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Article

BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite with high visible-light photocatalytic activity prepared by an ultrasonic hydrothermal method for removing dye and pharmaceutical

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ABSTRACT

A BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite with a high visible-light response and a low photoinduced electron-hole pair recombination rate was successfully synthesized using an ultrasonic-hydrothermal method. The texture, structure, optical, and photocatalytic properties of the composite were characterized. The results showed that the composite had a sheet flower-like structure with a large specific surface area. Ultraviolet-visible diffuse reflection spectra and photoluminescence spectra showed that the composite had an excellent visible-light response and a low recombination rate of photoinduced electron hole pairs. The photocatalytic property of the composite was evaluated by the removal efficiency of rhodamine B and ciprofloxacin under visible-light illumination. The composite's reaction rate constant of removing rhodamine B (/ciprofloxacin) was approximately 8.14 (/4.94), 42.63 (/11.91) and 64.66 (/36.07) times that of Bi₁₂O₁₇Cl₂, P25, and BiOCl, respectively. Furthermore, the composite showed a wide applicable pH range and excellent reusability. Mechanism analysis showed that photogenerated holes played a dominant role and ·O₂⁻ also contributed to photocatalytic degradation. In summary, this study presents a high-efficiency photocatalyst for wastewater treatment.

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1. Introduction

As a low-energy and green technology, photocatalytic technology has attracted increasing attention in recent decades [1,2]. This technology can use solar energy to destroy organic and highly toxic macromolecules [3]. Many photocatalysts such as TiO₂, ZnO, V₂O₅, and WO₃ [4–7] have the advantages of high photosensitivity, low cost, natural nontoxicity, and environmental friendliness for photocatalytic and photoelectrochemical applications [8]. However, those photocatalysts respond only to ultraviolet light due to their wide band gap. Visible-light

catalyst development focused on ion doping, noble metal deposition, and catalyst compounding of traditional catalysts to reduce the width of the band gap [9–11]. That method is highly attractive for exploring new photocatalysts with relatively narrow band gaps and high photocatalytic activity for improving their reaction to visible light [12].

Recently, Bismuth-based semiconductors such as BiOX (X = Cl, Br, and I), Bi₂WO₆, and Bi₂MoO₆ have received significant attention due to their unique electronic structures and decent photocatalytic properties [13–15]. Among them, bismuth oxyhalides [BiOX (X = Cl, Br, and I)] have been confirmed as prom-

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ising photocatalysts for water treatment [16,17]. Bismuth oxychloride (BiOCl) has shown excellent photocatalytic activity under UV light and has achieved the complete degradation of Rhodamine B (RhB) in 40 min [18]. However, its band gap of 3.2 to 3.5 eV means that it cannot degrade pollutants effectively under visible light [19].

Different atomic ratios of Bi:O:Cl, such as Bi₃O₄Cl (2.60 eV), Bi₁₂O₁₇Cl₂ (2.10 eV), Bi₁₂O₁₅Cl₆ (2.86 eV), and Bi₂₄O₃₁Cl₁₀ (2.70 eV), have been synthesized in recent years [20–23]. Those catalysts have narrower band gaps than that of BiOCl and can absorb visible light. Recent research showed that a lower Cl/O ratio might reduce the band gap width of semiconductors and enhance their ability to use visible light [24]. Bi₁₂O₁₇Cl₂ has the lowest Cl/O ratio, and its band gap is the narrowest among those catalysts, so it has great potential for improving visible-light utilization efficiency. However, Bi₁₂O₁₇Cl₂ has a quick electron-hole recombination [25] that reduces the efficiency of photocatalytic reactions. On the other hand, BiOCl has high stability and a low photoelectron recombination rate. In addition, the structure of BiOCl and Bi₁₂O₁₇Cl₂ are similar, and their composite will maintain stability. Thus, combining BiOCl with Bi₁₂O₁₇Cl₂ will improve the latter's stability and delay electron-hole recombination, which will improve the photocatalytic ability of the photocatalyst and facilitate the removal of refractory organic pollutants.

However, a BiOCl-Bi₁₂O₁₇Cl₂ composite, synthesized by a solvothermal method via adjusting the basicity, showed an irregular morphology and insufficient photocatalytic activity. After 4 h of irradiation, only 21.19% to 73.32% pollutant removal was achieved for various pollutants including dyes and pharmaceuticals [26]. Furthermore, the waste solvent produced during preparation likely caused secondary pollution. To improve the catalytic activity and solve the waste solvent problem, an ultrasonication-assisted hydrothermal method was adopted. Ultrasonic waves can strengthen the mass transfer and thermal effects through cavitation [27]. The ultrasonic hydrothermal method can promote the dispersion of active materials on the surface of the carrier and introduce the active ingredients into the material structure, thereby generating more active parts to improve catalytic activity [28].

In this study, a BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite was synthesized using a novel ultrasonic hydrothermal method and was used for a visible-light catalytic reaction. Rh B and ciprofloxacin (CIP) were used as target pollutants. The removal efficiency and catalyst reusability were studied. The mechanism of the catalytic degradation was determined by active species experiments. The aim of this study was to develop a green, stable, and high-efficiency visible-light catalyst for the treatment of refractory organic pollutants.

2. Experimental

2.1. Chemicals

Potassium chloride (KCl) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Sodium hydroxide (NaOH), ethanol, and tert-butyl alcohol (TBA) were purchased from

Beijing Chemical Works, China. Bismuth nitrate pentahydrate [(Bi(NO₃)₃·5H₂O)], benzoquinone (BQ), and sodium oxalate (SO) were purchased from Shandong Xi Ya Chemical Industry Co., Ltd. RhB and CIP were purchased from Shanghai Macklin Biochemical Co., Ltd. P25, the typical commercial TiO₂, was purchased from Aladdin Industrial Corporation, Shanghai, China. All reagents used were of analytical grade.

2.2. Catalyst preparation

The BiOCl-Bi₁₂O₁₇Cl₂ catalyst was prepared using an ultrasonication-assisted hydrothermal method. In a typical synthesis process, 1.94 g of Bi(NO₃)₃·5H₂O (4 mmol) was added to 60 ml of aqueous solution with 0.298 g KCl (4 mmol) and stirred for 30 min to get a white suspension. Then, an ultrasonic treatment by an ultrasonic generator (0.4 W/cm³) (FB-1500, Aoran Technology Ltd, China) was conducted for 5 min, which resulted in a uniformly dispersed suspension. After the ultrasonic treatment, a NaOH aqueous solution (1.0 mol/L) was used to adjust the pH of the suspension to 12.6 along with vigorous stirring. The suspension was ultrasonically treated again for 30 min. After the second ultrasonic treatment, the suspension liquid was poured into a Teflon autoclave (100 ml) and kept at 160 °C for 24 h. The precipitate was collected and washed several times with deionized water and ethanol. Finally, the product was dried at 80 °C for 6 h. The synthesis process is schematically illustrated in Scheme S1. The, BiOCl and Bi₁₂O₁₇Cl₂ were prepared in accordance with previous reports [29,30].

2.3. Catalyst characterization

X-ray diffractometer (XRD) measurements of samples were performed on a D/max-rc diffractometer (Rigaku, Japan) using Cu radiation, and the scanned 2θ range was from 10° to 70°. The microstructure of the catalysts was observed using a Hitachi S-4700 scanning electron microscope (SEM). The high-resolution transmission electron microscopy (HRTEM) was investigated by using a Tecnai G2 20 (FEI Co., Holland) microscope operating at an accelerating voltage of 200 kV, and the sample powder was dispersed into ethanol by sonication and a very dilute suspension was dropped onto a nickel grid. The Brunauer-Emmett-Teller (BET) specific surface area measurement of the sample was made by a 3H-2000PS2 specific surface analysis instrument (BeiShiDe Instrument Technology Co. Ltd., China) using N₂ adsorption-desorption experiments. The ultraviolet-visible (UV-vis) diffuse reflection spectra (DRS) were measured on a UV-2700 UV-vis spectrophotometer (Shimadzu Corp., Japan) with BaSO₄ as a reference. The samples of X-ray photoelectron spectroscopy (XPS) were measured on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA). The photoluminescence (PL) spectra of the samples were measured using a Renishaw RM 1000 fluorescence spectrometer (Renishaw, UK) at room temperature.

2.4. Photocatalytic performance assessment

The photocatalytic activity of the catalysts was evaluated by the degradation of RhB (20 mg/L) and CIP (10 mg/L) under visible-light illumination (a 500 W xenon lamp with a 420 nm cut-off filter; the radiation flux was 15.1 mW/cm²). Typically, a given mass of the sample (ranging from 0.1 to 1.2 g/L) was added to a quartz condensation beaker with 200 mL of contaminant solution. Dark stirring was conducted for 1 hour before illumination to ensure the adsorption-desorption equilibrium. Immediately after that, approximately 3 to 4 mL of the reaction solution was taken out at a specified time, and particles were removed using a 0.22- μ m nitrocellulose filter. The residual RhB and CIP concentrations in the solution were measured using a TU-1900 UV-vis spectrometer (Beijing Purkinje General Instrument Co. Ltd.) at 554 and 277 nm, respectively.

For the reuse experiments, after one run of catalytic reaction, the catalyst was separated, washed by deionized water and ethanol, and then dried at 80 °C. Later, the catalyst was dispersed in another fresh 20 mg/L RhB or 10 mg/L CIP aqueous solution for the next run.

2.5. Potential photocatalytic mechanism experiments

For these experiments, the active species involved in the photocatalytic procedure were examined. The superoxide radical ($\cdot\text{O}_2^-$), holes (h^+), and the hydroxyl radical ($\cdot\text{OH}$) were consumed by adding benzoquinone (BQ, 1 mmol/L), sodium oxalate (SO, 1 mmol/L), and tert-butyl alcohol (TBA, 10 mmol/L), respectively [31,32]. Except for the addition of a scavenger, the active species was detected under the same conditions as the RhB photodegradation reaction. The test of the reactive radicals trapped with electron spin resonance (ESR) was carried out using a Bruker A300 (Bruker, German). Typically, 10 mg of photocatalyst was dissolved in 500 μ L of methanol (DMPO- $\cdot\text{O}_2^-$), after which 45 μ L DMPO was added, followed by ultrasonic dispersion for 10 min.

2.6. Data quality control

All experiments were repeated three times and the averaged values were reported.

3. Results and discussion

3.1. Characterization of BiOCl-Bi₁₂O₁₇Cl₂

3.1.1. XRD analysis

The crystal structures of BiOCl, Bi₁₂O₁₇Cl₂, and the BiOCl-Bi₁₂O₁₇Cl₂ composite were investigated using XRD analysis. Fig. 1 shows that all peaks of the BiOCl and Bi₁₂O₁₇Cl₂ consisted primarily of BiOCl (JCPDS card number 06-0249) and Bi₁₂O₁₇Cl₂ (JCPDS card number 37-0702), respectively. The sample prepared using the ultrasonic-assisted hydrothermal method was well indexed to the phases of both BiOCl and Bi₁₂O₁₇Cl₂. No impurity peaks were observed over the BiOCl-Bi₁₂O₁₇Cl₂ composite, demonstrating that the composite was synthesized successfully.

Fig. 1. XRD patterns of BiOCl, Bi₁₂O₁₇Cl₂, and BiOCl-Bi₁₂O₁₇Cl₂ composite.

3.1.2. XPS analysis

The chemical state and composition of the BiOCl-Bi₁₂O₁₇Cl₂ composite were studied using XPS analysis. Fig. 2 shows the XPS spectra of the composite. It can be seen that the peaks of the C, Bi, O, and Cl elements could be accurately identified. The high-resolution XPS spectra of the sample for Bi 4f (Fig. 2(b)) shows that the binding energies of Bi 4f_{5/2} and Bi 4f_{7/2} were 164.9 and 159.6 eV, respectively, corresponding to the characteristics of Bi³⁺ [33]. Fig. 2(c) shows the Cl 2p spectra. The Cl 2p_{1/2} and Cl 2p_{3/2} peaks were situated at 200 and 198.3 eV, respectively, which could be associated with Cl at the monovalent oxidation state [26], indicating that the BiOCl-Bi₁₂O₁₇Cl₂ composite did not affect the interlayered Cl⁻ [34]. Fig. 2(d) shows that the O 1s peak was deconvoluted into two peaks at 531.5 and 530.3 eV corresponding to the adsorption oxygen (O_{ads}) and lattice oxygen (O_{lat}), respectively [35,36]. The peak intensity of the lattice oxygen was much higher than that of the adsorption oxygen, which was different from that with BiOCl and Bi₁₂O₁₇Cl₂ [37,38]. Such a difference might have been caused by the interaction between BiOCl and Bi₁₂O₁₇Cl₂ in the composite. This would expedite catalytic reactions, as the lattice oxygen plays an important role in catalytic performance and is directly involved in oxygen transport and catalytic reactions [39].

3.1.3. SEM analysis

The morphologies of the as-synthesized samples were examined by SEM. Fig. 3 shows SEM images of Bi₁₂O₁₇Cl₂ and the BiOCl-Bi₁₂O₁₇Cl₂ composite. As observed, the Bi₁₂O₁₇Cl₂ exhibited an irregular agglomeration of particles, and the average thickness was 100 to 200 nm. The nanocomposite showed a sheet flower-like structure with a uniformly ordered and dispersed arrangement, and the average thickness was 20 to 50 nm. These characteristics were significantly different from those of Bi₁₂O₁₇Cl₂. This could have been due to the cavitation effect of the ultrasonic waves that may have caused a uniform distribution, prevented agglomeration, and reduced the particle size, which could have given the catalyst a larger specific surface area to promote adsorption and degrade pollutants [40,41]. It has been reported that during the hydrothermal reaction, the thickness of the composite was less than that of the Bi₃O₄Cl through the crystallization, dissolution and recrystallization.

Fig. 2. XPS spectroscopy spectra of the BiOCl-Bi₁₂O₁₇Cl₂ composite. (a) Survey; (b) Bi 4f; (c) Cl 2p; (d) O 1s.

tallization procedures [34]. Therefore, we speculate that the difference of morphology between Bi₁₂O₁₇Cl₂ and the BiOCl-Bi₁₂O₁₇Cl₂ composite was caused by both a hydrothermal reaction and the ultrasound effects. In addition, the lesser thickness of the nanosheets indicated a relatively high catalytic activity, which could be attributed to the high electron mobility and low electron injection barrier on the surface of the sheet [42].

3.1.4. HRTEM analysis

The prepared samples were further characterized by HRTEM. Fig. 4 shows HRTEM images of Bi₁₂O₁₇Cl₂ and the BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite. As shown in Fig. 4(a), the slim

lattice fringes of Bi₁₂O₁₇Cl₂, with intervals of approximately 0.3175 nm, corresponded to the (319) plane of Bi₁₂O₁₇Cl₂. The slim lattice fringes, with spacing of 0.3177 and 0.2990 nm in Fig. 5(b), were indexed to the (212) plane of BiOCl and the (315) plane of Bi₁₂O₁₇Cl₂, respectively. In order to further determine the phase formation, the corresponding Fast Fourier Transform (FFT) image is provided. The insets of Figs. 5(a) and 5(b) exhibited a clear point array and were indexed to the (319) plane of Bi₁₂O₁₇Cl₂, the (212) plane of BiOCl, and the (316) plane of Bi₁₂O₁₇Cl₂, respectively. These above results demonstrated that the BiOCl-Bi₁₂O₁₇Cl₂ heterojunction was successfully synthesized by introducing ultrasound.

3.1.5. Nitrogen adsorption-desorption analysis

Nitrogen adsorption-desorption were used to test the pore

Fig. 3. SEM images of the Bi₁₂O₁₇Cl₂ (a, b) and the BiOCl-Bi₁₂O₁₇Cl₂ (c, d) composites.

Fig. 4. HRTEM images of Bi₁₂O₁₇Cl₂ (a) and BiOCl-Bi₁₂O₁₇Cl₂ (b).

Fig. 5. N_2 adsorption-desorption isotherm of $BiOCl-Bi_{12}O_{17}Cl_2$ composite.

structure of the $BiOCl-Bi_{12}O_{17}Cl_2$ composite, and the results are shown in Fig. 5. The adsorption-desorption isotherm can be classified as Type IV, and the hysteresis loops of Type H3 reveal the formation of slit-like pores due to the aggregations of the flake particles [43]. The hysteresis loop was at a relative pressure (p/p_0) between 0.2 and 1.0, indicating that capillary condensation occurred in the mesoporous structure. The average specific surface area of the $BiOCl-Bi_{12}O_{17}Cl_2$ composite was $16.491 \text{ m}^2/\text{g}$, greater than the reported that of the $Bi_{12}O_{17}Cl_2$ [33,44,45]. The pore volume and diameter of the composite were 0.031 ml/g and 2.491 nm , respectively. The higher surface area increased the pollutant adsorption capacity of the catalyst, which could have accelerated the reaction rate.

3.1.6. UV-vis analysis

The UV-vis (DRS) of $BiOCl$, $Bi_{12}O_{17}Cl_2$, and $BiOCl-Bi_{12}O_{17}Cl_2$ are shown in Fig. 6(a). The maximum absorption wavelengths of $BiOCl$, $Bi_{12}O_{17}Cl_2$, and $BiOCl-Bi_{12}O_{17}Cl_2$ were approximately 370, 510, and 490 nm, respectively, suggesting their ability to absorb UV light and visible light. The light absorption edge of the composite was between that of $BiOCl$ and $Bi_{12}O_{17}Cl_2$. The band gap energies of these catalysts were calculated using the following equation [46]:

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (1)$$

where α , A , E_g , and ν are the absorption coefficient, a con-

Fig. 7. PL spectra of $Bi_{12}O_{17}Cl_2$ and the $BiOCl-Bi_{12}O_{17}Cl_2$ composites.

stant, the band gap energy, and the light frequency, respectively. The value of n ($n = 1$ or 4) is a constant, depending on the characteristic of the semiconductor transition. As shown in Fig. 6(b), the band gap energy was 3.25, 2.20, and 2.39 eV for $BiOCl$, $Bi_{12}O_{17}Cl_2$, and the composite respectively, which was similar to previous reports [47,48]. These results indicate that the $BiOCl-Bi_{12}O_{17}Cl_2$ composite had a matching energy band position, which was conducive to photocatalytic degradation of organic pollutants under visible-light illumination.

3.1.7. PL analysis

The migration, transformation, and separation of charge carriers of photoinduced electron holes can be investigated by PL spectra. Generally, a decrease of PL intensity can result in a decrease of recombination rate [49]. As shown in Fig. 7, the peak of the composite was significantly lower than that of $Bi_{12}O_{17}Cl_2$, indicating that the composite had a lower recombination rate of photogenerated carriers. Thus, the PL results manifested that the photocatalytic activity of the composite should be greater than that of $Bi_{12}O_{17}Cl_2$. Therefore, we achieved the combination of the stability of $BiOCl$ and the high visible-light absorption capacity of $Bi_{12}O_{17}Cl_2$.

3.2. Photocatalytic activity of the $BiOCl-Bi_{12}O_{17}Cl_2$ nanocomposite

3.2.1. RhB and CIP removal efficiency with different catalysts

To evaluate the $BiOCl-Bi_{12}O_{17}Cl_2$ composite for its adsorp-

Fig. 6. UV-vis DRS (a) and band gap energies (b) of $BiOCl$, $Bi_{12}O_{17}Cl_2$, and $BiOCl-Bi_{12}O_{17}Cl_2$.

Fig. 8. Adsorption and catalytic performances and kinetic constants of RhB (a, b) and CIP (c, d) by different catalysts. Reaction conditions: RhB concentration = 20 mg/L, CIP concentration = 10 mg/L, catalyst dose = 1.0 g/L.

tion and visible light photocatalytic activity, several catalysts (BiOCl , $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, and P25) were compared. As shown in Fig. 8(a), P25, BiOCl , and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ displayed poor adsorption and photocatalytic performance. In contrast, the $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite showed excellent adsorption: 67.9% of RhB was adsorbed within 60 min, and the composite adsorption performance was approximately 2.10, 14.50, and 8.95 times that of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, BiOCl , and P25, respectively. During the following catalytic photodegradation, the remaining RhB was completely removed after 30 min. As shown in Fig. 8(b), the composite showed the highest visible light activity, and the reaction rate constant was approximately 8.14, 64.66, and 42.63 times that of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, BiOCl , and P25 respectively.

Similarly, as shown in Fig. 8(b), 34.2% of CIP was adsorbed within 60 min, and the composite adsorption performance was approximately 1.22, 4.44, and 8.34 times that of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, BiOCl , and P25, respectively. From Fig. 8(d), we can see that the composite also showed the highest visible light activity, and the reaction rate constant was approximately 4.94, 11.91, and 36.07 times that of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, BiOCl , and P25 respectively. These results showed that the composite had greater adsorption performance and catalytic properties than those of the other catalysts. These results might have been because the ultrasonic method had the important advantage of distributing the active species, which inhibited the aggregation of particles and made the surface of the particles rougher [50]. This would have helped to increase the specific surface area, adsorption capacity, and catalytic degradation ability of the catalyst. In addition, the removal efficiency of RhB by $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ was better than that of CIP, and this phenomenon can be explained by the photosensitization effect of the dyes, which could pro-

mote the dye's degradation under visible light.

3.2.2. Effects of catalyst dose and initial pH on catalytic performance

To investigate the effect of the $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ dose, we varied the catalyst dose from 0.1 to 1.2 g/L. As shown in Figs. 9 (a, b, e and f), the adsorption performance, removal efficiency, and reaction rate constant of RhB and CIP gradually improved with an increase of the catalyst dose. This was because by adding more catalyst, more active sites were obtained, which increased the adsorption and catalytic efficiency of RhB and CIP. Considering cost and efficiency, 0.5 and 0.8 g/L of catalyst were used in the following experiments for degrading RhB and CIP, respectively. These doses were lower than those in previous reports [44,51,52].

The effects of the initial pH value on the degradation of RhB and CIP were further investigated. As shown in Figs. 9(c) and 9(d), the adsorption and photocatalytic performances of the catalyst were enhanced under acidic conditions, where RhB could have been completely removed in 30 min. When the initial pH was 5, the catalyst showed the highest reaction rate constant. However, the RhB could not be adsorbed by the catalyst under alkaline conditions. As shown in Figs. 9(g) and 9(h), when the CIP pH was 7, the catalyst had the highest adsorption and photocatalytic performances. This confirmed that the degradation processes of RhB and CIP were pH-sensitive, as previously reported [53–55]. Thus, the composite catalyst adsorbed and removed RhB well in a range of neutral and strong acid solutions, while it adsorbed and removed CIP well in a range of strong acid and weak base solutions. This has great significance for practical applications.

Fig. 9. Effects of catalyst dose (a, b) and initial pH (c, d) on $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ activity in RhB degradation; Effects of catalyst dose (e, f) and initial pH (g, h) on $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ activity in CIP degradation.

3.2.3. Reusability of $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$

For future practical applications, the stability of catalyst should be considered. A recycling photodegradation test was performed to test the durability of $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$, and the results are shown in Fig. 10. The $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst had good reusability, the RhB contaminant was almost completely

removed after only four runs, and the CIP contaminant was almost completely removed after only five runs. Therefore, the composite had excellent reusability.

3.3. The possible photocatalytic mechanism for degrading RhB

To determine the main active species in the photodegrada-

Fig. 10. Reusability of $\text{BiOCl-Bi}_{12}\text{O}_{17}\text{Cl}_2$ in RhB (a) and CIP (b) degradation. Reaction conditions: the catalyst dose for degrading RhB and CIP were 0.5 and 0.8 g/L, respectively; the RhB and CIP pH were 5 and 7, respectively.

Fig. 11. (a) Effects of various scavengers on the catalytic photodegradation of RhB; (b) DMPO spin-trapping electron spin resonance spectra in a methanol dispersion for DMPO- $\cdot\text{O}_2^-$.

tion of RhB, active species trapping experiments were carried out. As shown in Fig. 11(a), the reaction was not affected by adding tert-butyl alcohol, a scavenger for $\cdot\text{OH}$. The degradation of RhB was significantly suppressed with the addition of sodium oxalate (a scavenger for h^+) and slightly suppressed with the addition of benzoquinone (a scavenger for $\cdot\text{O}_2^-$). These results show that photogenerated holes played a leading role in the photocatalytic decomposition of RhB, while $\cdot\text{O}_2^-$ promoted the photocatalytic decomposition of RhB.

To further confirm the existence of $\cdot\text{O}_2^-$ radical species, the ESR technique was performed. As shown in Fig. 11b, no ESR signals could be detected in the dark, but the DMPO- $\cdot\text{O}_2^-$ signal could be observed under visible-light irradiation. This result further suggesting that $\cdot\text{O}_2^-$ are generated in the photocatalytic reaction system.

Based on the above analysis, the possible processes for RhB degradation can be described in Eqs. (2) – (6):

The valence band (VB) and conduction band (CB) energies of BiOCl and Bi₁₂O₁₇Cl₂ were evaluated by using Eqs. (7) and (8) [15].

$$E_{\text{VB}} = X - E^e + 0.5E_g \quad (7)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (8)$$

where X , E_g , and E^e are the electronegativity of the semiconductor, the band gap energy, and the energy of free electrons on the hydrogen scale, respectively. Here, X is calculated from the electronegativity of the constituent atoms, and E^e is the energy of free electrons on the hydrogen scale (approximately 4.5 eV). The X values of BiOCl and Bi₁₂O₁₇Cl₂ are approximately 6.64 and 6.31 eV. The band gaps of BiOCl and Bi₁₂O₁₇Cl₂ were 3.25 and 2.2 eV (Fig. 6(b)). For BiOCl, E_{VB} and E_{CB} were estimated to be 3.77 and 0.52 eV, and those of Bi₁₂O₁₇Cl₂ were estimated to be 2.91 and 0.71 eV in this study. The Fermi level of BiOCl was located close to the VB, while the Fermi level of Bi₁₂O₁₇Cl₂ was close to the CB [26]. The coupling of BiOCl and Bi₁₂O₁₇Cl₂ enabled the Fermi level to shift to the same level [15]; thus, the VB of BiOCl shifted to an energy level lower than that of Bi₁₂O₁₇Cl₂ (Fig. 12(a)).

Based on the preceding discussion, a potential photocatalytic mechanism of the BiOCl-Bi₁₂O₁₇Cl₂ composite is proposed. As shown in Fig. 12(b), when exposed to visible light, charge carriers in the BiOCl-Bi₁₂O₁₇Cl₂ composite were excited. The band gap width of the catalyst and the reactive species can be obtained from Fig. 6(b) and Fig. 11 respectively. Because the CB position of BiOCl was more negative, the photoexcited electron of BiOCl in the CB would have been transferred to the CB of Bi₁₂O₁₇Cl₂ [33,57]. In contrast, the valence band hole (h^+) of Bi₁₂O₁₇Cl₂ was transferred to the valence band of BiOCl, which had lower energy [26]. The electrons in the CB of Bi₁₂O₁₇Cl₂ could further react with oxygen absorbed on the semiconductor surface and produced superoxide radicals ($\cdot\text{O}_2^-$) [32]. The produced h^+ and $\cdot\text{O}_2^-$ have strong oxidation capacity, so organic pollutants can be oxidized into small molecules: CO₂ and H₂O.

4. Conclusions

In summary, a BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite was synthesized by a novel one-step ultrasound-assisted hydrothermal method. SEM and BTE results showed that the nanocomposite had good dispersion and a flower-like structure with a high specific surface area and an average thickness of 20 to 50 nm. UV-vis diffuse reflection spectra and PL spectra analyses showed that the nanocomposite had good visible-light absorption, and a much lower photogenerated electron-hole recombination rate than that of Bi₁₂O₁₇Cl₂. The catalyst's kinetic constants of RhB (/CIP) were approximately 8.14/(4.94), 64.66/(11.91), and 42.63/(36.07) times those of Bi₁₂O₁₇Cl₂, BiOCl, and P25, respectively. Suitable morphology, structure,

Fig. 12. (a) Scheme of energy bands of BiOCl and Bi₁₂O₁₇Cl₂; (b) proposed mechanism of BiOCl-Bi₁₂O₁₇Cl₂ catalytic visible-light degradation of RhB.

and photoelectric properties were the reasons for the excellent photocatalytic performance of the nanocomposite photocatalyst. Further, it showed a wide pH range for application and an excellent reusability. Mechanism studies showed that the main reactive species were photogenerated holes and $\cdot\text{O}_2^-$. This research developed a green, stable, and high-efficiency visible-light photocatalyst, which is a valuable contribution to the area of BiOCl-based photocatalysts.

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Graphical Abstract

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BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite with high visible-light photocatalytic activity prepared by an ultrasonic hydrothermal method for removing dye and pharmaceutical

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Synthesis process of BiOCl-Bi₁₂O₁₇Cl₂ nanocomposite and the mechanism of photocatalytic degradation of organic pollutants.

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超声水热法制备高可见光催化活性的BiOCl-Bi₁₂O₁₇Cl₂纳米复合材料去除染料和药物废水

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摘要: 光催化作为一种环境友好型、低能耗的技术, 在环境净化等领域倍受关注. 传统光催化剂, 如TiO₂, ZnO, V₂O₅和WO₃等具有较高的光敏性, 其价格低廉, 自然无毒, 常用于光电反应的应用当中. 然而, 这些催化剂具有较宽的禁带宽度, 只能在紫外光下响应. 为此, 设计一种较窄带隙的高可见光活性的光催化剂具有一定的意义. 近年来, 氯化铋光催化剂受到了越来越多的关注, 其在紫外光下具有非常优异的光催化性能. 并且, 研究者们已成功合成出非化学计量比的氯化铋, 如Bi₃O₄Cl (2.60 eV), Bi₁₂O₁₇Cl₂ (2.10 eV), Bi₁₂O₁₅Cl₆ (2.86 eV)和Bi₂₄O₃₁Cl₁₀ (2.70 eV)等光催化剂. 研究表明, 较低的Cl/O比可能会减小催化剂的带隙宽度, 并提高其光催化性能; 其中Bi₁₂O₁₇Cl₂的Cl/O比最小, 是最有潜力的氯化铋光催化剂. 然而, Bi₁₂O₁₇Cl₂具有较高的光生电子空穴复合率, 会极大的减弱其光催化活性. 因此, 将Bi₁₂O₁₇Cl₂与具有高稳定性、结构相似且空穴复合率低的BiOCl相结合, 将会极大提高在可见光下Bi₁₂O₁₇Cl₂的光催化活性. 本文采用了超声水热法成功制备了具有高可见光催化活性的BiOCl-Bi₁₂O₁₇Cl₂纳米复合材料, 用于去除染料和药物废水. 扫描电子显微镜和比表面积分析仪的结果表明, 纳米复合材料具有良好的分散性, 结构为花瓣形状, 其平均厚度为20至50 nm, 且具有较高的比表面积. 紫外-可见漫反射和光致发光光谱分析表明, 纳米复合材料具有良好的可见光吸收性能, 并且光生电子空穴复合率远低于Bi₁₂O₁₇Cl₂. 其在可见光下降解罗丹明B (环丙沙星)的动力学常数分别约为Bi₁₂O₁₇Cl₂, BiOCl和P25的8.14 (/4.94), 64.66 (/11.91)和42.63 (/36.07)倍. 合适的形态、结构和光电性能是此纳米复合光催化剂具有优异光催化性能的原因.

此外, 该催化剂还显示出较宽的pH适用范围和优异的可重复利用性, 有利于实际利用. 机理研究表明, 降解罗丹明B的主要活性物质是光生空穴和超氧自由基. 总之, 本文开发了一种绿色、稳定、高效的可见光光催化剂, 对BiOCl基的光催化剂的研究作出了一定的贡献.

关键词: BiOCl-Bi₁₂O₁₇Cl₂; 纳米复合材料; 绿色技术; 可见光光催化

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