Solar Photocatalytic Degradation of Trace Organic Pollutants in Water by Bi(0)-Doped Bismuth Oxyhalide Thin Films

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ABSTRACT: Herein, we demonstrate the fabrication of Bi(0)-doped bismuth oxyhalide solid solution films for the removal of trace organic pollutants (TrOPs) in water. With the advantage of a viscous AlOOH sol, very high loadings (75 wt%) of bismuth oxyhalides were embedded within the thin films and calcined at 500 °C to develop porous alumina composite coatings. Various concentrations of Bi(0) doping were tested for their photocatalytic activity. Seven TrOPs including ipromide (IPM), iohexol (IHX), iopamidol (IPM), sulamethoxazole (SMX), carbamazepine, venlafaxine, and bezafibrate (BZF) were selected for this study based on their occurrence and detection in effluents and surface waters worldwide. In all tests, with the exception of IPM, 3% Bi(0)-doped BiOCl0.875Br0.125 showed highest activity, which can be attributed to its unique, highly organized, and compact morphology besides its well-matched energy band positions. Although IPM, IHX, IPM, and SMX are susceptible to photolysis, still the photocatalytic activity significantly augmented the removal of all tested compounds. In addition, analysis of the surface charge excluded electrostatic interactions and confirmed the ion-exchange adsorption mechanism for the high degradation rate of BZF in the presence of bismuth oxyhalides.

INTRODUCTION

Rapid economic growth, intensified industrialization, and acceleration in population growth rate have led to an increase in the use of pharmaceuticals, personal care products, pesticides, and herbicides. Most of these consumed compounds are only moderately or poorly metabolized in the human body, whereas others are excreted totally intact,¹ which results in the occurrence of trace organic pollutants (TrOPs) in wastewater and in drinking water sources and consequently in agricultural crops. In addition, most pharmaceuticals resist typical microbial degradation,² and thus, both wastewater and water treatment facilities are inefficient or only partially effective in the removal of TrOPs.²c,³ These persistent pharmaceuticals and their mixtures are found in the environment at concentrations of ng L⁻¹ to μg L⁻¹ levels in secondary effluents and receiving surface waters worldwide. In this context, Rodil et al.⁴ (2012) found that 19 out of 53 different emerging pollutants present in raw wastewater were at a concentration greater than 0.1 μg L⁻¹; 11 of them persisted even at wastewater treatment plant (WWTP) effluents at a concentration greater than 0.1 μg L⁻¹. In another study, Verlicchi et al. (2012)⁵ discovered that the concentrations of contaminants can be as high as 57 μg L⁻¹ (for tramadol) in WWTP secondary effluents.

In countries where water resources are limited, there is a great demand for the recycle and reuse of industrial and domestic wastewater. As a result, TrOPs enter the aquatic environment and eventually affect drinking water sources. The acute and chronic effects of pharmaceutical compounds on the ecosystem and on human health are not yet fully understood.⁶ Consequently, there is a growing need for effective, cost-effective, and environmentally benign water treatment technologies. An emerging technology for the destruction of persistent organic pollutants is photocatalysis. Titanium oxide (TiO₂) is the most widely studied photocatalyst⁷ in photo-decomposing TrOPs in surface water⁸ and in WWTP effluents.⁹ TiO₂ is rather limited as it can utilize only a narrow portion of the solar spectrum.¹⁰

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Recently, bismuth-based compounds have shown potential as photocatalysts because of their efficacious absorbance in the UVA and visible ranges and their nontoxic nature. In fact, bismuth oxyhalides (BiOX, X = Cl, Br, and I) have evolved as a new family of visible light-driven photocatalysts. The layered heterojunction structure of BiOX crystals can provide large enough space to polarize the related atoms and orbitals. The induced dipole can separate the photogenerated hole—electron pairs efficiently, enhancing the photocatalytic activity.10 In addition, indirect transition band gap can reduce the undesired recombination probability.11 To increase their photocapacity, numerous approaches were considered. These include doping, sensitization, formation of defects, exposing active facets, use of cocatalysts, graphene coupling, etc.12 It has been proved both theoretically and experimentally that these mixed bismuth oxyhalide solid solutions are more active in comparison with their monohalide counterparts. We also reported a very simple and practical approach for fabricating mixed bismuth oxyhalide solid solutions at ambient conditions.13 It has established the high degradation rate of rhodamine B using BiOX (BiOCl{sub 0.875}Br{sub 0.125}) under visible light.13 In another study, the high oxidation potential of the BiOX hole h{sub +} resulted in direct bacterial oxidation of Escherichia coli by its adsorption onto the catalyst surface.14

Much effort has been expended to immobilize catalysts and photocatalysts on thin films mainly to avoid the problems associated with handling catalyst suspensions. Little is known about the effects of the coating characteristics of bismuth-based sol—gel thin films on their photocatalytic activity toward the removal of micropollutants. The goal of this study is to demonstrate the ability of bismuth oxyhalide thin films doped with various bismuth(0) concentrations to photocatalytically degrade iopromide (IPRM), iohexol (IHX), iopamidol (IPMD), sulfamethoxazole (SMX), carbamazepine (CBZ), venlafaxine (VLX), and bezafibrate (BZF) in water. These compounds (Supporting Information Table S1 and Figure S1) were selected because of their frequent detection in WWTPs, surface waters, and groundwaters.15 This paper also addresses electrostatic interactions of the TrOP-immobilized catalysts (measured by zeta potential obtained from streaming potential measurements) on the photodegradation of target pollutants.

**RESULTS AND DISCUSSION**

**Fabrication and Analysis of Bismuth-Doped Bismuth Oxyhalide Particles.** In this study, an easy, scalable, and general approach for fabricating bismuth-doped bismuth oxyhalide solid solutions immobilized on thin films for solar enhanced photocatalytic degradation of TrOPs in water was demonstrated. The solid solutions of mixed bismuth oxyhalides (BiOCl{sub x}Br{sub 1−x}) were synthesized at room temperature. Among several possible compositions, BiOCl{sub 0.875}Br{sub 0.125} was selected taking into consideration its superior photocapacity as realized in our previous study.13 A further improvement in the harvested photoefficiency was achieved via doping of BiOCl{sub 0.875}Br{sub 0.125} with Bi(0). To benchmark the efficacy of our developed materials, a commercially available TiO{sub 2} (P25) photocatalyst was also examined.

Morphologies of these powders (BiOCl{sub 0.875}Br{sub 0.125}, 1% Bi−BiOCl{sub 0.875}Br{sub 0.125}, 2% Bi−BiOCl{sub 0.875}Br{sub 0.125}, and 3% Bi−BiOCl{sub 0.875}Br{sub 0.125}) along with that of TiO{sub 2} (for comparison) were investigated by extra-high-resolution scanning electron microscopy (SEM) (Figure 1). The formation of microspheres (∼2−8 μm) was evident for all bismuth powders, which are composed of very thin (∼10−20 nm) porous nanosheets (magnified portion on 1% Bi−BiOCl{sub 0.875}Br{sub 0.125} particles; Supporting Information Figure S2). The size of the particles gradually increased with increasing the doping of Bi(0), from 1 to 3%. Interestingly, relatively higher Bi(0) doping allowed the sheets to be arranged in a more compact and ordered fashion, which can be correlated with the electrostatic interaction between Bi{sup +} and BH{sub 4}− ions. However, higher amounts of BH{sub 4}− ions and high (4%) loading of Bi(0) shattered the structure of the microparticles and resulted in broken particles (Supporting Information Figure S3).

In comparison, the dimension of the TiO{sub 2} particles was found to be ∼20−40 nm. X-ray diffraction (XRD) patterns of the TiO{sub 2} particles show the presence of mainly the anatase (86.4%) form with small portion of rutile (13.6%) crystallites. All BiOCl{sub 1−x}Br{sub x} particles provided typical peaks for BiOCl{sub 0.875}Br{sub 0.125} as shown in Figure 2. Formation of Bi(0) was confirmed by X-ray photoelectron spectroscopy analysis, and representative spectra are given in Figure S4 (Supporting...
Herein, Bi(0) doping was varied from 0 to 3 mol% with respect to BiOCl0.875Br0.125 and the sample was designated as 1−3% Bi−BiOCl0.875Br0.125.

Brunauer−Emmett−Teller (BET) surface areas and the band gaps of the powders are given in Table 1. It was observed that the surface areas of the bismuth oxyhalides remain almost unchanged (∼27−30 m²/g). Interestingly, the absorption edge (λmax) of BiOCl0.875Br0.125 was shifted toward longer wavelengths with increasing % Bi(0) doping, as shown in Table 1. Consequently, the band gap values were also decreased with an increase in the Bi(0) content. It is well known that semiconductor materials with the absorption edge in the longer wavelength (visible region) and lower band gap values show better visible light-driven photocatalysis.

Table 1. Estimated BET Surface Areas, Band Gaps, and Absorbance Edges (λmax) of the Photocatalysts

| Photocatalyst | Surface Area (m²/g) | Band Gap (eV) | λmax Absorbance Edge (nm) |
|---------------|---------------------|---------------|--------------------------|
| TiO2 (Degussa P25) | 49.73 | 3.31 | 374 |
| BiOCl0.875Br0.125 | 26.87 | 2.94 | 421 |
| 1% Bi−BiOCl0.875Br0.125 | 28.32 | 2.81 | 440 |
| 2% Bi−BiOCl0.875Br0.125 | 27.78 | 2.69 | 460 |
| 3% Bi−BiOCl0.875Br0.125 | 30.04 | 2.58 | 480 |

that the surface areas of the bismuth oxyhalides remain almost uncharged (∼27−30 m²/g). Interestingly, the absorption edge (λmax) of BiOCl0.875Br0.125 was shifted toward longer wavelengths with increasing % Bi(0) doping, as shown in Table 1. Consequently, the band gap values were also decreased with an increase in the Bi(0) content. It is well known that semiconductor materials with the absorption edge in the longer wavelength (visible region) and lower band gap values show better visible light-driven photocatalysis. This result motivated us to study the photocatalytic efficiency of Bi(0)-doped BiOCl0.875Br0.125 toward the decomposition of TrOPs.

Characterization of Bismuth-Doped Bismuth Oxyhalide Thin Films. The synthesized BiOX powders (75 wt %) were loaded on alumina-based matrices (25 wt %) for forming thin films as described in the Experimental Section. A highly viscous but stable AIOOH sol helped to disperse these high amounts of bismuth oxyhalide particles within the sol, which was further deposited on a glass surface, followed by a concomitant heat treatment to obtain a stable film (Supporting Information Figure S5). During the calcinations process, AIOOH was converted into γ-Al₂O₃. Pure alumina films and TiO₂ (75 wt %)-loaded films were also synthesized for comparative photocatalytic studies. Morphologies of the films were studied by high-resolution SEM and are presented in the loading of TiO₂ particles within the alumina surface. The SEM image of one representative BiOX film (3% Bi−BiOCl0.875Br0.125) is shown in Figure 3c−e. The image (Figure 3d) from the top surface of the film shows that the bismuth oxyhalide particles are well distributed throughout the surface of the composite film. The higher magnification image (Figure 3e) clearly indicates the presence of bismuth oxyhalide particles within the alumina support. Cross-sectional image of the film is presented in Figure 3e, revealing a thickness of the composite films of ∼3 µm. The stability of the coatings was tested by the ASTM-D3359 method, and the adhesion of coatings was found to be very high (class 5B).

Zeta Potential of Bismuth-Doped Bismuth Oxyhalide Thin Films. Electrostatic attraction and repulsion in aqueous systems are driven by the surface charge and thus by the solid surface zeta potential. Opposite charges at a certain pH indicate that electrostatic forces contribute to the adhesion of water constituents (e.g., organic molecules) to the film layer. In addition, zeta potential measurements can imply whether film deposition was uniform along the sample and whether the film is stable in an aqueous environment. The zeta potential (ζ) as a function of pH for the reference samples (i.e., uncoated, Al₂O₃-coated, and TiO₂-coated microscope glass slides) and bismuth oxyhalide-deposited samples is presented in Figure 4. Table 2 summarizes the points of zero charge (PZCs) of the examined samples.
The uncoated glass sample was found to be the most acidic (PZC 2.7, Table 2) owing to the high density of surface silanol groups. The PZC value for the reference Al₂O₃-coated glass slide was 8.2 (Table 2), which is in the range for Al₂O₃. The TiO₂-coated sample resulted in a PZC of 4.3 with a slightly amphoteric behavior (Figure 4) as expected from the literature. PZCs of bismuth oxyhalide samples with lowest and highest degrees of Bi dopant were 5.1 (BiOCl₀.₈₇₅Br₀.₁₂₅) and 5.0 (3% Bi−BiOCl₀.₈₇₅Br₀.₁₂₅). The samples BiOCl₀.₈₇₅Br₀.₁₂₅ and 3% Bi-doped BiOCl₀.₈₇₅Br₀.₁₂₅ show similar data curves as expected. The doping of 1−3 w/w % Bi to the bismuth oxyhalide is not expected to affect surface charge since the concentration is low but mostly as the doped Bi is incorporated in the lattice structure and should not migrate to the photocatalyst outer surface as mentioned above. Upon the deposition of the photocatalytic films, the sol−gel solution contains 25% Al₂O₃ and 75% bismuth oxyhalide, giving a homogenously mixed coating. In case of partial dissolution of this homogenous (25% Al/75% Bi) coating at the measuring conditions, a more acidic glass surface will be exposed.

**Photocatalytic Activity of Bismuth-Doped Bismuth Oxyhalide Thin Films.** The fabricated films were tested for the photodegradation of certain TrOPs under solar light. Several studies report the adsorption of organic compounds on the semiconductor surface as a critical step for photodegradation, whereas others suggest that adsorption may increase the reaction rate but is not essential in the presence of hydroxyl radicals. A distinction should be made between dark adsorption to the catalyst surface and adsorption occurring in the course of the photocatalytic process (photoadsorption) while the catalyst is exposed to radiation.

Dark adsorption of the TrOPs to the examined photocatalytic thin films (i.e., after a 60 min equilibration time) was found to be insignificant for all contaminants except for BZF. BZF is a lipid regulator used for the treatment of hyperlipidemia. Because of its wide use, unmetabolized BZF is released to the environment with potential toxic effects. Interestingly, BZF, which is negatively charged (pKₐ = 3.8, Table S1) and hydrophobic (log D 1.8−2.8, Table S1), displayed an increasing dark adsorption with increasing Bi doping percentage to the bismuth oxyhalide samples but not to TiO₂ (Figure 5). According to the measured PZC of the TiO₂-

![Zeta potential vs pH of various types of photocatalytic films and references (Al₂O₃ and glass).](image)

Table 2. PZC Summary

|                | glass | Al₂O₃ ref | TiO₂ pure | 3% Bi-doped BiOCl₀.₈₇₅Br₀.₁₂₅ |
|----------------|-------|-----------|-----------|-------------------------------|
| PZC            | 2.7   | 8.2       | 4.3       | 5.1                           | 5.0                           |

![Degree of adsorption of BZF measured in the dark prior to irradiation.](image)

coated sample (Table 2), electrostatic repulsion between the negatively charged TiO₂ photocatalyst and BZF is expected. However, the isoelectric points of bismuth oxyhalide samples are also lower than those in experimental conditions (water pH ≈ 5.5) (Table 2), and consequently electrostatic attraction forces between BZF and these samples may not be the main mechanism. Furthermore, the pure Al₂O₃-coated sample shows a negligible adsorption of BZF in the dark, which confirms that the adsorption process is not driven by electrostatic attraction.

A hydrophobic interaction can be considered as a possible explanation. Lester et al. (2014) studied the particulate BiOCl₀.₈₇₅Br₀.₁₂₅ photocatalyst for the removal of four micropollutants: CBZ, ibuprofen, BZF, and propranolol. A similar adsorption conduct was realized for the negatively charged BZF, whereas dark adsorption of propranolol (positively charged) was negligible. The hydrophobic nature of BZF cannot be the main reason for this favorable interaction as CBZ (a neutral and hydrophobic compound) did not exhibit significant dark adsorption to the bismuth oxyhalide films in this work as well as to the particulate BiOCl₀.₈₇₅Br₀.₁₂₅ photocatalyst. It was suggested that ion exchange is the dominant adsorption mechanism for charged compounds. In this case, the adsorbing phase is the positively charged [Bi₂O₃]²⁺ layer, while the halogen atoms (i.e., Cl⁻/Br⁻) function as counter ions. Although most TrOPs do not exhibit dark adsorption to the thin-film-coated catalyst surface, a sorption−desorption mechanism may occur under light irradiation when the catalyst is “active”.

**The photocatalytic efficiency of BiOCl₀.₈₇₅Br₀.₁₂₅ films doped with different concentrations of metallic bismuth toward degradation of the chosen TrOPs under solar simulator irradiation is presented in Figure 6. IPMD, IHX, IPRM, and particularly SMX are susceptible to photolysis (solar light without the photocatalyst−Al₂O₃ ref sample) with 25 ± 4, 30 ± 6, 18 ± 1, and 44 ± 0.7% removal, respectively. However, exposure to light significantly increased the destruction of all of the abovementioned compounds. The molecular CBZ, VLX, and BZF were found to be notably stable toward exposure to radiation but showed meaningful degradation due to the**

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photocatalytic effect in the following order BZF > VLX > CBZ. Particularly, a high rate of degradation was realized for BZF with 70–79% removal with the bismuth oxyhalide films. In this case, the importance of dark adsorption was found to be correlated with the efficacy of the photocatalytic degradation. Considerable adsorption of rhodamine B (pKₐ = 4.2 and log D = 0.5 at pH 5) to BiOCl₀.₈₇₅Br₀.₁₂₅ compared to TiO₂ facilitated enhanced degradation of free rhodamine B, indicating the significance of close proximity between active sites on the catalyst and the decomposing dissolved molecule. On the basis of literature support and our observed results, it is suggested that initially adsorption of TrOPs on the surface of the films occurs, which is followed by the decomposition of the TrOPs under solar light illumination, as shown in the scheme (Figure 7).

Amongst the bismuth oxyhalide-deposited films, the sample 3% Bi–BiOCl₀.₈₇₅Br₀.₁₂₅ showed the highest destruction rate for most of the tested compounds, except for IPMD, where TiO₂ outperformed the bismuth thin film-coated surfaces. The highest efficiencies of 3% Bi–BiOCl₀.₈₇₅Br₀.₁₂₅ can be correlated with the lowest band gap (Table 1) as well as with the highly organized and compact morphology of the particles as observed in the SEM images (Figure 2). However, further increase of the bismuth doping (4%) did not result in improved performance (data not shown) because of the resulting broken microstructure (Supporting Information Figure S3).

CONCLUSIONS

In summary, we have described the synthesis of stable Bi(0)-doped bismuth oxyhalide thin films and their application as photocatalytic substrates for the removal of TrOPs. Diverse coatings of BiOCl₀.₈₇₅Br₀.₁₂₅ with variable Bi(0) loadings were synthesized. The notable efficiencies of the 3% Bi–BiOCl₀.₈₇₅Br₀.₁₂₅ films toward degradation of the selected TrOPs under solar irradiation can be correlated with their unique morphology and with the well-matched band positions. The negatively charged hydrophobic compound BZF exhibited extremely strong affinity to the bismuth oxyhalide films and high degradation rate accordingly. Analysis of the surface charge excluded electrostatic interactions between the compound and the bismuth films. This result rather strengthened the previously suggested ion-exchange adsorption mechanism owing to the unique structure of the bismuth oxyhalides.

EXPERIMENTAL SECTION

Materials and Reagents. Aluminum tri-sec-butoxide (ASB) Al[OCH(CH₃)C₂H₅]₃, bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O), cetyltrimethylammonium bromide (CTAB, ≥ 99%), cetyltrimethylammonium chloride (CTAC, 25 wt % in water), and glacial acetic acid were purchased from Sigma-Aldrich. Seven TrOPs were selected for this study, based on their physicochemical properties (Supporting Information Table S1). All standards (purity > 99%) were obtained from Sigma-Aldrich, except for IPRM and IPMD (European Pharmacopeia reference standards, France). Stock solutions were prepared by dissolving in deionized (DI) water (Direct-Q3 UV system, Millipore-France). LC-grade methanol and water were purchased from Bio-Lab (Jerusalem, Israel).

Synthesis of an AlOOH Sol. ASB (Al[OCH(CH₃)C₂H₅]₃, 20 g) was placed in a 250 mL round-bottom flask, followed by the addition of 146 g of boiled water while stirring under reflux conditions (~82 °C). After 1 h of reflux, 0.7 mL of concentrated HCl was added. Then, the sol was stirred vigorously under reflux for 48 h. After completion of the reaction, an equivalent wt % of AlOOH within the sol was determined to be 2.45. Part of the sol was concentrated to about 7–8 equivalent wt % to AlOOH content by distilling off the solvent (i.e., secondary butanol and water) using a rotary evaporator. A stoichiometric amount of methanol was then added to the sol to maintain the AlOOH content at 4 wt %.
Syntheses of BiOX Powders. Bismuth nitrate (14.69 g) was dissolved in DI water (50 mL) and glacial acetic acid (40 mL) in a 250 mL beaker and stirred at room temperature for 30 min until a clear, transparent solution was formed. Then, CTAB (1.38 g, dissolved in 25 mL of ethanol and 10 mL of water) and CTAC (33.92 g of 25 wt % aqueous solution) were added to the above solution in one batch. Finally, sodium borohydride [11.456, 22.912, and 34.364 mg for Bi(0) doping of 1, 2, and 3%, respectively] and ethanol (20 mL) were added to the reaction mixture, which was then stirred for an additional 60 min at room temperature. The precipitate thus formed was filtered and washed five times with ethanol (50 mL) and five times with water (200 mL) to remove the nonreactive organic species. The off-white solid was then dried (in air) and became ready for use. In the case of pure BiOCl0.875Br0.125, the procedure was same except the addition of NaBH4.

Preparation of an AIOOH/BiOX Composite Sol. BiOCl (480 mg) was ultrasonicated in 2 mL of 1-propanol for ~1−2 min, followed by the addition of 4 mL of 4 wt % AIOOH sol, and then again ultrasonicated for ~1−2 min. The sol became highly viscous and showed gel-like appearance.

Coating Procedure. A microscope glass slide (25 mm × 75 mm) was coated with the composite AIOOH/BiOX sol. A volume of 2−3 drops of this sol was placed on the glass slide, and coating was done by a wire-bar coating deposition method, using a K101 K Control Coater from RK Print Coat Instruments Ltd. The films were dried at room temperature for ~30 min and allowed to heat at 500 °C for 10 h. The rate of heating was maintained at 1 °C/min. The adhesion of the film was tested by the standard method (ASTM D3359).

Characterizations. Sample morphology was observed by an extra-high-resolution scanning electron microscope (Magnet TM 400L). XRD patterns were collected by using Bruker AXS D8 ADVANCE. Band gaps were estimated from the analysis of diffuse reflectance spectra obtained from a UV−visible spectrometer with an attached integrating sphere (JASCO V-650 Series ISV-722). Surface area was determined by N2 sorption analysis (BET method) using NOVA-1200e instrument.

Zeta Potential Measurement. Zeta potentials of TiO2, BiOCl0.875Br0.125, and 1−3% Bi-doped BiOCl0.875Br0.125-coated glass films (25 mm × 75 mm) were determined from streaming potential measurements using an electrokinetic analyzer equipped with conductivity and pH electrodes (SurPASS3, Anton Paar GmbH, Austria). The coated glass samples were mounted to a clamping cell opposite to a reference sample (polypropylene foil). A spacer separates the sample and the reference to form a rectangular capillary with a gap of approximately 100 μm. A 0.001 M KCl solution was used as the background electrolyte, and the pH was adjusted with 0.05 M HCl/NaOH to identify the PZC (i.e., the pH at which the electrokinetic charge density diminishes and thus ζ = 0 mV). Before starting the measurement, the samples were carefully rinsed with the measuring electrolyte. Zeta potential was calculated from the streaming potentials using the Helmholtz−Smoluchowski equation.

Photocatalytic Activity. Coated slides were immersed in a 90 mm × 50 mm Pyrex glass dish containing 30 mL of aqueous solution (DI water) spiked with seven TrOPs at initial concentrations of 100 μg L−1 (each compound). For each experiment, 3−4 slides were used with a surface of 18.5 cm2. Water height above the sample was ~4.7 mm. The examined solution was stirred for 60 min in the dark to ensure the adsorption/desorption equilibrium of the TrOPs on the catalyst prior to irradiation. The solution was then irradiated under a solar simulator for 60 min, with gentle stirring, during which samples of 0.3 mL were taken periodically.

Irradiation experiments were carried out with a 150 W ozone-free Xe arc lamp solar simulator (Sciencetech Inc., SS150W, Canada) achieving a consistent incident irradiation of ~500 W m−2 integrated between 280 and 950 nm, including an UVA irradiance of ~21.5 W m−2 and an UVB irradiance of 0.9 W m−2, as previously described by Mamane et al. (2014). The TrOPs were analyzed by high-performance liquid chromatography (Agilent 1100 series; ACE-RP phenyl column 2.1 mm × 250 mm) coupled with a mass spectrometer (Q-ToFMS, Waters Premier). The column temperature was 40 °C, the flow rate was 0.5 mL min−1, and the injected sample volume was 100 μL. The mobile phase consisted of water (A) and methanol (B) and was adjusted to pH 3 with formic acid. The eluent gradient started with 10% eluent B for 1 min, followed by a 4 min linear gradient to 90% B, a 5 min isocratic elution at 90% B, and a 2 min linear gradient back to 10% B, which was maintained for 4 min for equilibration. The Q-Tof MS was operated in the positive mode, with a limit of quantification of 0.1 μg L−1.

All experiments were performed in triplicate, and relative standard deviations were less than 10%. The photocatalytic efficiency was expressed as percent removal:

\[
\text{Removal (%) } = \left( \frac{C_0 - C_f}{C_0} \right) \times 100
\]

where C0 is the initial pollutant concentration after equilibrium and Cf is the pollutant concentration after t hours of irradiation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00759.

Structure and physicochemical properties of the TrOPs, SEM micrographs of 1% Bi−BiOCl0.875Br0.125 and 4% Bi−BiOCl0.875Br0.125 particles, high-resolution Bi 4f XPS spectra of 3% Bi−BiOCl0.875Br0.125 and image of one representative 3% Bi−BiOCl0.875Br0.125-loaded alumina film (PDF)

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Notes

The authors declare no competing financial interest.

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