Preparation, Characterization, and Photocatalytic Performance of Ag/BiOBr$_{0.85}$I$_{0.15}$ Nanocomposites

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Abstract: In the present paper, a series of Ag/BiOBr$_{0.85}$I$_{0.15}$ composite nanoparticles with different silver loading were prepared by a combined solvothermal and photocatalytic reduction method. The composite samples have been characterized by XRD, XPS, SEM, EDX, TEM, UV-Vis, and N$_2$ adsorption/desorption techniques. The characterization results showed that BiOBr$_{0.85}$I$_{0.15}$ composite nanoparticles have a tetragonal phase structure. Silver nanoparticles are uniformly distributed on the BiOBr$_{0.85}$I$_{0.15}$, which results in surface plasmon resonance absorption, effectively increasing the visible light absorption ability of BiOBr$_{0.85}$I$_{0.15}$. The photocatalytic activity of the samples was evaluated by photocatalytic degradation of ammonia nitrogen in circulating aquaculture water under simulated sunlight irradiation. The effect of the Ag loading amount on the photocatalytic degradation of ammonia nitrogen was investigated. Silver loading of 1% (molar ratio) can effectively improve the degradation capacity of the catalyst for ammonia nitrogen in water. The recycling experiments show that 1%Ag/BiOBr$_{0.85}$I$_{0.15}$ has good photocatalytic stability. ESR characterization and oxidation species scavenging experimental results suggest that h$^+$, O$_2^-$, and ·O$_2$− are the main oxidizing species in the photocatalytic system.

Keywords: Ag/BiOBr$_{0.85}$I$_{0.15}$; silver loading; photocatalysis; ammonia nitrogen degradation

1. Introduction

Advanced oxidation processes (AOPs) have been widely studied and applied to organic wastewater treatment because of their high capability to oxidize and remove organic compounds and pathogens originated from agricultural, industrial, and domestic activities [1–4]. Photocatalysis technology is one of the most effective AOPs for pollutant degradation [5,6]. Under the excitation of light, the electrons of the semiconductor transit from the valence band to the conduction band, thus forming photogenerated electrons in the conduction band and photogenerated holes in the valence band. The oxidative photogenerated holes and reductive electrons can directly react with pollutants on the surface of the semiconductor, leading to their degradation. Moreover, photocatalysis reaction can produce reactive oxygen species (ROS), which play a key role in the oxidative degradation of organic compounds due to their high reactivity [5–8].

So far, many semiconductors have been studied as photocatalysts, such as TiO$_2$ [9–11], ZnO [12,13], CdS [14,15], SrTiO$_3$ [16], and so forth. Much attention has been paid to improving the photocatalytic ability of semiconductors. However, since the conventional photocatalysts with wide band gaps can only be excited under UV-light irradiation, their practical application has been greatly limited. Because ultraviolet energy accounts for only 4% of solar energy, visible light-driven photocatalysts attract more attention [17]. Therefore, visible-light-responsive photocatalysts have also been prepared, and proved to be effective in the degradation of organic dyes and toxic and bio-refractory organic compounds in water, such as g-C$_3$N$_4$ [18,19], WO$_3$ [20], Ag$_5$PO$_4$ [21,22], Ag$_3$VO$_4$ [23,24], etc. In recent years, Bi-based compounds have been found to have high visible light photocatalytic activity, such as BiVO$_4$ [25,26], Bi$_2$O$_3$ [27], Bi$_2$Ti$_2$O$_7$ [28], Bi$_2$WO$_6$ [29], BiOBr [30], BiOI [31],
AgBiO$_3$ [32], etc. They possess narrow band gaps for their hybridized O 2p and Bi 6s valence bands, which makes them have high visible light catalytic activity [33].

Some solid solutions have been constructed as photocatalysts, showing good catalytic ability in the degradation of pollutants under visible light irradiation. Xu et al. [34] synthesized Zn$_x$Cd$_{1-x}$S solid solution photocatalysts which were extremely active for methylene blue photodegradation under visible light illumination. Zhang et al. [35] synthesized two-dimensional BiOCl$_x$Br$_{1-x}$ solid solution with exposed [001] facets and tunable band gaps by using solvothermal methods. The BiOCl$_{0.5}$Br$_{0.5}$ sample exhibited the highest photocatalytic activity for degrading rhodamine B. Wang et al. [36] developed a BiOBr$_x$I$_{1-x}$ solid solution to degrade 4-chlorophenol under visible light and found that the BiOBr$_{0.85}$I$_{0.15}$ sample showed very good catalytic activity.

On the other hand, much research work has focused on preventing the rapid recombination of photogenerated electrons and holes through a variety of methods to improve the photocatalytic degradation efficiency, such as semiconductor composite [37,38], ion doping [39,40], noble metal deposition [41,42], and so on. Noble metals on the surface of semiconductors can form a Schottky barrier at the contact interface between noble metals and semiconductors, inhibit the recombination of photogenerated hole–electron pairs, and prolong the lifetime of photogenerated carriers.

As the content of ammonia nitrogen (NH$_4^+$-N) is a very important water quality index that affects the aquatic environment of aquaculture, the degradation of ammonia nitrogen is very important. On the other hand, the aquaculture water system contains a variety of nitrogen-containing organic compounds from fish feed residues, fish excreta, and secretions, which may produce ammonia after a series of transformations. In recent years, there have been studies on the direct removal of NH$_4^+$-N through a photocatalytic reaction. Under the action of oxygen-containing free radicals, ammonia can gradually lose hydrogen atoms and finally convert to N$_2$ [43]. In this research, a series of Ag/BiOBr$_{0.85}$I$_{0.15}$ composite nanoparticles with different silver loading were synthesized via the solvothermal method and the photocatalytic reduction method. The composition, structure, morphology, and optical properties of the photocatalysts were characterized. The photocatalytic activity of the catalysts was investigated by the degradation of NH$_4^+$-N in aquaculture wastewater under simulated sunlight irradiation. The photocatalytic mechanism of the photocatalyst was also discussed.

2. Preparation and Experimental Details

2.1. Photocatalyst Preparation

The solvothermal method was used to synthesize the BiOBr$_{0.85}$I$_{0.15}$ nanoparticles [36]. In a typical process, 1.215 g bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) (Sinopharm Chemical Reagent, Shanghai, China) and 1.000 g polyvinylpyrrolidone (PVP, K-30) (Zhanyun Chemical, Shanghai, China) were mixed with 60 mL glycerol (Zhanyun Chemical, Shanghai, China) and 60 mL H$_2$O. The mixture was stirred to form solution A. Then, 0.219 g sodium bromide (NaBr) (Zhanyun Chemical, Shanghai, China) and 0.0622 g potassium iodide (KI) (Zhanyun Chemical, Shanghai, China) was dissolved into another 20 mL H$_2$O under magnetic stirring to form solution B. Subsequently, under constant agitation, solution B was added to solution A drop by drop in 1 h at room temperature. The suspension was transferred into 50 mL Teflon-lined stainless-steel autoclaves for hydrothermal treatment, and kept at 150 °C for 8 h, and then cooled down to room temperature naturally. After filtration, the product was washed with deionized water and absolute ethanol three times, respectively, to remove other impurities, and then dried at 80 °C for 12 h.

Ag nanoparticles were deposited on the surface of BiOBr$_{0.85}$I$_{0.15}$ by a photo-reduction approach [44]. The composite photocatalyst, 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ (molar ratio of Ag to BiOBr$_{0.85}$I$_{0.15}$ = 0.01:1), was prepared as follows: 0.0054 g AgNO$_3$ was dissolved in 50 mL methanol under stirring. Then, 1.000 g of BiOBr$_{0.85}$I$_{0.15}$ nanoparticles were added into the methanol solution while vigorously stirring to form a suspension. The suspension was irradiated with an ultraviolet lamp (λ = 365 nm, 30 w) for 6.0 min. The radiation intensity
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received at the reaction liquid surface was 12.38 W/m² (CAS 140CT Array Spectrometer, Instrument Systems, Munich, Germany). The photocatalytic reduction of silver ions enables the synthesis of Ag/BiOBr₀.₈₅I₀.₁₅. Then, the suspension was filtered and washed with deionized water and absolute ethanol, respectively. Finally, the product was dried at 80 °C for 2.0 h in an electric vacuum drying oven.

2.2. Characterization and Analysis

A transmission electron microscope, Talos F200X TEM (Thermo Scientific, Waltham, MA, USA), was used with about 0.005 g of the sample to obtain the morphology of the photocatalyst. A scanning electron microscope, ZEISS SUPRA 40 SEM (Carl Zeiss Microscopy GmbH, Oberkochen, Germany), was used with about 0.01 g sample to obtain the surface microstructure images of the catalysts, and energy-dispersive X-ray spectroscopy (EDAX) elemental mapping was conducted using a Bruker XFlash 6110 detector (Bruker, Karlsruhe, Germany). X-ray diffraction (XRD) of the nanoparticles was measured by a D8 Advance X-ray diffractometer (Bruker, Germany, λ = 1.5418 Å, Cu Kα radiation) with a scanning speed of 5° min⁻¹, using about 0.2 g of the sample. X-ray photo-electron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fisher Scientific, USA) with monochromatic Al Kα X-ray radiation at 1486.71 eV was applied to identify the surface element composition and chemical states of the as-prepared samples of the nanoparticles, using about 0.03 g of the sample. The specific surface area of the catalysts was determined by an ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) with an analysis bath temperature of 77 K, using about 1 g of the sample. Electron spin resonance (ESR) spectroscopy (Bruker EMX 10/12 spectrometer, Karlsruhe, Germany) was used to investigate the generation of reactive oxygen radicals in the photoreaction system. Hydroxyl radical and superoxide anion radical were captured by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), and singlet oxygen was captured by 2,2,6,6-tetramethylpiperidine (TEMP). The UV-vis diffuse reflectance spectra (DRS) of samples were obtained by a spectrophotometer (UV270, Shimadzu, Kyoto, Japan), using the BaSO₄ as the reflectance sample with about 0.02 g of the sample.

The NH₄⁺-N in water samples was analyzed using chromogenic spectrophotometry by a DR2800 multi parameter water quality analyzer (HACH Company, Loveland, CO, USA), following the HACH Water Analysis Handbook (HACH, Beijing, China, 2010). The NH₄⁺-N was determined by the salicylic acid method.

The transient photocurrents of the as-prepared samples were investigated on an Electrochemical Working Station (CHI660E, Chenhua Instruments Co., Shanghai, China) in a standard three-electrode electrochemical quartz cell with Na₂SO₄ (0.5 M) electrolyte solution. A 500 W Xe light with a filter (λ > 400 nm) was employed as the light source. FTO glass with coated photocatalysts was used as the working electrode. A Pt foil and an Ag/AgCl electrode served as the counter and reference electrode, respectively. The working electrodes were prepared by the spin-coating method. The 10-mg powder sample was dispersed in 1 mL of absolute ethanol, and then 50 µL of Nafion ethanol solution was added, and the uniform suspension was formed by ultrasonic treatment for 30 min. Then, 150 µL of the suspension was added to the ITO glass and dried at room temperature to form a working electrode. The changes of the photoinduced current intensity with time were measured by controlling the cycle light on and off (turn on the light for 20 s, and then turn off the light for another 20 s).

2.3. Photocatalytic Experiments

A certain amount (for example, 0.08 g) of photocatalyst was accurately weighed and added to a beaker containing 100 mL of the water sample from a freshwater-recirculating aquaculture system. The water sample was filtered by an 0.22-µm membrane before photocatalytic degradation. The main water quality parameters of the filtered water sample are pH, 8.0; chemical oxygen demand (COD), 88 mg/L; total organic carbon (TOC), 55 mg/L; and ammonia nitrogen (NH₄⁺-N), 50 mg/L. The catalysts in the water sample
were dispersed by ultrasonic wave for 2.0 min. Subsequently, the suspension was stirred for 60 min in the dark to reach an adsorption–desorption equilibrium on the surface of the catalyst. The photocatalytic degradation of the water sample started under the irradiation of a 300 W xenon lamp. The distance between the light source and the liquid level was 15 cm. The radiation intensity received at the liquid surface of the degradation reaction was 7.416 W/m² (CAS 140CT Array Spectrometer, Instrument Systems, Munich, Germany). The temperature of the degradation system was controlled by a cold trap using constant temperature cooling water. Then, 2.0 mL reaction suspension was taken out at certain intervals. All aliquots were filtered through a 0.22-µm filter membrane before analysis.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

Figure 1 shows the XRD patterns of BiOBr, BiOI, and Ag/BiOBr0.85I0.15 composite catalysts with different silver contents. The diffraction peaks of BiOBr at 2θ = 11.04°, 25.38°, 31.92°, 32.40°, 39.56°, 46.40°, and 57.30° correspond to {001}, {101}, {102}, {110}, {112}, {200}, and {212} crystal planes of the BiOBr crystal, respectively. The position of the BiOBr diffraction peak is consistent with the standard XRD pattern of the standard tetragonal phase BiOBr (JCPDS No. 01-073-2061) of the space group, P4/nmm (129). Its unit cell parameters are a = b = 3.984 Å, c = 9.128 Å. The diffraction peaks of BiOI at 2θ = 10.16°, 30.10°, 32.14°, 37.62°, 45.86°, 51.78°, and 55.56° correspond to {001}, {102}, {110}, {103}, {200}, {114}, and {212} crystal planes of the BiOI crystal, respectively. The position of the BiOI diffraction peak is consistent with the standard XRD pattern of the standard tetragonal phase BiOI (JCPDS No. 01-073-2062). The unit cell parameters are a = b = 3.984 Å, c = 9.128 Å. The diffraction peaks of BiOBr0.85I0.15 at 2θ = 10.88°, 25.38°, 31.74°, 32.40°, 39.36°, 46.44°, and 57.14° correspond to {001}, {101}, {102}, {110}, {103}, {200}, and {212} crystal planes of the BiOBr0.85I0.15 crystal, respectively [36].

In BiOBr0.85I0.15 and Ag/BiOBr0.85I0.15 composite catalysts with different silver contents, the ratio of I to Br is 0.15:0.85. Therefore, the XRD spectrum of the composite catalyst is closer to that of BiOBr. The diffraction peak of BiOBr0.85I0.15 is high and sharp, indicating that the samples have good crystallinity. In order to get the lattice parameters, a and c, of the synthesized BiOBr0.85I0.15 crystal, the Le Bail fitting was used to refine the XRD data (Fullprof, FullProf_Suite Windows (64 bits), Juan Rodríguez-Carvajal, Laboratory Léon Brillouin (CEA-CNRS), CEA/Saclay, France, https://www.ill.eu/sites/fullprof/php/downloads.html). The
lattice parameters, a and c, obtained by fitting are 3.930 Å and 8.270 Å, which is close to the calculated results of the solid solution using Vegard’s Law. Compared with BiOBr$_{0.85}$I$_{0.15}$, the characteristic diffraction peak of Ag/BiOBr$_{0.85}$I$_{0.15}$ has almost no change. Due to the very low concentration and high dispersion of silver in the composite sample, the XRD spectrum shows almost no silver diffraction peak.

3.2. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Energy-Dispersive X-ray (EDX)

Because the SEM and TEM images of the as-prepared samples look very similar, only the pictures of the BiOBr$_{0.85}$I$_{0.15}$ and 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ are presented. Figure 2a–c show the morphology and microstructure of the BiOBr$_{0.85}$I$_{0.15}$ composite catalyst. It can be seen from Figure 2a that the BiOBr$_{0.85}$I$_{0.15}$ is an irregular lump structure composed of many two-dimensional nanosheets with a width of 0.2–1.0 µm and a thickness of about 10–20 nm. Figure 2c shows that the width of the irregular lump structure is about 4.0–10.0 µm. Figure 2d–f show the morphology and microstructure of 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ composite. In terms of morphology, 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ has no obvious difference from BiOBr$_{0.85}$I$_{0.15}$, and also presents an irregular lump structure with a porous surface.

Figure 2. SEM images of BiOBr$_{0.85}$I$_{0.15}$, (a–c); 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$, (d–f).

Figure 3a,b show the TEM and HRTEM images of the prepared BiOBr$_{0.85}$I$_{0.15}$ composite. Figure 3b shows the BiOBr$_{0.85}$I$_{0.15}$ with high crystallinity and clear lattice stripes. The
continuous lattice stripes with a crystal plane spacing of 0.282 nm match well with the [110] plane of tetragonal-phase BiOBr (JCPDs No. 01-073-2061). Figure 3c,d show the TEM and HRTEM images of the prepared 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ composite. Figure 3d also shows the continuous lattice stripes with a crystal plane spacing of 0.282 nm, which match well with the [110] crystal plane of tetragonal-phase BiOBr [45].

Figure 3. TEM images of BiOBr$_{0.85}$I$_{0.15}$, (a,b); 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$, (c,d).

The elemental composition and distribution of the 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ sample are presented in Figure 4. The composite catalyst only contains Bi, O, Br, I, and Ag elements, which is consistent with the theoretical element composition of the composite photocatalyst sample. In addition, the distribution of the above five elements is very uniform, which indicates that silver nanoparticles are uniformly loaded on BiOBr$_{0.85}$I$_{0.15}$ composite nanoparticles. According to the test results of EDX, the rough atomic concentrations of I and Br of the sample surface are 4.76% and 30.18%, respectively. The concentration ratio of I to Br is 15.77:100, which is close to 0.15:0.85 (17.65:100).
3.3. X-ray Photoelectron Spectroscopy (XPS)

The XPS spectra of the BiOBr$_{0.85}$I$_{0.15}$ and 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ samples in Figure 5 provide the chemical composition and valence state of the surface elements. All the XPS peak positions are calibrated by C 1s as reference, with a binding energy of 284.8 eV. Figure 5a shows the survey spectra of the BiOBr$_{0.85}$I$_{0.15}$ and 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$. Only C, O, Bi, Br, and I are detected in BiOBr$_{0.85}$I$_{0.15}$, and C, O, Bi, Br, I, and Ag in 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$, which indicates the high purity of the samples. The Ag3d$_{5/2}$ and Ag3d$_{3/2}$ spin-orbital splitting photoelectrons for 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ in Figure 5b are located at binding energies of 368.0 and 374.0 eV, respectively, which are assigned to metallic-state Ag [46].

As shown in Figure 5c, the two peaks at about 164.5 eV and 159.2 eV are attributed to Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$, respectively, which are characteristic of Bi$^{3+}$ in the BiOX material [47]. The two peaks in Figure 5d can be identified from the Br 3d spectra. The peak at 69.5 eV corresponds to the Br 3d$_{3/2}$, whereas the peak located at 68.4 eV can be attributed to Br 3d$_{3/2}$ in Ag/BiOBr$_{0.85}$I$_{0.15}$ and BiOBr$_{0.85}$I$_{0.15}$, respectively, indicating the presence of Br$^{-}$. Figure 5e shows the high-resolution XPS spectra of the O 1s, which can be fitted into two peaks. The peak at about 530.0 eV are attributed to the Bi-O bonds in [Bi$_2$O$_2$] slabs of the BiOX layered structure, and the small peaks at 531.2 eV are assigned to the hydroxyl groups on the surface in Ag/BiOBr$_{0.85}$I$_{0.15}$ and BiOBr$_{0.85}$I$_{0.15}$ samples, respectively. The two peaks located at 630.5 and 619.0 eV in Figure 5f correspond to I 3d$_{3/2}$ and I 3d$_{5/2}$ in the BiOBr$_{0.85}$I$_{0.15}$ structure, respectively [36]. As a result, the chemical compositions
and valence states presented in the XPS spectra are consistent with the composition of the Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15} and BiOB\textsubscript{0.85}I\textsubscript{0.15}.

![XPS spectra](image)

**Figure 5.** XPS spectra of BiOB\textsubscript{0.85}I\textsubscript{0.15} (sample ①) and 1.0% Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15} (sample ②): survey spectra (a), Ag 3d (b), Bi 4f (c), Br 3d (d), O 1s (e), and I 3d (f).

### 3.4. N\textsubscript{2} Adsorption–Desorption Isotherms

The N\textsubscript{2} adsorption–desorption isotherms of the samples are presented in Figure 6. The BET surface areas of the as-prepared samples were tested and calculated to be 13.30, 12.23, 11.89, 11.80, and 11.29 m\textsuperscript{2}/g for the BiOB\textsubscript{0.85}I\textsubscript{0.15}, 0.5% Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15}, 1.0% Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15}, 1.5% Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15}, and 3.0% Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15} samples, respectively. The BET surface areas of Ag/BiOB\textsubscript{0.85}I\textsubscript{0.15} samples are a little smaller than that of the BiOB\textsubscript{0.85}I\textsubscript{0.15} sample. With the increase of silver loading, the specific surface areas of the samples decreased slightly.
The UV-visible diffuse reflectance spectra of the samples in the range of 200–800 nm are shown in Figure 7a. The BiOBr$_{0.85}$ sample has a stronger absorption of UV light than that of visible light. In the visible region, the light absorption capacity of the sample decreases significantly with the increase of wavelength. With the increase of the silver loading, the absorption of light, especially visible light by the Ag/BiOBr$_{0.85}$I$_{0.15}$ composite, increases significantly. In fact, the as-prepared BiOBr$_{0.85}$I$_{0.15}$ is orange-yellow. Silver nanoparticles are black, which is due to the absorption of visible light caused by surface plasmon resonance. The color of the Ag/BiOBr$_{0.85}$I$_{0.15}$ catalysts become darker with the increase of silver loading.

Figure 7. UV-vis diffuse reflectance spectra (a); the bandgap value, estimated by a related curve of $(\alpha h\nu)^{0.5}$ versus photon energy (b); and the VB-XPS spectra of BiOBr, BiOI, and BiOBr$_{0.85}$I$_{0.15}$ (c).
The bandgap value can be estimated by a related curve of \((\alpha \nu)^{0.5}\) versus photon energy \((\nu)\) according to the Kubelka–Munk function, \(\alpha \nu = \frac{A(h\nu - E_g)^{n/2}}{\nu}\), where \(\alpha\), \(h\), \(\nu\), and \(A\) stand for absorption coefficient, Planck constant, light frequency, and proportionality, respectively [48]. The value of \(n\) is determined by the optical transition mode of the semiconductor. For BiOBr and BiOI, the value of \(n\) is 4 [36].

It can be seen from Figure 7b that the band gap values of BiOBr and BiOI are estimated to be 2.39 eV and 1.58 eV, respectively, and the band gap of the BiOBr\(_{0.85}\)I\(_{0.15}\) composite is 1.98 eV. The band gap energy of the composite is between the energy of BiOBr and BiOI, and is obviously smaller than that of BiOBr, which enhances its absorption of visible light, and is conducive to the photocatalytic reaction.

As shown in Figure 7c, the valence band X-ray photoelectron spectra (VB-XPS) of the samples were investigated. The valence band potential of BiOBr, BiOI, and BiOBr\(_{0.85}\)I\(_{0.15}\) were found to be at 1.22, 0.76, and 0.98 eV, respectively. According to the equation of \(E_{CB} = E_g - E_{VB}\) [49], the conduction band (CB) edges of BiOBr, BiOI, and BiOBr\(_{0.85}\)I\(_{0.15}\) are calculated to be \(-1.17\), \(-0.82\), and \(-1.00\) eV, respectively; this indicates that BiOBr\(_{0.85}\)I\(_{0.15}\) has elevated oxidizing ability compared to BiOI, through a higher VB position.

3.6. Electron Spin Resonance (ESR) Spectroscopy

ESR technology is used to detect reactive oxygen species (-OH, \(^1\)O\(_2\), and -O\(_2^-\)) during the photodegradation process. Figure 8a–c show the ESR signals of DMPO-\(\cdot\)OH, TEMP-\(^1\)O\(_2\), and DMPO-\(\cdot\)O\(_2^-\) adduct with or without light irradiation, respectively. The signals of the reactive oxygen species are almost undetectable or not obvious in the dark. Under visible light irradiation, the six characteristic peaks of DMPO-\(\cdot\)O\(_2^-\) and three characteristic peaks of TEMP-\(^1\)O\(_2\) are very strong, but the four characteristic peaks of -OH are not significant [36,50]. \(\cdot\)OH, \(^1\)O\(_2\), and -O\(_2^-\) are detected in the visible photocatalytic degradation system, which confirmed that these free radicals are produced in the photocatalytic process over Ag/BiOBr\(_{0.85}\)I\(_{0.15}\) nanoparticles. Moreover, \(^1\)O\(_2\) and -O\(_2^-\) are the main oxidation species, whereas -OH is not important under the reaction condition.

![Figure 8. The ESR spectra of DMPO-\(\cdot\)OH (a), the ESR spectra of TEMP-\(^1\)O\(_2\) (b), and the ESR spectra of DMPO-\(\cdot\)O\(_2^-\) (c) (the sample is 1.0% Ag/BiOBr\(_{0.85}\)I\(_{0.15}\) irradiated under the xenon lamp light for 80 s).](image-url)
In photocatalysis, holes can oxidize H₂O or OH⁻ to generate ·OH, whereas ·O₂⁻ is mainly generated by O₂ capturing e⁻. The generation of ·OH depends on whether the E_VB is higher than the redox potential of ·OH/OH⁻ (1.99 eV), and the generation of ·O₂⁻ depends on whether the E_CB of the semiconductor is lower than the redox potential of ·O₂⁻/O₂ (−0.33 eV) [36]. As is stated above, the E_VB and E_CB of BiOBr_{0.85I_{0.15}} are calculated to be 0.98 eV and −1.00 eV, respectively. Therefore, in the photocatalyst surface, ·O₂⁻ can be directly produced, but it is difficult to directly produce ·OH. However, ·OH can be generated by further reduction of ·O₂⁻, which is an indirect way to form ·OH. The ¹O₂ is likely to be formed by the oxidation of ·O₂⁻, which is generated by the reduction of surface-adsorbed O₂ [51]. Moreover, semiconductor catalysts can produce photogenerated electron–hole pairs (excitons, e⁻−h⁺) under UV or visible light radiation. The electrostatic Coulomb interaction of photogenerated exciton usually produces a strong exciton effect, and the accompanying energy transfer can excite O₂ to produce ¹O₂ [52]. The relevant reactions are as follows.

\[ e^- + O_2 \rightarrow O_2^- \]  
(1)
\[ O_2^- + e^- + 2H^+ \rightarrow H_2O \]  
(2)
\[ O_2^- + H_2O \rightarrow \cdot OH + OH^- + O_2 \]  
(3)
\[ O_2^- + h^+ \rightarrow ¹O_2 \]  
(4)
Catalyst + hν \rightarrow Catalyst^*  
(5)
Catalyst^* + 3O₂ \rightarrow Catalyst + ¹O₂  
(6)

3.7. Photocatalytic Degradation of Ammonia Nitrogen

Figure 9 shows the ability of the as-prepared catalysts to degrade NH₄⁺-N in the water sample from the recirculating aquaculture system. The photocatalytic capability comparison between BiOBr_{0.85I_{0.15}} and Ag/BiOBr_{0.85I_{0.15}} samples with different Ag loading is shown in Figure 9a. Under the blank condition, the NH₄⁺-N value decreased slowly to 73.6% in 8 h under the light irradiation, which implied that the light radiation alone could degrade about 26% of NH₄⁺-N in the water sample. In the presence of BiOBr_{0.85I_{0.15}}, about 32% NH₄⁺-N was degraded within 8 h. Compared with the degradation result of the blank experiment, the addition of BiOBr_{0.85I_{0.15}} did not obviously improve the degradation efficiency of NH₄⁺-N. The degradation rates of NH₄⁺-N in the presence of the photocatalysts, 0.5% Ag/ BiOBr_{0.85I_{0.15}}, 1.0% Ag/ BiOBr_{0.85I_{0.15}}, and 1.5% Ag/BiOBr_{0.85I_{0.15}}, were 40.8%, 52.2%, and 46.2%, respectively. However, the catalytic capacity of the photocatalyst did not continue to increase with the increase of silver loading. The degradation rate of NH₄⁺-N with 3.0% Ag/ BiOBr_{0.85I_{0.15}} was 30.8%, which is significantly lower than that of 1.0% Ag/BiOBr_{0.85I_{0.15}}. The 1.0% Ag/BiOBr_{0.85I_{0.15}} showed the best photocatalytic ability.

Ag nanoparticles on the surface of semiconductors can become electron capture centers, which can improve the separation efficiency of carriers, effectively inhibit the recombination of photogenerated electrons–holes, thus accelerating the photocatalytic reaction rate and improving the photocatalytic activity of Ag/BiOBr_{0.85I_{0.15}} nanoparticles. However, Ag nanoparticles may become the recombination center of carriers when the Ag loading is further increased. On the other hand, too many Ag nanoparticles covering the surface of the catalyst will also affect the effective absorption of light by the catalyst [53].

Figure 10 shows that the 1.0% Ag/BiOBr_{0.85I_{0.15}} nanocomposite displays the highest photocurrent response. It proves that the loading of Ag nanoparticles could enhance the separation efficiency of photogenerated charges of the catalyst. The photocurrent of the 0.5% Ag/BiOBr_{0.85I_{0.15}} sample is close to or slightly higher than that of BiOBr_{0.85I_{0.15}}. The photocurrent of 1.5% Ag/BiOBr_{0.85I_{0.15}} is significantly lower than that of BiOBr_{0.85I_{0.15}}. The results are basically in line with the actual degradation performance of the catalysts. However, it is worth noting that the photocurrent of 3.0% Ag/BiOBr_{0.85I_{0.15}} is higher than that of 1.5% Ag/BiOBr_{0.85I_{0.15}}, and also higher than that of BiOBr_{0.85I_{0.15}} samples. This may be due to the significant increase of the photocurrent generated by the surface.
plasmon resonance of silver nanoparticles. The surface plasmon resonance photocurrent increases significantly with the increase of silver loading. However, since the oxidation of photogenerated holes on the surface of silver nanoparticles is not strong, although the actual photocurrent increases, it cannot effectively promote the degradation performance of the composite catalyst [54,55].

The results shown in Figure 9a indicate that the photocatalysts with different silver loading have different removal effects on NH$_4^+$-N. It is worth noting that the degradation
curves of the experiments with catalysts show significant fluctuation within 8 h, especially a remarkable rise in the initial 1~3 h, whereas the whole degradation curve of the blank experiment shows a downward trend. The fluctuation of the degradation curve implies the complexity of the photodegradation process. The significant increase of the NH$_4^+$-N value in the degradation process may be related to the photocatalytic transformation of nitrogen-containing compounds. There are many complex nitrogen-containing organic compounds in the water of the recirculating aquaculture system, which mainly come from the feed, excreta, and secretions of fish. The existence of the photocatalyst makes the reaction system produce more active oxygen radicals and holes (h$^+$), which leads to a series of subsequent reactions to convert organic nitrogen into NH$_4^+$-N. With the transformation of nitrogen-containing organic matter into NH$_4^+$-N under the photocatalytic condition, the NH$_4^+$-N value increased in the first a few hours, and then began to decline in a fluctuating way, and was, finally, significantly lower than the initial value [56]. Under the same photoreaction condition, different photocatalysts have different conversion rates of nitrogen-containing organic compounds and degradation rates of NH$_4^+$-N, so the fluctuation of their degradation curves is not completely synchronous.

Figure 9b shows the recycling stability of 1.0% Ag/BiOBr$_{0.85}$ used for removing NH$_4^+$-N. It indicates that the 1.0% Ag/BiOBr$_{0.85}$ sample kept stable photocatalytic activity after four-times cycling usage under the simulated sunlight radiation.

The effect of catalyst dosage on the NH$_4^+$-N degradation rate is shown in Figure 9c. The removing rates of NH$_4^+$-N are 33.8%, 48.7%, 52.2%, and 44.7%, respectively, when the photocatalyst dosage increased from 0.02 g/L to 0.12 g/L. With the increase of catalyst dosage, the final degradation rate of NH$_4^+$-N in 8 h increased first, and then decreased. This may be because when the separation efficiency of the photogenerated electron–hole pairs is certain, the greater the amount of the photocatalyst, and the greater the number of surface active sites involved in the catalytic reaction, so as to improve the degradation rate of NH$_4^+$-N. However, when the dosage increased to a certain amount, the removing rate of NH$_4^+$-N decreased. This may be due to the serious agglomeration of photocatalytic materials due to excessive dosage, resulting in the reduction of the surface area effectively used for the catalytic reaction. Moreover, it will also make the solution turbid, and the suspended particles in the solution will scatter the light to prevent the catalyst from making full use of light and to reduce the photocatalytic efficiency.

In order to investigate the main active species in the photocatalytic degradation of NH$_4^+$-N in recirculating aquaculture water under simulated sunlight, active species scavengers, sodium oxalate, isopropanol, and nitrogen (N$_2$), were added to consume or reduce the active species hole (h$^+$), ·OH, ·O$_2^-$, and 1O$_2$, respectively [36,57]. The concentration of ammonium oxalate and isopropanol is about 5 mM. In the beginning of degradation, the water sample was flushed with nitrogen to remove most of the oxygen. The effect of scavengers on NH$_4^+$-N degradation is presented in Figure 9d. The degradation rate of NH$_4^+$-N decreased from 52.2% to 41.2%, 34.5%, and 28.3% after aerating N$_2$ or adding isopropanol and sodium oxalate, respectively, which indicated the degradation efficiency was obviously inhibited. The results suggest that in this degradation system, the important oxidation species are h$^+$, ·O$_2^-$, and 1O$_2$. ·OH radicals make a minor contribution to NH$_4^+$-N degradation. This is consistent with the ESR characterization results.

4. Conclusions

In this work, a series of Ag/BiOBr$_{0.85}$ photocatalysts with different Ag loading (0.5, 1.0, 1.5, and 3.0 mol%) were successfully synthesized through a solvothermal and photoreduction method. The as-prepared photocatalysts were applied to the photocatalytic degradation of NH$_4^+$-N in circulating aquaculture water. The influence of Ag loading on the photocatalytic activity of Ag/BiOBr$_{0.85}$ photocatalysts was investigated. The ESR detection and free radical scavenging experiment results suggest that h$^+$, 1O$_2$, and ·O$_2^-$ are the main oxidation species in the photocatalytic reaction system. The degradation results showed that the appropriate amount of silver loading (0.5, 1.0, and 1.5 mol%) could improve
the catalytic activity of the catalyst, but a further increase of silver loading will inhibit the photocatalytic degradation ability of the catalyst. Among the synthesized photocatalysts, the 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ sample showed the highest photoactivity for the NH$_4^+$-N degradation; this may be due to the inhibition of the recombinaction of photogenerated electrons–holes. The 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ sample also displayed stable photocatalytic activity after four-times cycling usage under the simulated sunlight radiation. Therefore, 1.0% Ag/BiOBr$_{0.85}$I$_{0.15}$ nanocomposites are good candidates for applications as sunlight photocatalysts.

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