Journal of Hazardous Materials 344 (2018) 42–54

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Research paper

Three-dimensional Ag_2O/Bi_5O_7I *p–n* heterojunction photocatalyst harnessing UV–vis–NIR broad spectrum for photodegradation of organic pollutants

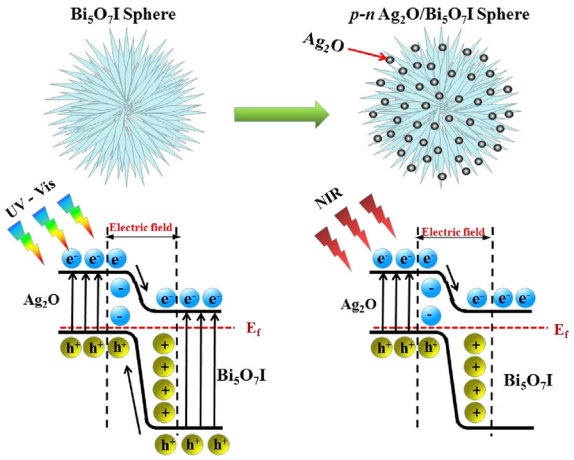
Yannan Chen[a], Gangqiang Zhu[a,*], Mirabbos Hojamberdiev[a,c], Jianzhi Gao[a,*], Runliang Zhu[b], Chenghui Wang[a], Xiumei Wei[a], Peng Liu[a]

[a] School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, PR China
[b] Guangdong Provincial Key Laboratory of Mineral Physics and Material Research & Development, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China
[c] Department of Natural and Mathematic Sciences, Turin Polytechnic University in Tashkent, Kichik Halqa Yo'li 17, Tashkent 100095, Uzbekistan

HIGHLIGHTS

- A novel *p–n* heterojunction photocatalyst of Ag_2O nanoparticles-loaded Bi_5O_7I microspheres is reported.
- The Ag_2O/Bi_5O_7I composite exhibited wide-spectrum response from ultraviolet to near-infrared.
- Ag_2O/Bi_5O_7I showed high photocatalytic activity for organic pollutants under visible and near-infrared light irradiation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 June 2017
Received in revised form 6 October 2017
Accepted 7 October 2017
Available online 7 October 2017

Keywords:
Silver oxide
Bismuth oxyiodide
Heterojunction
Photocatalyst
Wide-spectrum response

ABSTRACT

Ag_2O nanoparticles-loaded Bi_5O_7I microspheres forming a three dimensional Ag_2O/Bi_5O_7I *p–n* heterojunction photocatalyst with wide-spectrum response were synthesized in this study. The results of transmission electron microscopy observations revealed that the Ag_2O nanoparticles with the diameter of *ca.* 10–20 nm were distributed on the surfaces of Bi_5O_7I nanosheets. The as-synthesized Ag_2O/Bi_5O_7I exhibited an excellent wide-spectrum response to wavelengths ranging from ultraviolet (UV) to near-infrared (NIR), indicating its potential for effective utilization of solar energy. Compared with pure Bi_5O_7I, the Ag_2O/Bi_5O_7I composite also demonstrated excellent photocatalytic activity for the degradation of Bisphenol A and phenol in aqueous solution under visible LED light irradiation. Among samples, the 20% Ag_2O/Bi_5O_7I composite photocatalyst showed the highest photocatalytic activity for the degradation of Bisphenol A and phenol in aqueous solution. In addition, the 20% Ag_2O/Bi_5O_7I composite also exhibited a photocatalytic activity for the degradation of Bisphenol A under NIR light irradiation. The improved photocatalytic activity is attributed to the formation of a *p-n* heterojunction between Ag_2O and Bi_5O_7I,

* Corresponding authors.
E-mail address: zgq2006@snnu.edu.cn (G. Zhu).

https://doi.org/10.1016/j.jhazmat.2017.10.015

allowing the efficient utilization of solar energy (from UV to NIR) and high separation efficiency of photogenerated electron-hole pairs. The present work is desirable to explore a possible avenue for the full utilization of solar energy.

1. Introduction

With the technological development, the environmental pollution and energy shortage have become the two most severe crises in the world. Since the Honda-Fujishima effect was first reported, semiconductor-based photocatalysis has attracted extensive attention due to its potential application in environmental remediation and energy conversion by utilizing solar energy [1,2]. However, many large band gap (E_g > 3.0 eV) metal oxide photocatalysts, such as TiO_2 [3], ZnO [4,5], SnO_2 [6], etc. can only be activated under UV irradiation (λ < 388 nm) which accounts for less than 5% of solar energy [7]. In contrast, the visible light and infrared light making up 44% and 53% of solar spectrum, respectively, remain unutilized [3]. Therefore, many researchers have been heavily concentrated at developing the visible-light-responsive photocatalysts in the past twenty years. To further improve the absorbance and utilization of solar energy, much effort has been made to design photocatalysts with near-infrared light response. Over the past years, the researches on near-infrared-light-responsive photocatalysts primarily focused on upconversion luminescence of rare earth elements through doping and loading of narrow band-gap NIR-responsive semiconductors [3]. However, the upconversion materials usually absorb NIR light and emit UV or visible light at a certain wavelength, and the efficient utilization of solar energy is limited because of its very narrow absorption range [3,7]. Hence, the most promising photocatalysts should be compatible to utilize a full spectrum of the solar light, including UV, UV–vis, Vis-NIR, and NIR. It is still challenging to develop photocatalytic materials that are not only activated by a wide spectrum of solar light ranging from UV to NIR but also possess high charge separation efficiency.

Bismuth oxyiodides ($Bi_xO_yI_z$) – based photocatalysts have been demonstrated to have excellent visible light photocatalytic activity for the removal of organic pollutants and reduction of CO_2 [8–10]. $Bi_xO_yI_z$ has a unique layered crystal structure formed from the $[Bi_2O_2]^{2+}$ and double I^- layers. Therefore, it creates an internal static electric field that is perpendicular to each layer, promoting the effective separation of photo-generated electron-hole pairs [11–13]. As a member of the $Bi_xO_yI_z$ family, BiOI is a good visible-light-active photocatalyst with a narrow band-gap of 1.8 eV [14]. However, BiOI has an insufficient reduction ability due to its positive conduction band and a relatively high recombination of electron and holes [9,15–17]. Previously, Lei et al. [15] found that BiOI has a low thermal stability. Therefore, novel bismuth-rich oxyiodides, including $Bi_4O_5I_2$ [18], $Bi_7O_9I_3$ [19], Bi_5O_7I [20], etc., later received much attention. Bi_5O_7I is an *n*-type semiconductor having higher thermal stability than other bismuth oxyiodides [21]. In addition, Bi_5O_7I possesses more positively positioned valence band edge compared with BiOI and can provide more active holes to oxidize various organic pollutants [22–24]. However, Bi_5O_7I has a relatively wide band-gap than other bismuth oxyiodides. To further improve its photocatalytic activity, various metals were doped in and narrow band-gap semiconductors were coupled with Bi_5O_7I [25,26].

Recently, silver(I) oxide (Ag_2O) has been of particular interest due to its photocatalytic activity for the degradation of organic pollutants under visible light irradiation. The band-gap of Ag_2O is reported to be 1.2 eV with the bottom of the conduction band (CB) located at 0.2 eV and the top of the valence band (VB) positioned at 1.4 eV in comparison with Fermi energy (E_F), implying that Ag_2O can be a NIR light – responsive photocatalyst [27]. Ag_2O is a typical *p*-type semiconductor and widely used as a photo-sensitizer to regulate the light response of wide band-gap *n*-type semiconductors (e.g., Ag_2O/TiO_2, Ag_2O/ZnO, etc.) to form a *p–n* heterojunction and to improve their photocatalytic activities [28–32].

Here, we synthesized a three dimensional Ag_2O/Bi_5O_7I *p–n* heterojunction photocatalyst by loading silver(I) oxide (Ag_2O) nanoparticles on Bi_5O_7I microspheres and studied its photocatalytic activity for the degradation of Bisphenol A and phenol under UV, visible, and near-infrared light irradiation. It was found that the as-synthesized Ag_2O/Bi_5O_7I *p–n* heterojunction photocatalyst exhibits excellent photocatalytic activity for the degradation of Bisphenol A and phenol due to the effective utilization of solar light and efficient charge separation. The photo-stability and possible mechanisms for the degradation of Bisphenol A and phenol over Ag_2O/Bi_5O_7I are presented.

2. Experimental

2.1. Synthesis of porous Bi_5O_7I microspheres

All reagents obtained from Aladdin Reagents (Shanghai) Co., Ltd. (China) were of analytical grade and used without further purification. Uniform Bi_5O_7I microspheres were obtained by thermal conversion [25,33] of precursor BiOI microspheres synthesized by an ethylene glycol-assisted solvothermal method [14]. First, 2.85 mmol of $Bi(NO)_3{\cdot}5H_2O$ (donated as solution A) and 3 mmol of KI (donated as solution B) were separately dissolved in 25 mL of ethylene glycol (EG) under constant stirring for 30 min at room temperature. Then solution B was dropwise added into solution A and stirred continuously for 1 h. Afterward, the mixed transparent solution was transferred into an 80 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 12 h. After hydrothermal reaction, the autoclave was cooled gradually to room temperature, and the orange-colored precipitates were collected by centrifugation, washed with deionized water for several times, and dried in vacuum at 80 °C for 12 h. Uniform Bi_5O_7I microspheres were obtained by thermal treatment of BiOI microspheres at 450 °C for 2 h in a muffle furnace [25,33].

2.2. Synthesis of Ag_2O and Ag_2O/Bi_5O_7I p–n heterojunction photocatalyst

A certain amount of the as-synthesized Bi_5O_7I microspheres was added into 50 mL aqueous solution of $AgNO_3$ (99.9%) and stirred for 30 min. The mass ratio of Ag_2O to Ag_2O/Bi_5O_7I was controlled at 5, 10, 15, 20, 25 and 100 wt%. Afterward, NaOH aqueous solution was introduced into the suspension to adjust the pH to 14 and stirred for 2 h. Finally, the resulting precipitates were collected by centrifugation, washed with deionized water for several times, and dried at 60 °C for 12 h.

2.3. Characterization

The crystalline structures of the samples were analyzed by X-ray diffraction (XRD) using a D/max-2550 X-ray diffractometer