



Hydrothermal synthesis and visible-light photocatalytic activity of α -Fe₂O₃/TiO₂ composite hollow microspheres

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Abstract

Novel α -Fe₂O₃/TiO₂ composite hollow spheres were successfully synthesized by a template-assisted precipitation reaction using urea as a precipitating agent and carbon spheres as templates in a mixed solvent of water and ethanol, and then calcined at 400 °C for 4 h. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, nitrogen adsorption–desorption isotherms, and vibrating sample magnetometer. The influence of calcination temperature and the molar ratio of titanium to iron (*R*) on the photocatalytic activity of the samples was investigated. The results indicated that the composite spheres show magnetic characteristics at room temperature and good photocatalytic activity under visible-light irradiation compare to the single-component α -Fe₂O₃ particles. This method can be further applied to synthesize nanocomposites of magnetic metal oxide and other metal oxide.

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1. Introduction

In recent years, micrometer- and nanometer-sized hollow structures have attracted a great deal of attention because of their low density, high surface area, good surface permeability and large light-harvesting efficiencies [1–4]. Moreover, these materials can be widely applied in photoelectric devices, catalysis, drug delivery, chromatography separation, and chemical reactors [5–9]. Various synthetic methods were explored to prepare hollow nanomaterials including Ionic liquids (ILs), self-assembly techniques, hydrothermal techniques, template-assisted techniques, and chemically induced self-transformation [10–12]. Up to now, template-assisted synthetic method has proved to be the most-applied and most effective route to fabricate inorganic hollow structures.

Titanium dioxide (TiO₂), as one of the most important transition-metal functional oxides, has attracted extensive attention during the past decades for its superior physical and chemical properties and a wide variety of potential use in diverse fields such as solar energy conversion, environmental purification, and water treatment [13–16]. In particular, TiO₂ hollow nanomaterials and nanocomposites have received more and more attention owing to their high photocatalytic activity, chemical stability, low cost and nontoxicity [17,18]. However, because of its wide band-gap energy (3.02 eV), TiO₂ can only harvest the spectrum with wave lengths in the near-ultraviolet (UV) region shorter than 387 nm, which accounts for merely 4–5% of the solar spectrum. Moreover, TiO₂ follows a relatively high electron–hole recombination rate, which is detrimental to its photoactivity. To solve this issue, different approaches such as transition metal doping, inorganic dye-sensitizing, valuable metal deposition and coupling titania with other semiconductors have been devoted to enhancing the photocatalytic activity of TiO₂ in which the response of the semiconductor was extended toward the visible region [19–21]. Up to now, it is still a great

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challenge to effectively immobilize or separate the TiO_2 particles in the photocatalytic system. Magnetic separation provides a very convenient approach for removing and recycling magnetic particles/composites by applying an appropriate magnetic field [22,23]. Compared to conventional nanopowder photocatalysts, TiO_2 magnetic composites such as $\text{Fe}_2\text{O}_3\text{-TiO}_2$ or $\text{Fe}_3\text{O}_4\text{-TiO}_2$ can be regarded as a promising photocatalyst for the environmental purification at the industrial scale as they can be more readily separated from the slurry system by the magnetic separation after photocatalytic reaction and recycled. Very recently, Yu et al. [24] fabricate a hierarchical porous $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2@\text{TiO}_2$ composite photocatalyst with superior photocatalytic properties by an effective three-step approach. Mou et al. [25] developed an asymmetric shrinkage approach for the fabrication of magnetic $\gamma\text{-Fe}_2\text{O}_3/\text{TiO}_2$ Janus hollow bowls (JHBs) by constructing a precursor solution pair during the solvents evaporation process. Moreover the as-obtained products show an efficient visible-light photocatalytic activity and convenient magnetic separation for water purification.

Herein, novel $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ composite hollow spheres are successfully fabricated using carbon spheres prepared from saccharide solution as templates, and their visible-light photocatalytic activity and environment application are carefully investigated. In addition, we also investigated the effects of the molar ratio of iron to titanium (R) on the microstructures and properties, especially on the photocatalytic property.

2. Experimental

2.1. Synthesis of carbon spheres

All the reagents used in the experiments were in analytical grade (purchased from SCRC Chemical Co., China) and used without further purification. Carbon spheres were synthesized by the hydrothermal approach as reported previously [26]. In a typical synthesis, 6.0 g glucose was dissolved in 60 mL of distilled water under constant stirring. Then the aqueous solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, maintained at 180°C for 4 h. The black or puce precipitates were washed with distilled water and ethanol three times and dried at 60°C for 8 h. In general, a longer hydrothermal reaction time results in the formation of larger carbonaceous polysaccharide spheres.

2.2. Synthesis of $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ hollow structures

The $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ hollow structures were prepared as follows: 1.8 g $\text{CO}(\text{NH}_2)_2$ and 0.3 g carbon spheres were dissolved in 54 mL ethanol/water mixed solvents with given volume ratio ($V_e/V_w=48\text{ mL}/6\text{ mL}$). After vigorously magnetic stirring for 30 min by using a magnetic stirrer, a certain amount of FeCl_3 and tetrabutyl titanate (TBOT) was added into the above solution under vigorously stirring for another 10 min. The molar ratio of titanium to iron (R) varied from 2:1 to 2:3 (2:1, 2:1.5, 2:2, and 2:3). The mixture was then transferred into a 100 ml Teflon-lined stainless steel autoclave and sealed, and the autoclave was placed in a pre-heated oven

at 60°C for 48 h and naturally cooled down to room temperature. The $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ precursor thus obtained was collected by centrifugation, washed with distilled water and dried under vacuum at 60°C for 10 h. Finally, the prepared sample was heated in an air atmosphere to a certain temperature (400°C) and held at this temperature for 4 h to remove the carbon spheres template.

2.3. Characterization

The X-ray diffraction patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=0.1546\text{ nm}$). The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, JEOL JXA-840A) and transmission electron microscopy (TEM) with a Japan JEM-100CX II transmission electron microscopy. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of the powders was analyzed by nitrogen adsorption in an ASAP2020 surface area and porosity analyzer (Micromeritics, USA). All the samples were degassed at 180°C prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.25. Desorption isotherm was used to determine the pore size distribution via the Barret–Joyner–Halender (BJH) method with cylindrical pore size [27]. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.994 was used to determine the pore volume and average pore sizes. Magnetic properties of the samples were measured by a model 4HF vibrating sample magnetometer (VSM, ADE Co. Ltd., USA).

2.4. Photocatalytic activity test

The evaluation of photocatalytic activity of the prepared samples for the photocatalytic decolorization of RhB aqueous solution was performed at ambient temperature. A 300 W halogen–tungsten through a UV-cutoff filter ($>400\text{ nm}$, $13.0 \pm 0.5\text{ mW cm}^2$ at 420 nm), which was positioned 10 cm away from the reactor, was used as a visible light source to trigger the photocatalytic reaction. Experiments were as follows: 0.05 g of the prepared $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ powder was dispersed in a 20 mL of RhB aqueous solution with a concentration of $1 \times 10^{-5}\text{ M}$ in a reaction cell. Before illumination, the suspensions were magnetically stirred in the dark for 60 min to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst powders and RhB. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove photocatalyst powders. The filtrates were analyzed by recording the variations of the absorption-band maximum (553 nm) of RhB in the UV–vis spectrum. Total organic carbon of the solution was analyzed with the Apollo9000 TOC analyzer.

3. Results and discussion

Fig. 1 shows XRD patterns of the $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ samples prepared at $R=2:1.5$ at 60°C for 48 h and calcined at 400°C

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