Colloids and Surfaces B: Biointerfaces 161 (2018) 528–536

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Full Length Article

# Enhanced bacterial disinfection by $Bi_2MoO_6$-AgBr under visible light irradiation

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ARTICLE INFO

*Article history:*
Received 21 August 2017
Received in revised form 29 October 2017
Accepted 7 November 2017
Available online 8 November 2017

*Keywords:*
AgBr modified $Bi_2MoO_6$
Visible light irradiation
Bacterial disinfection
Photocatalysis
Active species

ABSTRACT

$Bi_2MoO_6$–AgBr hybrid photocatalyst was synthesized via a mixed solvothermal-precipitation method. The as-synthesized photocatalysts were well characterized by Powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopic (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscope (HRTEM), UV–vis diffuse reflectance spectra (DRS), as well as photoluminescence spectra (PL). The visible light driven (VLD) disinfection activity of $Bi_2MoO_6$–AgBr was tested using *Escherichia coli* as the model bacteria. Complete disinfection of $3 \times 10^6$ CFU $mL^{-1}$ viable cell density was observed in 90 min under visible light irradiation for $Bi_2MoO_6$–AgBr with the optimal AgBr amount. $Ag^+$ released from the photocatalysts did not affect the inactivation process due to the low concentration. Whereas, photo-generated holes, $H_2O_2$ and $^{\bullet}O_2^-$ were the main active species involved in the photocatalytic disinfection reaction. The presence of $O_2$ and direct contact between photocatalysts and bacterial cells were found to be indispensable for the cell inactivation. In addition, neutral and slight alkaline conditions was beneficial for the disinfection process.


## 1. Introduction

Due to the advantages of high efficiency, energy saving as well as reduced secondary pollution, photocatalysis has been considered as a promising and environmentally friendly technology to treat polluted water (such as organic matter or microbe contamination) [1–3]. Therefore, after the first report of $TiO_2$ application in water decontamination [4], great efforts have paid to develop and utilize different types of photocatalysts to treat polluted water (especially to disinfect waterborne pathogens) over past decades [5–9]. Among different types of photocatalyts, visible light active photocatalysts have drawn increasing attention due to their in-situ formation of highly reactive species under visible light irradiation [9,10]. A variety of visible light driven (VLD) photocatalysts such as Ti-based [9–11], Bi-based [1,12,13], Ag-based [14–16], natural minerals [17,18], as well as metal-free photocatalysis [19–21] have been recently fabricated to disinfect bacteria in water.

With the proper band gap (~2.7 eV) [5], $Bi_2MoO_6$, a layered Aurivillus-related oxide with sandwiched structure of perovskite $(MoO_4)^{2-}$ slabs and $(Bi_2O_2)^{2+}$ sheets [13], has been demonstrated to have good visible light absorption and could be used to degrade organic contaminants [22]. For example, Bi et al. [23] found $Bi_2MoO_6$ nanocrystals contained strong decomposition activity of Rhodamine B (RhB) under visible light irradiation. However, pure $Bi_2MoO_6$ showed relatively poor quantum yield [24] due to the fast recombination of photo-generated electron ($e^-$) and $h^+$ [22]. To improve the separation efficiency of $e^-$-$h^+$ pair, heterojunction modified with various other materials were widely used and found to be effective [5,25–27]. For instance, Liang et al. [28] found that the photocatalytic degradation of RhB was greatly enhanced by $Bi_2MoO_6$-g-$C_3N_4$ heterojunction relative to $Bi_2MoO_6$. Xu et al. [26] showed that the antimicrobial effects against *E. coli* was improved by modified $Bi_2MoO_6$ with $Bi_2O_3$ due to the improved separation of photo-generated $e^-$ and $h^+$.

Due to the excellent antibacterial capacity, silver bromide (AgBr) has been widely employed to disinfect bacteria in water [6,29,30]. Moreover, with a proper band gap (~2.6 eV), AgBr contains strong visible light absorption [15]. AgBr thus have been widely employed to modify semiconductors (via the improvement of $e^-$ and $h^+$ separation) and enhance their photocatalytic activities [7,15,30]. For example, Deng et al. [30] found that modified g-$C_3N_4$ with AgBr could significantly increase cell disinfection efficiency under visible light irradiation. Thus, combining $Bi_2MoO_6$ with AgBr is expected to improve the disinfection efficiency under visible light irradiation. However, the photocatalytic disinfection activity of the $Bi_2MoO_6$–AgBr heterojunction has not been investigated.

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https://doi.org/10.1016/j.colsurfb.2017.11.019
0927-7765/

In this work, AgBr modified $Bi_2MoO_6$ was synthesized by adsorption–deposition method. The as-synthesized photocatalysts were well characterized with using various technologies including XRD, XPS, SEM-EDX, HRTEM, DRS, and PL. The VLD disinfection activity of $Bi_2MoO_6$–AgBr against Gram-negative *Escherichia coli* (*E. coli*) was investigated. The possible photocatalytic mechanisms contributed to cell disinfection were systematically explored. The effects of pH on cell inactivation by $Bi_2MoO_6$–AgBr were also verified.

## 2. Materials and methods

### 2.1. Materials

$AgNO_3$, KBr, NaOH, HCl, NaCl, $FeCl_2{\cdot}4H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$, sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), ethanol, ethylene glycol, odium oxalate ($Na_2C_2O_4$), potassium dichromate, ammonium molybdate, bacto-yeast extract, tryptone, potassium chromate, nitroblue tetrazolium (NBT) and terephthalic acid (TA) were purchased from Sinopharm Corporation Ltd. (Shanghai, China). KI, 4-hydroxy-2,2,6,6-tetramet-hylpiperidinyloxy (TEMPOL) and isopropanol (IPA) were purchased from Sigma-Aldich Chemical Co. (St Louis, MO). All the chemicals were analytical grade and used without further purification.

### 2.2. Synthesis and characterization of $Bi_2MoO_6$-AgBr

$Bi_2MoO_6$ was synthesized by a mixed solvothermal method. In detail, 1.94 g $Bi(NO_3)_3{\cdot}5H_2O$ was completely dissolved in 20 mL ethylene glycol, and then 0.484 g $Na_2MoO_4{\cdot}2H_2O$ was added into the solution. Subsequently, the solution was sonicated to form clear solution and stirred for 30 min. After that, 60 mL absolute ethanol was added and then stirred for another 30 min. The resultant mixture was sealed in a 100 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 15 h. The yellow precipitate was filtered and washed with ethanol and deionized water for three times, respectively, and then dried at 60 °C for 12 h. Finally, the solids were calcined at 400 °C for 1.5 h to remove the organic impurities.

$Bi_2MoO_6$-AgBr was synthesized by adsorption–deposition method. In a typical experiment, 30 mg $AgNO_3$ was dispersed in 100 mL ethylene glycol, and 600 mg of as-synthesized $Bi_2MoO_6$ was then added. Subsequently, the mixture was sonicated for 10 min and stirred for 1 h at room temperature (25 °C) under dark condition to form solution A. Solution B was obtained by dissolving 21 mg KBr in 20 mL ethylene glycol. The solution B was then dropwise added into solution A with continuous stirring. After that, the mixture was further stirred for 2 h and the products were collected by filtration, washed with ethanol and deionized water for at least three times. Finally, AgBr modified $Bi_2MoO_6$ with 5% silver (BA5) was collected after being dried for 24 h at 60 °C. Composites with different contents of AgBr (denoted as BAx, x = 5, 10, 15, 20) were also prepared according to the same procedure with different dosage of $AgNO_3$ and KBr. Pure AgBr was also prepared via precipitation method in ethylene glycol.

To characterize the structure, constituent and morphology of the as-synthesized photocatalysts, different techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and high resolution transmission electron microscope (HRTEM) were employed. In addition, the UV–vis diffuse reflectance spectra (DRS) and Photoluminescence (PL) spectra were also employed to characterize the optical properties. The detailed information could be found in the Supplementary Information.

### 2.3. Bacteria preparation

*E. coli* ATCC15597 was employed as the model cells in present study. The bacterial cells were cultivated in thermostatic incubator at 37 °C with a shaking speed of 200 rpm for 16 h by using Luria Broth (LB) growth medium (10 g/L tryptone, 5 g/L bacto-yeast extract, and 10 g/L NaCl) as growth media. The cells were harvested by centrifugation (5000 × *g* for 8 min) and washed with proper sterilized physiological saline (0.9% of NaCl at pH 7.0) to remove the residual growth medium for three times. Finally, the harvested cells were re-suspended in certain amount of sterilized physiological saline solutions to yield the viable cell density of the stock suspension around $3 \times 10^8$ colony forming unit per mL (CFU $mL^{-1}$).

### 2.4. Disinfection experiments

A Xenon arc lamp (300 W, CEL-HXF300, Beijing Jin Yuan Technology Co.) was used as light source in the photocatalytic disinfection experiments and a 100 mL double wall beaker was chosen as the reactor. The light intensity in the center of the reaction suspension was $90 \pm 2$ mW/$cm^2$ according to a solar power meter (TM-207, Tenmars Electronics Co.). The schematic diagram of the photocatalytic experimental set-up was provided in Fig. S1 and the irradiance spectrum of the arc lamp was given in Fig. S2. During the experiments, the suspension of bacterial cells and photocatalysts were introduced into a double wall beaker. To ensure a constant temperature of 25.0 °C, a circulating cooling water bath was employed at outer layer of the reactor to remove the heat from the light.

Prior to the experiments, all glass apparatuses utilized were sterilized by an autoclave at 121 °C for 20 min. In a typical disinfection experiment, 6 mg $Bi_2MoO_6$-AgBr was added into 49.5 mL sterilized deionized water, and 0.5 mL of the bacterial stock solution was added after complete mixture. The initial viable cell concentration was about $3 \times 10^6$ CFU $mL^{-1}$. The cell suspension was stirred with a magnetic stirrer throughout the duration of experiment. 0.5 mL of the water samples were collected at different time intervals and then serially diluted with sterilized deionized water to yield the viable cell density. Details of viable cell determination could be found in the Supplementary Information. To make comparison, disinfection experiments were also conducted under dark condition. Experiments without $Bi_2MoO_6$-AgBr under visible light irradiation were also conducted as blank control. Three parallel experiments were conducted for each set of experiments.

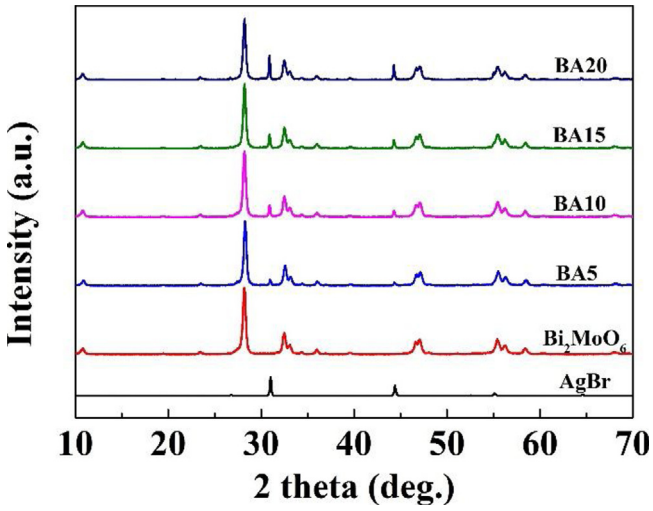


**Fig. 1.** XRD patterns of AgBr, $Bi_2MoO_6$ and $Bi_2MoO_6$-AgBr (BAx: x = 5, 10, 15, 20).