Journal of Photochemistry & Photobiology A: Chemistry 364 (2018) 240–249

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

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

$BiOCl/Fe_2O_3$ heterojunction nanoplates with enhanced visible-light-driven photocatalytic performance for degrading organic pollutants and reducing Cr(VI)

Kai Li[a,b], Yujun Liang[a,b,*], Jian Yang[a,b], Hang Zhang[a,b], Gui Yang[a,b], Wen Lei[a,b,c]

[a] Engineering Research Center of Nano-Geo Materials of Ministry of Education, China University of Geosciences, Wuhan 430074, PR China
[b] Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China
[c] School of Electrical, Electronic and Computer Engineering, The University of Western Australia, 35 Stirling Highway Crawley, WA 6009, Australia

ARTICLE INFO

Keywords:
BiOCl
Fe_2O_3
In-situ oxidation
Visible-light-driven
Photocatalytic activity
Cr(VI) reduction

ABSTRACT

In this study, a series of novel $BiOCl/Fe_2O_3$ (FB) heterojunctions were synthesized through an *in-situ* oxidation method by using elemental Bi nanospheres as Bi source while $FeCl_3$ as Fe source and oxidizing agent. The visible-light-driven (VLD) photocatalytic activity of FB heterojunctions in degrading organic pollutants and reducing Cr (VI) was enhanced significantly in comparison with pure BiOCl and Fe_2O_3. This enhancement of photocatalytic performance was mainly due to the formation of heterojunction between BiOCl and Fe_2O_3, which remarkably promoted the separation and transfer efficiency of photo-generated charge carriers. This work demonstrates an effective approach for the fabrication of Bi-based heterostructured photocatalytic systems from *in-situ* oxidation of elemental Bi by using metal cations as oxidizing agents, which exhibits great potential applications in energy conversion and environmental purification.

1. Introduction

Recently, semiconductor photocatalytic technology has been widely applied in the field of solar energy conversion, catalytic synthesis and environment purification [1–5] while considerable efforts have been paid on developing semiconductor photocatalysts with high photocatalytic performance in the past few decades [6–8]. Profited from the layer crystal structure existed in the majority of related compounds in which Bi^{3+} with s^2 configuration, Bi-based semiconductors, especially bismuth oxyhalides, exhibit excellent photocatalytic activity and aroused great attention of researchers [9–12]. As is known, the crystallize process of bismuth oxyhalides leads to the construction of layered-structure interleaved with $[Bi_2O_2]$ slabs and double halogen atoms slabs, thus creating a strong internal electrostatic field (IEF) and favoring for the separation of photo-generated electron-hole pairs [13–15]. Moreover, the oxygen vacancies existed in the BiOX matrix could capture and store the photo-generated electrons effectively, which restrains the recombination of photoinduced charge carriers and enhance the photocatalytic activity of BiOX significantly [16,17] In recent years, micro- and nano-structured BiOX photocatalysts have been investigated as efficient photocatalysts, including nanosheets [18], nanotubes [19], nanoflowers [20,21] and microspheres [22]. However, the utilization of surfactant and organic solvents during the construction of these micro- and nano-structures could cause several limitations, such as complex synthesis processes, increased production costs, and lower photocatalytic activities as well as pollution. Therefore, it presents a serious challenge to study a simple, cost effective and environmental friendly method for fabricating BiOX photocatalysts. As is known, the *in-situ* conversion of elemental Bi nanospheres into BiOX photocatalysts could provide a potential solution to overcome those drawbacks, which ensuring both high crystallinity and controllable morphology of the products. It was reported by Liu et al. that BiOCl film with flower-like hierarchical structures was obtained by dipping Bi spherical film in a mixed solution of H_2O_2 and HCl for 2 min [23]. While Bi and Lu et al. took Bi nanospheres and NaBr for the fabrication of flower-like BiOBr nanoarchitectures *via* a simple hydrolysis route using $Fe(NO_3)_3{\cdot}9H_2O$ as oxidizer at room temperature [24]. Nevertheless, the recombination of photogenerated electron-hole pairs within these single semiconductor photocatalytic systems is still efficient and results in the decrease of quantum efficiency, thus doing harm to the photocatalytic performance of the photocatalysts [25,26]. Besides, the Fe^{3+} remained in the reaction solution could be wasteful and cause some other environmental problem. How can we make full use of them and convert them into effective components of the final products?

Nowadays, Fe_2O_3 has been widely applied in magnetism [27], sensors [28] and lithium ion batteries [29] due to its abundant, low-

* Corresponding author at: Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China.
E-mail address: yujunliang@sohu.com (Y. Liang).

https://doi.org/10.1016/j.jphotochem.2018.06.001
Received 17 March 2018; Received in revised form 30 May 2018; Accepted 1 June 2018

cost, none-toxicity and high physical-chemical stability. Besides, as a kind of semiconductor, it has also been applied in photocatalysis [30–32]. Since its energy band could well match those of BiOCl, a stable heterojunction would form when coupling Fe_2O_3 with BiOCl, which favoring for the separation of photogenerated electron-hole pairs and accelerating their transfer from one component to another, thus refraining their recombination effectively and leading to the improvement of photocatalytic efficiency. Moreover, the narrow band gap of Fe_2O_3 could also contribute to the adsorption of light spectrum range of the heterojunction.

Therefore, based on the above discussion, in this work, we demonstrated an *in-situ* oxidation method for converting elemental Bi nanospheres into BiOCl/Fe_2O_3 heterojunction by using $FeCl_3$ as Fe source and oxidizing agent, and were then used for photocatalytic degradation of organic pollutants and reduction of aqueous Cr(VI) under visible lights irradiation. Specifically, BiOCl nanoplates with Fe_2O_3 nanoparticles attached to their surfaces were obtained *via* a simple hydrothermal treatment. The formation mechanism of the heterojunction was discussed in details and the photocatalytic activities of the BiOCl/Fe_2O_3 heterojunction was also been investigated. The as-prepared BiOCl/Fe_2O_3 heterojunctions exhibited enhanced photocatalytic performance in comparison with pure BiOCl and Fe_2O_3 under visible light irradiation. Moreover, the BiOCl/Fe_2O_3 heterojunction also presented an improved photocatalytic efficiency for the reduction of Cr (VI). In addition, the catalyst exhibited the optimum photocatalytic activity when $FeCl_3$ and Bi was 1.5:1 (m/m) in the formation process and the photostability was excellent after five times recycling photocatalytic reactions.

2. Experimental section

2.1. Synthesis of Bi nanospheres

All the reagents were of analytical purity and purchased from Sinopharm Chemical Reagent Co., Ltd, China. In a typical synthesis, 0.0012 mol of $Bi(NO_3)_3{\cdot}5H_2O$ was added into 30 mL of ethylene glycol with magnetic stirring at room temperature for 20 min to obtain a transparent solution (solution 1). While 0.2 g of glucose was dissolved in 10 mL of deionized water to form another transparent solution (solution 2). Thereafter, the solution 2 was added to the solution 1 dropwise under continuously stirring for 30 min to form a homogeneous mixture. Finally, the obtained mixture was transferred into a Telfon-lined oxidation-resisting steel autoclave, and heated at 180 °C for 8 h, then cooling down to room temperature naturally. The precipitant was collected by centrifugation, followed by washing several times with deionized water and ethanol before drying in vacuum at 80 °C for 8 h.

2.2. Synthesis of BiOCl/Fe_2O_3 heterojunction nanoplates

A one-pot strategy was adopted for the synthesis of BiOCl/Fe_2O_3 heterojunction nanoplates. Specifically, 20 mg of Bi nanospheres were dispersed in 20 mL of deionized water with ultrasonication for 5 min. Then, 20 mL of $FeCl_3$ solution (containing 0.1 mmol of $FeCl_3$) was added to the dispersion dropwise under continuous stirring. After stirring for 20 min, the mixture was poured into a Telfon-lined oxidation-resisting steel autoclave, and kept at 180 °C for 24 h, then cooling down to room temperature naturally. The product was recovered by centrifugation and washed by deionized water and ethanol several times to remove the extra ions and wastes, then drying at 80 °C for 8 h. In order to obtain a catalyst with the optimum photocatalytic performance, a series of BiOCl/Fe_2O_3 heterojunctions were prepared with various molar ratios of $FeCl_3$ to Bi (0.5/1.0, 1.0/1.0, 1.5/1.0, 2.0/1.0), the corresponding products were referred to as FB50%, FB100%, FB150% and FB200%, respectively. For comparison, pure Fe_2O_3 was also prepared similarly without adding Bi nanospheres while bare BiOCl was prepared by following the methods reported in our previous work [33].

2.3. Characterization

The phase composition of as-prepared samples were characterized by powder X-ray diffraction (XRD) method on a Bruker D8 Focus diffractometer (Bruker, Kalsruhe, Germany) with Cu-Kα (λ = 1.540598 Å) radiation over the 2θ range of 5.0–70°. The mass ratio of the components among as-prepared samples was investigated by inductively coupled plasma mass spectrometry (ICP-MS) (Elan DRC-e, PerkinElmer, America). The morphology of as-prepared samples were observed by a field emission scanning electron microscopy (SEM, SU8010, Hitachi, Japan), while the crystal structure of sample FB150% was studied with transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Tecnai G2 T20, FEI, America). The textural properties of the samples were analyzed by N_2 adsorption/desorption method using automatic surface area analyzer (ASAP2020, US). X-ray photoelectron spectroscopy (XPS) analysis for the FB150% sample was carried out on a Thermo ESCALAB 250X spectrometer (America) using a 150 W Al Kα X-ray source. The UV–vis diffused reflectance spectra (DRS) of the samples were recorded with an UV–vis-near-IR spectrometer (UV3600-MPC3100). The photoluminescence (PL) emission spectra were taken by using fluorescence spectrometer (Fluoromax-4 P, Horiba Jobin Yvon, New Jersey, USA.) equipped with a 450 W xenon lamp as the excitation source. The photocurrent measurements were performed by using a CHI 660B (Chenhua, China) electrochemical workstation with a standard three-electrode cell at room temperature.

2.4. Photocatalytic activity test

The photocatalytic activity of as-prepared samples was evaluated by the degradation MO and RhB molecules and reduction of Cr(VI) under visible light illumination, which were undertaken with a multi-channel photochemistry reaction system (PCX50B, Beijing Perfectlight Co. Ltd., China) equipped with 5 W LED lamps as the light source. The wavelengths of the LED lamps are greater than 420 nm. For the degradation of MO or RhB, 10 mg of photocatalyst was dispersed into 50 mL of dye aqueous solution (10 mg L^{-1}). Prior to irradiation, the suspension was magnetically stirred in dark for 30 min to establish adsorption-desorption equilibrium. The suspension then reacted under visible light irradiation at room temperature while 5 mL solution was taken out at a fixed time interval. The experiments for the reduction of Cr(VI) were carried out as follows: the Cr(VI) aqueous solution was prepared by dissolving $K_2Cr_2O_7$ and citric acid with deionized water. Then, 50 mg of as-prepared samples was added into 50 mL of Cr(VI) aqueous solution (100 mg L^{-1}, pH = 2.5). Prior to illumination, the suspension was stirred in dark for 30 min to establish adsorption-desorption equilibrium. The suspension then reacted under visible light irradiation at room temperature. During the photochemistry reaction process, 5 mL of the suspension was taken out and centrifuged to remove the photocatalyst for analysis. The quantitative determination of both organic dyes and aqueous Cr(VI) was performed by measuring the absorption peak intensity using an UV–vis spectrophotometer (UV-1800PC, Shanghai Mapada Co. Ltd., China).

2.5. Active species trapping experiments

In order to study the main active species that played major role in photocatalytic reaction, $(NH_4)_2C_2O_4$ (0.2 mM), 1, 4-benzoquinone (BQ, 0.2 mM) and isopropanol (IPA, 0.2 mM) were used as the scavengers of h^+, $\cdot O_2^-$, and ·OH during the photocatalytic activity test, respectively.

3. Results and discussion

3.1. Characterization of as-prepared samples

In order to study the phase composition and crystal structure, XRD measurements were undertaken on the as-prepared samples while the