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Full Length Article

Enhancement mechanism of fiddlehead-shaped TiO_2-$BiVO_4$ type II heterojunction in SPEC towards RhB degradation and detoxification

Yaqi Wang[a,1], Nan Lu[a,1], Min Luo[a], Lingyun Fan[a], Kun Zhao[b], Jiao Qu[a], Jiunian Guan[a,*], Xing Yuan[a,*]

[a] School of Environment, Northeast Normal University, Changchun 130117, PR China
[b] School of Environmental Science & Technology, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

Type II heterojunction TiO_2-$BiVO_4$ composite films were designed via modified sol-gel-hydrothermal method for solar photoelectrocatalysis (SPEC) to restrain the recombination of electrons and holes as well as expand light absorption range. Fiddlehead-shaped morphology resulted in a larger specific surface area (157.63 $m^2 \cdot g^{-1}$) and an intensification of light-harvesting efficiency. In comparison with photocatalytic (PC) system (79.3%), the degradation efficiency of RhB increased significantly to 93.9% in SPEC system. The enhancement mechanism and degradation path of SPEC systems was further discussed based on energy band adjustment, main active group determination, and quantum chemical calculation. Furthermore, the acute ecotoxicity of RhB and its degradation products were tested by *Vibrio fischeri*. The ecotoxicity was almost completely eliminated in SPEC system but it increased in PC system. The nanocomposite film also represented an excellent recyclability and stability, which may greatly reduce the economic cost and limit the probability of secondary pollution. Therefore, TiO_2-$BiVO_4$ nanocomposite films exhibited great potential in SPEC, providing a sustainable and harmless technique to treat organic wastewater.

1. Introduction

Compared with photocatalysis (PC), photoelectrocatalysis (PEC) method has emerged to eliminate a broad-range of organic contaminants from wastewaters with an enhanced removal capability by adding an external bias potential onto the electrodes loaded by catalysts [1–3]. Recently, solar photoelectrocatalysis (SPEC) has been developed as a novel field in PEC which not only promotes the charges transferring but also utilizes free green energy source of sunlight [4,5]. Various semiconductors have been applied as the driving catalysts in PEC system, among which n-type semiconductor TiO_2 is preferable to the others because of its unique physiochemical, optical and electrical properties [6,7]. However, TiO_2's inherent drawbacks, i.e. poor visible light utilization efficiency and recombination of the electrons and holes limit its application in PEC, especially in SPEC.

N-type semiconductor bismuth vanadate ($BiVO_4$) is characterized by narrow band gap (~2.4 eV) with a broad light absorbance range (to 520 nm) [8]. Moreover, the largely dispersed valence band of monoclinic $BiVO_4$ facilitates mobility of the photogenerated holes [9,10] and n-n junction could promote the separation of the photo-generated charges [11]. Thus, the TiO_2 materials modified by $BiVO_4$ may provide an efficient approach to extend spectral response to visible light and improve quantum efficiency by the heterojunction between TiO_2 and $BiVO_4$ [12,13]. However, it should be noted that type I alignment between TiO_2 and $BiVO_4$ band edges defects the lattice matching degrees, which exerts an adverse influence on degrading organic pollutants [14,15]. Thus, TiO_2-$BiVO_4$ with an excellent heterojunction type may possess a considerable prospect in SPEC treatment, whereas the enhancement mechanism is needed to investigate in depth [16].

The activity of catalysts is strongly related to its morphology, such as shape, particle size distribution, and pore structure type [17–19]. In the current study, fiddlehead-shaped TiO_2-$BiVO_4$ nanocomposite films were attained by a modified sol-gel-hydrothermal method, which promoted light utilization due to the bionic effect i.e. the plants expose themselves to the sunlight as far as possible through the stretched leaves. The special three-dimensional structure resulted in a larger specific surface area (157.63 $m^2 \cdot g^{-1}$) in comparison with commercial TiO_2 P25 (*ca.* 50 $m^2 \cdot g^{-1}$) and $BiVO_4$ (< 10 $m^2 \cdot g^{-1}$) [20,21]. In TiO_2-$BiVO_4$ nanocomposite, pore structures constituted by microporous and mesoporous (2–30 nm) made more active sites exposed to the

* Corresponding authors.
E-mail addresses: guanjn461@nenu.edu.cn (J. Guan), yuanx@nenu.edu.cn (X. Yuan).
[1] These authors contributed equally.

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surrounding media, which may facilitate efficient transportations of reactants and products.

Currently, treatment efficiency generally relies on concentration determination of organic pollutants, nevertheless, they cannot be completely mineralized to CO_2 and H_2O by most treatment techniques but generate certain intermediates that may be more toxic. It is still a challenge to identify the intermediate products in PC/PEC system based on current analysis methods. Aquatic toxicity evaluation provides an efficient way to assess the adverse effects of chemicals on aquatic organisms without determination of its composition and properties. *Vibrio fischeri* is commonly applied to evaluate the toxicity variation with quick response time [22]. Furthermore, as a breakthrough, quantum chemical calculation [23,24] was employed to explore the intermediates as well as their toxicity in the current PC and PEC system [25].

The fiddlehead-shaped TiO_2-$BiVO_4$ type II heterojunction nanocomposite films with broad absorbance spectrum were designed and synthesized controllably via the modified sol-gel-hydrothermal method for SPEC. The chemical composition, optical properties, pore structure, morphology, and heterojunction of as-prepared materials were well-characterized. The performances of TiO_2-$BiVO_4$ nanocomposite films in PC and SPEC system were evaluated and compared by degradation experiments and toxicity tests towards RhB. The enhancement mechanism and degradation path towards RhB in SPEC system was revealed based on energy band adjustment, active group determination and quantum chemical calculation. Recyclability and stability of the nanocomposite films were also tested for the practical application.

2. Experimental

2.1. Reagents

Titanium tetraisopropoxide (TTIP, 98%) was purchased from Sigma-Aldrich Corporation. Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, AR), nitric acid (HNO_3, AR), ammonium vanadate (NH_4VO_3, AR), sodium hydroxide (NaOH, AR), isopropanol ($CH_3CHOHCH_3$, AR), glacial acetic acid (CH_3COOH, AR), ethanol (CH_3CH_2OH, AR), and Rhodamine B (RhB, AR) were purchased from China Pharmaceutical Group. Double distilled water (ddH_2O) was utilized throughout the experimental procedures.

2.2. Catalyst preparation

Solution A: 2 ml TTIP was added into 6 ml isopropanol and stirred at room temperature for 1 h; Solution B: certain amount (mass percent: 1%, 5% and 20%) of self-prepared $BiVO_4$ (specific preparation method is provided in Supporting Information), 1.6 ml $CH_3CHOHCH_3$, and ddH_2O were mixed and ultrasonically dispersed for 30 min. Solution B was dropwise added into solution A and kept stirring to appear a transparent sol. 0.5 ml CH_3COOH was added to inhibit the hydrolysis and avoid the agglomeration during sol-gel preparation process. The resulting colloid was transferred into a Teflon-lined autoclave, heated to 473 K with a rate of 2 $K \cdot min^{-1}$ and then kept constantly for 2 h. The hydrogel was transferred into a beaker and deposited onto conductive quartz glasses (50 mm × 15 mm × 1 mm) by spin-coating, solution was dripped at 500 rpm for 6s, while spin-coating was performed at 2000 rpm for 30 s. The composite film was aged at 293 K for 24 h. For comparison, pure TiO_2 film was prepared by the same method.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.08.239.

2.3. Catalyst characterization

The composition and structure of as-prepared catalysts were determined by Electron Spectrum (a XL30ESEM-FEG instrument), Fourier Transform Infrared Spectroscopy (a Nicolet Magna 560 IR spectrophotometer) and X-ray Photoelectron Spectroscopy (an Escalab 250 XPS instrument) analysis. Nitrogen adsorption/desorption isotherms were measured using a Leeman-Prodigy system, Brunauere Emmette Teller (BET) method was applied to calculate the specific surface area and pore diameter of the catalysts. The morphological properties were analyzed by Field-emission Scanning Electron Microscopy (FESEM, XL30ESEM-FEG). UV–vis Absorbance Spectra were obtained by a Cary 500 UV–vis-NIR spectrophotometer. Crystalline structures were characterized by a Rigaku D/max-2500 X-ray diffractometer (Cu Kα radiation, $\lambda = 0.154$ nm) and a JEM-2010 high resolution transmission electron microscope (HRTEM).

2.4. Experiment setting in EC, PC and PEC system

In EC system, 100 ml RhB solution was placed in a self-designed quartz reactor, the electric field was provided by an electrochemical workstation (CHI760E, Shanghai Chenhua Co. Ltd., China) with the voltage set as 2, 4, and 6 V respectively, running time was 19,800 s, signal interval was 2.72 s, sensitivity was 100 μA/V. In PC system, the simulated solar light was provided by a PLS-SXE300 Xe lamp (300 W, light intensity is 200 $mW\,cm^{-2}$, Beijing Trusttech Co. Ltd., China) equipped with a filter to cut most of IR irradiation (780–1100 nm), which matched natural solar light well (Fig. S1), and placed *ca.* 15 cm above the reactor. TiO_2 or TiO_2-$BiVO_4$ films (the catalyst loading amount: *ca.* 5.0 mg) were immobilized and immersed in 100 ml RhB solution. In PEC system, electrochemical workstation and Xe lamp were assembled to provide electric field and simulated sunlight simultaneously. The films, Pt wire, and Ag/AgCl acted as working electrode, counter electrode and reference electrode (data 1 Fig. S1). In EC, PC and PEC system, RhB solution were firstly stirred for 30 min to ensure the adsorption-desorption equilibrium, then sampled every 30 min to determine the concentration of RhB by a UV–vis Absorption Spectrometer (Shimadzu UV-2450) at 554 nm.

2.5. Acute toxicity test

The acute toxicity of RhB during the degradation process in PC and SPEC system was evaluated by *photobacterium phosphoreum* (*Vibrio fischeri* 5269, Chinese Academy of Sciences, Nanjing) as the indicator. The cultivation of *Vibrio fischeri* and toxicity evaluation procedure were conducted according to ISO 11348-7 method. Samples were taken every 60 min and exposed to *Vibrio fischeri* in a medium containing 2% w/v NaCl for 5 min. The luminosity was measured by a DXY-2 biotoxicity testing instrument. The experiments were carried out in triplicate.

2.6. Mathematical simulation

Quantum chemical calculation was done by Gaussian 09 program to explore the degradation mechanisms in PC and SPEC system. Stationary point geometries were optimized using DFT functional B3LYP method with the 6-31G (d) basis set. Harmonic vibrational frequencies were calculated at the same level to identify all stationary points as either minima (zero imaginary frequency) or transition states (TSs; only one imaginary frequency). Intrinsic reaction coordinate calculations were conducted to confirm that each TS connected with the products. In-silico toxicity prediction was executed by TOPKAT (Discovery Studio 2.5.5, USA).

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Chemical composition and structure of TiO_2-$BiVO_4$ nanocomposite film

The elements of Bi, V, Ti, and O dispersed uniformly in the as-prepared TiO_2-$BiVO_4$ nanocomposite films (Fig. S2). In FT-IR spectroscopy (Fig. 1), it can be concluded that TiO_2-$BiVO_4$ nanocomposite film