

Synthesis and shell structure design of hollow silica nanoparticles using polyelectrolyte as template

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Abstract. Hollow silica (SiO_2) nanoparticles with tunable shell microstructures were synthesized in ethanol solvent by using a polyelectrolyte as template. The polyelectrolyte template was composed of poly (acrylic acid) (PAA) with small amount of ammonia solution (NH_4OH) and prepared by dispersion of the PAA- NH_4OH mixture in ethanol. Upon the addition of silica precursor, tetraethoxysilane (TEOS), into the PAA- NH_4OH /ethanol suspension, a certain thickness of SiO_2 shell could be gradually formed outside the template through the sol-gel reaction of TEOS, which was supposed to be driven by the catalytic effect of NH_4^+ ions suspended on the surface of the template. By varying the NH_4OH amount in reaction solution, it was found that the hollow SiO_2 nanoparticles could be obtained only in the case of NH_4OH amount below a critical value. Furthermore, it was found that the water amount in reaction solution had a significant influence on the shell microstructure of hollow SiO_2 . The shells formed in water-free solution were thick, rough and rich of mesopores, which became relatively thinner, smoother and richer of micropores if the water amount was gradually increased within a limited range. Therefore, it was thought to be possible for the controllable synthesis and shell structure design of hollow SiO_2 nanoparticles by optimizing the NH_4OH and water amount in reaction solution.

1. Introduction

Hollow silica (SiO_2) nanoparticles, with a unique structure of hollow interior and solid shell, can provide solid/liquid loading, thermal/electrical insulation, special optical properties, and so on [1,2]. Therefore, they have received increasing attention and have been applied in diverse fields including catalysis, drug delivery, security protection, biological detection, etc.

The current approaches to the synthesis of hollow SiO_2 nanoparticles are generally divided into two categories: (1) sacrificial template method and (2) template-free method. Of the two methods, the first one is the most effective and commonly used strategy, because it is relatively easy to control the shape and size of the resulting hollow SiO_2 nanoparticles by a simple copy surrounding the template and a subsequent removal of the template [3]. It is thus clear that the template type would be an important determining factor for the synthesis of different shapes/sizes of hollow SiO_2 nanoparticles. According to previous reports, organic templates (e.g. surfactant micelles, co-polymer micelles, etc.) mostly contributed to the formation of spherical SiO_2 hollow structure [4], while inorganic templates (compound or metal particles) might result in a shape diversity of SiO_2 hollow structure, such as rod, cubic, needle, cocoon and sphere [5,6].



The forming mechanism of the SiO₂ shell on those templates could be illustrated by either of the two following processes. One is a consecutive adsorption of pre-deposited particles on the template surface, during which the shell thickness of hollow particle was determined by the size and adsorbed amount of the pre-deposited particles [7]. The other is a precursor react, i.e. sol-gel reaction, on the template surface, where the shell thickness depended on the ratio of precursor/template [8]. In addition, the microstructure (mesopores and micropores) of the SiO₂ shell was found to be tunable by properly adjusting the sol-gel conditions, e.g. reaction time, pH value, etc [9-12]. Considering the importance of the shell thickness and shell microstructure in determining the physical and chemical properties of the hollow SiO₂ nanoparticles, it is necessary to strength the research on the two factors.

Recently, Yu and his co-workers reported a unique technique to prepare hollow SiO₂ nanoparticles using a polyelectrolyte as template [13]. The template was a mixture of poly (acrylic acid) (PAA) and ammonia solution (NH₄OH), and was insoluble in ethanol. Upon the addition of silica source (tetraethoxysilane, TEOS) into ethanol where PAA-NH₄OH template dispersed, TEOS transferred into SiO₂ shell on the template surface via a sol-gel reaction for over 10-hour stirring. A significant advantage of this method is that the template removal process is simple and environmental friendly. Although the Yu's group has showed a controllable synthesis of the hollow SiO₂ particles in particle size and shell thickness, by changing the amount of PAA and TEOS. The formation mechanism of the SiO₂ shell on the PAA-NH₄OH template was still not clear and the shell microstructure of the hollow SiO₂ particles was never mentioned. So, the purpose of our work here was mainly focused on studying the two points. First, the formation mechanism was investigated by varying the NH₄OH amount in reaction solution. Then, the shell microstructure was examined by changing the water amount in reaction.

2. Experimental section

2.1. Synthesis of hollow silica particle

Synthesis of hollow silica nanoparticles without addition of water was conducted according to Yu's groups [13]. A 0.08 g of poly (acrylic acid) (PAA, molecular weight 5,000) powder was dissolved in 1.5 ml of ammonium hydroxide solution (NH₄OH, 25 wt%) under stirring condition. The PAA-NH₄OH solution was dropped in 30 ml of ethanol (EtOH) and stirred to form PAA-NH₄OH template suspension. Then, 0.15 ml of tetraethoxysilane (TEOS) was separately added in the suspension per 2 h during 10 h stirring. After another 4 h stirring, the suspension was separated and washed by ethanol and distilled water using centrifugation. The precipitates were dried and hollow silica particles were obtained. To study the effect of NH₄OH and water content on the formation and shell microstructure of the hollow SiO₂ particles, the PAA-NH₄OH mixture was dropped in EtOH (30 ml) with addition of different NH₄OH amount (1.5, 3.0, 6.0 ml) and water amount (0.1, 1.0, 2.0 ml), respectively, and the following procedure was the same as described above.

2.2. Characterizations

Surface morphology and hollow structure of the obtained samples were observed by a scanning electron microscope (SEM), a scanning transmission electron microscope (STEM, JSM-7000F, JEOL Ltd.), and a transmission electron microscope (TEM, 2000-EX, JEOL Ltd.). Particle size of template suspension was measured by a particle size analyzer using dynamic light scattering (Zetasizer Nano, Marvern Instruments Ltd.). Specific surface areas of hollow particles were calculated by applying Brunauer-Emmett-Teller (BET) equation to nitrogen adsorption isotherms, which were measured by a surface area analyzer based on the volumetric method (BEL-Sorp max, BEL Japan, Inc.). The cross-sectional area of nitrogen molecule was taken as 0.162 nm². Existence of pore in the silica shell was investigated by t-plot method, using nonporous silica as the standard reference absorbent for the determination of pore sizes.

3. Results and discussion

Figure 1 shows SEM and TEM micrographs of a) PAA-NH₄OH template and b) hollow silica nanoparticles, which were prepared according to Yu's group [13]. The template shapes were totally spherical and have wide particle size distribution from several tens of nm to several hundreds of nm (Fig. 1a)). The shape and size distribution of the hollow silica nanoparticles (Fig. 1b)) were similar to that of the template. It can be said that the hollow silica nanoparticles formed as a replica of the PAA-NH₄OH template.

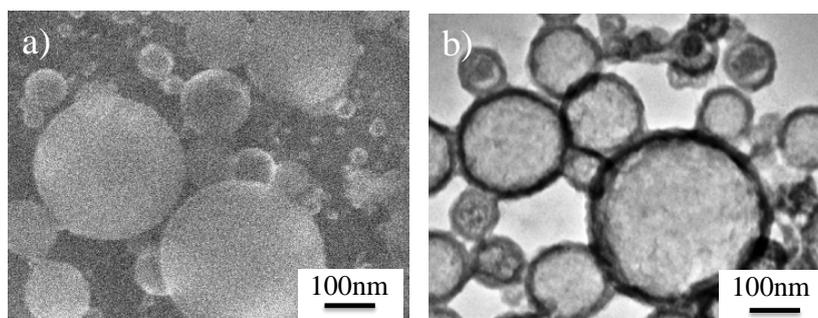


Figure 1. Microscopic observations of a) polyelectrolyte template and b) hollow silica particles by SEM and TEM, respectively.

Figure 2 shows change in particle size of PAA-NH₄OH template as a function of different NH₄OH amounts from 1.5 ml to 6.0 ml with PAA amount kept constant. In less than 1.5 ml NH₄OH, as-received PAA powder didn't completely dissolve in the NH₄OH solution. The amount of NH₄OH over 1.5 ml seems to be enough for preparation of PAA-NH₄OH mixture. The size of PAA-NH₄OH template significantly decreased with increase in NH₄OH amount. For 1.5, 3.0, 4.0, 5.0, 6.0 ml NH₄OH amounts, synthesis of hollow particles were attempted in the same way as described above.

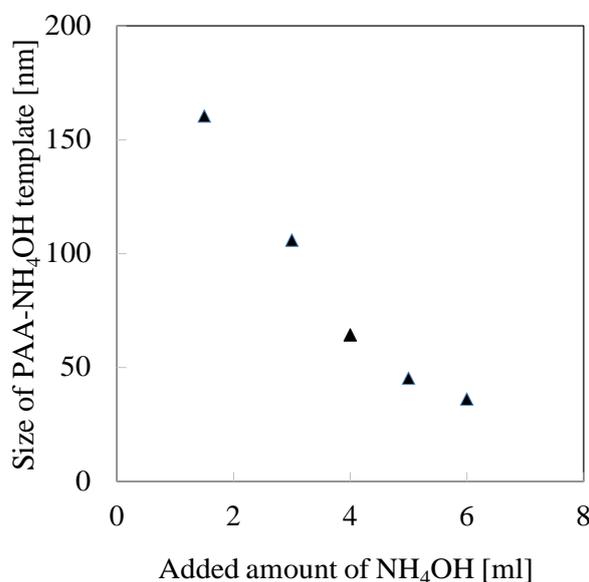


Figure 2. Particle size of PAA-NH₄OH template as a function of NH₄OH amount.

Figure 3 shows STEM images of obtained samples with NH₄OH additions of a) 1.5, b) 3.0, c) 6.0 ml, respectively. In the 1.5 ml NH₄OH addition, hollow particles were obtained (Fig. 3a)). They were spherical particles with wide particle size distribution. While in the range of 3.0 and 6.0 ml additions,

only dense nanoparticles were observed without hollow silica nanoparticles as shown in Fig. 3b) and c). When PAA-NH₄OH mixture was dropped in EtOH, insoluble PAA-NH₄OH mixture forms spherical droplet in EtOH. In the droplet, PAA molecules aggregate each other owing to their intra- and inter-molecular interactions through hydrogen bond, ionic interaction between negative PAA and positive NH₄⁺ ion. When TEOS was added in the PAA-NH₄OH/EtOH suspension, only hollow silica particles were obtained with the NH₄OH of 1.5 ml without dense particle formation (Fig. 3a)). Therefore, it can be said that NH₄⁺ ion in the droplet works as a catalyst for sol-gel reaction of TEOS and the hydrolyzed TEOS reacts at only the PAA-NH₄OH droplet surface. An increase in NH₄OH in the droplet means increases in both NH₄⁺ ion and water in the droplet. The increasing water in the droplet makes the droplet difficult to maintain the shape in EtOH, because effect of the interactions becomes low. To keep the droplet shape, the excess water in the droplet will leak from the droplet to outer phase EtOH. This could be a reason why that particle size decreased with increase in NH₄OH as shown in Fig. 2. Along with the water leakage, polarity of EtOH increases. The increasing NH₄⁺ ions in the droplet also leak to EtOH, because higher polarity is favourable for NH₄⁺. The NH₄⁺ ions in the outer phase EtOH work as sol-gel catalyst in advance of that in the droplet. When TEOS added in the suspension, the hydrolyzation and condensation of TEOS easily occur in EtOH using the leaked NH₄⁺ ion as a catalyst before TEOS approach to the droplet surface. Therefore, dense silica nanoparticles were formed with excess amount of NH₄OH, which is over than 3.0 ml in this experiment.

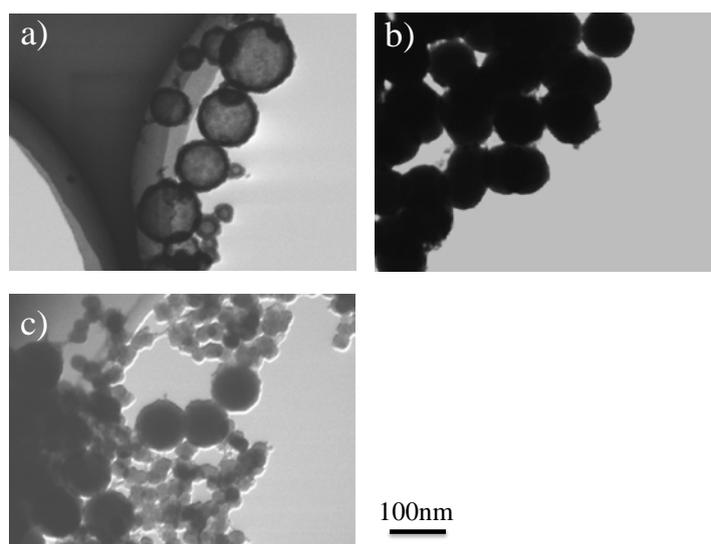


Figure 3. STEM images of obtained samples with NH₄OH additions of a) 1.5, b) 3.0, c) 6.0 ml.

From these results, if the conditions were optimum, TEOS reacts at only the PAA-NH₄OH droplet surface and only hollow silica nanoparticles were obtained. To design silica shell microstructure of the hollow nanoparticles, control of sol-gel reaction rate at the droplet surface is required. According to our previous results, sol-gel conditions like pH and reaction time control silica shell formation, e.g., coarse silica shell forms at low pH and for short time reaction and vice versa [12]. Here, polarity of EtOH where the PAA-NH₄OH droplets were dispersed was focused. Effect of water addition in the outer phase EtOH on microstructure of silica shell was investigated with 1.5 ml of NH₄OH kept constant.

Figure 4 shows STEM images of obtained samples prepared a) without water addition, with b) 0.1, c) 1.0, d) 2.0 ml water additions. In Fig. 4a)b)c), hollow silica particles were observed and their shell morphologies were changed with water amounts. Without water addition (Fig. 4a)), the silica shell was relative thick and rough silica shell surface was observed. With 0.1 ml addition (Fig. 4b)), the

silica shell thickness decreased and the shell surface roughness also slightly decreased. In these hollow particles without water and with 0.1 ml, fine silica particles which composed of silica shell were recognized. On the other hands, with water addition of 1.0 ml (Fig. 4c)), the shell thickness significantly decreased and smoothness of the silica shell increased compared to the former two hollow particles. The fine silica particles were not recognized in the silica shell and it seems to have the highest density silica shell in the three. With further water addition up to 2.0 ml (Fig. 4d)), hollow particles were not formed and only dense particles were observed. When PAA-NH₄OH mixture was dropped in EtOH, the PAA-NH₄OH droplets form “soft” PAA aggregation by NH₄⁺ ions linkage including water. In the droplets, these molecules move freely during stirring, therefore NH₄⁺ ions which appeared at the droplet surface by chance can work as sol-gel catalyst when TEOS approaches to the droplet surface. This is the reason why this technique needs long time to form silica shell coating at the droplet surface. When water added in the outer phase EtOH, polarity of EtOH increases because of water’s high polarity. Because TEOS is rather hydrophobic before hydrolyzation owing to their alkoxide groups, TEOS approaching rate to the droplet surface depends on the reaction solvent polarity. In other words, when EtOH polarity increases by water addition, TEOS approaching rate becomes slowly. By comparing Fig. 4a) (without water) with Fig. 4c) (with 1.0 ml addition), TEOS approaching rate can be faster in the former and slower in the latter. In the latter, for the small amount of TEOS by slower TEOS approaching, there were rich NH₄⁺ catalyst in/at the droplet, which results in dense and thin silica shell formation (Fig. 4c)). When the excess amount of water added in EtOH, the PAA-NH₄OH droplet could be unstable because PAA-NH₄OH droplet dissolves in water. In the droplet, PAA molecular movement becomes more active and silica shell formation at such unstable droplet surface must be difficult. Therefore, only dense particles were formed as shown in Fig. 4d).

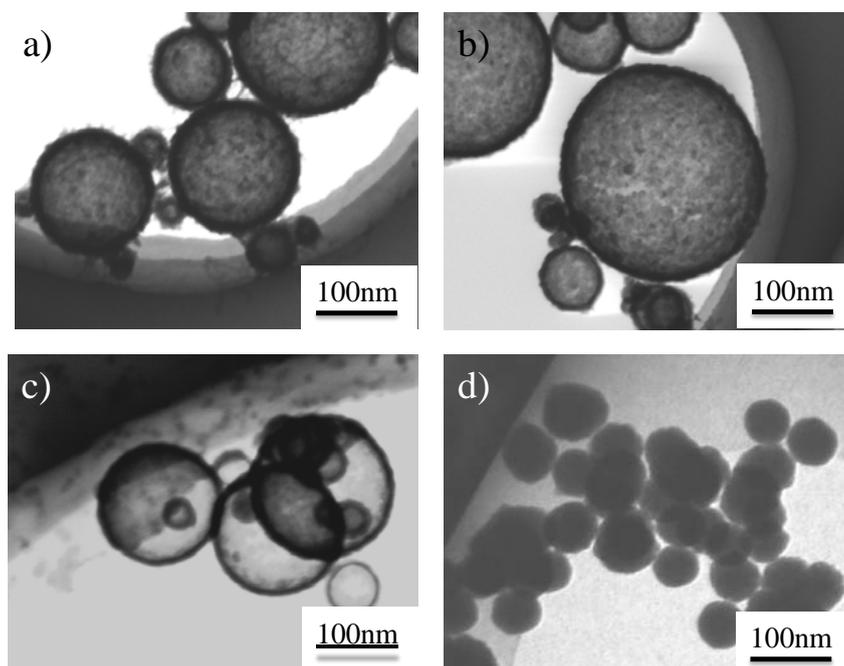


Figure 4. STEM images of the samples prepared (a) without water addition, with addition of (b) 0.1, (c) 1.0, (d) 2.0ml water in EtOH.

Shell microstructures of the hollow particles without water addition, with 0.1, 1.0 ml addition were investigated. Figure 5 shows the nitrogen gas adsorption/desorption isotherms of them (left) and a representative *t*-plot (right). The specific surface areas of them were calculated as 181, 71, 469 m²/g by BET equation, and pore sizes of them were calculated as 2.2, 2.0, 1.3 nm by *t*-plot. The hollow

particles, synthesized without and with 0.1 ml water addition, have mesopores in their silica shells. While the hollow particles synthesized with 1.0 ml water addition have micropores in the silica shell. It indicates possibility that water addition in EtOH controls silica shell microstructure of hollow particles.

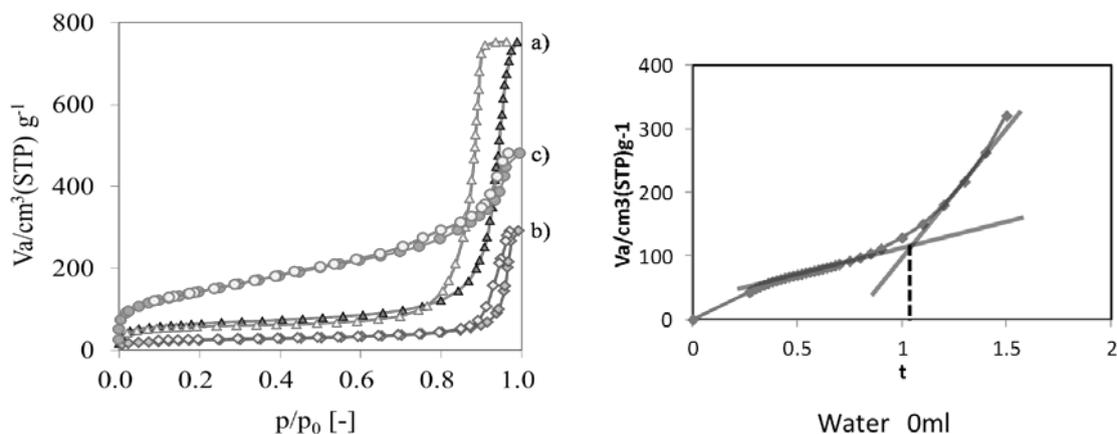


Figure 5. N₂ adsorption/desorption and a representative *t*-plot of the obtained hollow silica particles (a) without and with (b) 0.1, (c) 1.0 ml water in EtOH.

4. Conclusion

The controllable synthesis and shell structure design of hollow SiO₂ nanoparticles were achieved by optimizing the NH₄OH and water amount in reaction solution. In the case of NH₄OH amount below a critical value, hollow SiO₂ nanoparticles could be obtained. Furthermore, the shells formed in water-free solution were thick, rough and rich of mesopores, which became relatively thinner, smoother and richer of micropores if the water amount was gradually increased within a limited range.

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