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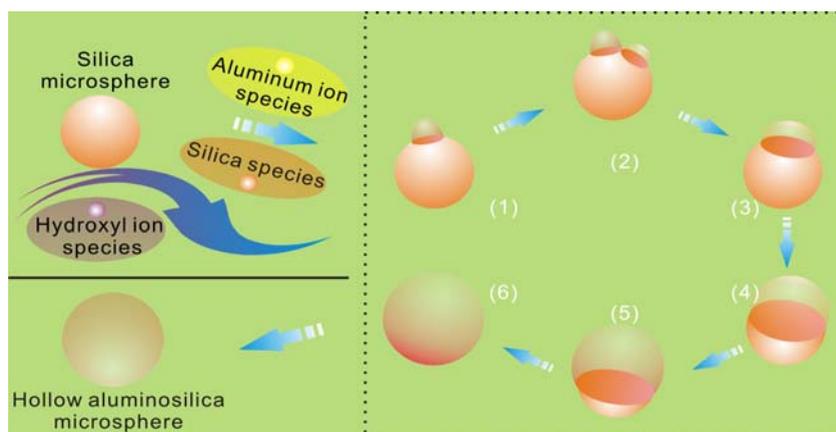


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Monodispersed hollow aluminosilica microspheres with thin shell structures have been successfully synthesized via a facile, novel method.

A facile and novel approach for preparing monodispersed hollow aluminosilica microspheres with thin shell structures

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Abstract;

Monodispersed hollow aluminosilica microspheres (HAMs) with thin shell structures have been successfully synthesized via a novel method. The facial strategy is simple, efficient, and highly controllable. NaAlO₂ aqueous solution is firstly employed as an alkaline solution to directly etch silica microspheres hard templates without additional surfactants for forming monodispersed hollow microspheres. On the basis of the proposed formation mechanism of etching followed by co-assembly, the size of HAMs is fully dependent on the size of silica spheres hard templates.

Keywords: aluminosilica microspheres, thin shell, hollow, silica template.

1 Introduction

Hollow nano- and microspheres with well-defined structures have been of

particular interest because of their low density, increased surface area and high porosity.¹⁻¹² The excellent properties make them good candidates for the potential applications in catalysis, chromatography, the protection of biologically active agents, fillers (or pigments, coatings), waste removal, and large biomolecular-release systems.^{5, 7, 10, 13-20}

In the past decade, efforts have been made in the design and synthesis of hollow mesoporous structures with desired components.^{1, 4-6, 13, 15, 16, 21-36} Various synthetic strategies have been developed to prepare this type of nanostructured inorganic materials, including template-directed synthesis, Kirkendall or ostwald ripening effect, ship-in-bottle techniques, bubble-assisted method and selective etching.^{1, 4-6, 13, 15, 16, 21-39} Among the strategies, the template-directed synthesis method is particularly interesting and frequently used to fabricate hollow spheres with homogeneous, dense layers. For example, Xia et al. successfully synthesize hollow platinum spheres with spherical colloids of amorphous selenium as templates.⁴⁰ Our group use ZnO nanorods as templates to fabricate TiO₂ hollow nanotubes.⁴¹ In addition, silica nanospheres have been widely used as hard templates, which obtained great success in the synthesis of mesoporous structures with various shell components and functional cores.^{7, 12, 19, 35, 42-45}

Among the silica-based templating method, the selective etching process is essential. When dispersed in a solution with etching agent, amorphous silica colloids undergo a spontaneous morphology change from solid to hollow spheres. The etching agents reported up to date are including NaBH₄, NaOH, NH₃ · 3H₂O, Na₂CO₃, HCl

and HF solution.^{7, 12, 19, 35, 42-45} It is well-known that incorporation of aluminum into the silica network can provide mesoporous silica with preferable properties in acidity and stability in various chemical and physical environments.⁴³⁻⁴⁶ Therefore, mesoporous aluminosilica shells are a benefit for upgrading and applications of hollow mesoporous structures. In previous studies, conventional mesoporous aluminosilicas, such as Al-MCM-41 are usually obtained by co-assembly of cationic surfactants (i.e. CTAB), aluminate species (i.e. NaAlO_2), and silicate species in a hot alkaline solution. Tetraethyl orthosilicate (TEOS) and sodium silicate (Na_2SiO_3) are the most widely used silica precursors.⁴⁶⁻⁴⁹ Although these approaches are easy to control the structures parameters of mesopores, the morphologies of as-synthesized mesoporous aluminosilicas are always irregular. Most importantly, the application of surfactants such as CTAB will be inevitable to bring in additional components to mesoporous aluminosilicas, which will be disadvantageous for their practical performance. Consequently, it is highly desirable that the etching of silica materials to form hollow spheres without using surfactants in alkaline solution media with aluminate species.

Herein, we show that amorphous silica spheres can also be hollowed out in NaAlO_2 solution by using a novel method without additional surfactants. In comparison with other techniques, the primary differences and advantages of this as-proposed approach are: a) our method by using novel growth process to fabricate the hollow spheres is very simple and highly reproducible; b) No additional templates or protective surfactants are needed. Thus, as-prepared hollow spheres should have

relatively clean surfaces, which are important in some application areas with strict surface chemistry requirements, such as catalysis, electrochemistry, sensing, etc; c) the size of the hollow microspheres is very uniform and easily controllable because it is fully dependent on the uniformity and size of the starting amorphous silica spheres.

2 Experimental

All reagents were of analytical grade and used without further purification. In a typical experiment, 0.1g of silica microspheres was dispersed to form a homogeneous suspension in 20mL of deionized water by ultrasonication. 1.02g of sodium aluminate (NaAlO_2) was dissolved in 30mL of deionized water by stirring. The above solutions were then mixed to form a homogeneous suspension and transferred to a Teflon autoclave (70mL) and heated to a temperature of 140°C for 28min. After the reaction system was naturally cooled to room temperature, the white precipitates was separated from solution and thoroughly washed several times with deionized water and absolutely ethanol, and then dried in a vacuum oven at 50°C for 6h.

Field emission scanning electron microscope (FESEM) images were taken on a FESEM (Quanta 200 FEG) operated at an accelerating voltage of 10.0kV. Transmission electron microscope (TEM) images were obtained on a JEOL JEM-2010 high resolution transmission electron microscope, equipped with X-ray energy dispersive spectroscopy (EDS) capabilities, working at an acceleration voltage of 200 kV. The specific surface areas of the samples were measured with Micromeritics ASAP 2020 M+C Brunauer-Emmet-Teller (BET) equipment by using

nitrogen adsorption and desorption.

3 Results and discussion

3.1 Synthesis of hollow aluminosilica microspheres (HAMs) with thin shell structures

In previous studies, conventional aluminosilicas are usually obtained by co-assembly of cationic surfactants, aluminate species, and silicate species in a hot alkaline solution.^{7, 43, 44, 48-50} Although these approaches are easy to control the structure parameters of hollow structures, the application of surfactants such as CTAB will be inevitable to bring in additional components to mesoporous aluminosilicas, which will be disadvantageous for their practical performance. In this study, NaAlO₂ aqueous solution is firstly employed as an alkaline solution to directly etch silica microspheres hard templates without additional surfactants.

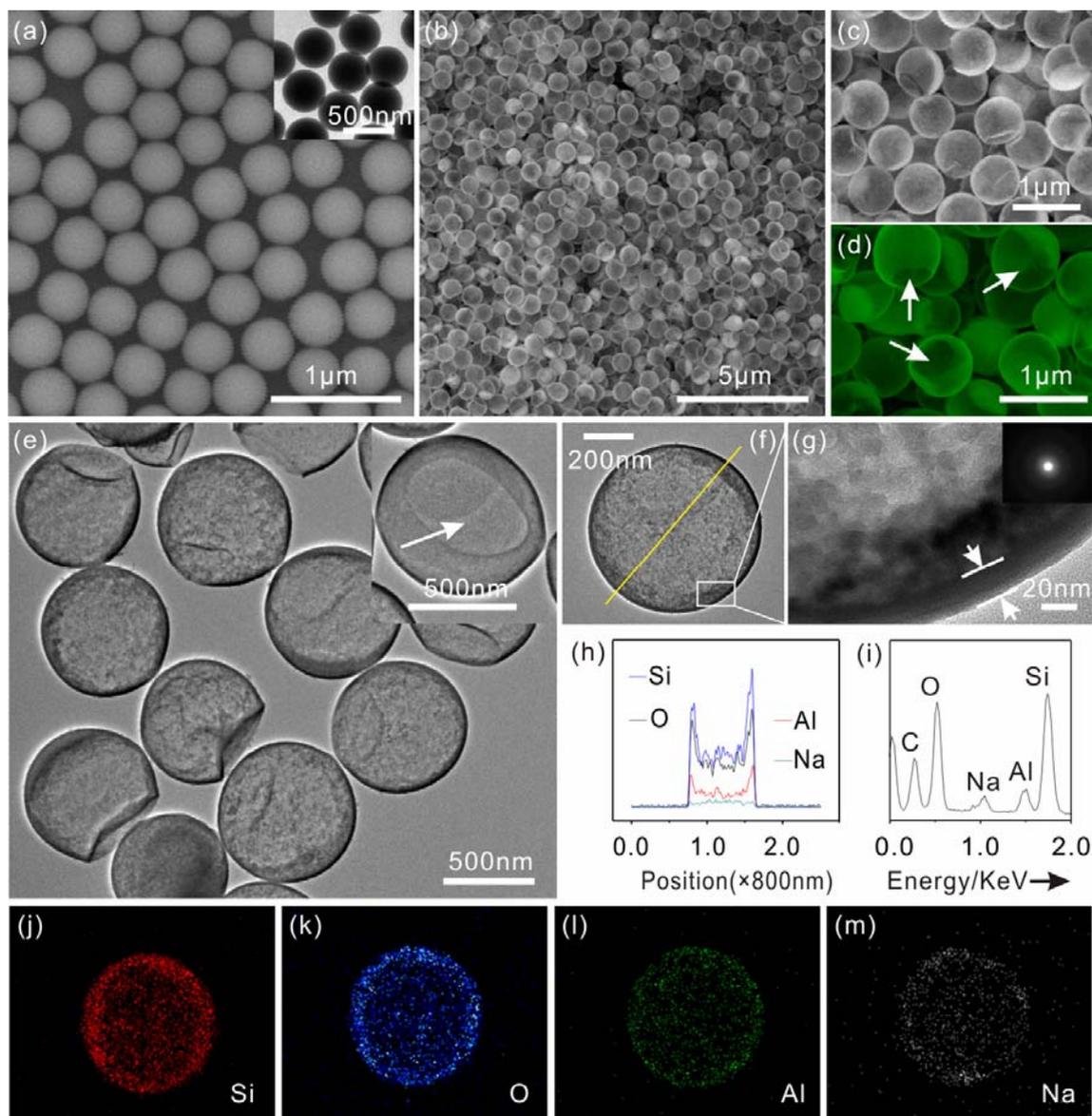


Figure 1. (a) SEM and TEM (inset) images of silica microspheres, (b) SEM and (c, d) high-magnification SEM images of the hollow aluminosilica microspheres (HAMs) with thin shell structures, (e, f) TEM and (g) HRTEM images of the HAMs with thin shell structures (Inset in (g): corresponding SAED pattern), (h) EDS line scanning results, (i) EDS spectrum and (j-m) elemental mapping images of single HAM.

Figure 1(a) shows SEM and TEM (inset) images of the silica microspheres as silica precursors. It is clear that the sample is composed of nearly monodispersed spherical particles with a diameter of about 450nm as the precursor for synthesis of hollow aluminosilica microspheres (HAMs) with thin shell structures. After going through a facile reaction condition in which silica microspheres are treated with a hot NaAlO_2

aqueous solution, silica microspheres are directly converted into many monodispersed and uniform HAMs with thin shell structures (Figure 1 (b)). And the as-synthesized HAMs possess well-defined thin shells and cavities, shown in Figure 1(c-f). The high-magnification SEM and TEM images (indicated by the arrow in Figure 1 (d) and (e)) reveal that there are some broken places on the shells of the HAMs. The broken places also show that the shells of the HAMs have very thin structures. As revealed in the HRTEM image (Figure 1(g)), the as-synthesized HAMs have a uniform shell with an average thickness of 20nm. More interestingly, the average diameter of the HAMs is about 720nm, which is larger than that of the initial silica microspheres. HRTEM image shown in Figure 1(g) reveals that the obtained HAMs are amorphous, which is consistent with the SAED pattern (see inset of Figure 1(g)).

To further investigate the hollow structure, TEM elemental line scanning and mapping analysis are employed to identify the obtained HAMs with thin shell structures. From the corresponding EDS line scanning results (Figure 1(h)), it is noted that the Si, O, Al and Na seem to concentrate more at the edge than in the HAM center. Figure 1(i) is the EDS spectrum of single HAMs, in which Si, O, Al and Na are all present. The elemental mapping images in Figure 1(j)–(m) also clearly show the distribution of the Si, O, Al and Na in single HAM. The elemental signals are dominant in the shell region, indicating the formation of a hollow structure.

Figure 2 and its inset are the representative nitrogen adsorption-desorption isotherms and corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution curves of the a) silica microspheres and b) HAMs with thin shell structures, respectively. It can be seen that the HAMs with thin shell structures have a type IV isotherm with a type H3 hysteresis loop. The BET surface area and the pore volume have been estimated to be $48.9\text{m}^2\text{ g}^{-1}$ and $0.121\text{cm}^3\text{ g}^{-1}$, respectively. The pore size distribution curve of the HAMs with thin shell structures exhibits a broad peak in the range of 7–110nm with a maximum at 80nm. The result indicates that there are some mesopores/macropores in the HAMs. However, the porous nature of the silica microspheres can be neglected due to the small specific surface area ($9.2\text{m}^2\text{ g}^{-1}$) and total pore volume (0.016cm^3).

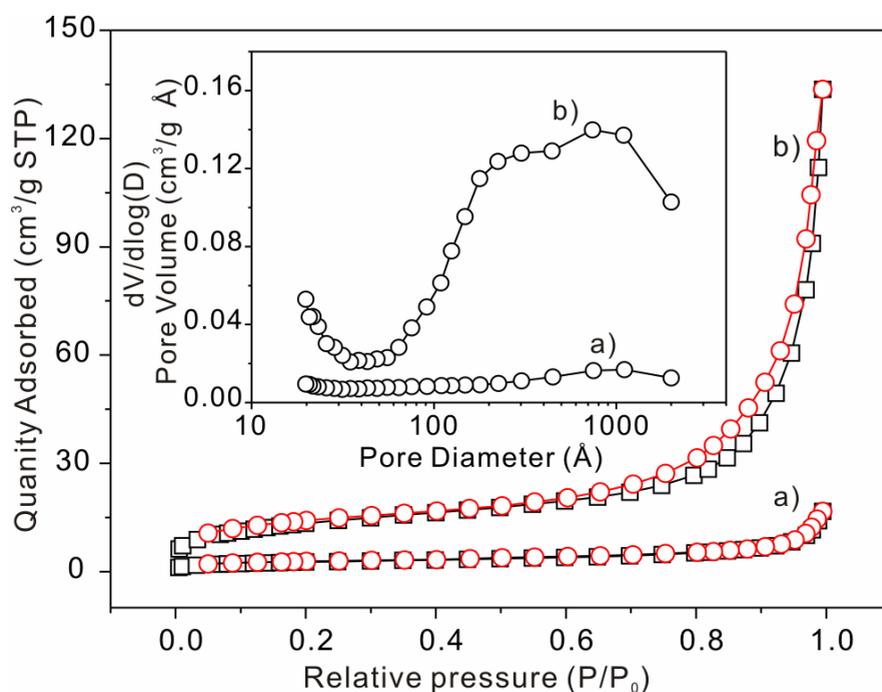


Figure 2. N_2 adsorption-desorption isotherms with pore size distributions (inset) of the a) silica microspheres and b) HAMs with thin shell structures

3.2 Formation mechanism of hollow aluminosilica microspheres with thin shell structures

The formation of hollow aluminosilica microspheres is hypothesized to occur by etching silica under alkaline conditions and meanwhile by assembling silicate and aluminium ion species. To understand such a mechanism, we carry out time dependent experiments in which samples are collected at different time intervals. Figure 3(b) presents the product synthesized with reaction time of 3min. It is clear that a bubble-like structure on the surface of silica microsphere is observed. When prolonging the reaction time to 7min, two bubble-like structures appear on the surface of silica microsphere as shown in Figure 3(c). Interestingly, after reaction time of 11min, the two bubble-like structures coalesce into one bubble-like structure (see Figure 3(d)). Furthermore, the bubble-like structure becomes larger while silica microsphere continues shrunken when the reaction time is up to 16min, as shown in Figure 3(e). When the reaction time is longer than 20min, the size of the bubble-like

structure become larger and larger; meanwhile, the silica gradually disappeared, as shown in Figure 3(f) and (g). Continuing to increase the reaction time to 28 min (Figure 3(h)), all of the silica disappeared completely and a HAM is formed.

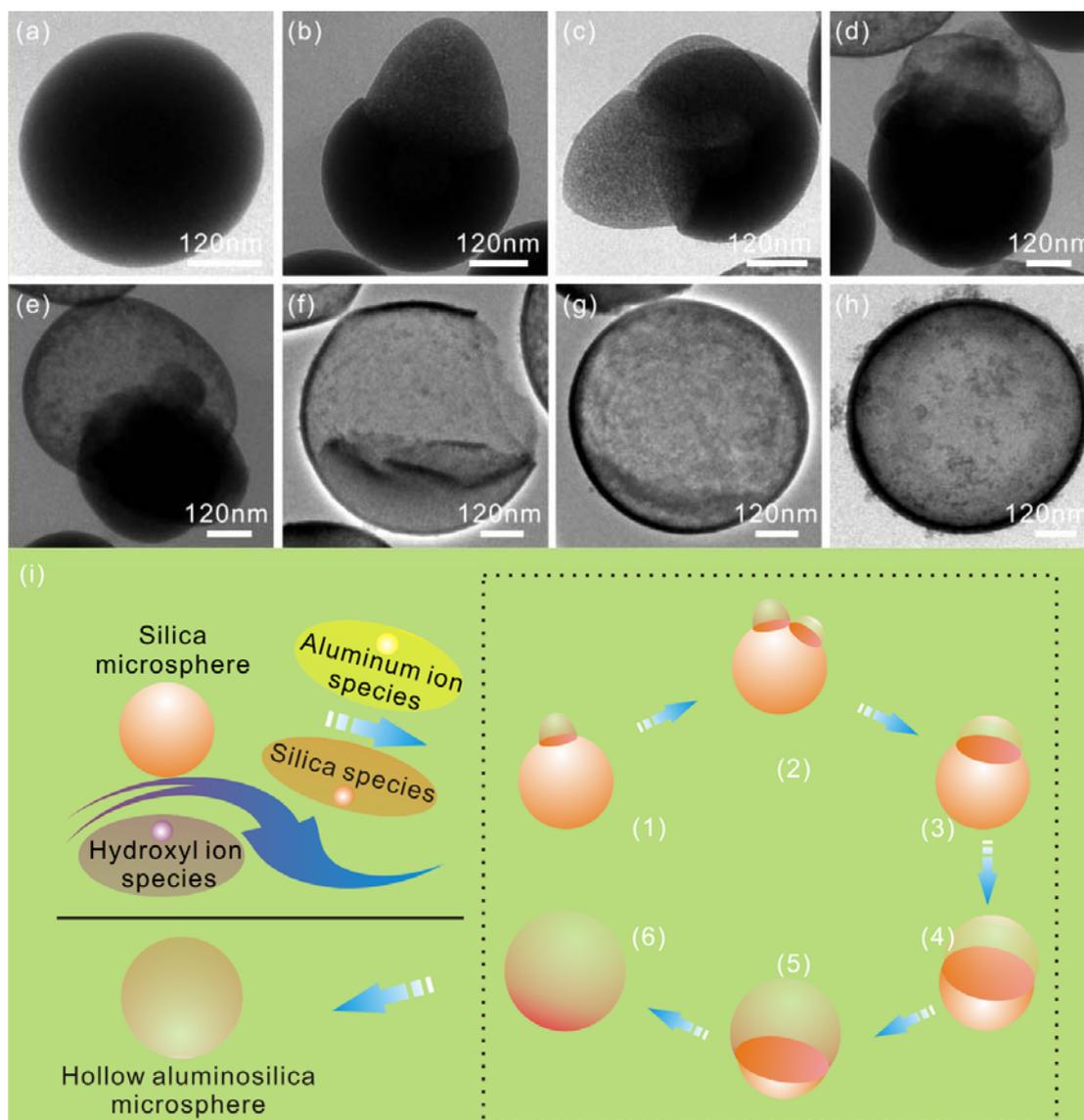


Figure 3. (a-h) TEM images of the morphological evolution in the time-dependent experiments carried out by using 0.1g of silica microspheres with a diameter of approximately 450nm: (a) 0min, (b) 3min, (c) 7min, (d) 11min, (e) 16min, (f) 20min, (g) 25min, and (h) 28min. (i) Schematic illustration for the formation of the HAMs with thin shell structures.

Generally, aluminate anions at high temperature undergo the following chemical reactions:⁵¹



When the solution is heated at 140 °C, $\text{Al}(\text{OH})_3$ would be formed on the basis of the hydrolysis reaction through Equation (1). Under alkaline conditions, the newly formed $\text{Al}(\text{OH})_3$ could be further hydrolysed to aluminum ion (Al^{3+}) and hydroxyl ion (OH^-) through Equation (2), expectably.

According to Equation (3), the aqueous solution having higher concentration of sodium aluminate is strong alkaline. The disappearance of the silica indicates that the silica is etched gradually under the alkaline reaction condition. At the same time, the continuously generated silicate species etch-release from silica and the aluminate species can assemble to form the aluminosilica bubble-like shell on the surface of silica microsphere observed during the formation of HAMs. From the TEM images (a-h) of the morphological evolution in the time-dependent experiments, the whole assembly growth process of the HAMs is similar to that of blowing bubble process.

On the basis of the growth process of HAMs, the formation mechanism of HAMs is proposed as illustrated in Figure 3(i): (1) the silica templates are slowly etched under the alkaline condition to provide soluble silicate species. The released soluble silicate species are then assembled with aluminate species on the surface of silica to form the aluminosilica shell. At the initial reaction stage, the aluminosilica shell looks like a small bubble. (2-3) With the increase of reaction time, two small bubble-like aluminosilica shells appear on the surface of silica microsphere. After that, they coalesce into one bubble-like aluminosilica shell. (4-6) Along with the etching of silica spheres, the bubble-like aluminosilica shells grow continuously. Finally, the HAMs with thin shell structures form when the silica is entirely etched.

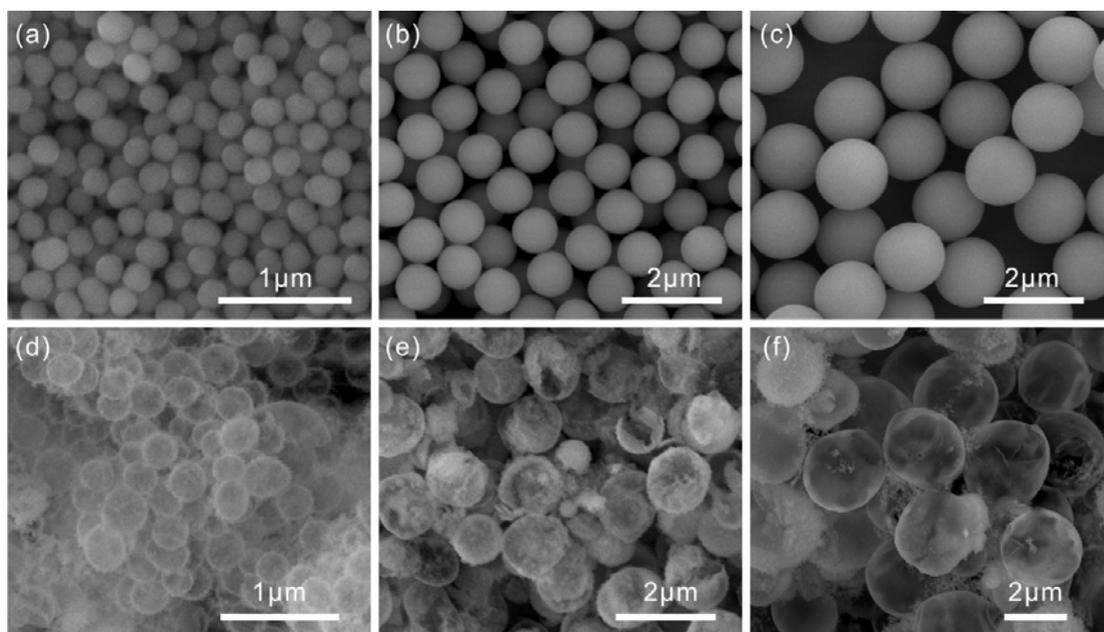


Figure 4. SEM images of silica microspheres with different diameter: (a) 200nm, (b)1000nm, and (c)1500nm; the corresponding SEM images of as-prepared HAMS obtained by etching different silica spheres hard templates: (d) 200nm, (e)1000nm, and (f)1500nm , respectively.

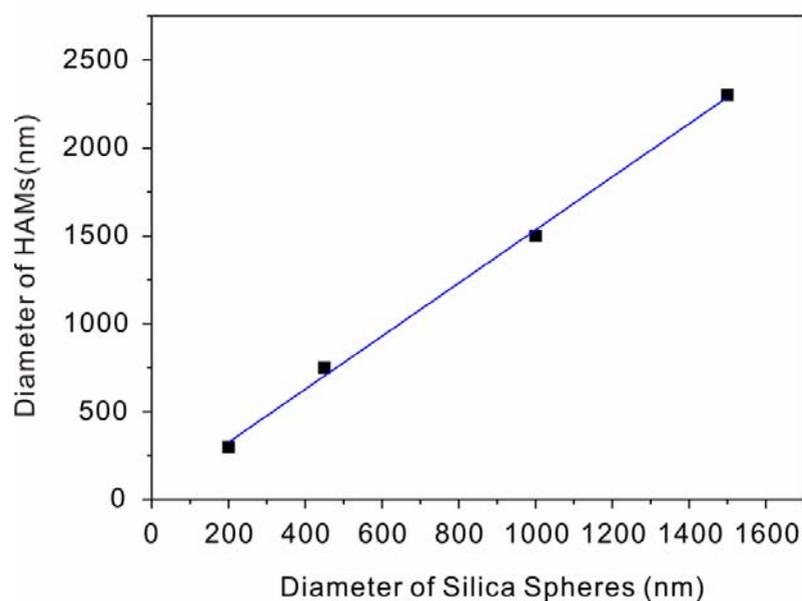


Figure 5. The diameter of as-prepared HAMS depending on the size of the silica spheres.

This facile strategy is simple, efficient and highly controllable. On the basis of the proposed formation mechanism of etching followed by co-assembly, the size of

HAMs is fully dependent on the size of silica spheres hard templates. Beside we have successfully prepared HAM with diameter of 720nm by etching silica sphere hard template with diameter of 450nm, as shown in Figure 1. To further demonstrate this issue, we investigate the effect of size of silica templates to diameter of as-prepared HAMs through the novel method. Figure 4 depicts typical FESEM images of the silica spheres with varying diameter (200nm, 1000nm and 1500 nm). At the end of the reaction, the HAMs with thin shell structures are certainly formed and corresponding diameter of as-prepared HAMs with thin shell structures is increased from 300 nm, 1500nm, and to 2300nm, respectively. Interestingly, it is found that there is a linear relation between the diameter of silica sphere (200, 450, 1000, and 1500nm) and the diameter of corresponding HAMs (300, 720, 1500, and 2300nm), which means the size of as-prepared HAMs is strongly dependent on the diameter of silica spheres (Figure 5). More importantly, through this method, the size of HAMs is easily tunable. Thus, according to practical requirements, HAMs with different size can be obtained by using silica spheres with the corresponding size as template.

4 Conclusions

In summary, we have proposed a facile and novel method for successfully synthesizing monodispersed hollow aluminosilica microspheres with thin shell structures. Such a synthetic strategy is remarkably effective and reproducible. Through this method, the size of HAMs is easily tunable. On the basis of the proposed formation mechanism of etching followed by co-assembly, the size of HAMs is fully dependent on the size of silica spheres hard templates. The product possesses a high BET surface area of $48.9\text{m}^2\text{ g}^{-1}$ and a large pore volume of $0.121\text{cm}^3\text{ g}^{-1}$. The excellent hollow structures of the product reported in this work are powerful platforms for nanoreactors. We believe that the strategy reported herein will stimulate chemists to explore its further promising applications, such as confined catalysis and controlled release.

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