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Research Paper

Magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions with wide-spectrum response and magnetic separation

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ABSTRACT

The solar-light-harvesting and separation of nanostructured photocatalysts in slurry systems are key issues in fields of photocatalysis. Herein, magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions (M-Fe_2O_3/b-TiO_2) are fabricated through wet-impregnation and surface hydrogenation strategy, which show wide-spectrum response and magnetic separation. The decreased specific surfaces, pore sizes and pore volumes from ~80 to 67 $m^2 g^{-1}$, ~12 to 10.3 nm, and ~0.20 to 0.16 $cm^3 g^{-1}$, respectively, all confirm the efficient loading of magnetic Fe_2O_3. The M-Fe_2O_3/b-TiO_2 with narrow bandgap of ~2.41 eV extends the photoresponse from UV to near infrared region and exhibits excellent solar-driven photocatalytic degradation performance and long-term stability for complete mineralization methyl orange and high-toxic herbicide metribuzin. The photocatalytic reaction apparent rate constant k for metribuzin is ~ 9 times higher than that of pristine TiO_2 under AM 1.5 irradiation. Especially for single-wavelength of 950 nm, the degradation ratio is up to 4%. The enhancement is attributed to Ti^{3+} and magnetic Fe_2O_3 with narrow bandgap facilitating solar-light-harvesting, the hollow structure benefiting mass transport, and the heterojunctions favoring the spatial separation of photogenerated electron-hole pairs. The magnetic separation is conducive to recycle of photocatalysts, which favors practical applications in environment.

1. Introduction

With the fast development of the textile industry, lots of industrial sewage spread poisonous chemicals into soil and water resources [1–3]. The pollution of water with agrochemical can pose a significant destruction to aquatic ecosystems and drinking water resources [4–7]. What is worse, the triazine compounds have been the most widely used pesticides in recent decades, which bring about insurmountable environmental problems [8,9]. The photocatalytic oxidation, as one of the green technologies that have advantages of high-efficiency, non-selective oxidation, and low-cost, has been recognized as an important and effective candidate to remove the toxic and harmful contaminants in aqueous environment [10–14]. Titanium dioxide (TiO_2) is one of the most important photocatalysts due to its cheapness, excellent physical and chemical stability and high efficiency [15,16]. However, the large bandgap (~3.2 eV) for anatase TiO_2 limits its utilization ratio of solar energy [17,18]. Although some approaches including metal and non-metal doping were used for narrowing the bandgap of TiO_2, the visible-light-driven photocatalytic performance and long-term stability are unsatisfactory [19,20]. Fortunately, Chen and coworkers discovered black TiO_2 nanomaterials via surface hydrogenation strategy recently, which narrowed the bandgap and extended the photoresponse from ultraviolet to visible light and/or near infrared region [21]. The excellent solar-driven photocatalytic performance represented a breakthrough for wide-spectrum response TiO_2 materials. Since then, numerous efforts have been made to synthesize various black TiO_2 nanomaterials and the visible-light-driven photocatalytic performance is indeed improved obviously [22,23].

So far, the separation of nanostructured photocatalysts in slurry systems is a difficult subject which needs to be solved urgently. Although some approaches, such as centrifugation, sedimentation and vacuum filtration, have been adopted, the separation effectiveness of photocatalysts is not satisfactory [24,25]. Magnetic separation may be a good choice for their separation, because the magnetic photocatalysts can be separated easily when the applied magnetic field appears. Of various magnetic materials, magnetic ferric oxide (Fe_2O_3) has drawn the most attention due to its earth-abundant, low-cost, excellent ferromagnetism, narrow bandgap and high chemical and physical stability [26,27]. The narrowed bandgap of ~2.24 eV could extend the photoresponse to visible light region [28]. Therefore, magnetic Fe_2O_3 is a

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good candidate for efficient absorption of long-wavelength light and magnetic separation. Some strategies have been taken for synthesizing magnetic Fe_2O_3/TiO_2 composites, which represented excellent separation effect [29–31]. However, the low quantum efficiency for traditional TiO_2 material is still beyond the requirement for practical applications. Mesoporous black TiO_2 hollow spheres would be ideal candidates for further improving the solar-driven photocatalytic performance because the unique hollow structures are beneficial for efficient light utilization and offering good hosts to load magnetic Fe_2O_3. Therefore, to fabricate magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions will satisfy the requirement of both wide-spectrum response and magnetic separation simultaneously.

Herein, we demonstrate a facile wet-impregnation and surface hydrogenation route to synthesize magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions. The resultant heterojunctions are considered as photocatalysts with wide-spectrum response and magnetic separation, which exhibit excellent solar-driven photocatalytic performance and long-term stability for complete mineralization methyl orange and metribuzin. The novel magnetic heterojunctions photocatalysts will have widespread practical applications in environmental fields.

2. Experimental section

2.1. Chemicals

N,*N*-dimethylformamide (DMF), ethanol (EtOH), ethylenediamine, ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), methanol and potassium hydroxide (KOH) were of analytical grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Tetrabutyltitanate (TBOT), hydroxylammonium chloride, sulfanilic acid, 1-naphthylamine and anhydrous oxalic acid were purchased from Aladdin Industrial Inc. All chemicals were used as received without further purification. Deionized water was used for all experiments.

2.2. Synthesis of magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions

The synthesis of mesoporous black TiO_2 hollow spheres was according to literature [32]. The preparation of magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions was through wet-impregnation and surface hydrogenation route. Typically, different amounts of $Fe(NO_3)_3{\cdot}9H_2O$and 100 mg of TiO_2 hollow spheres were mixed evenly in 30 mL ethanol to form a mixed solution. The mixture was stirred for 6 h at room temperature and then dried at 60 °C in oven overnight. Finally, the samples were calcined at 400 °C for 5 h in Air, with a temperature ramping rate of 5 °C min^{-1}. Before being calcined in a H_2 flow at 200 °C for 3 h under normal pressure conditions with a constant heating rate of 10 °C min^{-1}, the samples were deaerated under an inert gas flow (N_2) for 0.5 h. The resultant materials were denoted as M-Fe_2O_3/b-TiO_2. The loading amounts of Fe_2O_3were testified to be 9, 13, 16, 19 and 24%, respectively, according to Inductively Coupled Plasma (Optima 8300 (PerkinElmer, USA) ICP-OES). To provide a comparison with the M-Fe_2O_3/b-TiO_2 sample, magnetic Fe_2O_3/mesoporous black TiO_2 hollow sphere heterojunctions was also synthesized under the same conditions without the H_2 calcined (denoted as M-Fe_2O_3/TiO_2).

2.3. Characterization

X-ray diffraction (XRD) patterns was performed on a Bruker D8 Advance diffractometer by using Cu Kα radiation (λ = 1.5406 Å, 40 kV, 40 mA). Raman measurements were obtained with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The laser beam was focused with a 50 objective lens to a ca. 1 μm spot on the surface of the sample. Scanning electron microscopy (SEM) using a Hitachi S-4800 instrument operated at 15 kV. The transmission electron microscopy (TEM) experiments were obtained on a JEOL JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as sample holders. X-ray photoelectron spectroscopy (XPS, Kratos, ULTRA AXIS DLD) was recorded to study the surface states with monochrome Al Kα (1486.6 eV) radiation. All binding energies were calibrated by referencing to C 1speak at 284.6 eV. UV/vis adsorption spectra were conducted on a UV/vis spectrophotometer (Lambda 950 (PerkinElmer, USA)) in the range of 200–1800 nm, with fine $BaSO_4$ powders as reference. The bandgaps were estimated by extrapolating a linear part of the plots to $(\alpha h\nu)^2$ = 0.Nitrogenadsorption-desorption isotherms at 77 K were collected on anAUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. All samples were degassed under vacuum at 180 °C for at least 8 h before measurement. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area. Pore-size distribution was measured from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherms. The magnetic hysteresis loops were made by a LakeShore 7404 (USA) vibrating sample magnetometer (VSM).

2.4. Photocatalytic activity

Photocatalytic test was evaluated by the photocatalytic decomposition of methyl orange (MO) and metribuzin ($C_8H_{14}N_4OS$) under AM 1.5 irradiation. The light intensity was calibrated to 100 mW cm^{-2} before measurement. In a typical experiment, the photocatalyst (50 mg) was added to 100 mL metribuzin solution (10 mg L^{-1}) or MO solution (10 mg L^{-1}). The suspension was irradiated with a 300 W Xe lamp equipped with an AM 1.5 filter. To confirm the stability of the photocatalysts, we recycled the catalysts after experiments by deionized water and ethanol cleaning several times, and then drying at 60 °C for 6 h to remove the residual reactants and reactivate the adsorption and catalytic performance. The residual MO and metribuzin concentration was analyzed by total organic carbon (TOC, TOC-VCPN (SHIMADZU) analyser). The single wavelength efficiency was performed using metribuzin solution (0.1 mg L^{-1}). Before irradiation, the suspensions were magnetically stirred in the dark for 20 min to establish adsorption/desorption equilibrium between the organic and the surface of the catalyst at room temperature. The single-wavelength efficiency was irradiated with a 300 W Xe lamp with a bandpass filter (365, 420, 520 and 950 nm) system.

2.5. Photoelectrochemical measurement

Photoelectrochemical properties were investigated using a Princeton Versa STAT 3 in a standard three electrode configurations with M-Fe_2O_3/b-TiO_2 and TiO_2 materials used as photoanodes, Pt foil as the counter electrode, an Ag/AgCl reference electrode in home-built crystal equipment containing 1 M KOH solution. The KOH solution was purged with N_2 and used as the electrolyte. The photoanodes were prepared by an easy spray coating method, using a glass-rod to roll a paste containing 30 mg of powders and 2 mL of EtOH on a transparent FTO glass-substrate with an effective diaphragm area 1 cm^2 (TCO, fluorine doped SnO_2 layer, 20 Ω/square, Nippon sheet glass, Japan), followed by calcining 120 min at 400 °C under a N_2 atmosphere with a constant heating rate of 5 °C min^{-1}. An AM 1.5 power system (Oriel, USA) was used as the light irradiation source.

3. Results and discussion

3.1. Crystal structure and morphology ofM-Fe_2O_3/b-TiO_2 heterojunctions

After surface hydrogenation, the X-ray diffraction (XRD) patterns of both M-Fe_2O_3/TiO_2 and M-Fe_2O_3/b-TiO_2 heterojunctions (Fig. 1A) show five obvious crystal peaks at 2θ = 25.2–55.2°, which could be