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# Microwave-assisted synthesis of bismuth oxybromochloride nanoflakes for visible light photodegradation of pollutants

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ABSTRACT

$BiOBr_xCl_{1-x}$ ($0<x<1$) nanoflakes with lateral dimensions of ~1 μm and thickness of < 100 nm were synthesized using bismuth nitrate pentahydrate, potassium bromide and sodium chloride by a microwave-assisted synthesis method. The X-ray diffraction (XRD) studies confirmed the formation of pure crystalline phase of $BiOBr_xCl_{1-x}$. The UV–visible diffuse reflectance and photoluminescence (PL) spectroscopies revealed the indirect band gap of ~2.82 eV for the bismuth oxybromochloride nanoflakes. Visible light-assisted photocatalytic studies showed that the degradation efficiency of the as-prepared $BiOBr_xCl_{1-x}$ for (100 mL of 10 mg $L^{-1}$) Rhodamine B (RhB), Natural Red 4 (N-Red) dye solutions was 98.14% and for the colorless organic pentachlorophenol (PCP) solution was 91.09% over 150 min. The possible mechanisms involved in the visible light photodegradation of the pollutants by $BiOBr_xCl_{1-x}$ photocatalyst were also discussed.



## 1. Introduction

The photoactivity of semiconductors gives rise to their significant roles in environmental pollution control and biological applications [1–3]. Accordingly, scientists have been attempting to prepare new classes of semiconductors with high photocatalytic activities to solve the problem of disposed textural dyes [4–8]. Bismuth based compounds (already applied in cosmetics, pharmaceuticals and catalyst industries [9,10]) have recently proved their efficient photocatalytic properties [11,12]. To date, different bismuth based compounds have been used in photodegradation processes such as: $BiPO_4$ [13], $(BiO)_2CO_3$ [14], $CaBiO_2Cl$ [15], $Bi_2WO_6$ [16], $Bi_{3.25}Eu_{0.75}Ti_3O_{12}$ [17], Au–$Bi_2S_3$ [18] and $Bi(Mg_{3/8}Fe_{2/8}Ti_{3/8})O_3$ [19]. Among different Bi-based photocatalysts, bismuth oxyhalides (BiOX) have captivated the interest of scientists, astoundingly [20,21]. Different strategies have been developed to improve the photocatalytic activities of bismuth oxyhalides. For instance, $Bi_2S_3$-sensitized BiOCl showed superior performance than that of single BiOCl, $Bi_2S_3$ and $TiO_2$ (P25) in RhB photodegradation [22].

As a result of similar crystal structures, BiOCl, BiOBr and BiOI compounds can form solid solutions [23]. Keller et al. [24] reported the unlimited solubility of the BiOX/BiOY (X, Y=Cl, Br, I) systems for the first time. The flower-like BiOCl/BiOBr composite showed higher photocatalytic activity than single BiOCl and BiOBr [25]. The reaction rate constant for bisphenol-A photodegradation by BiOI/BiOCl composite was reported to be more than 4 and 20 times greater than that of pure BiOI and P25, respectively [26]. In addition to bismuth oxyhalide composites (BiOX/BiOY), the alloyed compounds containing more than one type of halogen with the general formula of $BiOX_xY_{1-x}$ have also showed more enhanced performance than single bismuth oxyhalides. The flower-like nanostructure of $BiOCl_{0.875}Br_{0.125}$ synthesized by a solution method using cetyltrimethylammonium halides and acetic acid exhibited an excellent activity in RhB and pharmaceuticals photodegradation [27,28]. Furthermore, the solvothermally prepared three-dimensional I-doped BiOClBr crystals demonstrated both efficient adsorption and photocatalytic activities [29]. Na et al. reported the synthesis of $BiOBr_{0.7}Cl_{0.3}$ microspheres and investigated their adsorption/photocatalytic activity toward methylene blue, Rhodamine B and methyl orange dyes. They showed that the composition of the catalyst, structure of the dye and also the dye-photosensitization path could highly influence the dye removal process [30]. Ren et al. likewise showed that $BiOM_xR_{1-x}$ (M, R=Cl, Br, I)

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solid solutions possess superior photocatalytic activity than the pure ones (BiOM) due to the broadened range of visible light response [31].

Additionally, in the recent years, much more attention has been given to the two-dimensional nanostructured materials such as nanoflakes and nanosheets. This is because of their distinguished characteristics including their large surface areas, structural anisotropy, nearly perfect crystallinity, quantum confinement effects and thin thickness [32].

The necessity of precise control of solution acidity and the harsh synthetis conditions for the controlled growth of BiOX nanostructures have motivated the scientists to devise green and facile preparation methods such as microwave (MW) synthesis [33]. Percy LeBaron Spencer, an American inventor, accidentally discovered the heating effect of microwaves for the first time in 1945 [34] and Komarneni and Roy [35] were the beginners of microwave-assisted inorganic synthesis in liquid phase, in 1985. Microwave-assisted heating is also a valuable technique in medicinal chemistry and drug discovery applications [36]. To date, different bismuth based compounds have been prepared by microwave-assisted method such as: BiOX [37,38], $BiO_{1.84}H_{0.08}$ [39], $Bi_2Fe_4O_9$ [40], $Bi_2S_3$ [41], Bi [42], $BiVO_4$ [43], $Bi_{24}O_{31}Br_{10}$ [44] and $Bi_7O_9I_3$ [45].

In this research, contrary to all the above-mentioned researches, we have successfully prepared $BiOBr_xCl_{1-x}$ nanoflakes without the use of any templates, acid or base, organic solvents, high temperatures, solvothermal and/or sonication processes. To the best of our knowledge, this is the first report on the rapid microwave synthesis of $BiOBr_xCl_{1-x}$ nanoflakes starting from the simple initial reagents in an aqueous solution. In this research, visible light photocatalytic performance of the microwave synthesized $BiOBr_xCl_{1-x}$ nanoflakes in photodegradation of RhB, N-Red and PCP pollutants was also evaluated.

## 2. Materials and methods

### 2.1. Chemicals and synthesis

Bismuth nitrate pentahydrate (98.0%) was purchased from SAMCHUN CHEMICALS Company, Korea. All the other reagents were purchased from the Merck Company and used without further purification. RhB, N-Red and PCP [46–48] were employed as the model pollutants and deionized (DI) water was used to prepare the solutions. $Bi(NO_3)_3 \cdot 5H_2O$ (2.91 g), KBr (0.36 g) and NaCl (0.17 g) in DI water (40 mL) were used as the initial reagents to fabricate the product. The reaction was carried out in a domestic microwave instrument (Household microwave oven, Samsung GE 280, Frequency 2.45 GHz and a maximum output of 900 W) at 450 W for 23 min in a Pyrex container (open atmosphere). The microwave frequency was 2.45 GHz and the reaction temperature did not reach higher than 95 °C. Then the reaction mixture was cooled to room temperature, naturally. The microwave heating at high temperatures becomes difficult for pure water and therefore, temperature control of the reaction will be acquired by the periodic delays during synthesis [34]. Consequently, we had a 2 min delay after every 2 min microwave processing. It is proved that the uniform and high heating rates is observed at the edges rather than the center (three times faster than the center) and hence, the load is placed on the edge of the turntable [49]. Before starting the procedure, the mixture was stirred for 10 min to disperse the reagents in the solution. The product was washed with DI water for several times to purify the product from the initial reagents or possible by-products and dried at room temperature.

### 2.2. Characterization

FTIR spectrum of the product was recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 $cm^{-1}$ using KBr pellets. The powder XRD measurement was performed using a JEOL diffractometer with monochromatic Cu Kα radiation ($\lambda = 1.5418$ Å). For SEM, the samples were firstly coated by a thin Au layer using a desktop sputtering system (Nanostructured Coating Co., Iran). SEM images of the products were taken by a MIRA3/TESCAN microscope (from Czech Republic) at an accelerating voltage of 10.00 kV. The energy dispersive X-ray spectroscopy (EDS) study was done on a SAMx instrument (Producer country of hardware: England and producer country of software: France) with gold coating to discover the elements present in the product. Diffuse-reflectance spectrum (DRS) was obtained by a Shimadzu (MPC-2200) spectrophotometer. Room temperature photoluminescence spectrum was taken on a PL-Perkin-Elmer LS55 equipped with a 450 W Xe lamp as the excitation source (excitation wavelength = 200 nm). The UV–vis absorption studies were performed at room temperature in the wavelength range of 190–800 nm on a UV–vis spectrophotometer (Shimadzu UV–1700).

### 2.3. Photocatalytic test

RhB, N-Red and PCP were used as the representative pollutants to analyze the photocatalytic performance of the as-prepared $BiOBr_xCl_{1-x}$. The photodegradation experiments were carried out under the following conditions: 0.05 g of the photocatalyst was added to 100 mL pollutant aqueous solution with the initial concentration of 10 mg $L^{-1}$ at room temperature and at neutral pH. The suspensions were stirred using a magnetic stirrer for 1 h in the dark to fix an adsorption–desorption equilibrium. The concentration of the remained pollutants were measured using a UV–vis spectrophotometer at the appropriate wavelengths that correspond to the maximum absorptions of RhB (554 nm), N-Red (525 nm) and PCP (318 nm). The reaction vessel was subjected to light irradiation in the photo-reactor to carry out the photodegradation process. The visible light irradiation was supplied by a 500 W high-pressure mercury-vapor lamp ($\lambda = 546.8$ nm) that was mounted 10 cm away from the reaction solution. The mercury lamp (HWL 500 W, 225 V, E40) was purchased from the OSRAM Co. in China. The RhB and N-Red solutions were kept at room temperature during the photocatalytic process by a water bath equipped with a circulating system. At identified irradiation time intervals, the specific portions of the suspension were taken from the reaction vessel, centrifuged at 14,000 rpm for 10 min and analyzed by UV–vis spectrophotometer.

## 3. Results and discussion

### 3.1. Synthesis process

The advantages of MW synthesis method include: (1) It increases the heating rate of the synthesis mixture and hence the reaction rate [50,51]. (2) It provides a more uniform heating. (3) It changes the association between species within the synthesis mixture. (4) It can superheat the synthesis mixture. (5) Hot spots are created. (6) The minimal usage of templates and suppression of undesired phases will be possible. (7) The low operating costs and energy consumption are achievable by MW method. (8) MW heating produces better morphologies [52] and more crystalline nanoparticles at lower temperatures [53,54] than conventionally fabricated counterparts.

There are three types of heating by microwaves: (1) dielectric