



Highly photocatalytic active thiomolybdate $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters/BiOBr nanocomposite with enhanced sulfur tolerance



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ARTICLE INFO

Article history:

Received 11 August 2015

Received in revised form 6 October 2015

Accepted 11 October 2015

Available online 23 October 2015

Keywords:

Photocatalyst

$\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr

$[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters

Sulfur tolerant

ABSTRACT

The sulfur tolerant $\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr nanocomposite photocatalysts were facilely fabricated by a hydrothermal method. The characterizations including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDS), UV–vis diffuse reflection spectroscopy (DRS) and photoluminescence (PL) investigate the structures, elemental composition, morphologies and photocatalytic activities of $\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr nanocomposite. The 5.0 wt% $\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr composite sample showed highest visible-light-driven photocatalytic activity for decolorization of organic dyes including Rhodamine B (RhB) and sulfur containing methylene blue (MB). The decolorization of RhB was dominated by the direct hole and the generated $\cdot\text{O}_2^-$ radicals oxidation process. Our 5.0 wt% $\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr nanocomposite exhibited comparable photocatalytic activity as the state of art 1 wt% BiOBr/Pt composite for photocatalytic decolorization of RhB. The 5.0 wt% $\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr composite possessed better sulfur resistance than 1.0 wt% Pt/BiOBr composite.

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1. Introduction

Semiconductor photocatalysis technique, a “green” method for environmental remediation and the conversion of solar energy into chemical energy, has attracted tremendous research attention [1–3]. Unfortunately, the classical and most widely used photocatalysts of TiO_2 can only utilize the UV light, which covers only 4% of the whole solar spectrum. Many different techniques and novel photocatalysts have been developed to extend their activities to the visible light. Recently, an important class of ternary compounds of bismuth oxyhalides (BiOX , $X = \text{Cl}, \text{Br}, \text{I}$) have been widely investigated due to their excellent visible light photocatalytic activities [4–14]. Among these BiOX photocatalysts, BiOBr is of great research interest owing to its stability, suitable band gap and superior photocatalytic abilities. BiOBr has a layered structure of $[\text{Bi}_2\text{O}_2]$ slabs intercalated with double slabs of bromine atoms. Furthermore, BiOBr possesses indirect-transition band-gap (2.75 eV), leading to a better photocatalytic oxidation and reduction performance under visible light irradiation due to its longer lifetime charge carriers [4,15–17]. Until now, BiOBr has been widely utilized in photocatalytic applications such as photodegradation of

dyes, nitrogen oxide and microcystin-LR [6,12,18,19], and so many different methods have been reported to prepare various BiOBr micro/nanostructures [20–27]. Co-catalyst is another most popular approach to enhance photocatalysts’ activities by promote charge separation and charge transfer. Platinum and other noble metals are widely adopted as co-catalyst for enhancing photocatalysis due to their high activities with negligible overpotential even under high reaction rates. However, the scarcity and high cost of noble metals especially platinum limit their large scale application [28]. In addition, industrial wastewater from the dye industry usually contain considerable amounts of sulfur compound such as S^{2-} which tends to poison these noble metal co-catalysts especially platinum.

Recently, molybdenum sulfide materials (MoS_x) have emerged as one of most of popular low-cost, earth-abundant alternatives to Pt and other noble metals for their unique electronic and chemical properties [29]. The small $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters, reported by Kibsgaard et al. [28], inherently expose a significant number of active edge sites. The enhanced catalytic activity of the $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters complex is attributed to their three different types of sulfur ligands, which locate intrinsically as edge sulfur atoms. Such unique structure could potentially enable $[\text{Mo}_3\text{S}_{13}]^{2-}$ -based catalysts comparable to the best precious-metal catalysts such as platinum [28]. Besides, previous reports have demonstrate its excellent stability when used as electrocatalysts and co-catalyst [28,30–32]. In this report, we prepared the $\text{Mo}_3\text{S}_{13}^{2-}$ /BiOBr

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nanocomposites via a facile hydro-thermal method. We investigate the photodegradation of RhB under visible light irradiation catalyzed by our $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ nanocomposites in a sulfur-containing dye wastewater. The $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters prove to be a highly active and low-cost co-catalyst for BiOBr, which not only exhibit enhanced photocatalytic activity comparable to Pt but also showed much better sulfur tolerance. A photocatalytic mechanism for the $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ composites is also discussed.

2. Experimental

2.1. Chemicals

TiO_2 powders (Degussa P25, ca. 80% anatase) were used as received. Bismuth(III) nitrate pentahydrate, ethylenediamine tetraacetic acid disodium salt dihydrate (EDTA-2Na), *tert*-butanol (TBA), Rhodamine B (RhB), ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), chloroplatinic acid hexahydrate, carbon disulfide, toluene and ethanol were of analytical purity and were used as received. All of them were purchased from Sinopharm Chemical Reagent Co., Ltd. Cetyltrimethylammonium bromide (CTAB) and barium sulfate were purchased from Aladdin Industrial Corporation. Ammonium polysulfide solution was purchased from Xiya reagent.

2.2. Materials synthesis

2.2.1. Synthesis of $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters

The thiomolybdate $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}\cdot n\text{H}_2\text{O}$ ($n=0-2$) was prepared according to Kibsgaard et al. [28]. A 4.0 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dissolved in 20 mL of water in an Erlenmeyer flask. An ammonium polysulfide solution was added and the flask was covered with a watch glass. The solution was then kept on an oil bath (96°C) for five days without stirring. Dark-red crystals of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}\cdot n\text{H}_2\text{O}$ precipitated and the obtained samples were centrifuged and washed three times with distilled water and ethanol. In order to remove excess sulfur, the $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}\cdot n\text{H}_2\text{O}$ crystals were heated in hot toluene (80°C) for 3 h. Finally, the crystals were dried in air.

2.2.2. The preparation of $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ and Pt/BiOBr

1.0 mmol $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ and 2.2 mmol of cetyltrimethylammonium bromide (CTAB) were added into a 50 mL beaker, and then 20 mL deionized water and 1 mL ethanol were added followed by stirring for 20 min. Different amounts of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$ solution were added into the mixture solution and stirred for 10 min, then the solution was transferred into a 25 mL Teflon-lined autoclave and heated at 140°C for 18 h. The obtained samples were centrifuged and washed three times with distilled water and ethanol. Finally, the samples were dried at 60°C for 4 h before further characterization. The weight contents of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$ in the composite photocatalysts were 1 wt%, 3 wt%, 5 wt% and 6.5 wt%. For comparison, pure BiOBr was synthesized using the similar processes and 1 wt% Pt/BiOBr composite were synthesized according to the previous report [33]. 1 wt% Pt/ TiO_2 and 5 wt% $\text{Mo}_3\text{S}_{13}^{2-}/\text{TiO}_2$ was also prepared according to previous reports [34].

2.3. Characterization

The crystal structures of the samples were characterized by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 40 mA. The data were recorded at a scan rate of $10^\circ \text{ min}^{-1}$ in the 2θ range from 10° to 80° . The morphologies of $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ nanocomposites were carried out on a field-emission scanning electron

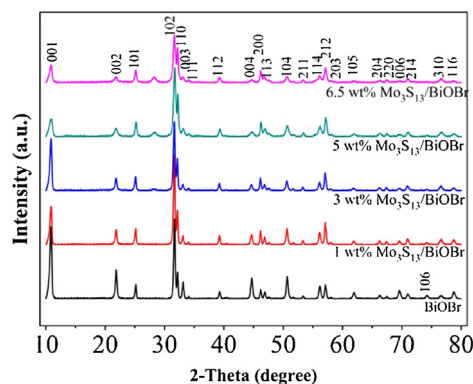


Fig. 1. XRD patterns of BiOBr and $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ composites with different mass ratios of $[\text{Mo}_3\text{S}_{13}]^{2-}$.

microscope equipped with an energy-dispersive X-ray spectroscope (EDS) operating at an acceleration voltage of 25 kV (FEI & Oxford Sirion 200 & INCA X-Act). The elemental composition of samples were determined by inductively coupled plasma optical emission spectrometer (ICP-AES, iCAP 6300, Thermo, USA). The surface analysis was investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), and the spectra calibrated to the C 1s peak at 284.6 eV. Transmission electron microscopy (TEM) micrographs were obtained using a JEOL-JEM-2010 microscope (JEOL, Japan) operating at 200 kV. Diffuse reflectance spectra (DRS) were measured in the range of 200–800 nm using a UV–vis spectrophotometer (Shimadzu UV-2450, Japan). BaSO_4 was used as the reflectance standard material. Photoluminescence (PL) measurements of the $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ composites were carried out using an excitation wavelength of 360 nm by fluorescence spectrophotometer (F-380, Tianjin Gangdong SCI. & TECH. Development Co., Ltd.). The slit width for the measurements was 10 nm. Powder samples were used without further treatment.

2.4. Photocatalytic activity evaluation

The visible light ($\lambda \geq 420 \text{ nm}$) photocatalytic activities of the composite powders were evaluated by the degradation of RhB and MB using a 150 W Halogen lamp (Cealight, CEL-TCH150) as the light source. 0.02 g photocatalysts were added into 50 mL RhB solution with a concentration 10 mg/L in the photocatalysis reactor. For the degradation of 5 mg/L MB solution, 0.05 g photocatalysts were added into 50 mL MB solution. Prior to irradiation, the solution was stirred for 30 min in the dark to reach the adsorption–desorption equilibrium of organic dyes (RhB and MB) on the surface of samples. During irradiation, approximately 3 mL of the suspension was taken periodically at different time interval, and then the photocatalyst powder and the solution were separated from solution by centrifugation. The concentration of RhB and MB was analyzed under its characteristic absorption wavelength of 553 and 664 nm on a UV–vis spectrophotometer (Agilent Cary 60, Agilent). For the regeneration test of the photocatalyst, 5 consecutive cycles of MB were tested, and the samples were washed thoroughly with DI water and dried after each cycle.

3. Results and discussion

Through a facile hydrothermal route, the assembled BiOBr nanosheets and the $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ composites with different mass ratios were synthesized. Fig. 1 shows the XRD patterns of BiOBr and the $\text{Mo}_3\text{S}_{13}^{2-}/\text{BiOBr}$ composites with different mass ratios. XRD pattern (Fig. 1) reveals that all these samples have the characteristic diffraction peaks attributing to tetragonal BiOBr

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