Efficient fabrication and photocatalytic properties of TiO$_2$ hollow spheres

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Titania hollow spheres were synthesized via the styrene-methyl methacrylate copolymer (PSMMA) spheres as templates in conjunction with the sol–gel method without any surfactant or polyelectrolyte. Uniform TiO$_2$ hollow spheres were made up of loosely aggregated anatase-phase nanoparticles. Compared to TiO$_2$ nanoparticles (NPs), TiO$_2$ hollow spheres exhibited a higher photocatalytic activity for the degradation of methyl orange (MO), which may be attributed to their larger specific surface area, more abundant porous structure and larger band-gap energy. In addition, the hollow spheres catalysts can be recycled.

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1. Introduction

Titania, in particular nanosized TiO$_2$, has been proved to be the most popular photocatalyst for the elimination of environmental pollutants [1–3]. In recent years, TiO$_2$ nanostructures have attracted much attention due to their unique physicochemical properties and potential applications. To enhance the catalytic performance, nanostructured TiO$_2$ with various morphologies and textures, including nanotubes, nanorods and porous spheres, has been synthesized [4–6]. Among them, hollow spheres have increasingly attracted tremendous interest as a special class of materials compared to the solid counterparts, due to their higher specific surface area, lower density, better permeation and greater light-harvesting capacity [7,8].

Many methods such as the spray-drying technique [9], template-directed approach [10,11] and hydrothermal [8] have been employed to synthesize TiO$_2$ hollow spheres. It has been proven that using hard templates, especially polymer templates to fabricate hollow spherical structure of inorganic materials, is successful [12]. Generally, the polymer as templates needs to be modified by polyelectrolyte, surfactant or concentrated sulfuric acid to enhance the interaction between templates and the coating particles [13–15]. For example, Nakashima and coworkers [16] synthesized titania hollow spheres by employing sulfonated-polystyrene (PS) particles as templates and investigated their photocatalytic properties. It is very difficult to remove the sulfate species from TiO$_2$ completely using sulfonated PS or Ti(SO$_4$)$_2$ as the raw materials. Moreover, the sulfate species preserved in TiO$_2$ would influence their properties [16,17]. At this point, it is difficult to clarify that the influence on the catalytic performance is from the morphology or surface sulfate species. In addition, although there are a lot of investigations on the photocatalytic activities of dense titania, there still are few works on hollow particles, especially on hollow spherical nanostructures [18].

Herein, the titania hollow spheres were obtained via the styrene-methyl methacrylate copolymer (PSMMA) spheres as templates in conjunction with the sol–gel method without any surfactant or polyelectrolyte. This was an effective approach for fabrication of TiO$_2$ with a uniform hollow spherical structure and relatively pure chemical composition, which should be in favor of the clear research on the potential correlations between the morphology of TiO$_2$ nanomaterials and their properties. The photocatalytic activity of the TiO$_2$ hollow spheres was evaluated by photocatalytic decolorization of methyl orange (MO) aqueous solution under the UV-light illumination. Compared with the TiO$_2$ nanoparticles (NPs) with irregular morphology, TiO$_2$ with hollow spherical morphology exhibited much better photocatalytic activity, and the possible reasons were also discussed.

2. Experimental

2.1. Preparation of TiO$_2$ hollow spheres

Styrene-methyl methacrylate copolymer (PSMMA) spheres were prepared by radical co-polymerization of styrene and methyl...
methacrylate using ammonium persulfate as the initiator [19]. One gram of PSMMA templates were dispersed in the mixture of 100 ml absolute ethanol and 5 ml tetrabutyl titanate (TBT). After stirring for 16 h in a closed bottle, the TBT swollen particles were separated by centrifugation and redispersed into ethanol/water (1:1 v/v) for the sol–gel process. The coating process was repeated twice as described above. Finally the coated particles were dried and calcined at 500 °C for 4 h in air. For comparison, TiO2 nanoparticles (NPs) were prepared via hydrolysis of TBT in ethanol/water (1:1 v/v) and via calcinations.

2.2. Characterization

Thermogravimetry and differential thermal analysis (TG/DTA) of the coated particles were carried out on a Netzsch thermalanalyzer STA 449 C (air atmosphere, heating rate 10 °C/min). The size and morphology of the products were observed by using a transmission electron microscope (Tecnai 12 TEM) with an accelerating voltage of 120 kV and a field-emission scanning electron microscope (S-4800 FESEM) with the energy dispersive X-ray (EDX) spectrum analysis capability, operating at accelerating voltages of 20 kV. The possible impurity sulfur element in hollow spheres from ammonium persulfate was detected on elemental analyzer (Vario EL, Elemental) by Dumas combustion method and by thermal conduction detection (TCD) (detection limit ≤0.1%). Fourier transformation infrared (FTIR) measurements were performed on a Nicolet 5700 spectrometer (KBr tablet). Nitrogen adsorption–desorption property at 77 K was characterized by a Micromeritics ASAP 2020 apparatus. X-ray diffraction (XRD) was collected on a Philips X’pert Pro diffractometer with Ni-filtered CuKα radiation (0.15418 nm). UV–visible diffuse reflectance spectra (DRS) were observed with a UV–visible spectrophotometer (UV-2401PC, Shimadzu).

2.3. Measurement of photocatalytic activity

The photocatalytic activities of the TiO2 hollow spheres for the degradation of methylene orange (MO) in an aqueous solution were measured under irradiation with a 300 W high-pressure mercury lamp. The reaction suspension was prepared by adding the sample (40 mg) into 80 ml of an MO (20 mg/l) solution under stirring. For comparison, the activities of TiO2 NPs were also measured as the reference under the same experimental conditions.

3. Results and discussion

3.1. The TG/DTA of the coated particles

Fig. 1 shows the TG/DTA curves for the coated particles in air. The weight loss in 25–200 °C is ~12 wt%, which should be attributed to the removal of adsorbed water on the particles. And the other two weight losses of 49.8% and 15.6% in 320–395 °C and 395–500 °C with their corresponding exothermic peaks should be attributed to the thermal degradation and combustion of the PSMA templates, respectively [20]. In addition, the decomposition of titania-bonded groups unhydrolyzed–OR is also in the temperature region of 395–500 °C [12]. When the temperature is higher than 500 °C, the weight of the sample is stable, indicating that all the templates can be removed at 500 °C. According to the TG/DTA results, the coated particles were calcined at 500 °C in air to remove the PSMA templates in the present experiments.

3.2. Characterization of the TiO2 hollow spheres

As shown in Fig. 2a, PSMMA spheres as templates are monodispersed and with a diameter of ~300 nm. The void size of TiO2 hollow spheres is ~280 nm with the average wall thickness of about 20 nm (Fig. 2b and c). Significantly, TEM image (Fig. 2c) with the higher magnification reveals that the shell of TiO2 hollow spheres is made up of the aggregation of the nanoparticles with a diameter of 10–20 nm. SEM image (Fig. 2e) also indicates that the products have the uniform spherical morphology and the shell is made of small particles. The inset in Fig. 2e is the image of a broken sphere, which further confirms the presence of hollow structures. EDX analysis spectrum can give the chemical composition of the hollow spheres catalyst on the surface. As shown in Fig. 2f, only the high-intensity peaks for titanium (4.5, 4.9 and 0.45 keV) and oxygen (0.52 keV) are observed, while no peaks of other extraneous elements are detected besides Au (originating from the conductive gold coating prior to SEM imaging) and C (arising from the underlying conductive carbon tapes). This result indicates that hollow spherical catalyst on the surface is composed of Ti and O elements without sulfur element. Furthermore, elemental analysis does not detect sulfur element in the bulk of the catalyst, which further confirms the purity of the hollow spherical samples. In addition, the TEM image of TiO2 NPs (Fig. 2d) shows that particles are irregular with a diameter of 20–40 nm.

Fig. 3 shows the FTIR data of samples to confirm the formation of the inorganic shells and the removal of organic components. The FTIR spectrum in Fig. 3a reveals the typical absorption bands of the phenyl group (700, 1542, 1493, 1601 and 3026 cm–1) for PSMMA latex. Besides, two peaks at 2924 and 2850 cm–1 can be ascribed to the stretching vibrations of CH2 and CH3. In the FTIR spectrum of the coated particles (Fig. 3b), most of the characteristic peaks from the copolymer can still be observed. Additionally, a broad band of Ti–O stretch appears from 400 to 800 cm–1. Then, the characteristic bands for the PSMA latex disappear in the spectrum of the hollow spheres (Fig. 3c), indicating that PSMA has been removed from the coated particles by calcinations at 500 °C. The main peak at 400–800 cm–1 is due to Ti–O stretching and Ti–O–Ti bridging stretching modes of TiO2 [10].

According to nitrogen adsorption–desorption results, the Brunauer–Emmett–Teller (BET) surface area and pore structure data of samples are given in Table 1. It is noteworthy that BET surface area and pore volume of TiO2 hollow spheres are both much larger, compared to those of TiO2 NPs. These textural pores should arise from the inter-particle porosity of samples.

Fig. 4A shows the XRD patterns. As presented in Fig. 4A(c), the coated particles are amorphous. After calcinations, the hollow spherical TiO2 and irregular titania NPs (b and a of Fig. 4A) are both...
in good agreement with anatase crystallographic structure (JCPDS No. 21-1272) ((d) of Fig. 4A). According to the Debye–Scherrer equation, the average crystallite size of the TiO$_2$ hollow spheres and TiO$_2$ NPs is determined to be ~16 nm and 25 nm, respectively, which is basically in accordance with the results from the TEM.

The optical band gaps of the samples were studied by means of an UV–visible spectrometer. Fig. 4B shows the typical UV–visible DRS of TiO$_2$ hollow spheres and NPs. The onset wavelength ($\lambda_{onset}$) in the spectrum of TiO$_2$ NPs (spectrum a) is ~389 nm, while the $\lambda_{onset}$ of the TiO$_2$ hollow spheres (spectrum b) is ~378 nm. The obvious blue shift of the absorption edges may result from the quantum-size effect [16], due to the smaller average crystal size of the TiO$_2$ hollow spheres. The band-gap energies ($E_g$) calculated on the basis of the corresponding absorption edges are about 3.29 eV (TiO$_2$ hollow spheres) and 3.19 eV (TiO$_2$ NPs).

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ hollow spheres</td>
<td>81.1</td>
<td>0.23</td>
<td>9.8</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>39.1</td>
<td>0.14</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Fig. 2. Transmission electron microscope (TEM) images of styrene-methyl methacrylate copolymer (PSMMA) templates (a), TiO$_2$ hollow spheres (b and c) and TiO$_2$ nanoparticles (NPs) (d), scanning electron microscope (SEM) images (e) and energy dispersive X-ray (EDX) spectrum (f) of TiO$_2$ hollow spheres. The inset in (e) is the image of a typical broken sphere.

Fig. 3. Fourier transformation infrared (FTIR) spectra of styrene-methyl methacrylate copolymer (PSMMA) templates (a), coated particles (b) and TiO$_2$ hollow spheres (c).
3.3. Photocatalytic activity of TiO2 hollow spheres

To characterize the photocatalytic efficiency of TiO2 hollow spheres, MO was used as a model pollutant. Fig. 5A displays the absorption spectra of MO solution after lamp irradiation for different times. Almost all of the MO molecules were decomposed after 20 min at the presence of the TiO2 hollow spheres. The result of blank experiment in the presence of catalysts without UV irradiation \((A/A_0 = 0.995)\) \((A_0\) and \(A\) are the absorbance of MO solution before and after stirring for 40 min, respectively) indicated that the adsorption of MO on the surface of hollow spheres photocatalysts was negligible and that MO molecules could not be degraded at this condition.

To approach the influence of the morphology of TiO2 catalysts on the photocatalytic properties, anatase-phase TiO2 NPs (ca. 25 nm, BET 39.1 m²/g) were used as references. As illustrated in Fig. 5B, we plotted the MO degradation \(C/C_0\) \((C_0\) and \(C\) are the equilibrium concentration of MO before and after UV irradiation, respectively) versus UV-light irradiation time in the presence of various photocatalysts. It is obvious that the TiO2 hollow spheres exhibited better photocatalytic activity than TiO2 NPs, indicating that hollow structures could improve their photocatalytic performance. Additionally, the blank experiment was also carried out under ultraviolet (UV) irradiation without catalysts (Fig. 5B) and the results revealed that the MO molecules could not be degraded at this condition.

The higher photocatalytic activity of the TiO2 hollow spheres may attribute to the following three main factors: the enhancement of specific surface area, porous structure and band-gap energy. Firstly, the hollow spherical products are with larger BET

![Fig. 4. X-ray diffraction (XRD) patterns (A) and room-temperature UV–visible diffuse reflectance spectra (DRS) (B) of samples: TiO2 nanoparticles (NPs) (a), TiO2 hollow spheres (b), the coated particles (c) and standard data for anatase TiO2 (JCPDS No. 21-1272) (d).](image)

![Fig. 5. (A) Absorption spectra of a solution of methylene orange (MO) in the presence of TiO2 hollow spheres under ultraviolet- (UV) light. (B) The degradation of MO in the presence of various photocatalysts and under exposure to UV-light. (C) Cycles of the photocatalytic degradation of MO in the presence of TiO2 hollow spheres. (D) Transmission electron microscope (TEM) images of TiO2 hollow spheres catalysts after the third-run reaction.](image)
surface area (ca. 81.1 m²/g versus titania NPs ca. 39.1 m²/g). It is generally acknowledged that the catalytic process is mainly related to the adsorption and desorption of molecules on the surface of the catalyst. The larger specific surface area of hollow spheres may result in more reactant adsorption/desorption sites for catalytic reaction. Secondly, the higher photocatalytic activity of the hollow spheres may be associated with their porous structure [21]. The bigger pore volume of hollow spherical catalyst (0.23 cm³/g versus titania NPs ca. 0.14 cm³/g) enables storage of more molecules, provides more efficient transport channels for the reactant molecules and allows rapid diffusion of various reactants and products during the reaction. Thirdly, the higher band-gap energy (3.29 eV versus titania NPs ca. 3.19 eV) owing to the quantum-size effect means more powerful redox ability; moreover, the larger $E_g$ will also be beneficial for the separation of the photogenerated hole and electron pairs [18]. Considering the unique structure of TiO₂ hollow spheres, the reflections of UV-light within the sphere interior voids may also influence their photocatalytic performance [22,23].

Since the stability of catalysts is important for their practical application, cycles of the photocatalytic degradation of MO in the presence of the TiO₂ hollow spheres were also carried out. After three cycles of the photocatalytic degradation of MO, the catalyst did not exhibit any significant loss of photocatalytic activity, as shown in Fig. 5C. The TEM image (Fig. 5D) of the catalyst after the third-run photocatalytic reaction showed that hollow spherical nanostructure of catalysts was maintained very well. Therefore, the hollow spheres catalysts have good stability at current experimental conditions. These results suggested that TiO₂ with hollow spherical nanostructures would be a potential photocatalyst for this reaction.

4. Conclusion

Anatase-phase TiO₂ hollow spheres were prepared by using PSMMMA spheres as the templates in conjunction with the sol–gel method without any surfactant or polyelectrolyte. Compared with TiO₂ NPs, hollow spherical TiO₂ exhibited better catalytic activity for the photocatalytic degradation of MO aqueous solution, which may be attributed to their larger specific surface area, more abundant porous structure and a larger band-gap energy.

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