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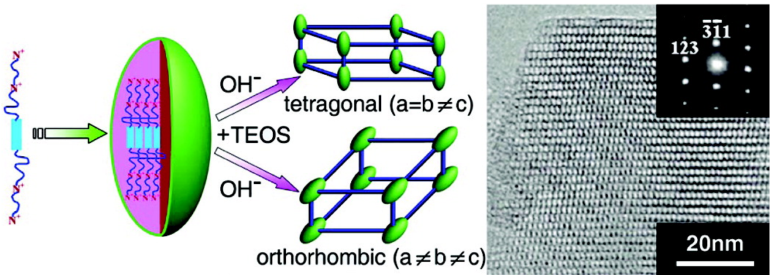

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Three-Dimensional Low Symmetry Mesoporous Silica Structures Templated from Tetra-Headgroup Rigid Bolaform Quaternary Ammonium Surfactant

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Abstract: Two kinds of highly ordered mesoporous silica materials (FDU-11, FDU-13) with novel three-dimensional (3-D) tetragonal and orthorhombic structures were synthesized by using tetra-headgroup rigid bolaform quaternary ammonium surfactant $[(CH_3)_3NCH_2CH_2CH_2N(CH_3)_2CH_2(CH_2)_{11}OC_6H_4C_6H_4O(CH_2)_{11}CH_2N(CH_3)_2CH_2CH_2CH_2N(CH_3)_3\cdot 4Br]$ ($C_{3-12-12-3}$) as a template under alkaline conditions. High-resolution transmission electron microscopy (HRTEM), small-angle X-ray scattering (SAXS), and X-ray diffraction (XRD) show that mesoporous silica FDU-11 has primitive tetragonal $P4/mmm$ structure with cell parameters $a = b = 8.46$ nm, $c = 5.22$ nm, and c/a ratio = 0.617. N_2 sorption isotherms show that calcined FDU-11 has a high BET surface area of ~1490 m^2/g, a uniform pore size of ~2.72 nm, and a pore volume of ~1.88 cm^3/g. Mesoporous silica FDU-13 has primitive orthorhombic $Pmmm$ structure. The cell parameters are $a = 9.81$, $b = 5.67$, and $c = 3.66$ nm. N_2 sorption isotherms show that calcined FDU-13 has a high BET surface area of 1210 m^2/g, a uniform mesopore size of ~1.76 nm, and a large pore volume of ~1.83 cm^3/g. Such low symmetries for 3-D mesostructures (tetragonal and orthorhombic system) have not been observed before even in amphiphilic liquid crystals, which maybe resulted from an oblate aggregation of the bolaform surfactant and its strong electrostatic interaction with inorganic precursor. A probable mechanism has been proposed for the formation of such a 3-D low symmetrical mesostructure. These results will further extend the synthesis of mesoporous materials and may open up new opportunities for their new applications in catalysis, separation, and nanoscience.

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1. Introduction

Ordered mesoporous materials[1−8] prepared from soft chemistry[9−13] by using surfactants and block copolymers as the structure-directing agents or templates have received a great deal of attention because of their large surface area (up to 1500 m^2/g), uniform pore size distribution (~1.5−40 nm), and their potential applications in catalysis,[14−19] separation technology,[20−24] nanoscience,[25,26] and biomaterials engineering.[27−31] Great efforts

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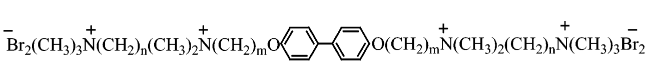
have been performed toward the synthesis of mesoporous materials with different mesostructures, compositions, as well as morphologies through several approaches such as hydrothermal process under acidic and basic media, sol−gel process, and evaporation-induce self-assembly (EISA). Among these efforts, the synthesis of mesoporous materials with novel mesostructures is the most challenging and somewhat difficult, and only a few new mesostructures have been reported during the past a few years.[30,32−41] However, it is very important for both fundamental research and applications to develop new catalysts, adsorbents, delivery hosts, microdevices, and nanoreactors. Surfactants, the structure-directing agents of the mesoporous materials, play a key role for the self-assembly of the ordered mesostructure because they can be aggregated in aqueous solution[42−45] and give rise to a wide range of mesophases with different structure upon interacting with the inorganic precursor species in the presence of acid or base catalysts.[46] For example, MCM-41,[1] SBA-15,[32,47] FSM-16,[3,4] SBA-3[46] (2-D hexagonal $p6mm$), MCM-48,[2] FDU-5,[48] KIT-6[49] (cubic $Ia\bar{3}d$), SBA-1, SBA-6[50,51,33] (cubic $Pm\bar{3}n$), SBA-16,[32,33] FDU-1[34,36,52−56] (cubic $Im\bar{3}m$), and FDU-12[30,57] (cubic $Fm\bar{3}m$), FDU-2,[35] AMS-8[37,39,41] (cubic $Fd\bar{3}m$), SBA-2[58−61] and SBA-12[32,62] (intergrowth 3-D hexagonal $P6_3/mmc$ and cubic $Fm\bar{3}m$), and SBA-8[63] (2-D rectangular centered $c2mm$) have been synthesized via electrostatic Coulombic interaction and double layer hydrogen bond interaction through S^+I^-, S^-I^+, $S^+X^-I^+$, and $S^\circ H^+X^-I^+$ pathways (where S^+ is cationic surfactant, I is inorganic precursor species, and X is counterion).[64] It is surprising to note that the symmetries for all the above mesostructures are high in cubic and hexagonal systems except the 2-D SBA-8 mesostructure, which is derived from 2-D hexagonal structure by “pushing or drawing” along the [100] direction. This is not difficult to understand since the self-assembly of surfactant molecules and/or cooperative assembly of surfactant−inorganic precursor composites are driven by weak Coulombic or van der Waals forces; therefore, close-packing mesostructures of cubic or hexagonal symmetries can be easily formed. If the driving force between silicates and surfactant assembly is stronger, the low symmetrical mesostructure could be formed. Recently, Falcaro et al. and Besson et al. found that during the formation of mesoporous silica films by EISA, the low symmetrical mesostructure such as orthorhombic face-centered (space group, $Fmmm$) structure may be formed in the presence of triblock copolymer templates[65,66] due to the strong interface tension. However, because of the lack of convincing evidence from transmission electron microscopy (TEM) images, this mesostructure could not be confirmed as a distorted cubic $Im\bar{3}m$ structure induced by ethanol evaporation during the EISA.[67−69] To the best of our knowledge, a highly ordered silica mesostructure with relatively low symmetry such as tetragonal or orthorhombic system has not been reported yet.

In general, the formation of mesostructure depends excessively on the nature of the surfactants, such as the volume of hydrophilic headgroup, the molecular shape (flexible or rigid) and the charge density distribution.[14,58,59,64] Therefore, a rational design of the surfactant provides a direct and efficient pathway to synthesize mesoporous materials with desired structures.

Tetra-headgroup rigid bolaform surfactants (denoted as $C_{n-m-m-n}$), refer to a kind of multicharged cationic surfactants, are related to gemini surfactants, in which four hydrophilic headgroups separated by different methylene chains are attached by one variable-length hydrophobic linker with a rigid biphenol group.[35,52,57,58,69,70] Their formula is shown below:



n = 2, 3, 4; m = 8, 10, 12

The high charge density, rigid biphenol rodlike unit, and flexible hydrophobic coil segment in the tetra-headgroup bolaform surfactant ($C_{n-m-m-n}$) can increase the interaction between inorganic silicate precursors and organic surfactant molecules and the aggregation force of the surfactant molecules via $\pi-\pi$ interaction, it may facilitate formation of low symmetrical

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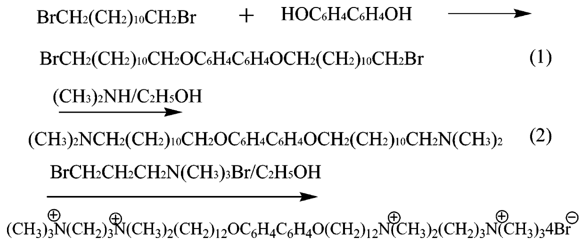
Scheme 1. Synthesis of Tetra-Headgroup Rigid Bolaform Quaternary Ammonium Surfactant



mesostructure, and creation of a new kind of highly ordered mesoporous silica materials can be expected.[70]

Here, we report the synthesis of two new 3-D highly ordered mesoporous silica with low symmetrical structures (tetragonal *P*4/*mmm* and orthorhombic *Pmmm* structure) (denoted as FDU-11 and FDU-13, respectively) by using multicharged rigid bolaform surfactant ($C_{3-12-12-3}$) as a structure-directing agent under base condition. X-ray diffraction (XRD), small-angle X-ray scattering (SAXS), high-resolution transmission electron microscopy (HRTEM), and N_2 sorption measurements show that the obtained mesoporous silica materials with low symmetrical structure possess highly ordered regularity, high surface area (up to 1490 m^2/g), large pore volume (up to 1.88 cm^3/g), and a narrow pore size distribution ($\sim$1.76−2.1 nm). A formation mechanism has been proposed for the synthesis of these mesoporous silica with low symmetrical structure based on the cooperative-assemble interaction between the organic surfactant and inorganic precursor species.

2. Experimental Section

Materials. The chemicals used for the synthesis—tetraethyl orthosilicate (TEOS), 1,12-dibromododecane [$Br(CH_2)_{12}Br$], and (3-bromopropyl) trimethylammonium bromide—were bought from Aldrich, and 4, 4′-biphenol (97%) was purchased from Acros. Other reagents were obtained from China Chemical Reagent Corporation. All chemicals mentioned here were used without further purification.

Synthesis of Tetra-Headgroup Rigid Bolaform Surfactant. The synthesis of tetra-headgroup rigid bolaform quaternary ammonium surfactant $C_{3-12-12-3}$ was carried out as in previous reports[70−75] and was performed as outlined in Scheme 1. Detailed synthesis of surfactant $C_{3-12-12-3}$ is as follows.

A mixture of 4,4′-biphenol (5.00 g, 26.9 mmol) in 200 mL of ethanol, 3.20 g (57.1 mmol) of KOH, and 44.0 g (134 mmol) of 1,12-dibromododecane was refluxed under N_2 environment for 20 h. After cooling to room temperature, the reaction mixture was filtered and washed repeatedly with hot C_2H_5OH several times to obtain intermediate **1**, $BrCH_2(CH_2)_{10}CH_2OC_6H_4C_6H_4OCH_2(CH_2)_{10}CH_2N(CH_3)_2$ (mp 114.6 °C). ^1H NMR (400M, $CDCl_3$), δ (ppm): 7.48 (d, 4H, Ar−H), 6.94 (d, 4H, H−Ar−O), 3.99 (t, 4H, OCH_2), 3.42 (t, CH_2Br), 1.83 (m, 8H, $OCH_2\mathbf{CH_2}$, $\mathbf{CH_2}CH_2Br$), 1.41 (m, 8H, $\mathbf{CH_2}(CH_2)_6\mathbf{CH_2}$), 1.29 (m, 24H, $(CH_2)_6$). EI-MS *m*/*z* for $C_{36}H_{56}O_2Br_2$ found: (186, 100%); (678, 3.23%); (680, 6.23%); (682, 3.32%); (55, 12.91%); (69.92, 9.2%); (157, 7.56%); (434, 2.08%). Calculated: 680.

A quantity of 10.0 g (14.7 mmol) of intermediate **1** in 100 mL of benzene was allowed to react with 13.0 g (295 mmol) of ethanolic $HN(CH_3)_2$ in an ampule at 80 °C for 20 h. After the solvent was removed, the residue was treated with KOH and recrystallized from C_2H_5OH three times to obtain intermediate **2**, $(CH_3)_2NCH_2(CH_2)_{10}CH_2OC_6H_4C_6H_4OCH_2(CH_2)_{10}CH_2N(CH_3)_2$ (mp 100.7 °C). ^1H NMR (400M, $CDCl_3$), δ (ppm): 7.48 (d, 4H, Ar−H), 6.96 (d, 4H, H−Ar−O), 3.99 (t, 4H, OCH_2), 2.29 (t, 16H, $\mathbf{CH_2}N(\mathbf{CH_3})_2$), 1.80 (m, 4H, $\mathbf{CH_2}CH_2N(CH_3)_2$), 1.47 (m, 8H, $OCH_2\mathbf{CH_2}(CH_2)_7\mathbf{CH_2}CH_2CH_2N(CH_3)_2$), 1.29 (m, 28H, $(CH_2)_7$). ESI-MS *m*/*z* for $C_{40}H_{68}O_2N_2$ ($[M + H]^+$) found: 609.5. Calculated: 609.

A quantity of 2.50 g (4.01 mmol) of the intermediate **2** was further dissolved in 100 mL of C_2H_5OH, and 2.68 g (10.3 mmol) of (3-bromopropyl)trimethylammonium bromide was added to this solution. The resulting mixture was heated while being stirred at 78 °C for 5 days under refluxing condition. The solvent was evaporated by using a rotary evaporator until a white viscous liquid was obtained. The viscous liquid was cooled in a refrigerator (5 °C) to enhance the precipitation. The resulting precipitate was filtered, washed with cool ethyl acetate, and dried in a vacuum desiccator. The white precipitate was further purified by column chromatography (Sephadex LH-20) using methanol as an eluent and identified as final product $C_{3-12-12-3}$ (hygroscopic) by ^1H NMR spectra after dissolution in CH_3OD. ^1H NMR (400M, CH_3OD), δ (ppm): 7.45 (m, 4H, Ar−H), 6.91 (m, 4H, H−Ar−O), 3.94 (t, 4H, OCH_2), 3.49 (m, 12H, $N(CH_3)_2$), 3.26 (s, 18H, $N(CH_3)_3$), 3.19 (s, 12H, CH_2N), 2.38 (m, 4H, $N(CH_3)_2CH_2\mathbf{CH_2}CH_2N(CH_3)_3$), 1.75 (m, 8H, $\mathbf{CH_2}(CH_2)_8\mathbf{CH_2}$), 1.33 (m, 32H, $(CH_2)_8$). ESI-MS *m*/*z* for $C_{52}H_{98}O_2N_4Br_4$ ($[M - Br]^+$) found: 1051.5. Calculated: 1051.5.

Synthesis of Mesoporous Silica. Mesoporous silica materials (FDU-11) were hydrothermally prepared under base condition at room temperature with the composition of $C_{3-12-12-3}$/TEOS/NaOH/H_2O = 1:21.7:13:5070 (molar ratio). In a typical preparation, 0.520 g of bolaform surfactant $C_{3-12-12-3}$ was dissolved in 30.0 g of distilled water, and to this mixture, 12.0 g of NaOH (0.5 M) was added under stirring. After complete dissolution of the surfactant, 2.08 g TEOS (10.0 mmol) was added to the solution, and the mixture was further stirred for 12 h. The resultant product was filtered, washed with distilled water, and dried at ambient temperature. Template free sample was obtained after calcination for 6 h at 550 °C in air.

The synthesis procedure of mesoporous silica, FDU-13, was carried out by a procedure similar to that described for FDU-11 except for the molar ratio of TEOS to the surfactant. Typical synthesis of FDU-13 was as follows: 0.500 g of tetra-headgroup rigid bolaform surfactant $C_{3-12-12-3}$ was dissolved in 30.0 g of distilled water, and to this mixture, 12.0 g of NaOH (0.5 M) was added under stirring. The obtained solution of a template was homogenized for 30 min under vigorous stirring, and 1.62 g of TEOS was added to obtain a reaction mixture with the following molar composition: $C_{3-12-12-3}$/TEOS/NaOH/H_2O = 1:17.6:13.6:5273 (molar ratio). The mixture was vigorously stirred for 12 h, and the resultant product was filtered, washed with distilled water, and dried at ambient temperature. The calcination was carried out in air for 6 h at 550 °C to remove the organic surfactant.

Measurements. SAXS profiles were recorded on a homemade camera with imaging plate at transmission mode under vacuum at 40 kV and 35 mA. Cu Kα X-ray with a wavelength of (*l*) 1.5418 Å was used. The 2-D isotropic diffraction patterns were transformed into a 1-D radial average of the scattering intensity. Powder XRD patterns were recorded with Bruker D4 powder X-ray diffractometer using Cu Kα radiation. TEM images were taken with a JEM-3010 at 300 kV, and electron diffraction (ED) patterns were recorded with a slow-scan CCD using low-dose conditions. Nitrogen adsorption measurements were carried out on a Tristar 3000 volumetric adsorption analyzer. Before the adsorption measurements, the samples were outgassed at 200 °C in the port of the adsorption analyzer. The surface area of the samples was calculated by using the Barrett−Emmett−Teller (BET) method at low relative pressure (P_0/P < 0.2), and the pore volume

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was calculated from the adsorption volume at relative pressure ($P_0/P = 0.998$). The pore size distribution was calculated from the adsorption branch of the isotherms by using the Barrett−Joyner−Halenda (BJH) method. Although it has recently been found that the BJH model has been somewhat problematic to calculate the pore size, the model has been widely adopted in the mesostructured materials community for the comparison. Scanning electron micrographs (SEM) were taken on a XL 30 Philips 25 kV.

3. Results and Discussion

Mesoporous Silica FDU-11 with 3-D Tetragonal Structure. As-synthesized mesoporous silica FDU-11 prepared by using rigid bolaform tetra-headgroup amphiphile ($C_{3-12-12-3}$) as a structure-directing agent shows well-resolved XRD peaks (Figure 1) at 2θ of ∼1−7° which are quite different from those for the mesoporous silica structures reported previously. Two intense and well-resolved diffraction peaks are observed at 2θ of ∼1−2°. The ratio for *d*-spacing of the two adjacent intense XRD peaks is closed to $\sqrt{5}:\sqrt{8}$. Several weak poorly resolved diffraction peaks and one intense diffraction peak can be observed at 2θ of ∼2−3.5° and ∼3.6°, respectively. The ratio for *d*-spacing of three intense XRD peaks is about $\sqrt{5}:\sqrt{8}:\sqrt{17}$. If we suppose that the mesostructure is cubic or hexagonal phase, the corresponding cell parameter could not index the other XRD peaks, and thus cubic and hexagonal mesophases are ruled out and 3-D low-symmetrical mesostructure is suggested. After calcination at 550 °C for 6 h in air, the XRD pattern becomes more resolved and the diffraction peaks shift to higher angles, suggesting that the shrinkage has occurred during the calcination. These XRD peaks can be indexed to 110, 001, 210, 220, 002, 320, 400, and 302 Bragg reflections (see Supporting Information (SI) Table S1), respectively, suggesting that mesoporous silica FDU-11 has a 3-D tetragonal mesostructure. The cell parameters calculated are $a = 8.51$, $c = 5.26$ nm, and $c/a = 0.618$ (see SI Table S1).

To more accurately obtain the diffraction indexation, the SAXS pattern of the calcined FDU-11 prepared by using rigid bolaform tetra-headgroup amphiphile ($C_{3-12-12-3}$) as a structure-directing agent was measured. As shown in Figure 2, more resolved pattern and more diffraction peaks can be observed compared with the XRD case of calcined FDU-11. Five obvious intense diffraction peaks with *d*-spacings of 8.622, 5.999, 5.224, 3.784, and 3.241 nm were measured in the range of $q = \sim 0.5-2$ nm^{-1}. In addition, several relatively weak diffraction peaks are also resolved in the range of $q = \sim 2-3.5$ nm^{-1}, corresponding to *d*-spacings of 2.951, 2.607, 2.390, 2.080, 2.043, 1.938, and 1.869 nm. The value of d_1, d_2, d_4, d_6, d_9, and d_{10} shows systematic *hkl* reflection conditions, where $1/d_1:1/d_2:1/d_4:1/d_6:1/d_9:1/d_{10} = \sqrt{1}:\sqrt{2}:\sqrt{5}:\sqrt{8}:\sqrt{16}:\sqrt{17}$. Combined with the fact that threefold symmetry has not been observed in both ED and HRTEM images FDU-11therefore does not belong to a cubic or hexagonal system and is supposed to be tetragonal symmetry. The reflection conditions are consistent with tetragonal structure (where $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$) according to the principle of crystallography. All these reflection peaks observed in the calcined FDU-11 can be indexed to 100, 110, 001, 210, 201, 220, 002, 112, 400, 410, 302, and 312 Bragg reflections (see SI Table S2), respectively. $P4$, $P\bar{4}$, $P4/m$, $P422$, $P4mm$, $P\bar{4}2m$ ($P\bar{4}m2$), and $P4/mmm$ are possible space groups, and $P4/mmm$ is warily chosen as the highest space group for the calcined FDU-11. The obtained lattice constants, *a* and *c*, are 8.46 and 5.22 nm, respectively, which is similar to the values obtained from XRD, further suggesting a 3-D tetragonal mesostructure. In addition, the corresponding cell parameter ratio c/a is 0.617, which is in good agreement with that obtained from XRD measurement.

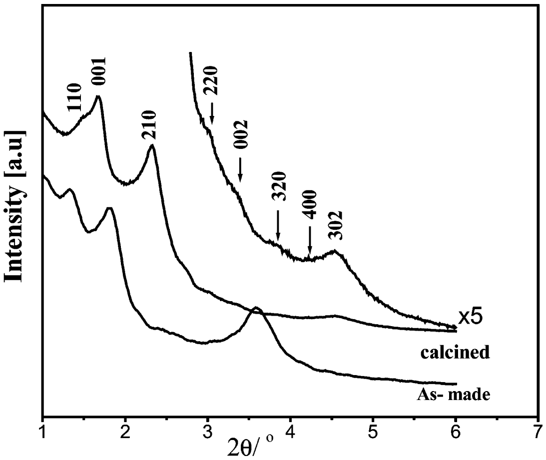

Figure 1. XRD patterns for the mesoporous silica products FDU-11 prepared from bolaform surfactant $C_{3-12-12-3}$ under base condition.

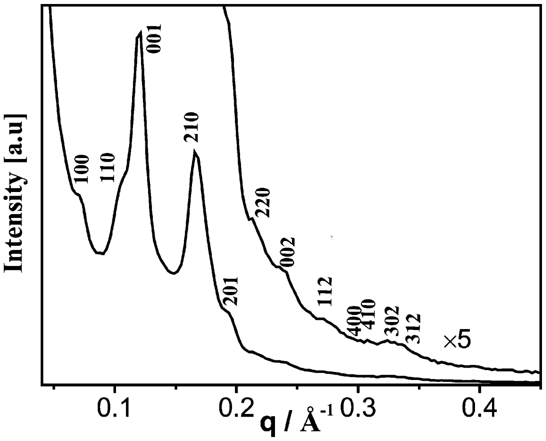

Figure 2. SAXS pattern for calcined mesoporous silica FDU-11 templated by tetra-headgroup rigid bolaform surfactant $C_{3-12-12-3}$.

The SEM image (Figure 3A) shows that the calcined mesoporous silica FDU-11 products have uniform short rodlike square morphology with the size of about ∼0.5−1.0 μm, implying that FDU-11 products have a tetragonal mesostructure.

TEM images and corresponding selected area electron diffraction (SAED) patterns (Figure 4) further confirm that mesoporous silica FDU-11 prepared by using tetra-headgroup rigid bolaform surfactant $C_{3-12-12-3}$ has 3-D tetragonal structure. The electron diffraction pattern in Figure 4A shows a fourfold symmetry that belongs to the crystal system of either cubic or tetragonal symmetry. This is a critical character of the tetragonal system distinguished from the hexagonal or orthorhombic system. A threefold axis from all the TEM measurements is not observed for the calcined FDU-11 samples. Therefore, the cubic system is excluded, and the tetragonal system can be considered. Taking account of the cell parameter ratio ($c/a = 0.617$), we can index representative TEM images and corresponding SAED (Figure 4B,C) that exhibit highly ordered regularity in large domain by tetragonal system taken along the

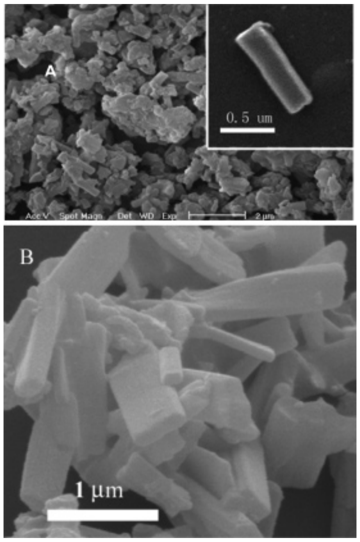

Figure 3. SEM images and corresponding large magnification images (inset) for calcined mesoporous silica prepared by using bolaform surfactant $C_{3-12-12-3}$ as a structure-direction agent under base condition. (A) FDU-11 with tetragonal *P*4/*mmm* mesostructure, and (B) FDU-13 with orthorhombic *Pmmm* mesostructure.

[232] and [−12−1] zone axes. The corresponding ED patterns (insets in Figure 4B,C) can be indexed according to the tetragonal system. Similar to the solution from the SAXS pattern, *P*4, *P*$\bar{4}$, *P*4/*m*, *P*422, *P*4*mm*, *P*$\bar{4}$2*m* (*P*$\bar{4}$*m*2), and *P*4/*mmm* are possible solutions based on the indexation from ED. We choose space groups of *P*4/*mmm* as a possible solution because of the highest space group for the calcined FDU-11.

N_2 adsorption and desorption isotherm curves of the calcined FDU-11 (Figure 5a) show a typical type IV isotherm with a small H1 hysteresis loop, implying its complexity 3-D pore connectivity mesostructure. The calcined FDU-11 has a BET surface area of 1490 cm^2/g and a pore volume of 1.88 cm^3/g. The pore size mean value with a very narrow distribution (Figure 5a, inset) calculated from the adsorption branch with the BJH method is 2.72 nm. The pore size can be slightly adjusted from 1.76 to 2.72 nm by varying the linker length of the tetra-headgroup cationic surfactant $C_{3-m-m-3}$ (m = 8, 10, 12).

Mesoporous Silica FDU-13 with Orthorhombic Structure. More interesting, another kind of new mesoporous silica materials with orthorhombic *Pmmm* structure can be prepared from tetra-headgroup rigid bolaform surfactant $C_{3-12-12-3}$ by decreasing the TEOS/$C_{3-12-12-3}$ ratio from 21.7 to 17.6 (molar ratio). As-synthesized mesoporous silica FDU-13 shows a well-resolved XRD pattern (Figure 6) at 2θ of ∼1−7° which is more resolved than that for FDU-11. Two strongly adjacent intense diffraction peaks are observed at 2θ of ∼1−2°, and another intense diffraction peak is observed at 2θ of 3.786°. The ratio for *d*-spacings of three strong intense XRD peaks is about $\sqrt{5}:\sqrt{8}:\sqrt{32}$. Several resolved XRD peaks including a shoulder peak at 2θ of 2.117° can also be observed. After calcinations at 550 °C for 6 h in air, the small-angle XRD pattern (Figure 6) for calcined FDU-13 becomes more resolved and the diffraction peaks shift to higher angles, like that for FDU-11. Two strong intense diffractions at $2\theta = \sim 1-5°$ corresponding to the *d*-spacings of 5.048 and 3.743 nm are observed. Other diffraction peaks in this region corresponding to *d*-spacings of 5.889, 3.451, 3.078, 2.832, 2.517, 2.248, and 1.872 nm, respectively, can also be observed. Combined with HRTEM results (see below), all these diffraction peaks can be indexed as orthorhombic structures of 010, 110, 001, 101, 011, 120, 220, 121, and 002 Bragg reflections (see SI Table S3). *P*222, *Pmm*2 (*Pm*2*m*, *P*2 *mm*), and *Pmmm* are possible space groups, and *Pmmm* is cautiously chosen because of its highest space group. The obtained lattice parameters *a*, *b*, and *c* are 9.80, 5.89, and 3.74 nm, respectively.

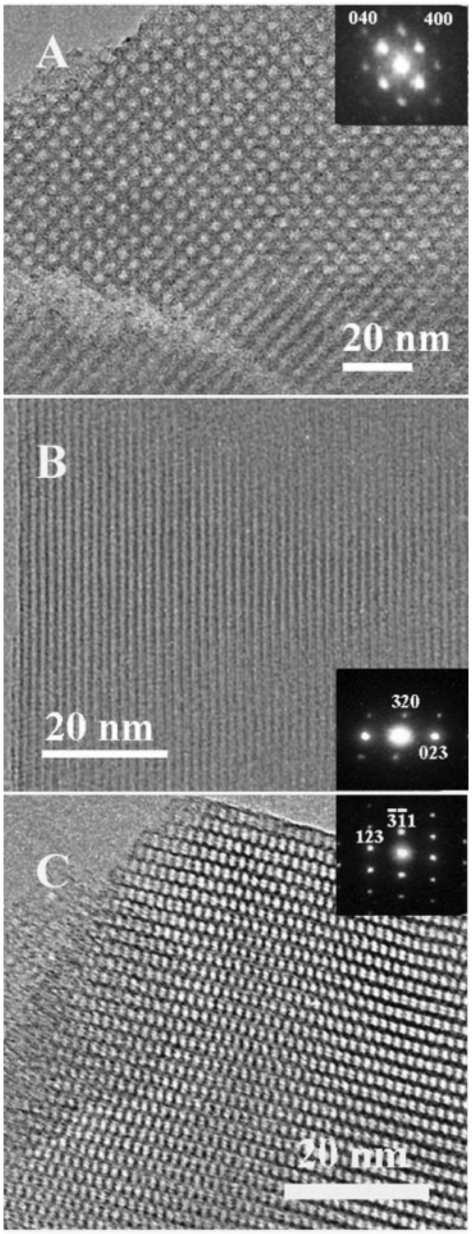

Figure 4. TEM images and SAED patterns (insets) for calcined mesoporous silica prepared by using bolaform surfactant $C_{3-12-12-3}$, along (A) [001], (B) [2−32], and (C) [−12−1] zone axes.

The SAXS pattern (Figure 7) for calcined FDU-13 prepared by using rigid bolaform surfactant ($C_{3-12-12-3}$) as a structure-directing agent is more resolved than the XRD pattern. Four intense diffraction peaks with *d*-spacings of 5.671, 4.911, 3.662, and 3.351 nm are resolved in the range of $q = \sim 1.0-2.0$ nm^{-1}. In addition, several weak diffraction peaks are also well-resolved in the range of $q = \sim 2.0-3.2$ nm^{-1}, corresponding to *d*-spacings of 3.049, 2.828, 2.717, 2.652, 2.527, 2.454, 2.266, and 2.163 nm. Through the trial and error method, we found that the

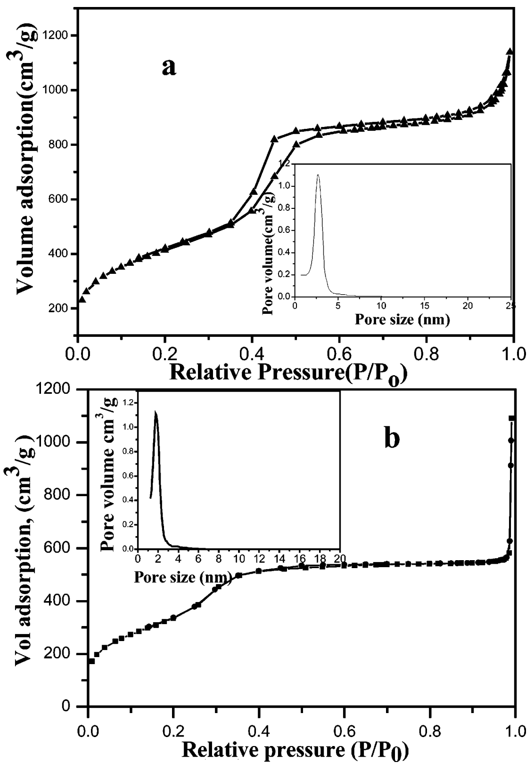

Figure 5. N_2 adsorption and desorption isotherm curves and corresponding pore size distribution curves (inset) for the calcined mesoporous silica FDU-11 (a) and FDU-13 (b) template by bolaform surfactant $C_{3-12-12-3}$.

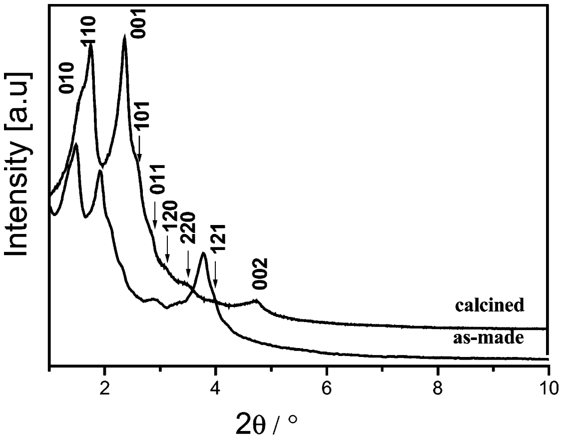

Figure 6. XRD patterns for mesoporous silica FDU-13 with orthorhombic *Pmmm* structure prepared from bolaform surfactant $C_{3-12-12-3}$ under base conditions.

reflection conditions are consistent with orthorhombic system (where $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$ according to the principle of crystallography) if the cell parameters *a*, *b*, and *c* are supposed as 9.81, 5.67, and 3.66 nm, which is in agreement with that obtained from XRD measurements. All these reflection peaks observed can be indexed to 010, 110, 001, 101, 011, 020, 120, 211, 220, 301, 021, and 121 Bragg reflections (see SI Table S4), respectively. Similar to above XRD indexation, *P*222, *Pmm*2 (*Pm*2*m*, *P*2*mm*), and *Pmmm* are possible space groups, and *Pmmm* is warily chosen as the highest space group.

The SEM image (Figure 3B) of the calcined FDU-13 displays rodlike rectangle morphology, a little different from that of mesoporous silica FDU-11. The rods of FDU-13 are longer than that of silica FDU-11.

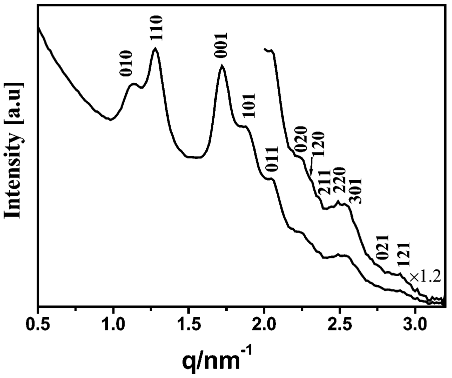

Figure 7. SAXS pattern for calcined mesoporous silica FDU-13 with orthorhombic *Pmmm* structure prepared from bolaform surfactant $C_{3-12-12-3}$ under base conditions.

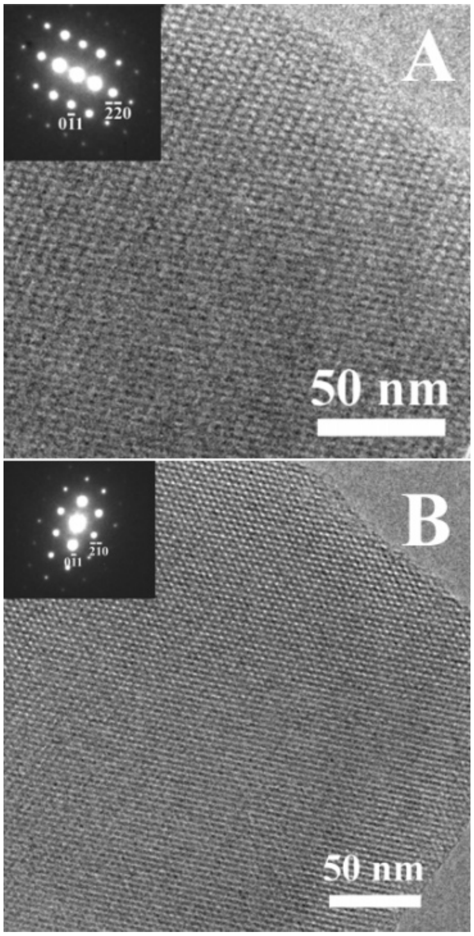

Figure 8. TEM images and SAED patterns (insets) for calcined mesoporous silica FDU-13 prepared by using bolaform surfactant $C_{3-12-12-3}$, along (A) [1−1−1] and (B) [1−2−2] zone axes.

The silica FDU-13 mesostructure could be resolved thoroughly by HRTEM from a set of TEM images and corresponding SAED patterns obtained through the sample tilting, further confirming that the calcined FDU-13 has 3-D low symmetrical orthorhombic mesostructure (possible space group of *Pmmm*), as shown in Figure 8A,B. From all the TEM observations, the symmetry fold is found as high as twofold axis, whereas threefold, fourfold, and sixfold axes could not be found for calcined FDU-13 samples, suggesting that cubic, hexagonal, and tetragonal systems are excluded and a low symmetry system such as an orthorhombic system can be considered. A

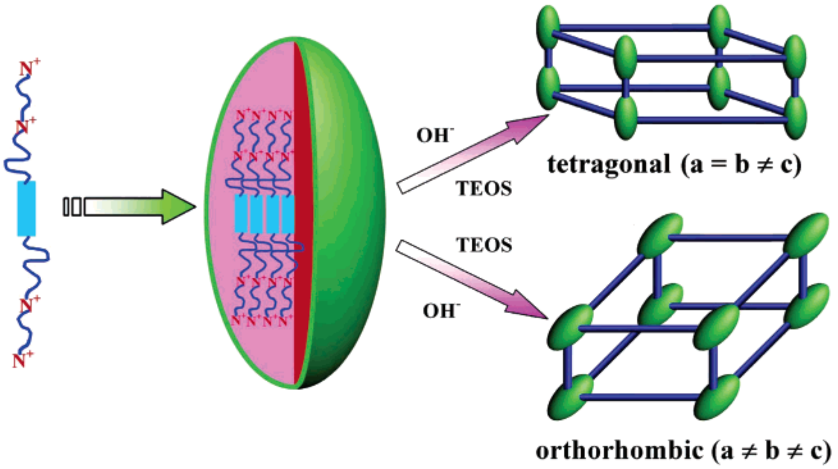

Figure 9. Representative schematic drawings of the formation mechanism for synthesis of low symmetrical mesostructured silica materials template with tetra-headgroup rigid bolaform surfactant $C_{3-12-12-3}$.

set of well-resolved ED patterns taken through the sample tilting (for example, see insets in Figure 8A,B along the [1−1−1], [1−2−2] zone axes) can be well-indexed to the orthorhombic system. Similar to the solution from the SAXS pattern, *P*222, *Pmm*2 (*Pm*2*m*, *P*2*mm*), and *Pmmm* are possible solutions, and we chose the space group *Pmmm* as a possible solution because it is the highest space group. The cell parameters for orthorhombic mesostructure calculated from ED patterns with [1−1−1] and [1−2−2] are $a = 9.72$, $b = 5.65$, and $c = 3.79$ nm, which is commensurate with the values calculated from XRD and SAXS measurements. Although the cell parameters from TEM are slightly different from those from SAXS and XRD, taking into account the systemic error from TEM, XRD, and SAXS patterns, the difference is acceptable.

N_2 adsorption and desorption isotherms (Figure 5b) of the calcined FDU-13 with orthorhombic structure also exhibit representative type IV curves without a hysteresis loop, similar to that of the mesoporous silica materials templated from cationic surfactants, implying that FDU-13 have uniform mesopore connectivity. The BET surface area for calcined FDU-13 is found to be as high as 1210 m^2/g as compared with the silica FDU-11, the uniform BJH mesopore size is about 1.76 nm, and the pore volume is about 1.83 cm^3/g.

To the best of our knowledge, low symmetrical mesostructures with tetragonal *P*4/*mmm* and orthorhombic *Pmmm* space groups have not been observed yet in mesoporous silica structures and even in the lyotropic liquid crystal systems, and their analogues were regarded as one of the most complex yet discovered.[76] The formation mechanism of mesoporous silica with low symmetrical structure templated with tetra-headgroup rigid bolaform surfactant may be difficult to be fully understood at this time. We speculate that the formation of the mesostructures is probably related to the rigid biphenol hydrophobic unit and high charge density of the bolaform surfactant. The aggregation behavior of the bolaform surfactant is similar to that for the coil−rod−coil molecules in aqueous solution,[77] where the inner core of the supramolecular structure is constituted by the discrete rod bundle due to $\pi-\pi$ interaction between biphenols. This kind of supramolecular structure give rises to the formation of the oblate aggregates by the parallel self-organization instead of spherical micelles. We speculate that the oblate aggregate for the bolaform surfactant is responsible for the formation of unusual 3-D packing which is different from cubic or hexagonal symmetry mesophases upon cooperative interacting with the inorganic precursor species (Figure 9). In addition, the ζ-potential of the bolaform surfactant under the synthesis condition is as high as ~31 mv, suggesting a strong electrostatic interaction between the surfactant and the silicate precursors, which facilitates cooperative organization of the silica−surfactant composite.[70] Therefore, the oblate shape of supramolecular aggregation may quickly be fastened by the condensation of the silicate precursors in aqueous solution, and consequently the low symmetric mesostructures are formed.

It should be noted that careful control of the concentration of alkalinity is very essential to obtain the ordered mesoporous silica with low symmetrical structures such as FDU-11 and FDU-13. High pH (>13.5) in the initial aqueous solution results in the formation of unknown mesostructure silica, while low pH (<11.0) in the initial aqueous solution leads to the formation of silica gel. The optimized pH value for synthesis of these mesoporous silica with low symmetrical structures is 13.0−13.3. An unknown silica mesostructure was obtained upon heating the solution containing tetragonal or orthorhombic structure silica at 80 °C for 1 day, suggesting a new mesostructure that is being resolved now in our laboratory.

4. Conclusion

Two well-ordered 3-D mesoporous silica with low symmetrical tetragonal (possible space group *P*4/*mmm*) and orthorhombic (possible space group *Pmmm*) structures have been synthesized in the presence of the tetra-headgroup rigid bolaform surfactant under basic conditions. The lattice constants *a* and *c* in the tetragonal structure are 8.46 and 5.22 nm, respectively, and the corresponding *c*/*a* ratio is 0.617. The lattice parameters (*a*, *b*, and *c*) in the orthorhombic structure are 9.81, 5.67, and 3.66 nm, respectively. The new mesoporous silicas have highly ordered regularity, relatively high surface area (up to 1490 m^2/g), large pore volume (up to 1.88 cm^3/g), and a narrow distribution pore size (~1.76−2.72 nm). The ability to prepare well-defined 3-D low symmetrical mesostructure will open up

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new opportunities for both fundamental studies and their applications in catalysis, adsorption, and separation.

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Supporting Information Available: XRD and SAXS data for FDU-11; XRD and SAXS data for FDU-13. This material is available free of charge via the Internet at http://pubs.acs.org.

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