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One template approach to synthesize C-doped titania hollow spheres with high visible-light photocatalytic activity

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HIGHLIGHTS

- ▶ C-doped titania hollow spheres (THS) were prepared by a facile one template method.
- ▶ THS interconnected with each other to form unique hollow three-dimensional network.
- ▶ The formation mechanism of the hollow three-dimensional network was proposed.
- ▶ The as-prepared THS presented much higher photocatalytic activity than commercial P25.

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ABSTRACT

Carbon-doped titania hollow spheres (THS) with unique hollow three-dimensional network structure were synthesized by a facile method using carbon spheres as template. The resultant samples, such as carbon spheres, carbon spheres coated with titania precursor, and final THS were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectrometer (EDS), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectra (FTIR), Brunauer–Emmett–Teller (BET) and UV–vis absorption spectrum. Based on the results of these characterizations, a reasonable formation mechanism of the hollow three-dimensional network structure was proposed. The photocatalytic activity of as-prepared THS was evaluated by decoloration of methylene blue solution under visible light irradiation. Results indicated that THS possessed higher visible light-induced photocatalytic activity than commercial P25, which could be attributed to its visible light absorption characteristic created by C-doping and the unique hollow three-dimensional network structure.

1. Introduction

In recent years, the research of a variety of photocatalytic materials, such as TiO_2, ZnO, CdS, WO_3, has attracted much attention because of their potentials in solving global energy and environmental problems [1–4]. Among these photocatalysts, titania (TiO_2) is the most important one because of its biological and chemical inertness, nontoxicity, cost effectiveness, and strong oxidizing power under ultraviolet light (UV) and visible light irradiation [5]. However, the photocatalytic activity of TiO_2 is limited by several factors, such as restrictive light absorption (only responsive to UV with wavelength below 387 nm due to its wide band-gap), fast charge-carrier recombination and low interfacial charge-transfer rate of photogenerated carriers, which severely restrict its practical applications and commerce [5–7].

In order to improve the photocatalytic activity of titania, many measures have been taken by previous scientists [8–10]. Ions doping and morphology control are considered as two of very promising strategies. Anion doping has proven to be an effective method for extending the photoresponse of TiO_2 into the wide visible light region. As one of the most promising anions, carbon-doped or modified TiO_2 photocatalysts have been investigated with emphasis in the past few years. For example, Lettmann et al. found carbon-containing TiO_2 was capable to photodegrade p-chlorophenol with visible light (>400 nm) [11]. Khan and co-workers found C-doped TiO_2 could absorb light at wavelengths below 535 nm [12]. Sakthivel and Kisch developed a carbon-modified TiO_2 which could even respond to the indoor daylight [13]. Park et al. reported that carbon-doped TiO_2 had more efficient water splitting under visible light (>420 nm) than pure TiO_2 nanotube [14]. On the other hand, some investigations show the photocatalytic activity of titania can be further improved by controlling its morphology properly [15,16]. Therefore, titania with different morphology, such as nanorods, nanotubes, nanowires, nanosheets, and nanoporous spheres have been successfully prepared by a variety of approaches [17–21]. Among these titania materials, titania hollow spheres (THS) have been considered as the potential candidate due to the intrinsic

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shape-dependent properties, including low density, good surface permeability, tunable pore structure, as well as high light-harvesting efficiency [22–25].

In current work, we synthesized C-doped THS by a facile one template method. It is worth mentioning that the as-prepared THS interconnect with each other through smaller pores to form hollow three-dimensional network structure, which was found to dramatically enhance the photocatalytic activity of TiO_2.

2. Experimental section

2.1. Preparation of carbon spheres

Glucose (20 g) was dissolved in 120 mL of deionized water to form a clear solution. The solution was then sealed in a 200 mL Teflon-lined autoclave and maintained at 180 °C for 4 h. After cooling to ambient temperature naturally, the products of the hydrothermal reaction were collected and washed with water and ethanol for three times, respectively. Finally, the products were dried at 80 °C for 4 h in an oven, resulting in carbon spheres (abbreviated as CS).

2.2. Preparation of titania hollow spheres

CS (0.4 g) was added into 20 mL of ethanol and stirred vigorously for 30 min in a sealed beaker. Then, the other solution including 5 mL of titanium isopropoxide and 20 mL of ethanol was added drop-by-drop into the beaker under vigorous stirring. Subsequently, the mixture was stirred vigorously for 1 h. Next, the products were centrifugated, washed and re-dispersed in water and in ethanol for three cycles, respectively. The resultant solid products were placed in the air at room temperature for 12 h, and then were dried at 80 °C for 4 h in an oven, resulting in the carbon–titania composite spheres (carbon spheres coated with titania precursor structure, abbreviated as CS + Ti for convenience). Finally, the above titania–carbon composite spheres were calcined at 600 °C in nitrogen atmosphere for 1 h, and then calcined at 600 °C in air for 4 h, resulting in THS.

2.3. Characterizations

Scanning electron microscopy (SEM) images were obtained by an S-4800 (Hitachi, Japan) equipment. X-ray diffraction (XRD) patterns were recorded at room temperature with an X'pert PROMPD diffractometer (PANalytical, Holand) with copper $K_{\alpha 1}$ radiation. The surface elements composition over the desired region of sample were detected by an energy dispersive X-ray spectrometer (EDS) attached to the SEM. X-ray photoelectron spectroscopy (XPS) analyses were tested on a PHI5300 analyzer (Perkin Elmer, America) with aluminum K_{α} radiation. Fourier transform infrared (FTIR) spectra were obtained by a Nicolet FTIR spectrometer (Magna-750) at ambient conditions. The nitrogen adsorption measurements were carried out at 77 K using an ASAP 2010 analyzer (Micromeritics, USA), and the Barrett–Joyner–Halenda (BJH) pore diameter distribution curves were obtained from the desorption branch and specific surface areas were obtained according to the Brunauer–Emmett–Teller (BET) model. Ultraviolet–visible (UV–vis) absorption spectra were recorded by a UV-2450 spectrophotometer (Shimadzu, Japan) equipped with an integrating sphere, and the baseline correction was done using a calibrated sample of barium sulfate.

2.4. Experimental procedures of photocatalytic decoloration

The photocatalytic experiment was carried out in a photo reaction system by using methylene blue (MB) as a model pollutant. A 1000 W Xe lamp equipped with a 420 nm cut-off glass filter (removing the UV irradiation below 420 nm wavelength), positioned in the center of a water-cooled quartz jacket, was used to offer visible light irradiation. At the side of quartz jacket, a 50-mL cylindrical vessel was used as the reactive bottle to load reaction solution. The distance between lamp and reactive bottle was 40 mm. In the bottom of the reactive bottle, a magnetic stirrer was equipped to achieve effective dispersion. The temperature of the reaction solution was maintained at 30 ± 0.5 °C by cooling water. 25 mg of photocatalyst powder was added into 50 mL of 10 mg/L MB solution to form suspension (pH = 6.98). Then, the suspension was irradiated with visible light (wavelength longer than 420 nm). During the irradiation, the suspension was stirred continuously. For comparison, the commercial Degussa P25 was also examined under the same conditions. At given time interval, 3 mL of suspension was taken out and immediately centrifuged to eliminate the solid particles. The absorbance of the filtrate was measured by a spectrophotometer at the maximum absorbance peak 665 nm.

3. Results and discussion

3.1. Morphology

From the SEM image shown in Fig. 1a, it can be observed that the as-prepared carbon spheres have smooth surface and almost uniform diameters (about 230 nm). Furthermore, these carbon spheres interconnect with each other intimately to form three-dimensional network array. The surface of sample CS + Ti looks a bit rough due to the fact that these carbon spheres with smooth surface have been coated by a layer of titania precursor (Fig. 1b). After calcination, THS with a diameter of approximately 200 nm are obtained, as shown in Fig. 1c, and a shrinkage of about 15% occurred due to the removal of template and the contraction of titania precursor. From the broken spheres shown in Fig. 1d, it can be clearly observed that these spheres possess hollow structure with a wall thickness of approximately 20 nm. In addition, it is noteworthy that THS interconnect with each other through smaller pores of about 50 nm (as shown in inset in Fig. 1d) to form hollow three-dimensional network structure, which is expected to offer an excellent pathway facilitating the transmission and diffusion of guest species.

3.2. Crystal phase and surface elements composition

To determine the crystal phase of the as-prepared samples, XRD measurements were carried out and the results are shown in Fig. 2a. The broad diffraction peak appeared at $2\theta = 22°$ (as observed in the XRD pattern of CS) corresponds to the (002) reflection of carbon [26], implying carbon spheres can be obtained by the hydrothermal reaction of glucose solution. After titania precursor was coated on carbon spheres, the XRD pattern of CS + Ti is not much change in comparison with that of CS, suggesting titania precursor anchored on the surface of CS is still amorphous structure. Once the carbon–titania composite spheres are calcined at 600 °C, most of titania precursor is transformed into anatase TiO_2, and a small portion is transformed into rutile TiO_2 (as shown in the XRD pattern of THS, the peak at $2\theta = 27.5°$ can be assigned to the (110) plane of rutile TiO_2 [27,28]). The weight fraction of anatase can be calculated using $X_A\ (\%) = 100/(1 + (1.265 I_R/I_A))$ (where X_A is the mass fraction of anatase, I_A and I_R are the X-ray integrated intensities of (101) peak of the anatase and (110) peak of rutile, respectively), and the result of calculation indicates that the as-prepared THS are composed of 78.4% anatase and 21.6% rutile. In addition, the crystal size of anatase in sample THS is 18.8 nm by applying the Scherrer equation $D = K\lambda/\beta\cos\theta$ (where K is a shape factor, about 0.89, λ is the X-ray wavelength, β is the FWHM of the diffraction line, and θ is the diffraction angle) [29,30].