

Nonionic Block Copolymer and Anionic Mixed Surfactants Directed Synthesis of Highly Ordered Mesoporous Silica with Bicontinuous Cubic Structure

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Mesoporous silica with $Ia\bar{3}d$ structure has been successfully prepared by using mixed surfactants of commercially available nonionic block copolymer P123 (EO₂₀PO₇₀EO₂₀) and anionic sodium dodecyl sulfate (SDS) as structure-directing agents through an acid-catalyzed silica sol–gel process. XRD, TEM, and N₂ sorption measurements show that the products have highly ordered bicontinuous cubic mesostructure with high surface area (~770 m²/g), large pore volume (~1.5 cm³/g), and uniform pore size (~10 nm). Effects of preparation parameters on the formation of the mesostructure have been extensively investigated. It is found that the molar ratios of SDS/P123 between 2.1 and 2.5 and that of silicic species to P123 in the range from 40 to 75 are favorable for the formation of highly ordered $Ia\bar{3}d$ mesostructure. Prolonging hydrothermal treatment time leads to almost unchanged cell parameters of the products, whereas there is obvious increase of the pore sizes and pore volume. The results show that resultant template-free mesoporous silica products have excellent thermal stability, and they are more stable in N₂ atmosphere than in air. Morphologies of the resultant materials can be further controlled by adding inorganic salt (such as Na₂SO₄) into the mixed surfactants system. Coral- and petaline-like mesoporous silica with continuous skeletons can be obtained. Understanding this synthesis system might be useful for economical and large-scale production of mesoporous materials with controllable structures.

Introduction

Since the pioneering discovery of surfactant-templated mesoporous materials reported by Mobil researchers,^{1,2} there has been a growing interest due to their emerging applications in areas such as adsorption, separation, catalysis, drug delivery, photonic and electronic devices, etc.^{3–8} Cationic long-chain quaternary ammonium surfactants such as cetyltrimethylammonium bromide (CTAB) have first been used to prepare highly ordered mesoporous materials.^{1,2} Later, anionic surfactants,⁹ neutral amine surfactants,¹⁰ nonionic poly(ethylene oxide) (PEO) surfactants,¹¹ and block copoly-

mers^{12,13} have been widely studied to synthesize mesoporous materials with various structures and tunable pore sizes. Recently, Che et al. reported several new mesoporous silica structures templated by anionic surfactant molecules in combination with aminosilane or quaternized aminosilane as co-structure-directing agent.^{14–16}

In addition to the above-mentioned templates, highly ordered mesoporous materials can also be prepared by using mixed surfactants as templates. Li and co-workers reported the synthesis of MCM-48 by using the mixture of cationic–anionic or cationic–nonionic surfactants system.^{17–20} M41S type and vesicle-like mesoscopically ordered silica materials were also synthesized by cationic–anionic mixing surfactants.^{21,22} Using the cationic alkyltrimethylammonium bro-

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mides and nonionic PEO alkyl ethers surfactant mixtures as structure-directing agents, Ryoo and co-workers successfully prepared MCM-48 molecular sieves with a remarkably high product yield.²³ Stable ordered mesoporous silica-based materials have also been prepared by using mixtures of cationic fluorocarbon and hydrocarbon polymer surfactants through a high-temperature hydrothermal process.²⁴ By adjusting the hydrophilic/hydrophobic volume ratio (V_H/V_L) of the mixed templating agents, mesoporous materials with different structure symmetries can be “rationally” designed and prepared by using mixed nonionic surfactants.²⁵ However, no report on the synthesis of mesoporous materials by using mixed anionic–nonionic surfactants system has been published until now. In view of the facts that both anionic and nonionic surfactants are very cheap and have been widely used in industrial fields in the processing of their various formulations, research on the synthesis of mesoporous materials templated by anionic–nonionic mixed surfactants may not only be theoretically important, but also provide more options for economical and large-scale productions of mesoporous materials with controllable structures.

In this paper, highly ordered mesoporous silica with bicontinuous cubic structure (space group $Ia\bar{3}d$) has been successfully prepared by using commercially available anionic surfactant sodium dodecyl sulfate (SDS) and nonionic block copolymer P123 mixed surfactants as structure-directing agents through an acid-catalyzed silica sol–gel process. The effects of preparation parameters on the formation of mesostructure have been extensively investigated. The morphology of mesoporous silica materials can be further controlled by the addition of inorganic salts.

Experimental Section

Synthesis. All chemicals were used as received without purification. Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer EO₂₀PO₇₀EO₂₀ denoted P123 (Mw = 5800) was purchased from Aldrich. Other chemicals were purchased from Shanghai Chemical Company. Millipore distilled water was used in all experiments.

A typical synthesis of cubic $Ia\bar{3}d$ mesoporous silica was as follows. P123 (1.00 g) and SDS (0.115 g) were dissolved in a mixture of 26.0 g of water and 12.0 g of HCl of 2.0 M at 30 °C. To this solution, 2.15 g of tetraethyl orthosilicate (TEOS) was added under vigorous stirring. The final reactant molar composition of P123/SDS/HCl/H₂O/TEOS was 1.00:2.30:139:1.20 × 10⁴:59.8. The reaction mixture was stirred at the same temperature for 1 day, then sealed within a Teflon autoclave and heated at 100 °C for another 24 h (referred to as hydrothermal treatment time). The solid products were collected by filtration, washed with water, and dried in air at room temperature. The resultant powders were calcined at 550 °C for 5 h in air to remove the templates, and the final mesoporous silica materials were obtained.

To control the morphology of the products, Na₂SO₄ solution with different concentrations (0.01–0.5 M) was used instead of water,

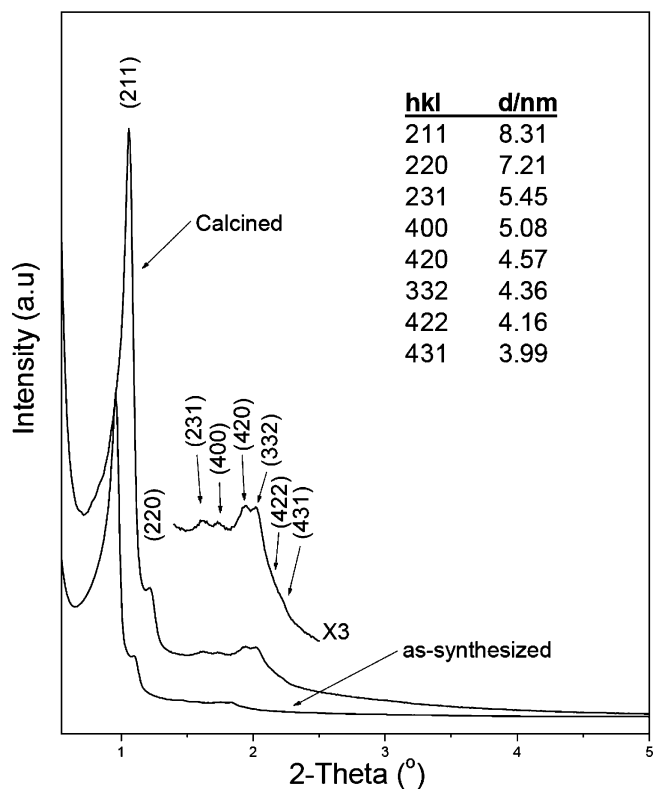


Figure 1. XRD patterns of the as-synthesized and calcined cubic $Ia\bar{3}d$ mesoporous materials prepared with hydrothermal treatment time for 1 day by using the mixed surfactant of SDS and P123.

and the mixture was kept in static condition after stirring for 30 min after the adding of TEOS. Except for these differences, other conditions were identical with the procedures described above.

Characterization. The structural quality of the mesoporous silica products was monitored by low-angle X-ray diffraction (XRD), recorded on a German Bruker D4 X-ray diffractometer with Ni-filtered Cu K α radiation. Transmission electron microscopy (TEM) images were obtained with a JEOL 2011 microscope operated at 200 kV. For TEM measurements, the samples were prepared by dispersing the powder samples in ethanol; after that they were dispersed and dried on the carbon film on a Cu grid. Scanning electron microscopy (SEM) images were obtained on a Philips XL30 microscope operated at 20 kV. Nitrogen adsorption/desorption isotherms were measured at –196 °C by using a Micromeritics ASAP Tristar 3000 system. The samples were degassed at 180 °C overnight on a vacuum line.

Results and Discussion

$Ia\bar{3}d$ Mesostructured Silica Templated by SDS–P123 Mixed Surfactants. XRD patterns of as-synthesized and calcined mesoporous silica materials prepared by nonionic P123 and anionic SDS mixed surfactants at 30 °C are shown in Figure 1. For as-synthesized mesoporous silica product, its XRD pattern shows characteristic diffraction peaks of bicontinuous cubic structure (Figure 1a). After calcination at 550 °C in air, much stronger diffraction peaks can be observed for the surfactant-removed products. Figure 1b shows eight well-resolved diffraction peaks that can be indexed to (211), (220), (321), (400), (420), (332), (422), and (431) reflections of the bicontinuous cubic structure (space group $Ia\bar{3}d$), indicating that the highly ordered mesostructure of the material is thermally stable. The cell

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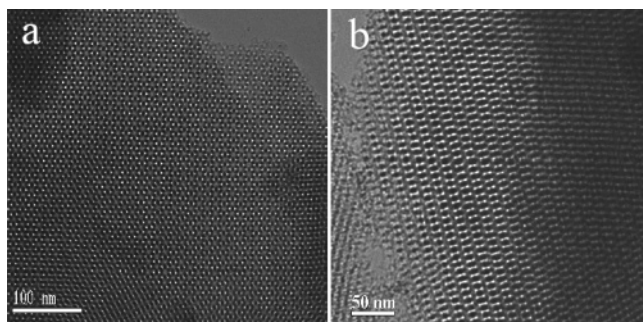


Figure 2. TEM images of calcined cubic $Ia\bar{3}d$ mesoporous silica prepared from mixed surfactant of SDS and P123 taken along (a) [111] and (b) [311] zone axis, respectively.

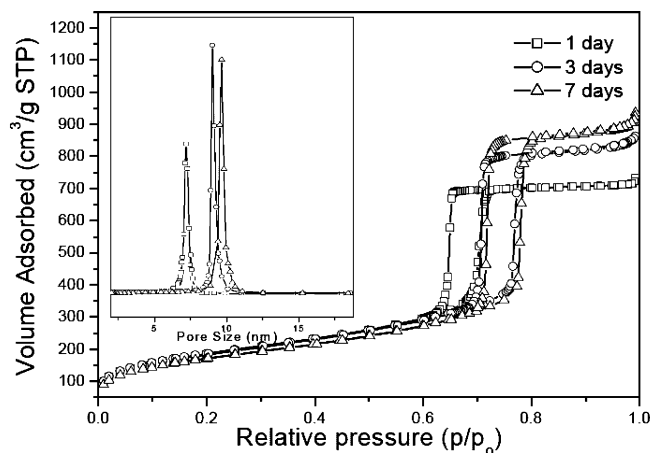


Figure 3. N_2 sorption isotherms and pore size distribution curves (inset) of the calcined mesoporous silica prepared by mixed surfactant of SDS and P123 with different hydrothermal treatment times.

parameters, a , are 22.6 and 20.4 nm for as-synthesized and calcined samples, respectively.

TEM images further confirm that the mesoporous silica prepared by using mixed templates of nonionic block copolymer and anionic surfactants have bicontinuous cubic mesostructure. As shown in Figure 2, the representative TEM images viewed along [111] and [311] directions reveal that these products consist of large ordered domains of cubic $Ia\bar{3}d$ structure. The cell parameter, a , obtained from TEM analysis is 20.3 nm for the calcined sample, in good agreement with that calculated from XRD measurements.

The nitrogen adsorption–desorption isotherms and corresponding pore size distribution of the calcined products are shown in Figure 3. The calcined silica materials prepared by hydrothermally heating at 100 °C for 24 h yield a type IV isotherm with a sharp capillary condensation step at high relative pressures ($P/P_0 = 0.7–0.8$), and an H_1 -type hysteresis loop. This result is in agreement with that from a large-pore cubic ($Ia\bar{3}d$) mesoporous silica reported previously,^{26–29} suggesting typical ordered mesoporous materials with bicontinuous channels. A narrow pore size distribution with a

Table 1. Physical Properties of the $Ia\bar{3}d$ Structured Mesoporous Silica

sample ^a	a (nm)	pore size (nm)	pore volume (cm ³ /g)	surface area (m ² /g)
4a	20.4	7.1	1.13	768
4b	20.8	9.0	1.33	700
4c	21.0	9.8	1.48	713
7a	18.8	5.5	0.78	475
7b	17.0	4.6	0.48	338
8a	20.1	6.5	1.03	738
8c	20.3	6.4	1.00	730
8e	20.6	6.3	1.05	746

^a 4a, 4b, and 4c denote the sample shown in Figure 4a, b, and c; 7a and 7b denote that shown in Figure 7a and b; and 8a, 8c, and 8e denote that shown in Figure 8a, c, and e, respectively.

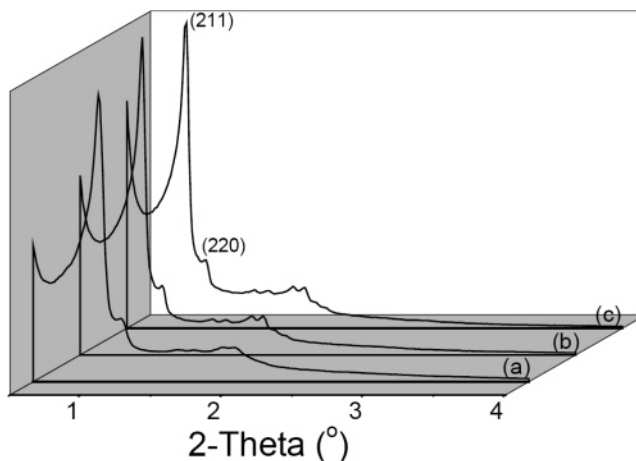


Figure 4. XRD patterns of the calcined cubic $Ia\bar{3}d$ mesoporous silica prepared with hydrothermal treatment for (a) 1 day, (b) 3 days, and (c) 7 days.

mean value of 7.1 nm is calculated from the adsorption branch by Barrett–Joyner–Halenda (BJH) method. Although the BJH model is known to underestimate pore size,^{30,31} it has been widely adopted in the mesostructured materials community for comparison. The calcined mesoporous material has a BET surface area of 768 m²/g and a pore volume of 1.13 cm³/g (Table 1).

The influence of hydrothermal treatment time on mesostructure of the final materials has been studied. XRD patterns of the calcined samples under different hydrothermal treatment times for 1, 3, and 7 days are shown in Figure 4. All products show well-resolved diffraction peaks and characteristic XRD patterns of $Ia\bar{3}d$ mesostructure, suggesting the high quality of resultant mesoporous materials. The corresponding XRD analyses show that prolonging the treatment time from 1 day to 3 or 7 days leads to a slight increase in cell parameters of the products from 20.4 to 20.8 or 21.0 nm (Table 1). It is noted that the XRD peaks at relatively high angles are relatively more resolved for the materials with longer hydrothermal treatment time. Such observation might be attributed to the fact that the wall framework is more condensed with increasing hydrothermal treatment time, leading to higher wall-pore contrast of final mesoporous materials. For the samples with different hydrothermal treatment time, there are steep changes from the adsorption

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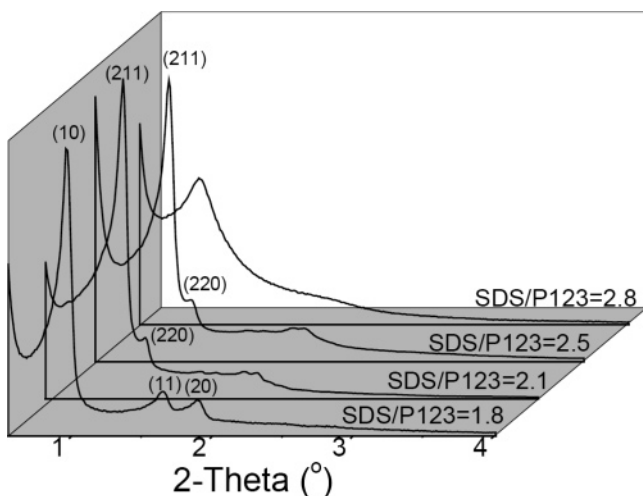


Figure 5. XRD patterns of the calcined mesoporous silica synthesized with different SDS/P123 molar ratios.

and desorption branches at high relative pressures ($P/P_0 = 0.6-0.8$) in their N_2 sorption isotherms, indicating that all of them have fairly narrow pore size distribution. With the increase of hydrothermal treatment time, the obvious shifts for both adsorption and desorption branches to higher relative pressures can be observed in the N_2 sorption isotherms (Figure 3), suggesting that the pore sizes are enlarged. When hydrothermal treatment (at 100 °C) time is increased from 1 day to 3 or 7 days, the pore sizes of resultant products can be increased from 7.1 to 9.0 or 9.8 nm (Table 1, Figure 3). Meanwhile, the pore volumes increase from 1.13 to 1.33 or 1.48 cm^3/g . These results suggest that the hydrothermal treatment is an efficient method to enlarge the pore size and pore volume, while the bicontinuous cubic structure directed by the anionic surfactant and nonionic block copolymer binary system is still highly ordered.

To investigate the effect of SDS molecules on the formation of mesostructure in final silica materials, further experiments were conducted by varying SDS/P123 molar ratio in this mixed surfactants system. XRD patterns (Figure 5) show that highly ordered mesoporous silica with bicontinuous cubic $Ia\bar{3}d$ mesostructure can be formed when the molar ratio of SDS/P123 is between 2.1 and 2.5. When the ratio is below 2.1, hexagonal $p6m$ mesoporous silica materials are obtained. On the other hand, increasing the SDS/P123 molar ratio up to 2.8, products with disordered mesostructure form as indicated by its broad XRD diffraction peak. These results suggest that the bicontinuous cubic $Ia\bar{3}d$ mesostructure can be prepared in a narrow range. Studies on micellization behavior of the triblock copolymers and anionic mixed surfactants showed that SDS molecules prefer binding to the more hydrophobic PPO blocks than to the hydrophilic PEO blocks even when the SDS concentration is far below its critical micelle concentration (CMC) and this interaction could lead to the formation of mixed surfactants micelles with the PPO blocks existing in a more or less extended conformation.³²⁻³⁴ By increasing the concentration of the anionic surfactant in this mixed surfactants system, SDS molecules bound to copolymers would be saturated;

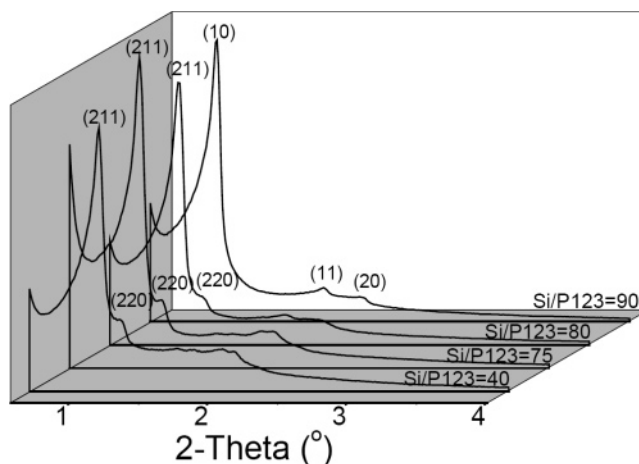


Figure 6. XRD patterns of the calcined mesoporous silica synthesized with different Si/P123 molar ratios.

further adding anionic surfactant might lead to the breakdown of mixed micelles to smaller aggregates.³²⁻³⁴ Therefore, when the molar ratio of SDS/P123 is between 2.1 and 2.5, the mixed surfactant micelles could get the larger hydrophobic volume due to the binding of SDS molecules onto the more hydrophobic PPO blocks and lower hydrophilic/hydrophobic volume ratio (V_H/V_L) and smaller interface curvature, which favor the formation of $Ia\bar{3}d$ mesostructured materials. This result is similar to the *n*-butanol-P123 mixed system reported by Ryoo and co-workers.²⁶ While the molar ratio of SDS/P123 is below 2.1, the small quantity of SDS molecules bound to the PPO blocks could not significantly affect the V_H/V_L ratio and the hexagonal $p6m$ mesophase could be formed. On the other hand, the more SDS molecules added into the solution might disturb the self-organization of the block copolymer and result in disordered mesostructure.

The effect of the silicic species to P123 molar ratio (Si/P123) on the formation of final mesoporous materials was also investigated in this mixed surfactants system. As shown in the XRD patterns (Figure 6), the highly ordered mesoporous silica with $Ia\bar{3}d$ structure can be prepared when the molar ratio of Si/P123 is between 40 and 75. By increasing the Si/P123 molar ratio to 80, only mesoporous silica with mixed structures of $p6m$ and $Ia\bar{3}d$ can be obtained as evidenced from the XRD and TEM analysis. Further increasing the Si/P123 molar ratio to 90, the hexagonal $p6m$ silica mesophase forms. In fact, adding TEOS into this system will simultaneously increase the molar quantity of silicic species and that of ethanol molecules released by hydrolysis of TEOS. To make sure of the effect of ethanol on the formation of silica mesostructure in this system, a further experiment was carried out by fixing the molar ratio of Si/P123 at 60 and adding 1.27 g of ethanol into the precursor solution (in this case, the total quantity of ethanol in this system equals that generated by TEOS with an Si/P123 molar ratio of 100). XRD pattern of the resultant silica reveals that highly ordered cubic $Ia\bar{3}d$ mesostructured silica can be obtained from solution, suggesting that the molar

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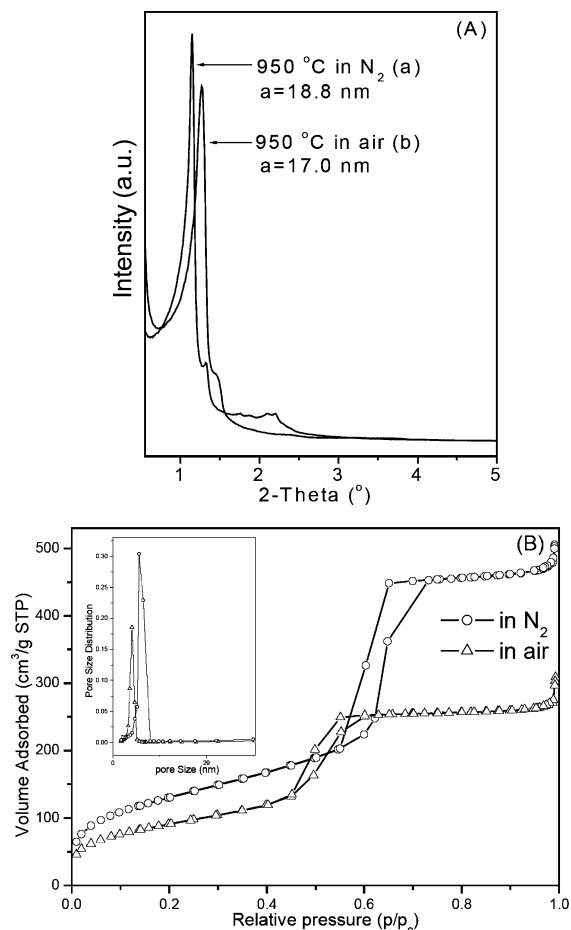


Figure 7. (A) XRD patterns and (B) N₂ sorption isotherms and pore size distribution curves (inset) of the mesoporous silica samples calcined at 950 °C in air and N₂, respectively.

ratio of Si/P123 is the major factor for the formation of the silica mesostructure, while ethanol released by hydrolysis of TEOS molecules has a minor effect in this process.

Besides SDS surfactant, other anionic surfactants such as sodium dodecyl benzene sulfonate (SDBS) can also be used to prepare the highly ordered silica with $Ia\bar{3}d$ mesostructure in the presence of nonionic P123 block copolymer. In this case, the favorable molar ratio of P123/SDBS for $Ia\bar{3}d$ mesostructure is 1.00:1.25, slightly smaller than that of P123/SDS.

It is noted that the obtained mesoporous materials are very stable. When the products were calcined at 950 °C in N₂ or in air for 4 h, the mesostructures could be retained as illustrated by corresponding XRD and nitrogen sorption studies (Figure 7). Compared with the materials calcined at 550 °C, the shrinkage in the cell parameters is only 7.84% or 16.7% for resultant products calcined in N₂ or in air, respectively. N₂ sorption measurements show BET surface area of 475 or 338 m²/g, pore volume of 0.782 or 0.478 cm³/g, and a narrow pore size distribution with the maximum at ca. 5.5 or 4.6 nm for the materials calcined at 950 °C in N₂ or in air, respectively (Table 1). About 66% or 41% for the pore volume and 62% or 44% for surface area are retained after calcination in N₂ or in air at 950 °C, respectively, indicating that the mesostructure has high thermal stability, and it is more stable in N₂ than in air.

Morphology of Highly Ordered Mesoporous Silica with Cubic $Ia\bar{3}d$ Structure. Recently, lots of efforts have been made to prepare mesoporous materials with $Ia\bar{3}d$ structure in the presence of nonionic block copolymer,^{26–29,35,36} however, research on simultaneous control of these materials at both macro- and meso-structure in acid media has not yet been reported. In this contribution, several mesostructured silica materials with different morphologies were obtained by adding inorganic salt with different concentration.

Figure 8 shows representative SEM images for these mesostructured materials synthesized in Na₂SO₄ solution. Mesoporous silica with macropores ca. 2–10 μm in diameter precipitates from the solution when the Na₂SO₄ concentration is 0.01 M, and it can be seen that the adjacent macropores are interconnected by some small pores ca. 0.1–1 μm (Figure 8a and b). XRD pattern (Figure 9) of this sample shows that silica skeletons of this material uniquely consist of pure bicontinuous cubic mesostructure. By increasing the Na₂SO₄ concentration up to 0.10 M, coral-like mesoporous silica materials with co-continuous gel skeletons and macropores in the micrometer range are obtained. SEM image at low magnification reveals that this material is very homogeneous even at hundreds of micrometers scale (Figure 8c and d). When Na₂SO₄ concentration increases to 0.20 M, petaline-like mesoporous silica (Figure 8e and f) is obtained. XRD patterns show that both coral-like and petaline-like materials have highly ordered $Ia\bar{3}d$ mesostructures (Figure 9). Nitrogen sorption isotherms reveal that these materials have high BET surface areas, large pore volume, and fairly narrow pore size distribution (Table 1).

It is well-known that a phase separation process is usually observed during the cooperative assembly of silicates species and surfactants, and various macro-structures, depending on the relative onset of phase separation and sol–gel transition, can be retained in the inorganic skeletons by gelation transition.^{37–41} For systems with similar starting composition, particle aggregates are usually obtained by the early phase separation relative to sol–gel transition; inversely, morphology with isolated macropores is the result of sol–gel transition that takes place relatively earlier than the phase separation process. Under the reaction condition between the above-mentioned two cases, materials with continuous gel skeletons and macropores form due to the concurrent phase separation and sol–gel transition.^{37–41} In the present mixed surfactant system with abundant 0.60 M HCl aqueous solution, the sol–gel transition kinetics of silica depends weakly on the solution composition. Morphologies of the final mesoporous materials, therefore, might be mainly determined by phase separation tendency of the surfactants–silica composite. It is found that there is an obvious decrease

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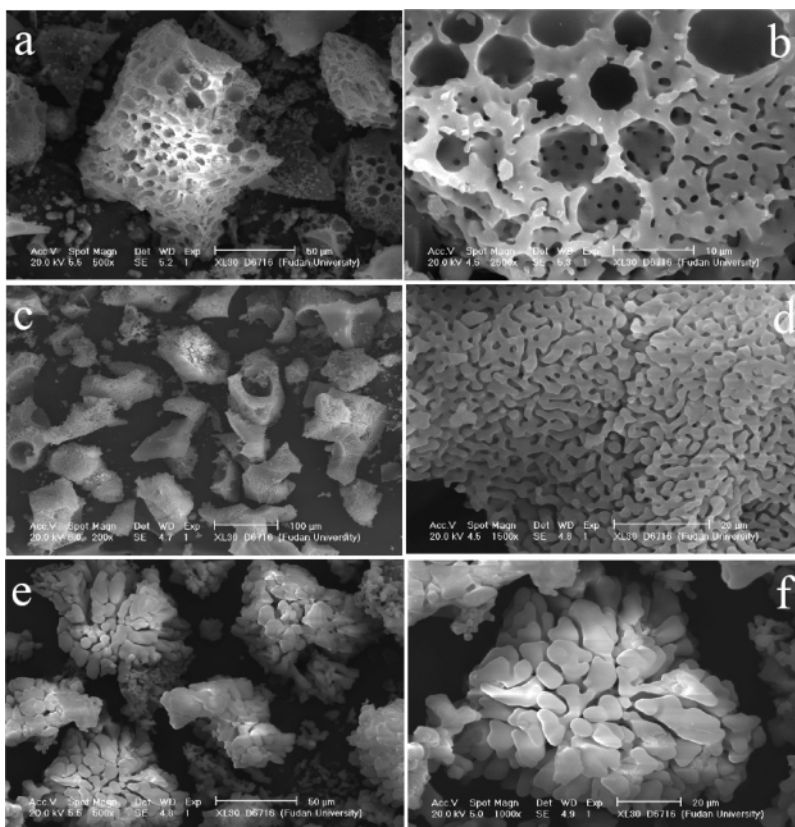


Figure 8. SEM images with different magnification of the $Ia\bar{3}d$ structured mesoporous silica synthesized from (a) and (b) 0.01, (c) and (d) 0.10, and (e) and (f) 0.20 M Na_2SO_4 solution.

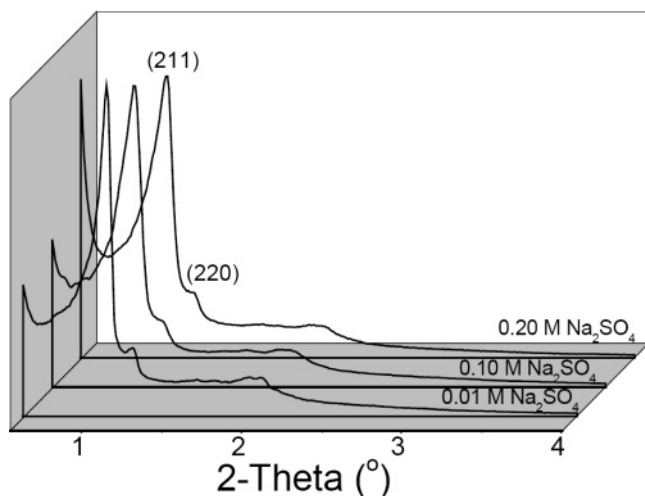


Figure 9. XRD patterns of the calcined mesoporous silica prepared from Na_2SO_4 solutions with different concentrations.

in phase separation time (the period from adding of TEOS to the time when precipitate is first observed in solution) of the surfactants–silica composites with the increasing of Na_2SO_4 concentration. When Na_2SO_4 concentration is 0.01 M, at least 145 ± 3 min is needed for the occurrence of phase separation. Increasing Na_2SO_4 concentration from 0.01 to 0.10 M, the time shortens to 128 ± 3 min; further increasing the salt concentration to 0.20 M, only 119 ± 3 min is required. These results suggest that the phase separation process is largely accelerated relative to gelation transition of the silicic oligomers with the increase of inorganic salt concentration in the mixed surfactants system, and similar

phenomenon has been discussed in our previous paper based on the well-known Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.⁴² It is proposed that phase separation process of the surfactants–silica composites is relatively slow and comparable to their gelation transition in the system with low salt concentration (0.01–0.1 M), therefore, materials with interconnected macroporous morphology are observed (Figure 8b and d). Increasing salt concentration to 0.2 M may induce a faster phase separation process of the surfactants–silica composites than their gelation transition, and leads to the mesoporous silica formed by the aggregation of small particles (Figure 8e and f). In this case, surface free energy of the liquid crystal-like composite derived from the phase separation process has considerable influence upon morphology of the final solid phase, which favors the formation of spherical particles in order to minimize its surface area.⁴²

Conclusions

Highly ordered mesoporous silica with bicontinuous cubic $Ia\bar{3}d$ structure has been successfully prepared by using mixed surfactants of commercially available anionic SDS and nonionic P123 as structure-directing agents through an acid-catalyzed silica sol–gel process. The molar ratios of SDS/P123 between 2.1 and 2.5 and that of Si/P123 in the range from 40 to 75 are favorable for the formation of highly ordered $Ia\bar{3}d$ mesostructure. The products have large pore

(42) Yu, C. Z.; Fan, J.; Tian, B. Z.; Zhao, D. Y. *Chem. Mater.* **2004**, *16*, 889.

volume ($\sim 1.5 \text{ cm}^3/\text{g}$), uniform pore size ($\sim 10 \text{ nm}$), and excellent thermal stability in N_2 atmosphere. The morphology of the final products can be further varied by adding inorganic salt Na_2SO_4 into the synthesis system. The obtained mesostructured silica materials might find applications as catalyst supports, antibacterial substrates, or in the immobilization and controlled release of biomolecules, and protein separation.

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