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Visible-light-induced Fe-doped $BiVO_4$ photocatalyst for contaminated water treatment

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ABSTRACT

A monoclinic–tetragonal heterostructured $BiVO_4$ photocatalyst doped with varying quantities of Fe was synthesized by a microwave–hydrothermal method and employed in the photodegradation of ibuprofen and inactivation of *Escherichia coli* under irradiation with visible light. An improvement in the photocatalytic activity for the Fe-doped $BiVO_4$ was confirmed relative to that determined for the undoped $BiVO_4$. The in-gap state formed between the valence band and conduction band of $BiVO_4$ as a result of doping, as established by first principles DFT calculations, facilitates an easy transition of electrons from the valence band to the conduction band. This transition enhances the tendency of electron–hole separation and improves the visible light absorption capacity, thereby improving the photocatalytic activity. Among the various concentrations of Fe dopant examined, the highest visible light photoactivity is demonstrated for the 1 wt% Fe-doped $BiVO_4$ photocatalyst, which degrades 80% of ibuprofen within 180 min and inactivates 90% of *Escherichia coli* within 5 h. No decrease in the efficiency of the 1 wt% Fe-doped $BiVO_4$ photocatalyst was observed during the degradation of ibuprofen over three consecutive cycles, thereby demonstrating the stability of the semiconductor towards photocorrosion. Possible mechanisms for both the enhanced photocatalytic activity and the degradation of ibuprofen are proposed on the basis of the experimental observations.

1. Introduction

Clean water is essential for the sustenance of all living organisms. The rapid progress of industrialization and surge in population growth has resulted in a tremendous increase in the rate of water quality deterioration [1,2]. Water pollutants such as effluents from pharmaceutical industries can often pose a significant risk to both living organisms and ecosystems. Similarly, the direct discharge of sewage and animal waste into water sources is the main pathway through which *Escherichia coli (E. coli)* can reach water resources, causing serious hemorrhagic diarrhea and potentially even long-term or fatal complications in humans [3]. Removal of these pollutants and pathogens from contaminated water is a pressing matter in order to prevent potential negative effects on both human health and the environment [4,5]. Different techniques such as chlorination, ozonation, ultraviolet (UV)-irradiation treatment, and advanced filtration processes have been in practice for wastewater treatment [6]. These conventional methods suffer from drawbacks such as the formation of hazardous byproducts [7], and, therefore, researchers are now searching for alternative green technologies in order to solve the abovementioned problem. One such plausible technology involves the use of photocatalytic semiconductors based on the advanced oxidation process (AOP), capable of utilizing renewable solar energy to activate chemical reactions, which has already been applied intensively in this field [4,8].

Following the discovery of photocatalytic splitting of water on the TiO_2 electrode by Honda and Fujishima in 1972, a significant effort was devoted to the development of TiO_2 as an efficient material. Since then, TiO_2 has been applied with varied success to a number of processes, including hydrogen production, effluent detoxification and disinfection, and organic synthesis [9–11]. The relatively high quantum yield and high stability of TiO_2 towards

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photocorrosion are the key reasons for the prevalent use of this semiconductor, which has essentially become a synonym for a photocatalyst. However, the moderate photocatalytic reaction rates and a mismatch between the energy band gap and the sunlight spectra in the UV range, as a consequence of which this catalyst can utilize less than 5% of the solar energy impinging on the Earth's surface, limit its applications as a potential and sustainable photocatalyst. Therefore, significant efforts have been devoted in the last few years to the search for new materials that can overcome the limitations of TiO_2 [12,13].

Among the various potential photocatalysts, Bi-based materials, and $BiVO_4$ in particular, have been recognized as efficient visible light responsive photocatalysts as a result of their attractive properties such as a narrow band gap (2.4 eV), visible light responsiveness, n-type character, non-toxic nature, high stability towards photocorrosion, cost-effectiveness, relatively strong oxidation properties for decomposition of organic pollutants, and their promising application as photoanode materials for water splitting [14–16]. Three crystalline phases of synthetic $BiVO_4$ are known: (i) the tetragonal zircon structure and the (ii) monoclinic and (iii) tetragonal scheelite structures [17]. Among these, the monoclinic scheelite phase (m-$BiVO_4$) has been identified as catalytically the most active pristine $BiVO_4$ species under visible light irradiation. This activity can be attributed to the fact that m-$BiVO_4$ has a more asymmetric local environment around each Bi^{3+} ion than t-$BiVO_4$ [18]. Nonetheless, as a result of the facile electron–hole recombination, slow carrier transport, and slow water oxidation kinetics, the photocatalytic activity of the single component $BiVO_4$ is not suitable for practical application yet and requires further optimization [19]. To date, many strategies have been investigated in order to overcome these limitations, including cocatalyst loading, construction of heterostructures, and substitution of the metal cation/anion [20–23].

In this work, we have prepared a Fe-doped $BiVO_4$ semiconductor using a simple microwave–hydrothermal procedure. The effect of Fe doping on the photocatalytic degradation of ibuprofen (IBP) and inactivation of *E. coli* are studied under visible light irradiation. The possible mechanism of IBP degradation and the rationale for the improved catalytic activity of the Fe-doped $BiVO_4$ system are discussed.

2. Experimental

2.1. Sample preparation

$Bi(NO_3)_3.5H_2O$ (purity 99%) and NH_4VO_3 (purity 99%) were received from Sigma Aldrich. Typically, 5 mmol of $Bi(NO_3)_3.5H_2O$ was dissolved in 20 mL of 4 M HNO_3 (Daejung Chemical) to give solution A. In another beaker, 5 mmol of NH_4VO_3 was dissolved in 20 mL 4 M NaOH (purity 98%) obtained from Samchun Chemical, producing solution B. The solutions were stirred for 30 min in order to ensure the complete dissolution of the chemicals. Solution B was slowly poured into solution A under constant stirring. A specific amount of $Fe(NO_3)_3.9H_2O$ (purity 99%) obtained from Acros Organics was added to the mixture to give solutions with 0.5 wt%, 1.0 wt%, 1.5 wt%, and 3.0 wt% of Fe. The pH of these mixtures was adjusted to 8 using NaOH. Each mixture was stirred for 30 min and transferred into a Teflon-lined vessel for the microwave treatment. In each case, the mixture was heated at 180 °C for 3 h and the resulting yellow precipitate was washed with distilled water and ethanol several times, and dried overnight at 80 °C. The dried samples were calcined at 200 °C for 2 h. A similar procedure was used in the preparation of undoped $BiVO_4$. The composition and the corresponding abbreviation of all samples are listed in Table 1.

2.2. Characterization and measurements

The morphology and particle size of the prepared samples were characterized by scanning electron microscopy (SEM, nano-eye, SNE 2000 M). The elemental composition and distribution of the elements in the samples were examined by energy-dispersive X-ray spectroscopy (EDX, Oxford instruments, X-max^N 50) and field emission scanning electron microscopy (FE-SEM, JSM-6700F). The Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained from the nitrogen adsorption-desorption method using micrometrics, ASAP 2020 automatic analyzer at 77 K. The actual doping concentration of Fe in the sample was determined by ICP-MS analysis (Perkin Elmer Sciex Elan 6100 ICP-MS system). The crystallinity and the phase purity of all samples were determined by powder X-ray diffraction (XRD) using an X-ray diffractometer with Cu Kα (λ = 0.15406 nm) (Rigaku, D/max. 2200HR). UV–vis diffuse reflectance spectra (UV–Vis/DRS) were recorded on a UV–Vis-NIR spectrophotometer (JASCO-V 570). Raman spectra were recorded on a Raman spectrometer (Horiba, LabRam, HR 800) at an excitation wavelength of 532.15 nm. FT-IR spectra were collected using a Vertex-70 infrared spectrometer. In order to understand the electronic environment and the chemical composition of the prepared samples, X-ray photoelectron (XPS) spectra were recorded on a MultiLab 2000 system with an Al Kα source at 15 kV and 200 W. The photocatalytic performances of the synthesized samples were evaluated by examining the degradation of 20 mgL^{-1} solutions of ibuprofen (IBP) and the deactivation of *E. coli* under visible light irradiation. The light source was obtained from a solar simulator using 150 W short arc lamp with a 420 nm UV cut-off filter (portable solar simulator, PEC-L01, Peccell, Am 1.5G). A UV–vis spectrometer (Mega-2100) was used to record the absorbance of IBP at various time intervals.

2.3. Photocatalytic activity tests

2.3.1. Ibuprofen degradation test

In a typical photodegradation experiment, 0.1 g of the photocatalyst powder was placed in a quartz photoreactor and 70 mL of an aqueous solution of IBP (20 mgL^{-1}) was added. Prior to irradiation, each suspension was stirred magnetically in the dark for 30 min in order to establish absorption-desorption equilibrium between the dye and the surface of the catalyst under normal atmospheric conditions. A 150 W short arc lamp with a 420 nm UV cut-off filter was used as a visible light source for the photocatalysis. The incident light intensity on the sample during the experiment is 150 $mWcm^{-2}$ and the total energy per second (power) received by the sample is 20 W. At selected time intervals, aliquots of the mixed solution were collected for analysis and centrifuged to remove the catalyst particulates. The residual IBP concentration was measured using a UV–vis spectrophotometer. The degradation pathway was finally monitored by HPLC followed by HR/MS measurement. Details of the HPLC and HR/MS measurement has been provided in the materials and methods (Supplementary Information, S3).

2.3.2. E. coli *inactivation test*

Escherichia coli DH5α (New England Biolabs® Inc., USA) was used for the bacterial inhibition assays. The cells were grown in 50 mL of Luria-Bertuni (LB) broth medium at 37 °C overnight, with agitation at 220 rpm. The cells were centrifuged and washed with phosphate buffer saline (PBS, pH 7.2). The washed cells were resuspended in the same PBS buffer in such a way that the final optical density (OD) of the cells measured at 600 nm using a spectrophotometer (Optizen, Mecasys Co., Ltd., South Korea) was approximately 1.0. The cells (10 mL) were placed in several 25 mL screw-cap sterile glass tubes. 200 μg/mL (final concentration) of the photocatalytic powder was added to these cell suspensions. The photocatalytic