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Preparation of TiO_2 hollow microspheres by a novel vesicle template method and their enhanced photocatalytic properties

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Abstract

TiO_2 hollow microspheres were successfully prepared via a novel vesicle template method. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, nitrogen adsorption and UV–vis absorbance spectra. It was demonstrated that TiO_2 hollow microspheres with diameter of about 1 μm were self-assembled by one-dimensional (1-D) TiO_2 nanorods. The photocatalytic property of TiO_2 hollow microspheres was investigated by decomposing methylene blue (MB) under simulated sunlight. The result shows that specific surface area of TiO_2 hollow microspheres reaches 155 m^2/g and photocatalytic efficiency of these microspheres is higher than that of the commercial TiO_2 (Degussa P25). The enhanced photocatalytic activity of the as-prepared TiO_2 microspheres here could result from their high specific surface area, the hollow structure and 1-D TiO_2 nanorod structure.

Keywords: D. TiO_2; Hollow microspheres; Photocatalysis; Vesicle template method

1. Introduction

Over the past decades, considerable efforts have been paid to synthesize TiO_2 nanostructures because of their desirable physical and chemical properties [1–4]. Meanwhile, with the development of nano-technology, dimensionality and size of the materials have been regarded as critical factors that may bring novel and promising properties. TiO_2 materials with various dimensionality and size, including nanoparticles (zero-dimensional, 0-D), nanorods (1-D), nanosheets (2-D), and hollow spheres (3-D), have been prepared [5–9]. Among them, 3-D TiO_2 hollow spheres have aroused special attention and are expected to have potential applications in photocatalysts, dye-sensitized solar cells, and gas sensors due to its dimension and high surface area [10–12]. As photocatalyst, TiO_2 hollow microspheres possess high surface area, low density, delivering ability, surface permeability and high light harvesting capacities, which can enhance energy conversion efficiency and photocatalytic activity of TiO_2 [9].

It has been reported that 1-D TiO_2 nanorod structure can facilitate charge transfer and thus retards the recombination of photogenerated electrons and holes [13,14]. However, the assembly of 1-D TiO_2 nanorods to form 3-D TiO_2 hollow microspheres has been rarely reported. Therefore, controlled organization of primary 1-D TiO_2 nanorods units into 3-D TiO_2 hollow microspheres remains a significant challenge.

Generally, fabrication of TiO_2 hollow microspheres is based on hard or soft template, such as silica, carbon spheres, block copolymers, surfactants and bubbles [15–19]. Here we provide a novel vesicle template method to synthesize TiO_2 hollow microspheres, which are self-assembled with uniform 1-D TiO_2 nanorods. For this work, surfactant (Tween 60) and linear polymer (PEG1000) were selected to form vesicles which possess preferable stability [20,21]. The photocatalytic activity of TiO_2 hollow microspheres was investigated by decomposing methylene blue (MB) under simulated sunlight. Moreover, a possible formation mechanism of TiO_2 hollow microspheres was proposed on the basis of experimental results.

2. Experimental

2.1. Materials and synthesis

All the chemicals were of analytic grade and used without further purification. Titanium isopropoxide (97%, TIP) isopropyl and isopropyl alcohol (IPA) were used as the titanium precursor

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and the solvent, respectively; Tween 60 and polyethylene glycol 1000 (PEG1000) were served as template agents. In a typical synthesis, 0.05 g Tween 60 and 0.1 g PEG1000 were dissolved in 42 ml IPA. The solution was stirred until it is clarifying, and 1.5 mL TIP was added by ultrasonic dispersion for 10 min. The prepared solution was transferred into a Teflon-lined autoclave (60 mL) and heated at 180 °C for 24 h. After reaction, the autoclave was cooled to room temperature naturally. The precipitate was collected via centrifugation and washed completely with ethanol and deionized water several times to remove the impurities and dried at 60 °C overnight.

The commercial TiO_2 (Degussa P25) was employed as the reference sample. It is mostly in anatase form and has a specific surface area of 50 m^2/g corresponding to a mean particle size of ca. 30 nm.

2.2. Characterization

X-ray diffraction patterns were obtained with a Rigaku D/Max diffractometer which operates at 40 kV, 30 mA with Bragg–Brentano geometry by Cu Kα radiation (λ=1.5405 Å). The scan ranged from 20° to 80° (2θ degree) at the scanning rate of 3 deg/min. The morphologies of samples were characterized using field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4700) and transmission electron microscopy (TEM, Tecnai G220, FEI). The S_{BET} of the samples was performed by nitrogen physical adsorption at 77 K (Micromeritics ASAP 2010). Before measurement, the samples were degassed at 150 °C. UV–vis absorbance spectra of TiO_2 samples were obtained in the range of 200–800 nm using a Japan Shimadzu UV240 UV–vis spectrophotometer equipped with an integrating sphere, and $BaSO_4$ was employed as the reference.

2.3. Photocatalytic degradation of MB solution

The photocatalytic activity of TiO_2 hollow microspheres was evaluated by degradation of MB under simulated sunlight. A 500 W Xe lamp was employed and the photocatalytic experiment was carried out in a 0.5 L cylindrical glass reactor. The photocatalyst powders (0.05 g) and methylene blue aqueous solutions (300 mL, 10 mg/L) were mixed in a beaker. The suspension was maintained in the dark for 1 h in order to reach adsorption/desorption equilibrium before photocatalytic reaction. Methylene blue aqueous solutions (5 mL) were taken out of the reactor at a defined time interval, and were measured by the UV–vis spectrophotometer. The percentage of degradation (W) was calculated by using

$$W=[1-(A/A_0)]100\% \qquad (1)$$

Where A_0 is the absorbance of MB before irradiation and A_i is the absorbance of MB measured under irradiation every 20 min.

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction (XRD) patterns of TiO_2 hollow microspheres are shown in Fig. 1. It can be observed that all the identified peaks of the sample can be indexed to anatase TiO_2 (JCPDS card no. 21-1272). The diffraction peaks of TiO_2 hollow microspheres have no response to crystalline impurities, indicating that the anatase TiO_2 with superior crystallinity and high phase purity is achieved. Moreover, the average crystallite size of the sample is about 16.9 nm according to the Scherrer's formula.

3.2. Morphology analysis and proposed formation mechanism

The morphology of the samples was investigated by SEM and TEM. The typical SEM images of the samples are presented in Fig. 2(a–c) at different magnifications. The morphology of TiO_2 samples is microsphere with a diameter of about 1 μm, which is shown in the Fig. 2(a), and it is found that the TiO_2 microspheres were connected together in disorder. A high magnification SEM image is shown in Fig. 2(b). It can be seen that the microspheres were self-assembled with uniform 1-D TiO_2 nanorods. These nanorods, possessing diameter of about 20 nm and length of about one hundred nanometers, were wrapped around each other to form microspheres. In Fig. 2(c), the hollow interior of the TiO_2 microsphere is clearly visible in the SEM image of a broken microsphere. The porous wall and hollow interior structure of TiO_2 microspheres were further confirmed by TEM shown in Fig. 3. These results indicate that TiO_2 microspheres with a typical structure of hollow interior and porous spherical surface were prepared successfully.

A proposed formation mechanism model of TiO_2 hollow microspheres is shown in Fig. 4. At first, the additive of the PEG, Tween can form stable vesicles in the initial mix [20,21], which acts as a soft template for the formation of hollow microspheres. The coordination interaction among metallic species Ti^{4+} and PEG chains leads to aggregation of Ti^{4+}–PEG [22,23]. As the reaction temperature increases gradually, more and more TiO_2 nanoparticles nucleate and grow during the alcoholysis process. With the reaction proceeding, TiO_2 nanoparticles grew into TiO_2 nanorods and then aggregated into

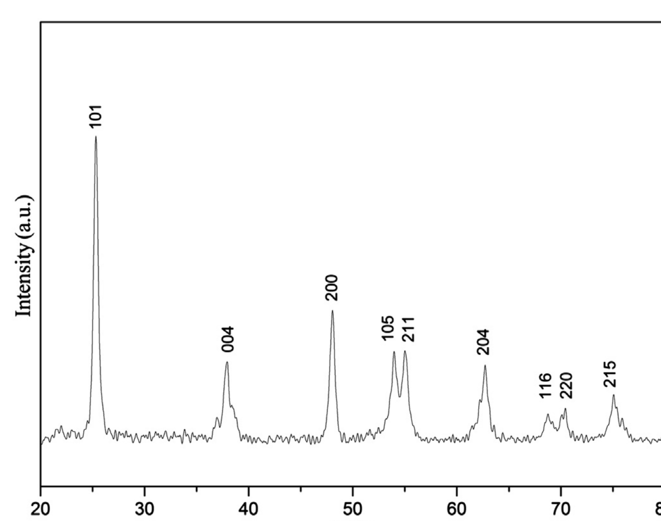

Fig. 1. XRD patterns of TiO_2 hollow microspheres.

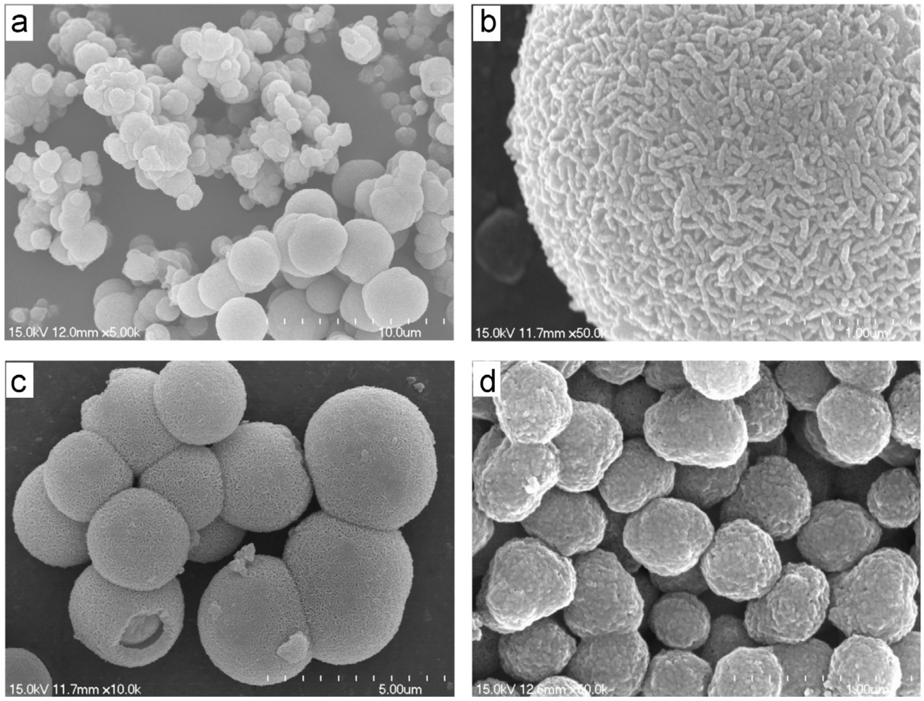

Fig. 2. SEM images: (a) overall morphology of hollow TiO_2 microspheres; (b) the surface of TiO_2 microspheres showing the self-assembled nanorods; (c) an individual broken TiO_2 microspheres showing the hollow interior and (d) the as-synthesized TiO_2 samples without PEG1000.

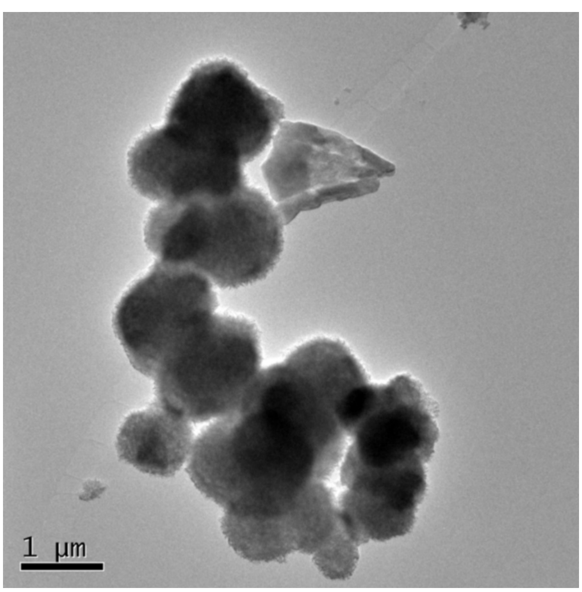

Fig. 3. TEM images of TiO_2 hollow microspheres.

TiO_2 hollow microsphere. In this study, the introduction of PEG is crucial to obtain a spherical organization of nanorods; no spherical organization of nanorods is obtained in the absence of PEG under the current synthetic conditions, which is presented in Fig. 2(d).

3.3. BET surface areas analysis

The nitrogen adsorption–desorption experiment was employed in order to further examine the open porous network structure of the TiO_2 microspheres. The pore size distribution curve determined by the Barrett–Joyner–Halenda (BJH) method from desorption branch of a nitrogen isotherm is shown in Fig. 5. Two sharp peaks located at 3.6 nm and 5.9 nm can be observed respectively, which provide a further evidence of mesoporous structure with relatively narrow pore size distribution. The N_2 adsorption–desorption isotherm is shown in the inset of Fig. 5. It gives a type-IV isotherm with a type-H3 hysteresis loop, indicating the existence of well-developed mesoporous structure [24]. All of these results clearly confirm the mesoporous structure, which leads to high specific surface area of 155 m^2/g calculated by the Brunauer –Emmett–Teller (BET) method.

It is well known that high specific area can lead to strong adsorption performance [25]. A simple adsorption contrast has been made in Fig. 6. Photographs (a) and (c) are the results of the MB solutions (10 mg/L) added with P25 and TiO_2 hollow microspheres respectively, and photograph (b) is the MB solution with nothing added. Apparently, the MB solution added with P25 still kept blue color. Meanwhile, the MB solution added with TiO_2 hollow microspheres became nearly colorless and blue precipitation formed, indicating that TiO_2 hollow microspheres have strong adsorption performance.

3.4. UV–vis absorbance spectra

The UV–vis absorbance spectra were employed to demonstrate the light absorption. The UV–vis absorbance spectra of TiO_2 hollow microspheres and P25 are shown in Fig. 7. It can be observed that both TiO_2 hollow microspheres and P25 have the same band gap energies as well as the strong adsorption in the UV region. Particularly, in the part of visible light region

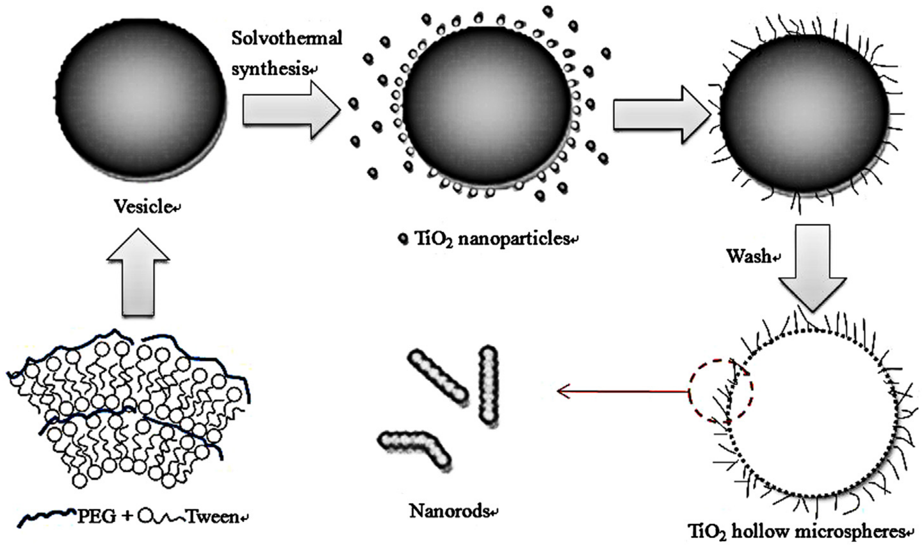

Fig. 4. Schematic of proposed reaction mechanism for the formation of TiO_2 hollow microspheres with nanorods structure.

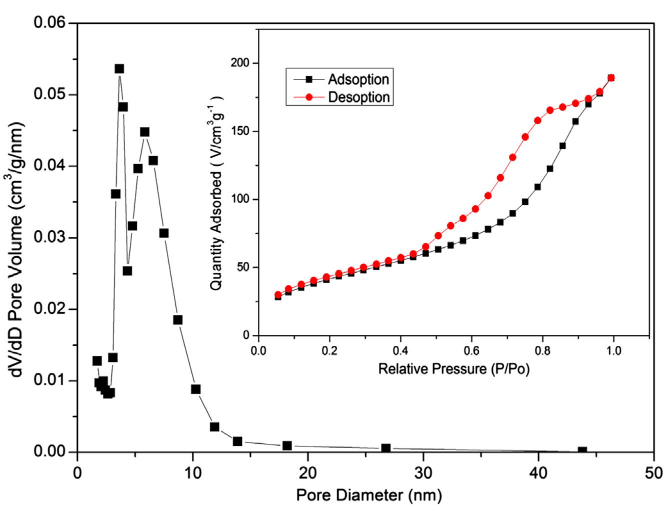

Fig. 5. Pore size distribution curve and corresponding nitrogen adsorption–desorption isotherm of TiO_2 hollow microspheres (inset).

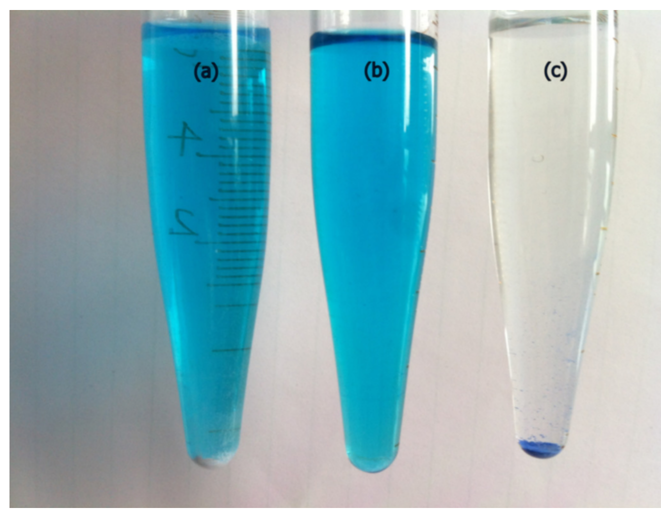

Fig. 6. Photographs of the MB solutions: (a) with addition of P25; (b) without addition and (c) with addition of TiO_2 hollow microspheres.

(400–500 nm), TiO_2 hollow microspheres have a stronger adsorption than P25. This phenomenon can be explained by the hollow structure which can absorb more photons [9]. This structure allows the light to scatter inside their interior hollows and reflect multiply, which can improve the use efficiency of the light source and enhance photocatalytic activity [26,27].

3.5. Photocatalytic activity

The photocatalytic activity of TiO_2 hollow microspheres and P25 was investigated. The 500 W Xe lamp was chosen to simulate the sunlight, and methylene blue (MB) was selected as model dye. The photocatalytic results were shown in Fig. 8. It could be observed that TiO_2 hollow microspheres have higher catalytic efficiency than P25. The reasons are possibly attributed to three aspects: firstly, enlarged specific surface areas and thus provide more reaction sites for mass transfer. Secondly, the enhanced light absorption capability by permitting more light reflections and multiple-scattering inside its interior. Thirdly, enhanced charge transfer facilitated by 1D TiO_2 nanorod structure and thus retards the recombination of photogenerated electrons and holes [13,27,28]. Furthermore, TiO_2 hollow microspheres can be easily recycled by a simple filtration. As shown in Fig. 9, the photocatalytic ability had no obvious decrease in five cycles for the MB, indicating that TiO_2 hollow microspheres have superior stability, which is important to its practical environmental applications.

4. Conclusion

In summary, TiO_2 hollow microspheres were successfully prepared by a novel vesicle template method. TiO_2 hollow microspheres with an average diameter of about 1 μm are self-assembled with uniform 1-D TiO_2 nanorods, meanwhile

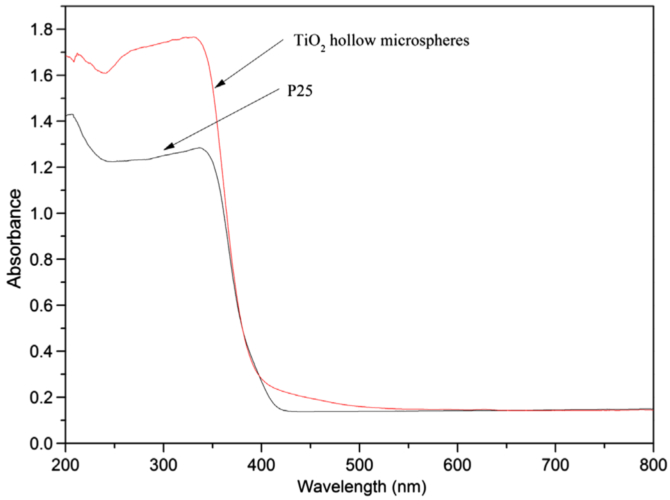

Fig. 7. UV–vis absorbance spectra of TiO_2 hollow microspheres and P25.

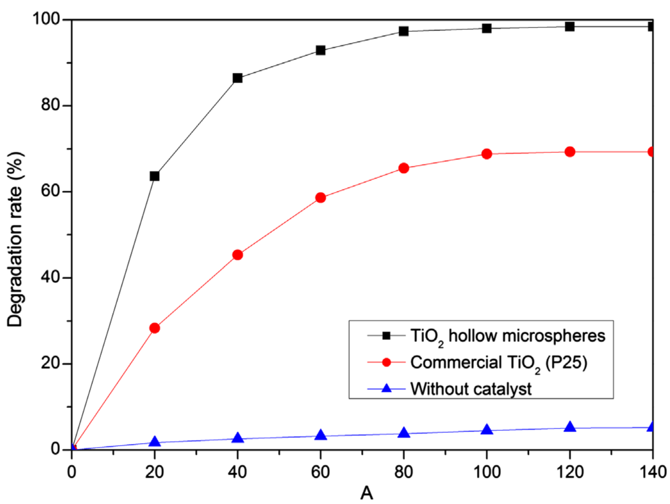

Fig. 8. Photocatalytic degradation of methylene blue (10 mg/L) under simulated sunlight irradiation using TiO_2 hollow microspheres and P25 as the catalyst.

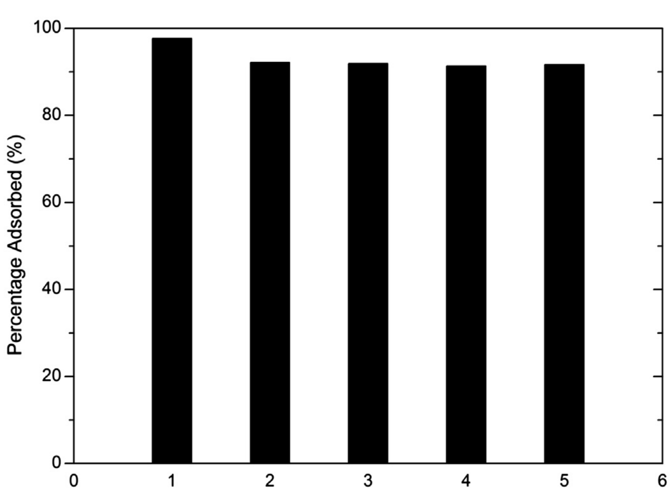

Fig. 9. Reusability of TiO_2 hollow microspheres.

forming well-developed mesoporous wall. They possess enhanced photocatalytic efficiency and strong adsorption performance compared with P25. Reason can be attributed to their high surface area which can improve catalytic reaction efficiency, the hollow structure which can enhance light harvesting, and one-dimensional TiO_2 nanorod structure which can facilitate charge transfer. The vesicle template method is simple and it provides a novel pathway to the synthesis of hollow spheres, possessing potential application for catalyst, environment and others.

Acknowledgments

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