Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Synthesis and enhanced visible light photocatalytic activity of WO_3-$BiOCl_xBr_{1-x}$ heterojunctions with tunable energy band structure

Yi Ling Qi[a], Yi Fan Zheng[b], Xu Chun Song[a,*]

[a] Department of Chemistry, Fujian Normal University, Fuzhou 350007, PR China
[b] Research Center of Analysis and Measurement, Zhejiang University of Technology, Hangzhou 310014, PR China

ARTICLE INFO

Keywords:
WO_3
$BiOCl_xBr_{1-x}$
Heterojunction
Solid solutions
Photocatalytic

ABSTRACT

A series of WO_3-$BiOCl_xBr_{1-x}$ heterojunctions with tunable energy band structure were successfully synthesized via a hydrothermal method. The photocatalytic activities and reaction mechanism of WO_3-$BiOCl_xBr_{1-x}$ composites were investigated by decomposition of Rhodamine B (RhB). The light absorption ability, energy band structure and photocatalytic activity in WO_3-$BiOCl_xBr_{1-x}$ heterojunctions could be adjusted by changing the mole ratio of Br and Cl. The results revealed that the WO_3-$BiOCl_xBr_{1-x}$ composites exhibited the highest photocatalytic activities than pure WO_3 and $BiOCl_xBr_{1-x}$ under visible light irradiation. The photocatalytic property of WO_3-BiOCl can be strengthened mainly owing to the enhanced light absorption ability, while the photocatalytic activities of WO_3-$BiOCl_xBr_{1-x}$ (x = 0, 0.25, 0.5 and 0.75) composites could be enhanced by restricting the recombination of photo-generated electrons and holes. Among them, 5% WO_3-$BiOCl_{0.25}Br_{0.75}$ heterojunction shows the highest photocatalytic activity with RhB completely decomposed in 6 min, this can be contributed to the synergetic effects of energy band structure and light absorption ability. Moreover, the holes and superoxide radical anions were considered as the active species during photocatalytic oxidation process, and the possible mechanism of the enhancement of the photocatalytic property was proposed.

1. Introduction

Semiconductor photocatalysis has attracted a great deal of attention as a promising green energy technology for the degradation of organic pollutants under solar light. In the past few decades, a lot of researches have been devoted to the development of photocatalysts. Bismuth oxyhalides compounds BiOX (X = Cl, Br, I) [1–3], as a new category of potential photocatalysts, have been extensively researched and attracted great interest. BiOX (X = Cl, Br, I) as lamellar-structured photocatalysts have been demonstrated to be promising semiconductor catalysts for decomposing a wide range of organic pollutants due to its good chemical stability [4–6]. As we known, the lamellar structure may be beneficial for restraining the recombination opportunities of the photo-induced electron–hole pairs. In addition, it has been proved that BiOX (X = Cl, Br, I) can improve the photocatalytic activity by forming a series of solid solutions. The high quality solid solutions such as Kim et al. [7] have been successfully synthesized the $BiOCl_{1-x}I_x$ via a hydrothermal process, and exhibit higher photocatalytic activities under solar light for the degradation of RhB, methyl orange and so on. Coincidentally, the $BiOCl_xBr_{1-x}$ [8–10] and $BiOBr_xI_{1-x}$ [11] ($0 \le x \le 1$) nanocrystals have also been successfully synthesized to improve catalytic property. Zhang and Wang et al. [8–10] summarized the reasons for the high photocatalytic property of $BiOCl_xBr_{1-x}$ and $BiOBr_xI_{1-x}$ owing to the deep VB edge position and the structure with an internal electric field between each X halide layers and interfacial $[Bi_2O_2]^{2+}$ cation layer. Meanwhile, there are many reports that depicted a lot of solid solutions can be continuously adjusted the band gap by changing its composition [12–17]. The construction of solid solutions leads to the changes of the band gap, the fundamental electronic structure and the crystalline form, all of which can influence the photocatalytic performance [18–21].

Among various semiconductor materials, tungsten oxide (WO_3) has been mostly investigated for the high chemical stability, low cost and electrical properties. Besides, WO_3 is an eco-friendly and stable semiconductor catalyst in acidic and oxidative environments. Therefore, WO_3 has attracted much attention as a feasible candidate for making composite photocatalyst [22]. WO_3 as a visible light-responsive photocatalyst can absorb up to about 480 nm. The narrow band gap energy of WO_3 semiconductor is approximately 2.40–2.80 eV which enables it to produce an efficient photo-induced electrons and holes under irradiation by visible light [23]. These superior properties indicate that WO_3 semiconductor should be an ideal candidate and a

* Corresponding author.
E-mail address: songxuchunfj@163.com (X.C. Song).

http://dx.doi.org/10.1016/j.ceramint.2017.06.093
Received 4 December 2016; Received in revised form 1 May 2017; Accepted 14 June 2017

potential material in photocatalytic fields. However, there are still very few reports concerning the photodegradation of organic contaminants over WO_3 alone due to poor photocatalytic activity. Recently, the combining of WO_3 has attracted a great number of interests, such as WO_3/BiOCl [24,25], WO_3/BiOI [26], WO_3/BiOBr [27], Bi_2O_3/WO_3 [28], WO_3/$ZnWO_4$ [29] and so on. Although there are some reports about BiOX-containing WO_3 heterojunction catalysts, the $BiOCl_xBr_{1-x}$ solid solutions combining with WO_3 has not been researched so far. Therefore, these previous efforts stimulate us to investigate and find available methods and cheap raw materials. Herein, the WO_3-$BiOCl_xBr_{1-x}$ composites are synthesized with the adjustment of the energy band, which is never been discussed.

In this paper, the WO_3-$BiOCl_xBr_{1-x}$ (x = 0, 0.25, 0.5, 0.75 and 1) heterojunction with high photocatalytic activities has already been successfully synthesized through a facial hydrothermal process for the first time. And the photocatalytic properties of the as-prepared photocatalysts were evaluated by decomposition of Rhodamine B (RhB). Compared with pure WO_3 and $BiOCl_xBr_{1-x}$, the WO_3-$BiOCl_xBr_{1-x}$ heterojunction possesses the enhanced photocatalytic activity under visible-light irradiation. Moreover, a possible mechanism of the WO_3-$BiOCl_xBr_{1-x}$ heterojunction regarding photocatalytic process was investigated according to the experimental results in depth. Meanwhile, we also discuss the tunable energy band of WO_3-$BiOCl_xBr_{1-x}$ heterojunction in this work.

2. Experimental section

2.1. Sample preparation

2.1.1. Synthesis of WO_3 precursor

All chemicals were of analytical purity and used without other purification. The WO_3 powder was prepared via a hydrothermal method. Firstly, 1.3196 g $Na_2WO_4{\cdot}2H_2O$ (Alaadin) was dissolved in 30 mL distilled water with strongly stirring. After 10 min, 10 mL HCl (Sinopharm Chemical Reagent Co., Ltd) was dropped into the above solution under strongly stirring. After another 30 min, the final mixture solution was transferred into a 50 mL of Teflon-lined stainless steel tank for hydrothermal. The temperature of this system maintained at 160 °C for 12 h. After the autoclave was cooled to room temperature naturally, the WO_3 solid products was collected via centrifugal separation and washed by deionized water for three times, then dried at 60 °C in oven overnight for further synthesis.

2.1.2. Preparation of a series of WO_3-$BiOCl_xBr_{1-x}$

To prepare the WO_3-$BiOCl_xBr_{1-x}$ composites, $BiOCl_xBr_{1-x}$ (x = 0, 0.25, 0.5, 0.75 and 1) with different mole ratios of WO_3 (2%, 5% and 10%) were synthesized through a facile hydrothermal method. Taking 5% WO_3-BiOCl (x = 1) as an example, 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ (2.4254 g) was dispersed in 20 mL deionized water to form the solution A. Then 0.2632 mmol WO_3 (0.0610 g) was added into the solution A under continuous stirring to form the solution B. At the same time, 5 mmol KCl (0.3728 g) were dissolved in 20 mL deionized water to form the solution C. Then, the solution B and the solution C were stirred for 30 min at room temperature. After that, the solution C was added into solution B drop by drop with strongly stirring. Afterwards, 2 mol/L NaOH was dropped into the resulting suspension solution to adjust the pH value to 7.0 under strongly stirring for another 30 min. Finally, the suspension solution was transferred into a 50 mL of stainless steel tank with an inner Teflon-lined. The temperature of the suspension solution maintained at 160 °C for 12 h before cooling them naturally to room temperature. The product was washed with distilled water for several times, collected and dried at 60 °C. Similarly, a series of WO_3-$BiOCl_xBr_{1-x}$ (x = 0, 0.25, 0.5, 0.75 and 1) composites with 2% WO_3-$BiOCl_xBr_{1-x}$, 5% WO_3-$BiOCl_xBr_{1-x}$ and 10% WO_3-$BiOCl_xBr_{1-x}$ were successfully synthesized in the same way by changing the amount of $Bi(NO_3)_3{\cdot}5H_2O$, KCl, KBr and WO_3 according to the mol ratios and the percentage.

For the sake of comparison, the pure $BiOCl_xBr_{1-x}$ solid solutions were also synthesized. First of all, 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ (2.4254 g) was dispersed in 20 mL distilled water and the stoichiometric amounts of KBr and KCl also got dissolved in 20 mL distilled water, respectively. Afterwards, synthesis of $BiOCl_xBr_{1-x}$ solid solutions follows the similar procedure except that the WO_3 was not added into suspension solution. Finally, all the as-obtained products were dried at 60 °C for further characterization.

2.2. Characterization

The phase compositions of the WO_3-$BiOCl_xBr_{1-x}$ heterojunction were measured by X-ray diffraction (XRD) researches using an X-ray diffractometer (Thermo ARL SCINTAG X'TRA) equipped with Cu Ka radiation (λ = 0.154056 nm) under 40 kV and 40 mA, and the 2θ ranging from 20° to 70°. The morphologies of the obtained samples were analyzed by a Hitachi S-4700 SEM which the scanning voltage was 15 kV. The TEM and HRTEM images were measured over Tecnai G2 F30, which the acceleration voltage was 200 kV. Chemical compositions of as-prepared products were characterized using Energy-dispersive X-ray detector (EDS, Thermo Noran VANTAG-ESI). A Lambda 850 UV–vis spectrophotometer was used for products, in which the $BaSO_4$ was acted as a reference. The electrochemical workstation (CHI-660C, China) with a conventional three-electrode chemical cell was used to measure the photocurrent of samples. ITO glass coupled with the as-synthesized samples (0.1 mg) worked as the working electrode. A saturated Ag–AgCl electrode and a platinum wire were served as the reference electrode and counter, respectively. The 0.1 M Na_2SO_4 aqueous liquor was used as electrolyte.

2.3. Photocatalytic experiments

In order to evaluate the photocatalytic activities of the as-prepared samples, the first step was taken 0.1 g of the fabricated sample to disperse in 200 mL RhB solution (2×10^{-5} mol/L) or methyl orange (MO) solution through continuously stirring for 30 min in a dark place to guarantee the adsorption-desorption equilibrium between the sample and RhB (MO) dye. The concentration of MO over sample was 10 mg/L. Then the as-prepared products above were illuminated by a PLS-SXE300 xenon lamp with a 420 nm cut off filter in each experiment. At every interval of 3 min, took sample from the suspension followed by centrifugation (7000 rpm, 3 min) in order to remove the catalyst powders. Finally, the RhB (MO) concentration was evaluated by measuring the maximum absorbance at 553 nm with a UV759S UV–Vis spectrophotometer.

3. Results and discussion

The crystal structure and the composition of the as-prepared samples are characterized by XRD in Fig. 1. The typical XRD patterns of the as-prepared BiOCl, $BiOCl_{0.75}Br_{0.25}$, $BiOCl_{0.5}Br_{0.5}$, $BiOCl_{0.25}Br_{0.75}$ and BiOBr solid solutions are showed in Fig. 1a. The diffraction patterns of products for x = 1 can be indexed to the standard card of tetragonal (*P4/nmm*) for pure BiOCl (JCPDS No. 06–0249), the XRD patterns for x = 0 can be indexed as structure of pure BiOBr (JCPDS No. 09–0393), individually. It is shown that the angle of $BiOCl_xBr_{1-x}$ diffraction peaks shifted to a smaller angle sequentially with the increasing amount of Br, which is closely connected to the radius of Br^- ions is bigger than that of Cl^- ions (0.196 versus 0.181 nm). A similar phenomenon has also been reported [8–10]. The diffraction peaks shift of $BiOCl_xBr_{1-x}$ in the XRD patterns imply that there is no physical mixture compound of BiOCl and BiOBr in the formation process, but the $BiOCl_xBr_{1-x}$ solid solutions. The average crystallite size can be calculated by using the Scherrer equation ($D = K\lambda/\beta\cos\theta$, where D, λ, β and θ are crystallite size, X-ray wavelength, full width at half-maximum intensity in radians and Bragg angle, respectively).