Chemical Engineering Journal 251 (2014) 371–380

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Mechanism of 2,4-dinitrophenol photocatalytic degradation by ζ-Bi_2O_3/Bi_2MoO_6 composites under solar and visible light irradiation

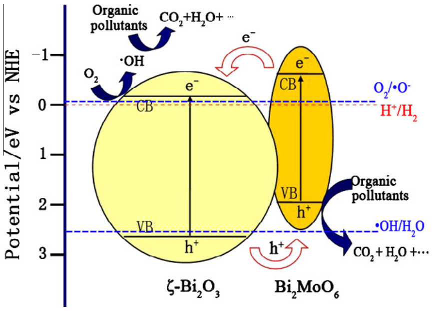
Jun Ma [a], Long-Zhu Zhang [a], Yue-Hua Wang [a,*], Si-Liang Lei [a], Xu-Biao Luo [a], Su-Hua Chen [a], Gui-Sheng Zeng [a], Jian-Ping Zou [a,*], Sheng-Lian Luo [a], Chak-Tong Au [a,b]

[a] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang, Jiangxi 330063, PR China
[b] Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

HIGHLIGHTS

- *Facile method:* The catalysts were synthesized by facile hydrothermal method without any templates.
- *Good properties:* 20BBM exhibits the best property of degradations of 2,4-DNP among the reported catalysts.
- *Effect of H_2O_2:* H_2O_2 improving the activity of photodegradation of 2,4-DNP is firstly demonstrated.
- *New mechanism:* New photocatalytic mechanisms for the heterostructured composites are proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form 21 April 2014
Accepted 21 April 2014
Available online 30 April 2014

Keywords:
Photocatalyst
Degradation
Persistent organic pollutants
Radicals

ABSTRACT

The ζ-Bi_2O_3/Bi_2MoO_6 composites were synthesized by a one-pot template-free hydrothermal method, and were systematically characterized by powder X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, UV–vis diffuse reflectance spectroscopy, and Raman spectroscopy. Based on the results of 2,4-dinitrophenol (2,4-DNP) degradation under simulated solar or visible light irradiation over the as-prepared materials, it is found that photocatalytic efficiency is closely related to the compositions of the materials, and the 20%ζ-Bi_2O_3/Bi_2MoO_6 catalyst performs the best. With the addition of H_2O_2 (5.0 mmol/L), there is marked improvement of photocatalytic activity. Related mechanisms for the photocatalytic degradation of 2,4-DNP and photocatalytic enhancement of the ζ-Bi_2O_3/Bi_2MoO_6 composites have been put forward.

1. Introduction

Alkyl nitrophenols are common pollutants found in urban and agricultural wastes [1–3]. Of the six possible forms of dinitrophenol, 2,4-Dinitrophenol (2,4-DNP) is the most important because it has been extensively used in the manufacture of wood preservatives, pesticides, medicament for obesity, vinyl aromatics, dyes, photochemicals, and explosives [1–8]. Despite the benefits, the use of 2,4-DNP is undesirable because it is a kind of persistent organic pollutants low in biodegradability and harmful to human health. Unfortunately, the removal of 2,4-DNP from aqueous effluents is a complex issue because it cannot be removed by conventional technologies for wastewater treatment. To destroy 2,4-DNP, advanced oxidation technologies (AOT) such as Fenton oxidation [1,2], TiO_2 photocatalysis [3–11] and electrocatalytic oxidation [12,13] have to be used. Till now, the removal efficiency of 2,4-DNP based on AOT is low and the TiO_2 photocatalysts can only absorb UV light. What is more, the related degradation mechanism of 2,4-DNP and the photocatalytic enhancement mechanism of catalyst have not been properly investigated. Therefore, it is vital

---

* Corresponding authors. Tel./fax: +86 791 83953373 (J.-P. Zou).
E-mail addresses: yh_wang04@126.com (Y.-H. Wang), zjp_112@126.com (J.-P. Zou).

http://dx.doi.org/10.1016/j.cej.2014.04.085
1385-8947/

to develop new photocatalysts that are low-cost, highly-efficient and reactive under solar or visible light irradiation for the degradation of 2,4-DNP.

Bismuth compounds Bi_2O_3 and Bi_2MoO_6 have attracted considerable attention because of their dielectric nature, visible light activity, catalytic behavior, and thermal stability [14–16]. Recently, there are reports showing that Bi_2MoO_6 and Bi_2O_3 can act as good photocatalysts for the degradation of organic compounds under visible-light irradiation [17–21]. As well known, compared to single-component photocatalysts, the heterostructured counterparts are much more superior in terms of photocatalytic activity.

Considering that Bi_2O_3 and Bi_2MoO_6 can be combined to create interfaces with matching band potentials [14,22–24]. We prepared Bi_2O_3/Bi_2MoO_6 photocatalysts (denoted as BBM hereinafter) containing an unidentified bismuth oxide (denoted as ζ-Bi_2O_3 hereinafter) by a one-step hydrothermal method. The catalysts show activity superior to ζ-Bi_2O_3 or Bi_2MoO_6 and its performance is better than any of that reported in the literature for 2,4-DNP photodegradation. Noteworthily, it is demonstrated the first time that photocatalytic efficiency in the photodegradation of 2,4-DNP can be markedly improved by adding H_2O_2. The main objective of this work is to investigate the photocatalytic degradation of 2,4-DNP over the BBM catalysts under simulated solar and visible light irradiation. To obtain insights into the degradation of persistent organic pollutants over composite catalysts, we investigated the enhancement mechanism of BBM and the reaction mechanism of 2,4-DNP photocatalytic degradation over BBM.

2. Experimental section

2.1. Materials and measurement

All chemicals were analytically pure and used without further purification. The crystalline phases of samples were identified by X-ray diffraction (XRD, Bruker D8 ADVANCE) using graphite monochromatized Cu Kα (λ = 1.5406 Å) radiation. The XRD data for indexing and cell-parameter calculations were collected with a scanning speed of 2°/min in the 2θ range between 10° and 70°. The morphology of samples was observed with scanning electron microscope (SEM, FEI, Holland) and transmission electron microscope (TEM, JEM-2010). Composition analyses on several randomly selected samples of the as-prepared catalysts were performed on a field-emission scanning electron microscope equipped with an energy dispersive X-ray spectroscope (EDS). The Bi/Mo molar ratio of as-prepared catalysts was estimated based on the averaged value of several randomly selected samples. The Bi/Mo molar ratio of the as-prepared samples was also determined based on data collected over an inductively coupled plasma atomic emission spectrometer (ICP-AES; Vista-MPX, VARIAN). X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1486.7 eV). UV–vis diffuse reflectance spectra were recorded with a PE Lambda 900 UV/Vis spectrophotometer at room temperature and were converted to absorbance spectrum by the Kubelka–Munk method. Raman measurements were performed using a JY LabRam HR800 spectrometer equipped with a microscope. Laser radiation (λ = 514.5 nm) was used as excitation source at 5 mW. Photoluminescence analyses were performed on an F-7000 (Hitachi-High-Technologies Corporation) fluorescence spectrometer. The Brunauer–Emmett–Teller (BET) surface areas of samples were measured by means of N_2 adsorption over a NOVA 2000e (Quantachrome) equipment.

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell with a working electrode, a platinum wire (as counter electrode), and a standard calomel electrode (in saturated KCl as reference electrode). The working electrodes were prepared by dip-coating: 20 mg of photocatalyst was suspended in 5 mL ethanol to produce a slurry, which was then dip-coated onto a 2 cm × 0.5 cm fluorine-tin oxide (FTO) glass electrode with a sheet resistance of 15 Ω. After drying under ambient condition, the films were sintered at 400 °C for 1 h. The electrolyte (0.5 M K_2SO_4) was purged with nitrogen. For photocurrent measurements, a 300 W xenon lamp with a 420 nm cutoff filter was used as visible light source and the other conditions were similar to those of electrochemical measurements.

2.2. Syntheses

2.2.1. Synthesis of ζ-Bi_2O_3

The ζ-Bi_2O_3 was synthesized by a hydrothermal method. In a typical procedure, 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ (>99.5% purity) was dissolved in 10 mL distilled water under magnetic stirring for 30 min. Then ammonia solution (5 mol/L) was added to adjust the solution to a pH of 1.0. After being stirred for 30 min at room temperature and followed by ultrasonic treatment for 30 min, the mixture was hydrothermally treated in a 50 mL Teflon-lined stainless steel autoclave at 150 °C for 5 h. Finally, the obtained solid was calcined at 300 °C for 5 h.

2.2.2. Synthesis of pure Bi_2MoO_6

The pure Bi_2MoO_6 was synthesized by a hydrothermal method. In a typical procedure, 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ (>99.5% for purity) was dissolved in 10 mL distilled water under magnetic stirring for 30 min. Stoichiometric amounts of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.36 mmol, >99.5% for purity) was dissolved in 10 mL distilled water, and added to the above prepared solution slowly. Then ammonia solution (5 mol/L) was added to adjust pH value of the mixed solution to 1.0. After ultrasonic treatment for 30 min, the mixture was hydrothermally treated in a 50 mL Teflon-lined stainless steel autoclave at 150 °C for 5 h. Finally, the obtained samples were calcined at 300 °C for 5 h.

2.2.3. Syntheses of ζ-Bi_2O_3/Bi_2MoO_6 composites

The ζ-Bi_2O_3/Bi_2MoO_6 composites were prepared by a hydrothermal method. In order to achieve ζ-Bi_2O_3/Bi_2MoO_6 of a designated ratio, a certain amount of (5–10 mmol) $Bi(NO_3)_3{\cdot}5H_2O$ (>99.5% for purity) was dissolved in 10 mL distilled water under magnetic stirring for 30 min. In the mean time, 0.36 mmol $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (purity > 99.5%) was dissolved in 10 mL distilled water. Slowly the latter was added to the former while the pH of the mixture was adjusted to 1.0 using an ammonia solution (5 mol/L). For example, 6 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and 0.36 mmol $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were used to generate the 20%ζ-Bi_2O_3/Bi_2MoO_6 catalyst (ζ-Bi_2O_3/Bi_2MoO_6 molar ratio being 20%). After ultrasonic treatment for 30 min, the mixture was hydrothermally treated in a 50 mL Teflon-lined stainless steel autoclave at 150 °C for 5 h. Finally, the obtained sample was calcined at 300 °C for 5 h. Hereinafter, the composite ζ-Bi_2O_3/Bi_2MoO_6 catalysts with ζ-Bi_2O_3/Bi_2MoO_6 molar ratio being 5% (1/20), 10% (1/10), 20% (1/5), 30% (3/10), 50% (1/2), and 100% (1/1) are denoted as 5BBM, 10BBM, 20BBM, 30BBM, 50BBM and 100BBM, respectively. The calculated contents of ζ-Bi_2O_3 among the ζ-Bi_2O_3/Bi_2MoO_6 composites are consistent with the nominal values based on the results of ICP-AES (Table S1).

2.3. Photocatalytic reactions

Photocatalytic activities of the samples were evaluated for the degradation of 2,4-DNP under simulated solar or visible-light irradiation. A 300 W Xe lamp was used as simulated solar or visible light source (cutoff filter applied for the latter, λ > 420 nm). In the