



## Research article

## Two-dimensional bismuth oxybromide coupled with molybdenum disulphide for enhanced dye degradation using low power energy-saving light bulb



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## ABSTRACT

In the present work, two-dimensional bismuth oxybromide (BiOBr) was synthesized and coupled with co-catalyst molybdenum disulphide (MoS<sub>2</sub>) via a simple hydrothermal process. The photoactivity of the resulting hybrid photocatalyst (MoS<sub>2</sub>/BiOBr) was evaluated under the irradiation of 15 W energy-saving light bulb at ambient condition using Reactive Black 5 (RB5) as model dye solution. The photo-degradation of RB5 by BiOBr loaded with 0.2 wt% MoS<sub>2</sub> (MoBi-2) exhibited more than 1.4 and 5.0 folds of enhancement over pristine BiOBr and titanium dioxide (Degussa, P25), respectively. The increased photocatalytic performance was a result of an efficient migration of excited electrons from BiOBr to MoS<sub>2</sub>, prolonging the electron-hole pairs recombination rate. A possible charge transfer diagram of this hybrid composite photocatalyst, and the reaction mechanism for the photodegradation of RB5 were proposed.

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### 1. Introduction

With the expansion of textile industries, the release of dye-tainted water to the environment has become one of the major sources of water pollution around the world (Liu et al., 2013). Reactive dyes, particularly azo dyes, which constitute 60–70% of all dyes produced, are the largest and most important dye class of synthetic organic dyes used in textile industry (Tunc et al., 2012, 2013). An estimated 50% of reactive dyes maybe lost in the effluent after dying process (Duman et al., 2016). Owing to their high alkalinities and strong colours, azo dyes can cause severe consequences to human health and marine life if left untreated. Numerous methods have been proposed to remove dyes from water, which include coagulation, adsorption, biodegradation and advanced oxidation process (AOP). Among the methods proposed, the more promising technology for dye removal is through AOP due

to its non-selectivity to a wide range of dyes and its ability to be carried out under relatively mild conditions. In general, AOP involves two stages: (1) the formation of a strong oxidant; and (2) the reaction of the oxidants with organic contaminants such as dyes. Simultaneously, photocatalysis has been regarded as an important route for AOP, and has been gaining incessant research interest due to the simplicity of the process. Furthermore, the photocatalytic degradation and mineralization of dyes to environmentally benign products is also one of the main reasons for the process popularity.

In recent years, there has been abundant advancement in the development of photocatalysts for organic pollution degradation (Das and Dutta, 2015; Suárez et al., 2016; Sun et al., 2015; Xu et al., 2015). Among them, by far the most researched photocatalyst for liquid and gaseous organic pollutant degradation is TiO<sub>2</sub> due to its stability and inexpensiveness. However, the main drawback of TiO<sub>2</sub> is its inability to absorb light in the visible region. Of late, bismuth oxybromide (BiOBr) has also garnered immense attention from chemists and material scientists worldwide. As one of the simplest members of the Sillén family, the unique layered structure of BiOBr which consists of alternating [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> layers and Br<sup>-</sup> layers enable

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the formation of internal static electric field (Li et al., 2014a). In addition, the highly dispersive band structures of BiOBr which are made up of charge carriers with light effective mass are beneficial for the transfer of photogenerated charge carriers (Kong et al., 2016; Shang et al., 2014). Other remarkable properties of BiOBr include its low cost, non-toxicity, high chemical and optical stability, visible light responsiveness ( $E_g = 2.8\text{--}3.0$  eV) and strong oxidation power (Li et al., 2014b, 2014c). Despite that, practical application of BiOBr is still hindered by the rapid recombination of electron-hole pairs. Thus, tremendous efforts have been devoted to enhancing its photocatalytic activity by means of coupling BiOBr with a wide range of co-catalysts, such as g-C<sub>3</sub>N<sub>4</sub> (Ye et al., 2013), TiO<sub>2</sub> (Wang et al., 2015b), CQDs (Di et al., 2016) and Cu<sub>2</sub>S quantum dots (Wang et al., 2015a). Molybdenum disulphide (MoS<sub>2</sub>) is a 2D semiconductor material comprising of hexagonal stacking of Mo atoms sandwiched between two layers of S atoms through weak Van der Waals interaction. MoS<sub>2</sub> has been largely applied in the field of photocatalysis due to its capability of harnessing a wide range of solar spectrum ( $E_g = 1.2\text{--}1.9$  eV), its stability against photocorrosion and its unique electronics and chemical properties (Chou et al., 2013; Zong et al., 2009). Owing to these properties, many researchers have reported that by introducing MoS<sub>2</sub> as co-catalyst, the photocatalytic performances of the resulting composites could be improved significantly (Li et al., 2011; Zhang et al., 2015; Zhou et al., 2013).

In the present work, we demonstrate the successful hybridisation of MoS<sub>2</sub> with 2D-BiOBr. The composite displayed high photocatalytic activity towards the photodegradation of Reactive Black 5 (RB5), despite only using a low-powered energy saving light bulb as the light source. A plausible photocatalytic mechanism for the enhanced photodegradation performance by the hybrid composite was proposed.

## 2. Experimental

### 2.1. Material synthesis

MoS<sub>2</sub> was synthesized using hydrothermal method reported elsewhere (Zhang et al., 2014). In brief, sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) and thioacetamide (C<sub>2</sub>H<sub>5</sub>NS) were used as precursors and dissolved in deionised water before transferred into a Teflon lined stainless steel autoclave. The mixture was subsequently heated at 240 °C for 24 h. Following that, the solution was left to cool to room temperature naturally. The solid precipitates were then collected and washed with deionised water.

To fabricate MoS<sub>2</sub>/BiOBr, a predetermined amount of MoS<sub>2</sub> was first added into a solution containing potassium bromide (KBr) with the aid of sonication. Following that, bismuth (III) nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) was added slowly into the mixture under vigorous stirring for 1 h. The mixtures were then transferred into a Teflon lined autoclave and heated at 160 °C for 12 h. The precipitated samples were collected and washed with deionised water and ethanol. The MoS<sub>2</sub>/BiOBr samples synthesized with 0.1, 0.2, 0.3, 0.4 and 0.5 wt% of MoS<sub>2</sub> were denoted as MoBi-x, i.e. MoBi-1, MoBi-2, MoBi-3, MoBi-4 and MoBi-5 respectively. For comparison, pristine BiOBr was synthesized following the same method but without MoS<sub>2</sub>.

### 2.2. Materials characterisation

The morphology of the as-prepared samples was analysed using field-emission scanning electron microscope (FE-SEM) (Hitachi SU8010) and transmission electron microscope (TEM) (TECNAI G2 F20) with an accelerating voltage of 200 kV. Preparation was done by suspending the samples in ethanol using bath sonicator for

10 min at 40 kHz and a few drops of the suspension solution were dropped onto silicon wafer and copper grid for FE-SEM and TEM analysis respectively. The powder X-ray diffraction (XRD) patterns of the samples were determined using Bruker D8 Discover X-Ray diffractometer with CuK<sub>α</sub> radiation ( $\lambda = 0.15406$  nm) at a scan rate of 0.02 s<sup>-1</sup>. The optical properties of the samples were determined with ultraviolet–visible (UV–Vis) spectrophotometer (Agilent Cary 100) in the range of 200–800 nm. Photoluminescence (PL) measurements were carried out using LS 55 PerkinElmer fluorescence spectrophotometer at an excitation wavelength of 320 nm. The emission spectra were scanned from 550 to 750 nm. Kubelka-Munk (KM) function and the extrapolation of the Tauc plot,  $[F(R) \times hv]^{1/2}$  vs.  $hv$  were employed to determine the optical absorption edge of the samples.

### 2.3. Photocatalytic experiments

Photodegradation of Reactive Black 5 (RB5) was carried out in a black box. 50 mg of the photocatalyst samples were suspended in 100 mL of RB5 aqueous solution with a concentration of 10 ppm. The mixture was stirred in the dark to establish RB5 absorption-desorption equilibrium for 90 min before the light was switched on. The aliquot was sampled at a 30-min interval for 3 h and analysed with a spectrophotometer (Thermo Genesys 10 UV). The light source used for this study was a commercially available household energy saving light bulb (Philips Tornado 15 W) (see Fig. 1 for light spectrum). The distance between the light source and the solution was fixed at approximately 3 cm.

### 2.4. Trapping experiments for radicals and holes

The photocatalytic mechanisms for the developed photocatalyst were investigated through the effects of holes (h<sup>+</sup>), hydroxyl (•OH) and superoxide radicals (•O<sub>2</sub><sup>-</sup>) in degradation of RB5. Several quencher species such as isopropanol, triethanolamine and benzoquinone were used in this study. The concentration of each quencher added prior to the addition of photocatalyst was 10 mM. The analysis method was similar to photocatalytic dye degradation process as described earlier.

### 2.5. Analysis of hydroxyl radicals (•OH)

In order to examine the formation of •OH radicals, terephthalic acid was used as a probe molecule under the irradiation of a light source. Terephthalic acid reacts with generated •OH radicals to form 2-hydroxyterephthalic acid that can be detected by PL at the wavelength of 425 nm. The experimental methods for this analysis were the same as photocatalytic degradation of RB5 except 5 mM of

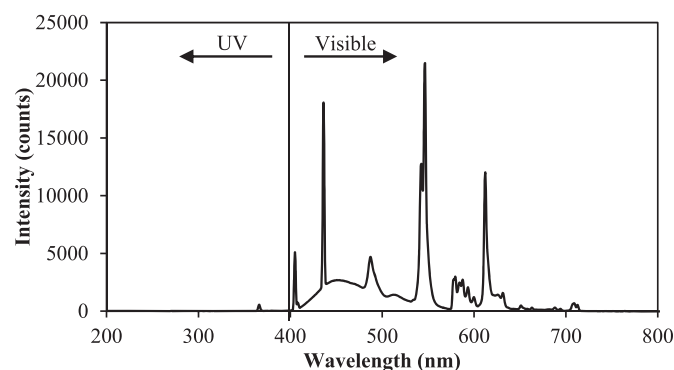


Fig. 1. Light spectrum of energy saving light bulb used for photodegradation studies.

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