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Synthesis of Hollow Silica by Stöber Method with Double Polymers as Templates

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The hollow SiO_2 spheres with uniform size were synthesized by a modified Stöber method under the control of polyelectrolytes (PSS and PAA) as templates. This synthetic route includes the formation of spherical colloid micelle in ethanol solution, hydrolysis of TEOS under control of ammonia, and the removal of polyelectrolyte by washing or calcination. Hollow silica spheres with controllable core diameters between 100 and 270 nm and wall thickness between 15 and 50 nm have been synthesized. The influence of template solution concentration and solvent and dispersant on the formation of silica hollow spheres is studied and reported in detail.

Key Words : Hollow silica, Polyelectrolyte, Stöber method, Double polymers as templates, Colloid micelle

Introduction

The synthesis of hollow nanoparticles has attracted much attention in chemistry and materials community because of their low density, large specific area, low coefficients of thermal expansion, low refractive index, mechanical and thermal stabilities, and surface permeability.[1] Such hollow nanoparticles have a wide variety of potential application in cosmetics, catalysis, coatings, composite materials, dyes, inks, artificial cells, and fillers.[2-6] Furthermore, their hollow structure can be used as microencapsulate for drugs in the pharmaceutical fields.[7] Silica is demonstrated to be a nontoxic, highly biocompatible, and mechanically stable material, so it has many more practical applications in the areas mentioned above.[8] Various methods, such as templating, sonochemical, and hydrothermal have been reported for the preparation of silica spheres with hollow structures.[9-13] Traditionally, hollow silica spheres at the sub-micrometer or nanometer scale with tunable wall thickness were fabricated by organic template methods or sacrificial-core techniques.[14,15] Here in this study, the hollow silica nano-spheres were synthesized using Stöber method with double electrolyte component for micelle to optimize the reaction conditions and to obtain the product with uniform size and well defined morphologies. Poly (styrene sulfonate acid) sodium salt (PSS, Mw = 70 000) and poly (acrylic acid) (PAA, Mw = 1 800) were used to make the templates and which are easily removed by washing with base or calcination. Tetraethyl orthosilicate (TEOS) was used as the silica source. The main advantage of this method is the formation of size controlled uniform hollow silica with commonly and cheaply available chemicals with good yield enabling the large scale synthesis for specific applications.

Experimental

Materials Tetraethoxysilane (TEOS), methyltrimethoxysilane (MTMS), ethanol (95%), ammonia solution (28%), polystyrene sulfonate (PSS, Mw = 70 000), polyacrylic acid (PAA, Mw = 1 800), methanol, propylene glycol methyl ether acetate (PGMEA) were purchased from Sigma Aldrich. Distilled water was used in all our experiments.

Characterization. Size and shape of the silica synthesized in the present work were studied using TEM and SEM. TEM observations were performed on a JEOL Model JEM-1200EX, working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on to copper grids. SEM images were obtained with Hitachi S-4800 instrument. For structural analysis XRD patterns were recorded in the 2θ ranging from 10° to 80° with a scanning step of 0.01° using the Rigaku-D/max-III diffractogram with Cu-K_α radiation. Thermogravimetric analysis (TGA) was carried out using a Diamond TG/DTA thermal analyzer (STAR^e SW10.00) with a heating rate of 10 $K \cdot min^{-1}$ from room temperature to 900 °C in an air flow. The composition of particles was investigated by using energy-dispersive X-ray spectroscopy (EDS, JEOL Model JEM-1200EX). The samples were prepared by the same way with TEM analysis.

Synthesis of Hollow Silica. At room temperature, 0.042 g PSS and 0.022 g PAA were dissolved in 1.5 mL of ammonia hydroxide, and then mixed with 30 mL of ethanol. The solution became cloudy after adding ethanol. This solution was called template solution. 1 mL of TEOS was injected slowly into the template solution under vigorous magnetic stirring. The reaction was kept in for 12 h before adding MTMS to modify the surface of silica spheres.[17] After 5 h, the resulting white colloids were centrifuged and washed five times with distilled water and dried at 50 °C for several hours or calcined at 500 °C for 2 hours. The detail of reaction conditions in each experiment are reported in Table 1.

Results and Discussion

The powder X-ray diffraction (XRD) pattern of the as-prepared particles (Fig. 1) indicates that the particles are amorphous with a single broad peak centered at about 23°, which is characteristic diffraction of amorphous silica. TEM

Table 1. Reaction conditions of each experiment

Sample	Template solution				Precursor solution	Additives
	PSS (g)	PAA (g)	NH_4OH (mL)	C_2H_5OH (mL)		
S_0	0.042	0.022	1.5	30	1 mL TEOS	0.1 mL MTMS
S_1	0.084	0.00	1.5	30	1 mL TEOS	0.1 mL MTMS
S_2	0.00	0.03	1.5	30	1 mL TEOS	0.1 mL MTMS
S_3	0.042	0.022	1.5	30	0.375 mL TEOS + 37.125 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_4	0.042	0.022	1.5	30	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_5	0.042	0.022	1.5	30	0.75 ml TEOS + 74.25 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_6	0.042	0.022	1.5	30	1.00 mL TEOS + 99 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_7	0.042	0.022	1.5	60	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_8	0.042	0.022	1.5	90	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_9	0.042	0.022	1.5	150	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_{10}	0.042	0.022	1.5	300	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH

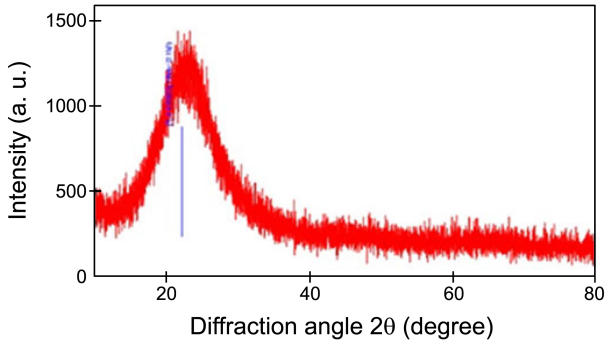

Figure 1. X-ray diffraction pattern of silica spheres using double polymers as templates.

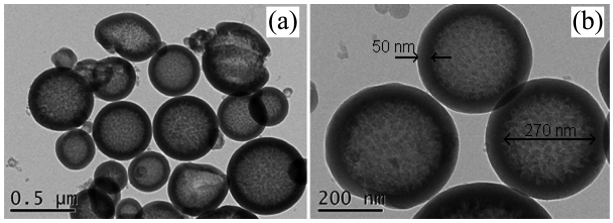

Figure 2. TEM image of silica spheres using double polymers as templates.

image (Fig. 2) of the particles prepared with double polymer template demonstrates that silica spheres are hollow structures with core diameter of 260 nm and with shell thickness of 50 nm. For comparison, the experiments with PAA and PSS separately as templates are examined for their effects on the formation of hollow spheres. For this work 0.03 g PAA and 0.084 g PSS were used. The TEM results as shown in Figure 3 suggest that the sample which was synthesized by PAA (Fig. 3(a)) does not possess the hollow structure where as the sample which was synthesized using PSS (Fig. 3(b)) possess the hollow structure but the spheres are non-uniform. TEOS was added to the solution as a precursor for silica formation. MTMS is used to modify the surface of silica spheres and help them avoid the aggregation. Hollow spheres with different wall thickness can be prepared by

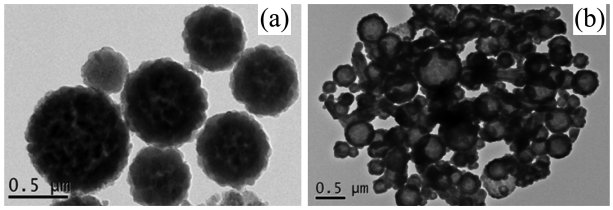

Figure 3. TEM image of silica spheres using single polymer: (a) PAA and (b) PSS as templates.

tuning the amount of TEOS. Here in this work we used 0.375, 0.50, 0.75, and 1.0 mL of TEOS. The TEOS used in our work was diluted in ethanol to 1% by volume. All other experimental conditions were same as explained above in the hollow silica preparation section above. When the volume of TEOS is 0.375 mL; the as-prepared products almost dissolved after washing. This may be due to the formation of very thin and weak walls with small quantity of TEOS. When we increase the volume of TEOS to 0.5 mL, the wall thickness is about 35 nm (Fig. 4(a) and 4(d)), and no free silica spheres are found. With 0.75 mL TEOS, the wall thickness increased up to 40 nm with slightly rougher morphology (Fig. 4(b) and 4(e)). With more TEOS added to the reaction (1.00 mL), the wall thickness increases up to 45 nm (Fig. 4(c) and 4(f)). Moreover, many solid silica spheres are

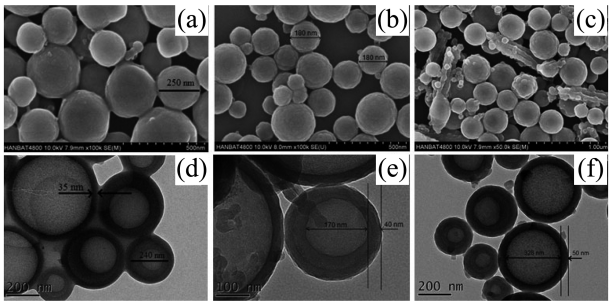

Figure 4. SEM and TEM images of hollow silica spheres obtained using various amount of TEOS: (a, d) 0.50 mL; (b, e) 0.75 mL; (c, f) 1.00 mL.

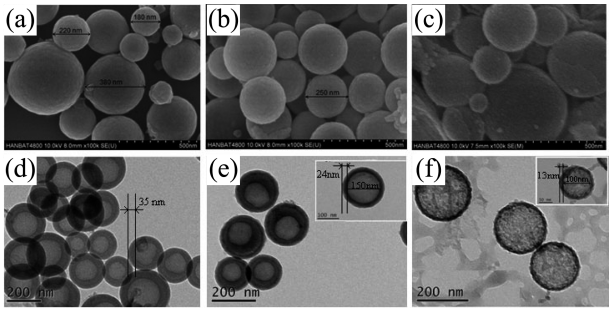

Figure 5. SEM and TEM images of hollow silica obtained using various amount of C_2H_5OH: (a, d) 60 mL, (b, e) 90 mL, (c, f) 150 mL.

also found in this case. Hence 0.5 mL of TEOS was chosen as the optimized volume. With the ratio of PSS: PAA = 0.042 g: 0.022 g, and TEOS = 0.5 mL constant, we varied the template solution concentration by diluting with various volumes of ethanol: 60 mL, 90 mL, 150 mL and 300 mL. Figure 5 shows the SEM and corresponding TEM image of the hollow silica spheres obtained with various amount of ethanol. The microscopic images shown in Figure 5(a) & 5(d) reveal that the sample prepared with template solution diluted by 60 mL ethanol is more uniform than the sample prepared with template solution prepared with 30 mL ethanol (Fig. 2). The shell thickness is ~35 nm. With 90 mL ethanol, further uniformity in size and shape of hollow silica achieved (Fig. 5(b) & 5(e)) with reduced shell thickness and core diameter of 24 and 150 nm respectively. Figure 5(c) and 5(f) shows the SEM and TEM image of the hollow silica spheres prepared with 150 mL ethanol. In this case, shell thickness of hollow silica is reduced to 13 nm but the outer surface of particles become rougher along with the presence of some broken particles as shown in the SEM. The products prepared with excess ethanol (300 mL) diluted template; dissolved completely after washing several times by water. Based on the uniformity in size and shape and also stability after washing, 90 mL ethanol was found to be the optimum volume for synthesis of hollow silica. We represent the sample prepared under this optimum condition as '*standard sample*'. TEM image of the standard sample shows obviously the presence of another layer inside particles. TGA of this sample was checked and the result figured out that polyelectrolytes still remain in this sample.

The following section explains the TGA results in detail. The thermo gravimetric analysis (TGA) of PSS and PAA was investigated by using a Diamond TG/DTA thermal analyzer (STAR^{e}SW10.00) with a heating rate of 10 K·min^{-1} from room temperature to 900 °C in an air flow. As shown in Figure 6, the weight loss starts around 200 °C for PAA and occurs very rapidly. Whereas, the degradation rate for PSS is very slow compare to the PAA. TGA data for PSS shows that the degradation starts around 400 and at around 500 weight loss of the PSS occurs very rapidly. The standard sample TGA was also checked using similar experimental conditions. The TGA curve for the standard sample is shown in Figure 7. It shows first weight loss stage around 100 °C

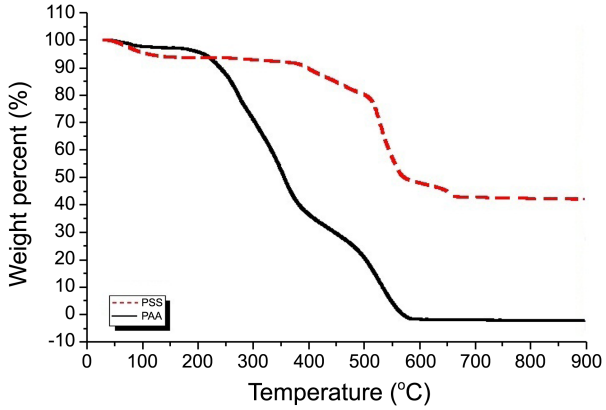

Figure 6. TGA curve of PSS and PAA.

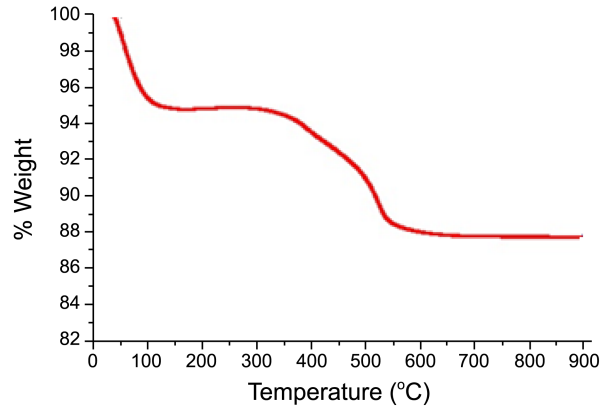

Figure 7. TGA curve of standard sample.

which is attributed to the evaporation of physically adsorbed water and residual solvent. The weight loss stage around 200 °C is not observed and the weight loss stage around 400 °C indicated that only PSS still remain in the sample after washing. To remove the PSS completely, we washed the spheres with 0.1 M NaOH. TEM images of base washed silica spheres with clear core are observed as shown in Figure 8, which reveals the complete removal of PSS. To investigate the effect of solvent to the formation of hollow silica, ethanol was replaced by methanol and propylene glycol methyl ether acetate (PGMEA). The experimental condition in each case is reported in Table 2. In this experiment, ethanol was replaced by methanol while keeping all other conditions constant. But after washing two times in water, all the white colloids were dissolved completely. This result can be ex-

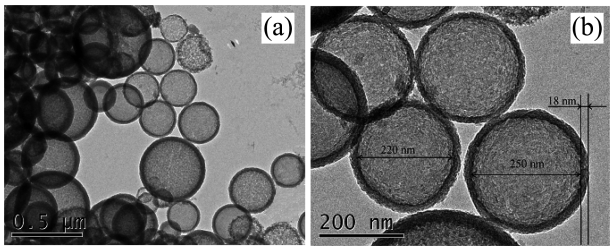

Figure 8. TEM images of hollow silica after washing by 0.1 NaOH. (a) 500 nm and (b) 200 nm scale bar.

Table 2. Reaction conditions with various solvents except ethanol

Sample	Template solution				Precursor solution	Additives
	PSS (g)	PAA (g)	NH_4OH (mL)	Other Solvent		
S_{11}	0.042	0.022	1.5	30 mL CH_3OH	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH
S_{12}	0.042	0.022	1.5	30 mL PGMEA	0.50 mL TEOS + 49.5 mL C_2H_5OH	0.1 mL MTMS + 9.9 mL C_2H_5OH

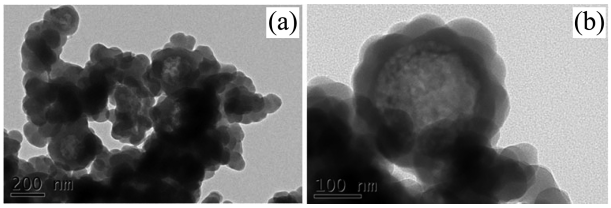

Figure 9. TEM images of the silica synthesized with PGMEA as solvent.

plained by the difference in polarity of methanol compared to ethanol. The second solvent we used in this work is propylene glycol methyl ether acetate (PGMEA). The particles were prepared with the same approach as mentioned above by only replacing ethanol with PGMEA. After the reaction, the resulting white colloids were washed five times in water, dried at 50 °C for several hours and calcined at 500 °C for 2 hours. The TEM image (Fig. 9) indicates that the formation of few hollow structures of silica. Although the shape and size of the particles are not uniform, many compact silica particles were obtained with this solvent. These results suggest that ethanol is the suitable solvent with proper polarity for the formation of good micelle to prepare good quality silica spheres.

Conclusion

Preparation of uniform hollow silica spheres with controlled core diameter (100 to 300 nm) and wall thickness (13-50 nm) has been demonstrated. PSS and PAA combined water soluble polymer was used as the template solution to promote the formation of well-defined core templates. This route involves the formation of spherical colloid aggregates in ethanol solution, hydrolysis of TEOS under the control of ammonia, sodium hydroxide and the removal of polyelectrolyte by washing or calcination. The effect of polyelectrolytes template, template solution concentration, and solvents were investigated to find the optimized conditions for the preparation. Use of double electrolytes, PAA and PSS, was required to form good quality hollow silica. The function of PAA is to reduce the pH of solution and to make the surface of hollow smoother while PSS was critical for the formation of hollow structure. Suitable solvent with proper polarity such as ethanol, was required to create good micelle to form best hollow structure. Washing with base enables the long chain PSS polymer probably by partially dissolving the silica cluster to create the porous channel to release the core polymer chain effectively. The incorporation of functional dye molecules into the polyelectrolyte aggregates is ongoing. The product can be applied in industry field such as coating, catalyst and so on.

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