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A novel ordered cubic mesoporous silica templated with tri-head group quaternary ammonium surfactant†

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An ordered mesoporous silica with novel cubic structure (space group *Fd*3*m*) has been synthesized by using tri-head group quaternary ammonium surfactants [$C_mH_{2m+1}N^+(CH_3)_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2N^+(CH_3)_3\cdot3Br^-$] ($C_{m\text{-}2\text{-}3\text{-}1}$, m = 14, 16, 18) as the structure-directing agents under basic conditions at low temperature.

The synthesis of ordered mesoporous materials[1] by using amphiphilic surfactants as the structure-directing agents or templates is an area of expeditious growth with numerous applications, such as separation technology, catalysis, biosensor and microelectronic devices. The pore structures of these materials are largely determined by the structure and polarity of the organic groups. The cooperative assembly developed by Stucky and coworkers[2] has been proved to be a powerful approach to create novel mesostructures with well defined interactions of inorganic species and organic surfactants. Compared with two-dimensional (2D) mesoporous materials such as MCM-41[1] or SBA-15,[3] 3D cubic periodic ordered materials have advantages in applications such as catalysis and molecule separation due to their interconnected pores and channels. Considering the phase diagrams from amphiphilic surfactant liquid crystals,[4] most cubic liquid crystal phases, for example, those with space groups *Ia*3*d*, *Pm*3*n*, *Im*3*m*, have been replicated into silica mesostructures such as MCM-48,[3] SBA-1, SBA-6,[5] SBA-16, FDU-1.[6] It has been noted that the last common cubic liquid crystal phase, with space group *Fd*3*m*, has not been used to synthesize periodic silica mesostructures, although an uncertain face-centered cubic silica mesostructure was claimed by Kim *et al.*[7]

Tri-head group surfactant amphiphiles [$C_mH_{2m+1}N^+(CH_3)_2C_nH_{2n}N^+(CH_3)_2C_sH_{2s}N^+(CH_3)_3\cdot3Br^-$] (designated $C_{m\text{-}n\text{-}s\text{-}1}$) are a kind of multicharge cationic surfactant with three head groups separated by different methylene chains and a variable length hydrophobic tail and are closely related to Gemini surfactants $C_mH_{2m+1}N(CH_3)_2C_sH_{2s}N(CH_3)_2C_pH_{2p+1}Br_2$ ($C_{m\text{-}s\text{-}p}$).[8] The higher charge in the former enables it to interact strongly with water molecules and to have new amphiphile self-aggregation[9] easily. Consequently, using such surfactants, novel mesostructured silica can be expected.

Here, we report our recent synthesis of a novel cubic silica mesostructure (space group *Fd*3*m* Q^{227}) by using the tri-head group quaternary ammonium surfactants $C_{m\text{-}2\text{-}3\text{-}1}$ (m = 14, 16, 18) as the structure-directing agents under basic conditions at low temperature. The obtained mesoporous materials have a uniform nanopore size (~3.0 nm) and a large surface area (~960 $m^2\ g^{-1}$).

$C_{m\text{-}2\text{-}3\text{-}1}$ surfactants were synthesized by reaction of the correponding bromoalkane with tetramethylethylenediamine and (3-bromopropyl)trimethylammonium bromide through two steps,[10] and their structures were confirmed by NMR (see ESI†). The mesoporous silica materials, designed FDU-2, were synthesized at low temperature under basic conditions. In a typical preparation, 0.6 g (0.84 mmol) $C_{18\text{-}2\text{-}3\text{-}1}$ surfactant was dissolved in 24.0 g of distilled water and 9.6 g of 0.5 M NaOH was then added with stirring at 17 °C. To this solution, 1.6 g (7.7 mmol) TEOS (tetraethoxysilane) was added with vigorous magnetic stirring. The resulting gel mixture was stirred for at least 6 h. The solid product was recovered by filtration, washed with water and dried at room temperature. Calcination was carried out in an oven at 500 °C in air for 8 h.

The small angle X-ray diffraction (XRD) pattern (Fig. 1) for the as-synthesized mesoporous silica sample shows two intense diffraction peaks at 2θ = 1.637 and 1.934°. In addition, three well-resolved diffraction peaks at 2θ = 3–5° are also observed. These peaks can be indexed as (220), (311), (333), (440) and (622) of space group *Fd*3*m* (Q^{227}). After calcination at 500 °C in air, the two intense diffraction peaks are shifted to slightly higher angle (2θ = 1.980 and 2.373) due to shrinkage (Fig. 1). Four well-resolved diffraction peaks at 2θ of 3–5° can be observed. These reflection peaks for calcined products can be successfully indexed as (220), (311), (331), (333), (442), and (622), respectively, into a cubic unit cell with space group *Fd*3*m*. The cell parameters calculated from the XRD patterns for as-synthesized and calcined products are 15.3 nm and 12.6 nm, respectively.

Transmission electron micrographs (TEM) further confirm that the mesostructure prepared by using tri-head group surfactants has cubic space group *Fd*3*m*. TEM images of calcined sample show large domains with ordered 3D arrays. Three typical images along [100], [111] and [110] with corresponding selected area electron diffraction (SAED) patterns (Fig. 2A, B, C) show that the calcined mesoporous silica clearly has a face-centred cubic mesostructure. Double-spots are also observed obviously along the [110] direction in Fig. 2C; this is the critical characterization of the *Fd*3*m* space group which is different from other face-centered cubic structures. The cell parameter is evaluated to be 12.1 nm, in agreement with

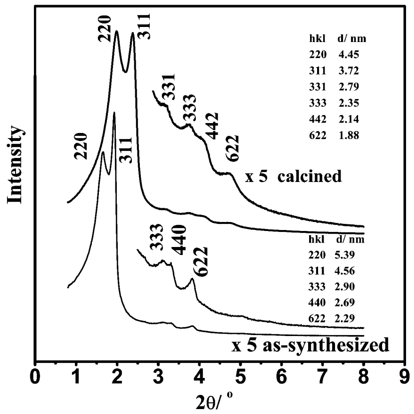

Fig. 1 XRD patterns for the mesoporous silica products prepared from $C_{18\text{-}2\text{-}3\text{-}1}$ under basic conditions.

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† Electronic supplementary information (ESI) available: projections of a typical diamond structure with *Fd*3*m* space group; ^1H NMR data; elemental analysis; SEM image; experimental characterization. See http://www.rsc.org/suppdata/cc/b2/b206993h/

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that determined from the XRD data. Scanning electron micrograph images show that the mesostructured silica products have non-uniform particle morphology with the size of about 1-2 μm, which are similar to that for MCM-41 prepared under basic conditions.[1]

N_2 adsorption–desorption isotherms of the calcined products (Fig. 3) exhibit a typical IV type curve without a hysteresis loop. The pore-size distribution calculated from the Barrett–Joyner–Halanda (BJH) model for the calcined sample (Fig. 3 inset) is rather narrow with a mean pore size of 3.02 nm. The calcined silica product has a Brunauer–Emmett–Teller (BET) surface area of 964 $m^2\ g^{-1}$ and a pore volume of 0.98 $cm^3\ g^{-1}$. The pore size for calcined mesoporous silica can be slightly adjusted from 2.3–3.0 nm by varying the chain length of the tri-head group surfactant $C_{m\text{-}2\text{-}3\text{-}1}$ (m = 14, 16, 18).

Although most lyotropic cubic phases include the typical ones with space groups *Pm*3*n*, *Im*3*m* and *Ia*3d have been duplicated to silica mesostructures,[3,5,6] to the best of our knowledge, a mesoporus silica structure with cubic *Fd*3*m* symmetry has not been reported previously. The packing behavior and the high charge density in the tri-head group quaternary ammonium surfactant may result in strong interactions with the silicate species and play a key role in the formation of 3D face-centered cubic silica mesostructure.

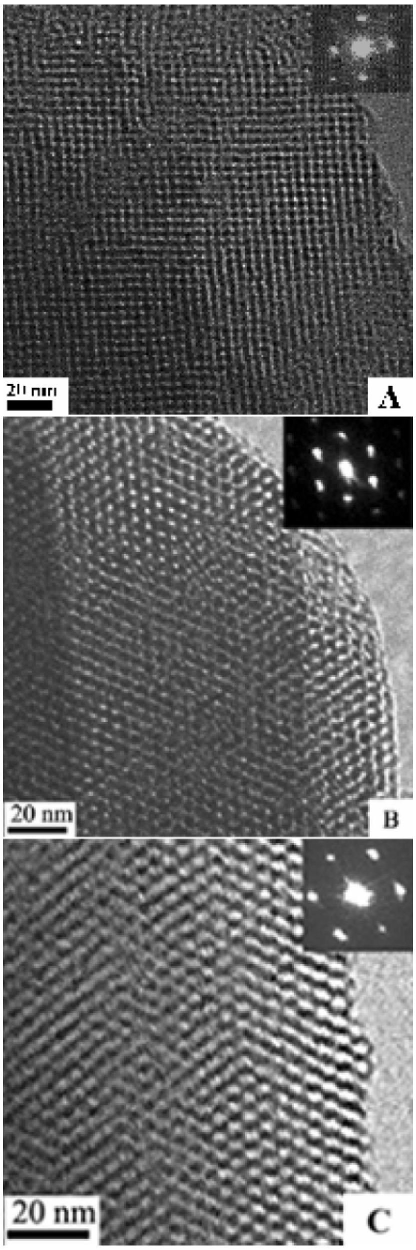

Fig. 2 TEM images and SAED patterns (insets) for calcined mesoporous silica prepared using $C_{18\text{-}2\text{-}3\text{-}1}$ surfactant, along (A) the [100], (B) the [111] and (C) the [110] directions.

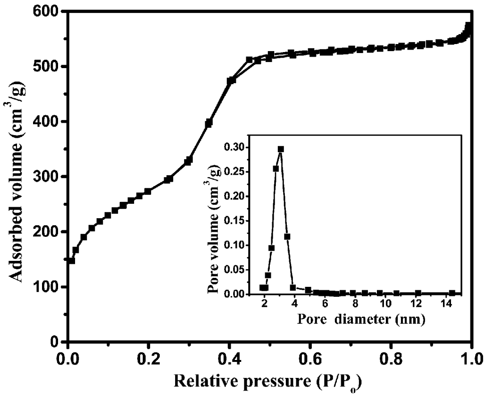

Fig. 3 Nitrogen adsorption–desorption isotherm curves and BJH pore size distribution plot (inset) of calcined mesoporous silica.

It should be noted that the cubic mesoporous silica can only be formed in a relatively narrow pH range of 13.0–13.3 and at low temperature (13–19 °C). The low temperature favors the formation of the face-centered cubic mesophase, which may be related to the low temperature phase (*Fd*3*m*) for the surfactant liquid crystal. A higher pH value, or a higher synthesis temperature, yields a mixture of the cubic phase and the 2D hexagonal phase with space group *p*6*mm*. A high quality mesoporous silica MCM-41 can be obtained by heating the solution containing FDU-2 at 100 °C for two days.

In conclusion, novel cubic *Fd*3*m* mesoporous silica materials have been successfully synthesized at low temperature by using tri-head group quaternary ammonium surfactants as the structure-directing agents. Further investigations on the complete mesopore network are being carried out in these laboratories.

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