction, the value of  $d_{100}$  relative to  $d_{111}$  is equal to 0.866 (I) and 1.224 (P), respectively, from geometrical calculations. From bright/dark TEM images [Fig. 2(a) and (b)] for calcined FDU-1, the value of  $d_{100}/d_{111}$  is estimated as 0.88, giving further evidence that the mesostructure is centered cubic with  $Im\bar{3}m$  space group. The cell parameter,  $a$ , is estimated as 170 Å from TEM images, in good agreement with the value determined from the XRD data. Moreover, TEM measurements also reveal that all areas for calcined FDU-1 have well ordered mesoscopic arrays and a three-dimensional caged structure can be observed along the edge of the sample [Fig. 2(b)], indicating that calcined FDU-1 has a high quality caged cubic mesostructure.

Calcined cubic mesoporous silica FDU-1 synthesized using B50-6600 yields a type IV isotherm with a large type-H<sub>1</sub> hysteresis loop (Fig. 3).<sup>11</sup> A narrow pore-size distribution (FWHM *ca.* 10 Å) with a mean value of 120 Å (BJH model) is also obtained from the adsorption branch, indicating that FDU-1 has well defined uniform pore dimensions. The calcined cubic mesoporous silica has a pore volume of 0.77 cm<sup>3</sup> g<sup>-1</sup> and a BET surface area of 740 m<sup>2</sup> g<sup>-1</sup>. Although the cell parameter for FDU-1 is similar to that of SBA-16 (176 Å), the pore size and pore volume for FDU-1 are much larger than those (54 Å, 0.45 cm<sup>3</sup> g<sup>-1</sup>, respectively) for SBA-16,<sup>2b</sup> suggesting that the pore size is very dependent on hydrophobic domains. More hydrophobic PBO segments relative to PPO segments yields a larger

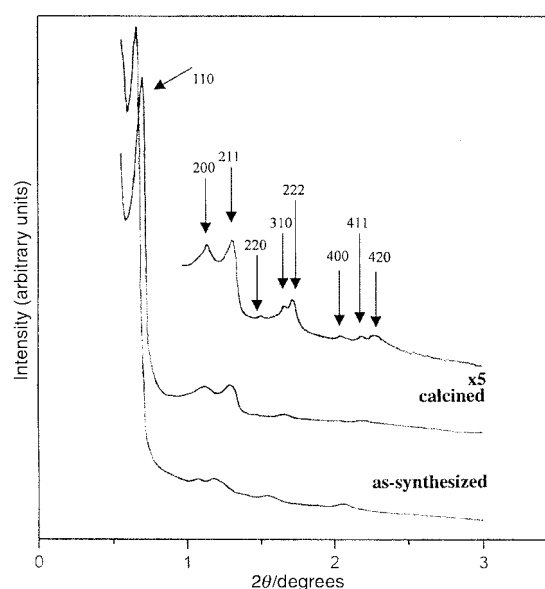
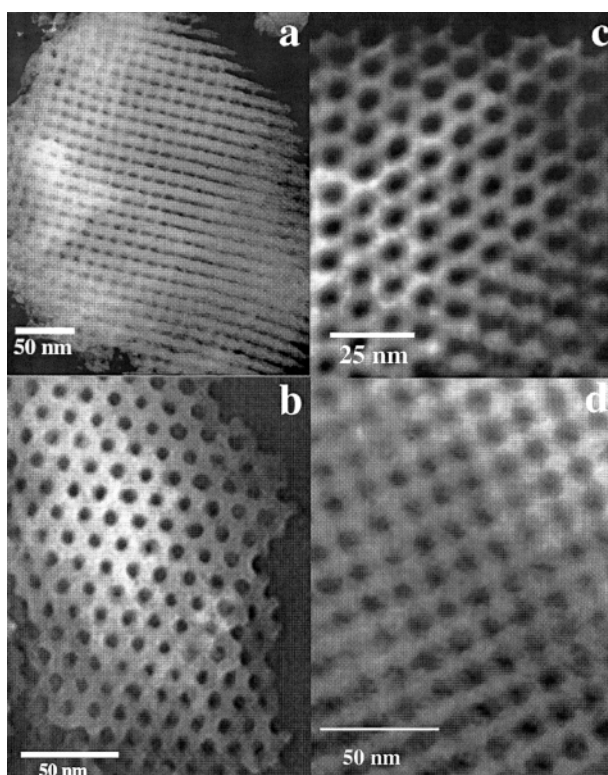


Fig. 1 XRD patterns of as-synthesized and calcined cubic mesoporous silica FDU-1 prepared using  $EO_{39}BO_{47}EO_{39}$  triblock copolymer as the structure-directing agent at room temperature. XRD patterns were recorded with a Rigaku D/Max-IIA using Cu-K $\alpha$  radiation.

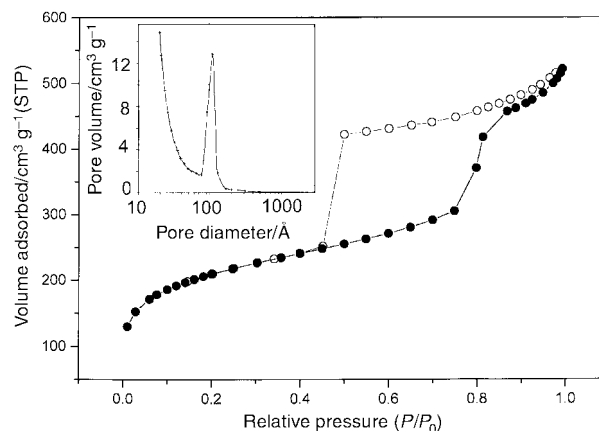
mesopore size. To the best of our knowledge, FDU-1 has the largest pore sizes among all reported cubic silica structures.

Cubic mesoporous silica can be synthesized over a relatively wide range of reaction mixture compositions at temperatures of 0–60 °C. At room temperature, the cubic structure can be synthesized over a range of PEO–PBO–PEO concentrations (0.6–2.4 wt%), with cell parameters ( $a$ ) in the range 200 to 178 Å. Moreover, a low temperature such as 0 °C yields a large cell parameter ( $a$  up to 220 Å), but may lead to slight disorder for FDU-1 according to XRD and TEM. At higher temperatures, the cell parameter and crystalline quality for FDU-1 remain almost unchanged. Addition of swelling agents, such as 1,3,5-trimethylbenzene (TBM), can slightly enlarge the cell parameter (up to 220 Å) with a highly ordered mesostructure. Fig. 2(d) shows a TEM image of calcined FDU-1 obtained with TMB. The cell parameter is estimated as 220 Å, in agreement with that determined from XRD.

Despite of such large lattice dimensions, calcined cubic FDU-1 is hydrothermally stable. After calcined FDU-1 was heated in boiling water for more than 9 days, at least five diffraction peaks can be observed in the XRD pattern and the intensity for the (110) reflection was even increased after the treatment, indicating that large pore mesoporous FDU-1 is hydrothermally stable.



**Fig. 2** TEM images of calcined cubic FDU-1 synthesized using EO<sub>39</sub>BO<sub>47</sub>EO<sub>39</sub> triblock copolymer without TMB at room temperature: (a) along the [100] direction, (b) along the [111] direction and (c) along the [110] direction; (d) calcined cubic FDU-1 synthesized with TMB as the swelling agent. TEM photographs were obtained with a JEM-1200EX microscope operated at 80 kV. For TEM measurements, the samples were ground, embedded in epoxy resin, and ultramicrotomed except the sample in Fig. 2(a), which was prepared by dispersing the powder products as a slurry in acetone and subsequently deposited and dried on a holey carbon film on a Cu grid.



**Fig. 3** Nitrogen adsorption–desorption isotherm plots and pore size distribution curve of calcined mesoporous silica FDU-1. N<sub>2</sub> adsorption measurements were performed at 77 K using a Micromeritics ASAP 2000 analyzer utilizing Barrett–Emmett–Teller (BET) calculations for surface area and Barrett–Joyner–Halanda (BJH) calculations for pore volume and pore size distributions for the adsorption branch of the isotherm.

In summary, highly ordered, large cage-structured cubic mesoporous silica FDU-1 has been synthesized with the hydrophobic PBO containing triblock PEO–PBO–PEO copolymer as a template. The new large cage structure and high hydrothermal stability for the resulting cubic mesoporous silica are expected to be of great value in electrochemistry, catalysis and separation for large molecules.

This work was supported by the National Science Foundation of China (Grant No. 29925309 and 29873012) and National Education Ministry. We thank the Dow Company for providing block copolymer surfactants.

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Communication b000603n