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Enhanced visible-light-driven peroxymonosulfate activation for antibiotic mineralization using electrosynthesized nanostructured bismuth oxyiodides thin films

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ABSTRACT

The search for non-specific catalysts capable of removing a wide range of organic contaminants remains a key challenge given their increasing presence in aquatic environments. In this ongoing exploration, this work proposes the use of bismuth oxyiodides as activators of ecological oxidative radicals, wherein raw substances like peroxymonosulfate (PMS) gain prominence due to the valuable efficiency of the radicals they can generate. For BiOI, serving as a precursor to the photocatalysts, the effect of the electroactive solution components on its electrochemical preparation was analyzed using the voltamperometric technique. The compositional and structural characterization confirmed successful formation. Deposit annealing treatments result in new species such as Bi₇O₉I₃ at 250°C and, primarily, Bi₅O₇I at 420 or 520°C—species that also exhibit visible light absorption, paving the way for their use under sunlight. Initially, a single tetracycline (TC) solution was employed to test the degradation and mineralization capability of the prepared films, assessing the impact of the solution's pH, the presence of PMS, light irradiation, and annealing temperature. The annealing temperature increases the catalytic effect. It is noteworthy that for all bismuth iodide films, the highest catalytic activity was observed when combining PMS and visible light irradiation, showcasing a synergistic improvement. This trend holds for multipollutant solutions as well. In a crucial role for the material's application, the results demonstrate that annealing temperatures below 450°C promote films that reasonably maintain their activity and chemical stability after continuous reuse.

1. Introduction

Antibiotic pollution is a pressing global issue, with these compounds persisting in water systems, posing risks to ecosystems and human health. Continuous release from various sources leads to their accumulation in water bodies, impacting aquatic ecosystems and potentially fostering antibiotic-resistant bacteria [1–3]. Antibiotics are released into the environment due to incomplete absorption and/or metabolization by organisms (30–90% ejected), primarily excreted in urine and feces. The main issue stems from their frequent application, not only through mistreating undiagnosed diseases but also from consuming animals

treated with these agents and improper disposal. Urgent action is required to address this concern and tackle the challenges of antibiotic pollution for the environment and human well-being [2–5].

Traditional water treatment methods, including biological degradation, chemical oxidation, and filtration, prove inefficient in achieving rapid and complete removal of contaminants. Various alternative methods, such as membrane processes, adsorption, photochemical processes, electrochemical processes, and photocatalysis have been employed to address antibiotic presence in water systems [6–8]. The need for more efficient and versatile water treatment methods has led to the exploration of advanced oxidation processes (AOPs), which involve

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Received 26 January 2024; Received in revised form 12 March 2024; Accepted 18 March 2024 Available online 19 March 2024 2213-3437/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/). generating highly reactive radicals for enhanced pollutant removal [9, 10]. The search for cost-effective and versatile technologies continues due to the increasing demand for non-polluted water and the limitations of conventional treatments [11–13].

Photocatalysis holds significant potential for the treatment of wastewater and pretreatment of drinking water [14,15]. When a photon with energy equal to or higher than the photocatalyst band gap energy is absorbed, it ejects an electron from the valence band to the conductive band, simultaneously creating a positively charged vacancy or hole. The generated electron and hole are highly reactive and play a crucial role to reduce and oxidize contaminants [16-18]. Bismuth based photocatalysts are notable for their responsiveness to visible light, enhancing catalytic reactions under solar-light irradiation (given that only 3-5% of sunlight falls within the ultraviolet domain) [18–21]. Bismuth oxyiodide (BiOI) possesses the smallest optical band gap energy among bismuth oxyhalides, approximately 1.8 eV, resulting in strong absorption of visible light. In addition, the uniquely layered structures of bismuth oxyhalides create an internal static electric field between positive and anionic slabs, facilitating the effective separation of photogenerated electron-hole pairs [22–24]. Consequently, BiOI thin films exhibit potential in degrading pollutants like antibiotics in water, prompting an exploration of their use in photocatalysis and highlighting their attributes for mitigating waterborne pollutants [25,26].

Electrodeposition is a cost-effective method for producing BiOI thin films, crucial for practical applications due to scalability. The complexity of the electrodeposition process arises from the formation of a new phase on the substrate, involving multiple stages related to matter transport, electron transfer, and the creation of new structures. This electrosynthesis process provides precise control over film thickness and composition using simple equipment and easily available materials. Despite the widespread use of electrodeposition for BiOI synthesis, there is a limited number of studies that thoroughly analyze the electrodeposition process [27–31]. A comprehensive understanding of its dynamics is paramount for optimizing film growth and morphology [15]. This optimization is crucial to enhance surface area, crystallinity, and defect densities, all of which play a pivotal role in enhancing the efficiency of the film for photocatalytic applications [32–34].

Peroxymonosulfate (PMS) emerges as a potent oxidizing agent in water treatment, holding substantial promise for degrading and mineralizing organic contaminants through the generation of sulfate radicals [35–37]. Despite its favorable oxidizing power, its reaction with organic pollutants does not always yield the expected kinetic outcome. Various activation methods, including thermal activation, alkaline activation, radiation activation, transition metal ions, oxide, carbonaceous-based materials, and hybrid activation systems, have been explored over the past decade [38–43]. Recently, the visible-light activation of PMS, facilitated by photocatalysts, has proven to enhance degradation efficiency. This approach broadens the spectrum of targeted pollutants, thanks to the synergistic interaction between PMS activation and the photocatalytic generation of highly reactive radicals [35,40].

In the present analysis, the BiOI electrodeposition process has been scrutinized and elucidated through a voltammetric examination of bath components, coupled with an analysis of the chemical composition and structure of the resultant deposits. The electrochemical study yielded various deposits, and the influence of an annealing process in an oxygen atmosphere on the chemical composition, structure, morphology, and optical properties of the materials was explored [44]. The non-annealed and annealed deposits were subjected to investigation as activators for PMS both in the absence of light and under visible-light irradiation for the degradation/mineralization of antibiotics [23]. The focus of the investigation was on the evaluation of PMS activation using visible light for the degradation of commonplace waterborne antibiotics. Emphasis was placed on comprehending degradation kinetics, optimizing conditions for PMS activation in conjunction with BiOI photocatalysis, and striving for the complete mineralization of antibiotics into inert byproducts. The study aimed to reveal the synergistic interplay between

visible-light-activated PMS catalysis and BiOI photocatalysis, with the ultimate goal of enhancing degradation kinetics and treatment efficiency. The significance of this research lies in the potential to revolutionize water treatment by establishing a sustainable approach to mineralize antibiotics, thereby improving water quality and mitigating the environmental impact of antibiotic pollution.

2. Experimental section

2.1. Electrochemical deposition and characterization of BiOI thin films

The electrochemical experiments were performed in a threeelectrode cell system connected to a potentiostat/galvanostat (Autolab PGSTAT30) with NOVA software. Fluorine-doped tin oxide glass (FTO; Sigma-Aldrich, resistivity $\sim 7\Omega$ sq⁻¹, 2.2 mm thickness) substrate was used as working electrode (0.8 cm² area), Pt wire spiral was used as counter electrode, and Ag/AgCl (3 M) electrode as reference electrode. FTO was cleaned in an ethanol-water mixture, and ultrasonically in MilliQ water for 15 min each. The experimental setup allowed precise control and monitoring of electrochemical processes throughout the investigation. For the synthesis of BiOI film, a solution consisting of bismuth nitrate from pentahydrate (Bi(NO₃)₃·5H₂O, Sigma- Aldrich, \geq 98%), potassium iodide (KI, Panreac, \geq 99%), nitric acid (HNO₃, Fischer Chemical, 65%), *p*-benzoquinone (Sigma-Aldrich, \geq 98%), ethanol (Panreac, \geq 96% v/v), and MilliQ treated water was used. The electrochemical bath solution for the deposition of BiOI on the FTO electrode consisted of 40 mM Bi(NO3)3 and 400 mM KI solution which was adjusted to pH=1.7 by adding HNO₃. Furthermore, 20 mL of pbenzoquinone in ethanol solution was added to 50 mL of first solution, and stirred for 15 min. In order to elucidate the intricate electrodeposition dynamics of BiOI thin films, cyclic voltammetry was employed systematically to monitor the electrochemical behavior of distinct components within the electrochemical bath. The electrochemical baths under investigation are outlined in Table 1. The ionic strength of the diverse electrochemical media was consistently controlled and modified using KNO₃. Prior to each experiment, all solutions underwent deaeration through argon bubbling, and the experimental environment was maintained under an argon atmosphere throughout the duration of the study.

After the electrodeposition of BiOI films, the samples underwent an annealing treatment in an air atmosphere at various temperatures. The annealing conditions included temperatures of 250°C, 420°C, and 520°C for 4 hours, with a gradual increase at a slope of 2°C per minute from 20°C. The nanostructured BiOI-based films were characterized using different techniques. The surface morphology and architecture of electrodeposits were analyzed by using a field emission scanning electron microscopy (FE-SEM; JEDL J-7100) equipped with an energy dispersive X-ray spectroscopy (EDX) detector. The elemental composition was determined with an X-ray spectroscopy (EDX) equipment. Surface chemical composition of the samples was characterized using X-ray photoelectron spectrometry (XPS; PHI Quantera SXM). Samples underwent irradiation with monochromated X-rays of Al K_{α} source at a spot size of 200 µm at ultra-high vacuum. The ejected electrons were collected at a 45-degree emission angle, directed towards a hemispherical capacitor analyzer in fixed-analyzer-transmission mode. All measurements were recorded with an active low-voltage ion gun and

Table 1			
Electrochemical	baths	com	osition.

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Solution	Solution Concentration / M		Solvent (V:V)	рН	
	Bi(NO ₃) ₃	кі	p-BQ	H2O/EtOH	
S1	0.029	0.289	0.041	70:20	3.4
S2	0.029	0.289	0	70:20	3.4
S3	0	0.289	0.041	70:20	3.4
S4	0.029	0	0	70:20	0.3

electron neutralizer. According to the ISO 15472:2010, the calibration of spectrometer was done employing etched clean surfaces of pure copper, silver, and gold to ensure an accuracy < 0.2 eV. Survey spectra were obtained at a pass energy of 280 eV with a step size of 1 eV, while high-resolution spectra were collected using a pass energy of 55 eV with a finer step size of 0.05 eV. X-ray diffraction (XRD) profiles of the fabricated samples were obtained by implementing θ - 2 θ scans (Bruker D8 Discover). Recorded profiles covered a scan range of 20 – 90° at a step size and step time of 0.05 ° and 0.5 s, respectively. The UV–visible diffused reflectance spectra were acquired utilizing a PerkinElmer Lambda 900 UV spectrophotometer (PerkinElmer).

2.2. Antibiotic degradation/mineralization experiments

The chemical stability of TC, in absence of light, was investigated over a 30-day period. The effect of pH on the chemical stability was also examined. To conduct the study, 1000 mL of single-pollutant TC solutions (20 ppm) were incubated at 20°C in dark and stagnant conditions. The temporal changes in UV–vis spectra were monitored using a UV–vis spectrophotometer (Shimadzu UV-1800). Additionally, the total organic carbon (TOC) content in the single-pollutant solutions was determined using the high-temperature combustion method with TOC-V_{CSH} equipment (Shimadzu), featuring a high-sensitivity column. All experiments were conducted in triplicate.

Various experiments were conducted to investigate the impact of visible light irradiation, the presence of PMS - (oxone - Merck), which contains KHSO₅·0.5KHSO₄·0.5 K₂SO₄ -, and the simultaneous combination of visible light irradiation and PMS on TC degradation and mineralization. Independent experiments were carried out for each factor. To analyze the effect of visible light irradiation, 3 mL of a TC solution (20 ppm) at pH=6 or pH=8 was exposed to a 1.6 W cylinder of a white LED strip (2.2 $\times 10^{-3}$ W cm⁻²). The LED strip was turned on at different time intervals (to facilitate measurements) over a 150-minute period. Readings were taken at various wavelengths ranging from 250 to 500 nm. For the evaluation of PMS effect, 50 µL of a 150 mM PMS solution was added to 3 mL of TC solution (20 ppm) at pH=6 or pH=8 in dark conditions. The absorbance at the maximum was measured every 0.5 s for 150 min. Finally, to assess the simultaneous effect of visible light irradiation and PMS presence, 50 μL of a 150 mM PMS solution was added to 3 mL of TC solution (20 ppm) at pH=6 or pH=8. The solution was also illuminated with a 1.6 W cylinder of a white LED strip (2.2 $\times 10^{-3}$ W cm⁻²), which was turned on at different time intervals over 150 min. The absorbance at the maximum was rapidly measured at different intervals during this period. Mineralization of each resulting solution after 150 min was determined by measuring the TOC. All experiments were also conducted in triplicate.

The impact of visible light, PMS, and the combined influence of light and PMS was systematically assessed in conjunction with non-annealed BiOI deposits. In each experiment, the photocatalyst was allowed to interact with 3 mL of TC solution, at pH=6 and pH=8, for 40 minutes in darkness to establish adsorption-desorption equilibrium. Subsequently, under different conditions-visible light irradiation, addition of 50 µL of a 150 mM PMS solution, or the simultaneous application of both factors-the experiments were initiated. The absorbance at the absorption maximum was measured using a UV-vis spectrophotometer at various time intervals. Additionally, after 150 minutes, TOC was determined to gauge mineralization. The same set of experiments, limited to combined influence of PMS and visible light irradiation, was conducted for various samples of annealed BiOI. The system's efficacy was evaluated by examining the degradation and mineralization of additional 20 ppm single-pollutant solutions at pH=7.0. This set included methylene blue (MB), levofloxacin (LEV), and ciprofloxacin (CIP), as well as multipollutant solutions containing 5 ppm each of TC, MB, LEV, and CIP, conducted over a 150-minute duration. The investigation encompassed both thermally treated and untreated deposits, employing simultaneous PMS presence and visible light irradiation. All experiments were

conducted in triplicate.

Furthermore, the reusability of both thermally treated and untreated deposits was examined under PMS and visible light irradiation, over 12 cycles of 150 minutes each. Degradation was assessed through absorption measurements with a UV–vis spectrophotometer, while mineralization was monitored through TOC measurements at the end of each cycle. Additionally, the morphology of reused deposits was analyzed using FE-SEM, and the bismuth content in the resulting solutions from all 12 cycles was determined to evaluate the chemical stability of the photocatalyst (inductively coupled plasma mass spectrometry; ICP-MS). Furthermore, the released bismuth was determined after 72 hours of continuous irradiation, employing ICP-MS.

Finally, to investigate the role of hydroxyl and sulfate radicals in the TC degradation process, experiments were repeated with radical scavengers. Specifically, methanol (MeOH) and tert-butyl alcohol (TBA) were alternately added to experiments involving PMS and visible light. MeOH, capturing both hydroxyl and sulfate radicals, and TBA, capturing only hydroxyl radicals, were utilized. By comparing degradation values in the presence of these agents, the distinct effects of each radical species could be discerned.

3. Results and discussion

3.1. Electrochemical study

To determine the optimal deposition conditions for the BiOI film, cyclic voltammetry was employed to analyze the electrochemical behavior of the bath (solution S1). Additionally, p-benzoquinone-free bath (solution S2), bismuth-free bath (solution S3) and an acidic bismuth bath lacking KI and p-BQ (solution S4) were utilized to elucidate the possible electrochemical processes involved in BiOI film deposition. The ionic strength of the various electrochemical media was standardized and adjusted using KNO₃. It is noteworthy that Bi(NO₃)₃ exhibits limited solubility in water, except under acidic conditions near a pH of zero. Under moderately acidic conditions, the solubility of Bi(NO₃)₃ was enhanced by incorporating KI, which promoted the formation of the [BiI₄]⁻ complex [28,45,46].

Fig. 1a illustrates the cyclic voltammetry of solution S2, showcasing an increase in current density from -0.23 V, culminating in a peak centered at -0.4 V (R1 reduction). For potentials more negative than -0.23 V, XPS analysis confirmed the electrodeposition of Bi(0). The black line represented the voltamperometric response of a bare substrate in a solution with the same ionic strength, comprising potassium nitrate, ethanol, and water. In Figure S1, the cyclic voltammetry of solution S4 is depicted, corresponding to a bismuth-pure acid solution. Starting from -0.05 V, a rise in reduction current was observed, reaching a peak at -0.24 V, indicating the electrodeposition of Bi(0). The quantity of deposited Bi(0) in this acidic bath surpasses that in solution S2. Notably, the presence of the [BiI₄]⁻ complex delays the reduction potential compared to the acidic bismuth-pure solution. In both systems, under hydrodynamic conditions, the reduction current attained a stationary value, and the anodic peak rose, signifying an increased deposition of Bi (0). This affirmed that the observed anodic peak was indeed associated with the oxidation of the previously reduced Bi(0) [28].

In the analysis of bath S3 (bismuth-free), the reduction of p-BQ was investigated in the presence of KI, as depicted in Fig. 1b. In the absence of KI, a singular, reversible-looking redox process was observed, exhibiting an apparent half-wave potential. The electrochemical reduction, whether in buffered or unbuffered solutions in acidic media, is posited to involve two successive rounds of electron transfer coupled with proton acceptance (chemical reaction), where a 2-electron and 2-proton reaction yields hydroquinone as the final product. It is noteworthy that the reduction of p-BQ in aqueous solution consumes protons [47,48]. Consequently, in the absence of a buffer, the reduction of p-BQ induces an increase in pH near the electrode. Given that protons play a pivotal role in the overall redox process, the redox potential becomes



Fig. 1. Cyclic voltammetry profile recorded on FTO substrates at 25°C with a scan rate of 50 mV s⁻¹ for (a) p-benzoquinone-free solution (solution S2), (b) bismuth-free solution (solution S3) and (c) electrodeposition bath (solution S1). (d) Cyclic voltammetry profiles on FTO substrates at 25°C with a scan rate of 50 mV s⁻¹, showcasing various cathodic limits of the electrodeposition bath (solution S1) (e) Chronoamperometric transients on the on FTO substrate from solution S1 at different applied potentials.

pH-dependent, trending towards more negative potentials with an increase in pH. This serves as an effective strategy to locally elevate the pH at the electrified interface of the cathode. In the presence of KI, a similar local increase in pH at the electrified interface is observed. The process closely mirrors that observed and described for p-BQ alone, with the additional observation that the oxidation peak (peak O2) was significantly diminished in the presence of KI. An alternative method for locally increasing the pH at the electrode interface is by reducing nitrate. However, this proves to be an unfavorable option for BiOI electrode-position due to the fact that Bi(III) ions in the solution undergo reduction to metal before nitrate reduction takes place [28,47].

In the examination of solution S1, designated for the electrodeposition of BiOI, it was observed that the cathodic current initiated an increase from a potential of 0.1 V mirroring the phenomenon observed in the case of solution S3 (a bismuth-free solution). This occurrence stemmed from the reduction of p-BQ to p-hydroquinone, inducing a localized increase in pH at the electrode interface (Fig. 1c). It is wellknown that [BiI4]⁻ complex, characterized as a bulky anion, exhibits a proclivity to precipitate with equally bulky cations through the formation of ion pairs. When subjected to heat or in the presence of hydroxyl ions, precipitation occurs, yielding an orange solid of BiOI [45,46]. Hence, it is anticipated that the reduction of p-BQ will initiate the precipitation of BiOI. Consequently, the formation of BiOI is attributed to electroprecipitation rather than undergoing a classical electrodeposition process. As the potential becomes more negative, the reduction current experiences a significant increase, concurrently involving two processes: the electroprecipitation of BiOI and electroreduction of Bi(III) to Bi(0). During the anodic scan, an oxidation peak was observed (peak O3), ostensibly attributable to the oxidation of Bi(0). This current intensifies under hydrodynamic conditions, where the deposition of Bi(0) holds greater significance due to the relatively unaffected pH of the interface. In Fig. 1d, cyclic voltammetries at different cathodic limits reveal that at cathodic limits more positive than -0.3 V, no anodic peak is observed, indicating negligible Bi(0) reduction. At limits more negative than -0.3 V, an anodic peak (O3 peak) is observed, but it does not increase when progressing to more negative limits—only showing an increase in hydrodynamic conditions. This can be explained by the higher concentration of p-BQ relative to the concentration of Bi(III), demonstrating that the predominant process is the electroprecipitation of BiOI [28].

To explore the reduction mechanism at low potentials more comprehensively, chronoamperometries were carried out across various potentials (depicted in Fig. 1e) using solution S1. The observed trend unveils a progressive growth process initiating from -0.2 V. In order to deepen our understanding of the dynamics governing the electroprecipitation of BiOI, multiple deposits were prepared by applying a constant potential under static conditions (without stirring) in a bismuth solution (S1). Fig. 2 illustrates the morphology of the deposited films, which were prepared at distinct constant potentials ranging from -0.1 V



Fig. 2. FE-SEM micrographs of deposits prepared at (a) -0.1 V, (b) -0.2 V, (c) -0.27 V, (d) -0.3 V, (e) -0.4 V and (f) -0.6 V vs Ag|AgCl. Scale bar: 100 nm.

to -0.6 V while maintaining a constant charge density. The results exhibit two markedly different morphologies, possibly attributed first to the electroprecipitation of BiOI and subsequently to the simultaneous electroprecipitation of BiOI and the electrodeposition of Bi(0). At potentials between -0.1 and -0.3 V, the deposits manifest as nanoplates, with a broader appearance at higher potentials. Conversely, at more negative potentials, a mixed morphology emerges, characterized by a combination of nanoplates and more compact spongy structures.

To analyze the surface chemistry of deposits further, XPS spectra for Bi 4 f, I 3d, and O 1 s were conducted (depicted in Fig. 3a). The Bi 4 f XPS spectra of samples prepared at potentials more positive than -0.3 V reveal two peaks with binding energies of 159.2 and 164.5 eV, ascribed to Bi³⁺ 4 f_{7/2} and Bi³⁺ 4 f_{5/2} signals for the Bi-O bond of [Bi₂O₂]²⁺, consistent with the formation of BiOI films. As the applied potential becomes more negative, the relevance of two new peaks with binding energies at 157.2 eV and 162.5 eV, corresponding to the Bi-metal bond, increases. This suggests that with a more negative potential, the deposition of Bi(0) gains prominence—underscoring the importance of noting that as the charge density of the deposit increases, the deposition of Bi(0) becomes more significant. Even at more negative potentials, at lower charge densities, the deposit predominantly consists of BiOI. In the I 3d spectra of deposits, two peaks situated at 619.2 eV and 630.6 eV were identified, corresponding to I $3d_{5/2}$ and I $3d_{3/2}$. The intensity of these peaks diminishes with the application of more negative potentials. For potentials exceeding -0.3 V, the O 1 s deconvoluted spectra exhibit two distinct peaks at 530.1 eV and 531.8 eV, corresponding to Bi-O and I-O coordination, respectively. Furthermore, at potentials more negative than -0.3 V, a peak located at 528.2 eV becomes more prominent, indicating the presence of superficial bismuth oxides. It is noteworthy that Bi(0) aids in the decomposition of PMS without producing sulfate radicals. Thus, it is desirable for the catalysts to have minimal amounts of Bi(0).

In Fig. 3b, the X-ray diffraction profiles of the substrate and deposits are observed in relation to the electrodeposition potential. It has been demonstrated that, up to a potential of -0.3 V, the predominant electroprecipitation was of BiOI, while at more negative potentials, there was simultaneous BiOI electroprecipitation and Bi(0) electrodeposition. Several peaks corresponding to the substrate, primarily SnO₂ (JCPDS card No. 46–1088) from the fluorine-doped tin oxide substrates, were observed in all diffractograms. The formation of BiOI was identified in all cases, as evident reflection peaks at approximately $2\theta = 29.4^{\circ}$, 31.6° , 39.4° , 45.5° , and 55.2° were observed. These reflection peaks corresponded to the crystal planes of (102), (110), (004), (200), and (212), respectively, aligning with the standard card for the tetragonal phase of



Fig. 3. (a) XPS spectra of Bi 4 f, I 3d, and O 1 s and (b) XRD difractograms of deposits prepared at -0.1 V, -0.2 V, -0.25 V, -0.27 V, -0.3 V, -0.35 V, -0.4 V and -0.6 V vs Ag|AgCl.

BiOI (JCPDS card No. 73–2062). The XRD result indicated that BiOI with high crystallinity and purity could be successfully synthesized using the electroprecipitation process. Moreover, for deposits obtained at potentials more negative than -0.2 V, new small peaks emerged at approximately $2\theta = 27.2^{\circ}$ and 29.1° , potentially corresponding to the crystal planes (001) and (012) of metallic bismuth (JCPDS card No. 44–1246). However, these peaks were minimal and did not amplify as the potential became more negative. Conversely, the peaks corresponding to BiOI noticeably decreased as the applied potential became more negative. Based on these findings, a potential of -0.2 V was selected for the preparation of photocatalysts intended for the removal of antibiotics through the photocatalytic activation of PMS.

3.2. Study of annealing temperature effect on optoelectronic properties of BiOI thin films

The thermal treatment of BiOI can lead to its solid transformation into $Bi_7O_9I_3$ and Bi_5O_7I , contingent upon the annealing temperature. This annealing process not only influences the crystal structure but also alters the photocatalytic activity [49,50]. However, to the best of our knowledge, no investigation has been undertaken to examine the impact of BiOI, $Bi_7O_9I_3$, and Bi_5O_7I on the photocatalytic activation of PMS in water treatment processes. Several studies have demonstrated that the bandgap energy of bismuth oxyiodides, such as BiOI, $Bi_4O_5I_2$, $Bi_7O_9I_3$, and Bi_5O_7I , may gradually increase with the substitution of I with O in their structures [44,49].

In accordance with findings from the literature, three treatment temperatures have been chosen to produce Bi7O9I3 (at 250°C) and Bi5O7I (at 420 and 520°C) [23,44,50]. Following the thermal treatment, observable changes were evident to the naked eye (Figure S2), aligning with the formation of BiOI, Bi₇O₉I₃, and Bi₅O₇I. The color of the BiOI films appeared deep orange, and upon treatment at 250°C and subsequent transformation into Bi₇O₉I₃, the film adopted a slightly yellowish hue. At temperatures of 420°C and 520°C, the color of the BiOI film turned light yellow. These alterations were noticeable at both the micro and nanometric scales, bringing about significant changes in deposit morphology (Fig. 4). With increasing annealing temperature, there was a reduction in uniformity, accompanied by distortions in morphology. At 250°C, the overall morphology remained relatively intact, although the edges became thicker and more straightened. A temperature of 420°C resulted in a spongier morphology characterized by branched wires. Despite these changes, traces of the original BiOI morphology were still discernible in certain areas of the sample. Upon reaching 520°C, a morphology akin to that observed at 420°C was noted, featuring much thicker wires or columns and more rounded tips. The evolution of the atomic ratio between bismuth and iodine with varying annealing temperatures presented an intriguing avenue for analysis.

The atomic concentration of each deposit has been determined posttreatment. It is worth noting that, oxygen concentration has not been incorporated due to its inherent challenges in quantitative analysis—owing to low x-ray fluorescence yields, self-absorption, and detector efficiency issues. Table 2 provides a comprehensive overview of the atomic ratios of Bi and I in the distinct deposits, along with the Bi/I ratio for each sample. In the case of the non-thermally treated sample, the ratio approximated 1, aligning with the characteristics of BiOI. At 250°C, a Bi/I ratio of approximately 2.6 was observed, indicating a slight elevation likely attributed to the substitution of iodine by oxygen in the structure, resembling the atomic ratio of Bi₇O₉I₃, which stood at about Table 2

Atomic composition of bismuth oxoiodide, expressed as the percentage of bismuth and iodine.

Annealing temperature / °C	Bi / at%	I / at%	Bi/I
RT (no annealing treatment)	50.2	49.8	~1.0
250	72.3	27.7	~2.6
420	85.3	14.7	~5.8
520	87.7	12.3	~7.1

2.3. The ratio increased to approximately 5.8 at 420°C and further to around 7.1 at 520°C. The former aligned closely with the structure of Bi_5O_7I , while the latter suggested a marginally higher sublimation of iodine. Based on these results, the reduction in atomic concentration of iodine and the concurrent increase in the concentration of oxygen may have contributed to structural defects, thereby modifying the optical bandgap energy and mitigating recombination effects.

In Fig. 5a, it is evident that the chemical nature of the surfaces remained unchanged during the heat treatment—an anticipated outcome. Conversely, the signal of the iodine 3d peaks was notably lower for samples treated at 420°C and 520°C, indicating iodine sublimation and subsequent replacement with oxygen. This resulted in a decrease in the relative amount of iodine signal and an increase in the amount of oxygen. The oxygen 1 s spectrum, depicted in the same figure, also revealed higher intensity for deposits treated at elevated temperatures.

Fig. 5b illustrates the XRD diffractograms of each structure. Omitting commentary on the substrate and the non-thermally treated BiOI, previously discussed, the samples treated at 250°C exhibited peaks at approximately $2\theta = 29.1^{\circ}$, 31.2° , 36.1° , and 45.4° , corresponding to the (012), (110), (112), and (024) planes, respectively. All diffraction peaks precisely matched those of Bi₇O₉I₃ (JCPDS card No. 38–0669). Notably, these peaks could be assigned to the ones discussed in the preceding section on BiOI, given their practically imperceptible differences except for a slight shift to smaller angles. This shift may be attributed to the increased bismuth and oxygen content in the Bi₇O₉I₃ lattice crystal. For



Fig. 4. FE-SEM micrographs of deposits prepared at -0.2 V vs Ag|AgCl: (a) non-annealed and annealed at (b) 250°C, (c) 420°C and (d) 520°C. Scale bar: 100 nm.



Fig. 5. (a) XPS spectra depicting Bi 4 f, I 3d, and O 1 s, (b) XRD diffractograms, and (c) UV-vis diffused reflectance absorption spectra for non-annealed deposits and deposits annealed at 250°C, 420°C, and 520°C.

samples annealed at 420°C and 520 °C, significant differences emerged. In comparison to BiOI and Bi₇O₉I₃, new diffraction peaks appeared at 28.2°, 31.1°, 33.1°, 33.4°, and 53.6°, corresponding to the (312), (004), (204), (020), and (316) planes, respectively. These could be assigned to the orthorhombic phase of Bi₅O₇I (JCPDS card No. 40–0548).

In Fig. 5c, the UV–vis diffused reflectance spectra of each deposit are presented. The optical properties of the material are crucial parameters for predicting the potential and performance of devices in photocatalytic applications. In all cases, the photocatalysts exhibited visible light absorption—an aspect of great importance for the application investigated in this study. The intention is to utilize these materials under sunlight irradiation, with more than 40% falling within the visible domain and less than approximately 5% in the ultraviolet zone. This made them suitable for deployment in areas with fewer resources or developing countries. Analysis of the spectra revealed that thermally treated deposits exhibited a greater capacity to absorb light, with those treated at 420°C and 520°C showing very similar behavior. The optical bandgap of each material was determined through Tauc plot analysis, yielding values of approximately 1.93 eV for BiOI, 1.87 eV for Bi₇O₉I₃

(250°C), 2.09 eV for Bi₅O₇I (420°C), and 2.11 eV for Bi₅O₇I (520°C). Based on these characterizations, all the materials appeared to be suitable for promoting the photocatalytic activation of PMS facilitating the oxidation of organic pollutants and the generation of reactive species through the photocatalytic activity of the materials themselves.

3.3. PMS catalytic degradation and mineralization of tetracycline by BiOI thin films

The analysis initially focused on the persistence of the pollutant over a 30-day period in the absence of light. Two solutions containing 20 ppm TC at pH=6.0 and pH=8.0 were examined by periodically recording UV–vis spectra (Figure S3). At pH=6.0, the maximum absorbance value decreased by approximately 16%, and at pH=8.0, it decreased by approximately 20%. However, no significant alterations were observed in the UV–vis spectra. While there was a slight decrease in TC concentration over the 30-day period, it was crucial to note that the TOC of both solutions remained virtually constant. Given the potential modification of TC over time, which could lead to the generation of more harmful species for aquatic biota, it is imperative to conclude that finding a method to eliminate these antibiotic types is essential. The persistence of these substances in water bodies for extended periods demands proactive measures, considering the potential environmental risks linked to their prolonged presence.

Subsequently, the impact of light (photolysis), PMS, and the combined effect of light and PMS on TC degradation and mineralization was assessed (Fig. 6a), in the absence of a photocatalyst. Following 150 min of visible light irradiation, degradations of approximately 10% and mineralization ranging between 2% and 3% were observed, irrespective of pH. The introduction of PMS exhibited pH-dependent efficiency, leading to degradations of about 30% and mineralization levels of approximately 13% at pH=6.0. In contrast, more modest values were noted at pH=8.0, with degradation around 10% and mineralization around 4%. This disparity can be attributed to electrostatic repulsion between TC anions and PMS anions. At pH=6.0, TC primarily exists in the zwitterionic form, with a net charge of zero, while at pH=8.0, the species is predominantly negatively charged. Note that PMS, a pH-sensitive oxidizing agent, exhibits instability at pH < 6 and pH > 12 (maintaining stability at neutral pH). It is advisable to operate at a pH close to neutral. The activation of PMS was enhanced in the presence of visible light, resulting in degradations of approximately 44% (pH=6.0) and 27% (pH=8.0), alongside mineralizations of 16% (pH=6.0) and 8% (pH=8.0). However, it is noteworthy that the activation of PMS in response to light is more pronounced when photocatalysts or inorganic ions are present. Light alone not only boosts TC degradation through photolysis but also synergistically enhances the activation and decomposition of PMS.

An examination of the impacts of light, PMS, and their combined influence on TC degradation and mineralization was conducted using as prepared BiOI photocatalyst, as depicted in Fig. 6b. In the presence of the photocatalyst and a visible light source, TC degradation efficiency



Fig. 6. (a) Tetracycline (20 ppm) degradation and mineralization performances in the absence of catalysts under visible light irradiation (photolysis), presence of PMS in dark conditions, and both simultaneously under visible light irradiation and PMS presence at pH=6.0 and pH=8.0 after 150 min of treatment. (b) Tetracycline degradation performance of BiOI under visible light irradiation, in the presence of PMS in dark conditions, and both simultaneously under visible light irradiation and PMS presence at pH=6.0 and pH=8.0 after 150 min of treatment. (c) Tetracycline (20 ppm) degradation and (d) tetracycline (20 ppm) mineralization performances of bismuth oxoiodides non-thermally treated and annealed at 250°C, 420°C, and 520°C under both simultaneously visible light irradiation and PMS presence at pH=6.0 and pH=8.0 during 150 min of treatment. (e) Degradation and fiberalization performances of bismuth oxoiodides non-thermally treated and annealed at 250°C, 420°C, and 520°C under both simultaneously visible light irradiation and PMS presence at pH=6.0 and pH=8.0 during 150 min of treatment. (e) Degradation and mineralization performances of bismuth oxoiodides non-thermally treated and annealed at 250°C, 420°C, and 520°C under both simultaneously visible light irradiation and PMS presence at pH=7.0 for treating single-pollutant solutions of methylene blue (20 ppm), levofloxacin (20 ppm), and a multipollutant solution (MP) of tetracycline (5 ppm), methylene blue (5 ppm), levofloxacin (5 ppm), and ciprofloxacin (5 ppm), and ciprofloxacin (5 ppm), and ciprofloxacin (5 ppm) after 150 min of treatment. Temperature is maintained at 20°C. The error bars indicate the standard deviations from three replicate experiments.

ranged from approximately 30-36% over 150 minutes, accompanied by mineralization levels ranging from about 14-16%. In the system involving the photocatalyst and PMS but without visible light irradiation, degradation varied from 32% to 45%, with mineralization levels ranging from 17% to 24%, depending on the pH of the reaction medium. The introduction of visible light irradiation into the system with the coexistence of the photocatalyst and PMS resulted in a gradual degradation of TC, reaching degradation rates between 66% and 75%, and mineralization levels between 36% and 44%. In all instances, elevated rates of degradation and mineralization were observed at pH=6 compared to pH=8. This can be elucidated as a result of electrostatic effects stemming from repulsions between anionic species, which are predominant at pH=8. Significantly, the efficiency of TC degradation and mineralization experienced a substantial increase in the visible light-assisted PMS activation system. This implies the realization of an effective synergistic system involving photocatalysis and PMS activation on the BiOI films. The heightened rates of degradation and mineralization, observed upon introducing PMS into the system containing a photocatalyst irradiated with visible light, can be ascribed to the generation of electrons and holes at the photocatalyst interface. These generated electrons facilitate the breakdown of the peroxide bond in PMS, yielding $SO_4^{\bullet-}$ and $^{\bullet}OH$, thereby amplifying the photocatalytic formation of other reactive species. These include the production of °OH and ${}^{\circ}O_{2}^{-}$ radicals resulting from the reaction between the holes and water molecules, as well as the reaction of photoelectrons with dissolved oxygen in the aqueous medium. It is important to note that bismuthbased semiconductors typically do not have the capability to produce hydroxyl radicals. Instead, most hydroxyl radicals are generated through the radical decomposition of PMS and the reaction of sulfate radicals with water molecules or hydroxide ions. However, these processes collectively impede electron-hole recombination, supplying a greater number of electrons and holes to drive photocatalytic reactions.

To investigate the possible influence of calcination temperatures on the PMS-photocatalytic degradation/mineralization of TC under visible light irradiation, the degradation (Fig. 6c) and mineralization (Fig. 6d) of TC from BiOI and samples annealed treated at 250°C (predominantly Bi₇O₉I₃ phases) and at 420°C and 520°C (mainly Bi₅O₇I phases) were compared. Lower levels of degradation and mineralization were evident in non-annealed catalysts compared to their heat-treated counterparts. As the calcination temperature increased, the catalytic efficiency in degrading and mineralizing TC rose. Specifically, degradation increased from approximately 66% (pH=8) to 75% (pH=6), and mineralization increased from approximately 36% (pH=8) to 44% (pH=6) for BiOI. Meanwhile, utilizing the annealed catalyst at 420°C yielded degradations of approximately 83% (pH=8) and 98% (pH=6), with mineralizations of approximately 49% (pH=8) and 61% (pH=6). The performance of TC degradation/mineralization consistently improved with higher calcination temperatures, and 520 °C appeared to be the optimal temperature. At elevated annealing temperatures, a decline in catalyst integrity occurred, resulting in significant mass losses. This phenomenon was absent when experiments were carried out without PMS. In the absence of PMS and under visible light irradiation, the uncalcined catalyst demonstrated the highest catalytic activity, aligning with observed optoelectronic properties and existing literature. Repeating the experiment in the dark (with PMS but without visible light irradiation) yielded a consistent trend, wherein the catalyst calcined at 520°C emerged as the most active material. The highest catalytic activity was observed in the presence of PMS, showing a synergistic enhancement with visible light irradiation. This outcome is ascribed to the evolving chemical nature resulting from an increase in calcination temperature, leading to a higher relative amount of Bi(III). Despite a lower observed catalytic activity at pH=8, the results exhibit a similar trend as observed at pH=6. The catalytic activity of the system was further evaluated based on the degradation and mineralization of three additional organic pollutants (MB, CIP, and LEV). In Fig. 6e, it was demonstrated that, for both single-pollutant solutions (MB, CIP, or LEV)

and a multi-pollutant solution (TC, MB, CIP, and LEV), the most efficient material was the catalyst annealed at 520°C. In all instances, a uniform behavior akin to TC was observed. Particularly noteworthy was the attainment of higher levels of degradation and mineralization for MB, LEV, and CIP compared to TC. In the case of the multi-pollutant solution, an approximate 96% mineralization was achieved with the film calcined at 520°C. Although various contaminants exhibit distinct degradation and mineralization mechanisms involving different reactive species at different stages, the catalyst's heterogeneous surface, with its array of active centers, was ideally suited to facilitate interactions between molecules of differing chemical nature and the catalyst surface. This may promote the simultaneous mineralization of diverse organic pollutants.

The evaluation of catalyst reusability and its chemical and photochemical stability constitutes crucial parameters to assess suitability and potential. In Fig. 7a, it was observed that the nonannealed catalyst and those calcined at 250°C and 420°C maintained nearly constant mineralization values over 12 cycles, without any rejuvenation treatment between cycles. However, the catalyst annealed at 520°C exhibited a progressive reduction in catalytic activity upon reuse, decreasing by approximately 39% between the first and twelfth cycle. The catalyst with initially higher catalytic activity experienced a decline in performance with repeated use, and attempts to recover its activity through thermal treatment proved unsuccessful. At pH=8, the results exhibit a similar trend as observed at pH=6. In Fig. 7b, the amount of detectable bismuth in the water resulting from these 12 cycles, in solutions containing TC and PMS, was depicted. The catalyst annealed at 520°C released a greater amount of bismuth, while the uncalcined catalyst showed no bismuth detection. For the catalysts calcined at 250°C and 420°C, the released bismuth levels were an order of magnitude lower than the catalyst annealed at 520°C. As the calcination temperature increased, the dissolved bismuth in the medium post-use also increased. Fig. 7c illustrates the amount of dissolved bismuth when the catalyst was exposed to visible light, in the absence of TC and PMS, over a 72-hour period. This trend mirrored that observed in the presence of pollutant and PMS. It was noteworthy that, in all cases, catalyst dissolution remained below 0.6% of the catalyst. Figure S4 displays FE-SEM micrographs of each catalyst after 72 hours of irradiation, revealing changes in morphology only in the case of the catalyst annealed at 520°C. Consequently, both BiOI and catalysts thermally-treated at 250°C to 420°C exhibited favorable reusability and demonstrated high chemical and photochemical stability. The XRD patterns of the reused photocatalysts, obtained both during the reusability test and after the 72hour irradiation period, unequivocally confirmed their structural stability. Notably, no discernible alterations were observed in the XRD patterns (Figure S5).

In the investigation of the impact of free radicals on TC degradation during visible-light activation of PMS with bismuth oxoiodides-both non-thermally treated and annealed at 250°C, 420°C, and 520°C-under simultaneous visible light irradiation and PMS presence at pH=6.0 and pH=8.0 over a 150-minute treatment period, MeOH and TBA were employed as scavengers. MeOH effectively quenches hydroxyl and sulfate radicals, while TBA specifically quenches hydroxyl radicals due to its faster kinetics with hydroxyl radicals compared to sulfate radicals [51-53]. As depicted in Fig. 7d, the addition of MeOH (50 mM) led to a significant reduction in degradation rates, dropping below 10% for all bismuth oxoiodides. Conversely, the addition of TBA (50 mM) resulted in a less pronounced reduction in degradation, with rates equal to or even higher than 50%. Importantly, hydroxyl radicals originate not only from semiconductor irradiation but also from sulfate radicals reacting with hydroxide ions and water molecules. In this study, the main source of hydroxyl radicals was shown to be the latter process. This was evident from the similar degradation rates observed when PMS was absent, both in the presence and absence of TBA during photocatalyst irradiation. Consequently, while sulfate and hydroxyl radicals are generated during PMS activation and visible light irradiation using bismuth oxoiodides,



Fig. 7. (a) Tetracycline (20 ppm) degradation and mineralization performances of bismuth oxoiodides, non-thermally treated and annealed at 250°C, 420°C, and 520°C, under both simultaneous visible light irradiation and PMS presence at pH=6.0 and pH=8.0 during 150 min of treatment for 12 reusability cycles (without rejuvenation treatment). Released bismuth (b) during twelve consecutive reusability cycles for degrading 20 ppm of TC at pH=6.0 and pH=8.0 (the colors used to indicate pH are the same as in Fig. 7a) and (c) after 72 h of continuous visible light irradiation. (d) Trapping experiments of sulfate and hydroxyl radicals during TC degradation under both simultaneous visible light irradiation and PMS presence at pH=6.0 and pH=8.0 during 150 min of treatment.

sulfate radicals appear to exert a predominant influence on the degradation process. Visible light irradiation not only enhances the degradation and mineralization of TC, facilitated by the increased formation of hydroxyl radicals, holes, and other reactive species due to electron photoexcitation, but also synergistically activates the formation of sulfate radicals.

4. Conclusions

This study initially addresses the effective electrochemical preparation of BiOI as a raw material for various photocatalysts. Analysis of the role of electroactive solution components confirms the electroprecipitation of Bi(III)-iodine species, promoted by the substantial local variation of pH that occurs in the electrode environment when benzoquinone is reduced. Knowledge of this combination of factors allows the establishment of the appropriate potential range for BiOI obtention and opens the way for the future preparation of other mixed bismuth compounds. After the compositional and structural characterization of the as-prepared material at -0.2 V vs Ag|AgCl, its capacity to absorb visible light was confirmed as a crucial factor for the photocatalytic activity performance with sunlight. The comparison of degradation and mineralization results for TC solutions at pH 6 and 8 using the as-prepared material as: i) photocatalyst (under radiation), ii) PMS activator (dark conditions), or iii) combining radiation and PMS allows us to conclude that the PMS-irradiation combination is favorable. This combination

results in degradation values between 66% and 75% and mineralization values between 36% and 44%, with the highest values obtained from the pH 6 solution, a behavior related to the different ionic forms of tetracycline in this pH range. After the thermal treatment of the films at different temperatures, the characterization allows the identification of new species such as Bi₇O₉I₃ after treatment at 250°C, and mainly Bi₅O₇I at 420 or 520°C. Using these thermally treated materials, combining radiation and PMS, a moderate increase in the effectiveness of the remediation process at both pHs was observed, demonstrating the effectiveness of the thermal treatment. Likewise, as observed using the as-prepared films, degradation and mineralization are favored at pH 6 of the TC solution. The versatility of materials as PMS activators in the presence of radiation was demonstrated, using different single solutions at 20 ppm and a multipollutant solution (tetracycline, methylene blue, levofloxacin, and ciprofloxacin), achieving degradation and mineralization percentages similar or even higher, evidencing that the combination of PMS and radiation procedure is a suitable general procedure and its performance also depends on the nature of the contaminants. After being subjected to 12 successive cycles of 150 minutes, the substrates exhibited a quasi-stable behavior, with the exception of those that underwent heat treatment at 520°C. The study confirms the substrates treated under 450°C are both chemically stable and reusable. The low levels of bismuth, measured in parts per billion, and the minimal decrease in mineralization observed after cycles support this conclusion. Bi₅O₇I (420°C) proved to be the most effective catalyst, producing

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superior degradation yields within the MP solution. Additionally, it demonstrated exceptional reusability, a pivotal factor for scaling up operations. Electrochemically prepared bismuth oxyiodide films are multifunctional photocatalysts capable of eliminating various types of contaminants. They also offer potential for the development of more efficient and effective photocatalysts.

CRediT authorship contribution statement

Mohammad Alinezhadfar: Writing – original draft, Methodology, Investigation, Formal analysis. **Elvira Gómez:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Funding acquisition, Conceptualization. **Laura Huidobro:** Writing – original draft, Methodology, Investigation, Formal analysis. **Queralt Bautista:** Methodology, Investigation, Formal analysis. **Albert Serrà:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization.

Declaration of Competing Interest

Authors declare no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.112545.

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