Research Article

A Convenient and Templated Method for the Fabrication of Monodisperse Micrometer Hollow Titania Spheres

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A simple and widely applicable methodology was presented to synthesize monodisperse micrometer hollow titania spheres (HTS) based on the templating method. It was performed by using the preformed poly(styrene-acrylic acid) (PSA) as template spheres which was mixed with tetrabutyltitanate (TBOT) in an ethanol solvent under steam treatment. The HTS which were obtained by the calcination of PSA/TiO₂ composite core-shell spheres had a narrow particle size distribution and commendable surface topography characterized by SEM. The calcined HTS at 500°C displayed crystalline reflection peaks that were characteristic to the anatase phase by XRD. Moreover, some key influencing factors including TBOT concentration and reaction time were analyzed. As expected, the diameter of HTS could be readily controlled by altering the size of PSA template spheres. In addition, the approach was also applied to fabricate hollow zirconia spheres and other inorganic spheres.

1. Introduction

Titania has been extensively studied due to the advantages including unique optical, electrical, high refractive index, and chemical attributes. Hollow titania sphere was well known for high porosity, photovoltaic, and photocatalytic properties, along with its applications as catalyst [1], filler [2], whitener [3], UV absorber, photonic crystal [4, 5], and a large bimolecular release system [6]. However, the sensitivity of titania precursors to moisture led to the great difficulties of controlling the precipitation, the particle morphology, and monodispersity [7, 8], defining the further wide applications of titania spheres.

A variety of chemical and physicochemical methods have been employed to synthesize HTS, such as nozzle reactor approaches (spray drying or pyrolysis) [9], emulsion/phase separation techniques [10], emulsion/interfacial polymerization strategies [11], self-assembly processes [12], and surface living polymerization [13]. Among these methods, the morphology and microstructures were significantly influenced by the preparative conditions, and the precise optimization of the reaction conditions (concentration of reagents, pH, temperature, and mixing methods) was required to obtain uniform coatings without the occurrence of aggregation of

the coated titania particles [14, 15]. Though many efforts have been made to synthesize HTS, developing an effective way to better control the size and morphology was still a great challenge. Furthermore, until now, the reports about fabricating HTS in micrometer scale were scarce.

Recently, the templating method has been proved as a successful method to fabricate such hollow spherical structure of inorganic materials, such as zinc sulfide-coated polystyrene [16] or silica spheres [17, 18] and core-shell latex spheres with semiconductors [19–22]. For the templating method, the apparent advantage was that the shape and cavity size of formed hollow structures were directly determined by template spheres. In the templating method, monodisperse PSA latex was commonly used as colloidal template, because it was readily available in a wide range of sizes. In the previous study [23, 24], a series of micrometer scale monodisperse PSA spheres in dispersion polymerization has been successfully fabricated, which confirmed the high uniformity of titania coating on the PSA template spheres.

In this study, we reported a new, simple, and efficient water vapor-induced hydrolysis route for postsynthesis coating of titania on the preformed positively charged PSA template spheres as shown in Scheme 1. This method was to

SCHEME 1: Diagram of the formation of HTS.

implement the conventional sol-gel condensation in ethanol solvent. In this procedure, the generated water vapor was bubbled through the TBOT/ethanol solution and impelled the hydrolysis of TBOT to product titania molecules. The generated negative titania molecular precursors deposited on the surface of cationic PSA template spheres to form PSA/TiO₂ composite core-shell spheres. In this case, we did not require careful optimization of the solution conditions to produce uniform coatings on PSA template spheres. Both electrostatic attraction and surface precipitation ensured that the titania molecular precursors were captured by the PSA template spheres, resulting in more uniform nanoparticle coverage. The HTS prepared by this method showed high monodispersity and preferable surface topography. The diameter and the shell thickness of HTS were flexible and tuned by altering the size of PSA template spheres and TBOT concentration, respectively. Furthermore, the zirconia coating hollow spheres with zirconium dichloride oxide (ZrOCl₂·8H₂O) were also successfully obtained. This approach not only proved to be a facile, low-cost, and environmentally benign way to fabricate HTS but also offered a versatile and effective route for the preparation of other hollow spheres, such as SiO₂ and ZrO₂.

2. Experimental

2.1. Materials. Styrene (St), polyvinylpyrrolidone (PVP), anhydrous ethanol, α -methylacrylic acid (AA), 2,2'-azobisisobutyronitrile (AIBN), TBOT, and ZrOCl₂·8H₂O were all purchased from Sinopharm Chemical Reagent Co., Ltd. 2-(Methacryloyl) ethyltrimethylammonium chloride (MTC) and sodium methyl allyl sulfonate (SMAS) were purchased from Zibo Wanduofu Chemical Reagent Co., Ltd. and used as the cationic monomer. Ethylene glycol dimethacrylate (EGDMA) was prepared in our laboratory and used as the crosslinking agent. It was stored at 4°C before use. Deionized water was prepared in our laboratory and applied in all polymerization and treatment processes.

2.2. Preparation of Cationic PSA Template Spheres. St, PVP, AA, AIBN, EGDMA, anhydrous ethanol, and water were charged into a 250 mL three-neck round-bottomed flask

which was equipped with a mechanical stirrer, a thermometer, a N₂ inlet, a Graham condenser, and a heating mantle. The reaction system was deoxygenated by bubbling nitrogen gas and then heated to 72°C under stirred condition. After 5 h, MTC was dispersed in anhydrous ethanol and then added into the reaction system. The reaction lasted for 6 h at 72°C. The latex emulsion was separated centrifugally and washed twice with ethanol. The formula of fabricating a series of micrometer scale PSA template spheres was presented in the previous study [23]. The obtained white precipitate was air dried to use as follows.

2.3. Preparation of HTS. The fabrication of HTS was shown in Scheme 1. In the typical procedure, water (30 mL) was placed inside an erlenmeyer of 50 mL capacity. The prepared cationic PSA powder and TBOT were redispersed into anhydrous ethanol in 50 mL beaker under gentle stirring. In the subsequent coating process, the water was stirred and heated to 80°C for a specified time, and then water vapor that evaporated from the water bath slowly got through the funnel and entered the mixed suspension to react with TBOT, continuously generating white precipitate to deposit on the prepared PSA spheres slowly. After the treatment, the final latex was stirred at ambient temperature until the solvent was fully evaporated. The solid material was washed three times with anhydrous ethanol and heated in a vacuum oven at 90°C for 12 h. Finally, the dried material was calcined in a muffle furnace at 500°C to generate hollow structure.

In order to investigate the effect of TBOT concentration and reaction time on the forming of HTS, we also performed some contrast experiments following the same procedure mentioned previously. We systematically studied the hollow titania spheres under the condition of different amounts of TBOT and different reaction time (3 h, 9 h, and 15 h). The formula used in this study was as follows: PSA: 1.5 g, absolute ethanol: 20 mL, TBOT: varied from 0.5 to 2.0 g. Furthermore, a series of monodisperse micrometer HTS were fabricated based on altering the size of PSA template spheres referencing to the previous study [23].

2.4. Preparation of Hollow Zirconia Spheres. In the same experimental facility, the different sizes of hollow zirconia spheres with controllable diameters were synthesized following the same procedure mentioned above. In the subsequent process, SMAS was used as anionic surfactant instead of MTC to obtain the anionic PSA spheres, and ZrOCl₂·8H₂O was used as zirconia precursor to generate zirconia in sol-gel process by this approach. Finally, the PSA/ZrO₂ composite spheres were calcined in a muffle furnace to generate hollow zirconia spheres.

2.5. Characterization. The morphology of the products was characterized by SEM (JSM-6380LV). Before the examination, the products were sputtered with gold. TGA was performed using STA 449C instruments. The composite spheres were heated from the ambient temperature to 800°C at a rate of 5°C/min under oxygen purge. The infrared spectra were recorded with FTIR (Nicolet IR100) in the range of

FIGURE 1: SEM images of hollow titania spheres under different TBOT volumes: (a) 0.5 g; (b) 1.0 g; (c) 1.5 g, and (d) 2.0 g.

FIGURE 2: TG curves of the as-synthesized PSA/TiO₂ composite spheres under different TBOT volumes: (a) 0.5 g; (b) 1.0 g; (c) 1.5 g, and (d) 2.0 g. The composite spheres were heated from the ambient temperature to 800°C at a rate of 5°C/min under oxygen purge.

400~4000 cm⁻¹. The sample was prepared by the usual KBr pellet method. The purity and composition of the products were characterized by powder XRD with D8 Advance X-ray diffractometer (Cu Ka, $\lambda = 0.02$ nm, 30 mA, 40 kV).

3. Results and Discussion

In the previous study, they have developed a facile method to fabricate a series of monodisperse micrometer PSA template spheres in dispersion polymerization [23]. The PSA spheres were flexibly controlled in diameter by altering the initial water volume and the crosslinking agent EGDMA concentration, which simultaneously possessed the favorable surface topography. In the current study, the employment of monodisperse PSA template sphere was a key to the self-assembly of titania spheres into homogeneous crystalline arrays with large domain size. The water vapor-induced internal hydrolysis method was reported to fabricate HTS based on the templating method. In addition, the procedure using TBOT precursor was adopted to ensure coating uniformity.

Figure 1 showed a series of coating reactions in which the TBOT concentration was varied on a scale of 0.5 g in glass vials to establish the concentration ranges in which HTS were formed without aggregation. The volume of ethanol, and PSA spheres remained constant in all the coating reactions (1.5 g PSA, 20 mL ethanol and reaction time 15 h). When less than 0.5 g of TBOT was used, there was no spherical structure as exemplified by Figure 1(a). It demonstrated that TBOT was not enough to coat the PSA template spheres to form titania shell. When the amount of TBOT was increased to 1.0 g, the spherical structure appeared as shown in Figure 1(b). Figure 1(c) showed the SEM image of HTS when the amount was 1.5 g. The HTS were obtained hardly any coagulation and secondary nucleation of titania on the surface of HTS. However, when the TBOT content continued

FIGURE 3: SEM images of hollow titania spheres under the TBOT volume 1.5 g and different reaction times: (a) PSA template spheres, 0 h; (b) 3 h; (c) 9 h, and (d) 15 h.

FIGURE 4: SEM images, FESEM images, and the size distribution histogram of the HTS with different diameters under the reaction time 15 h.

FIGURE 5: FT-IR spectra of (a) PSA/TiO₂ composite spheres dried at 90°C and (b) HTS obtained by annealing at 500°C.

FIGURE 6: XRD patterns of (a) PSA/TiO₂ composite spheres dried at 90°C and (b) HTS obtained by annealing at 500°C.

to be increased to 2.0 g, HTS were disfigured and a lot of secondary nucleation of titania could be observed (Figure 1(d)). The reason was that the faster hydrolysis and condensation of TBOT as a result of higher TBOT content resulted in the nucleation of secondary titania particles. Simultaneously, the generated titania nanoparticles did not maintain stable and severely aggregated in solution to deposit onto the surface of PSA template spheres. In this case, the shell thickness of the HTS was also confined by the concentration of TBOT which contrarily decreased the shell thickness of HTS with increasing the TBOT content [25].

The compositions of PSA/TiO₂ composite core-shell spheres were investigated by TG curves as shown in Figure 2. According to the TG curves, the PSA/TiO₂ composite spheres eliminated most of their weight in the temperature range of 270~320°C. The evaporation of physically adsorbed water, the desorption of physisorbed template molecules, and the evaporation of residual solvent in the sample occurred in turn. The later weight loss was induced by the oxidative decomposition of PSA template spheres. The PSA cores were completely removed at about 500°C and the residual titania accounted for about 11%, 18%, 21%, and 32% in proportion corresponding to the Figures 2(a), 2(b), 2(c), and 2(d), respectively. On the other hand, the results revealed that the shell thickness of HTS was increased with the addition of TBOT content in specified concentration range.

The effect of reaction time could be observed using three different reaction times (3 h, 9 h, and 15 h), while other process parameters remained the same (1.5 g TBOT, 1.5 g PSA, and 20 mL ethanol). Figure 3 showed the SEM of PSA template spheres and HTS at three different times. Figure 3(a) displayed the PSA template spheres with controllable micrometer-sized diameters and consistent spherical feature. In the shorter reaction time (3 h), the prepared titania

was irregular particles, and there were few of spherical structure with some residual precursor chemicals as exemplified by Figure 3(b), which indicated that there was only a bit of TBOT to be hydrolyzed, leading to the incomplete coating in the sol-gel process. As the reaction time was increased to 9 h, a lot of spherical titania particles were observed in Figure 3(c). When the reaction time was further increased to 15 h, the titania particles became more spherical as observed in Figure 3(d). Furthermore, the size of HTS was uniform as indicated by the size distribution histogram (Figures 4(c) and 4(d)). Based on these results, although the precipitation of titania occurred in a short time, it was 15 h at least to ensure that the titania nanoparticles were completely coated on PSA template spheres. It was beneficial for the formation of uniform HTS with favorable surface topography as shown in the inset FESEM images (Figure 4).

As exemplified by the intentionally broken sample (data not shown), it indeed showed a vivid hollow structure with hollow cavity. The approximate shell thickness was also observed at ca. 150 nm, which could be controlled by changing the amount of TBOT in sol-gel process. The mean shell thickness estimated increased from ca. 100 nm to 200 nm, accompanying the molar ratio of TBOT/ethanol which increased from 0.007 to 0.013, respectively. Figure 4 showed different sizes of HTS with controllable diameters and favorable surface topography. The HTS were uniform observed by the size distribution histogram (Figures 4(c) and 4(d)) and the surface topography was commendable as shown in the inset FESEM images.

FT-IR spectrum (Figure 5) of titania spheres had broad bands between 3200 and 3600 cm⁻¹, indicating the presence of hydroxyl groups on the titania surface. Two peaks appeared at approximately 3403 and 1632 cm⁻¹, which were characteristic of stretching and bending vibrations of water molecules,

FIGURE 7: SEM images of the hollow zirconia spheres with different diameters: (a) $1.6\ \mu\text{m}$ and (b) $5.5\ \mu\text{m}$.

revealing the presence of water molecules adsorbed on the dried titania spheres. A weaker absorption peak at $1401\ \text{cm}^{-1}$ revealed the stretching vibration of little residual organic groups. Both the peak at $1103\ \text{cm}^{-1}$ and the strong peaks near $1627\ \text{cm}^{-1}$ agreed with the Ti–O bond which implied the asymmetric stretching vibration and the anatase phase of titania, respectively. The band at $500\ \text{cm}^{-1}$ was associated with the Ti–O–Ti stretching mode of titania [26].

Figure 6 showed the XRD results of PSA/TiO₂ composite spheres and corresponding HTS after thermal treatment. The results showed that as-prepared PSA/TiO₂ composite spheres had no diffraction peaks, indicating that the powder obtained was amorphous (Figure 6(a)). After heat treatment at 500°C , the HTS were turned into anatase phase from amorphous phase (Figure 6(b)). The calcination at 500°C not only removed the template but also made the formation of anatase phase [26]. There were no other peaks observed, indicating that the structured HTS were of high purity.

In addition, to further verify the viability of this approach, we also successfully fabricated hollow zirconia spheres using preformed negatively charged PSA particles as template spheres and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as zirconia precursor. Figure 7 showed different diameters of controllable monodisperse micrometer hollow zirconia spheres. The previous results demonstrated that the approach could be easily extended to the preparation of other metal oxide hollow spheres.

4. Conclusion

In summary, a simple and easily scalable approach has been offered for producing well-defined, size tunable HTS by means of modified sol-gel condensation method in ethanol solvent. In this process, the water vapor promoted the hydrolysis of TBOT to form titania coating spheres, which was very simple and achievable. Besides, this approach offered a great deal of control on the diameter and the shell thickness of HTS. We believed that this method could be extended to prepare other inorganic hollow spheres and broaden a variety of applications in magnetics, electronics, photonic crystals, and heat preservation material.

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