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Novel synthesis of $PbBiO_2Cl$/BiOCl nanocomposite with enhanced visible-driven-light photocatalytic activity

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ABSTRACT

The first synthetic study on $PbBiO_2Cl$/BiOCl nanocomposite preparation using a controlled hydrothermal method is reported. The composition and morphologies of the samples could be controlled by adjusting some growth parameters, including reaction pH, Pb/Bi molar ratio, and temperature. All the samples are characterized by XRD, TEM, XPS, SEM-EDS, FT-IR, 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 $2.763 \times 10^{-1}\ h^{-1}$ once $PbBiO_2Cl$/BiOCl is used as the photocatalyst for the degradation of CV; which is 3.01 and 2.12 times higher than the reaction rate constant of $PbBiO_2Cl$ and BiOCl being the photocatalysts, respectively. This study reveals that $PbBiO_2Cl$/BiOCl 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. The results reveal that the reactive O_2^{-}, OH, h^{+}, $^{1}O_2$ play the major roles in 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 an important component [3]. CV, a cationic triphenylmethane dye, was 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 was 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 was studied using several systems to generate active species, including heterojunctions BiOI/g-C_3N_4 [6], BiOI/GO [7], $SrFeO_{3-x}$/g-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. As shown in Table 1, mixed oxide based photocatalysts have obtained remarkable interests in recent years because of their suitable band gaps, stability, and relatively superior photocatalytic activities. It is found that the mixed oxide based photocatalysts shows higher photocatalytic activities than pure metal oxide based photocatalysts for the photocatalytic degradation of remediation [8–10,12–15].

During the last two decades, besides the focused work on TiO_2 modifications, many efforts were made to develop other novel efficient photocatalysts [16–19]. Recently, Bi-based oxychlorides have drawn our attentions to their potential application as novel photocatalysts owing to their unique layered structures and high chemical stabilities [13,20,21]. The original Bi-based oxychlordie is the Sillén family expressed by $[M_2O_2][Cl_m]$ (m = 1–3) [22,23] where bismuth oxide-based fluorite-like layers, $[M_2O_2]$, are inter-grown with single, double, or triple chlorine layers to construct such compositions as $PbBiO_2Cl$, BiOCl, et al. Sillen's phases are an adaptive structure series of oxyhalides originally investigated by Sillen and co-workers 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

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Table 1
Photocatalytic properties of mixed oxide based photocatalysts for the degradation of remediation under visible light irradiation.

Mixed oxide based photocatalyst	Mass fraction of mixed oxide (%)	Parameters of photocatalytic experiments	Photocatalytic activity	Reference Photocatalyst/ photocatalytic activity	Enhancement factor	Reference
$SrFeO_{3-x}/g\text{-}C_3N_4$	4	Crystal violet Chloramphenicol	95% decomposition in 24 h 97% decomposition in 24 h	$g\text{-}C_3N_4$: 21% $SrFeO_{3-x}$: 1%	– 4.77 4.8	[8]
$Bi_3O_4Cl/Bi_{24}O_{31}Br_{10}$	–	Crystal violet	99% in 48 h	–	–	[9]
$PbBiO_2Br/BiOBr$	–	Crystal violet	98% in 72 h.	$PbBiO_2Br$: 33% BiOBr: 50%	3 2	[10]
$SrBiO_2Br$	5%	Rhodamine B	68% in 12 h.	–	– 7.3	[13]
$F\text{-}Bi_2MoO_6$	20%F	Rhodamine B	88.0% in 100 min.	Bi_2MoO_6: 30%	3.5	[15]
		Phenol	45.3% in 100 min.	Bi_2MoO_6: 11.2%	8.9	
		Bisphenol A	74.7% in 100 min.	Bi_2MoO_6: 33%	3.0	
		4-Chlorophenol	33.6% in 100 min.	Bi_2MoO_6: 53%	1.9	
$PbBiO_2I$	–	Nitrobenzene	4%	–	–	[14]
Bi_2WO_6	–	Crystal violet	92.1% in 24 h	–	–	[12]

halogen layers. Two examples of these phases are BiOCl and $PbBiO_2Cl$ which consist of $[M_2O_2]$ + 2 halogen and $[M_2O_2]$ + 1 halogen layers respectively. The Aurivillius intergrowth phases consist of perovskite blocks sandwiched between the $[Bi_2O_2]^{2+}$ slabs and can 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+} [25]. The extended Bi-based oxychlorides are the Sille'n–Aurivillius intergrowth $[Bi_2O_2][A_{n-1}B_nO_{3n+1}][Bi_2O_2][Cl_m]$ [13,21] where the Aurivillius family $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$ is intergrown with the structure-similarity Sillén 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 [21] and pigments [26].

Bi-based layered structure compounds, within Aurivillius family, such as Bi_2WO_6 [27], $Bi_4Ti_3O_{12}$ [28], $BiVO_4$ [29], BiOX (X = Cl, Br, I) [9,30–32], 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, inducing efficient separation of photo-generated electron-hole pairs and then improving the photocatalytic efficiency [33]. Many inorganic materials have modular structures, where individual units are responsible for different functions. 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 [25]. Previous reports discussed mainly electronic reasons for the different photocatalytic activity of layered $PbBiO_2X$-type materials (X = Cl, Br, I) [10,14,34–36]. 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. In the case of bismuth compounds, the metal position was statistically occupied by lead and bismuth with the ratio 1:1 [37,38]. It was reported that the band gaps of $PbBiO_2I$ [14], $PbBiO_2Br$ [10,34], and $PbBiO_2Cl$ [35] 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.

Recently, the development of visible-light-driven photocatalysts has obtained considerable attention as an alternative in wastewater treatment. An effective and simple tactic to improve the photocatalytic activity of a photocatalyst is the incorporation of a heterostructure, because heterojunctions have great potential for tuning the wished electronic properties of photocatalysts and efficiently separating the photogenerated electron–hole pairs [39–41]. So far, a heterojunction concerned $PbBiO_2Br$, such as $PbBiO_2Br/BiOBr$ and $PbBiO_2Br/NbSe_2$, has been reported and exhibited the enhanced photocatalytic efficiency [10,42]. Therefore, it is feasible for $PbBiO_2Br$ being partly transformed into $NbSe_2$ via a thermodynamically favored direction through the ion exchange reaction, which allows the exchange between the component ions and the incoming species [43], to consequently obtain the $PbBiO_2Br/NbSe_2$ heterojunction.

To the best of our knowledge, nanocomposite semiconductors consisting of $PbBiO_2Cl$ and BiOCl have not yet been reported in the literature. This is the first report that $PbBiO_2Cl/BiOCl$ composites are prepared by a template-free hydrothermal method. Through degrading CV and 2-HBA in aqueous solution under visible-light irradiation, the photocatalytic activities of $PbBiO_2Cl/BiOCl$ composites are further discussed.

2. Experimental details

2.1. Materials

$Pb(NO_3)_2{\cdot}H_2O$, ammonium oxalate (Osaka), 2-hydroxybenzoic acid (salicylic acid), $Bi(NO_3)_3{\cdot}5H_2O$ (Katayama), CV dye (TCI), *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 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. 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 X-ray diffraction (XRD) patterns were recorded on a MAC Science MXP18 equipped with Cu-Kα radiation, operating at 40 kV and 80 mA. 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 Al-Kα radiation was generated at 15 kV. High resolution X-ray photoelectron spectroscopy (HRXPS)