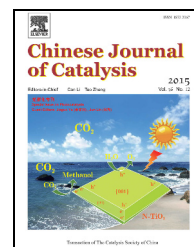


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Fabrication of TiO₂ hollow microspheres using K₃PW₁₂O₄₀ as template

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ABSTRACT

Fabrication of TiO₂ hollow microspheres (TiO₂-HMSs) has attracted considerable attention owing to their low density, high photoreactivity, and easy to separate and reuse. A fluoride-free method for the fabrication of TiO₂-HMSs is reported by refluxing a mixed solution of H₃PW₁₂O₄₀ (0.4 mmol), KCl (2.5 mmol) and Ti(SO₄)₂ (2–25 mmol) at 125 °C for 8 h, followed by decomposition of the K₃PW₁₂O₄₀ (KPW) template in basic solution. The prepared TiO₂-HMSs are characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy. The activities of the photocatalysts are evaluated by photocatalytic degradation of Brilliant Red X-3B, an anionic dye, under UV irradiation. It is observed that the TiO₂-HMSs exhibit diameters of approximately 0.5–1 μm, and the photocatalytic activity of TiO₂-HMSs initially increases and then decreases with an increasing amount of Ti(SO₄)₂. The TiO₂-HMSs prepared in the presence of 4 mmol Ti(SO₄)₂ exhibit the highest photocatalytic activity, which is 2.1 times higher than TiO₂ nanoparticles (prepared in the absence of the KPW template). The enhanced photocatalytic activity of the prepared TiO₂-HMSs is ascribed to the improved crystallization, coupling effect between TiO₂ and the residual KPW template, and the unique hollow structures of TiO₂-HMSs.

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1. Introduction

In the last several decades, a wide variety of hollow inorganic nanostructures have received considerable attention [1–9] because of their promising applications, including drug delivery, photocatalytic redox reactions and water splitting, clean energy conversion and storage, gas sensing, and heavy-metal ion sequestration. TiO₂ is a very important multifunctional material because of its peculiar and fascinating physicochemical properties and has a wide variety of potential

uses in diverse fields, such as solar energy conversion, environmental purification and water treatment [10–12].

Recently, TiO₂ hollow microspheres (TiO₂-HMSs) have received increasing attention owing to their low density, high specific surface areas and good photocatalytic activity [5,13–19]. Many strategies for the fabrication of TiO₂-HMSs have been reported, including templating methods [20–22] and templating-free methods [17,23,24]. For example, the fabrication of TiO₂-HMSs using SiO₂ microspheres as templates and TiF₄ as the precursor, where sacrifice of the template (SiO₂

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microspheres) was achieved by *in situ* hydrofluoric acid (HF) etching, has been reported [21]. Yu et al. [13,25] also reported the fabrication of TiO₂-HMSs by fluoride-induced self-transformation (FIST) in the presence of fluorides, such as (NH₄)₂TiF₆ and NH₄F, a method based on the template-free Ostwald ripening process. Our group also reported the fabrication of TiO₂ hollow structures by the H₂O₂-assisted FIST method [18,26,27]. However, the presence of F can produce highly corrosive and toxic HF during the synthesis for the etching of solid cores, thus decreasing the practicality of this synthetic approach [23,28]. Therefore, the challenge remains for the synthesis of TiO₂-HMSs in a F-free process.

Herein, we report a facile F-free method for the fabrication of TiO₂-HMSs using Ti(SO₄)₂ as precursor and K₃PW₁₂O₄₀ (KPW) as template. It should be noted that the template, KPW, can be easily removed in diluted NaOH solution [29].

2. Experimental

2.1. Preparation of TiO₂-HMSs

KCl solution (25 mL, 2.5 mol/L) was mixed with H₃PW₁₂O₄₀ solution (5.0 mL, 0.4 mol/L) in a 250-mL flask under magnetic stirring to form a white milk-like KPW suspension. Ti(SO₄)₂ (2–25 mmol) was added into the flask and heated under reflux (approximately 125 °C) for 8 h. After cooling to room temperature, the solid products were collected by filtration, and the resultant cake was dispersed in NaOH solution (75 mL, 1.0 mol/L). After stirring for 1 h, the precipitate was collected by filtration and sequentially washed by distilled water until the pH of the filtrate was between 6 and 7. The prepared TiO₂ samples were labeled as Tx, where x represents the amount of Ti(SO₄)₂ used in reaction (Table 1). For example, T4 represents the sample prepared in the presence of 4 mmol of Ti(SO₄)₂ in the presence of the KPW template. For comparison, TiO₂ particles (Tp), by direct hydrolysis of Ti(SO₄)₂ in the absence of the KPW template, were also prepared.

2.2. Characterization

The X-ray diffraction (XRD) patterns were obtained on a D8-advance X-ray diffractometer (Bruker, German) using Cu K_α radiation at a scanning rate of 0.02°/s and a step size of 0.02° in the 2θ range of 10°–70°. The accelerated voltage and applied current were 15 kV and 20 mA, respectively. The morphologies of the photocatalysts are characterized by transmission electron microscopy (TEM, Tecnai G20, USA) using an acceleration voltage of 200 kV and field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) with an acceleration voltage of 10 kV. Fourier transform infrared spectroscopy (FTIR) was performed using a NEXUS-470 infrared spectrometer (Nicolet Co., USA). Diffuse reflectance spectroscopy (DRS) was performed on dry-processed disk samples using a ultraviolet-visible (UV-Vis) spectrophotometer (Lambda, Bio 35, PE Co., USA). X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Multilab 2000 XPS system with a monochromatic Mg K_α source and a charge neutralizer. All the

Table 1

Starting materials and characterization results of the photocatalysts.

Sample	Starting materials (mmol)			Characterization results	
	H ₃ PW ₁₂ O ₄₀	KCl	Ti(SO ₄) ₂	Relative Crystallinity *	Band gap (eV)
Tp	—	—	4	1.80	3.19
T2	0.4	2.5	2	1.00	3.20
T4	0.4	2.5	4	2.03	3.19
T8	0.4	2.5	8	1.47	3.18
T25	0.4	2.5	25	1.35	3.18

Reaction conditions: EtOH/Acid = 5:1, 60 °C.

* Evaluated via the relative intensity of anatase (101) plane diffraction peak using T2 sample as reference.

binding energies were referenced to the C 1s peak at 284.4 eV of the surface adventitious carbon.

2.3. Evaluation of the photocatalytic activity

The photocatalytic activity of the photocatalyst was evaluated by degradation of Brilliant Red X-3B (X3B), an anionic dye, under irradiation of a 3 W LED lamp (UVEC-4 II, Shenzhen Lamplic Tech. Co., Ltd., China) with a wavelength of 365±10 nm. Prior to irradiation, the suspensions were first sonicated, to ensure the photocatalyst was uniformly dispersed, and then shaken overnight in the dark, to establish the adsorption-desorption equilibrium. During the photocatalytic reaction, the reactor was mechanically stirred at a constant rate. The concentration of TiO₂ was 1.0 g/L, and the initial concentration of dye used was 1.0×10⁻⁴ mol/L. At given intervals of irradiation, small volume aliquots were withdrawn and centrifuged. The supernatant fluid was then analyzed by an Agilent 8451 spectrometer at 510 nm for X3B.

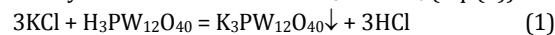
2.4. Powder photoluminescence spectra

Photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The excitation wavelength was 300 nm. Both of the widths for excitation and emission slits were 5.0 nm. The scanning speed was 1200 nm/min and the photomultiplier tube voltage was 700 V.

3. Results and discussion

3.1. Structure of the template

Figure 1(a) shows the TEM image of the prepared KPW templates. It can be seen that the templates are solid microspheres with diameters of approximately 0.5–1.0 μm. Observations at high magnification show that the surface of the templates is fairly smooth (Fig. 1(b)). Consistent with literature previous report [29], XRD characterization results (Fig. 1(c)) show that the prepared template is KPW. KPW microspheres were formed by the reaction of KCl and H₃PW₁₂O₄₀ (Eq. (1)).



According to a previous report [29], KPW exhibits a weak solubility in water, which makes it a good candidate to be used as a template for the fabrication of TiO₂-HMSs.

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