Heterostructured $\alpha$-Bi$_2$O$_3$/BiOCl Nanosheet for Photocatalytic Applications

Daoguang Teng $^{1,\dagger}$, Jie Qu $^{1,\dagger}$, Peng Li $^1$, Peng Jin $^1$, Jie Zhang $^2$, Ying Zhang $^1,*$ and Yijun Cao $^1,*$

$^1$ School of Chemical Engineering and Zhongyuan Critical Metals Laboratory, Zhengzhou University, Zhengzhou 450001, China
$^2$ School of Ecology and Environment, Zhengzhou University, Zhengzhou 450001, China
* Correspondence: zhangying777@zzu.edu.cn (Y.Z.); yijuncao@zzu.edu.cn (Y.C.)
† These authors contributed equally to the work.

Abstract: Photocatalytic degradation of organic pollutants in wastewater is recognized as a promising technology. However, photocatalyst Bi$_2$O$_3$ responds to visible light and suffers from low quantum yield. In this study, the $\alpha$-Bi$_2$O$_3$ was synthesized and used for removing Cl$^-$ in acidic solutions to transform BiOCl. A heterostructured $\alpha$-Bi$_2$O$_3$/BiOCl nanosheet can be fabricated by coupling Bi$_2$O$_3$ (narrow band gap) with layered BiOCl (rapid photoelectron transmission). During the degradation of Rhodamine B (RhB), the Bi$_2$O$_3$/BiOCl composite material presented excellent photocatalytic activity. Under visible light irradiation for 60 min, the Bi$_2$O$_3$/BiOCl photocatalyst delivered a superior removal rate of 99.9%, which was much higher than pristine Bi$_2$O$_3$ (36.0%) and BiOCl (74.4%). Radical quenching experiments and electron spin resonance spectra further confirmed the dominant effect of electron holes $h^+$ and superoxide radical anions $\cdot O_2^-$ for the photodegradation process. This work develops a green strategy to synthesize a high-performance photocatalyst for organic dye degradation.

Keywords: Bi$_2$O$_3$; dechlorination; heterostructure; photocatalytic degradation; organic dye

1. Introduction

Current industrial productions generate large amounts of pollutants. Hazardous organic contaminants that exist in industrial wastewater can endanger the whole ecosystem and human health [1]. Rhodamine B (RhB, C$_{28}$H$_{31}$ClN$_3$O$_3$) is one of the most commonly used cationic dyes applied in the textile, painting, medicine and cosmetic industries [2]. Due to its high solubility in aqueous solutions and organic solvents, RhB compound has strong irritation to the skin, eyes and respiratory tract, and can even have potential carcinogenic effects [3,4]. The common removal methods of RhB include adsorption, ion exchange, photocatalytic degradation and biological treatment [5–8]. Among these methods, photocatalytic degradation is recognized as an effective technology with a high removal rate [9].

It is critical to develop a highly efficient photocatalyst for the photocatalytic degradation process. TiO$_2$ is a classical photocatalyst with a wide band gap (3.2 eV) that only allows it to be excited under ultraviolet (UV) light radiation (which only occupies ~5% of the solar light) [10,11]. In last decade, various visible light responding metal oxides/sulfides have attracted attention, such as WO$_3$ (2.7 eV), Bi$_2$O$_3$ (2.6–2.8 eV), SrNbO$_3$ (2.3 eV) and CdS (2.4 eV) [12–15]. Due to low toxicity, bismuth-based semiconductor Bi$_2$O$_3$ has emerged as an alternative candidate [16]. Generally, Bi$_2$O$_3$ has two common polymorphs: monoclinic $\alpha$ phase (~2.8 eV) and tetragonal $\beta$ phase (~2.6 eV) [17]. Previous studies mainly focused on the $\beta$-Bi$_2$O$_3$. For example, Brezesinski et al. [18] used $\beta$-Bi$_2$O$_3$ to decompose RhB and the catalyst showed a degradation rate of ~80% within 2.5 h. However, the $\beta$-Bi$_2$O$_3$ is a thermodynamic metastable phase [19], and there were few reports about stable $\alpha$-Bi$_2$O$_3$. 

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Currently, the low quantum yield originating from the rapid recombination of photogenerated electron-hole pairs limits the practical application of α-Bi$_2$O$_3$ [20]. To improve photocatalytic performances of Bi$_2$O$_3$, heterostructure is an available approach [21]. The heterogeneous interface between different compositions in heterostructure-based material can modify electronic band structure [22,23]. Due to same element of Bi and the close band gap of ~3.5 eV, BiOCl is an ideal composition matched to Bi$_2$O$_3$ [24]. Furthermore, the layered structure of BiOCl can shorten photoelectron transmission distance and accelerate the separation of photogenerated electron-hole pairs [25,26]. Combing a narrow band gap with a distinctive nanostructure is an appealing strategy to simultaneously achieve visible light response and high quantum yield. The BiOCl is usually prepared through the reaction between Bi$_2$O$_3$ and HCl [27]. It is still a huge challenge to develop a green method for synthesizing a Bi$_2$O$_3$/BiOCl heterostructured photocatalyst.

Chloride ion (Cl$^-$) is also a common inorganic pollutant in strongly acidic wastewater from the metallurgical industry [28]. The high Cl$^-$ content could cause metal corrosion, soil salinization and human diseases. The conventional removal technique of Cl$^-$ in acidic wastewater is to use Cu(0) and Cu(II) for generating CuCl precipitate [29]. Unfortunately, the low removal efficiency (<60%) would lead to a high concentration of residual Cl$^-$ (>400 mg/L). In view of this, the Bi$_2$O$_3$ could be applied to capture Cl$^-$ in acidic wastewater and be transformed to the BiOCl product [30].

Herein, the as-prepared α-Bi$_2$O$_3$ was used to remove high concentration Cl$^-$ wastewater to generate the BiOCl. By coupling Bi$_2$O$_3$ with layered BiOCl, the α-Bi$_2$O$_3$/BiOCl composite material exhibited the nanosheet structure. The heterogeneous interface between Bi$_2$O$_3$ and BiOCl can serve as “heterojunction” to enhance the photocatalytic activity due to efficient charge separation and transfer across the interface [31,32]. In this case, the binary Bi$_2$O$_3$/BiOCl catalyst delivered a larger degradation rate of RhB under visible light irradiation than pristine Bi$_2$O$_3$ or BiOCl.

2. Experimental

2.1. Preparation of α-Bi$_2$O$_3$

All reagents were of analytical grade and purchased from Sinopharm Group Co. Ltd., Shanghai, China. On the basis of previous literature [19], 12.13 g of Bi(NO$_3$)$_3$·5H$_2$O (25 mmol) was dissolved in 50 mL of deionized H$_2$O and 4 mL of HNO$_3$ (68 wt%) under continuous stirring of 300 RPM for 10 min. NH$_3$·H$_2$O (28 wt%) was added dropwise into the above solution until pH was ~7, and then the solution was stirred under ultrasonic radiation at 80°C for 10 h. After filtration and drying, the residue was calcined at 500°C for 2 h to obtain the yellow α-Bi$_2$O$_3$ product.

2.2. Preparation of BiOCl and Bi$_2$O$_3$/BiOCl from Adsorbed Cl$^-$

BiOCl was synthetized by using Bi$_2$O$_3$ to adsorb Cl$^-$ in wastewater. Typically, 1.64 g of as-prepared Bi$_2$O$_3$ powder (3.52 mmol) was dissolved in 100 mL NaCl aqueous solution (initial Cl$^-$ concentration of 1000, 2000, 2500, 3000, or 4000 mg/L) under continuous stirring of 300 RPM for 10 min. NH$_3$·H$_2$O (28 wt%) was added dropwise into the above solution until pH was ~7, and then the solution was stirred under ultrasonic radiation at 80°C for 10 h. After filtration and drying, the residue was calcined at 500°C for 2 h to obtain the yellow α-Bi$_2$O$_3$ product.

2.3. Characterizations

Bruker AXS D8 ADVANCE diffractometer (Cu Kα source) (Bremen, Germany) was employed to characterize the X-ray diffraction (XRD) patterns. Surface functional groups
were tested using a Fourier transform infrared spectroscopy (FTIR) analyzer (Nicolet iS10, Thermo Fisher Scientific, Waltham, MA, USA) mixed with KBr. Element compositions were characterized by an ESCA LAB MK-II X-ray photoelectron spectrometer (XPS, VG Scientific, Uppsala, Sweden). Micromorphologies were investigated by the field emission scanning electron microscopy (FESEM, SU8010, Hitachi, Ibaraki, Japan) with an energy-dispersive spectrometer (EDS) and transmission electron microscopy (TEM, JEM-2100F, 200 kV, JEOL, Tokyo, Japan). Specific surface areas were analyzed at 77 K using the Brunauer–Emmett–Teller (BET) method via the Micromeritics analyzer (Autosotrb-IQ2-MP-XR, Norcross, GA, USA). Thermal behavior was analyzed by a thermogravimetric (TG) analyzer (NETZSCH, STA449F3, Selb, Germany) with a heating rate of 5 °C/min in a nitrogen atmosphere. The UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded on a UV-3600 PLUS spectrophotometer (Shimadzu, Kyoto, Japan). Electron spin resonance (ESR) spectra were obtained by Bruker EMXPLUS (Bremen, Germany). Intermediates of photocatalysis were detected by liquid chromatography-mass spectrometer (LC–MS, Ultimate 3000 UHPLC-Q Exactive, Thermo Fisher Scientific, Waltham, MA, USA) equipped with an electrospray ionization (ESI) positive ion mode.

2.4. Photocatalytic Degradation Measurement

The photocatalytic degradation performances of the materials were evaluated by using RhB solution. First, 20 mg Bi$_2$O$_3$ or Bi$_2$O$_3$/BiOCl was added into 100 mL RhB solution (20 mg/L) under stirring of 300 RPM at room temperature for 30 min in the dark, and then a 300 W Xe lamp (Asahi Spectra, MAX-303, Tokyo, Japan) was used for photocatalytic irradiation. The control experiments of adsorption were conducted as the same as photocatalytic degradation, but without light radiation during the whole process. The RhB concentration in the solution was analyzed using the ultraviolet-visible (UV–Vis) spectrophotometer (Shimadzu, UV-3600 PIUS, Kyoto, Japan) at wavelength of ~550 nm.

Radical quenching experiments were conducted to detect the dominant active species for RhB degradation. Isopropanol (IPA, 10 mmol/L), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 5 mmol/L) and 1,4-benzoquinone (BQ, 1 mmol/L) were employed to quench hydroxyl radical (·OH), hole (h$^+$) and superoxide radical (·O$_2^-$), respectively [34]. All the experiments were conducted under the same conditions as in the photocatalytic degradation test except for the addition of a separate scavenger.

Removal rate ($R_t$) of pollutant was calculated using Equation (2).

$$R_t = \frac{C_0 - C_t}{C_0} \times 100\%$$ (2)

where $C_0$ and $C_t$ are the concentration of pollutant at contact time of 0 and $t$, respectively.

Reaction kinetic study was evaluated using the pseudo first-order model of Equation (3) [17].

$$-\ln(C_t/C_0) = k \cdot t$$ (3)

where $k$ is the apparent rate constant of equation.

3. Results and Discussion

3.1. Physical Properties of Materials

According to Figure S1, Bi$_2$O$_3$ presented excellent adsorption capacity of Cl$^-$ in the acidic solution. Under the optimal conditions of pH = 1, initial Cl$^-$ concentration = 2500 mg/L, Bi$_3^+$:Cl$^-$ ratio = 1:1, contact time = 180 min and the removal rate of Cl$^-$ could be reached to >95%, which suggests that there is a low concentration of residual Cl$^-$ (<120 mg/L) [30]. The dechlorination products of BiOCl and Bi$_2$O$_3$/BiOCl were further used for photocatalysts.

The XRD patterns of Bi$_2$O$_3$, BiOCl and Bi$_2$O$_3$/BiOCl are illustrated in Figure 1a. For the Bi$_2$O$_3$, two sharp peaks located at around 27.5° and 33.3° could be attributed to the (120) and (200) planes of monoclinic α-Bi$_2$O$_3$ (JCPDS #72-0398), respectively [20]. Several
diffraction peaks at approximately 11.9°, 25.8°, 32.5° and 33.4° corresponded to the (001), (101), (110) and (102) planes of tetragonal BiOCl (JCPDS #85-0861), respectively [35]. The Bi$_2$O$_3$/BiOCl composite displayed a hybrid pattern with characteristic peaks of α-Bi$_2$O$_3$ and BiOCl, which suggests that it maintained the original crystal structure of the two compositions. All materials showed sharp diffraction peaks, which indicated their good crystallinity [19].

Figure 1. Physical properties of Bi$_2$O$_3$, BiOCl and Bi$_2$O$_3$/BiOCl: (a) XRD patterns, (b) FTIR spectra, (c) liquid nitrogen adsorption–desorption isotherms; high-resolution XPS spectra of (d) Bi 4f, (e) O 1s and (f) Cl 2p.

Figure 1b presented the FTIR spectra of three materials. For the Bi$_2$O$_3$, two broad absorption peaks at ~3450 and ~1620 cm$^{-1}$ could be classified as the stretching and bending vibrations of the O–H bond, respectively [20]. A peak located at ~850 cm$^{-1}$ was attributed to the stretching vibration of Bi–O–Bi bond, and a sharp peak at ~520 cm$^{-1}$ was assigned to the stretching vibration of Bi–O bond [36]. With regard to the BiOCl, the Bi–O–Bi peak disappeared and a new peak appeared at ~1380 cm$^{-1}$ (stretching vibration of Bi–Cl bond) [37]. The Bi$_2$O$_3$/BiOCl simultaneously contained the Bi–O–Bi and Bi–Cl peaks, which indicated the successful preparation of such composite material.

The porosities of Bi$_2$O$_3$, BiOCl and Bi$_2$O$_3$/BiOCl were characterized by the liquid nitrogen adsorption–desorption isotherms in Figure 1c. All materials exhibited type IV isotherms with a hysteresis loop, which suggests the existence of mesopores (2–50 nm) [38]. Among the three samples, the Bi$_2$O$_3$/BiOCl expressed the largest N$_2$ adsorption volume, which suggests its maximum specific surface area. Using the BET method, the surface area of Bi$_2$O$_3$/BiOCl was calculated as 11.2 m$^2$/g, which was much higher than the 2.3 m$^2$/g of Bi$_2$O$_3$ and 6.8 m$^2$/g of BiOCl. In addition, Figure S2 reveals the Barrett–Joyner–Halenda (BJH) pore size distributions of three samples [39]. Similarly, the Bi$_2$O$_3$/BiOCl composite delivered the largest pore volume with an average pore diameter of 20.7 nm (Table S1). The large surface area and pore volume of Bi$_2$O$_3$/BiOCl can expose more active site, which is beneficial for subsequent adsorption and photocatalysis [15,40].

The TG (25–900 °C) analysis was used to investigate the thermal stability of Bi$_2$O$_3$/BiOCl. From Figure S3, the small weight loss on the TG curve below 700 °C could be assigned to the absorbed water. Until the temperature rose to 700 °C, an obvious decline started to
appear at 700–800 °C, which can be attributed to the pyrolysis of the BiOCl composition [35]. The result revealed the excellent thermal stability of the Bi$_2$O$_3$/BiOCl material.

The XPS survey spectra of Bi$_2$O$_3$, BiOCl and Bi$_2$O$_3$/BiOCl is presented in Figure S4. For the Bi$_2$O$_3$, some obvious peaks at around 159, 285, 442 and 531 eV were attributed to the Bi 4f, C 1s, Bi 4d and O 1s, respectively [41]. Two new peaks appeared at 197 and 268 eV in BiOCl and Bi$_2$O$_3$/BiOCl spectra could correspond to the Cl 2p and Cl 2s. It confirmed the successful introduction of Cl$^-$ [37]. For the high-resolution Bi 4f spectra in Figure 1d, all samples displayed two spin-orbit doublet peaks of Bi 4f$_{7/2}$ (159.2 eV) and Bi 4f$_{5/2}$ (164.5 eV). The above doublet peaks could be attributed to the presence of Bi$^{3+}$ [38]. The O 1s spectra (Figure 1e) could be deconvoluted into two compositions. The peak at 529.8 eV was assigned to the lattice oxygen of Bi–O–Bi and the peaks at 531.3 eV originated from adsorbed oxygen in the water molecule (H–O–H) [27]. The Cl 2p high-resolution spectra (Figure 1f) also expressed two spin-orbit doublet peaks of Cl 2p$_{3/2}$ (198.0 eV) and Cl 2p$_{1/2}$ (199.5 eV) for the characteristic of Cl$^-$ [39].

Figure 2 shows the SEM images of three samples. As observed in Figure 2a, the as-prepared Bi$_2$O$_3$ was stacked by interlaced nanorods with irregular shapes [19,42]. These irregular nanorods had the particle size of 100–300 nm (Figure 2b). After chlorination, the nanorods disappeared and there were only irregular nanoflakes for the BiOCl (Figure 2c,d) [27,43]. For the Bi$_2$O$_3$/BiOCl composite, Figure 2e displayed a distinctive structure different from both Bi$_2$O$_3$ and BiOCl. The Bi$_2$O$_3$/BiOCl was assembled by numerous staggered nanosheets with a diameter of 80–200 nm (Figure 2f). Such a distinctive nanosheet array structure of Bi$_2$O$_3$/BiOCl can devote a large surface area and provide more active sites for photocatalytic reactions [26,33]. The mapping images (Figure 2g) detected the uniform distribution of Bi, Cl and O elements on Bi$_2$O$_3$/BiOCl [37,44].

![Figure 2. SEM images of (a,b) Bi$_2$O$_3$, (c,d) BiOCl and (e,f) Bi$_2$O$_3$/BiOCl; (g) mapping images of Bi, Cl and O elements on Bi$_2$O$_3$/BiOCl.](image)

The TEM images were used to further reveal the microstructure of Bi$_2$O$_3$/BiOCl. From Figure 3a,b, the Bi$_2$O$_3$/BiOCl presented a thin nanosheet structure, which was consistent with the SEM results. The high resolution TEM (HR-TEM) in Figure 3c showed clear
lattice fringes. These lattice fringes exhibited different arrangement directions with various crystalline domains, and could be attributed to Bi$_2$O$_3$ and BiOCl nanocrystallines [42]. For example, the lattice fringes with d-spacing of 0.33 nm were assigned to the (120) plane of Bi$_2$O$_3$, and the lattice fringes with d-spacing of 0.74 nm were assigned to the (001) plane of BiOCl (Figure 3d) [30,45]. A fast Fourier transform (FFT) image (inset in Figure 3d) illustrates regular lattice patterns for monoclinic crystal (Bi$_2$O$_3$) and tetragonal crystal (BiOCl), verifying two compositions of Bi$_2$O$_3$/BiOCl [30]. The heterogeneous interface of the material can modify electronic structure and improve the photocatalytic performances [46].

![Figure 3](image-url)  
Figure 3. (a,b) TEM images of Bi$_2$O$_3$/BiOCl nanosheet; (c,d) HR-TEM images of Bi$_2$O$_3$/BiOCl with clear lattice fringes (inset in figure d was the FFT patterns).

3.2. Photocatalytic Performances

UV–Vis DRS were conducted to characterize the optical absorption properties of Bi$_2$O$_3$, BiOCl and Bi$_2$O$_3$/BiOCl. As illustrated in Figure 4a, Bi$_2$O$_3$ and Bi$_2$O$_3$/BiOCl possessed strong absorption in the UV light region compared with that of BiOCl [47]. The absorption edges of Bi$_2$O$_3$, Bi$_2$O$_3$/BiOCl and BiOCl were 440, 380 and 360 nm, respectively. Band gap energy ($E_g$) of the semiconductor photocatalyst can be calculated according to the Beer-Lambert law (Equation (S1)) based on the absorption edge [17,48]. The $E_g$ values of Bi$_2$O$_3$ and BiOCl were calculated as 2.85 eV (Figure 4b) and 3.52 eV (Figure 4c). In addition, the positions of the valence band edge ($E_{VB}$) and conduction band edge ($E_{CB}$) for Bi$_2$O$_3$ and BiOCl were also estimated according to Equations (S2) and (S3) [17,49].
two compositions. Compared to pristine Bi$_2$O$_3$ or BiOCl, these hybrid compositions can modify band structure and enhance the photocatalytic activity [41,45].

RhB was employed as the target pollutant to investigate the photocatalytic performances of the materials. Figure 5a showed the adsorption effect of three samples in darkness. The RhB can exist stably in the solution during the whole process without any photocatalyst (blank curve) [37]. Adding the materials, all three curves achieved the adsorption–desorption equilibrium at a contact time of 30 min. In addition, the Bi$_2$O$_3$/BiOCl exhibited the maximum adsorption capacity (minimum $C_t/C_0$ value). The reason could be attributed to the large surface area of Bi$_2$O$_3$/BiOCl [38].

The optical properties of the materials are summarized in Table S2 and Figure 4d. Based on analysis above, the Bi$_2$O$_3$/BiOCl composite was a hybrid photocatalyst with two compositions. Compared to pristine Bi$_2$O$_3$ or BiOCl, these hybrid compositions can modify band structure and enhance the photocatalytic activity [41,45].

Figure 4. (a) UV–Vis DRS spectra of Bi$_2$O$_3$, BiOCl and Bi$_2$O$_3$/BiOCl; band gap energy $E_g$ of (b) Bi$_2$O$_3$ and (c) BiOCl; (d) schematic illustration of band gap structure of Bi$_2$O$_3$ and BiOCl.
The photodegradation behavior of RhB was displayed in Figure 5b. After the adsorption process in darkness for 30 min, there was no obvious degradation for RhB by using the Bi2O3. The Bi2O3/BiOCl composite presented significant degradation of its performance, with a total removal rate of ~99.9% at an irradiation time of 60 min (determined from the UV–Vis absorbance spectra of RhB in Figure 5c) [20]. By contrast, the total removal rates of Bi2O3 and BiOCl were only recorded as 36.0% and 74.4%, respectively. Accordingly, the removal rate of RhB increased as Bi2O3/BiOCl > BiOCl > Bi2O3 [41,42]. The surface area values of the catalysts exhibited the positive correlation with the removal rate of RhB, which suggests that the larger surface area can provide more active sites for photocatalytic reaction.

Figure 5d illustrated the pseudo first-order kinetic model of RhB photodegradation [17]. Using the linear fitting, the Bi2O3/BiOCl showed the steepest straight line with the largest slope value among three samples, which indicates its excellent photocatalytic activity [35,37]. The apparent rate constant k of kinetic equation was recorded in Figure 5e. As expected, the Bi2O3/BiOCl catalyst had the maximum k value of 0.1061 min⁻¹. The k value was almost 100 times higher than that of Bi2O3 (0.0013 min⁻¹).

Norfloxacin and tetracycline hydrochloride (TCHC) were used as targets to further estimate the photodegradation performances of Bi2O3/BiOCl. Similarly, after adsorption in darkness for 30 min, both the norfloxacin and TCHC expressed obvious degradation (Figure 5f). At irradiation time of 120 min, the total removal rates of norfloxacin and TCHC were recorded as 59% and 63%, respectively. The high removal rates of organic pollutants (e.g., RhB, norfloxacin and TCHC) demonstrated the availability of our Bi2O3/BiOCl photocatalyst [36,48].

The stability for the Bi2O3/BiOCl catalyst after 60 min photocatalytic degradation of RhB was evaluated. As shown in Figure 6a, the catalytic Bi2O3/BiOCl sample presented a similar XRD pattern to pristine Bi2O3/BiOCl, with significant characteristic peaks of
monoclinic Bi$_2$O$_3$ and tetragonal BiOCl. Such results confirmed the good structure stability of Bi$_2$O$_3$/BiOCl material [49,50].

![Figure 6](image)

Figure 6. Stability evaluation for Bi$_2$O$_3$/BiOCl after 60 min photocatalytic degradation of RhB: (a) XRD pattern of sample; XPS spectrum of (b) Bi 4f and (c) O 1s; (d) SEM image.

Figure 6b exhibited the high-resolution Bi 4f spectrum of Bi$_2$O$_3$/BiOCl after degradation testing. The sample showed two spin-orbit doublet peaks of Bi 4f$_{7/2}$ (159.0 eV) and Bi 4f$_{5/2}$ (164.3 eV) for the Bi$^{3+}$. For the O 1s spectrum (Figure 6c), it included two deconvolutional peaks: lattice oxygen in Bi–O–Bi (529.6 eV) and adsorbed oxygen in the water molecule (H–O–H) (531.8 eV). Compared to the pristine Bi$_2$O$_3$/BiOCl, the peak corresponding to the O was still maintained [41,45]. A slight shift toward a lower binding energy (~0.3 eV) of the Bi–O peak was ascribed to the lower oxidation state of Bi atoms [43].

As observed in Figure 6d, the catalytic Bi$_2$O$_3$/BiOCl sample still displayed the nanosheet shape. The results further demonstrated the potential application opportunity of the Bi$_2$O$_3$/BiOCl photocatalyst [50].

Radical quenching experiments were performed to explore the potential photodegradation mechanism of RhB using Bi$_2$O$_3$/BiOCl. IPA, EDTA-2Na and BQ were employed as scavengers to quench hydroxyl radicals (·OH), electron holes (h$^+$) and superoxide radical anions (·O$_2^-$), respectively [51]. From Figure 7a, adding the IPA into the system made almost no difference to the entire photocatalytic degradation rate. However, EDTA-2Na and BQ (especially EDTA-2Na) greatly inhibited Bi$_2$O$_3$/BiOCl from degrading RhB. In other words, ·OH did not play a role here while h$^+$ and ·O$_2^-$ dominated the photocatalytic degradation of RhB by Bi$_2$O$_3$/BiOCl [39,52]. Using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a capture agent, the ESR electron spin capture technology was performed to further detect the generation of ·OH and ·O$_2^-$. No ·OH signals appeared whether or not there was light (Figure S5). As for the ·O$_2^-$ active free radical, no signal was generated in the dark, while the obvious characteristic peak of the ·O$_2^-$ spectrum was observed after
light irradiation (Figure 7b) [35,53]. Therefore, ·O$_2^-$ was proven to be produced and ·OH was absent during the light reaction, which was inconsistent with the result of radical quenching experiments.

![Figure 7](image_url)

Figure 7. (a) Effects of different scavengers during the RhB photocatalytic degradation process; (b) ESR spectra by adding DMPO to capture ·O$_2^-$ with Bi$_2$O$_3$/BiOCl; (c) LC–MS (positive ESI scan) spectra of the photocatalytic degradation of RhB; (d) the probable degradation pathway of RhB by Bi$_2$O$_3$/BiOCl.

The main degradation route of RhB using Bi$_2$O$_3$/BiOCl was deduced according to LC–MS analysis, as shown in Figure 7c. The probable degradation pathway was present in Figure 7d based on the detected intermediates in Figure 7c. Generally, RhB degradation included five main steps: N-de-ethylation, chromophore cleavage, de-carboxylation, ring opening, and mineralization [35,52]. RhB was decomposed by Bi$_2$O$_3$/BiOCl into various molecular fragments step by step under light irradiation gradually, and was completely degraded into CO$_2$, H$_2$O, and finally NH$_4^+$ [52,54].

Figure 8 illustrates the synthesis process of the Bi$_2$O$_3$/BiOCl nanosheet and its photocatalytic degradation mechanism of RhB. The as-prepared α-Bi$_2$O$_3$ was used as an adsorbent to remove Cl$^-$ in acidic solution. The adsorbed Bi$_2$O$_3$ could transform the BiOCl and be further assembled into the heterostructured Bi$_2$O$_3$/BiOCl nanosheet [41]. Under visible light irradiation, the electrons on VB of Bi$_2$O$_3$/BiOCl were excited and transferred to CB of the material, leaving h$^+$ on the VB. These photogenerated e$^-$ can react with adsorbed O$_2$ on the Bi$_2$O$_3$/BiOCl surface to produce abundant ·O$_2^-$ [55,56]. Such highly oxidizing ·O$_2^-$ and h$^+$ can further react with RhB during the degradation process to generate small molecular substances (e.g., CO$_2$ and H$_2$O) [52,54].
Table 1. The photocatalytic degradation of RhB for some representative catalysts.

| Photocatalyst          | Dosage (mg/mL) | RhB Concentration (mg/L) | Light Source     | Reaction Time (min) | Removal Rate (%) | Ref.               |
|------------------------|----------------|--------------------------|------------------|---------------------|------------------|--------------------|
| Bi$_2$O$_3$/BiOCl      | 20/100         | 20                       | 300 W Xe lamp    | 60                  | 99.9             | This work          |
| Bi$_2$O$_3$/Bi$_2$S$_3$| 50/100         | 20                       | 300 W Xe lamp    | 90                  | 99.7             | [57]               |
| Ag$_2$O/TiO$_2$        | 130/100        | 4.8                      | visible-light     | 80                  | 87.7             | [10]               |
| MoS$_2$/NiFe           | 100/100        | 20                       | 300 W Xe lamp    | 120                 | 90               | [58]               |
| C$_3$N$_4$/ZnO         | 100/100        | 10                       | 300 W Xe lamp    | 90                  | 98.5             | [59]               |
| ZnO/Bi$_2$MoO$_6$      | 25/100         | 10                       | 15 W cool daylight lamp | 180            | 99.3             | [60]               |
| AgI/Bi$_2$O$_3$Br      | 20/100         | 50                       | 300 W Xe lamp    | 60                  | 98               | [61]               |
| Ti$_3$C$_2$/TiO$_2$/BiOCl | 100/100       | 10                       | 500 W Xe lamp    | 120                 | 84               | [49]               |

4. Conclusions

The as-prepared α-Bi$_2$O$_3$ was used to remove Cl$^-$ in acidic solutions to generate BiOCl. The α-Bi$_2$O$_3$/BiOCl heterostructured photocatalyst could be synthetized by coupling Bi$_2$O$_3$ with layered BiOCl. The composite material displayed the staggered nanosheet shape with a diameter of 80–200 nm. Both heterogeneous interface and nanosheet structure enhanced the photocatalytic activity of the material. For example, the Bi$_2$O$_3$/BiOCl binary catalyst delivered an excellent degradation rate of 99.9% for RhB at 60 min of visible light irradiation, which was much higher than 36.0% of Bi$_2$O$_3$ and 74.4% of BiOCl. Radical quenching experiments and ESR spectra confirmed that h$^+$ and ·O$_2^-$ dominated the photocatalytic degradation process of RhB. The probable intermediates of RhB during the photodegradation process were further investigated using the LC–MS analysis. This work constructed a heterostructured Bi$_2$O$_3$/BiOCl photocatalyst with high photocatalytic performances, which provided a new opportunity for potential commercial applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12203631/s1, Calculation of band gap energy $E_{\text{g}}$, valence band edge $E_{\text{VB}}$ and conduction band edge $E_{\text{CB}}$; removal rate of Cl$^-$ onto Bi$_2$O$_3$ (Figure S1), BJH pore size distributions (Figure S2), TG curve of Bi$_2$O$_3$/BiOCl (Figure S3), XPS survey spectra (Figure S4), ESR spectra for capturing ·OH (Figure S5); pore texture parameters of three samples (Table S1), optical properties of Bi$_2$O$_3$ and BiOCl (Table S2).
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References

1. Lim, S.; Shi, J.L.; Gunten, U.; McCurry, D.L. Ozonation of organic compounds in water and wastewater: A critical review. Water Res. 2022, 213, 118053. [CrossRef]
2. Li, K.; He, Y.; Xu, Y.; Wang, Y.; Jia, J. Degradation of Rhodamine B using an unconventional graded photoelectrode with wedge structure. Environ. Sci. Technol. 2011, 45, 7401–7407. [CrossRef] [PubMed]
3. Tang, X.; Feng, Q.; Liu, K.; Li, Z.; Wang, H. Fabrication of magnetic Fe3O4/silica nano composite with enhanced Fenton-like catalytic performance for Rhodamine B degradation. J. Mater. Sci. 2018, 53, 369–384. [CrossRef]
4. Liu, S.; Wang, Y.; Wang, B.; Huang, J.; Deng, S.; Yu, G. Regeneration of Rhodamine B saturated activated carbon by an electroperoxone process. J. Clean. Prod. 2017, 168, 584–594. [CrossRef]
5. Al-Gheethi, A.A.; Azhar, Q.M.; Kumar, P.S.; Yusuf, A.A.; Al-Buriahi, A.K.; Mohamed, R.M.S.R.; Al-shaibani, M.M. Sustainable approaches for removing Rhodamine B dye using agricultural waste adsorbents: A review. Chemosphere 2022, 287, 132080. [CrossRef]
6. Saruchi; Kumar, V; Kaith, B.S.; Jindal, R. Synthesis of hybrid ion exchanger for Rhodamine B dye removal: Equilibrium, kinetic and thermodynamic studies. Ind. Eng. Chem. Res. 2016, 55, 10492–10499. [CrossRef]
7. Ma, J.; Liu, Q.; Zhu, L.; Zou, J.; Wang, K.; Yang, M.; Komarneni, S. Visible light photocatalytic activity enhancement of Ag3PO4 dispersed on exfoliated bentonite for degradation of rhodamine B. Appl. Catal. B Environ. 2016, 182, 26–32. [CrossRef]
8. Rosa, A.L.D.; Carissimi, E.; Dotto, G.L.; Sander, H.L.; Feris, A. Biosorption of rhodamine B dye from dyeing stones effluents using the green microalgae Chlorella pyrenoidosa. J. Clean. Prod. 2018, 198, 1302–1310. [CrossRef]
9. Zhang, S.; Li, B.; Wang, X.; Zhao, G.; Hu, B.; Lu, Z.; Wen, T.; Chen, J.; Wang, X. Recent developments of two-dimensional graphene-based composites in visible-light photocatalysis for eliminating persistent organic pollutants from wastewater. Chem. Eng. J. 2020, 390, 124642. [CrossRef]
10. Liu, G.; Wang, G.; Hu, Z.; Su, Y.; Zhao, L. Ag3O nanoparticles decorated TiO2 nanofibers as a p-n heterojunction for enhanced photocatalytic decomposition of RhB under visible light irradiation. Appl. Surf. Sci. 2019, 465, 902–910. [CrossRef]
11. Song, R.; Chi, H.; Ma, Q.; Li, D.; Wang, X.; Gao, W.; Wang, H.; Wang, X.; Li, Z.; Li, C. Highly efficient degradation of persistent pollutants with 3D nanocone TiO2-based photoelectrocatalysis. J. Am. Chem. Soc. 2021, 143, 13664–13674. [PubMed]
12. Lange, M.A.; Krysiak, Y.; Hartmann, J.; Dewald, G.; Cerretti, G.; Tahir, M.N.; Panthöfer, M.; Barton, B.; Reich, T.; Zeier, W.G.; et al. Solid state fluorination on the minute scale: Synthesis of WO3−xFx with photocatalytic activity. Adv. Funct. Mater. 2020, 30, 1909051. [CrossRef]
13. Xu, X.; Randorn, C.; Irvine, P.E.J.T.S. A red metallic oxide photocatalyst. Nat. Mater. 2012, 11, 595–598. [CrossRef] [PubMed]
14. Cheng, L.; Xiang, Q.; Liao, Y.; Zhang, H. CdS-based photocatalysts. Energy Environ. Sci. 2018, 11, 1362–1391. [CrossRef]
15. Toe, C.Y.; Tsounis, C.; Zhang, J.; Masood, H.; Gunawan, D.; Scott, J.; Amal, R. Advancing photoforming of organics: Highlights on photocatalyst and system designs for selective oxidation reactions. Energy Environ. Sci. 2021, 14, 1140–1175. [CrossRef]
16. Riente, P.; Adams, A.M.; Albero, J.; Palomares, E.; Pericás, M.A. Light-driven organocatalysis using inexpensive, nontoxic BiO3 as the photocatalyst. Angew. Chem. Int. Ed. 2014, 53, 9613–9616. [CrossRef]
17. Xiao, X.; Hu, R.; Liu, C.; Xing, C.; Qian, C.; Zuo, X.; Nan, J.; Wang, L. Facile large-scale synthesis of β-Bi2O3 nanospheres as a highly efficient photocatalyst for the degradation of acetaldehyde under visible light irradiation. Appl. Catal. B Environ. 2013, 140–141, 433–443. [CrossRef]
18. Brezesinski, K.; Ostermann, R.; Hartmann, P.; Perlich, J.; Brezesinski, T. Exceptional photocatalytic activity of ordered mesoporous β-Bi2O3 thin films and electrospun nano fiber mats. Chem. Mater. 2010, 22, 3079–3085. [CrossRef]
19. Cheng, H.; Huang, B.; Lu, J.; Wang, Z.; Xu, B.; Qin, X.; Zhang, X.; Dai, Y. Synergistic effect of crystal and electronic structures on the visible-light-driven photocatalytic activity of Bi2O3 polymorphs. Phys. Chem. Chem. Phys. 2010, 12, 15468–15475. [CrossRef]
20. Bera, K.K.; Majumdar, R.; Chakraborty, M.; Bhattacharya, S.K. Phase control synthesis of α, β and α/β Bi2O3 hetero-junction with enhanced and synergistic photocatalytic activity on degradation of a toxic dye, Rhodamine-B under natural sunlight. J. Hazard Mater. 2018, 352, 182–191. [CrossRef]
21. Jiang, S.; Wang, L.; Hao, W.; Li, W.; Xin, H.; Wang, W.; Wang, T. Visible-light photocatalytic activity of S-doped α-Bi2O3. J. Phys. Chem. C 2015, 119, 14094–14101. [CrossRef]
22. Freitas, R.R.Q.; Mota, F.D.B.; Rivelino, R.; Castilho, C.M.C.D.; Kakanakova-Georgieva, A.; Gueorguiev, G.K. Spin-orbit-induced gap modification in buckled honeycomb XBi and XBi$_2$ (X = Al, Ga, and In) sheets. J. Phys. Condens. Matter 2015, 27, 485306. [CrossRef]

23. Hanif, M.A.; Akter, J.; Islam, M.A.; Lee, I.; Sapkota, K.P.; Shrestha, S.; Pandey, A.; Gyawali, N.; Hahn, J.R. Enhancement of visible-light photocatalytic activity of ZnO/ZnS/g-C$_3$N$_4$ by decreasing the bandgap and reducing the crystallite size via facile one-step fabrication. J. Photochem. Photobiol. A 2022, 431, 114066. [CrossRef]

24. Jia, Z.; Lv, R.; Guo, L.; Zhang, J.; Li, R.; Liu, J.; Fan, C. Rapid degradation of ciprofloxacin over BiOCl: Insight into the molecular structure transformation and antibacterial activity elimination. Sep. Purif. Technol. 2021, 257, 117872. [CrossRef]

25. Kakanakova-Georgieva, A.; Giannazzo, F.; Nicotra, G.; Cora, I.; Gueorguiev, G.K.; Persson, P.O.Á.; Pécz, B. Material proposal for 2D indium oxide. Appl. Surf. Sci. 2021, 548, 149275. [CrossRef]

26. Zhao, Y.; Zhang, S.; Shi, R.; Waterhouse, G.I.N.; Tang, J.; Zhang, T. Two-dimensional photocatalyst design: A critical review of recent experimental and computational advances. Mater. Today 2020, 34, 78–91. [CrossRef]

27. Ding, L.; Wei, R.; Chen, H.; Hu, J.; Li, J. Controllable synthesis of highly active BiOCl hierarchical microsphere self-assembled by nanosheets with tunable thickness. Appl. Catal. B Environ. 2015, 172, 91–99. [CrossRef]

28. Hu, X.; Zhu, F.; Kong, L.; Peng, X. Sulfate radical-based removal of chloride ion from strongly acidic wastewater: Kinetics and mechanism. J. Hazard. Mater. 2021, 410, 124540. [CrossRef]

29. Peng, X.; Dou, W.; Kong, L.; Hu, X.; Wang, X. Removal of chloride ions from strongly acidic wastewater using Cu(0)/Cu(II): Efficiency enhancement by UV irradiation and the mechanism for chloride ions removal. Environ. Sci. Technol. 2019, 53, 383–389. [CrossRef]

30. Huang, S.; Li, L.; Zhu, N.; Lou, Z.; Liu, W.; Cheng, J.; Wang, H.; Luo, P.; Wang, H. Removal and recovery of chloride ions in concentrated leachate by Bi(III) containing oxides quantum dots/two-dimensional flakes. J. Hazard. Mater. 2020, 382, 121041. [CrossRef]

31. Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X. Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances. Chem. Soc. Rev. 2014, 43, 5234–5244. [CrossRef] [PubMed]

32. Ruiz-Castillo, A.L.; Hinojosa-Reyes, M.; Camposeco-Solis, R.; Ruiz, F. Photocatalytic Activity of Bi$_2$O$_3$/BiOCl Heterojunctions Under UV and Visible Light Illumination for Degradation of Caffeine. Top. Catal. 2021, 65, 1071–1087. [CrossRef]

33. Guan, M.; Xiao, C.; Zhang, J.; Fan, S.; An, R.; Cheng, Q.; Xie, J.; Zhou, M.; Ye, B.; Xie, Y. Vacancy associates promoting solar-driven photocatalytic activity of ultrathin bismuth oxychloride nanosheets. J. Am. Chem. Soc. 2013, 135, 10411–10417. [CrossRef]

34. Zhang, P.; Rao, Y.; Huang, Y.; Chen, M.; Huang, T.; Ho, W.; Lee, S.; Zhong, J.; Cao, J. Transformation of amorphous Bi$_2$O$_3$ to crystal Bi$_2$O$_2$CO$_3$ on Bi nanospheres surface for photocatalytic NO oxidation: Intensified hot-electron transfer and reactive oxygen species generation. Chem. Eng. J. 2021, 420, 129814. [CrossRef]

35. Jiang, R.; Lu, G.; Zhou, R.; Dang, T.; Wang, M. Degradation and detoxification of propranolol by a molecular intercalation bismuth oxychloride semiconductor-organic framework. Chem. Eng. J. 2021, 423, 130222. [CrossRef]

36. Ortiz-Quinonez, J.L.; Zumeta-Dubé, I.; Díaz, D.; Nava-Etzana, N.; Cruz-Zaragoza, E.; Santiago-Jacinto, P. Bismuth oxide nanoparticles partially substituted with EuIII, MnIV, and SiIV: Structural, spectroscopic, and optical findings. Inorg. Chem. 2017, 56, 3394–3403. [CrossRef]

37. Zhong, Y.; Wu, C.; Feng, Y.; Chen, D.; Wang, Y.; Hao, D.; Ding, H. Enriched surface oxygen vacancies of BiOCl boosting efficient charge separation, whole visible-light absorption, and photo to thermal conversion. Appl. Surf. Sci. 2022, 585, 152666. [CrossRef]

38. Zhang, J.; Wang, Z.; Fan, M.; Tong, P.; Sun, J.; Dong, S.; Sun, J. Ultra-light and compressible 3D BiOCl / RGO aerogel with enriched synergistic effect of adsorption and photocatalytic degradation of oxtetracycline. J. Mater. Res. Technol. 2019, 8, 4577–4587. [CrossRef]

39. Zhao, Q.; Liu, X.; Xing, Y.; Liu, Z.; Du, C. Synthesizing Bi$_2$O$_3$/BiOCl heterojunctions by partial conversion of BiOCl. J. Mater. Sci. 2017, 52, 2117–2130. [CrossRef]

40. Cheng, G.; Xiong, J.; stadler, F. J. Facile template-free and fast refluxing synthesis of 3D desertrose-like BiOCl nanoarchitectures with superior photocatalytic activity. New J. Chem. 2013, 37, 3207–3213. [CrossRef]

41. Deng, F.; Zhang, Q.; Yang, L.; Luo, X.; Wang, A.; Luo, S.; Dionysiou, D.D. Visible-light-responsive graphene-functionalized Bi-bridge Z-scheme black BiOCl/BiO$_2$$_3$ heterojunction with oxygen vacancy and multiple charge transfer channels for efficient photocatalytic degradation of 2-nitrophenol and industrial wastewater treatment. Appl. Catal. B Environ. 2018, 238, 61–69. [CrossRef]

42. Nagar, A.; Basu, S. Fabrication of 3D porous peony flower-like β-Bi$_2$O$_3$/BiOCl heterostructure for synergistically boosting the visible-light-driven degradation of organic pollutants. Environ. Technol. Innovation 2021, 24, 101956. [CrossRef]

43. Song, Z.; Dong, X.; Wang, N.; Zhu, L.; Luo, Z.; Fang, J.; Xiong, C. Efficient photocatalytic defluorination of perfluorooctanoic acid over BiOCl nanosheets via a hole direct oxidation mechanism. Chem. Eng. J. 2017, 317, 925–934. [CrossRef]

44. Huang, J.; Chen, W.; Yu, X.; Fu, X.; Zhu, Y.; Zhang, Y. Fabrication of a ternary BiOCl/CQDs/rGO photocatalyst: The roles of CQDs and rGO in adsorption-photocatalytic removal of ciprofloxacin. Colloids Surf. A Physicochem. Eng. Asp. 2020, 597, 124758. [CrossRef]

45. Kong, S.; An, Z.; Zhang, W.; An, Z.; Yuan, M.; Chen, D. Preparation of hollow flower-like microspherical β-Bi$_2$O$_3$/BiOCl heterojunction and high photocatalytic property for tetracycline hydrochloride degradation. Nanomaterials 2020, 10, 57. [CrossRef] [PubMed]
46. Mushtaq, F.; Guerrero, M.; Sakar, M.S.; Hoop, M.; Lindo, A.M.; Sort, J.; Chen, X.; Nelson, B.J.; Pellicer, E.I.; Pané, S. Magnetically driven Bi₂O₃/BiOCl-based hybrid microrobots for photocatalytic water remediation. *J. Mater. Chem. A* 2015, 3, 23670–23676. [CrossRef]

47. Chai, S.Y.; Kim, Y.J.; Jung, M.H.; Chakraborty, A.K.; Jung, D.; Lee, W.I. Heterojunctioned BiOCl/Bi₂O₃, a new visible light photocatalyst. *J. Catal.* 2009, 262, 144–149. [CrossRef]

48. Priya, B.; Raizada, P.; Singh, N.; Thakur, P.; Singh, P. Adsorptional photocatalytic mineralization of oxytetracycline and ampicillin antibiotics using Bi₂O₃/BiOCl supported on graphene sand composite and chitosan. *J. Colloid Interface Sci.* 2016, 479, 271–283. [CrossRef]

49. Liu, H.; Yang, C.; Jin, X.; Zhong, J.; Li, J. One-pot hydrothermal synthesis of MXene Ti₃C₂/TiO₂/BiOCl ternary heterojunctions with improved separation of photoactivated carries and photocatalytic behavior toward elimination of contaminants. *Colloids Surf. A Physicochem. Eng. Asp.* 2020, 603, 125239. [CrossRef]

50. Ma, F.; Wu, Y.; Shao, Y.; Zhong, Y.; Lv, J.; Hao, X. 0D/2D nanocomposite visible light photocatalyst for highly stable and efficient hydrogen generation via recrystallization of CdS on MoS₂ nanosheets. *Nano Energy* 2016, 27, 466–474. [CrossRef]

51. Nosaka, Y.; Nosaka, A.Y. Generation and detection of reactive oxygen species in photocatalysis. *Chem. Rev.* 2017, 117, 11302–11336. [CrossRef] [PubMed]

52. Shi, H.; Xie, Y.; Wang, W.; Zhang, L.; Zhang, X.; Shi, Y.; Fan, J.; Tang, Z. In-situ construction of step-scheme MoS₂/Bi₄O₅Br₂ heterojunction with improved photocatalytic activity of Rhodamine B degradation and disinfection. *J. Colloid Interface Sci.* 2022, 623, 500–512. [CrossRef] [PubMed]

53. Dai, Z.; Qin, F.; Zhao, H.; Ding, J.; Liu, Y.; Chen, R. Crystal defect engineering of aurivillius Bi₂MoO₆ by Ce doping for increased reactive species production in photocatalysis. *ACS Catal.* 2016, 6, 3180–3192. [CrossRef]

54. Kang, Z.; Qin, N.I.; Lin, E.; Wu, J.; Yuan, B.; Bao, D. Effect of Bi₂WO₆ nanosheets on the ultrasonic degradation of organic dyes: Roles of adsorption and piezocatalysis. *J. Clean. Prod.* 2020, 261, 121125. [CrossRef]

55. Ghosh, I.; Khamrai, J.; Savateev, A.; Shlapakov, N.; Antonietti, M.; König, B. Organic semiconductor photocatalyst can bifunctionalize arenes and heteroarenes. *Science* 2019, 365, 360–366. [CrossRef] [PubMed]

56. Riente, P.; Fianchini, M.; Llanes, P.; Péricas, M.A.; Noël, T. Shedding light on the nature of the catalytically active species in photocatalytic reactions using Bi₂O₃ semiconductor. *Nat. Commun.* 2021, 12, 625. [CrossRef] [PubMed]

57. Sang, Y.; Cao, X.; Dai, G.; Wang, L.; Peng, Y.; Geng, B. Facile one-pot synthesis of novel hierarchical Bi₃O₅/Bi₂S₃ nanoflower photocatalyst with intrinsic p-n junction for efficient photocatalytic removals of RhB and Cr(VI). *J. Hazard. Mater.* 2020, 381, 120942. [CrossRef] [PubMed]

58. Nayak, S.; Swain, G.; Parida, K. Enhanced photocatalytic activities of RhB degradation and H₂ evolution from in situ formation of the electrostatic heterostructure MoS₂/ NiFe LDH nanoparticle through the Z-scheme mechanism via p–n heterojunctions. *ACS Appl. Mater. Interfaces* 2019, 11, 20923–20942. [CrossRef] [PubMed]

59. Zhong, Q.; Lan, H.; Zhang, M.; Zhu, H.; Bu, M. Preparation of heterostructure g-C₃N₄/ZnO nanorods for high photocatalytic activity on different pollutants (MB, RhB, Cr(VI) and eosin). *Ceram. Int.* 2020, 46, 12192–12199. [CrossRef]

60. Chankhanitha, T.; Nanan, S. Visible-light-driven photocatalytic degradation of ofloxacin (OFL) antibiotic and Rhodamine B (RhB) dye by solvothermally grown ZnO/Bi₂MoO₆ heterojunction. *J. Colloid Interface Sci.* 2021, 582, 412–427. [CrossRef]

61. Zhou, R.; Zhang, D.; Wang, P.; Huang, Y. Regulation of excitons dissociation in AgI/Bi₂O₃Br for advanced reactive oxygen species generation towards photodegradation. *Appl. Catal. B Environ.* 2021, 285, 119820. [CrossRef]