Synthesis of amino group functionalized monodispersed mesoporous silica nanospheres using anionic surfactant

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ABSTRACT

A series of anionic surfactant templated mesoporous silica (AMS) monodispersed nanospheres were synthesized by anionic surfactant, co-structure-directing agent (CSDA) bearing amino group, and silica source in the presence of nonionic surfactant. The amino group functionalized well-ordered cubic Fd-3m, bi-continuous cubic Ia-3d and disordered structures with tunable pore size from 2.2 to 9.2 nm and the particle size from 30 to 320 nm, have been synthesized by changing the type of the surfactant, the concentration of the nonionic and anionic surfactant and the reaction temperature. Loadings of the amino groups were determined in the range of 2.7–3.4 mmol/g. It has been found that, the higher concentration of the nonionic and the amino surfactant, the shorter chain length of the anionic surfactant and the higher reaction temperature favor the formation of mesoporous silica nanospheres with larger particle size. These functional AMS nanospheres may find potential use in catalysis, sensor devices and bio-applications, etc.

1. Introduction

Hybrid mesoporous materials with organic functionalization on the exterior and/or interior surfaces are of great interest because of their potential for new applications in separation, adsorption, catalysis, sensor design, drug delivery, and nanotechnology [1–5]. Massive efforts have been devoted to the mesoporous silicas with various organic functional groups [6–10]. Among these, amino group functionalized mesoporous materials are well known for their use in base-catalyzed reactions, waste-water treatment, further post-synthesis functionalization, immobilization of enzymes and other proteins and absorption of heavy metal ions and toxic oxanions [11–17].

The synthesis of functionalized mesoporous materials based on organosilanes can be commonly achieved by two strategies: the subsequent modification of a purely inorganic silica material by organosilanes (grafting), and the simultaneous condensation of organosilane and the silica source in a one-pot process (co-condensation). The post-synthesis grafting method typically results in inhomogeneous surface coverage of organic moieties due to their congregation near the entries of the mesopores and the exterior surfaces [18]. The co-condensation method is generally superior due to the relatively uniform distribution of the organic groups, which is, however, not chemically guaranteed. A higher loading of organic groups could be achieved by a one-pot functionalization without closing the mesopores [13], which may on the other hand deteriorate the mesoscopic ordering.

In 2004, Che et al. reported a co-structure-directing method to synthesize mesoporous materials based on electrostatic interactions between the headgroup of a surfactant and a co-structure-directing agent (CSDA) bearing opposite charges, and a regular array of the CSDA could be condensed on the surface of the mesopores in the expected ratios following the arrangement of the surfactant due to their interactions [19–23]. By using this method, we have succeeded in synthesizing a series of functionalized mesoporous silicas with various structures including tetragonal P42/mmm, three-dimensional (3D) hexagonal P63/mmc, cubic Pm-3n, Fm-3m, Fd-3m, two-dimensional (2D) hexagonal p6mm, bi-continuous cubic Ia-3d, Pn-3m, lamellar structures, modulated structures, and a chiral mesostructure with helically arranged mesopores [24]. Recently, by using guest probe molecules, we have proved that the arrangement of the quaternary ammonium groups on the mesopore surface of the extracted chiral mesostructured silicas is in a helical way, which is imprinted from the original chirality of the micelle [25].

Organic group functionalized, monodispersed mesoporous silica nanospheres have particularly attracted great attention due to their potential applications in chemical, material and biological fields. Various functionalized mesoporous silica nanospheres have been synthesized by post-synthesis and co-condensation methods

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Two nonionic surfactants, C16(EO)10 (Brij-56) and EO20PO70EO20, manipulated based on the dispersant effect of nonionic surfactant. Nucleation and the growth of the nanospheres could be well controlled by introducing a nonionic co-surfactant in the synthesis system, in which the dispersity of the AMS nanospheres has been achieved by introducing nonionic surfactant P123 in the synthesis gel above its cloud point, which disperses the nucleation sites and limits the diffusion of silicate oligomers in the synthesis of the nanospheres [32].

Herein we report a synthesis route of amino group functionalized AMS nanospheres with high monodispersity based on the self-assembly of various anionic surfactants, CSDA and inorganic source, in the presence of nonionic co-surfactants. In the synthesis, the negatively charged headgroup of the anionic surfactant and the positively charged amino group of the CSDA interact electrostatically. The alkoxysilane site of CSDA (3-aminopropyltrimethoxysilane, APS) is co-condensed with TEOs, to be assembled subsequently forming the silica framework. Improved monodispersity of the AMS nanospheres has been achieved by introducing a nonionic co-surfactant in the synthesis system, in which the nucleation and the growth of the nanospheres could be well manipulated based on the dispersant effect of nonionic surfactant. Two nonionic surfactants, C16(EO)10 (Brij-56) and EO20PO70EO20 (P123), have been used as the dispersant. Unlike P123, Brij-56 not only acts as a dispersant but also affects the formation of the micelles due to its compatibility with anionic surfactant in forming micelles. Various parameters that affect the morphological and porous properties of the nanospheres, such as the concentration of the nonionic and the anionic surfactant, chain length of the anionic surfactant and reaction temperature, have been discussed in the following sections in detail.

2. Experimental

2.1. Chemicals

All materials were used as purchased without further purification. Tetraethyl orthosilicate (TEOS), from SCRC, China; 3-aminopropyltrimethoxysilane (APS), from TCI; nonionic block copolymer EO30PO70EO30 (Pluronic P123), from Aldrich; nonionic surfactant C16(EO)10 (Brij-56), from Aldrich; Anionic surfactants N-lauroyl-L-glutamic acid (C12GluA), N-myristoyl-L-glutamic acid (C14GluA), N-palmitoyl-L-glutamic acid (C16GluA), N-stearoyl-L-glutamic acid (C18GluA), from Ajinomoto Co., Ltd.

2.2. Synthesis of mesoporous silica nanospheres

The mesoporous silica nanospheres were synthesized by using anionic surfactant as structure directing agent, APS as CSDA and TEOS as silica source in the presence of nonionic surfactant (Brij-56 or P123). In a typical synthesis, 0.207 g anionic surfactant C18GluA (0.5 mmol) and 0.3 g nonionic surfactant Brij-56 (0.44 mmol) were dissolved in 21 g deionized water (1268 mmol) at 80 °C. A mixture of 1.56 g TEOS (7.5 mmol) and 0.179 g APS (1 mmol) was added dropwise with stirring (one drop per second). The molar composition of the synthesis system is: 1C18GluA: 2APS: 15TEOS: 2335H2O (where x = 0.29, 0.88 and 1.46). The reaction temperature is 80 °C.

![Fig. 1. TEM images of mesoporous silica spheres synthesized with different Brij-56 concentrations of 0.5 wt.% (a), 1.5 wt.% (b) and 2.5 wt.% (c). The molar composition of the synthesis system is: 1C18GluA: 2APS: 15TEOS: 2335H2O: xBrij-56 (where x = 0.29, 0.88 and 1.46). The reaction temperature is 80 °C.](image-url)
samples were studied without any metal coating. An accelerating voltage of 1 kV (resolution: ca. 1.4 nm) was chosen for all mesoporous nanosphere samples. The N2 adsorption/desorption isotherms were measured at \(196^\circ C\) with Quantachrome Nova 4200E. The samples were pretreated at \(120^\circ C\) and \(1.33 \times 10^{-4}\) Pa for 3 h. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method and the pore size was obtained from the maxima of the pore size distribution curve calculated by the Barrett–Joyner–Halenda (BJH) method using the desorption branch of the isotherm. Solid-state \(^{13}\)C MAS NMR spectra of the mesoporous materials were collected on a Varian Mercury plus-400 NMR spectrometer at 100 MHz and a sample spinning frequency of 3 kHz. The elemental analysis of the materials was obtained from a Perkin–Elmer Series II CHNS/O Analyzer 2400. Dynamic light scattering (DLS) experiments were conducted via a Zetasizer instrument (Nano ZS90, Malvern Instruments). The scattering intensity autocorrelation decays were analyzed with the manufacturer’s program, DTS (Nano). The synthesis was performed in a 50 mL beaker and the reaction mixture was rapidly pipetted into a cuvette (1-cm path length) and added to the DLS apparatus at designed time.

3. Results and discussion

3.1. Effect of the concentration of Brij-56 on the morphology and the mesostructure of the AMS nanospheres

To investigate the effect of the concentration of the nonionic surfactant on the morphology and mesostructure of the nanospheres, the samples were synthesized with different Brij-56 concentrations in H2O. The molar ratios of other reagents were kept constant and the reaction temperatures were set at \(80^\circ C\). As shown in Fig. 1a–c, the diameter of the nanospheres increased.

![Table 1](image1)

<table>
<thead>
<tr>
<th>Brij-56 (wt.%)</th>
<th>Average particle diameter (nm)</th>
<th>Standard deviation (%)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Primary mesopore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
<th>Loading of amino groups (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 (a)</td>
<td>120</td>
<td>11.0</td>
<td>719</td>
<td>1.85</td>
<td>0.66</td>
<td>5.3</td>
<td>2.8</td>
</tr>
<tr>
<td>1.5 (b)</td>
<td>130</td>
<td>7.5</td>
<td>759</td>
<td>1.99</td>
<td>0.71</td>
<td>5.3</td>
<td>2.7</td>
</tr>
<tr>
<td>2.5 (c)</td>
<td>320</td>
<td>17.6</td>
<td>646</td>
<td>1.84</td>
<td>0.87</td>
<td>4.0, 9.2</td>
<td>2.9</td>
</tr>
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</table>

![Table 2](image2)

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<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>Average particle diameter (nm)</th>
<th>Standard deviation (%)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Primary mesopore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
<th>Loading of amino groups (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (a)</td>
<td>120</td>
<td>14.6</td>
<td>587</td>
<td>0.99</td>
<td>0.43</td>
<td>3.4</td>
<td>3.1</td>
</tr>
<tr>
<td>50 (b)</td>
<td>120</td>
<td>13.7</td>
<td>701</td>
<td>1.27</td>
<td>0.63</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td>70 (c)</td>
<td>150</td>
<td>12.4</td>
<td>632</td>
<td>1.46</td>
<td>0.71</td>
<td>5.3</td>
<td>2.8</td>
</tr>
<tr>
<td>80*</td>
<td>130</td>
<td>7.5</td>
<td>759</td>
<td>1.99</td>
<td>0.71</td>
<td>5.3</td>
<td>2.7</td>
</tr>
</tbody>
</table>

* The same sample shown in Table 1(b).
from ~120 to ~320 nm with increasing concentration of Brij-56 from 0.5 wt.% to 2.5 wt.%. The standard deviations of the size of the nanospheres were changed in the range of 7.5–17.6% (Table 1). The sample synthesized with 1.5 wt.% Brij-56 has the uniform particle size of ~130 nm with the highest monodispersity. However, a higher concentration (>2.5 wt.%) of Brij-56 gives a highly viscous solution, failing in producing mesoporous silicas of high quality. The structures of the samples were examined by TEM observation.

As shown in Fig. 1a1-2, the samples synthesized with low concentration of Brij-56 have ordered mesopores. However, it is difficult to determine the structure because of the poor crystallinity. The mesoporous nanospheres synthesized with higher concentration of Brij-56 (Fig. 1b2 and c2) possess disordered pore arrangement.

The XRD patterns of the samples synthesized with different Brij-56 concentrations are shown in Fig. 2A. All samples exhibited one reflection at 2θ = 0.6–6°, and no higher order X-ray reflections appeared due to the low long-range ordering of the mesostructure. Increasing the concentration of the Brij-56 gives rise to a shift of the main reflection to a lower angle, indicating the enlarged d-spacing of the resultant mesoporous material.

The N2 adsorption–desorption isotherms of the samples synthesized with different Brij-56 concentrations show type IV isotherms with a capillary condensation at relative pressure between 0.4 and 0.8. The samples synthesized with lower Brij-56 concentration (Fig. 2B—a and b) have large surface area (719 and 759 m² g⁻¹), large pore volume (1.93 and 2.15 cm³ g⁻¹) and pore diameter of 5.3 nm. A second nitrogen uptake step at relative pressures up to 0.9 could be attributed to the capillary condensation in voids between the packed nanospheres. The isotherm of the sample synthesized with highest Brij-56 concentrations (Fig. 2B—c) shows a large hysteresis loop with two steps in desorption branch (P/P₀ = 0.45–0.55 and 0.7–0.8), suggesting that this sample possesses two types of mesopores with the pore size of 4.0 nm and 9.2 nm, respectively. The surface area of this sample is 646 m² g⁻¹ and pore volume is 2.10 cm³ g⁻¹.

The presence of the functional groups on the mesopore nanoparticles after the removal of the surfactant was confirmed by the solid-state ¹³C MAS NMR spectrum (Fig. 3). The resonance signals at 8.8, 23.9, and 42.9 ppm correspond to C₁, CⅡ, and CⅢ of APS [8,21,33], respectively, revealing that the surfactant has been extracted from the mesopores, and the resultant mesoporous silica is functionalized with aminopropyl groups of APS.

Quantitative evaluation of the loading density of the functional groups was conducted by CHN elemental analysis. The loading amount of aminopropyl stemmed from APS was calculated as 2.7–2.9 mmol/g by the nitrogen content of the analytic result (Table 1), confirming that abundant amino groups were introduced into the mesopores without being affected by the addition of Brij-56. The swelling of the pore size with the Brij-56 addition could be explained by the introduction of Brij-56 in the anionic surfactant micelles. The cloud point of Brij-56 is in the range of 64–69 °C [34], and its hydrophobicity could be increased with increasing temperature due to the destruction of the hydrogen bond between Brij-56 and H₂O. Therefore, it can be considered that, at higher...
temperature, the highly hydrophobic Brij-56 tends to be associated with the hydrophobic part of the micelle formed amphiphilic molecules, acting as a swelling agent, which leads to disordered mesostructure and large mesopores as shown in Fig. 2B–c.

3.2. Effect of the reaction temperature on the morphology and the mesostructure

Reaction temperature is an important factor that affects the size and structure of the mesoporous particles, because thermodynamics of the liquid–crystal phases of surfactants and the kinetics of the hydrolysis and condensation of TEOS are highly dependent on temperature [35].

To investigate the influence of reaction temperature on the morphology and structure of the AMS nanospheres, samples were synthesized at different temperature of 30, 50, 70 and 80 °C, respectively, with the same chemical composition. The other reaction conditions for these samples were identical to those described in the experiment above. The morphological, structural and compositional properties of the materials are summarized in Table 2. The TEM images of the mesoporous silica nanospheres are shown in Fig. 4. It can be inferred that the average particle diameters are within the range of 120–150 nm when the reaction temperature increases from 30 to 80 °C, indicating that the size of the AMS nanospheres is not significantly affected by the reaction temperature. The standard deviations of the particle diameters decreased from 14.6% to 7.5% with increasing synthesis temperature in the range of 30–80 °C. The TEM images of the sample synthesized at 30 °C show highly ordered mesostructure, which can be assigned to bi-continues Ia-3d mesostructure. Fig. 4a2 shows the HRTEM image taken along [1 1 1] direction and the corresponding Fourier diffractogram (FD) of the sample, clearly showing the typical contrast of the Ia-3d type structure, and the unit-cell parameter is 113 Å calculated from the FDs. The samples synthesized at 50 °C show highly ordered mesostructure, which can be assigned to Ia-3d mesostructure. Fig. 4b2 shows the TEM image of the sample synthesized at 50 °C, and the mesostructure is also Ia-3d; however, the degree of crystallinity becomes lower. The sample synthesized at 70 °C has disordered mesopores as can be inferred from Fig. 4c2.

The XRD patterns of the samples synthesized at different temperature are shown in Fig. 5A. From the XRD patterns shown in Fig. 5A–a, it can be seen that the material has highly ordered mesopores with the cubic Ia-3d symmetry. The reciprocal spacing ratio of the first two reflections is close to $\sqrt{3}/2$, in agreement with the 211 and 220 reflections. The unit-cell parameter $a = 116$ Å. This mesophase has been extensively studied because it is common in liquid crystal systems and mesoporous silica phases. It is the first time that the Ia-3d mesostructure has been observed by using the anionic surfactant C16GluA with two head groups. The XRD patterns of the sample synthesized at 50 and 70 °C (Fig. 4A–b, c) show only one reflection at around $2\theta = 1.0–2.0^\circ$, indicating deteriorated or disordered mesophase.

Fig. 5B and C show the N2 adsorption–desorption isotherms and pore size distributions of the AMS nanospheres. The N2 adsorption–desorption isotherms show sharp capillary condensation steps in the relative pressure ($P/P_0$) of 0.4–0.8, which is characteristic for a mesoporous material. All samples had high specific surface area and large pore volumes (Table 2). The pore diameters evaluated by the BJH method are listed in Table 2. The pore diameter became larger (3.4–5.3 nm) with increasing the synthesis temperature, which is consistent with the TEM and XRD results. The steep uptake of nitrogen at $P/P_0 \sim 1$ is attributed to the cavities caused by aggregation of the nanospheres.

It can be concluded that lower temperature is favorable for the formation of AMS nanospheres with highly ordered bi-continuous Ia-3d structure. The temperature dependence of the mesostructure could be explained in terms of the surfactant packing behavior. The reaction temperature of 30 °C is blow the cloud point of Brij-56, and thus the alkyl chain of Brij-56 could insert into the hydrophobic part of the micelles of the anionic surfactant with the hydrophilic EO part remaining outside, forming micelles together with the anionic surfactant. It is worthy to note that bi-continues Ia-3d structure cannot be formed solely by controlling the charge density of the micelle surfaces via difference of ionization degree of the carboxylate surfactants with two head groups [21]. Such a system always gives a bi-continues Pn-3m mesophase, the silica wall of which follows a typical diamond minimal surface (D surface), in analogy to the gyroid minimal surface (G surface) as observed for the silica wall of Ia-3d [20]. In our experiments using Brij-56 as a co-surfactant at a low temperature, the incorporation of the Brij-56 into the micelles of the diprotic anionic surfactant is believed to account for the formation of the Ia-3d structure. As
the synthesis temperature increased, the Brij-56 became more hydrophobic and the highly hydrophobic Brij-56 tends to be associated with the hydrophobic part of the micelle formed by amphiphilic molecules. In this case, the co-surfactant Brij-56 behaves more like a swelling agent, which lies in the core of the anionic surfactant micelles, giving rise to disordered mesoporous structure with significant enlargement pore size (Table 2).

To further investigate the effect of Brij-56 on the mesostructure, AMS nanospheres were synthesized with different concentrations of Brij-56 at 30 °C (See Supplementary information, Fig. S1). When the Brij-56/C18GluA molar ratio is increased, the resultant mesostructure was obtained (Fig. 6c and d). The XRD pattern (Fig. 7A—a) of the sample synthesized by using C12GluA displays several reflections in the 2θ range of 1–4.5°, which can be indexed to 220 and 311 reflections on the basis of the cubic Fd-3m symmetry with unit-cell parameter of a = 114 Å. The samples synthesized with C16GluA and C18GluA show smaller particle size; however, only disordered mesostructure was obtained (Fig. 6c and d).

3.3. Effect of the alkyl chain length of surfactant CnGluA on the morphology and the mesostructure

The packing energetics of the surfactant depend greatly on its molecular geometry including the length of its alkyl chain [36], which could also affect the morphology of the mesoporous materials [37]. Here, anionic surfactants CnGluA (n = 12–18) with different alkyl chain length have been used in the synthesis of AMS nanospheres. As the TEM images shown in Fig. 6, mesoporous silica nanospheres were successfully synthesized by using C18GluA as the template, APS as the CSDA with addition of P123 as the dispersant.

The TEM images of the sample synthesized with C12GluA are shown in Fig. 6a, clearly revealing the [1 1 0] direction of the Fd-3m structure with stacking faults. Both cubic stacking (ABCABC) and hexagonal stacking (ABABAB) can be observed in a crystal. The stacking faults make streaks in the FDs along the [1 1 1] direction. Fig. 6b shows TEM images of the sample synthesized with C14GluA. The mesostructure is Fd-3m. Interestingly, a ten-fold quasicrystal-like FD is observed, which can be explained by the multiple twinning of the face centered cubic (fcc) structure. The particle growth layers, i.e., the stacking-fault planes, often share one or many stacking-fault layers with other domains, and therefore a fivefold center is created in the particle (marked by a circle). The AMS nanosphere materials synthesized with C16GluA and C18GluA show smaller particle size; however, only disordered mesostructure was obtained (Fig. 6c and d).

The N2 adsorption–desorption isotherms (Fig. 7B) are type IV, typical for mesoporous materials. The pore size increased from 2.2 to 3.4 nm with increasing the chain length of the anionic surfactant (Fig. 7C), which is reasonable because the mesopores derive from the alkyl chains of the surfactant. The N2 adsorption–desorption isotherms of the samples synthesized using C12GluA and C14GluA as the template exhibit well-reversible features without significant hysteresis loops due to the small mesopores. When the alkyl chain length of the anionic surfactant increased to 16 and 18, a second adsorption step at P/P0 > 0.9 is observed, due to the macroporosity caused by aggregation of the nanospheres. All of the samples maintained relatively high loading of amino groups of 2.9–3.4 mmol/g. The results of the morphological, porous and compositional characteristics of the nanospheres are summarized in Table 3.

The size of the mesoporous silica nanosphere is significantly affected by the type of the surfactant employed in the synthesis. It

![Fig. 7. XRD patterns (A), N2 adsorption–desorption isotherms (B) and pore size distributions (C) of the samples shown in Fig. 6.](image)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Average particle diameter (nm)</th>
<th>Standard deviation (%)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Primary mesopore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
<th>Loading of amino groups (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12GluA (a)</td>
<td>190</td>
<td>15.6</td>
<td>640</td>
<td>0.49</td>
<td>0.29</td>
<td>2.2</td>
<td>3.0</td>
</tr>
<tr>
<td>C14GluA (b)</td>
<td>100</td>
<td>13.1</td>
<td>794</td>
<td>1.01</td>
<td>0.43</td>
<td>3.2</td>
<td>2.9</td>
</tr>
<tr>
<td>C16GluA (c)</td>
<td>60</td>
<td>12.5</td>
<td>636</td>
<td>1.04</td>
<td>0.08</td>
<td>3.4</td>
<td>3.0</td>
</tr>
<tr>
<td>C18GluA (d)</td>
<td>50</td>
<td>11.2</td>
<td>669</td>
<td>1.20</td>
<td>0.02</td>
<td>3.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>
can be inferred from Table 3 that the diameter of the primary AMS nanospheres decreases from 190 to 50 nm with increasing the alkyl chain length of C18GluA in the presence of P123. This change in the particle size can be explained by the emulsification effect of the anionic surfactant with different chain length. The anionic surfactant used in the synthesis of AMS materials not only acts as the template for the mesopores but also stabilizes the surfactant-silicate micro-phase which further grows into large mesoporous solid. The anionic surfactant with longer alkyl chains readily emulsify and stabilize the surfactant/silicate micro-phase, giving rise to smaller particle size of the AMS nanospheres. As a result, the average particle size decreased from 190 to 50 nm with increasing the alkyl chain length of the surfactant from n = 12 to 18.

3.4. Effect of the surfactant concentration on the morphology and the mesostructure

It is well-known that the concentration of the surfactant is a critical factor affecting the structure and the size of the micelles and the templated mesoporous silica materials. In this work, we investigated the effect of surfactant concentration on the mesoporous structures and the particle size of AMS nanospheres, keeping the ratios of APS/C18GluA, TEOS/C18GluA and Brij-56/C18GluA constantly as 2, 15 and 0.6, respectively, and the reaction temperature, 80 °C.

Fig. 8 shows the TEM images of the AMS materials. The sample synthesized with high concentration surfactant (2%) shows large particle size (120–250 nm) with ordered mesostructure (Fig. 8a), however, the ordering is not high enough to determine the structure. The standard deviations of this sample is 26.9%. It can be inferred that the average particle size can be significantly reduced and the monodispersity can be improved by decreasing the concentration of the C18GluA from 2% to 0.3% (Table 4). The mesoporous nanospheres synthesized with low surfactant concentration possess disordered pore arrangement (Fig. 8b and c). The standard deviations of the size of the nanospheres synthesized with surfactant concentration of 0.7 and 0.3 were 12.8% and 7.4%, respectively, indicating the high monodispersity of the nanospheres. The sample synthesized with 0.3% surfactant concentration has the uniform particle size of ~30 nm with the highest monodispersity.

The XRD pattern (Fig. 9A—a) of the sample synthesized by C18GluA concentration of 2% displays two reflections in the 2θ range of 1–2°, however, the XRD pattern is not allowed structure determination because of the limited information. The samples synthesized with low surfactant concentration only show one broad reflection within the range of 2θ = 1.5–2.5° (0.7% and 0.3%), indicating disordered mesostructures, in good agreement with the result from TEM observations.

Fig 9B and C show the N2 adsorption–desorption isotherms and pore size distributions of the mesoporous silicas. All samples show type IV isotherms with sharp capillary condensation steps in the relative pressure (P/P0) of 0.4–0.8 and have high surface areas and pore volumes (Table 4). The steep uptake of nitrogen at P/P0 ~ 1 is attributed to the cavities caused by aggregation of the nanospheres.

It can be inferred that mesoporous silica nanospheres could be synthesized within a proper range of surfactant concentration. The nanospheres become smaller with decreasing the surfactant concentration. Generally, the formation of the AMS nanospheres includes the formation of clusters seeds their aggregation and separation into nanoparticles. The higher concentration of the reactants produces higher concentration of the clusters seed, and on the other hand facilitates their aggregation leading to the large particles. However, the changes in mesopore dimensions are observed with the surfactant concentrations, which might due to the different mesostructure formed with different surfactant concentration.

The redisperability of these particles in water is one of the crucial properties for potential use of these nanospheres, especially in biomedical applications. We found that although the nanoparticles

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![Fig. 8. TEM images of the mesoporous silica spheres synthesized with different surfactant concentrations of 2.0 wt.% (a), 0.7 wt.% (b) and 0.3 wt.% (c). The synthesis molar composition is 1C18GluA: 15TEOS: xH2O: 0.29Brij-56 (where x = 1168, 3336 and 7783). The reaction temperature is 80 °C.](image)

<table>
<thead>
<tr>
<th>C18GluA (wt.%)</th>
<th>Average particle diameter (nm)</th>
<th>Standard deviation (%)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Primary mesopore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
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<tbody>
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<td>2.0 (a)</td>
<td>210</td>
<td>26.9</td>
<td>773</td>
<td>1.33</td>
<td>0.88</td>
<td>4.3</td>
</tr>
<tr>
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<td>120</td>
<td>11.0</td>
<td>719</td>
<td>1.85</td>
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<td>5.3</td>
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<tr>
<td>0.7 (b)</td>
<td>60</td>
<td>12.8</td>
<td>689</td>
<td>1.15</td>
<td>0.32</td>
<td>4.0</td>
</tr>
<tr>
<td>0.3 (c)</td>
<td>30</td>
<td>7.4</td>
<td>775</td>
<td>1.39</td>
<td>0.17</td>
<td>3.8</td>
</tr>
</tbody>
</table>

* The same sample shown in Table 1(a).
aggregate after extraction and the drying process, the materials with different particle size can easily be redispersed by mild sonication (See Supplementary information, Fig. S2).

3.5. Morphological and structural transformation with reaction time

To investigate the morphological evolution of the mesoporous silica nanoparticles, the SEM images (Fig. 10) and DLS (Fig. 11) of the products synthesized with Brij-56/C18GluA molar ratio of 0.29 at 80 °C (Fig. 8 sample c), were monitored as a function of the reaction time.

The morphological transformation can be observed clearly from SEM images. At first, the morphology of larger, irregular particles was observed for the sample synthesized for 1 min. The large particles at the beginning of the synthesis also have been detected in DLS measurement (Fig. 11a). From SEM images, it can be seen that the spheres have emerged from the large particles and then separated quickly with keeping the constant particle size. The anionic lipid molecules would easily aggregate to form the oil-like large droplet before silica condensation processed. From DLS, a rapid decrease in oil droplet size was observed within the first 1 min and then decreased to around 70 nm, which remained almost constant for a long time. The aggregation of the nanoparticles to a large

Fig. 9. XRD patterns (A), N₂ adsorption–desorption isotherms (B) and pore size distributions (C) of the samples shown in Fig. 8.

Fig. 10. SEM images of as-synthesized products sampled at different reaction periods of the sample shown in Fig. 8b.

Fig. 11. Dynamic light scattering (DLS) profile of the products shown in Fig. 10 (A), Size distribution of the particles at different reaction periods of the products (B).
particle would be caused by sample drying process. It has been found that the particles size was increased with increasing Brij-56 concentration, and the formation rate from large particles to nanoparticles was almost not affected by the Brij-56 concentration.

The effect of the concentration of Brij-56 on the monodispersity of the AMS nanospheres can be explained in terms of the influence of Brij-56 on the born process of the nanospheres. The formation of the AMS nanospheres can be considered to be started from large oil-like droplet surfactant–silicate clusters which would be cross-linked and separated into small particles with silica condensation processed. The monodispersity of the born particle depends on the difference in the rate between the cluster cross-linking and separation. A higher degree of separation of the cluster leads to formation of more monodisperse particles. The presence of Brij-56 dramatically increases the viscosity of micellar solution, slowing down the cross-linking of surfactant–silicate clusters, which favors the separate process of the particles. The particle separation, driven by global surface tension forces, will minimize its surface free energy by forming monodisperse spheres. With low or high Brij-56 concentration, the degree of separation between the clusters was not adequate to produce monodisperse particles. With proper Brij-56 concentration, the slow cross-linking of the surfactant–silica clusters favors formation of monodisperse mesoporous silica nanospheres with uniform morphologies.

The concentration of Brij-56 affects not only the monodispersity of the AMS nanospheres but also the particle size. The higher the concentration of Brij-56, the larger the nanosphere grows. The particle size of the nanospheres would be controlled by the nucleation number of disordered clusters and the kinetic aggregation rate. The larger nucleation numbers and the slower aggregation rate, the smaller mesoporous nanosphere particles would be formed. The cluster numbers is controlled by the kinetics of the hydrolysis and condensation rates of TEOS. It is well-known that the Brij56 addition into TEOS–water reaction system significantly suppressed its hydrolysis and condensation rate, which is not favorable for both cluster formation and their aggregation. It can be considered that small cluster numbers would be formed in the presence of Brij-56 and decreased with increasing of Brij-56 addition amount. Then, the clusters would become large particle by aggregation with other clusters gradually. As mentioned above, here, we found that the particle size of the nanoparticles was significantly increased with addition of Brij-56 and with increasing its addition amount. Therefore, in this case, the small numbers of cluster seems predominant over the aggregation effect of Brij-56.

4. Conclusions

The addition of nonionic surfactant proved effective for tuning the size of the AMS nanospheres from 30 to 320 nm and for changing the mesoporous structure from ordered structure to disordered structure. Monodisperse AMS nanospheres could be obtained when the concentration of Brij-56 is 0.15%.

The reaction temperature plays an important role in the formation of the AMS nanospheres. The mesostructure changed from \( \text{I}_{0} \rightarrow \text{I}_{3} \text{d} \) to wormlike when the reaction temperature increased from 30 to 80 °C, while the monodispersity morphology could be achieved at 80 °C. At low temperature the Brij-56 could be incorporated into the anionic surfactant micelles changing its organic/inorganic interface curvature, and at high temperatures the Brij-56 acts more as a swelling agent of the mesopores. Other mesostructures can be also formed by using different anionic surfactants.

With addition of nonionic P123, mesoporous nanospheres could be synthesized by using C_{12}GlUA \((n = 12–18)\) as the template. When the alkyl chain length increased from \(n = 12\) to 18, the particle sizes decreased from 190 to 50 nm, due to better emulsionification ability of surfactant with longer chains, and the resultant mesostructure changed from cubic \( Fd-3m\) to disordered.

Higher concentration of anionic surfactant was found to favor the formation of larger AMS nanospheres with larger pore size, which could be explained by the favorable aggregation kinetics of the primary surfactant–silica clusters and the swelling effect. Thus, it has been found that higher concentration of the non-ionic surfactant leads to larger particle size, larger pore size and lower ordering of the mesostructure; higher concentration of the anionic surfactant produces larger particle size; larger pore size and higher ordering of the mesostructure; the shorter chain length of the anionic surfactant leads to larger particle size, smaller pore size and higher ordering of the mesostructure and the higher reaction temperature favors the formation of larger particle size, larger pore size and lower ordering of the mesostructure. It is predictable that new nanoparticles with designed particles size, pore size and mesoscopic ordering can be synthesized according to these rules.

After removal of the surfactant by extraction, AMS nanospheres functionalized with high loading of amino groups could be obtained, which could find potential use in catalysis, separation, adsorption, drug-delivery, and sensor devices, etc.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2010.10.025.

References