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Editor's choice paper

Improved photocatalytic Bi_2WO_6/BiOCl heterojunctions: One-step synthesis via an ionic-liquid assisted ultrasonic method and first-principles calculations

Shiwen Zhu[a,1], Chengyu Yang[a,1], Feng Li[a], Taohai Li[a,*], Meng Zhang[b,*], Wei Cao[c]

[a] College of Chemistry, Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105, China
[b] Department of Physics, East China University of Science and Technology, Shanghai 200237, China
[c] Nano and Molecular Materials Research Unit, Faculty of Science, University of Oulu, P.O. Box 3000, FIN-90014, Finland

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ABSTRACT

Bi_2WO_6/BiOCl heterojunctions with high photocatalytic activity and photocurrent property were synthesized via an ionic-liquid assisted ultrasonic irradiation at room temperature. The ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was used as the Cl source. Modifications of heterojunction structures and properties were realized just by changing the amount of [BMIM]Cl. Photocatalytic activities of Bi_2WO_6/BiOCl heterojunctions enable fast degradations of 2,4-dinitrophenol solution (DNP), rhodamine B (RhB) and quinoline blue (QB) under visible light and sunlight irradiation. Through first-principles calculations, the Bi-O bonding was found as junction structures at the interface, leading to band intercalations between the two parts besides the interface. Efficient charge (hole) transfers to two sides of the tungstate and chloride were enabled through interface during photocatalytic processes, resulting in longer electron-hole separations, and enhanced catalytic activities under sunlight radiation. The mechanism is crosschecked with transient photocurrent results where the BiOCl-Bi_2WO_6 heterojunction possess higher photocurrent than pure Bi_2WO_6 or BiOCl, ascribed to inhibition of electron-hole recombination in the photo processes.

1. Introduction

Semiconductor photocatalyst has been widely used for environmental pollutants removal and solar energy conversion [1–3]. Recently, Bi_2WO_6 has attracted extensive attention due to its narrow band gap (the band gap is 2.8 eV) and photocatalytic activity under visible light [4–6]. However, the photocatalytic activity of Bi_2WO_6 is low because of its high recombination probability between photogenerated electrons and holes, which limits its application in the fields of environmental protection. Fortunately, many attempts have been made to overcome these disadvantages, including controlling the morphologies [7,8], forming heterojunctions [9–11], and coupling with oxygen-evolution catalysts [12]. To be noted, the heterojunctions composed of two or more photocatalysts may efficiently promote the interfacial charge transfer and reduce the recombination of photoinduced electron-hole pairs, so it can improve energy transfer efficiency and enhance photocatalytic activity. So far, a lot of heterojunctions have been synthesized, such as WO_3/Bi_2WO_6 [13], TiO_2/Bi_2WO_6 [14,15], Bi_2O_3/Bi_2WO_6 [16], BiOBr/Bi_2WO_6 [17] and Bi_2S_3/Bi_2WO_6 [10].

Another bismuth compound, the BiOCl, has also unique materials properties such as high stability and relatively superior photocatalytic ability [18–20]. The crystal lattice of BiOCl matches well with that of Bi_2WO_6 [21], which makes it easy form Bi_2WO_6/BiOCl heterojunction. Up to now, only the solvothermal method has been used to synthesize Bi_2WO_6/BiOCl heterojunction. However, the reaction conditions are very rigorous, and high pressure, high reaction temperature and long reaction time are always needed. Therefore, development a mild and environment-friendly method for the synthesis of Bi_2WO_6/BiOCl is of great importance for broadening and improving their industrial applications.

In recent years, ultrasonic synthesis method has attracted considerable attentions owing to its rapid reaction rate, high efficiency, mild reaction conditions, high purity of products and environmentally friendly properties. The primary mechanism for sonochemistry is acoustic cavitation, including formation, growth,

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* Corresponding authors.
E-mail addresses: hnlth@xtu.edu.cn, lthxtu@hotmail.com (T. Li), mzhang@ecust.edu.cn (M. Zhang).

[1] Shiwen Zhu and Chengyu Yang contributed equally to this research and should be considered co-first authors.

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and implosive collapse of bubbles in a liquid. The rapid collapse of such bubbles results in intense local heating, high pressure, and extremely rapid cooling rates [22]. The unusual properties can drive many chemical reactions, such as redox, dissolution, and promotion of polymerization. The solvent of sonochemical reactions is critical, because the physical and chemical effects of cavitation are highly dependent on the contents of the collapsing bubble. Undoubtedly, solvents with low vapour pressure can be a good choice, which can minimize the participation of the solvent in reaction and maximize the temperatures and pressures of bubbles collapse [23]. Ionic liquids (ILs) have been widely used for the synthesis of semiconductor inorganic materials due to its high thermal stability, excellent dissolving ability, and negligible vapour pressure [24–31], which are potential solvents for sonochemical reactions.

Herein, combining the advantages of both ILs and ultrasound, ionic-liquid assisted ultrasonic method was developed to prepare Bi_2WO_6/BiOCl heterojunctions at room temperature. Ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was mainly used as a Cl source. And the photocatalytic activities were evaluated by the degradation of rhodamine B (RhB) and quinoline blue (QB) under visible light irradiation and sunlight irradiation. The obtained Bi_2WO_6/BiOCl heterojunctions exhibited high photocatalytic activity and stability. A first-principles calculation was carried out to explicate interfacial structures and band structures leading to materials properties. A possible photocatalytic mechanism for the enhanced photocatalytic activity of Bi_2WO_6/BiOCl was proposed. Transient photocurrent measurements were also carried out to further explicate charge transfer responses of the heterojunctions under visible light radiation.

2. Experimental section

2.1. Synthesis of Bi_2WO_6/BiOCl heterojunctions

All of the chemical reagents were analytical purity and used without further purification. The ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was added to the water solution (20 mL) of $Bi(NO_3)_3{\cdot}5H_2O$ (4.851 g, 10 mmo) and $Na_2WO_4{\cdot}2H_2O$ (2.42 g, 7 mmo). (The details were shown in Table 1). And the mixture was kept stirring for 20 min at room temperature. Afterwards, the mixture was transferred to ultrasonic bath (100 W, 40 kHz, Shu Mei KQ-250DB, china) and treated for 2 h. The precipitate was obtained after ultrasonic irradiation for 2 h, and it was purified by filtration and washing with water and ethanol several times. Finally, the products were dried at 70 °C for 12 h. Depending on the dosage of [BMIM]Cl (0 g, 0.5 g, 1 g), different composites can be synthesized and labelled as S1, S2 and S3, respectively.

For the purpose of comparison, sample S4 was prepared under the same conditions with sample S2 expect for ultrasonic treatment. To investigate the role of ionic liquid [BMIM]Cl in the synthesis of Bi_2WO_6/BiOCl composites, KCl was used as the Cl source for the preparation of Sample S5. (The detailed conditions are available in Table 1.

2.2. Characterization

The crystal structure of the prepared samples was characterized by powder X-ray diffraction (XRD) on a D8 CEVNCE apparatus diffractometer at 40 kV and 40 mA with Cu-Kα radiation. FT-IR spectrum was recorded in the range of 600–4000 cm^{-1} on a Shimadzu-8400S spectrometer. The composition of the as-prepared product was analyzed by an energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) with Al Kα X-rays (hv = 1486.6 eV) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties. The morphologies and microstructures characterizations were performed on the scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL JEM-2100F). Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (TRISTAR II3020, USA). UV–vis diffuse reflectance spectra were obtained for the dry pressed disk samples with a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan) using $BaSO_4$ as a reference.

2.3. Photocatalytic activity measurement

Photocatalytic activities of the products (50 mg) were evaluated by the degradation of the colorless dye 2,4-dinitrophenol solution (DNP, 10 mg/L, 50 mL), RhB solution (5 mg/L, 50 mL) and quinoline blue solution (5 mg/L, 50 mL) under visible light (Xe-lamp, 300 W with the 400 nm cutoff filter) and sunlight (Xiangtan, China, 14:30-16:30, 2014/07/10) irradiation for a period time. To eliminate the adsorption/desorption equilibrium effects of RhB and QB, all of the samples were magnetically stirred in dark for 30 min before the irradiation. The solution (4 mL) was taken out periodically and centrifuged to remove the catalysts. The UV–vis absorption spectra were recorded on a Lambda 25 UV–vis spectrophotometer (Perkin-Elmer, USA). The maximum absorption peak of DNP was at 360 nm, RhB was at 553 nm and QB was at 638 nm, which was used to detect the degradation of RhB and QB. The spectra scan range was 300–800 nm.

2.4. Determination of reactive species

To investigate the possible reactive species involved in the photocatalytic process, the trapping experiments of active species were conducted. Various scavengers, including benzoquinone (BQ, 2 mmo/L), tertiary butanol (t-BuOH, 10 mmo/L) and potassium iodide (KI, 5 mmo/L) were introduced into the solution of QB (5 mmg/L) to trap the active species. The experimental procedures were as follows: the photocatalyst (0.05 g) was dispersed in 50 mL of the QB (5 mg/L) aqueous solution. The solution was irradiated under visible light and 4 mL of sample was extracted periodically, centrifuged and measured on Lambda 25 UV–vis spectrophotometer.

2.5. Computational methods

All theoretical calculations were performed through the density functional theory (DFT) by using the Cambridge Serial Total Energy

Table 1
The synthetic conditions of Bi_2WO_6/BiOCl composites.

samples	$Bi(NO_3)_3{\cdot}5H_2O$/g	$Na_2WO_6{\cdot}2H_2O$/g	[BMIM]Cl/g	KCl/g	reaction condition
S1	4.85	2.42	0	0	ultrasound
S2	4.85	2.42	0.5	0	ultrasound
S3	4.85	2.42	1.0	0	ultrasound
S4	4.85	2.42	0.5	0	without ultrasound
S5	4.85	2.42	0	0.21	ultrasound