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Preparation of perovskites $PbBiO_2I/PbO$ exhibiting visible-light photocatalytic activity

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ABSTRACT

The first synthetic study on $PbBiO_2I/PbO$ nanocomposite preparation using a controlled hydrothermal method is reported. The morphologies and composition of the samples are controlled by adjusting some parameters, including reaction pH, Pb/Bi molar ratio, and temperature. All the samples are characterized by XRD, TEM, XPS, SEM-EDS, PL, BET, EPR, and UV–vis-DRS. The photodegradation activities are evaluated against the de-colorization of crystal violet (CV) and 2-hydroxybenzoic acid (2-HBA) in aqueous solution under visible light illumination. In particular, the catalytic performance illustrates the best reaction rate constant $1.159 \times 10^{-1}\,h^{-1}$ once $PbBiO_2I/PbO$ is used as the photocatalyst for the degradation of CV; which is 3 and 20 times higher than the reaction rate constants of $PbBiO_2I$ and PbO being the photocatalysts, respectively. This study reveals that $PbBiO_2I/PbO$ can be used for repressing the recombination of photo-generated electron-hole pairs and contribute to the enhanced photocatalytic activity of semiconductors in the visible-light-driven catalysis. The possible photocatalytic degradation mechanism is studied by using different active species through EPR and adding suitable scavengers. When being irradiated, two major active species, O_2^- and $^1O_2$, and a minor active species, h^+, can be produced for the CV degradation.

1. Introduction

The elimination of toxic chemicals from wastewater has become one of the most crucial aspects of contemporary pollution-control methods because of the hazardous effects of these chemicals on living beings and the environment. In face of an increasingly serious environmental pollution and energy crunch, photocatalysis, as a suitable technology, plays an important role in the degradation of pollutants and solar energy conversion [1,2]. For the practical applications of photocatalysis, an environmentally powerful and cheap photocatalyst is regarded as an important component [3]. CV, a cationic triphenylmethane dye, is found the use as colorants in industry and as antimicrobial agents [4]. However, great trouble about the thyroid peroxidase-catalyzed oxidation of the triphenylmethane class of dyes is arisen because the reactions might produce various *N*-de-alkylated primary and secondary aromatic amines, with the structures similar to aromatic amine carcinogens [5]. Photocatalytic degradation of CV has been studied using several systems to generate active species, including heterojunctions $BiOI/g\text{-}C_3N_4$ [6], BiOI/GO [7], $SrFeO_{3\text{-}x}/g\text{-}C_3N_4$ [8], BiOCl/BiOBr [9], $BiOBr/PbBiO_2Br$ [10], etc. and pure semiconductors $Bi_xAg_yO_z$ [11], Bi_2WO_6 [12], TiO_2 [13], etc.

Recently, Bi-based oxyhalides have drawn people's attention to their potential application as novel photocatalysts owing to their unique layered structures and high chemical stabilities [13,14,15]. Bi-based layered structure compounds, within Aurivillius family such as BiOX (X = Cl, Br, I) [9,16–18], Bi_2WO_6 [19], $Bi_4Ti_3O_{12}$ [20], $BiVO_4$ [21], etc., have been extensively explored as highly efficient photo-catalysts due to their unique layered structure and high catalytic activity. It is thought that the Bi 6 s and O 2p levels can make a largely dispersed hybridized valence band, which favors the mobility of photo-generated holes and the oxidation reaction of inducing efficient separation of photo-generated electron-hole pairs and then improving the photocatalytic efficiency [22].

Many inorganic materials have modular structures, where the individual units are responsible for different functions. Sillen's phases are an adaptive structure series of oxyhalides originally investigated by Sillen et al. in the 1940′s [24]. The structures of these compounds consist of $[M_2O_2]$ layers (M = Pb, Bi, Cd, Ba, Sr) intermixed with either halogen or metal halogen layers. Two examples of these phases are $PbBiO_2I$ which consist of $[M_2O_2]$ with 2 halogens and $[M_2O_2]$ with 1 halogen layer, respectively. The Aurivillius intergrowth phases consist of perovskite blocks sandwiched between the $[Bi_2O_2]^{2+}$ slabs and can

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be described with a general formula $[Bi_2O_2]$- $A_{n-1}B_nO_{3n+1}$, where A is a large alkali, alkali-earth, rare-earth, or Pb^{2+} cation, and B is a d^0 transition metal cation, such as Nb^{5+}, W^{6+}, Ta^{5+}, or Ti^{4+} [23]. The extended Bi-based oxychlorides are the Sillen–Aurivillius intergrowth $[Bi_2O_2][A_{n-1}B_nO_{3n+1}][Bi_2O_2][Cl_m]$ [13,15], where the Aurivillius family $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$ is inter-grown with the structure-similarity of Sillen family $[Bi_2O_2][Cl_m]$, X_m], where n is the number of perovskite layers and m is the number of halide layers, such as Bi_4TaO_8Cl, Bi_4NbO_8Cl, etc. These oxychloride compounds are of interest as selective oxidation catalysts [13], ferroelectric materials [15] and pigments [25].

The $[Bi_2O_2]^{2+}$ slabs with the α-PbO type structure as well as simple halide layers are effective spacers in some layered functional materials [23,26]. Previous reports mainly discussed the electronic reasons for the different photocatalytic activity of layered $PbBiO_2X$-type materials (X = Cl, Br, I) [10,27–30]. However, crystal-chemical arguments should also be taken into consideration to explain the photocatalytic properties of the compounds. A possible reason for the different catalytic activity of the oxides may be derived collectively from their crystal structures, their optic, and their redox properties. All the solid materials under discussion crystallize in a layered structure. They exhibit covalent metal oxygen layers $[PbBiO_2]^+$ separated by halide layers, which are stacked along [001]. One can assume that the crystal surface consists of metal oxygen layers, i.e., the metal atoms are expected to form the (001) surfaces [26]. In the case of bismuth compounds, the metal position was statistically occupied by lead and bismuth with the ratio 1:1 [31,32]. It was reported that the band gaps of $PbBiO_2I$ [27,33], $PbBiO_2Br$ [10,28,34,35], and $PbBiO_2Cl$ [29,36,37] were 2.39, 2.47, and 2.53 eV, respectively. It seemed that the gaps of all these semiconductors were in the visible-light range to catalyze the photocatalytic reaction.

So as to narrow the band gap (Eg) of BiOX and enhance the visible light-driven activity of the catalyst, we incorporated Pb^{2+} into $[Bi_2O_2]$ layers based on the structure of BiOX to form the derived compound of $PbBiO_2X$ [10,38]. $PbBiO_2X$ is supposed to show a narrower Eg than BiOX. Because the contribution of Pb $6s^2$ orbitals occupy higher energy states at the valence band maximum (VBM), and the contribution of Pb 6p orbitals occupy lower energy states at the conduction band minimum (CBM). The hybridized states of VBM and CBM can decrease the effective masses of holes and electrons, respectively, to favor a longer traveling distance for excited carriers. Just as expected, the experimentally evaluated E_g of $PbBiO_2X$ (X = Cl, Br, I; E_g = 2.53, 2.40, 2.29 eV) is much narrower than that of nano-metered BiOX (E_g = 3.38, 2.80, 2.57 eV) [6,10,30,38]. Then, the visible-light-response photocatalytic activity of the material is also higher than that of BiOX. In our judgment, the higher activity for photocatalytic degradation of dyes on $PbBiO_2X$ is not only attributed to the layered structure but also the hybridized band structure.

The development of visible-light-driven photocatalysts, as an alternative in toxic wastewater treatment, has recently obtained considerable attention. An effective and simple topic to improve the photocatalytic activity of a photocatalyst is the incorporation of a composite, because a composite has great potential for tuning the wished electronic properties of photocatalysts and efficiently separating the photogenerated electron–hole pairs. So far, a composite concerned $PbBiO_2Br$, such as $PbBiO_2Br/NbSe_2$ [39], $PbBiO_2Cl/BiOCl$ [38], and $PbBiO_2Br/BiOBr$ [10], has been reported and exhibited the enhanced photocatalytic activity.

Herein, we report another novel layered photocatalyst $PbBiO_2I$/PbO. To the best of our knowledge, nanocomposite semiconductors consisting of $PbBiO_2I$ and PbO have not yet been reported in the literature. This is the first report that $PbBiO_2I$/PbO composites are synthesized by a template-free hydrothermal method through degrading CV and 2-HBA in aqueous solution under visible-light irradiation. The photocatalytic efficiency of $PbBiO_2I$/PbO composites are further discussed.

2. Experimental details

2.1. Materials

CV dye (TCI), 2-hydroxybenzoic acid (salicylic acid), $Pb(NO_3)_2\cdot H_2O$, ammonium oxalate (Osaka), $Bi(NO_3)_3\cdot 5H_2O$ (Katayama), *p*-benzoquinone (Alfa aesar), sodium azide (Sigma-Aldrich), and isopropanol (Merck) were purchased and used without further purification. Reagent-grade HNO_3, NaOH, CH_3COONH_4, and HPLC-grade methanol were obtained from Merck.

2.2. Instruments and analytical methods

The X-ray diffraction (XRD) patterns were recorded on a MAC Science MXP18 equipped with Cu-Kα radiation, operating at 40 kV and 80 mA. The field-emission transmission electron microscopy (FE-TEM) images, selected area electron diffraction (SAED) patterns, high resolution transmission electron microscopy (HRTEM) images, and energy-dispersive X-ray spectra (EDS) were obtained using JEOL-2010 with an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) specific surface areas of the samples (S_{BET}) were measured with an automated system (Micrometrics Gemini) using nitrogen gas as the adsorbate at liquid nitrogen temperature. Field emission scanning electron microscopy-electron dispersive X-ray spectroscopy (FE-SEM-EDS) measurements were carried out using a JEOL JSM-7401F at an acceleration voltage of 15 kV. The Ultra-violet photoelectron spectroscopy (UPS) measurements were performed using ULVAC-PHI XPS, PHI Quantera SXM. UPS was used to measure the work function using He I emission (21.2 eV, ∼50 W) as the source of ultra-violet-light, and the take-off angle was 90°. Specimens were biased at −7.5 V DC to give low-energy secondary electrons extra energy to overcome the work function of the detector (4.4 eV) for acquiring the onset of secondary electrons. The work function of specimens was extracted from the UPS data using the width of the spectra. High resolution X-ray photoelectron spectroscopy (HRXPS) measurements were carried out using ULVAC-PHI. Waters ZQ LC/MS system, equipped with a binary pump, a photodiode array detector, an autosampler, and a micromass detector, was used for separation and identification. The amount of residual dye at each reaction cycle was determined by HPLC–MS. The HPLC-PDA-ESI–MS system was composed a Waters 1525 binary pump, a 2998 photodiode-array-detector, and a 717 plus auto-sampler. Besides, a ZQ-2000 micro-mass detector and an Atlantis ™ dC18 column (250 mm × 4.6 mm i.d., dp = 5 μm) were used for separation and identification. The column effluent was introduced into the ESI source of the mass spectrometer.

The amount of residual dye at each reaction cycle was determined by HPLC-PDA-ESI–MS. The analysis of organic intermediates was accomplished by HPLC-PDA-ESI–MS after the readjustment of chromatographic conditions in order to make the mobile phase (Solvent A and B) compatible with the working conditions of the mass spectrometer. Solvent A was 25 mM aqueous ammonium acetate buffer (pH 6.9), and solvent B was methanol. LC was carried out on an Atlantis ™ dC18 column (250 mm × 4.6 mm i.d., dp = 5 μm). The mobile phase flow rate was 1.0 mL/min. A linear gradient was run as follows: t = 0, A = 95, B = 5; t = 20, A = 50, B = 50; t = 35–40, A = 10, B = 90; t = 45, A = 95, B = 5. The column effluent was introduced into the ESI source of the mass spectrometer. The quadruple mass spectrometer equipped with an ESI interface with heated nebulizer probe at 350 °C was used with an ion source temperature of 80 °C. ESI was carried out with the vaporizer at 350 °C and nitrogen as sheath (80 psi) and auxiliary (20 psi) gas to assist with the preliminary nebulization and to initiate the ionization process. A discharge current of 5 μA was applied. Tube lens and capillary voltage were optimized for the maximum response during the perfusion of the CV standard.