Research Article

Control the Morphologies and the Pore Architectures of Mesoporous Silicas through a Dual-Templating Approach

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Mesoporous silica nanospheres were prepared using a chiral cationic low-molecular-weight amphiphile and organic solvents such as toluene, cyclohexane, and tetrachlorocarbon through a dual-templating approach. X-ray diffraction, nitrogen sorption, field emission scanning electron microscopy, and transmission electron microscopy techniques have been used to characterize the mesoporous silicas. The volume ratio of toluene to water plays an important role in controlling the morphologies and the pore architectures of the mesoporous silicas. It was also found that mesoporous silica nanoflakes can be prepared by adding tetrahydrofuran to the reaction mixtures.

1. Introduction

It has been two decades since the discovery of ordered mesoporous silica materials [1]. Recent reports are focused on the precise control of the pore size, accessibility, stability, morphologies, and surface functionalization of the mesoporous silicas, due to their versatile applications in chemical separation, catalysis, photonic devices, biosensors, and drug delivery [2]. Mesoporous silicas were usually prepared through a sol-gel approach using the organic self-assemblies of surfactants [3], lipid [4], low-molecular-weight gelators [5], or block copolymers [6] as template. Since these templates can self-assemble into varieties of nanostructures, the obtained silicas exhibit many kinds of nanostructures such as films [7, 8], spheres [9], fibers [10], tubes [11], and ribbons [12]. As the organization of the templates is sensitive to the surrounding conditions such as temperature, concentration, and solvents, varieties of silica nanostructures can be prepared only using single template, and the morphologies and pore architectures of mesoporous silicas are controllable via modification of preparation conditions.

Mesoporous silicas through a dual-templating approach have attracted much attention because of some special hollow-shell structures might be obtained by this way.

The hollow structures find applications in chromatography, nanocatalysts, bimolecular encapsulation, gene delivery, and drug storage and release due to their unique properties of large cavity, low density, high pore volume, and permeable mesoporous walls [13]. Generally, polymer beads, air bubbles, oil droplets, colloids, or vesicles have been used to control the sizes of hollow cores, while amphiphile self-assemblies have been used to control the diameters of the pores in the shells [14–18]. However, the exact structural nature of mesoporous silica through a dual-templating approach and their formation manner under different synthesis conditions remain unclear so far. Herein, mesoporous silicas using a chiral cationic low-molecular-weight amphiphile and organic solvents such as toluene, cyclohexane, tetrachlorocarbon, and tetrahydrofuran through a dual-templating approach were described. Nanospheres and nanoflakes had been obtained by tuning the kind and amount of the organic solvents precisely.

2. Experimental

2.1. Chemicals and Reagents. Tetraethyl orthosilicate (TEOS) was purchased from Aldrich. Toluene, cyclohexane, tetrahydrofuran, and tetrachlorocarbon were purchased from Sinopharm Chemical Reagent Co., Ltd.

FIGURE 1: Molecular structure of the compound L-18Phe6NEt₃Br.

2.2. Characterization. FT-IR spectrum was taken on a Nicolet 6700 spectrometer, using KBr pellets of the solids. The ¹H NMR spectrum was recorded on a Varian NMR 400 spectrometer in DMSO-*d*⁶ solutions using TMS as an internal standard. Elemental analysis was performed on a Perkin Elmer series II CHNS/O analyzer 2400. Circular dichroism (CD) and UV-Vis spectra were measured on an AVIV 410 spectrophotometer. TEM images were obtained using a TecnaiG220 microscope operating at 200 kV. FESEM images were taken on a Hitachi S-4800 microscope operating at 15 kV. Before taking the FESEM images, the sample surface was coated with platinum. Specific surface area and pore-size distribution were determined by the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods using N₂ desorption isotherms measured by a Micromeritics ASAP 2020 M+C instrument at 77 K. Small angle X-ray diffraction (SAXRD) pattern was taken on an X' Pert-Pro MPD X-ray diffractometer using Cu Kα radiation.

2.3. Preparation of Mesoporous Silica Nanostructures

2.3.1. Characterization of L-18Phe6NEt₃Br. Compound L-18Phe6NEt₃Br (Figure 1), which is composed of l-phenylalanine, was synthesized according to the literature [19]. FT-IR (KBr): 3294 cm⁻¹ (ν_{N-H}, amide A), 1651 cm⁻¹ (ν_{C=O}, amide I), 1543 cm⁻¹ (ν_{N-H}, amide II). ¹H NMR (300 MHz, DMSO-*d*⁶, TMS, 25°C): δ = 0.83 (*t*, *J* = 6.4 Hz, 3H; CH₃), 1.15 (*d*, *J* = 7.2 Hz, 3H; CHCH₃), 1.13–1.41 (*br*, 30H; alkyl), 1.69 (*m*, 2H; CONHCH₂CH₂), 1.99–2.08 (*m*, 2H; CH₂CH₂CONH), 2.67–2.75 (*m*, 2H; CH₂CONH), 2.87–3.01 (*m*, 2H; CONHCH₂), 4.35 (*q*, *J* = 7.8 Hz, 1H; PhCH₂CH), 4.48–4.65 (*t*, *J* = 7.2 Hz, 2H; PhCH₂), 7.21 (*m*, 1H; 1-PhH), 7.12 (*t*, *J* = 7.5 Hz, 1H; 3-PhH), 7.08 (*t*, *J* = 5.4 Hz, 1H; 2-PhH), 7.88 (*t*, *J* = 9.1 Hz, 1H; CONHCH₂), 7.99 (*d*, *J* = 7.8 Hz, 1H; CONHCH). Elemental analysis calcd(%): C, 67.41; H, 10.44; N, 6.05. Found: C, 65.63; H, 9.86; N, 5.91.

2.3.2. Synthetic Procedure for the Mesoporous Silica S0. A typical synthetic procedure was shown as follows: 200 mg (0.31 mmol) of L-18Phe6NEt₃Br was dissolved in 50.0 mL of deionized water. Then, 0.35 mL of aqueous NaOH (2.0 M) solution and 0.5 mL of toluene were added at the stirring rate of 1500 rpm at 80°C. 3.0 min later, 1.0 mL (4.5 mmol) of TEOS was dropped into the mixtures under stirring. The reaction mixture was kept at that temperature for 2.0 hrs. The

resultant white precipitate was filtered and dried to yield as-prepared mesoporous silica. L-18Phe6NEt₃Br was removed by extracting with a mixture of 80 mL of methanol and 10 mL of 36 wt% aqueous HCl solution. Finally, calcination was preformed at 550°C for 5.0 h under aerobic conditions, with a ramp rate of 1.0°C min⁻¹.

2.3.3. Synthetic Procedure for the Mesoporous Silicas S1 Series. Toluene was added into the reaction mixture. The toluene/water volume ratio was varied (0.01, 0.02, 0.04) while keeping the other reaction conditions constant. The obtained samples were named as S1-1, S1-2, and S1-3, respectively.

2.3.4. Synthetic Procedure for the Mesoporous Silica S2. The synthetic procedure is similar as that for S0, except for the addition of 1.0 mL of cyclohexane and that the reaction temperature is 65°C.

2.3.5. Synthetic Procedure for the Mesoporous Silica S3. The synthetic procedure is similar as that for S0, except for the addition of 1.5 mL of tetrachlorocarbon and that the reaction temperature is 65°C.

2.3.6. Synthetic Procedure for the Mesoporous Silica S4. The synthetic procedure is similar as that for S0, except for the addition of 1.0 mL of THF and that the reaction temperature is 65°C.

3. Results and Discussion

3.1. Characterization of L-18Phe6NEt₃Br. For a certain amphiphile, it can self-assemble into supramolecular structures through H-bondings, solvophobic associations, cationic-anionic and π-π interactions, and the self-assembly behaviors are sensitive to solvents, pH values, and temperatures [20, 21]. Compound L-18Phe6NEt₃Br causes viscous liquid in deionized water with a concentration of 10 g L⁻¹ at 25°C, and physical gels in cyclohexane, ethanol, and 1,4-dioxane, and shows low solubility in toluene, THF, and acetone. The CD and UV-Vis spectra of its aqueous solutions at a concentration of 10 g L⁻¹ are shown in Figure 2. The UV-Vis spectrum shows an absorption band at 259 nm attributed to the aromatic rings. A positive signal at 225 nm and a negative signal at 221 nm in the CD spectrum

FIGURE 2: CD and UV-Vis spectra of the compound **L-18Phe6NEt₃Br**.

FIGURE 3: FESEM images of the mesoporous silica nanostructures **S0** (a) and **S1** prepared in the mixtures of toluene and water (**S1-1** (b); **S1-2** (c); **S1-3** (d)).

FIGURE 4: TEM images of the mesoporous silica nanostructures **S0** (a), **S1-1** (b), **S1-2** (c), and **S1-3** (d).

FIGURE 5: SAXRD patterns of the mesoporous silica nanostructures **S0** (a), **S1-1** (b), **S1-2** (c), and **S1-3** (d).

FIGURE 6: N₂ adsorption-desorption Sorption isotherms (A) and BJH pore size distribution plots calculated from the desorption branch (B) of the mesoporous silica nanostructures **S0** (a), **S1-1** (b), **S1-2** (c), and **S1-3** (d).

are identified, indicating a right-handed staking among the chiral molecules.

3.2. Characterization of Mesoporous Silicas **S0 and **S1**.** The FESEM images of them were shown in Figure 3. For **S0**, nanospheres with diameters of 80–150 nm were identified (Figure 3(a)). When toluene was added into the reaction mixture at the toluene/water volume ratio of 0.01, 0.02, and 0.04, samples **S1-1**, **S1-2**, and **S1-3** were obtained, respectively. The FESEM images of them were shown in Figures 3(b) to 3(d). It was found that the toluene/water volume ratio played an important role in controlling the morphologies of the mesoporous silicas. For **S1-1**, nanospheres with sponge-like mesopores inside were identified (Figure 3(b)). The diameters of the nanospheres are about 80–150 nm. Fine toluene droplets were proposed as the templates for the sponge-like mesopores. For **S1-2**, hollow nanostructures with diameters about 80–300 nm were identified (Figure 3(c)). The fine toluene droplets were proposed to merge together and then acted as templates for the hollow nanostructures. The structure of **S1-3** is similar as **S1-2**. Hollow silica nanospheres with a large inner cavity of 150–200 nm were identified (Figure 3(d)). Namely, with increasing the toluene/water volume ratio, the morphologies of the silicas changed from solid spheres to hollow spheres.

The TEM images of **S0** and **S1** series were shown in Figure 4. For **S0**, partially hexagonally organized mesopores were identified (Figure 4(a)). It is difficult to discern whether the mesopores on the surface of spheres are close or open. These nanospheres are not hollow. For **S1-1**, the mesopores seem to be also hexagonally organized (Figure 4(b)). The pore diameter is estimated to be 5–8 nm. For **S1-2**, hollow silica nanococoons with coiled pore channels within the

shells were identified (Figure 4(c)). The linkage of the nanococoons induced the formation of the chambers. TEM image of **S1-3** samples confirmed the hollow spherical morphology (Figure 4(d)). The thickness of the shell is around 10 nm, and the circular pore channels can be clearly discerned within the shells (Figure 4(d)). The results shown in Figure 4 indicated that the silicas changed from spheres with hexagonally arranged pore channels to hollow spheres with single-layer of coiled ones in the walls, with increasing the toluene/water volume ratio.

The SAXRD patterns of the mesoporous silicas **S0**, **S1-1**, **S1-2**, and **S1-3** are shown in Figure 5. For **S0**, two well-resolved diffraction peaks at 2θ of 1.5° and 2.4° are identified, indicating a two-dimensional hexagonal symmetry, which consists with TEM images shown in Figure 4(a). For **S1-1**, only one broad diffraction peak at 2θ of 1.2° is identified, which indicates that this material does not exhibit a long range order. The d -spacing calculated from the diffraction peak is 3.8 nm. For **S1-2** and **S1-3**, no sharp diffraction peaks are identified, indicating a less ordered mesostructure, which consist with the TEM images shown in Figures 4(c) and 4(d). The addition of toluene destroyed the ordered arrangement the mesopores.

The mesoporosity of these samples was characterized using a nitrogen sorption analysis. They exhibit type-IV-like isotherms (Figure 6(A)). It is noticeable that the isotherms of **S0**, **S1-1**, and **S1-2** show two sharp capillary-condensation steps in the relative pressure range of 0.4–1.0, indicating the existence of two types narrow mesopore size distributions. The capillary-condensation step at ca. 0.42 in relative pressure is an indication of typical uniform mesopores in the shell, while that occurred at a relative pressure of 0.9 is probably a result of the hollow cores and voids among the

FIGURE 7: FESEM (a, c, and e) and TEM (b, d, and f) images of the mesoporous silica nanostructures **S2** (a and b), **S3** (c and d), and **S4** (e and f).

particles. For **S0**, **S1-1**, **S1-2**, and **S1-3**, the BET surface areas are 540, 752, 507, and 369 m²/g, and the BJH pore diameters determined from the desorption branch are 4.71, 5.3, 4.1, and 3.8 nm, respectively (Figure 6(B)). The change of surface area is due to the formation of larger hollow cavity inside the nanospheres.

It is reported that the addition of organic dopants can decrease the critical micelle concentration of surfactant and enhance the formation of rod-like or worm-like micelles. Lamellar structures are feasible to be formed by increasing the molarity of organic dopants [22]. Toluene, as a kind of water-immiscible organic dopant, can construct vesicles together with self-assembled amphiphile amino acid derivatives to form a hollow cavity structure through a vesicle templating process. Subsequently, amphiphile compound **L-18Phe6Net₃Br** with a strong positively charged $-N^+$ may interact with negatively charged silica species to build mesostructured walls around the vesicles by a liquid-crystal templating process [23], which determines the final structure of silica hollow spheres. When the addition amount of toluene is small, the fine vesicles destroy the regularity of hexagonal mesopores; therefore, some sponge-like mesopores appear inside silica nanospheres **S1-1** (Figure 3(b)). When more toluene is added to the reaction mixture, larger oil droplets may be formed due to phase separation and then act as hard template for the nanospheres. The amphiphile compound molecules act as soft template, accumulating on the oil-water interface, self-assembling, and interacting with silica species. When the oil droplet is removed, a hollow-shell structure forms. Meanwhile, the circular pore channels are formed on the shell after getting rid of the amphiphile compound (Figures 3(c) and 3(d)).

3.3. Characterization of Silicas S2, S3, and S4 Prepared Using Cyclohexane, Tetrachlorocarbon, and Tetrahydrofuran as the Organic Solvents, Respectively. Since the addition of organic solvents strongly affect the morphologies and pore architectures of mesoporous silicas [24], samples prepared in the mixture of water and other organic solvents as cyclohexane, tetrachlorocarbon, and THF are obtained and studied, which were named as **S2**, **S3**, and **S4**, respectively. For **S2**, the obtained products are nanospheres about 50–150 nm in diameter (Figure 7(a)). Mesopores uniformly distribute within the spheres (Figure 7(b)). **S3** is similar as **S2** (Figures 7(c) and 7(d)). However, the arrangement of the mesopores is not ordered. Both samples **S2** and **S3** are not hollow. Unlike above, four sphere-like samples **S0-S3**, **S4**, are flake-like (Figure 7(e)). The diameters and the thickness of the flakes are about 100–200 and 50 nm, respectively. The hexagonally arranged are parallel to the short axes of the nanoflakes with a pore diameter of about 6.0 nm (Figure 7(f)). THF is a water-miscible polar solvent, while cyclohexane and tetrachlorocarbon, are immiscible with water. The formation of these fine mesoporous silica flakes might be explained by the fact that **L-18Phe6Net₃Br** exhibits high solubility in THF. Then, **L-18Phe6Net₃Br** acted as a surfactant in the mixture of water and THF. Finally, the hexagonally arranged pore architecture was obtained. Such

nanoflakes with perpendicular pores have been also prepared through other approach [25]. These ordered perpendicular pore channels are expected to have potential applications in many fields such as separation membranes and hard templates for nanorods or nanofibers.

4. Summary

Mesoporous silica nanospheres, hollow nanospheres, and nanoflakes were prepared using a chiral cationic low-molecular-weight amphiphile and organic dopants, such as toluene, cyclohexane, tetrachlorocarbon, and THF through a dual-templating approach. Since the morphologies and pore architectures of mesoporous silicas could to be manipulated by adding organic dopants, more interesting structures are proposed to obtained through this dual-templating approach.

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