A systematic investigation of the formation of ordered mesoporous silicas using poly(ethylene oxide)-b-poly(methyl methacrylate) as the template†

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Two different approaches, the conventional solvent evaporation induced self-assembly (EISA) and the novel solvent evaporation induced aggregating assembly (EIAA), were employed to synthesize ordered mesoporous silicas (OMSs), respectively, by using amphiphilic diblock copolymer poly(ethylene oxide)-b-poly(methyl methacrylate) as the template, with an aim to systematically investigate the difference of the two approaches and their effect on the textural properties of the obtained porous materials. The mesoporous silicas synthesized via the two methods possess face centered cubic (fcc) mesostructure, large pore size and high surface area. However, compared with the OMSs with a film-like morphology from EISA, the OMSs from the EIAA have a particle-like morphology, thinner pore wall and higher surface area, which is favorable for their applications. More importantly, the novel EIAA process is more versatile and can be used to synthesize ordered mesoporous silicas and silica-based nanostructured materials with different morphologies. By introducing ethanol as the additive in the EIAA system, unique mesoporous silica spheres with a diameter of 1–5 μm, large pore size (~16.8 nm), huge window size (~8.9 nm), and high surface area (~482 m² g⁻¹) can be synthesized. Through increasing the content of water, uniform silica hollow spheres (20–40 nm in diameter) and silica nanotubes (diameter ~30 nm) can be obtained by using templates with higher and lower molecular weight, respectively.

1 Introduction

Ordered mesoporous silicas (OMSs) with a unique pore structure, large pore size and high surface area have been synthesized via the cooperative self-assembly of soft template molecules and inorganic silicates. They have shown great application potential in various fields, such as adsorption, separation, catalysis, and drug delivery. Various soft templates including low-molecular-weight surfactants (cationic, nonionic or anionic) and high-molecular-weight amphiphilic block copolymers have been extensively used to synthesize ordered mesoporous materials with tunable pore structure and size via solution-phase syntheses or the solvent evaporation induced self-assembly (EISA) method. Using low-molecular-weight surfactants as templates, the pore size of the obtained OMSs is usually smaller than 5.0 nm. In the past years, OMSs with larger pore sizes have attracted great interest among researchers because the large pore size is beneficial to accommodate large-size guest objects in adsorption/immobilization and loading metal (or metal oxide) nanoparticles for catalysis without pore blocking. The pore size of mesoporous materials is mainly determined by the hydrophobic volume of the soft templates. Therefore, the commercial block copolymers with long hydrophobic segments (i.e. poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide), poly(ethylene oxide)-b-poly(ethylene oxide), PEO-b-PPO-b-PEO) have been extensively used to synthesize OMSs with large pore size (up to 12 nm). Additionally, a novel kind of laboratory-made block copolymers such as poly(ethylene oxide)-b-polystyrene (PEO-b-PS), poly(isoprene)-b-poly(ethylene oxide) (PI-b-PEO), poly(ethylene-co-butylene)-b-poly(ethylene oxide) (KLE) and poly(ethylene oxide)-b-poly(methyl methacrylate) (PEO-b-PMMA) have been proved to be effective in synthesizing OMSs with large tunable pore size beyond 30 nm. These high-molecular-weight templates have various compositions and controllable molecular weights, which make them ideal templates for the synthesis of mesoporous silica with new mesostructures, functional pore walls and adjustable pore sizes. Due to the long hydrophobic chain and high molecular weight, these block copolymers are usually insoluble in water and even ethanol. In the conventional EISA approach, when these block copolymers are used as the soft template, organic
solvents such as THF are adopted to dissolve the block copolymers, and a stoichiometric amount of acidic water is added to hydrolyze the silica source. Unfortunately, in the obtained mesostructured organic–inorganic noncomposites, it is usually difficult to directly remove the template through calcination or solvent extraction, because the spherical micelles of block copolymers are tightly wrapped by the dense silica framework, making the organic templates inaccessible for oxygen during calcination or solvent during extraction. To solve this problem, Deng et al. first reported the successful removal of templates by hydrothermal treatment of the as-made mesostructured silica/template composites to generate micropores in the silica framework, followed with calcination in air; however, the obtained OMSs have low surface areas (<370 m² g⁻¹) and very small pore window sizes (<5.0 nm). Consequently, it is of great importance and interest to develop a new approach for controlling the inorganic–organic self-assembly, through which the pore wall thickness can be tuned, and the template molecules can be burned out easily, so as to create large-pore ordered mesoporous silicas with high surface areas, large pore volumes and large window sizes.

Recently, a selective solvent evaporation induced aggregating assembly (EIAA) method has been developed for the synthesis of OMSs in an acidic THF–water mixture by using water-insoluble high-molecular-weight amphiphilic diblock copolymer poly(ethylene oxide)-b-poly(methyl methacrylate) (PEO-b-PMMMA) as the template and tetraethyl orthosilicate (TEOS) as the silica precursor. Different from the EISA method where only a trace amount of water is allowed to be present in the system and the ordered mesostructure is formed at the solid–liquid or vapor–liquid interface after the evaporation of the solvent (THF), the EIAA method can be carried out in the presence of high water content, and the selective evaporation of THF from the THF–water mixture induces the occurrence of self-assembly at the liquid–liquid interface. Therefore, the unique liquid–liquid interface assembly endows the EIAA method with great flexibility in synthesizing large-pore ordered mesoporous silicas for use as the carriers for nanocatalysts, bio-enzymes and drug molecules. In order to extend the EIAA approach to synthesize other mesoporous materials, such as metal oxides and carbon, it is necessary to further conduct a comparable study between the conventional EISA and the EIAA approach, including the effect of the water content and organic additives (solvents) on the respectively yielded products.

It is noteworthy that, in the EIAA process, the evaporation rate of THF from the THF–H₂O mixture is slow, thus the process is easily controlled and the intermediate product can be collected by stopping the evaporation process. In our previous report, the evaporation of THF induced the formation of the hybrid PEO-b-PMMMA/SiO₂ spherical micelles with PMMA as the core and silica-associated PEO as the shell at the early stage. The discrete spherical micelles can be obtained by stopping the aggregating assembly process, which can be further converted to silica nanospheres by removing the template selectively. It is generally accepted that the block-copolymer-micelle templating synthesis is a facile method to synthesize silica hollow nanostructures (sphere, tube, etc.), which have been widely studied as a nanoreactor and nanocarrier for nanocatalysts and drugs. By carefully controlling the evaporation process, the EIAA method can be extended to the synthesis of silica hollow nanostructures.

In this paper, an amphiphilic diblock copolymer PEO-b-PMMMA with high molecular weight was used as the template to synthesize ordered mesoporous silica via the EISA and EIAA methods, respectively. The effect of water content, template compositions and organic additives on the obtained siliceous products was investigated in detail. The mesoporous silicas synthesized via the two methods possess the same mesostructure, i.e. face centered cubic (fcc) symmetry. However, compared with the OMSs with film-like morphology from EISA the OMSs from the EIAA have a particle-like morphology, larger pore size, thinner pore wall and higher surface area, which is favorable for their applications. More importantly, the novel EIAA process is more versatile and can be used to synthesize ordered mesoporous silicas and silica-based nanostructured materials with different morphologies. By introducing ethanol as the additive in the EIAA system, unique mesoporous silica spheres with a diameter of 1–5 μm, large pore size (~16.8 nm), huge window size (~8.9 nm), and high surface area (~482 m² g⁻¹) can be synthesized. Through increasing the content of water, uniform silica hollow spheres (20–40 nm in diameter) and silica nanotubes (diameter ~30 nm) can be obtained by using templates with higher and lower molecular weight, respectively.

2 Experimental

2.1 Chemicals

Monomethoxy poly(ethylene oxide) [M_w = 2 and 5 kg mol⁻¹, PEO-2k and PEO-5k] and 2-bromoisobutyl bromide were purchased from Aldrich. N,N,N',N',N″-Pentamethyldiethylenetriamine (PMDETA) was purchased from Acros. Methyl methacrylate (MMA), tetrahydrofuran (THF) (>99%), pyridine (>99%), cuprous chloride (CuCl), tetraethyl orthosilicate (TEOS) (AR), hydrochloric acid and anhydrous ether (>99%) were purchased from Shanghai Chemical Corp. MMA was purified by filtration using an Al₂O₃ column to remove the polymerization inhibitor. Millipore water was used in all experiments.

2.2 Synthesis of block copolymer

The block copolymer EO₄₄-b-MMA₄₀₃ (PDI: 1.07) was synthesized by using the atom transfer radical polymerization (ATRP) technique which involved two steps, i.e. the preparation of the macroinitiator and polymerization of MMA monomers. Typi-

cally, PEO-2k (4.0 g) was dissolved in a mixture solvent of THF (30 mL) and pyridine (15 mL). The resulting solution was cooled in an ice-water bath followed by dropwise addition of 2-bromoisobutyl bromide (1.38 g) under stirring. Afterwards, the solution was stirred at 30 °C for 12 h and then filtered to remove impurities. Subsequently, ether (60 mL) was added to the filtrate to obtain a white precipitate which was collected by filtration and then washed with ether. After vacuum drying at 25 °C, the PEO-Br macroinitiator was obtained. In the next step, EO₄₄-b-MMA₄₀₃ was synthesized by polymerizing MMA using PEO-Br as
an initiator. Typically, the PEO-Br (1.5 g) macroinitiator, CuCl (0.078 g), MMA (10 mL), PMDETA (0.14 g) and THF (20 mL) were added into an ampoule bottle. After the removal of air by bubbling with Ar gas, the reaction system was sealed and placed in a thermostatted oil bath at 60 °C for polymerization under stirring. After 4 h, the system was cooled to room temperature, and THF (50 mL) was added to dissolve the product. After that, the obtained solution was filtered through an Al2O3 column to remove the Cu complex. The cold ether (200 mL) was poured into the clear filtrate to precipitate the PEO-b-PMMA diblock copolymer which was collected by filtration and dried under vacuum. The high-molecular weight block copolymer EO125-b-MMA174 was synthesized using the same method as mentioned in our recent report.14

2.3 OMSs synthesized via EISA process

The diblock copolymer EO44-b-MMA103 (0.10 g) was first dissolved in THF (5.0 g), and 0.01 M HCl (0.5 g) and TEOS (0.5 g) were then added to the solution; after stirring for 0.5 h, the solution was poured into Petri dishes to evaporate THF at room temperature for 12 h. The transparent membranes were collected and ground into powder. The sample was denoted as as-made OMS-EISA. After direct calcination at 550 °C for 5 h in air, the sample was denoted as OMS-EISA. When the as-made sample was calcined in air after a hydrothermal treatment at 100 °C for 24 h in the aqueous solution (2 M HCl), the product was denoted as OMS-EISA-HT.

2.4 OMSs synthesized via EIAA process

The mesoporous silica samples were synthesized via an EIAA method in an acidic mixed solvent of THF and water by using TEOS as a silica source. For a typical synthesis, EO44-b-MMA103 (5.0 g) dissolved in THF solution (1 wt%) was mixed with 2 M HCl (2.5 g) solution with stirring. Then, TEOS (0.50 g) was added into the above transparent solution, and the composition of EO44-b-MMA103/THF/2 M HCl/TEOS mass ratio was 1 : 100 : 50 : 10. After that, the solution was left to stand for evaporation of THF at 25 °C in air in a hood. After 48 h, the white silica/PEO-b-PMMA composites were precipitated from the solution and collected by centrifugation, washed with water three times, and dried at 25 °C in air. The as-made sample was calcined directly at 550 °C in air for 5 h to remove the template. The obtained sample was denoted as OMS-EIAA. When other organic solvents were considered, the solvent (such as ethanol, CH3Cl) (2.0 g) was added into the original clear solution. The mesoporous silica nanotubes and hollow spheres were synthesized by increasing the amount of water in the initial clear solution by using EO44-b-MMA103 and EO125-b-MMA174 as the templates, respectively.

2.5 Measurement and characterization

Small angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The d-spacing values were calculated from the formula \( d = \frac{2\pi}{q} \). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in vacuum at 180 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. By using the Broekhoff–de Boer (BdB) spherical model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms, and the total pore volumes \( V \) were estimated from the adsorbed amount at a relative pressure \( P/P_0 \) of 0.995. The window size was calculated from the desorption branches. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope (Japan) operated at 200 kV. Field-emission scanning electron microscopy (FESEM) images were collected on a Hitachi Model S-4800 field emission scanning electron microscope.

3 Results and discussion

3.1 OMSs synthesized via EISA process

Since PMMA is a water insoluble polymer with strong hydrophobic property, PEO-b-PMMA diblock copolymers with a long PMMA chain are insoluble in water and ethanol despite the hydrophilicity of PEO segments. Consequently, THF, a good solvent for both segments of PEO-b-PMMA, was usually used as a solvent to dissolve the block copolymer. When the EISA method was used to synthesize OMSs, the diblock copolymer PEO-b-PMMA was dissolved in THF before adding a small amount of acid aqueous solution to catalyze the hydrolysis of TEOS. The clear solution was then poured onto a solid substrate for evaporation of THF. As the solvent evaporates, a transparent composite film was obtained and denoted as the as-made OMS-EISA.

The small angle X-ray scattering (SAXS) pattern of as-made OMS-EISA shows three resolved peaks with q-values of 0.287, 0.556 and 0.835 nm\(^{-1}\), which can be exactly indexed to the 111, 311 and 422 reflections of the face centered cubic (fcc) mesostructure with a space group of \( Fm\overline{3}m \) (Fig. 1). It indicates that the obtained silica/PEO-b-PMMA composites possess a highly ordered mesostructure through evaporation of THF. The unit cell parameter calculated from the SAXS data is about 37.9 nm. After direct calcination in air at 550 °C, the SAXS pattern of the obtained ordered mesoporous silica (denoted as OMS-EISA) shows three resolved scattering peaks, suggesting that the ordered mesostructure is well retained after calcination to
remove the block copolymer templates. The OMS-EISA has a unit cell parameter of 34.0 nm, reflecting a structural shrinkage of 10% after the calcination. The SAXS pattern of the OMS-EISA-HT sample obtained by hydrothermal treatment of the as-made OMS-EISA at 100 °C for 24 h and followed by calcination in air also shows three resolved peaks, indicating that the mesoporous silica is thermally stable. The unit cell parameter was calculated to be 36.5 nm. It reflects a structural shrinkage of 4%, smaller than that (10%) of the obtained sample without pre-hydrothermal treatment, owing to the highly cross-linked and stable silica framework obtained after the hydrothermal treatment.

Transmission electron microscopy (TEM) images and the corresponding fast Fourier transformations of the OMS-EISA-HT show that the sample has a high degree of periodicity and a spherical mesopore viewed from [211], [111] and [110] directions, respectively, which further confirms the fcc mesostructure (Fig. 2a–d). The unit cell parameter calculated from the TEM image is about 35 nm, consistent with the SAXS results. Nitrogen sorption isotherms of both OMS-EISA and OMS-EISA-HT show representative type IV curves with a sharp capillary condensation step in the relative pressure range of 0.80–0.90 (Fig. 1B). It indicates that ultra-large uniform mesopores were generated. A very large H₂-type hysteresis loop with delayed capillary evaporation located at a relative pressure of about 0.50 is observed, revealing cage-like mesopores with a window size smaller than 5.0 nm. The pore size calculated from the adsorption branches by using the BdB model is ~15.7 and 18.7 nm respectively (Fig. 1C). The larger pore size of OMS-EISA-HT is due to the small structure shrinkage during the calcination. The pore wall thicknesses calculated from the unit cell parameter and pore size results are 8.3 and 7.3 nm for OMS-EISA and OMS-EISA-HT, respectively. The texture properties, such as pore volume and surface area, of OMS-EISA and OMS-EISA-HT were summarized in Table 1. OMS-EISA-HT shows a higher total surface area and microporous surface area than those of OMS-EISA owing to increasing numbers of the micropores via hydrothermal treatment. The OMSs obtained via the EIAA process show a total surface area of 127 m² g⁻¹ and a microporous surface area of 127 m² g⁻¹, both larger than the corresponding values of OMS-EISA. The reason is that, in the EIAA process, the PEO segments of the templates can be inserted into the thin silica wall, which generates a greater number of micropores after calcination in air.

3.2 OMSs synthesized via EIAA process

3.2.1 EIAA process in THF–H₂O solution. The evaporation induced aggregating assembly (EIAA) method can also be applied to synthesize OMSs. Different from the EISA method, the mass ratio of water to PEO-b-PMMA (denoted as \( \text{R}_{\text{water/template}} \)) is ~50, much higher than that (\( \text{R}_{\text{water/template}} = 5 \)) of the EISA method. After the evaporation of THF, a turbid aqueous solution containing a white particle-like sample was obtained. The particles collected by centrifugation were denoted as the as-made OMS-EIAA.

The SAXS patterns of the as-made OMS-EIAA show four resolved scattering peaks which can be indexed to the 200, 222, and 622 reflections, corresponding to a fcc mesostructure with a space group of \( \text{Fm}\overline{3}m \). It indicates that the ordered mesostructure is formed in the solution phase. After calcination at 550 °C, the ordered mesostructure of the sample (denoted as OMS-EIAA) is well retained (Fig. 3A(b)). TEM images further confirm the ordered mesostructure (Fig. 2e and f), similar to our previous report. Nitrogen sorption isotherms of OMS-EIAA show typical type IV curves with a sharp capillary condensation step in the relative pressure range of 0.80–0.90 (Fig. 3B), indicative of large mesopores with uniform pore size. A very large H₂-type hysteresis loop reveals the spherical mesopore with small window size, which is similar to that of OMS-EISA. The pore size distributions are centered at 18.0 nm (Fig. 1C). The BET surface area and microporous surface area are 330 and 127 m² g⁻¹, respectively. It indicates that abundant micropores were formed in the pore walls, which is mainly generated by the PEO segments inserted in the silica framework.

Scanning electron microscopy (SEM) observation indicates that the OMS-EIAA (\( \text{R}_{\text{water/template}} = 50 \)) after calcination consists of particles with an irregular shape and a diameter of 0.5–5 μm (Fig. 4a). The magnified field emission scanning electron microscopy (FESEM) image clearly shows spherical mesopore arrays on the surface of the particles, revealing the closely packed spherical silica-template composite micelles (Fig. 4b). As \( \text{R}_{\text{water/template}} \) increases to 100, the particles become smaller and the diameter is about 250 nm (Fig. 4c). The FESEM image shows that the particles are actually large bundles of tubular mesopores (Fig. 4d). Further increasing the amount of water (\( \text{R}_{\text{water/template}} = 150 \) and 500), the size of the bundles decreases significantly (Fig. 4e) and even individual nanotubes can be
obtained (Fig. 4f). The TEM image further confirms the hollow structure of the silica nanotubes (Fig. 4g). These results mean that the water content not only affects the particles sizes but also changes the pore structures. The increase of water content can induce the phase transition of PEO-b-PMMA micelles from spherical micelles to rod-like micelles. Finally, the rod-like micelle can act as the template for the formation of silica nanotubes. Interestingly, when a higher molecular weight EO125-b-MMA174 was used as the template, due to the large curvature of the spherical micelles formed by the template, they remain in the diluted solution, and no tubular structure was observed even in the highly diluted system. As a result, silica hollow nanospheres with a diameter of 20–40 nm were obtained through the EIAA approach using EO125-b-MMA174 as the template, as revealed by the FESEM and TEM images (Fig. 5).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit cell parameter (nm)</th>
<th>Pore size (nm)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Pore wall thickness (nm)</th>
<th>Microporous surface area (m² g⁻¹)</th>
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<tr>
<td>OMS-EISA</td>
<td>34.0</td>
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<td>0.59</td>
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<td>228</td>
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<tr>
<td>OMS-EIAA</td>
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<td>127</td>
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<tr>
<td>OMS-EIAA-sphere</td>
<td>—</td>
<td>16.8</td>
<td>482</td>
<td>1.34</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Ordered mesoporous silica prepared using the EISA method via direct calcination in air.  
* Ordered mesoporous silica prepared using the EISA method via calcination in air after hydrothermal treatment.  
* Ordered mesoporous silica prepared using the EIAA method.  
* Ordered mesoporous silica sphere prepared using the EIAA method.  

The wall thickness was calculated from the formula 

\[ W_t = \sqrt{2a^2 - D} \]

where \( a \) represents the unit cell parameter and \( D \) is the pore size calculated from the N2 sorption measurement.  

* Calculated by the V-t method.

**Fig. 3** (A) SAXS patterns of the as-made OMS-EIAA (a) and OMS-EIAA (b). (B) Nitrogen sorption isotherms and (C) pore size distributions of the OMS-EIAA samples synthesized from the EIAA process.

**Fig. 4** SEM images (a and c) and FESEM images of the silica nanostructure synthesized with different mass ratios of water to EO44-b-MMA103 via the EIAA process: (a and b) 50; (c and d) 100; (e) 150; (f) 500. (g) TEM image of silica nanotubes.

**Fig. 5** SEM and TEM images of the silica hollow nanospheres synthesized in the presence of high content of water using high molecular weight EO125-b-MMA174 as the template.
micelles (Fig. 6b and inset). After calcination in air, the obtained mesoporous silica spheres were found to have fully opened spherical mesopores in the exterior surface (Fig. 6c). To gain information of the inner structure of the spheres, the calcined sample was slightly ground for FESEM characterization. In the inner surface, highly ordered mesopores with an open pore structure can be clearly identified, indicating highly accessible mesopores in the entire spheres (Fig. 6d). TEM images of the calcined samples confirm the spherical morphology and ordered mesostructure (Fig. 6e and f). Nitrogen sorption isotherms show type IV curves with a sharp capillary condensation step in the relative pressure range of 0.80–0.90 (Fig. 7a), indicating ultra-large mesopores with uniform size. A H1-type hysteresis loop reveals a large window size of ~8.9 nm calculated from the desorption branches. The pore size calculated from the adsorption branches by using the BJH model is 16.8 nm (Fig. 7b). The surface area and pore volume are 482 m² g⁻¹ and 1.34 cm³ g⁻¹, respectively.

3.2.3 EIAA process in THF–H₂O solution with other solvents as additives. When isopropanol was used as a co-solvent in the EIAA process, spherical mesoporous particles with a diameter of 2–5 μm were obtained, which is similar to the case of ethanol as the additive (Fig. S1af). Dichloromethane (CH₂Cl₂) is another frequently used solvent. After the evaporation of THF in the mixture of THF–H₂O–CH₂Cl₂, the obtained particles have a nearly spherical morphology and a broad size distribution in the range of 100 nm to 4.5 μm. The HRSEM image shows that the particles are composed of randomly packed short nanotubes; therefore rod-like micelles were involved during the dichloromethane-mediated EIAA process (Fig. S1bf). The result indicates that the introduction of dichloromethane solvent is unfavorable to form ordered mesostructures. When DMF is used as a co-solvent, during the EIAA process, two distinct layers of solution separated by a liquid interface were observed in the reaction system. SEM observation shows that the obtained particles have a spherical morphology with a broad diameter (Fig. S1df). TEM images reveal that mesocellular silica foam with a disordered mesostructure and spherical morphology is formed (Fig. S1df). The samples have a surface area of ~414 m² g⁻¹ and a pore volume of ~0.87 cm³ g⁻¹ from the nitrogen sorption isotherms.

3.3 Discussion

3.3.1 The difference between EISA and EIAA processes. When the EISA method is used to synthesize OMSs, the silicate oligomers can interact with the PEO segment of the diblock copolymer by hydrogen bonding, and thus a block copolymer/silica mesostructure is formed by organic–inorganic self-assembly at the liquid–solid (vapor) interface. After direct calcination, the template can be removed easily and the accessible mesopores were generated, owing to the high oxygen content of the PMMA segment. The block copolymer PEO-b-PMMA is an ideal template which can be decomposed easily during calcination, compared to other block copolymers (such as PEO-b-PS).

When the EIAA method is employed to fabricate OMSs, the evaporation of THF leads to the formation of spherical micelles with PMMA as a core surrounded by PEO shell at the liquid (oil-rich)–liquid (water-rich) interface. Simultaneously, silicate oligomers hydrolyzed from TEOS in the water-rich phase can associate with PEO moieties through hydrogen bonding (Scheme 1). With the continuous loss of the good solvent THF, the increasing concentration of the hybrid PEO-b-PMMA/SiO₂ micelles and condensation of the silica oligomers induce the
form of ordered mesostructures. The formation of the micelles and aggregation proceed at the liquid–liquid interface. When the amount of water further increases, the spherical micelles become elongated. Finally, the rod-like micelle was formed, while a large amount of water remained in the final solution. Owing to the hydrogen bonding between the silicates and the PEO segments, the silicate species are located in the PEO segment of the PEO-b-PMMA rod-like micelles. The high content of water also decreases the concentration of the hybrid PEO-b-PMMA/SiO$_2$ micelles, which prevents the aggregating process. Therefore, the particle size decreases as the water content increases. Finally, the individual nanotubes can be synthesized by using the PEO-b-PMMA rod-like micelle as the template.

3.3.2 Morphology. Owing to the different formation processes, the OMSs obtained by the two methods have dramatic differences in the morphology and pore structure. In the case of the EISA method, it is usually difficult to achieve an effective morphology control of the sample, and only a film-like sample is obtained due to the macroscopic solid–liquid interface assembly. In the case of the EIAA method, OMSs with particle-like and spherical morphologies can be fabricated, which is similar to the commonly used solution-phase synthesis using a water soluble template PEO-b-PPO-b-PEO.$^{14}$ The residual solvent in the EIAA process plays a key role in the formation of particle-like and spherical morphologies. The acid in the solution can control the hydrolysis and crosslinking rate of silica species. When the EISA method is used, the fast evaporation of the solvent leads to the quick increase of the acidity, which can accelerate the rate of hydrolysis and crosslinking of silica species. This process is very fast and thus hard to control. By contrast, the process of selective evaporation of THF in the acidic H$_2$O–THF solution is relatively slow, and the acidity of the solution increases gradually. This process provides the possibility of controlling the hydrolysis and crosslinking process of silica species, and the assembly process of composite micelles, and thus allowing for a precise control over the pore structure and morphology.

3.3.3 Pore structure. As mentioned above, the pore wall thickness of OMSs synthesized via the EISA and the EIAA process are ~8.3 and 3.1 nm, respectively, indicating that the EISA process can generate much thicker pore walls, which is consistent with previous reports.$^{14}$ The thick pore wall usually leads to the small window size, which is the main problem in the mesoporous materials with cage-like mesopores. Fortunately, the EIAA method provides an alternative route to synthesize OMSs with thin pore walls, which can be easily expanded to form large window sizes.$^{16}$ Additionally, the content of micropores in the OMS framework synthesized via the EISA process is much less than that from the EIAA process (Table 1). Such a difference is mainly due to the fact that different processes lead to different distributions of the PEO-b-PMMA block copolymers in the silica framework. When the EISA method is used, the predominant solvent in the solution is THF. As THF evaporates, the concentration of PEO-b-PMMA increases, resulting in the formation of PEO-b-PMMA spherical micelles with a PMMA core and a PEO shell. As the content of THF decreases continually, the PEO segment contracts gradually to surround the PMMA core. At the same time, the silica species adhere to the surface of the spherical micelle via hydrogen bonding between the PEO segment and the silica species, and thus a layer of silica is formed around the template micelles. Different from the EISA process, in the EIAA method, the main solvents are THF and water. Water is a selective solvent for PEO-b-PMMA because it is a good solvent for the PEO segment but a poor solvent for the PMMA segment. As the evaporation of THF proceeds, PEO-b-PMMA dissolved in the THF–H$_2$O mixture forms spherical micelles with a PMMA core and a PEO shell. To make the micelles stable, the PEO segment stretches as much as possible to form hydrogen bonding with water molecules, which makes the PEO shell loose. At the same time, the silica oligomers can enter the loose PEO shell by interacting with PEO via hydrogen bonding. As a result, parts of the silica oligomers are located in the PEO shell, which is different from that of the EISA, where most of the silica oligomers are on the outer surface of the PEO shell. After further condensation of silica species, the spherical micelles aggregate together and the ordered mesostructure is formed. These two different processes make the PEO segment locate in different positions in the mesostructured template/silica composites, namely, the PEO segments stay with the PMMA core in the EISA process but inserts into the silica frameworks partly in the EIAA process. The different locations also lead to the different microporous surface areas. The PEO segments inserted into the silica pore walls can produce more micropores when they are removed after calcination in air.

3.3.4 Silica nanotube and hollow nanosphere. The amount of water is one of the critical factors affecting the formation of PEO-b-PMMA micelles and their phase-separation structures.
When \( R_{\text{water/template}} \) is about 50, both EO\(_{44}\)-b-MMA\(_{103}\) and EO\(_{125}\)-b-MMA\(_{174}\) self-assemble into spherical micelles with a PMMA core and a PEO shell. The spherical micelles binding silica oligomers via the hydrogen bonding serve as the building units which further adopt an aggregating assembly to the ordered mesostructure with a fcc symmetry to decrease the interface energy driven by the crosslinking and condensation of the silica oligomers. As the water content increases, the amount of free silica oligomers in the solution increases, while the amount of silica oligomers associated with spherical micelles decreases significantly. As a result, the hydrophilic volume of the composite micelles decreases and the curvature becomes lower. Finally, EO\(_{44}\)-b-MMA\(_{103}\) spherical micelles elongate to form rod-like micelles. The increasing amount of water further decreases the number of silica oligomers on the EO\(_{44}\)-b-MMA\(_{103}\) rod-like micelle, leading to the formation of aggregated silica/PEO-b-PMMA rods and individual silica/PEO-b-PMMA rods (Scheme 1). When the high molecular weight EO\(_{125}\)-b-MMA\(_{174}\) was used as the template, the increasing amount of water can also decrease the amount of silica oligomers on the surface of PEO-b-PMMA micelles, which leads to individual spherical micelle composites. Finally, the individual silica hollow sphere can be obtained by removing the spherical templated micelles. By contrast, in the case of the EIAA process using EO\(_{125}\)-b-MMA\(_{174}\) as the template, the decrease of silica oligomer amount cannot induce the transition of spherical micelles to rod-like micelles, owing to the high molecular weight of the hydrophobic segments. EO\(_{125}\)-b-MMA\(_{174}\) with high molecular weight of hydrophobic segments tends to form spherical micelles with high curvature in the solution.

### 3.3.5 Organic solvent

Ethanol and isopropanol can be used as a selective solvent for PEO-b-PMMA as H\(_2\)O. When ethanol is used as the co-solvent in the EIAA process, the slow evaporation rate makes it remain in the solution during the evaporation of THF. The presence of ethanol can partially suppress the hydrolysis of the TEOS precursor, and thus slows down the aggregation process of the hybrid PEO-b-PMMA/SiO\(_2\) micelles. Therefore, mesostructured spheres with thermodynamically stable morphology can be obtained. Other solvents, such as CH\(_2\)Cl\(_2\), a good solvent for PEO-b-PMMA (DMF), are not suitable for use as the additive for the formation of OMSs because CH\(_2\)Cl\(_2\) is not miscible with water and DMF has a very slow evaporation rate. Too much amount of these solvents remained in the EIAA system can disturb the assembly of micelles and the formation of ordered mesostructures.

### 4 Conclusions

Two different methods, the conventional EISA and the newly developed EIAA, have been employed to synthesize ordered mesoporous silicas (OMSs) by using a water insoluble block copolymer PEO-b-PMMA as the soft template. The mesoporous silicas synthesized via the two methods have face centered cubic (fcc) mesostructures with \( Fm\overline{3}m \) symmetries, large pore size and high surface area. Interestingly, compared with the OMSs with a film-like morphology from EISA, the OMSs from the EIAA process have a particle-like morphology, thinner pore wall and higher surface area. In addition, the EIAA method can be extended to synthesize ordered mesoporous silica particles, silica nanotubes and hollow nanospheres by precisely controlling the evaporation process. By increasing the water content, uniform and discrete silica nanotubes and nanospheres were synthesized by using templates with lower and higher molecular weight, respectively. The addition of ethanol as the additive can slow down the aggregating process, resulting in unique mesoporous silica spheres. The mesoporous silica spheres have a large pore size (16.8 nm) and windows size (8.9 nm), high surface area (482 m\(^2\) g\(^{-1}\)) and pore volume (1.34 cm\(^3\) g\(^{-1}\)). Therefore, it can be expected that the newly developed EIAA approach can be widely used to design porous materials with different morphologies, pore structures and pore sizes for various applications in adsorption, separation, catalysis, and drug delivery, especially those involving molecules or nanoparticles of large size.

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### Notes and references