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Magnetically recoverable Bi_2WO_6–Fe_3O_4 composite photocatalysts: Fabrication and photocatalytic activity

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HIGHLIGHTS

- ▶ The Bi_2WO_6–Fe_3O_4 photocatalysts were synthesised by a simple hydrothermal route.
- ▶ Morphological modulation of the products could be easily realized by tuning the pH.
- ▶ The products can effectively photocatalyze the degradation of RhB as a probe reaction.
- ▶ The visible light photocatalysts can be easily harvested by a magnet.

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ABSTRACT

Three-dimensional (3D) hierarchical Bi_2WO_6–Fe_3O_4 microspheres were successfully synthesized by a simple hydrothermal route. These microspheres with average diameters of 2–3 μm are constructed by Bi_2WO_6 nanosheets, which are decorated by Fe_3O_4 nanoparticles with an average diameter of 150 nm. Morphological modulation of the obtained products could be easily realized by tuning the pH value of the reaction system. The photocatalytic properties of the composites were studied with the photo-degradation of Rhodamine B (RhB) as a probe reaction. Comparing with bulk Bi_2WO_6 (SSR-Bi_2WO_6) and TiO_2 (P25), Bi_2WO_6–Fe_3O_4 microspheres show improved photocatalytic activity under visible light irradiation, and can efficiently catalyze the degradation of RhB up to 98.6% within 150 min. Kinetic analysis reveals that the reaction rate constant k of Bi_2WO_6–Fe_3O_4 microspheres is over three times that of P25 and nearly seven times that of SSR-Bi_2WO_6. The Bi_2WO_6–Fe_3O_4 photocatalyst can be easily re-collected from the reaction system upon applying an external magnetic field. This kind of composite photocatalysts with easiness of separation can have potential applications in water treatment and environmental cleaning.

1. Introduction

Semiconductor photocatalysts have attracted much attention because of their applications in solving potential environmental and energy crises [1]. A high-performance photocatalyst should possess a structure appropriate for rapid separation of photogenerated charges, a large specific surface area for many catalytically active sites, and a fair response to visible light so as to maximally utilize sunlight energy [2–12]. Among various semiconductor visible light driven photocatalysts, the Aurivillius phase oxides with general formula $Bi_2A_{n-1}B_nO_{3n+3}$ (A = Ca, Sr, Ba, Pb, Na, K, and B = Ti, Nb, Ta, Mo, W, Fe) have gained much attention due to their layer structure and unique properties [13,14]. Bismuth tungstate (Bi_2WO_6), which is one of the simplest members of the Aurivillius oxide family, possesses excellent visible light driven photocatalytic activity besides many interesting physical properties such as ferroelectric piezoelectricity, pyroelectricity, nonlinear dielectric susceptibility, oxide anion conducting, and luminescent properties [15–20]. Since Kudo and Hijii first demonstrated the photocatalytic activity of Bi_2WO_6 for O_2 evolution in $AgNO_3$ solution [21], many research efforts have been focused on developing various Bi_2WO_6 micro-/nanostructure and investigating their photocatalytic performance under the visible light irradiation, such as square nanoplates [19], hierarchical hollow spheres [22], flower-like microstructures [23] and clew-like structures [24]. However, one important issue of the industrial application for Bi_2WO_6 catalysts is their separation. The obtained Bi_2WO_6 usually has a hydrophilic surface, which make it be easily dispersed in water and would enhance the catalytic properties, but will increase the difficulty of its

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separation and recollection from reaction system. This can increase the cost of industrial application and/or cause the treated water to be re-polluted.

Magnetic separation provides an effective way for removing and recycling magnetic particles/composites (such as magnetite, ferrite) by applying an appropriate external magnet. Such materials could combine the advantages of activity of catalysts with the merit of easy separation due to the incorporation of magnetic species. Recently, many research works have been carried out with this in mind. For instance, Yin et al. have successfully synthesized magnetic core/shell structured $Fe_3O_4/SiO_2/TiO_2$ nanocomposites with enhanced photocatalytic activity and fast magnetic separability by combining a sol–gel process with calcinations [25]. Wang et al. have developed diverse multifunctional Fe_3O_4/metal hybrid nanostructures with polymers as linkers [26]. Shen et al. have synthesized a novel $Fe_3O_4@C@Cu_2O$ nanostructure under the assistance of the interlayer reactive carbon [27]. However, the synthesis of these magnetic nanocomposites usually requires some linker shells (e.g., silica, polymers, carbon), which makes the synthesis route complicated and decreases the saturation magnetization (M_s) of the resultant composites, and as a result, limits their widespread industrial use. Fortunately, several studies have been performed on the magnetic composite materials such as $Fe_3O_4@Bi_2O_3$ [28], Fe_3O_4/hydroxyapatite [29], and Fe_3O_4/WO_3 [30] hierarchical core–shell structures. However, to the best of our knowledge, there is no report on the synthesis of $Bi_2WO_6–Fe_3O_4$ nanocomposites so far.

In the present work, we report for the first time the hydrothermal synthesis of 3D flower-like $Bi_2WO_6–Fe_3O_4$ hierarchical architectures. The as-grown microspheres consist of a number of interlaced two-dimensional (2D) Bi_2WO_6 nanosheets, and Fe_3O_4 nanoparticles are immobilized onto the nanosheets' surface. Morphologies of $Bi_2WO_6–Fe_3O_4$ composites can be tuned by adjusting pH value of the reaction system. It is worthy to note that the obtained hierarchical $Bi_2WO_6–Fe_3O_4$ microspheres not only display highly photocatalytic activity toward the decomposition of Rhodamine B (RhB) in aqueous solution, but also can be easily harvested by applying an external magnetic field.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$), sodium tungstate dihydrate ($Na_2WO_4·2H_2O$), sodium acetate (NaAc), iron (III) chloride hexahydrate ($FeCl_3·6H_2O$), polyethylene glycol-2000 (PEG-2000), ethylene glycol (EG), sodium hydroxide (NaOH), Rhodamine B (RhB), and ethanol were purchased from Shanghai Chemical Reagent Co., Ltd. (China). P25 (nanoscale TiO_2 powder, surface area $50\ m^2\ g^{-1}$) was purchased from Degussa AG (Germany). All chemicals in the study were analytical reagent grade and were used without further purification. Deionized water was used in all the experiments.

2.2. Preparation of Fe_3O_4 magnetic nanoparticles

The Fe_3O_4 nanoparticles were synthesized by a modified solvothermal method in polyol medium [31]. Briefly, 1.35 g of $FeCl_3·6H_2O$ was dissolved in 30 mL of ethylene glycol (EG) to form a clear solution, then 3.6 g of NaAc and 1.0 g of polyethylene glycol-2000 (PEG-2000) were added to this solution. The mixture was stirred vigorously to form homogeneous yellow solution and then sealed in a Teflon-lined stainless-steel autoclave with a capacity of 40 mL. The autoclave was heated to 200 °C and kept at this temperature for 8 h, and then allowed to cool to room temperature. The obtained black products were washed with deionized water and ethanol several times, and then dried in vacuum at 45 °C for 24 h.

2.3. Preparation of $Bi_2WO_6–Fe_3O_4$ composite photocatalyst

In a typical process, 0.485 g of $Bi(NO_3)_3·5H_2O$ was dissolved in 2 mL of 2 M nitric acid solution, and 0.165 g of $Na_2WO_4·2H_2O$ was dissolved in 2 mL of deionized water. The Na_2WO_4 solution was then added dropwise to the $Bi(NO_3)_3$ solution to form a white suspension. The pH value of the resulting suspension was adjusted to 3.0 by adding a dilute NaOH solution. 35 mg of the as-prepared magnetic Fe_3O_4 nanoparticles was ultrasonically dispersed in 15 mL of deionized water and then was added to the above mixed solution. After being further stirred for 30 min, the mixture was transferred to a 25 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 160 °C for 6 h, and then allowed to cool to room temperature. The obtained products were collected and thoroughly washed with deionized water and ethanol several times, then dried in vacuum at 45 °C for 12 h. For comparison, bulk Bi_2WO_6 powder was also prepared by a traditional solid-state reaction (named SSR-Bi_2WO_6) according to the reported method [32].

2.4. Characterization

The phase of as-synthesized products were characterized using X-ray diffraction (XRD, Shimadzu XRD-6000) with Cu Kα radiation ($\lambda = 1.5406$) at a scanning rate of $4°\ min^{-1}$. The composition, morphology, and size of the products were examined by field emission scanning electron microscopy (FE-SEM; JSM-7001F), energy dispersive X-ray spectroscopy (EDS, attached to FE-SEM), and transmission electron microscopy (TEM; JEOL-2100). Samples for TEM were prepared by dropping the products on a carbon-coated copper grid after ultrasonic dispersing in absolute ethanol and allowed them to dry in air before analysis. The photocatalytic activity measurement was conducted on a GHX-2 photochemical reactor (Science and Education equipment Co., Ltd., YangZhou, China) (Fig. 1) with a 500 W of tungsten lamp (Small500WR7S, Philips). The light intensity was measured with a FZ-A radiometer (China).

2.5. Photocatalytic activity measurement

The photocatalytic activities of the samples were evaluated by the degradation of Rhodamine B (RhB) under visible light irradiation. A 500 W tungsten lamp (Fig. S1) as the visible light source (the total intensity at the catalyst mixture surface is *ca.* $120\ mW\ cm^{-2}$, in which the UV light intensity is less than $10\ mW\ cm^{-2}$) was positioned at *ca.* 10 cm away from the reaction cell to trigger the photocatalytic reaction. There is a water layer between the reaction system and the lamp to remove the thermal effect of light. The experiments were performed at room temperature as follows: 0.1 g of the photocatalysts was added to 100 mL of RhB solution ($1.0 \times 10^{-5}\ mol\ L^{-1}$) in a Pyrex reactor. Before illumination, the suspensions were vigorously stirred in the dark for 60 min to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst and RhB (Fig. S2). The dispersion was then exposed to visible light irradiation under stirring. At given time intervals, 4 mL of the suspension was pipetted into a 5 mL centrifuge tube and centrifuged at 8000 rpm for 2 min to remove the remnant photocatalyst. The concentrations of the RhB were monitored by checking the absorbance at 553 nm using a UV-2450 (Shimadzu) spectrophotometer. In the recycle experiments, after $Bi_2WO_6–Fe_3O_4$ composites were separated from solution by an external magnetic field, they were washed with ethanol and deionized water before being re-dispersed in the dye solution (100 mL, $10^{-5}\ mol\ L^{-1}$) for another cycle.