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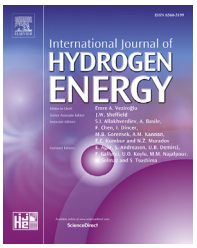

Enhanced photocatalytic H_2 production activity of Ag-doped Bi_2WO_6-graphene based photocatalysts

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ABSTRACT

Ag-doped Bi_2WO_6-graphene based photocatalysts were found to exhibit hydrogen production activity. The performance of Bi_2WO_6-graphene based photocatalysts were investigated and optimized in this study. The activity can be further improved by Ag-doping. The morphology, surface chemistry, and phase structure of the photocatalysts were investigated by Field emission scanning electron microscopy, Transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectra, and X-ray diffraction. UV–vis diffuse reflectance spectroscopy and zeta potential were measured to study the optical properties, bandgap and dispersion stability of the photocatalysts. The effects of forming Bi_2WO_6-graphene contact and Ag doping on the light absorption, band gap, dispersion stability, and photocatalytic H_2 production performance of the composite photocatalysts were evaluated. The improved photocatalytic performance is mainly owing to the Ag doping and high electrical conductivity of graphene.

Introduction

Bismuth-based nanomaterials, such as Bi_2WO_6, $BiVO_4$, BiOI, and BiOBr, were considered as potential photocatalysts with good photocatalytic activity [1–4]. The direct band gap of Bi_2WO_6 is 2.75 eV. Most of the Bi_2WO_6 related literatures were studied for the photocatalytic decomposition of pollutant or toxic waste [5–7]. However, it was reported that the performance of pristine Bi_2WO_6 photocatalyst was limited because of its fast charge recombination and low efficiency of light absorption [8,9]. Recombination of the photogenerated charge carriers can occur quickly and hinder the photocatalytic reaction.

In order to enhance the photocatalytic activity of the photocatalysts, some methods including doping [10], supporting by conductive substrate [11], loading metal [12], coupling with cocatalysts [13–15] have been carried out to improve the charge separation of photogenerated carriers. Introducing dopant in photocatalysts is a useful method to separate the photogenerated charge carriers. Introducing transition metal dopant can effectively change the electronic and optical properties of the host photocatalyst [16]. Donkova et al. found that introducing Cu dopant in ZnO resulted in the shift of absorption edge of ZnO, and hence changing the activity of photocatalyst [17]. Doping of photocatalyst can lead to a decrease in the band gap. It was reported that doping lead to an improved photocatalytic activity because of band-gap narrowing by creating dopant energy levels below the conduction band [18,19].

To improve the performance of photocatalysts, photogenerated electron-hole pairs should separate and migrate toward the photocatalyst surface and react with the reactants

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[20]. Incorporation of conductive carbon-based nanomaterials, such as graphene oxide, graphene, and carbon nanotube, can effectively increase the photocatalytic activity of the composite photocatalysts [21]. Graphene possesses high electrical conductivity, fast electron mobility, and a lot of adsorption sites on its surface. Graphene has been utilized in many fields, including sensors, electronics, and energy storage [22,23]. Composite photocatalysts coupled with graphene were reported to exhibit improved photocatalytic activity [24–27]. Yu et al. [28] reported the fabrication of graphene oxide-wrapped Bi_2WO_6 microspheres. The photocatalytic degradation activity of the Bi_2WO_6/graphene oxide (GO) photocatalyst was enhanced because of the rapid charge separation by wrapping with GO. Zhou et al. [29] studied the effect of graphene on the band structure and interfacial interaction of the Bi_2WO_6/graphene photocatalysts. The photocatalysts had better activity for the oxidation of NO, higher selectivity for forming ionic species, and larger photocurrent density than pristine Bi_2WO_6. Zhu et al. [30] developed a graphene–Bi_2WO_6 composite photocatalyst with high photocatalytic activity. The incorporated graphene can lead to not only decreased conduction band potential, but also a more negative reduction potential than H^+/H_2.

Ag-doped Bi_2WO_6 has been reported to act as photocatalyst for the degradation of hazardous materials, such as photocatalytic degradation of RhB dye and photocatalytic disinfection of *E. coli* [31–33]. Not all the photocatalysts possess both the activity for the degradation of pollutant and photocatalytic H_2 production. In this study, Bi_2WO_6-graphene based photocatalysts are found to exhibit photocatalytic hydrogen production activity. The effects of forming Bi_2WO_6-graphene contact and Ag doping on the light absorption, band gap, dispersion stability, and photocatalytic H_2 production performance and stability of the composite photocatalysts were investigated.

Experimental

Preparation of photocatalysts

Bi_2WO_6 photocatalyst

$Bi(NO_3)_3 \cdot 5H_2O$ (0.73 g) was dissolved in ethanol (20 mL). 0.25 g of $Na_2WO_4 \cdot 2H2O$ was dissolved in ethanol (20 mL). After mixing these two solutions, the mixture was transferred into a 100 mL autoclave with a PTEE container inside, which was heated at 160 °C for 24 h. After cooling, the precipitate was washed by ethanol and distilled water, and dried. Then, it was calcinated at 450 °C for 3 h to obtain the Bi_2WO_6 photocatalyst.

Bi_2WO_6/graphene photocatalyst

Bi_2WO_6 photocatalyst (0.1 g) was dispersed in 10 mL methanol. Certain amount of graphene was added to above solution. The dispersion mixture was ultrasonicated and stirred for 30 min at room temperature. The obtained samples were centrifuged. The precipitate was collected and dried to prepare the Bi_2WO_6/graphene photocatalyst.

Ag-doped Bi_2WO_6 photocatalyst

In a typical procedure, $Bi(NO_3)_3 \cdot 5H_2O$ (0.73 g) was dissolved in ethanol (20 mL). 0.25 g of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 20 mL ethanol. After mixing these two solutions, $AgNO_3$ was added into the solution and stirred. The mixture was transferred to a 100 mL autoclave with a PTEE container inside, which was kept at 160 °C for 24 h. Then, the sample was washed with ethanol and water. After drying, it was calcinated at 450 °C for 3 h to obtain Ag-doped Bi_2WO_6 photocatalyst.

Ag-doped Bi_2WO_6/graphene photocatalyst

In a typical procedure, 0.1 g of Ag-doped Bi_2WO_6 photocatalyst and certain amount of graphene were dispersed in 10 mL methanol. After centrifugation, the precipitate was collected and dried to obtain the Ag-doped Bi_2WO_6/graphene photocatalyst.

Nomenclature

The Bi_2WO_6/graphene photocatalysts were denoted as BGy. B and G represent Bi_2WO_6 and incoration of graphene, respectively. y means the weight ratio of graphene/Bi_2WO_6 is y%. The Ag-doped Bi_2WO_6/graphene photocatalysts were named as AxBGy. A, B, and G mean Ag doped sample, Bi_2WO_6, and incoration of graphene, respectively. x indicates the concentration of the $AgNO_3$ precursor is x mM. y means the weight ratio of graphene/Ag-doped Bi_2WO_6 is y%. The Ag-doped Bi_2WO_6 photocatalysts were denoted as AxB.

For example, BG1.5 means Bi_2WO_6/graphene photocatalyst with 1.5 wt% graphene. A2BG1.5 represents Ag-doped Bi_2WO_6/graphene photocatalyst with 1.5 wt% graphene and the concentration of the $AgNO_3$ precursor is 2 mM.

Catalyst characterization

X-ray photoelectron spectra (XPS) measurements were performed using a VGESCA scientific theta probe spectrometer. Transmission electron microscopy (TEM) images were monitored using a JEM-2010 electron microscope. The structures of the photocatalysts were recorded by a X-ray diffractometer (XRD, MACSCIENCE MXP3), scanning over 10°–80° two theta. The surface morphologies of the photocatalysts were monitored through a field-emission scanning electron microscope (FESEM, HITACHI S-4800). The diffuse reflection spectroscopy (DRS) of the photocatalyst was determined with a spectrophotometer (JASCO V-650). Raman spectra were measured by a Raman spectrometer (Tokyo Instruments Nanofinder 300) with 632.8 nm wavelength He–Ne laser and 488 nm semiconductor laser.

The zeta potential was measured by analyzing the dispersion using the NanoBrook 90Plus PALS (Brookhaven, USA). The dispersion was prepared by mixing photocatalyst in sacrificial aqueous solution. The pH values of the suspensions were adjusted with hydrochloride acid and sodium hydroxide by an automatic titrator. The zeta potential tests were performed by ZS Malvern Zetasizer. The dispersion stability of the photocatalyst was evaluated by the sedimentation test. 0.01 g photocatalyst was dispersed in 2 mL of aqueous sacrificial solution and stirred. Then, the stirring was stopped. Their dispersion stability can be evaluated by monitoring the photos of the photocatalyst dispersions at different time.

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