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Synthesis of porous hollow silica spheres using functionalized polystyrene latex spheres as templates

Chun Liu, Chen Ge, Aili Wang, Hengbo Yin†, Min Ren, Yunsheng Zhang, Longbao Yu, and Tingshun Jiang

Faculty of Chemistry and Chemical Engineering, Jiangsu University, Xuefu Road 301, Zhenjiang 212013, P. R. China
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Abstract−Uniform sized and integrated hollow silica spheres with porous shells were prepared by using sulfuric and carboxylic acid-functionalized polystyrene latex spheres as templates, sodium silicate as a precursor, and cetyltrimethylammonium bromide as a shell structure-directing agent. When polystyrene-methyl acrylic acid latex spheres were used as the templates, the pores in the shells of the resultant hollow silica spheres were composed of both micropores and mesopores. The pores in the shells of the hollow silica spheres were mainly composed of mesopores when sulfonated polystyrene-methyl acrylic acid latex spheres were used as the templates. The shell thickness and the specific surface area of the hollow silica spheres increased with the increase in the surface acidity of the latex spheres.

Key words: Hollow Silica Spheres, Sodium Silicate, Functionalized Polystyrene, Methyl Acrylic Acid, Sulfuric Acid

INTRODUCTION

Hollow spherical structured materials with porous shells have attracted intense interest from both scientific and technological viewpoints due to their good surface permeability, large specific area, low density, and high mechanical stability [1,2]. Hollow spherical structured materials, such as Fe_2O_3, Fe_3O_4, NiO, Co_3O_4, CeO_2, MgO, CuO, TiO_2, ZnO, Ta_2O_5, CdS, and SiO_2, were successfully synthesized [3-12]. Among them, hollow silica spheres with porous shells have potential applications for drug delivery [13,14], catalysis [15], hydrogen occlusion [16], adsorption, and coatings. Various approaches have been investigated for preparation of hollow silica spheres, such as sacrificial templates [13,17], oil/water/oil (O/W/O) microemulsions [18], water/oil (W/O) reverse emulsions [19], and sol-gel/emulsion [9] techniques.

For the commonly used sacrificial template approach, polystyrene latex [20], chitosan-polyacrylic acid [21], weakly cross-linked melamine-formaldehyde [20], calcium carbonate nanoparticles [17, 22], and assemblies of Fe_3O_4 nanocrystals [13] were used as templates. Hexadecyltrimethylammonium bromide [17], polydiallyldimethylammonium chloride [20], cetyltrimethylammonium bromide [22], and poly-L-lysine [23] were used as shell structure-directing agents. Tetraethoxysilane [13], silica nanoparticles or colloidal silica [20,21], and tetramethoxysilane [23] were used as precursors of silica.

Polystyrene latex sphere is an attractive template since uniform-sized polystyrene sphere can be easily and relatively inexpensively prepared. In the polystyrene latex templating approach, the amine layer adsorbed on the surface of the polystyrene latex sphere induces the formation of silica layer via electrostatic force. After calcination or dissolution, the polystyrene latex sphere and amine are removed, giving the formation of hollow silica sphere with porous shell. But there are still some challenges in the polystyrene latex templating approach. The combination extent between polystyrene latex sphere and amine affects the integrity of the resultant hollow silica sphere. Using silanes or silica nanoparticles as precursors of hollow silica sphere makes the cost high and the process complicated.

In our present work, in order to increase the combination extent between polystyrene latex sphere and cetyltrimethylammonium bromide, the surfaces of the polystyrene latex spheres were functionalized with acidic groups *via* copolymerization of styrene and methyl acrylic acid or sulfonation with sulfuric acid. Environmental friendly and low cost sodium silicate was used as a precursor of silica shells instead of silane. The evolution mechanism of hollow silica spheres was also investigated.

EXPERIMENTAL

1. Materials

The chemicals, such as sodium silicate ($Na_2SiO_3 \cdot 9H_2O$, 99%), cetyltrimethylammonium bromide (99%), sodium hydroxide (98%), styrene (99%), potassium persulfate (99.5%), concentrated sulfuric acid (98%), and methyl acrylic acid (98%), were purchased from China Chemical Reagent Co. Ltd. All the chemicals were of analytical grade and styrene was used after distillation. Distilled water was used throughout all of the experiments.

2. Preparation of Polystyrene and Acidic Group-functionalized Polystyrene Latex Spheres

Polystyrene and polystyrene-methyl acrylic acid latex spheres were prepared by an emulsifier-free emulsion polymerization method. Potassium persulfate ($K_2S_2O_8$) served as an initiator. The polystyrene and polystyrene-methyl acrylic acid latex spheres were prepared by changing the volume ratio of styrene to methyl acrylic acid. The preparation of polystyrene-methyl acrylic acid latex spheres was illustrated as follows. Styrene (50 ml), methyl acrylic acid (5 ml), and water (450 ml) were introduced into a 1,000 ml four-necked flask equipped with mechanical stirrer, reflux condenser, nitrogen inlet, and temperature controller. After deoxygenating the reaction mixture *via* bubbling nitrogen gas for 30 min, the temperature was increased to 70 °C and an aqueous solution of potassium persulfate

†To whom correspondence should be addressed.
E-mail: yin@ujs.edu.cn

(0.25 g in 10 ml of water) was added to start the polymerization process. The reaction was allowed to proceed for another 24 h and polystyrene-methyl acrylic acid latex was obtained as a stable dispersion in water with *ca.* 10% solid content. The preparation method of polystyrene latex was similar to that of polystyrene-methyl acrylic acid latex without using methyl acrylic acid. The as-prepared polystyrene and polystyrene-methyl acrylic acid latexes were centrifuged and washed with distilled water and ethanol, respectively.

For the preparation of sulfonated polystyrene-methyl acrylic acid latex, 55 ml of polystyrene-methyl acrylic acid latex (*ca.* 10%) aqueous suspension was transferred into a 500 ml beaker; then 200 ml of concentrated sulfuric acid (98%) was added dropwise and stirred at 40 °C for 4 h. The as-prepared sulfonated polystyrene-methyl acrylic acid latex was centrifuged and washed with distilled water and ethanol, respectively.

3. Preparation of Hollow Silica Spheres

Five grams of the as-prepared latex templates was ultrasonically treated in 150 ml of water for 20 min to obtain a well-dispersed suspension. The suspension was transferred into a 1,000 ml flask and heated to 80 °C in a water bath. Then an aqueous solution of cetyltrimethylammonium bromide (0.25 g in 5 ml of water) was added to the suspension and kept stirred for 1 h. The suspension was adjusted to a pH value of 7 by adding an NaOH (0.5 mol/*l*) aqueous solution. 300 ml of Na_2SiO_3 aqueous solution (0.1 mol/*l*) and 300 ml of sulfuric acid (0.1 mol/*l*) solution were added to the above-mentioned suspension with two constant flow pumps. The flow rate of the Na_2SiO_3 aqueous solution was kept constant and the feeding time was fixed at 3 h. The pH value of the reaction solution was kept at 7 during the coating process by adjusting the flow rate of the sulfuric acid. After feeding, the resultant suspension was aged for 3 h at a pH value of 9.5. The precipitate was filtrated and washed with distilled water until the conductivity of the filtrate was less than 20 mS/m. Then the washed precipitate was dried in an electric oven at 120 °C for 4 h. The as-prepared samples were heated from room temperature to 550 °C at a rate of 1 °C/min and kept at 550 °C for 4 h under atmospheric condition in order to oxidize the latex templates.

4. Characterization

Scanning electron microscopy (SEM, JSM 7001F) and transmission electron microscopy (TEM, Philips Tecnnai-12, operating at 120 kV) were used to investigate the morphologies of the latex templates, the silica-coated latex template core-shell composites, and the resultant hollow silica spheres. The samples for TEM inspection were dispersed in ethanol solution with ultrasonic treatment for 10 min. Then a few drops of the resultant suspension were dropped onto a copper grid coated with a layer of amorphous carbon. The Fourier transform infrared spectra of the samples were performed by the KBr pellet technique on a Fourier transform infrared spectrometer (Nicolet Nexus 470) to determine the interfacial chemical bonding structure. Nitrogen adsorption/desorption isotherms of the hollow silica spheres were obtained from a volumetric adsorption analyzer (Quantachrome Corporation, NOVA2000e). The sample was first degassed in vacuum at 300 °C for 1 h. Then the measurement was carried out at 77 K over a range of relative pressures (P/P_0), where P_0 is the saturated vapor pressure, from 0.1 to 1. The specific surface area and the pore size distribution were calculated by BET and BJH methods, respectively.

RESULTS AND DISCUSSION

1. Morphologies of Latex Templates, Silica-coated Latex Composites, and Hollow Silica Spheres

Fig. 1 shows the SEM images of the latex templates. All of the latex templates were spherical with uniform size. The average diameters of the polystyrene, the polystyrene-methyl acrylic acid, and the sulfonated polystyrene-methyl acrylic acid latex spheres were

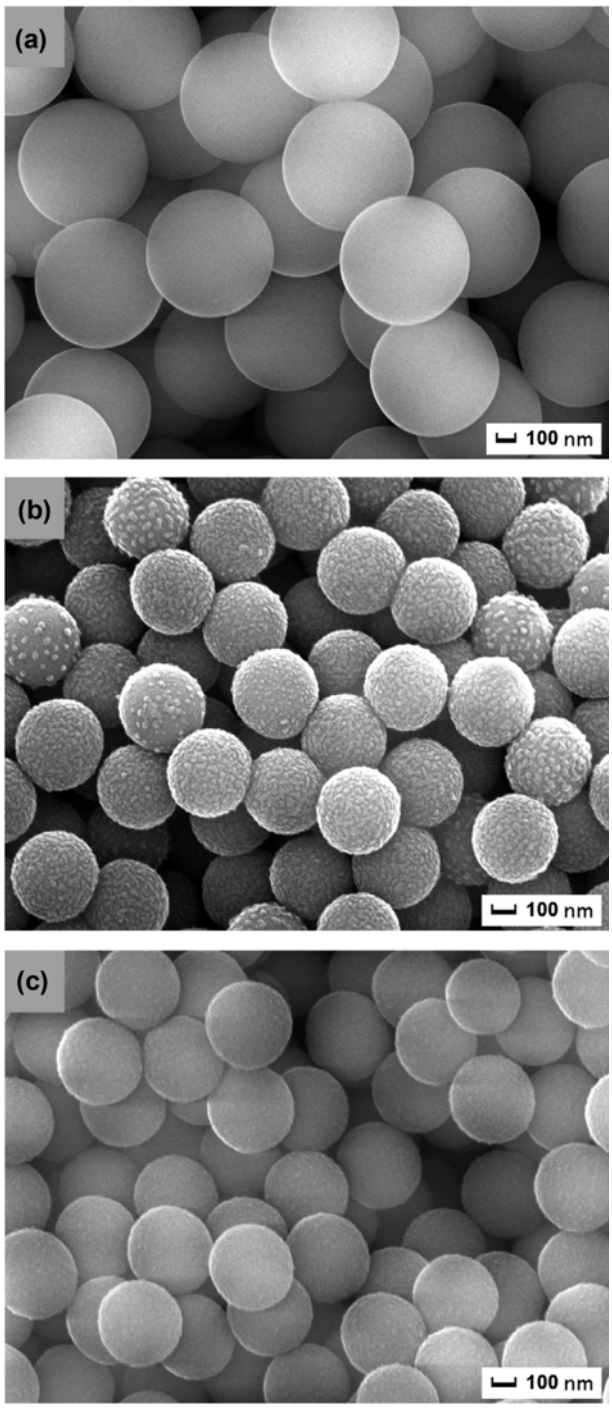


Fig. 1. SEM images of the latex templates. (a) polystyrene; (b) polystyrene-methyl acrylic acid; (c) sulfonated polystyrene-methyl acrylic acid.

650, 360, and 360 nm, respectively. The sizes of the polystyrene-methyl acrylic acid latex spheres were less than that of the polystyrene latex spheres by 290 nm. Sulfonation of the polystyrene-methyl acrylic acid latex spheres did not affect their size and morphology.

Fig. 2 shows the SEM images of the silica-coated latex template core-shell samples. All of the silica-coated latex samples were spherical. The average diameters of the silica-coated polystyrene, the silica-coated polystyrene-methyl acrylic acid, and the silica-coated sulfonated polystyrene-methyl acrylic acid latex spheres were 750, 380, and 440 nm, respectively.

Fig. 3 shows the SEM images of the hollow silica samples prepared by removing the latex templates by calcination. While the polystyrene latex spheres were used as templates, the resultant hollow silica spheres were incomplete. The average diameter of the

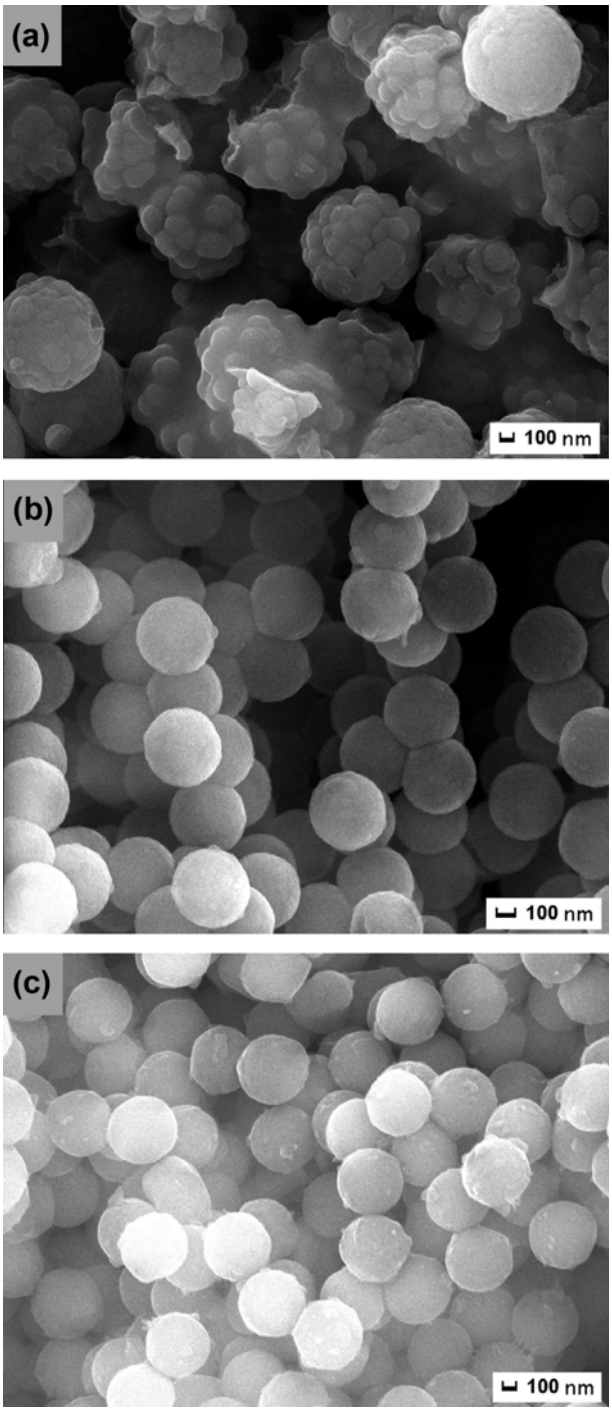


Fig. 2. SEM images of the silica-coated latex samples. (a) silica-coated polystyrene; (b) silica-coated polystyrene-methyl acrylic acid; (c) silica-coated sulfonated polystyrene-methyl acrylic acid.

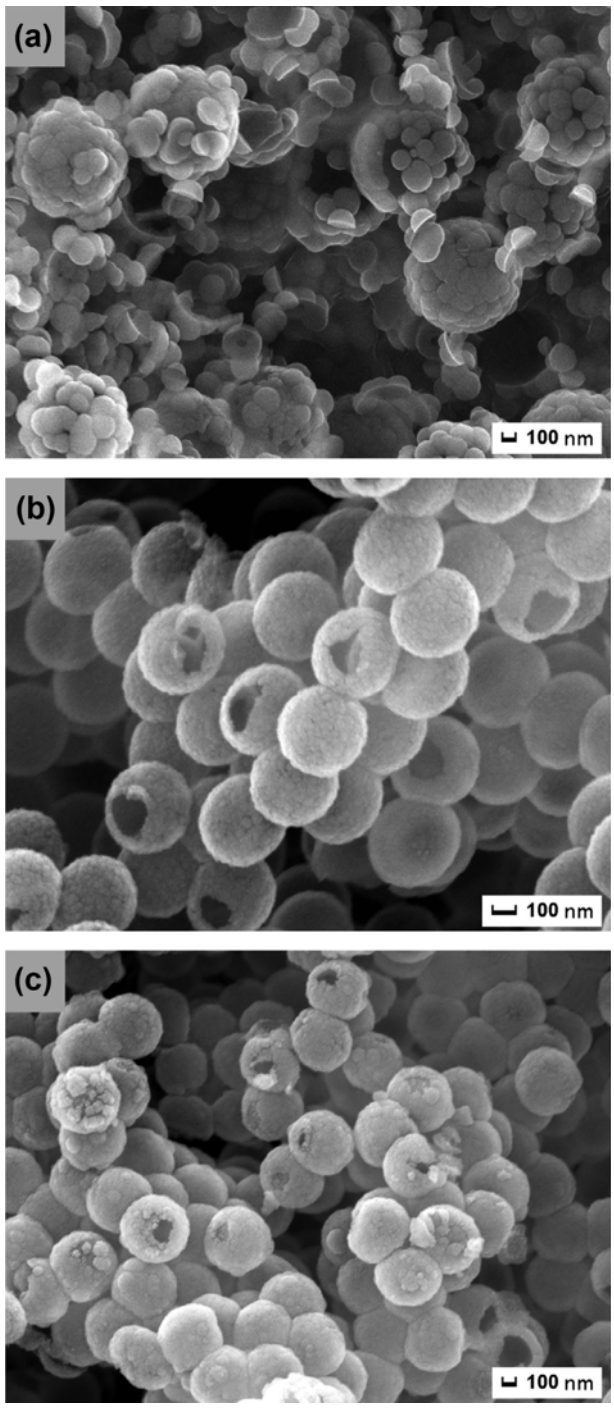


Fig. 3. SEM images of the hollow silica samples prepared by removing latex templates by calcination. The latex templates were (a) polystyrene, (b) polystyrene-methyl acrylic acid, and (c) sulfonated polystyrene-methyl acrylic acid.

hollow silica spheres was *ca.* 750 nm. Some of the hollow silica spheres collapsed and hemisphere- or bowl-like silica particles, which consisted of the shells of the hollow silica spheres, were formed in a large scale with an average diameter of 150 nm when the polystyrene cores were removed by calcination. While the polystyrene-methyl acrylic acid latex spheres were used as templates, uniform-sized hollow silica spheres were formed after the latex templates were removed by calcination. The average diameter of the resultant hollow silica spheres was 362 nm. There was an open hole in each hollow silica sphere with an average size of *ca.* 150 nm. The shells of the hollow silica spheres were composed of silica nanoparticles with an average size of *ca.* 10 nm, which was evaluated by magnified SEM image. While the sulfonated polystyrene-methyl acrylic acid latex spheres were used as templates, uniform-sized hollow silica spheres were formed after the latex templates were removed by calcination. The average diameter of the resultant hollow silica spheres was 421 nm. There was also an open hole in each hollow silica sphere with an average size of *ca.* 150 nm. The shells of the hollow silica spheres were composed of silica nanoparticles with an average size of *ca.* 10 nm, which was evaluated by magnified SEM image.

Fig. 4 shows the TEM images of the hollow silica samples. While the polystyrene-methyl acrylic acid latex spheres were used as templates, TEM image shows that uniform-sized hollow silica spheres were formed after the latex templates were removed by calcination. The average diameter of the resultant hollow silica spheres was 360 nm, consistent with that revealed by SEM analysis. The average thickness of the silica shells was *ca.* 18 nm. When the sulfonated polystyrene-methyl acrylic acid latex spheres were used as templates, TEM image shows that uniform sized hollow silica spheres were formed after the latex templates were removed by calcination. The average diameter of the resultant hollow silica spheres was 420 nm, consistent with that revealed by SEM analysis. The average thickness of the silica shells was *ca.* 51 nm.

The SEM and TEM results show that the carboxylic and sulfu-

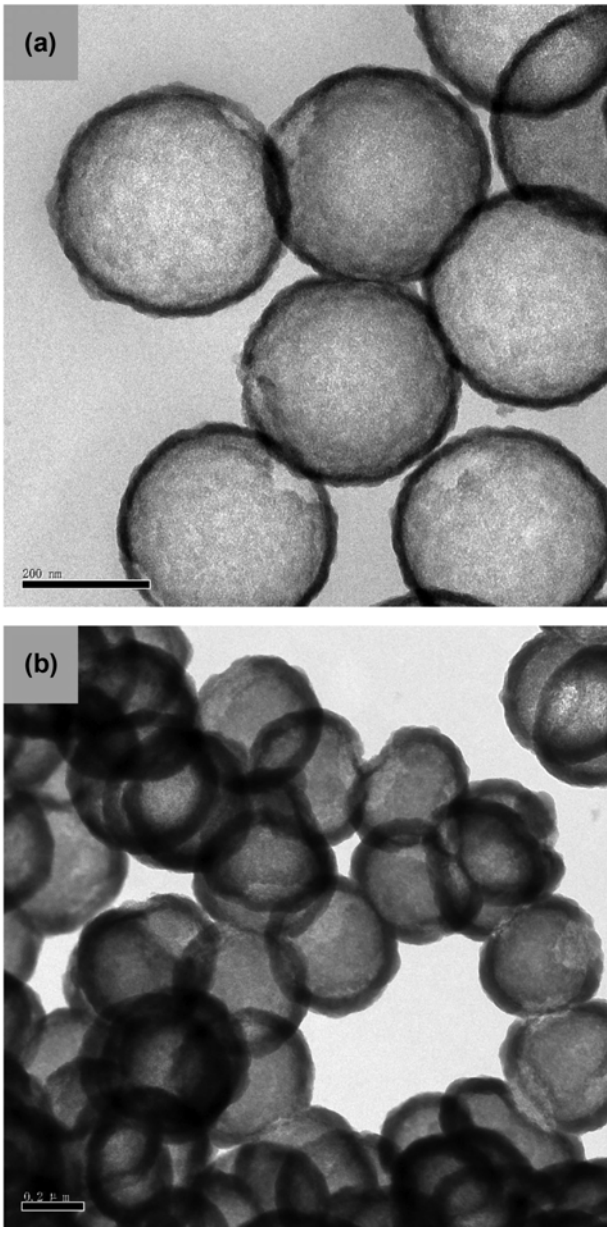


Fig. 4. TEM images of the hollow silica samples prepared by removing latex templates by calcination. The latex templates were (a) polystyrene-methyl acrylic acid and (b) sulfonated polystyrene-methyl acrylic acid.

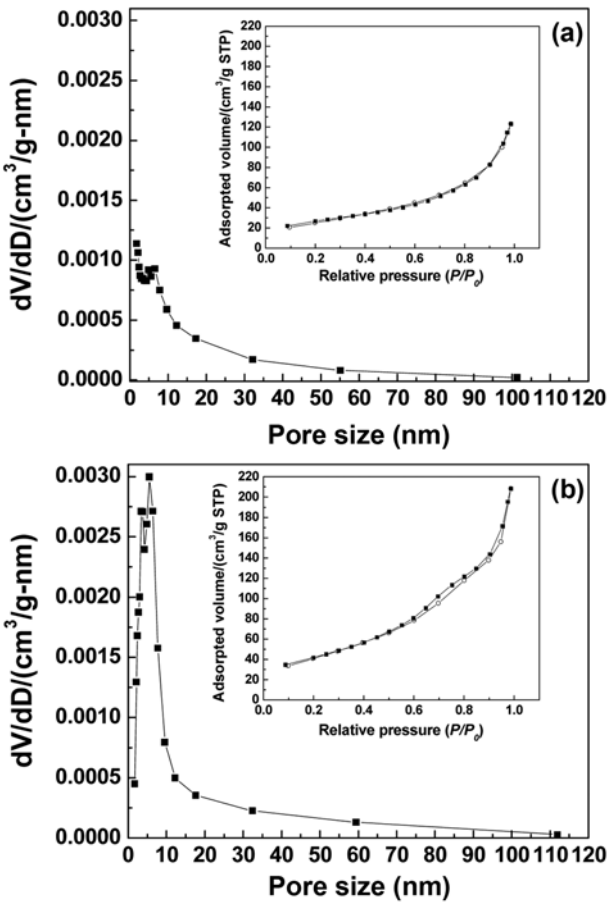


Fig. 5. Nitrogen adsorption/desorption isotherms and pore size distributions of the hollow silica samples prepared by using (a) polystyrene-methyl acrylic acid and (b) sulfonated polystyrene-methyl acrylic acid as the templates, respectively.

ric acid-functionalized polystyrene latex templates were beneficial to formation of intact hollow silica spheres as compared with the polystyrene latex template. The shell thickness of the hollow silica spheres prepared by using sulfonated polystyrene-methyl acrylic acid latex template was *ca.* three-times that using polystyrene-methyl acrylic acid latex template, revealing that the shell thickness increased with the increase in the acidity of the acidic functional groups.

2. Nitrogen Adsorption/Desorption

The nitrogen adsorption/desorption isotherms and the pore size distributions of the as-prepared hollow silica spheres are shown in Fig. 5. The specific surface area, the average pore size, and the pore volume of the hollow silica spheres prepared by using polystyrene-methyl acrylic acid latex template were 96.85 m^2/g, 1.78 nm, and 0.18 ml/g, respectively. While the sulfonated polystyrene-methyl acrylic acid latex spheres were used as templates, the specific surface area, the average pore size, and the pore volume of the resultant hollow silica spheres were 153.05 m^2/g, 5.57 nm, and 0.32 ml/g, respectively. The nitrogen adsorption/desorption isotherms and the pore size distribution revealed that the pores in the shells of the hollow silica spheres prepared by using the carboxylic acid-functionalized latex templates were composed of both micropores and mesopores. But while using the sulfonated latex templates, the pores in the silica shells were mainly composed of mesopores because the nitrogen adsorption/desorption isotherms were ascribed to IV type and the pore size distribution centered at 5.57 nm.

3. FT-IR Analysis

The FT-IR spectrum of the as-prepared polystyrene latex template is shown in Fig. 6(a); the observed strong IR absorption bands at 2,850-3,080, 1,600, 1,500, 750, 700, and 540 cm^{-1} are characteristic of the polystyrene [6,24]. The polystyrene-methyl acrylic acid latex template was characterized by the appearance of C=O vibration at 1,697.19 cm^{-1} (Fig. 6(b)) [25]. The sulfonated polystyrene-methyl acrylic acid latex template was characterized by the appearance of the band at 1,182.63 cm^{-1}, related with sulfonic group (-SO_3H) (Fig. 6(c)) [26]. The presence of sulfonic groups (-SO_3H) on the surfaces of polystyrene-methyl acrylic acid latex templates was certified by FTIR analysis. The peak intensity was weak due to the relatively small amount of sulfonic groups.

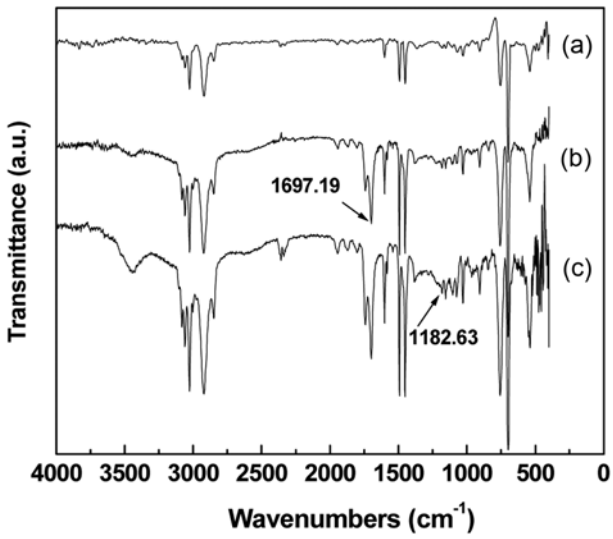


Fig. 6. FT-IR spectra of the latex templates. (a) polystyrene; (b) polystyrene-methyl acrylic acid; (c) sulfonated polystyrene-methyl acrylic acid.

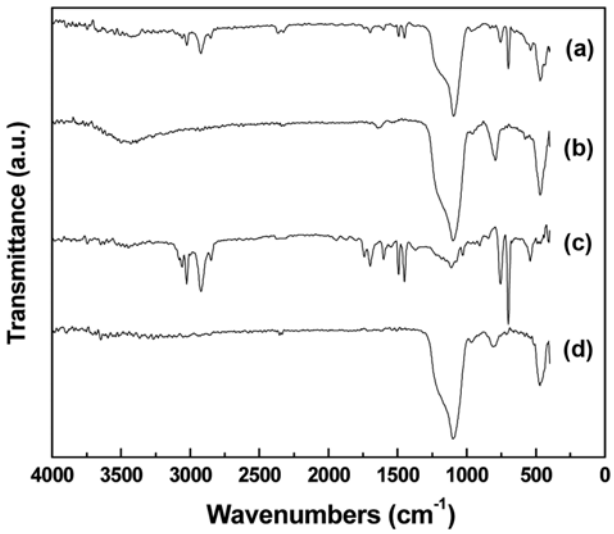
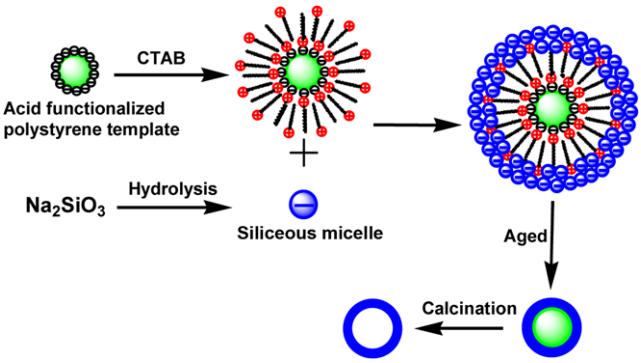


Fig. 7. FT-IR spectra of the silica-coated latex spheres and the hollow silica spheres. (a) the silica-coated polystyrene-methyl acrylic acid latex spheres; (b) the hollow silica spheres prepared by removing polystyrene-methyl acrylic acid latex template by calcination; (c) the silica-coated sulfonated polystyrene-methyl acrylic acid latex spheres; (d) the hollow silica spheres prepared by removing sulfonated polystyrene-methyl acrylic acid latex template by calcination.

The FT-IR spectra of the silica-coated latex spheres and the resultant hollow silica spheres are shown in Fig. 7. For the silica-coated latex samples (Fig. 7(a), (c)), a broad band assigned to Si-O-Si vibration appeared at 1,100 cm^{-1}, indicating that the polycondensation reaction of siliceous micelles took place at the latex surfaces [24]. The bands of the latex templates disappeared in the spectra for the hollow silica spheres (Fig. 7(b), (d)), meaning that the latex templates were completely removed by calcination. Furthermore, three strong bands near 1,100, 792, and 468 cm^{-1} assigned to Si-O-Si vibrations appeared in the spectra of the hollow silica spheres



Scheme 1. Evolution process of the hollow silica spheres prepared by using acid-functionalized polystyrene latex as a template, cetyltrimethylammonium bromide as a shell structure-directing agent, and sodium silicate as a starting material.

(Fig. 7(b), (d)), revealing that calcination caused further polycondensation among the silica gels.

4. Evolution Mechanism of Hollow Silica Spheres

The evolution mechanism of the hollow silica spheres prepared by using acidic group-functionalized polystyrene latex spheres as templates was proposed as Scheme 1. As certified by FT-IR analysis, the surfaces of the latex spheres were negatively charged by sulfonic and carboxylic groups. Cationic surfactant, cetyltrimethylammonium bromide, molecules were adsorbed on the acidic group-functionalized latex surfaces by electrostatic force. When the pH value of the reaction solution was at 7, Na_2SiO_3 was rapidly hydrolyzed to form a large number of negatively charged siliceous micelles [27]. The adsorbed layers of the cationic surfactant served as frameworks for deposition of the siliceous micelles on the surfaces of the latex templates by electrostatic force. The increase in the acidity of the latex spheres caused the increase in the amount of the adsorbed cationic surfactant, subsequently enhancing the deposition of the siliceous micelles. Silica layers were formed on the surfaces of the latex templates by polycondensation reaction in the coating process. The calcination treatment oxidized the latex templates completely and caused further polycondensation of the siliceous micelles to form silica shells by dehydration.

CONCLUSIONS

When polystyrene latex spheres were used as templates, cetyltrimethylammonium bromide as the shell structure-directing agent, and sodium silicate as the starting material, silica nanoparticles with an average diameter of 150 nm were coated on the surfaces of the polystyrene latex spheres. After calcination, incomplete hollow silica spheres were formed. When polystyrene-methyl acrylic acid and sulfonated polystyrene-methyl acrylic acid latex spheres were used as templates, cetyltrimethyl ammonium bromide molecules adsorbed on the negatively charged surfaces of the latex templates induced the deposition of siliceous micelles to form uniform silica coating layers. The latex templates were completely removed by calcination, giving intact hollow silica spheres. When sulfonated polystyrene-methyl acrylic acid latex spheres were used as templates, the shell thickness, specific surface area, pore size, and pore volume of the resultant hollow silica spheres were larger than those using polystyrene-methyl acrylic acid latex spheres as templates, respectively.

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