Preparation of Hollow Silica Microspheres via Poly(N-isopropylacrylamide)

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Core-shell structured SiO\textsubscript{2}/poly(N-isopropylacrylamide) (SiO\textsubscript{2}/PNIPAM) microspheres were successfully fabricated through hydrolysis and condensation reaction of tetraethyl orthosilicate (TEOS) on the surface of PNIPAM template at 50 °C. The PNIPAM template can be easily removed by water at room temperature so that SiO\textsubscript{2} hollow microspheres were finally obtained. The transmission electron microscope and scanning electron microscope observations indicated that SiO\textsubscript{2} hollow microspheres with an average diameter of 150 nm can be formed only if there are enough concentration of PNIPAM and TEOS, and the hydrolysis time of TEOS. FTIR analysis showed that part of PNIPAM remained on the wall of SiO\textsubscript{2} because of the strong interaction between PNIPAM and silica. This work provides a clean and efficient way to prepare hollow microspheres.

Key words: SiO\textsubscript{2} hollow microsphere, Poly(N-isopropylacrylamide), Tertraethyl orthosilicate, Soft template

I. INTRODUCTION

Hollow microspheres have been applied extensively in the fields of photoelectric material, filler and catalyst carrier because of their versatile advantages, such as better flow property, high specific surface area and low density [1, 2]. The inner spaces in hollow microspheres are expected to be utilized as micro-reactor, slow-release support and drug controlled release system [3–5]. The hollow microspheres of inorganic oxides have attracted special research interesting due to their abundant physical and chemical properties, good stability, easy producing technique, etc. [6–10].

Several methods have been developed to prepare inorganic hollow microspheres, such as microemulsion polymerization, template synthesis and spray reaction [11–13]. Metal materials (such as Pd, Ag and Au) [14–16], metal oxides (such as Al\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2} and TiO\textsubscript{2}) [17, 18], semiconductor materials, hydroxyapatite and SiO\textsubscript{2} are the main materials to construct the inorganic hollow microspheres through template synthesis. For the fabrication of hollow microspheres of inorganic oxides, organized surfactant assemblies [19, 20], block copolymer micelles [21, 22], inorganic (such as Au and Ag) colloidal nanoparticles [23, 24] and polymer latex particles [25] can be used as the template.

The preparation of SiO\textsubscript{2} hollow microspheres through template synthesis has become a research hotspot recently because of the versatile application of silica. Two steps are included in a common process of the preparation of SiO\textsubscript{2} hollow microspheres through template synthesis. First, a SiO\textsubscript{2} shell should be formed around the template through the hydrolysis and condensation reactions of tetraethyloxyorthosilicate (TEOS) or layer-by-layer self-assembly (LBL) [26–28]. Secondly, the template is removed by high temperature calcination, chemical etching and/or organic solvent extraction to obtain the designed SiO\textsubscript{2} hollow microspheres [29–32]. However, the two-stage method sometimes has a high cost because of the complex processes and produces energy waste and environment pollution. Moreover, this kind of treatment has the potential risk to destroy the SiO\textsubscript{2} shell and the structure and functional groups of other components. Therefore, researchers now search for various “soft template”, which can be removed without the need of high temperature calcination and the treatment of chemical reagents, to fabricate the SiO\textsubscript{2} hollow microspheres.

Poly(N-isopropylacrylamide) (PNIPAM) is a well-characterized thermo-responsive polymer, whose chains contain both hydrophilic amide groups and hydrophobic isopropyl groups. PNIPAM has a lower critical solution temperature (LCST) at about 32 °C [33, 34]. When the environmental temperature is lower than the LCST, PNIPAM is water-soluble and hydrophilic, existing in an extended chain form. However, once the temperature is above the LCST, PNIPAM undergoes a reversible phase transition to insoluble and hydrophobic aggregates. Inspired by this character of...
PNIPAM, Štěpánek et al. prepared composite microspheres with a PNIPAM hydrogel core and a silica shell through the inverse Pickering emulsion polymerization [35]. They found the silica shell cannot affect the thermo-responsive ability of the PNIPAM hydrogel core. The result implied that PNIPAM aggregates in aqueous solution at high temperature can be used as a soft template to prepare SiO$_2$ hollow microspheres because PNIPAM templates can be removed by water instead of other volatile or environmentally-unfriendly organic solvents.

II. EXPERIMENTS

2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) (0.01 g, 0.05 mmol, synthesized according to Ref.[36]). N-isopropyl-acrylamide (NIPAM) (0.6 g, 5.26 mmol, purchased from Aldrich and recrystallized from toluene/hexane (3/2, volume ratio)), 2,2-azoisobutyronitrile (AIBN, 98%, Sigma-Aldrich) (1.6 mg, 0.01 mmol) and tetrahydrofuran (THF, 5 mL) were mixed in a polymerization tube. After evacuation and nitrogen charge for three times, the tube was sealed in vacuum. The reaction was carried out at 60°C in oil bath. After 5 h, the polymerization tube was cooled with ice water. The reaction system was diluted with 5 mL of THF and then poured into a large amount of diethyl ether to let PNIPAM precipitate. The collected PNIPAM was vacuum dried at 30°C for 24 h.

A certain amount of TEOS was added into the aqueous solution of PNIPAM which had been kept at 50°C for a period of time. The system was stirred for another fixed time at 50°C, followed by being cooled to room temperature to let PNIPAM dissolve in water. The product was diluted with ethanol and separated by centrifugation.

The morphology of the SiO$_2$ hollow microspheres was observed by field emission scanning electron microscopy (FEI Sirion-2000, 5 kV) and transmission electron microscopy (TEM, H-7650, JEOL2011) at an accelerating voltage of 100 kV. The samples for TEM and SEM analysis were prepared by dispersing one drop of the ethanol suspension of the product on copper grids and then evaporating the ethanol in air. Fourier transform infrared (FT-IR) spectrometer (Bruker EQUIVOX-55) was utilized to record the infrared spectra of the samples at room temperature. The samples were mixed with potassium bromide (KBr) and pressed into pellets.

III. RESULTS AND DISCUSSION

A. Mechanism of hydrolysis and condensation reactions of TEOS

Fig.1 illustrates. In solution, the hydrolysis and condensation reaction of TEOS form polymeric species composed of Si–O–Si bonds. The process is very sensitive to the pH value of the environment [37]. Hydrolysis is rapid and complete when catalysts are employed. Ammonia is generally used in the processing. The polar silanol produced by the hydrolysis reaction will be attracted by amino groups on PNIPAM by their mutual electrostatic interaction. Therefore, the following hydrolysis and condensation reactions can occur on the surface of the PNIPAM aggregates.

B. Morphology of SiO$_2$ hollow microspheres

SiO$_2$ hollow microspheres were prepared through PNIPAM as the template, we first should let the hydrolysis and condensation of TEOS take place on the surface of the PNIPAM template and form core-shell structured SiO$_2$/PNIPAM composite microspheres. This process includes two steps in fact, i.e., the formation of PNIPAM template and the hydrolysis and condensation of TEOS on the template surface. The formation of PNIPAM template could be achieved at above LCST of PNIPAM because the hydrogen bonds between NIPAM units and water molecules will be destroyed with the increase of temperature so that the solubility of PNIPAM decreases at 50°C, resulting in the gradually precipitation of PNIPAM from the solution and the formation of spherical PNIPAM aggregates. Evidently, the phase transition is a kinetic process. The size of the aggregates depends on precipitation time and the concentration of PNIPAM. Thus the effect of pretreatment of PNIPAM solution at 50°C and the concentration of PNIPAM on the morphology of core-shell structured SiO$_2$/PNIPAM composite microspheres were investigated.

C. Effect of pretreatment and the concentration of PNIPAM on the morphology of SiO$_2$/PNIPAM composite microspheres

Figure 2 exhibits the morphology of the particles prepared after 5 and 10 h pretreatment of PNIPAM solution, followed by the hydrolysis of TEOS for 24 h.
FIG. 2 TEM images of the core-shell structured SiO$_2$/PNIPAM composite particles prepared after (a) 5 h and (b) 10 h pretreatment of PNIPAM solution, followed by the hydrolysis of TEOS for 24 h.

FIG. 3 TEM images of core-shell structured SiO$_2$/PNIPAM particles prepared from different concentration of PNIPAM (a) 2 mg/mL, (b) 10 mg/mL, and (c) 20 mg/mL.

The latex particles prepared after the pretreatment of PNIPAM solution at 50 °C for 5 h seem much smaller and agglomerate together. It means that 5 h is not enough for all PNIPAM to precipitate from the solution to be the template. However, 10 h of pretreatment on PNIPAM solutions at 50 °C is better for PNIPAM to precipitate from the solution to become the individual template of SiO$_2$ hollow microspheres.

Evidently, the concentration of PNIPMA determines the size of the PNIPMA aggregates, i.e., the size of template, if precipitation time is enough. Figure 3 shows the morphology of SiO$_2$/PNIPAM composite microspheres under different concentration of PNIPAM. When the concentration of PNIPAM is as low as 2 mg/mL, the amount of precipitated aggregates of PNIPAM is so little that the distribution of SiO$_2$/PNIPAM composite microspheres is sparse (see Fig.3(a)). The density of core-shell structured SiO$_2$/PNIPAM composite microspheres increase rapidly with the concentration of PNIPAM. When the concentration of PNIPAM increases up to 20 mg/mL, a large amount of core-shell structured SiO$_2$/PNIPAM composite microspheres were prepared and packed together, as shown in Fig.3(c).

When the prepared solution of core-shell structured SiO$_2$/PNIPAM composite microspheres is cooled to room temperature, the PNIPAM will be dissolved into water and SiO$_2$ hollow microspheres are formed finally. However, the formation process will be influenced by the volume concentration of TEOS and the hydrolysis time of TEOS.

D. Effect of the concentration and hydrolysis time of TEOS on the morphology of SiO$_2$ hollow microspheres

The morphology of SiO$_2$ microspheres prepared under different concentration of TEOS. Due to interactions between the amide groups on the side chains of PNIPAM and TEOS, TEOS can be adsorbed on the surface of the aggregates of PNIPAM and occur the hydrolysis and condensation process to form a silica layer. When the volume concentration of TEOS in water is small, e.g., 0.072, only collapsed irregular-shaped silica particles can be observed in Fig.4(a). The reason is the amount of silica is too little to form a complete silica layer around the aggregates of PNIPAM. After the PNIPAM template dissolves in water at room temperature, the silica layer collapses. No SiO$_2$ hollow microspheres can be observed. A complete and strong silica layer is formed until the concentration of TEOS is high enough.

Figure 4 shows the morphology of SiO$_2$ hollow microspheres prepared under different concentration of TEOS. When the concentration of PNIPAM is as low as 2 mg/mL, the amount of precipitated aggregates of PNIPAM is so little that the distribution of SiO$_2$/PNIPAM composite microspheres is sparse (see Fig.3(a)). The density of core-shell structured SiO$_2$/PNIPAM composite microspheres increase rapidly with the concentration of PNIPAM. When the concentration of PNIPAM increases up to 20 mg/mL, a large amount of core-shell structured SiO$_2$/PNIPAM composite microspheres were prepared and packed together, as shown in Fig.3(c).

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FIG. 5 TEM images of silica hollow particles prepared under different hydrolysis time of TEOS. (a) 96 h, (b) 144 h, and (c) 240 h. The volume concentration of TEOS in water is 0.2.

increases to 0.2. At this case, SiO$_2$ hollow microspheres with an average diameter of around 150 nm and an average shell thickness of 30 nm can be observed clearly, as displayed in Fig.4(b).

The effect of the hydrolysis time of TEOS on the morphology of SiO$_2$ hollow microspheres was investigated at a fixed volume concentration of TEOS in water (0.2 v/v). The results are exhibited in Fig.5. It can be observed that the thickness of the SiO$_2$ layer increase to a small extent when the hydrolysis time of TEOS increase from 96 h to 144 h, and levels off until 240 h. The corresponding SEM images of silica hollow particles prepared under different hydrolysis time of TEOS of 96 and 144 h are also shown in Fig.6 (a) and (b), respectively. The surface of SiO$_2$ hollow microspheres prepared after 144 h of the hydrolysis of TEOS seems much rougher than that prepared after 96 h of hydrolysis. It implies that the hydrolysis and condensation of TEOS will finish within 144 h.

E. FTIR analysis of SiO$_2$ hollow microspheres

The component of the prepared SiO$_2$ hollow microspheres can be analyzed by FTIR. The result is shown in Fig.7. The FTIR spectrum of prepared SiO$_2$ hollow microspheres (Fig.7(b)) shows three characteristic peaks of $\text{Si-O-Si}$, i.e., 1096, 800, 467 cm$^{-1}$, which is evidence of the existence of SiO$_2$. However, compared with the FTIR spectrum of the prepared PNIPAM (Fig.7(a)), two characteristic peaks of amide group (the stretching vibration of carbonyl group $\nu_{\text{C=O}}$: 1653 cm$^{-1}$ and the N–H deformation vibration of secondary amide $\nu_{\text{N-H}}$: 1547 cm$^{-1}$) remain in Fig.7(b). It means part of PNIPAM still remains on the wall of SiO$_2$ because of the strong interaction between PNIPAM and silica.

IV. CONCLUSION

SiO$_2$ hollow microspheres with an averaged diameter of 150 nm were successfully fabricated by using a thermo-sensitive polymer, PNIPAM, as soft template. By simply regulating the solution temperature with respect to the LCST of PNIPAM, PNIPAM chains can reversibly form aggregates in aqueous solution. Then the silica layer is in-situ fabricated around the PNIPAM aggregates through the hydrolysis and condensation reactions of TEOS occurring on the surface of the PNIPAM aggregates. If the concentration and hydrolysis time of TEOS is enough, SiO$_2$ hollow microspheres will be formed after the temperature lowers to room temperature to remove PNIPAM template by dissolving it into water.

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