Applied Catalysis B: Environmental 180 (2016) 219–226

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Enhanced visible-light activities of porous $BiFeO_3$ by coupling with nanocrystalline TiO_2 and mechanism

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ARTICLE INFO

Article history:
Received 21 March 2015
Received in revised form 30 May 2015
Accepted 19 June 2015
Available online 23 June 2015

Keywords:
Porous $BiFeO_3$
Coupling TiO_2
Charge transfer and separation
Visible photocatalysis
Pollutant degradation

ABSTRACT

In this work, different mole ratio percentage of nanocrystalline anatase TiO_2/porous nanosized $BiFeO_3$ (T/P-BFO) nanocomposites with effective contacts have been fabricated by putting the as-prepared P-BFO into the TiO_2 sol, followed by drying at 80 °C and then calcining at 450 °C for 2 h. The photoactivities of the obtained products for pollutant degradation and H_2 evolution were measured. It is clearly demonstrated by means of the steady-state surface photo-voltage spectra, the transient-state surface photovoltage responses, and the photoluminescence spectra that the photogenerated charge carriers in the T/P-BFO nanocomposites with a proper mole ratio percentage of TiO_2 (9%) display much long lifetime and high separation in comparison to the resulting P-BFO alone. This is well responsible for the enhanced activities for degrading gas-phase acetyldehyde, the liquid-phase phenol, and for producing H_2 under visible-light irradiation. Based on the measurements of formed hydroxyl radical amount and photoelectrochemical behavior, it is suggested that the improved separation of photogenerated charges in the fabricated T/P-BFO nanocomposite is mainly attributed to the spatial transfer of visible-light-excited ($\lambda \leq 500$ nm) high-energy electrons of P-BFO to TiO_2. This work will provide a feasible route to enhance the photoactivities of visible-light responsive oxide composites as photocatalysts for efficient solar energy utilization.

1. Introduction

To effectively address the consumption of fossil fuels, severe energy crises and serious environmental issues, modern society has been searching for renewable, low cost, and clean form of energy which will be used as an alternative source to fossil fuels. In this regard, photocatalytic degradation of pollutants and photocatalytic water splitting using solar energy to generate hydrogen offer a clean and environmentally friendly process [1]. Multiferroic materials have recently been used for applications in both photocatalysis and photovoltaics due to their narrow energy band gaps and ferroelectric properties, which allow them to absorb majority of the light in visible region. As a potential candidate for both pollutants degradation and water splitting, $BiFeO_3$ has attracted greater attention. Due to its high chemical stability, narrow band gap (2.0–2.7 eV), ferroelectric and ferromagnetic properties, BFO has been regarded as one of the third-generation visible-light responsive photocatalyst [2–5]. The ferroelectric properties of BFO with spontaneous polarization lead to the band bending that transports the photoinduced charge carriers (electrons and holes) in opposite directions, which enhances the reactivity and separation efficiency of the photo-generated charges [6]. However, the photocatalytic efficiency of BFO is still limited due to its low conduction band position compared to the hydrogen (or O_2) reduction level [7], and usually small surface areas for catalytic reactions.

To overcome these shortfalls and to improve the photocatalytic performance of BFO, elemental doping, fabricating with semiconductor metal oxides and synthesis of porous perovskite oxides with larger surface area are highly desirable [8–11]. As we know that, catalysis belongs to the class of surface reaction and there should be a good contact between the catalyst's surface and the substrates [12]. Moreover, the nanoparticles having no pores, the reaction takes place only on the external surface, limiting the catalytic performance of the material. To overcome this, the use of porous nanomaterials would be helpful, since porous material would absorb the reactants both on the surface and inside the pores, improving the contact area and hence the catalytic performances [13–15].

In addition, to improve the photocatalytic performance of BFO and to prolong the lifetime of the photogenerated charges and

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http://dx.doi.org/10.1016/j.apcatb.2015.06.035
0926-3373/

hence promote its separation, the construction of heterojunctional nanocomposites are widely used [16]. Zhang et al. [7] have fabricated BFO with TiO_2 by a pulsed laser deposition method. They investigated that titania can be made photochemically active under visible light with a wavelength of 460 nm by supporting on BFO substrate. Yang et al. [17] have fabricated one dimensional TiO_2 and BFO nanofibres by an electrospinning technique. They investigated that BFO/T nanocomposites exhibit high photocatalytic activity for degrading methylene blue under visible light irradiation, due to the excellent charge separation properties of the heterojunction formed between BFO and TiO_2. Further, the BFO/T nanofibres could be easily recycled without decrease in the photocatalytic performance due to large length to diameter ratio of the nanofibres. Recently Zhu and his co-workers [18] have fabricated BFO/TiO_2-NTs covered Ti electrode by ultrasonic immersion method. They demonstrated that under visible light irradiation, the BFO/TiO_2-NTs composites (grown on Ti sheet) exhibit significant photo-conversion efficiency than the unmodified TiO_2-NTs/Ti electrodes. This visible light enhanced photoelectrocatalytic efficiency for degrading rhodamine B is mainly attributed to the prolonged lifetime of the photogenerated charges via the applied bias and wider spectral response promoted by BFO. Thus, it is acceptable that the visible-light photoactivity of TiO_2 would be enhanced by coupling with a certain amount of BFO.

To the best of our knowledge, there is no previous report on the fabrication of nanocrystalline TiO_2-coupled porous BFO as efficient photocatalysts. In general case, due to the low CB position of P-BFO than TiO_2, the photogenerated electrons cannot be transferred to the CB of TiO_2. However, when a heterojunction is formed between TiO_2 and P-BFO, their Fermi levels tend to descend and rise up, respectively, since the Fermi level of TiO_2 is more negative than that of P-BFO. At the same time, an electric field is formed at the interface of the heterojunction nanocomposites. At equilibrium, the TiO_2 junction face becomes more positive than that of P-BFO. Thus, the visible-light excited electrons, especially for produced high-level ones, could transfer thermodynamically from the CB of BFO to TiO_2. It is worthy of noting, that it has been primarily demonstrated in our group that the visible-light photoactivities of Fe_2O_3 and $BiVO_4$ could be greatly improved after coupling with a proper amount of nanocrystalline TiO_2 [16,19]. Hence, it is feasible to couple TiO_2 with P-BFO for effective solar energy utilization.

Herein, P-BFO and T/P-BFO nanocomposites have been successfully prepared. It is demonstrated that the lifetime of photogenerated charge carriers of P-BFO could be prolonged by approximately millisecond timescales after a proper mole ratio percentage (9%) of TiO_2 is coupled, corresponding to the promoted charge separation. This promoted charge separation is responsible for the visible-light enhanced photocatalytic activities for pollutant degradation and water reduction. Moreover, it is suggested for the first time that the prolonged life-time and promoted separation of photogenerated charges in the fabricated T/P-BFO nanocomposites are attributed to the unusual spatial transfer of visible-light-excited ($\lambda \leq 500$ nm) high-energy electrons of P-BFO to TiO_2. This work will provide a feasible route to synthesize BFO-based nanophotocatalysts for efficient solar energy utilization, which is also applicable to other visible-light-responsive semiconducting composite nanomaterials.

2. Experimental

2.1. Chemicals and reagents

All the reagents were of analytical grade and used as-received without further purification. Deionized water was used throughout the reaction.

2.2. Synthesis of photocatalyst

2.2.1. Synthesis of P-BFO

Nanocrystalline P-BFO was synthesized by taking equimolar (0.04 M) amounts of $Bi(NO_3)_3{\cdot}5H_2O$ (19.4 g) and $Fe(NO_3)_3{\cdot}9H_2O$ (16.16 g) and dissolved in a beaker containing (30–50 vol%) of ethylene glycol and methanol. Then PS colloidal crystals were soaked in the metal precursor solution for 2 h. The solution was kept under stirring for 3 h. After that the solution was heated in a convection oven at 150 °C, until all the liquids were evaporated. To remove PS spheres, the obtained brown powder was calcined at 400 °C at a temp ramp of 1 °C/min. The powder was then calcined at 600 °C for 2 h at temp ramp of 5 °C/min to obtain nanocrystalline P-BFO.

2.2.2. Synthesis of T/P-BFO

To fabricate various samples of T/P-BFO nanocomposite powders, for each sample 2 g freshly prepared P-BFO was taken and dissolved into a mixed solution containing 10 mL water, 40 mL anhydrous ethanol, and 2 mL HNO_3 (68%), under stirring at room temperature. Then as-prepared solutions were ultrasonically treated for 1 h followed by vigorous magnetic stirring for 2 h. After that, 1:9 by volume of $Ti(OBu)_4$ solution was prepared by taking 10 mL of $Ti(OBu)_4$ and dissolved in 90 mL of anhydrous ethanol. The solution was then kept under continuous magnetic stirring for 1 h. From this stock solution, various molar ratio (i.e 3 mL, 6 mL, 9 mL and 12 mL) was added to the as-weighted (2 g) of the P-BFO samples and the mixture was stirred for 6 h. The reaction mixture was then dried in a convection oven at 85 °C, and finally calcined at 450 °C in air for 2 h. Different mole ratios of T/P-BFO nanocomposites were obtained. The nanocomposites were denoted by XT/P-BFO; in which *X* represent the mole ratio percentage of Ti to P-BFO.

2.3. Characterization

The materials were characterized by using various techniques. The crystal structures of the samples were determined with the help of XRD (Rigaku D/MAX-rA powder diffractometer, Japan), using Cu Kα radiation (α = 0.15418 nm), at an accelerating voltage of 30 kV, and emission current of 20 mA was employed. Transmission electron microscope (TEM) JEOL JEM-2010 at an accelerating voltage of 200 kV was used to record the electron micrographs of the samples. FT-IR spectra of the samples were collected with a Bruker Equinox 55 spectrometer, using KBr as diluents. The UV–vis diffuse reflection spectra (UV–vis DRS) of the samples were recorded with Shimadzu UV-2550 Spectrophotometer, using $BaSO_4$ as a reference. The N_2 adsorption–desorption isotherm of various samples were carried out by Micromeritics ASAP 2020 M system at the temperature of liquid nitrogen, while keeping the system out-gassed for 10 h at 300 °C prior to measurements. ST-2000 constant volume adsorption apparatus was used for the evaluation of BET surface area. The atmosphere-controlled SS-SPS measurement for samples was carried out with a home-built apparatus, equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). The powder sample was sandwiched between two indium tin oxide (ITO) glass electrodes, which were arranged in an atmosphere-controlled container with a quartz window, and a monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF XQ500W, Global xenon lamp power) through a double prism monochromator (SBP300). TS-SPV measurements for samples was collected by the process that the sample chamber connected an ITO glass as top electrode and a steel substrate as bottom electrode, and a 10 μ m thick mica spacer was placed between the ITO glass and the sample to decrease the space charge region at the ITO-sample interface. The samples were excited by a radiation pulse of 532 nm with 10 ns width from the second harmonic of a neodymium-doped