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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 2 θ 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 μ m. 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.

Fig. 1. TEM images (a, b) and XRD pattern (c) of the prepared KPW template.

3.2. Phase structure and morphology of TiO_2 photocatalyst

Phase structure and crystallization are important factors influencing the photocatalytic activity of TiO_2 [30]. Fig. 2 shows the XRD patterns of the TiO_2 photocatalysts. A broad peak at $2\theta = 25.3^\circ$, corresponding to the (101) plane diffraction of anatase TiO_2 (ICDD 21-1272), was observed for all the photocatalysts [31]. Upon increasing the amount of $\text{Ti}(\text{SO}_4)_2$ from 2 to 4 mmol, the relative crystallinity of anatase increased from 1.00 (T2) to 2.03 (T4), indicating an enhancement of crystallization. However, with a further increase in the amount of $\text{Ti}(\text{SO}_4)_2$ to 8 and 25 mmol, the relative crystallinity of anatase decreased to 1.47 (T8) and 1.35 (T25), respectively (Table 1). The relative crystallinity of anatase TiO_2 for the Tp sample is 1.80, which is larger than that of T2 but smaller than that of the T4 sample. In the absence of KPW, too many crystal nucleation centers are formed by direct hydrolysis of $\text{Ti}(\text{SO}_4)_2$, which results in the formation of smaller TiO_2 particle size (Tp). In the presence of the KPW template, however, nucleation of TiO_2 is favored at the surface of KPW template owing to the strong interaction be-

tween TiO_2 (positively charged) and KPW template (negatively charged). The limited nucleation centers lead to the formation of larger TiO_2 particle sizes (T4). Therefore, it is understanda-

Fig. 2. XRD patterns of the prepared TiO_2 samples, together with the expected diffraction peaks for anatase TiO_2 .

Fig. 3. TEM images of the prepared TiO_2 samples for Tp (a, b), T2 (c), T4 (d), T8 (e), and T25 (f).

Fig. 4. SEM images of the prepared TiO_2 samples for Tp (a), T2 (b), T4 (c, d), T8 (e), and T25 (f).

ble that T4 showed enhanced crystallization when compared with Tp, which was prepared in the same amount of $\text{Ti}(\text{SO}_4)_2$ precursor. However, with an increasing amount of $\text{Ti}(\text{SO}_4)_2$ precursor, the crystallization of TiO_2 -HMSs steadily decreases. This arises from the decreased relative concentration of KPW and increased acidity of solution. H_2SO_4 is formed during the hydrolysis of $\text{Ti}(\text{SO}_4)_2$ (Eq. (2)). The hydrolysis of $\text{Ti}(\text{SO}_4)_2$ is unfavorable in an acidic solution.

Figures 3 and 4 present the TEM and SEM images of the photocatalysts, respectively. In the absence of the KPW template, direct hydrolysis of $\text{Ti}(\text{SO}_4)_2$ resulted in only irregular TiO_2 particles (Fig. 3(a) and (b)). In the presence of the KPW template, TiO_2 -HMSs were formed (Fig. 3(c)–(e) and Fig. 4(b)–(e)) owing to the template-directed deposition and template-sacrificial dissolution (Scheme 1). When the concentration of $\text{Ti}(\text{SO}_4)_2$ was low, the obtained TiO_2 -HMSs were fragile (example of T2 in Fig. 3(c) and Fig. 4(b)), possibly owing to the fact that the wall of TiO_2 was thin. However, only solid aggrega-

Scheme 1. Strategy for fabrication of TiO_2 -HMSs using KPW solid microspheres as templates. (a) Hydrolysis of $\text{Ti}(\text{SO}_4)_2$ to form a layer of amorphous TiO_2 ; (b) Crystallization of TiO_2 from amorphous phase to anatase; (c) Decomposition of the core (KPW template) in basic solution. Gray, light red and dark red colors represent KPW template, amorphous and anatase phase TiO_2 , respectively.

tions of irregular TiO_2 microspheres were obtained if the concentration of $\text{Ti}(\text{SO}_4)_2$ was too high (example of T25 in Figs. 3(f) and 4(f)). This is because of the failure for etching of the KPW template by NaOH owing to the thick wall of TiO_2 on the surface of the KPW template. Perfect TiO_2 -HMSs were obtained (Fig. 3(d) and Fig. 4(c)–(d)) in the presence of 4 mmol $\text{Ti}(\text{SO}_4)_2$, and the inner diameters of the hollow microspheres were approximately 0.5–1 μm , consistent with the diameters of the KPW templates.

3.3. FT-IR and UV-Vis results

Figure 5 shows the FT-IR spectra of TiO_2 particles (Tp) and TiO_2 -HMSs (T4). It can be observed that the two samples showed similar spectra. The bands appearing at approximately 3414 cm^{-1} correspond to the stretching vibration of OH groups linked to Ti atoms (Ti-OH), and the bands at 1636 and 1619 cm^{-1} relate to the flexion vibration of OH groups in adsorbed water. These results confirm the presence of hydroxyl groups in the samples. The adsorbed water and hydroxyl groups are crucial to the photocatalytic reactions since they react with photo-excited holes on the catalyst surface to produce hydroxyl radicals, which are powerful oxidants. The band centered at 1383 cm^{-1} is assigned to the bending vibrations of the C-H bond in the species linking the -Ti-O-Ti- structural network. The intensity of the absorption at 1189 cm^{-1} is proposed to arise from Ti-O-Ti stretching. The peak at around 544 cm^{-1} was ascribed to the absorption bands of Ti-O and O-Ti-O flexion vibration [32].

Figure 6 compares the UV-Vis absorption spectra of TiO_2 particles (Tp) and TiO_2 -HMSs (T4). It can be clearly observed that the spectrum of T4 is almost the same with that of the Tp sample. It was reported that TiO_2 hollow structures allowed multiple reflections of UV-visible light within the interior cavity that facilitates more efficient use of the light source, which is important for an enhanced photocatalytic activity of TiO_2 [33]. However, in our present study, these TiO_2 samples showed similar light-harvesting ability with a bandgap of 3.18–3.20 eV (Table 1). The similar absorption spectra of these TiO_2 photocatalysts also reflect that the possibility of doping TiO_2 -HMSs by hetero elements, such as W and P, can be ruled out.

Fig. 5. FT-IR spectra of Tp and T4 samples, respectively.

Fig. 6. Optical absorption spectra of KPW template, Tp and T4.

3.4. XPS analysis

The XPS spectra of TiO_2 particles (Tp) and TiO_2 -HMSs (T4) are shown in Fig. 7(a). It can be determined that both the photocatalysts contain Ti, O and C with binding energies for Ti 2p at 458 eV, O 1s at 531 eV and C 1s at 284 eV. The C element is ascribed to the residual carbon from the precursor solution and the adventitious hydrocarbon from the XPS instrument [34]. A strong XPS signal of Na (binding energy of about 499 eV) and weak signal of element W can also be observed from the XPS survey spectrum of the T4 sample (Fig. 7). The element Na should arise from the residual NaOH on the surface of the photocatalyst, which was used to decompose the KPW template. High resolution XPS spectrum of the W element, shown in Fig. 7(b), shows a binding energy of approximately 249 eV ($\text{W } 4d_{5/2}$) and 261 eV ($\text{W } 4d_{3/2}$). The concentrations of W and P elements in the T4 sample were calculated to be 0.74 and 0.50 at%, respectively. This infers that KPW template was not completely removed after addition of NaOH. The UV-Vis absorption spectra and XPS characterization results suggest that W and P elements have not been doped into the lattice of TiO_2 -HMSs, and may still exist in the form of KPW. It has been reported that the photocatalytic activity of TiO_2 can be enhanced after modification by a polyoxometalate (POM), such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$, owing to the efficient electron transfer of POM from the conduction

band of TiO_2 [12,35–38]. The presence of residual KPW template, the salt of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, should also facilitate the enhancement of the photocatalytic activity of TiO_2 -HMSs.

3.5. Photocatalytic activity

To demonstrate the complex structure-function correlation, we examined the photocatalytic activity of the prepared samples using X3B degradation as a probe reaction. Fig. 8(a) shows the degradation profiles of X3B in the presence of TiO_2 under UV irradiation. It can be observed that the X3B dye is very stable, which shows little photo-bleaching in the absence of the TiO_2 photocatalyst [39].

From Fig. 8(a), it is clearly observed that, in the presence of TiO_2 , the concentration of X3B in solution decreases linearly with increasing the irradiation time, which obeys the kinetics of a pseudo-zero-order reaction rate equation. The slopes for the degradation curve (rate constants), which represent the photocatalytic activity of the photocatalyst, increase first and then decrease with increasing the amount of $\text{Ti}(\text{SO}_4)_2$ (Fig. 8(b)). The highest photocatalytic activity was achieved for the T4 sample (rate constant of $0.015 \mu\text{mol}/(\text{L}\cdot\text{min})$), which is approximately 2.1 times higher than that of Tp ($0.0073 \mu\text{mol}/(\text{L}\cdot\text{min})$).

The reasons for TiO_2 -HMSs of T4 showed the highest photoreactivity can be explained as the follow. First, good crystallization (Table 1) of the T4 sample is beneficial to reduce the number of defects, thus the recombination rates of photo-generated electrons and holes for the TiO_2 -HMSs are smaller. Therefore, it is not surprising that the photocatalytic activity of TiO_2 -HMSs increased with increasing the amount of $\text{Ti}(\text{SO}_4)_2$ from 2 to 4 mmol owing to enhanced crystallinity. Second, residual KPW template facilitates the removal of photo-generated electrons from the conduction band of TiO_2 , retarding the recombination (Fig. 7). Third, the photocatalytic activity can be enhanced owing to entrapment of organic pollutants into the hollow interiors [27].

However, the hydrolysis reaction of $\text{Ti}(\text{SO}_4)_2$ was restrained if the concentration of $\text{Ti}(\text{SO}_4)_2$ was too high owing to the formation of highly concentrated H_2SO_4 (Eq. (2)). Therefore, it is not surprising to observe that the crystallization of the TiO_2 sample decreased from 2.03 to 1.36 with the increase in the

Fig. 7. XPS survey spectra (a) and the corresponding high-resolution XPS spectra in W 4d region (b) for TiO_2 nanoparticles and TiO_2 hollow microspheres.

Fig. 8. Photocatalytic degradation profiles (a) and corresponding rate constants (b) of X3B dye in the presence of TiO_2 photocatalyst.

amount of $\text{Ti}(\text{SO}_4)_2$ from 4 to 25 mmol, which is consistent with the photocatalytic activity (Fig. 8). It is noteworthy that the relative crystallinity of Tp is 1.80, which is higher than that of the T8 and T25 samples. Hence, it is understandable that the photocatalytic activities of TiO_2 -HMSs of T8 and T25 are lower than Tp.

Although SiO_2 microspheres have been widely used as a hard template [21], the synthetic procedures are time- and energy-consuming. Additionally, surfactants, such as cetyltrimethylammonium bromide (CTAB) and Brij-56, are usually needed to fabricate monodispersed SiO_2 [40,41], which are costly and not environmentally-friendly. In the present study, however, the KPW template can be formed by simply mixing solutions of KCl and $\text{H}_3\text{PW}_{12}\text{O}_{40}$, which is very convenient.

Further experiments also indicate that hollow microspheres are readily separated from the slurry system by filtration or sedimentation after the photocatalytic reaction and can then be reused, which make them good photocatalysts for environmental purification.

4. Conclusions

A simple method for the fabrication of TiO_2 -HMSs was developed by using KPW microspheres as templates and $\text{Ti}(\text{SO}_4)_2$ as the precursor at 125°C . The photocatalytic activity of anatase TiO_2 -HMSs, prepared in the presence of 4 mmol $\text{Ti}(\text{SO}_4)_2$, showed the highest photocatalytic activity, which is 2.1 times

higher than that of TiO_2 nanoparticles. This enhancement is ascribed to the synergistic effect of good crystallinity, coupling with residual KPW template and the special hollow structure. The proposed route for the preparation of TiO_2 -HMSs has the merits of being simple, reproducible, and easily scaled-up, and is expected to find wide application in photocatalysis, catalysis, electrochemistry, separation, purification, drug delivery and so on.

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Graphical Abstract

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Fabrication of TiO_2 hollow microspheres using $\text{K}_3\text{PW}_{12}\text{O}_{40}$ as template

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A facile method for the fabrication of high photoreactive TiO_2 -HMSs is described. $\text{K}_3\text{PW}_{12}\text{O}_{40}$ (KPW) solid microspheres are used as templates, which can be decomposed in the presence of basic solution.

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磷钨酸钾模板法制备高活性二氧化钛空心微球

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摘要: TiO₂空心微球因具有低密度、高活性、易分离而有利于多次重复使用的优点而广受关注. 本文介绍一种无氟制备TiO₂空心微球的简单方法——磷钨酸钾(K₃PW₁₂O₄₀)模板法. 首先, 将H₃PW₁₂O₄₀和KCl溶液混匀, 得到白色牛奶状的K₃PW₁₂O₄₀模板(式(1)), 然后在磁力搅拌下加入一定量的Ti(SO₄)₂粉末, 加热至大约125 °C开始回流. 回流8 h后, 过滤洗涤. 滤饼分散在强NaOH溶液中, 原位除去K₃PW₁₂O₄₀模板(式(2)). 最后, 将催化剂洗涤到滤液为中性, 干燥后即得到TiO₂空心微球.

我们将所制备的TiO₂空心微球, 采用X射线衍射、透射电子显微镜、扫描电子显微镜、傅立叶红外光谱、固体粉末漫反射和X射线光电子能谱等进行了表征. 采用紫外光催化降解阴离子染料(活性嫣红X3B)来评价催化剂的性能.

实验结果显示: (1)所制TiO₂空心微球直径在0.5–1.0 μm; (2)磷钨酸钾模板剂充当晶核, 有利于空心微球的晶化; (3)加入的高浓度硫酸钛, 水解产生大量的硫酸, 抑制硫酸钛水解, 不利于TiO₂空心微球的晶化(式(3)); (4)催化剂的活性随着硫酸钛量的增加而先增后降. 4 mmol硫酸钛用量的TiO₂空心微球具有最高的光催化活性, 是TiO₂颗粒样品(无磷钨酸钾模板法制备)的2.1倍.

用该方法制备的TiO₂空心微球活性高可归因于以下主要原因: (1)TiO₂空心微球独特的孔结构; (2)良好的晶化程度(TiO₂样品晶化度越高, 越有利于光生载流子的分离, 抑制复合); (3)样品残余磷钨酸钾模板和TiO₂之间存在光生电子转移, 有利于空心微球TiO₂活性的提高. 该法具有操作简单、重复性好、易于批量制备的等优点, 有望广泛应用于(光)催化、电化学、分离与纯化以及药物缓释等领域.

关键词: 二氧化钛; 空心微球; 磷钨酸钾; 模板; 降解

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