Science of the Total Environment 647 (2019) 245–254

Contents lists available at ScienceDirect

Science of the Total Environment

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

Highly efficient photocatalytic removal of multiple refractory organic pollutants by $BiVO_4/CH_3COO(BiO)$ heterostructured nanocomposite

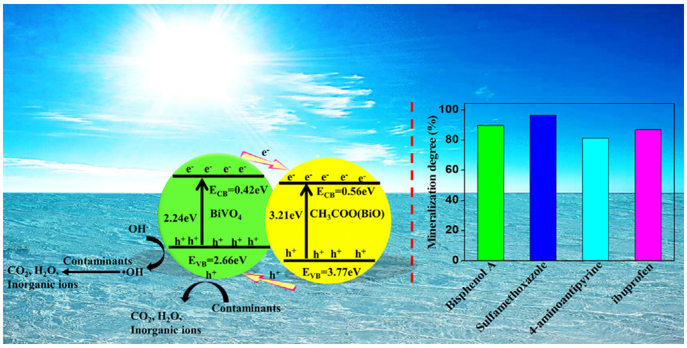
Xia Zhang, Yuhao Ma, Lulu Xi, Guifen Zhu, Xiang Li, Dongyang Shi, Jing Fan *

School of Environment, Henan Key Laboratory for Environmental Pollution Control, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, PR China

HIGHLIGHTS

- One-pot facile synthesis of $BiVO_4/CH_3COO(BiO)$ heterojunction was presented.
- The material showed high degradation and mineralization rate for multiple pollutants.
- The degradation mechanism of 4-AAP and IBP was proposed.
- Good activity of the heterojunction was maintained in real wastewater treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 June 2018
Received in revised form 27 July 2018
Accepted 30 July 2018
Available online 31 July 2018

Editor: Paola Verlicchi

Keywords:
$BiVO_4/CH_3COO(BiO)$
Heterojunction
Photocatalysis
Degradation
Organic pollutant
Mechanism

ABSTRACT

Highly efficient photocatalytic degradation of refractory organic contaminants in wastewater remains a great challenge due to low quantum efficiency and poor solar energy utilization of the currently employed photocatalysts. Herein, a novel $BiVO_4/CH_3COO(BiO)$ heterojunction photocatalyst is designed and prepared by a simple one-pot solvothermal method, and characterized by various techniques. By using this photocatalyst, degradation efficiency of four kinds of emerging refractory organic pollutants (sulfamethoxazole, bisphenol A, 4 aminoantipyrine and ibuprofen) in water is investigated under simulated solar irradiation. Then, total organic carbon is measured to determine the mineralization degree, and degradation intermediates of the pollutants are identified to propose their degradation pathway. It is found that under the given conditions, complete degradation of the pollutants is observed within the irradiation of 5–24 h, and 81–96% mineralization degree is achieved in 24 h. Furthermore, it is shown that the degradation kinetics can be described by pseudo-first order model. Based on the detected intermediates during the degradation process of 4 aminoantipyrine and ibuprofen, the degradation pathways of these two pollutants are suggested to involve cleavage of side chain, heterocyclic ring opening and hydroxylation of aromatic ring. In addition, the application of the $BiVO_4/CH_3COO(BiO)$ heterojunction photocatalyst in the purification of the spiked real wastewater is also investigated.

1. Introduction

Refractory organic contaminations are characterized by easy bioaccumulation and resistance to chemical oxidation and biological transformation due to their lipophilic and stable chemical structures. In

---

* Corresponding author.
E-mail address: fanjing@htu.cn (J. Fan).

https://doi.org/10.1016/j.scitotenv.2018.07.450
0048-9697/© 2018 Elsevier B.V. All rights reserved.

recent decades, an increasing occurrence of emerging organic contaminants with potential hazards, such as pharmaceuticals, metabolite, and plasticizer, has been frequently reported in a wide variety of water (Giraldo et al., 2010). These compounds have become a worldwide concern due to their extensive use, release and widespread distribution in environment (Rosal et al., 2010). In particular, low concentration (ng/L or μg/L) of such contaminants can lead to the problems of chronic toxicity, endocrine disruption, and the development of pathogen resistance (Hernando et al., 2006; Luo et al., 2014; Murgolo et al., 2015). Common methods, such as biodegradation, adsorption and chemical oxidative technique, are often used to remove such toxic organic substances from environmental matrices (Alvarino et al., 2015; Elmolla et al., 2010; Li and Zhang, 2010). Unfortunately, the complexity, low efficiency, essential post-treatment and possible secondary pollution make these methods less efficient for practical use (Cui et al., 2016; Yan et al., 2016). Comparatively speaking, "green" and "sustainable" heterogeneous photocatalysis becomes a promising alternative approach at present and is expected to play an important role in the decomposition of such pollutants because of its comprehensive merits of simplicity, eco-friendly, low-cost, gentle operation, and capability of simultaneously removal of multiple pollutants in complex water matrix (Chala et al., 2014; Zhang et al., 2017).

Recently, considerable attention has been drawn to the Bismuth-based organic acid salt semiconductor photocatalysts owing to their "green" elements composition and powerful oxidization properties resulted from deep valence band level dominated by O_2p (Duan et al., 2010; Xiao et al., 2015; Yang et al., 2015). Bismuth oxide acetate ($CH_3COO(BiO)$) is one of the most attractive photocatalysts and has been reported to exhibit excellent photocatalytic performance for the removal of organic dyes (Zhang et al., 2016). However, this photocatalyst can solely absorb UV light due to its wide bandgap, which greatly limits its applications. On the other hand, the photocatalytic efficiency of $CH_3COO(BiO)$ is also limited by the recombination of photogenerated e^-/h^+ pairs. Thus, efforts to reduce the recombination of the carriers and to improve its visible light responsive ability are extremely necessary. Contrast to individual photocatalyst, constructing composite photocatalyst has been recognized as effective strategy to simultaneously overcome the defect of the single photocatalyst (Grigioni et al., 2015). Particularly, the type-II semiconductor heterojunction with matchable band structures displays the best electron-hole separation, thus the selection of components for assembling unit composite system is crucial (Jia et al., 2017).

Yellow Bismuth vanadate ($BiVO_4$) has been recognized as a promising candidate photocatalyst capable of utilizing visible light, and extensively explored for decomposition of organic contaminants and water splitting (García Pérez et al., 2011; Kudo and Miseki, 2009; Tan et al., 2016), but its poor photo-activity resulted from high recombination of the photogenerated e^-/h^+ pairs limits its extensive application. As a result, $BiVO_4$ is often employed to combine with other semiconductor photocatalyst to form heterojunction, leading to simultaneous improvement of visible light capture and separation efficiency of carriers, and thus to the enhancement of activity (Chatchai et al., 2013; Madhusudan et al., 2011). In this context, types of heterojunction, matching degree of band structure and interface contact of the two materials greatly affect the extent of catalytic activity enhancement. Therefore, further researches on the design, preparation and properties of novel $BiVO_4$ based composite photocatalysts are of great significance for the practical application of photocatalysis technology.

In this work, we have designed and synthesized new $BiVO_4/CH_3COO(BiO)$ heterojunction by a facile simple one-pot solvothermal approach for the first time. Under simulated solar light irradiation, four representative emerging refractory organic compounds, including sulfamethoxazole, bisphenol A, 4 aminoantipyrine and ibuprofen, have been effectively degraded and mineralized by the $BiVO_4/CH_3COO(BiO)$ heterojunction in water.

2. Materials and methods

2.1. Chemical reagents

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), ammonium metavadate (NH_4VO_3), nitric acid (HNO_3, 65%), ammonia ($NH_3 \cdot H_2O$, 25%) and glacial acetic acid (CH_3COOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Sulfamethoxazole (SMX), bisphenol A (BPA), 4 aminoantipyrine (4 AAP) and ibuprofen (IBP) were acquired from Sigma-Aldrich (Steinheim, Germany). All these chemicals were analytical grade and used as received. Deionized water was used in solution preparations.

Here, sulfamethoxazole, bisphenol A, 4 aminoantipyrine and ibuprofen were selected as model compounds of pharmaceuticals, drug intermediates and endocrine disrupting chemicals, which are typical refractory organic contaminations. The selection of such organic compounds was based on their widespread occurrence in domestic sewage and diverse physicochemical properties (Gong and Chu, 2016; Kim et al., 2014; Loos et al., 2013). The chemical structure and main properties of these contaminants were summarized in Table 1.

2.2. Preparation of the photocatalysts

For the preparation of $BiVO_4/CH_3COO(BiO)$ composite, one-step solvothermal method was developed. In a typical procedure, 5.0 mmol of Bi $(NO_3)_3 \cdot 5H_2O$ was dissolved in 30 mL of mixed solvent of glacial acetic acid and deionized water (v/v = 2:1) to form solution A. Meanwhile, another solution was prepared by dissolving certain amount of NH_4VO_3 in 20 mL of diluted ammonia water (v/v = 1:1). Then, the ammonia solution containing NH_4VO_3 was added dropwise into solution A under vigorous stirring. Then, pH of the final suspension was adjusted to desired value (3.0, 5.5, 6.0, 7.0, 9.0, or 10.0) using ammonia. After stirring for 30 min, the resulting suspension was transferred into a 100 mL of Teflon-lined autoclave and heated at 160 °C for 20 h. Afterward cooling down naturally, the brilliant yellow precipitate was collected by centrifugation, washed by deionized water and absolute ethanol for several times, and then dried in an oven at 60 °C overnight. Meanwhile, changing the added amount of NH_4VO_3 (0.5, 1.0, 1.25, 1.5 or 2.0 mmol), $BiVO_4/CH_3COO(BiO)$ composites were synthesized and denoted as BCB-1, BCB-2, BCB-3, BCB-4, and BCB-5, respectively. For the sake of comparison, neat $BiVO_4$ and $CH_3COO(BiO)$ photocatalysts were also prepared by the same procedures but without the addition of CH_3COOH and NH_4VO_3.

2.3. Characterization of the photocatalysts

The crystal structure and phase composition of the as-prepared samples were analyzed by powder X-ray diffraction (XRD, D8 Focus, Bruker, German) with Cu Kα as a radiation source. The size and morphology of the as-prepared samples were observed with scanning electron microcopy (SEM, JSM-6390LV, Japan). Further microstructure characterization was performed on transmission electron microscopy (TEM) and high-resolution transmission spectroscopy (HRTEM, JEM-2100, Japan). Fourier transform infrared (FT-IR) spectra were recorded using a Spectrum 400 analyzer (Perkin-Elmer, USA), and KBr was used as reference. Surface properties of the samples were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, USA) with Al Kα X-ray irradiation. Binding energy values were calibrated to C 1s peak of 284.6 eV. The UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded over the range of 200–800 nm on an UV–vis spectrophotometer (Lambd 950, PerkinElmer, USA) using $BaSO_4$ as a reference. The room temperature photoluminescence (PL) emission spectra were measured using a fluorescence spectrophotometer (FP-6500, Japan) equipped with a Xenon lamp at an excitation wavelength of 300 nm.