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Article

Preparation of $\text{BiOCl}_{0.9}\text{I}_{0.1}/\beta\text{-Bi}_2\text{O}_3$ composite for degradation of tetracycline hydrochloride under simulated sunlight

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ABSTRACT

A novel and effective $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ composite catalyst was synthesized through a precipitation method. The structure, morphology, and optical properties of the samples were certified by X-ray diffraction, UV-Vis diffuse reflectance, scanning electron microscopy, and X-ray photoelectron spectroscopic characterizations. Photocatalytic experiments demonstrated that the synthesized $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ composite catalyst exhibited excellent photocatalytic performance toward the degradation of tetracycline hydrochloride (TCH) under simulated sunlight. Furthermore, the TCH degradation rate of $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ increased by 27.6% and 61.4% compared with those of the pure $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and pure $\beta\text{-Bi}_2\text{O}_3$, respectively. Due to the multiple vacancies and valence states possessed by $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$, namely Bi^{5+} , $\text{Bi}^{(3-x)+}$, $\text{Bi}^{5+-\text{O}}$, $\text{Bi}^{3+-\text{O}}$, I^- and I_3^- , the charge separation in photocatalysis reactions can be effectively promoted. The Mott-Schottky measurements indicate that the conduction band (CB) level of $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ becomes more negative relative to that of $\text{BiOCl}_{0.9}\text{I}_{0.1}$, guaranteeing an advantageous effect on the redox ability of the photocatalyst. This study provides a new bright spot for the construction of high-performance photocatalysts.

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1. Introduction

Along with the rapid development of domestic and foreign industries that engender impressive economic benefits, egregious environmental pollutants have been introduced to the planet, e.g., heavy metal ions, pesticides, and antibiotics. These pollutants not only affect the water and air quality but also seriously threaten human health [1,2]. Within the past several decades, a large number of antibiotics have emerged and are

still being accumulated globally. They are randomly discharged into natural environments, including surface water, groundwater, and sediments [2,3]. Tetracycline hydrochloride (TCH) is one of them; it is common and widely used in pharmaceutical care and veterinary fields [4,5]. The TCH residues in aquatic environment can induce the development of antibiotic-resistant pathogens and have a potential long-term detrimental effect on human health [6–8]. Moreover, TCH is difficult to eliminate [3,9]; thus, an increasing number of studies is cen-

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tered on its complete removal [10].

However, generally, the application of conventional physical adsorption and biodegradation methods to realize this objective is considered difficult owing to the cumbersome post-treatment challenges associated with adsorbents, high processing costs, and antibacterial properties [8]. In this case, advanced oxidation treatment has been considered in view of the possibility to generate superoxide free radicals ($\bullet\text{O}_2^-$) and hydroxyl radicals with strong oxidative abilities ($\bullet\text{OH}$, +2.4 eV) to decompose many recalcitrant organic contaminants [8,11].

- $\text{O}_2^- + \text{organic contaminants} \rightarrow \text{Degradation products}$,
- $\text{OH} + \text{h}^+ + \text{organic contaminants} \rightarrow \text{Degradation products}$.

Thus far, conventionally, the degradation of TCH has been carried out using the Fenton reagent [8,12] and photocatalytic oxidation [8,13–15]. Photocatalytic technology is considered as a practical method for degrading TCH due to its high efficiency, simple operation, and low cost [8]. Most photocatalytic processes employ TiO_2 -based photocatalysts; however, TiO_2 only responds to ultraviolet light, and its wide bandgap limits further practical application [13,14,16,17]. Therefore, exploring new semiconductor catalysts with visible-light-harvesting ability, high efficiency, and easy recycling is an effective way of effecting the degradation of tetracycline [18]. In recent years, bismuth oxyhalide (BiOX , $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) has attracted wide attention from researchers due to its unique layered crystal structure and optical properties [19–22]. BiOX ($\text{X} = \text{Cl}, \text{Br}$, and I) is a semiconductor with an indirect bandgap, and the recombination probability of the photogenerated carriers is relatively low [19–21,23,24]. These inherent structural advantages determine the intensive employment of BiOX in photocatalytic application [25–30].

Conversely, $\beta\text{-Bi}_2\text{O}_3$ is also a common germanium-containing semiconductor. Similarly, BiOX ($\text{X} = \text{Cl}, \text{Br}$ and I) exhibits good absorption of visible light; thus, it can significantly facilitate the production of superoxide and hydroxide species under exposure to sunlight [31]. Therefore, in this work, it is chosen for combination with $\text{BiOCl}_{0.9}\text{I}_{0.1}$, which has an indirect bandgap, to form a composite catalyst [32]. Due to the internal electrostatic field enrichment, $\text{BiOCl}_{x}\text{I}_{1-x}$ exhibits a relatively high photocatalytic activity [19]. After compounding with $\beta\text{-Bi}_2\text{O}_3$, the photocatalytic properties of the composite are evaluated by degrading $20 \text{ mg}\cdot\text{L}^{-1}$ of TCH under light irradiation. The relative valence band (VB) and conduction band (CB) edge positions and element valence states of the prepared samples were analyzed by analyzing the UV-vis diffuse reflec-

tance spectra, Mott-Schottky plots, and XPS spectra. The possible mechanism of the photocatalytic activity of the $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ complex in the degradation of TCH was discussed using energy band evaluation.

2. Experimental

2.1. Materials

$\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, KCl, KI, tetracycline hydrochloride, benzoquinone (BQ), triethanolamine (TEOA), isopropyl alcohol (IPA), and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents used were of analytical grade and were used without further purification.

2.2. Preparation of $\beta\text{-Bi}_2\text{O}_3$

In a typical synthesis, the $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ salt was first heated at 200°C for 1 h to evaporate the water molecules contained therein. Subsequently, the temperature was increased to 300°C for 2 h, after which it was maintained at 425°C for 2 h; the sample was naturally cooled in the furnace after the completion of the calcination.

2.3. Preparation of $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$

$\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ was synthesized by an oil bath method using ethylene glycol as a solvent. In a typical synthesis, 6 mmol of $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ was dissolved in 45 mL of ethylene glycol (EG) under magnetic stirring until the solid was completely dissolved. Thereafter, 0.6 mmol of KI and 5.4 mmol of KCl were added to 45 mL of deionized water, followed by stirring for 30 min under ultrasonic agitation. After the solid was dissolved, the $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ solution was transferred to a 90°C water bath and stirred for 10 min; subsequently, 0.285 g of $\beta\text{-Bi}_2\text{O}_3$ was added thereto and stirred for 10 min. Next, a mixed solution of KI and KCl was added dropwise to a mixed solution of $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ and $\beta\text{-Bi}_2\text{O}_3$, and further stirred at 90°C for 1 h. Finally, the prepared solution was filtered and dried at 80°C for 12 h to obtain a $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ composite. The preparation procedure for the $\text{BiOCl}_{0.9}\text{I}_{0.1}/5\%\beta\text{-Bi}_2\text{O}_3$, $\text{BiOCl}_{0.9}\text{I}_{0.1}/10\%\beta\text{-Bi}_2\text{O}_3$, and $\text{BiOCl}_{0.9}\text{I}_{0.1}/20\%\beta\text{-Bi}_2\text{O}_3$ catalysts was the same except that different amounts of $\beta\text{-Bi}_2\text{O}_3$ were employed.

2.4. Measurement of photocatalytic activity

Photocatalytic degradation experiments were carried out with a photocatalytic reaction device (XPA-G6) using a 350 W Xe lamp as the light source. The reactor was placed horizontally and surrounded by water to cool. A portion (20 mg) of the photocatalyst was dispersed in an aqueous solution of TCH (50 mL , $20 \text{ mg}\cdot\text{L}^{-1}$). The suspension was magnetically stirred under dark condition for 1 h to fully reach the adsorption/desorption equilibrium of the TCH molecules on the surface of the photocatalyst. Afterward, light was irradiated onto the tube containing the mixed solution, and about 5 mL of the suspension was

Scheme 1. Schematic of the synthesis of the $\text{BiOCl}_{0.9}\text{I}_{0.1}/\beta\text{-Bi}_2\text{O}_3$ photocatalyst.

continuously withdrawn from the reaction cell at intervals of 30 min for concentration analysis after centrifugation, and sampling was completed after 2 h of light irradiation. The degradation efficiency of the photocatalyst to TCH was evaluated by measuring the concentration of the centrifuged TCH solution using a UV-vis spectrophotometer (TU-1901, Beijing General).

3. Results and discussion

Fig. 1(a) and Fig. 1(b) show the morphologies of the $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ composites by SEM analysis, respectively. In Fig. 1(a), it is indicated that the pure $\text{BiOCl}_{0.9}\text{I}_{0.1}$ samples have a square nanosheet structure with a size of about 100 nm, which was regularly shaped and laminated. The basic morphology of the prepared $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ composite was compared with those of the pure $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and pure $\beta\text{-Bi}_2\text{O}_3$ catalysts, and the pure $\beta\text{-Bi}_2\text{O}_3$ exhibited a massive structure (Fig. S1). After forming the composite, the $\text{BiOCl}_{0.9}\text{I}_{0.1}$ nanosheets were embedded as a component in the $\beta\text{-Bi}_2\text{O}_3$ block that was exposed and combined with $\beta\text{-Bi}_2\text{O}_3$ blocks. At the same time, $\text{BiOCl}_{0.9}\text{I}_{0.1}$ nanosheets partially aggregated on the surface of the $\beta\text{-Bi}_2\text{O}_3$ into small flower-like microstructures covering the entire surface eventually. The presence of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ nanosheets greatly increased the specific surface area of the complex and provided more active sites for the reaction.

To further demonstrate that $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\beta\text{-Bi}_2\text{O}_3$ are well combined, the TEM and HRTEM results were analyzed. As shown in Fig. 2(a), the obtained $\text{BiOCl}_{0.9}\text{I}_{0.1}$ nanosheets were squares having a particle diameter of approximately 100 nm, and the distribution was uniform with a regular shape. As can be seen in Fig. 2(b), the $\text{BiOCl}_{0.9}\text{I}_{0.1}$ nanosheets were partially embedded in $\beta\text{-Bi}_2\text{O}_3$. Further, the lattice fringes observed in Fig. 2(c) correspond to the (110) crystal plane of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ ($d = 0.28$ nm). Similarly, the lattice fringes in Fig. 2(d) correspond to the (110) crystal faces of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ ($d = 0.28$ nm), while $d = 0.33$ nm corresponds to the (113) crystal faces of $\beta\text{-Bi}_2\text{O}_3$. Evidently, $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\beta\text{-Bi}_2\text{O}_3$ have been successfully combined.

Fig. 3(a) is the XRD patterns of the samples. The XRD diffraction peaks of $\text{BiOCl}_{0.9}\text{I}_{0.1}$, $\beta\text{-Bi}_2\text{O}_3$, and $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ can be seen from Fig. 3(a). The 11.59° , 25.72° , 32.35° , and 33.33° degrees represent the planes of (001), (101), (110), and

Fig. 1. SEM images of the as-synthesized samples. (a) $\text{BiOCl}_{0.9}\text{I}_{0.1}$; (b) $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$. (c–g) Elemental mapping of $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$.

Fig. 2. TEM images of pure $\text{BiOCl}_{0.9}\text{I}_{0.1}$ (a) and $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ (b). HRTEM images of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ (c) and $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ (d).

(102), respectively (Fig.S3). As compared with the peaks of BiOCl and $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$, the peaks of $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ shift slightly, which can be ascribed to the introduced I in BiOCl that forms the solid solution. The peaks of the samples are strong, indicating that these substances are crystalline. From the XRD diffraction peaks of the composite catalyst, only the diffraction peak of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ is observed, and the diffraction peak of $\beta\text{-Bi}_2\text{O}_3$ is not observed, from which the evidence of the combination is insignificant. In this case, to explicitly prove the incorporation, SEM, TEM, and XPS analyses were additionally conducted. Fig. 3(b) shows the diffuse reflectance spectra of the prepared pure $\text{BiOCl}_{0.9}\text{I}_{0.1}$, $\beta\text{-Bi}_2\text{O}_3$, and their complexes. Both $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\beta\text{-Bi}_2\text{O}_3$ exhibit strong absorptions in the visible light region. It is worth noting that a broad absorption peak near 310 nm can be observed in both $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and its composite, and the light absorption intensity of $\beta\text{-Bi}_2\text{O}_3$ is higher than that of $\text{BiOCl}_{0.9}\text{I}_{0.1}$. After the combination of the two semiconductors, the absorption intensity of the $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ composite increases with the $\beta\text{-Bi}_2\text{O}_3$ content, and the light absorption intensity is between those of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\beta\text{-Bi}_2\text{O}_3$. This phenomenon could be attributed to the coexistence of the two components: $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\beta\text{-Bi}_2\text{O}_3$ [33]. The bandgap of $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ was estimated, as shown in Fig. 3(c), and the $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ composite exhibited a narrow bandgap of 2.31 eV compared to 2.90 eV for $\beta\text{-Bi}_2\text{O}_3$ and 2.84 eV for $\text{BiOCl}_{0.9}\text{I}_{0.1}$, suggesting a more efficient light absorption [34]. The lower bandgap promoted the photon excitation from its VB to its CB, thereby effectively accelerating the migration process of the photogenerated carriers and greatly promoting the photocatalytic activity. Fig. 3(d) shows the PL of $\text{BiOCl}_{0.9}\text{I}_{0.1}$, $\beta\text{-Bi}_2\text{O}_3$, and $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$. It can be clearly seen that the strength of $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ is lower than those of the single components, $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\beta\text{-Bi}_2\text{O}_3$, implying that $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ can effectively inhibit the recombination of the photogenerated electron pairs [32].

To further study the electron transport of the samples during the photocatalytic reaction, the transient photocurrent responses and EIS Nyquist curves of each sample under illumina-

Fig. 3. (a) XRD patterns of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃. (b) UV-vis diffuse reflectance spectra of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃. (c) The bandgap of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃. (d) PL spectra of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃.

tion conditions were analyzed. Fig. 4(a) shows the transient photocurrent responses of the samples. It can be found that the transient photocurrent intensity of the pure BiOCl_{0.9}I_{0.1} is higher than that of the pure β-Bi₂O₃. This is because BiOCl_{0.9}I_{0.1} is more suitable as a catalyst for photocatalytic degradation, while β-Bi₂O₃ plays the role of a co-catalyst during the experiment. It can be seen from Fig. 4(a), that the photocurrent intensities of the composite catalysts are significantly higher than those of the pure BiOCl_{0.9}I_{0.1} and β-Bi₂O₃ catalysts, indicating that the separation efficiency of the photogenerated electrons and holes in the reaction process increases after the compounding. When the amount of β-Bi₂O₃ support increases, the transient photocurrent also increases. As the β-Bi₂O₃ loading reaches 15%, the transient photocurrent of the composite catalyst is the highest, which is highly favored by the reaction [32,35]. Fig. 4(b) shows the EIS Nyquist curves of the samples. It can be seen from Fig. 4(b), that the impedance of each sample is exactly one-to-one, corresponding to the transient photocurrent. A lower medium impedance implies that the transmission of photogenerated electrons is significantly favorable. It can be seen from Fig. 4(b), that the impedance of the BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃ composite catalyst is significantly smaller than that of the pure BiOCl_{0.9}I_{0.1} and β-Bi₂O₃ catalysts. In addition, with the increase in the β-Bi₂O₃ loading, the impedance of the composite catalyst declines. When the β-Bi₂O₃ loading reaches 15%, the impedance of the composite catalyst is the

lowest, further confirming that this proportion is optimal for photocatalytic reactions [36,37].

The complex was measured by testing the degradation of TCH in water under simulated sunlight. As shown in Fig. 5(a), the sample was observed to reach adsorption equilibrium after stirring for 30 min in the dark. After 120 min of illumination, the degradation rate of TCH in the samples containing the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composite reached 82.4%, while the degradation rate of TCH in the samples containing BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, BiOCl_{0.9}I_{0.1}/5%β-Bi₂O₃, BiOCl_{0.9}I_{0.1}/10%β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/20%β-Bi₂O₃ was only 54.8%, 21.0%, 70.0%, 73.2%, and 79.9%, respectively. The degradation of TCH can be described by the simplified first-order equation of the Langmuir-Hinshelwood model: $\ln(C_0/C_t) = kt$, where C_0 is the initial concentration of TCH; C_t , the concentration of TCH; k , the apparent first-order rate constant; and t , the light time. As shown in Fig. 5(b), the apparent rate constants of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, BiOCl_{0.9}I_{0.1}/5%β-Bi₂O₃, BiOCl_{0.9}I_{0.1}/10%β-Bi₂O₃, BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/20%β-Bi₂O₃ are 0.4×10^{-2} , 0.9×10^{-3} , 0.62×10^{-2} , 0.79×10^{-2} , 0.91×10^{-3} , and $0.96 \times 10^{-3} \text{ min}^{-1}$, respectively. Therefore, the photocatalytic activity of the BiOCl_{0.9}I_{0.1} nanosheet was effectively improved by combining it with β-Bi₂O₃ [33].

To explore the active substances involved in the TCH photodegradation, series scavenge trials were executed. As shown in Fig. 5(c), 1,4-benzoquinone (BQ, •O₂⁻ scavenger) and trieth-

Fig. 4. (a) Transient photocurrent responses of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃. (b) EIS Nyquist curves of BiOCl_{0.9}I_{0.1}, β-Bi₂O₃, and BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃.

Fig. 5. (a) Photocatalytic degradation curves of TCH over the various samples. (b) Apparent reaction rate constants (*k*) of TCH aqueous solutions over the various samples. (c) Plots of the reactive species trapping experiments of BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ for the degradation of TCH. (d) Recycling runs in the photocatalytic degradation of TCH by the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composites.

anolamine (TEOA, h⁺ scavenger) greatly inhibited the photodegradation efficiency of TCH. In contrast, the addition of isopropanol (IPA, •OH scavenger) only had a slight effect on the TCH photodegradation. Based on these results, we concluded that the main active species of the TCH photodegradation in BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃ are •O₂⁻ and •OH [38]. To investigate the recyclability of the BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃ composite catalyst, the sample powder, after the photocatalytic reaction, was collected and reused three times in the photocatalytic reaction, under the same conditions. As shown in Fig. 5(d), the photocatalytic activity of BiOCl_{0.9}I_{0.1}/x%β-Bi₂O₃ did not decrease sig-

nificantly during the three degradation cycles, indicating that BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ exhibits excellent stability and recyclability [18].

Fig. 6 shows the nitrogen adsorption-desorption isotherms for the BiOCl_{0.9}I_{0.1} nanosheets and BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ samples. It can be seen that sample exhibits a type IV isotherm, and the specific surface area measured of BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ is 139.09 m²·g⁻¹, which is higher than that of the pure BiOCl_{0.9}I_{0.1} (63.01 m²·g⁻¹). The relatively large specific surface area can provide the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ sample with more active sites, which are beneficial to the pho-

Fig. 6. Nitrogen adsorption-desorption isotherm of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ and $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$.

photocatalytic reaction [39].

To further analyze the electronic state of the elements in the $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ catalyst, XPS was conducted. Fig. 7 shows the XPS spectra of Bi 4f, O 1s, Cl 2p, and I 3d. The peak value of C 1s at the binding energy of 284.6 eV was employed as the reference. It can be seen from Fig. 7(a) that the Bi 4f_{5/2} and Bi 4f_{7/2} orbitals can fit three peaks, and the two main peaks at the binding energies of 159.54 and 164.81 eV correspond to Bi^{3+} . The fitted peaks at 160.80 and 165.85 eV correspond to Bi^{5+} [40]. The fitted peak at the binding energies of 158.41 and 163.83 eV correspond to $\text{Bi}^{(3-x)+}$, where the peaks can symbolize oxygen vacancies [19]. Fig. 7(b) shows the XPS spectrum of O 1s. It can be seen that there are three fitted peaks at 529.0,

530.35, and 533.32 eV, which are ascribed to $\text{Bi}^{5+}\text{-O}$, $\text{Bi}^{3+}\text{-O}$, and $\text{Bi}^{(3-x)+}\text{-O}$, respectively. A slight shift in the position was observed during the evaluation of the O species in $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ compared to the case with BiOCl , which might be attributed to a small amount of I added to BiOCl [19]. It can be seen from Fig. 7(c) that Cl 2p had two fitted peaks of Cl 2p_{3/2} and Cl 2p_{1/2} at binding energies of 198.07 and 199.5 eV, respectively [41]. Fig. 7(d) shows the XPS spectrum of I 3d. It was found that the peaks at both I 3d_{3/2} and I 3d_{5/2} can be fitted into three peaks. The binding energies are as follows: I^- at 618.63 and 629.83 eV, I^{3-} at 619.60 and 630.9 eV, and I^{5+} at 622.23 and 633.83 eV [32].

The mechanism of the electron transfer in the photocatalytic reaction is predicted. When visible light is irradiated onto the surface of the catalyst, $\text{BiOCl}_{0.9}\text{I}_{0.1}$ can generate photogenerated electrons (e^-). The photogenerated electrons can migrate from the VB to the CB of the catalyst, while an equal amount of photogenerated holes (h^+) can be generated on the VB. According to the model Schottky curve (Fig. S2), the $\beta\text{-Bi}_2\text{O}_3$ catalyst is also in a similar situation. Specifically, the CB potential of $\beta\text{-Bi}_2\text{O}_3$ (−0.4 eV) is more negative than that of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ (1.2 eV), while the VB potential of $\beta\text{-Bi}_2\text{O}_3$ (2.5 eV) is smaller than that of $\text{BiOCl}_{0.9}\text{I}_{0.1}$ (3.04 eV). When the catalyst and the cocatalyst are combined to form a composite catalyst, the CB and the VB positions between those of $\beta\text{-Bi}_2\text{O}_3$ and $\text{BiOCl}_{0.9}\text{I}_{0.1}$ can form a ladder structure. This structure facilitates the formation of a current loop by the charge transfer, which can effectively improve the separation efficiency of the photogenerated electrons and holes. In addition, the photogenerated electron, in the process of transport, can combine with the dissolved oxygen on the

Fig. 7. XPS spectra of Bi 4f (a), O 1s (b), Cl 2p (c), and I 3d (d).

Scheme 2. Proposed photocatalytic reaction processes and charge transfer of BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃.

surface of the composite to produce superoxide radicals $\bullet\text{O}_2^-$, which are active substances that can degrade TCH and combine with both H^+ to form $-\text{OOH}$ and H_2O_2 , and $-\text{OOH}$ to form hydroxyl radicals ($\bullet\text{OH}$) that are capable of completely oxidizing the pollutant. Moreover, since the VB potential of the catalyst is higher than the standard oxidation-reduction potential ($\bullet\text{OH}/\text{OH}^-$) (+2.4 eV) [42], it is suggested that the OH^- species in the reaction system can also transform into hydroxyl radicals $\bullet\text{OH}$; $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ can directly participate in the degradation reaction of TCH [43]. The reaction process can be generalized as follows:

4. Conclusions

In summary, the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composite was successfully synthesized through a simple oil bath method at 90 °C. The TEM and XPS images could prove that BiOCl_{0.9}I_{0.1} and β-Bi₂O₃ were successfully combined, and the (110) and (113) crystal lattice fringes of BiOCl_{0.9}I_{0.1} and β-Bi₂O₃ were clearly observed in the HRTEM image. The BET analysis showed that the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composite had a large specific surface area, providing more active sites for the reaction. The BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composite had a significantly reduced bandgap compared to those of the pure BiOCl_{0.9}I_{0.1} and pure β-Bi₂O₃ catalysts. The degradation rate by the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composite material of TCH in water was 82.4%, which was higher by 27.6% and 61.4% than those of the pure BiOCl_{0.9}I_{0.1} and pure β-Bi₂O₃ catalysts, respectively. Cyclic experiments showed that the BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃ composites exhibited good cycle stability.

References

- [1] R. Guo, X. Qi, X. Zhang, H. Zhang, X. Cheng, *Sep. Purif. Technol.*, **2019**, 211, 504–513.
- [2] M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo, M. A. H. Johir, D. Belhaj, *Bioresour. Technol.*, **2017**, 238, 306–312.
- [3] Z. Zeng, S. Ye, H. Wu, R. Xiao, G. Zeng, J. Liang, C. Zhang, J. Yu, Y. Fang, B. Song, *Sci. Total Environ.*, **2019**, 648, 206–217.
- [4] S. Farzamfar, M. Naseri-Nosar, H. Sahraeyima, A. Ehterami, A. Goodarzi, M. Rahmati, G. Ahmadi Lakalayeh, S. Ghorbani, A. Vaez, M. Salehi, *Int. J. Polym. Mater.*, **2018**, 68, 472–479.
- [5] X. Yu, Q. Yuan, M. Yang, R. Liu, S. Zhu, J. Li, W. Zhang, J. You, S. Xiong, Y. Hu, *Macromol. Mater. Eng.*, **2019**, 304, 1800755.

Graphical Abstract

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Preparation of BiOCl_{0.9}I_{0.1}/β-Bi₂O₃ composite for degradation of tetracycline hydrochloride under simulated sunlight

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β-Bi₂O₃ and element-doped BiOCl_{0.9}I_{0.1} were combined to construct a BiOCl_{0.9}I_{0.1}/β-Bi₂O₃ composite catalyst; compared with those of the pure β-Bi₂O₃, BiOCl_{0.9}I_{0.1} catalysts, the efficiency of the composite catalyst toward tetracycline hydrochloride degradation was significantly enhanced under simulated sunlight.

- [6] X. Xiao, R. Hu, C. Liu, C. Xing, X. Zuo, J. Nan, L. Wang, *Chem. Eng. J.*, **2013**, 225, 790–797.
- [7] J. Yu, J. Ran, *Energy Environ. Sci.*, **2011**, 4, 1364–1371.
- [8] R. Hao, X. Xiao, X. Zuo, J. Nan, W. Zhang, *J. Hazard. Mater.*, **2012**, 209–210, 137–145.
- [9] V. Homem, L. Santos, *J. Environ. Manage.*, **2011**, 92, 2304–2347.
- [10] B. Tiwari, B. Sellamuthu, Y. Ouarda, P. Drogui, R. D. Tyagi, G. Buelna, *Bioresour. Technol.*, **2017**, 224, 1–12.
- [11] J. S. Jeong, W. H. Song, W. J. Cooper, J. Y. Jung, J. Greaves, *Chemosphere*, **2010**, 78, 533–540.
- [12] I. R. Bautitz, R. F. P. Nogueira, *J. Photochem. Photobiol. A*, **2007**, 187, 33–39.
- [13] C. Reyes, J. Fernández, J. Freer, M. A. Mondaca, C. Zaror, S. Malato, H. D. Mansilla, *J. Photochem. Photobiol. A*, **2006**, 184, 141–146.
- [14] R. A. Palominos, M. A. Mondaca, A. Giraldo, G. Peñuela, M. Pérez-Moya, H. D. Mansilla, *Catal. Today*, **2009**, 144, 100–105.
- [15] X. F. Wu, H. Li, J. Z. Su, J. R. Zhang, Y. M. Feng, Y. N. Jia, L. S. Sun, W. G. Zhang, M. Zhang, C. Y. Zhang, *Appl. Surf. Sci.*, **2019**, 473, 992–1001.
- [16] L. Wang, S. Duan, P. Jin, H. She, J. Huang, Z. Lei, T. Zhang, Q. Wang, *Appl. Catal. B*, **2018**, 239, 599–608.
- [17] D. Gao, X. Wu, P. Wang, Y. Xu, H. Yu, J. Yu, *ACS Sustainable Chem. Eng.*, **2019**, 7, 10084–10094.
- [18] P. Xiao, D. Jiang, L. Ju, J. Jing, M. Chen, *Appl. Surf. Sci.*, **2018**, 433, 388–397.
- [19] G. Zhang, L. Cai, Y. Zhang, Y. Wei, *Chem. Eur. J.*, **2018**, 24, 7434–7444.
- [20] Z. Y. Zhao, W. W. Dai, *Inorg. Chem.*, **2014**, 53, 13001–13011.
- [21] X. Wu, Y. H. Ng, L. Wang, Y. Du, S. X. Dou, R. Amal, J. Scott, *J. Mater. Chem. A*, **2017**, 5, 8117–8124.
- [22] J. Jiang, K. Zhao, X. Xiao, L. Zhang, *J. Am. Chem. Soc.*, **2012**, 134, 4473–4476.
- [23] S. Zhou, P. Yue, J. Huang, L. Wang, H. She, Q. Wang, *Chem. Eng. J.*, **2019**, 371, 885–892.
- [24] Q. Wang, T. Niu, L. Wang, C. Yan, J. Huang, J. He, H. She, B. Su, Y. Bi, *Chem. Eng. J.*, **2018**, 337, 506–514.
- [25] J. Wang, Z. Zhang, X. Wang, Y. Shen, Y. Guo, P. K. Wong, R. Bai, *Chin. J. Catal.*, **2018**, 39, 1792–1803.
- [26] H. Yu, C. Cao, X. Wang, J. Yu, *J. Phys. Chem. C*, **2017**, 121, 13191–13201.
- [27] Y. Miao, Z. Lian, Y. Huo, H. Li, *Chin. J. Catal.*, **2018**, 39, 1411–1417.
- [28] J. Li, X. Wu, W. Pan, G. Zhang, H. Chen, *Angew. Chem. Int. Ed.*, **2018**, 57, 491–495.
- [29] X. Wang, D. Liao, H. Yu, J. Yu, *Dalton Trans.*, **2018**, 47, 6370–6377.
- [30] H. An, B. Lin, C. Xue, X. Yan, Y. Dai, J. Wei, G. Yang, *Chin. J. Catal.*, **2018**, 39, 654–663.
- [31] T. A. Gadhi, S. Hernández, M. Castellino, P. Jagdale, T. Husak, A. Hernández-Gordillo, A. Tagliaferro, N. Russo, *Catal. Today*, **2019**, 321–322, 135–145.
- [32] P. Yue, G. Zhang, X. Cao, B. Wang, Y. Zhang, Y. Wei, *Sep. Purif. Technol.*, **2019**, 213, 34–44.
- [33] Y. Shi, Z. Yang, Y. Liu, J. Yu, F. Wang, J. Tong, B. Su, Q. Wang, *RSC Adv.*, **2016**, 6, 39774–39783.
- [34] H. She, X. Ma, Z. Zhao, L. Wang, J. Huang, C. Li, Q. Wang, *Appl. Surf. Sci.*, **2019**, 489, 420–426.
- [35] R. B. Wei, Z. L. Huang, G. H. Gu, Z. Wang, L. Zeng, Y. Chen, Z. Q. Liu, *Appl. Catal. B*, **2018**, 231, 101–107.
- [36] H. She, Y. Sun, S. Li, J. Huang, L. Wang, G. Zhu, Q. Wang, *Appl. Catal. B*, **2019**, 245, 439–447.
- [37] X. F. Wu, Y. Sun, H. Li, Y. J. Wang, C. X. Zhang, J. R. Zhang, J. Z. Su, Y. W. Wang, Y. Zhang, C. Wang, M. Zhang, *J. Alloys Compd.*, **2018**, 740, 1197–1203.
- [38] W. Liu, D. Zhong, Z. Dai, Y. Liu, J. Wang, Z. Wang, J. Pan, *J. Alloys Compd.*, **2019**, 780, 907–916.
- [39] H. She, H. Zhou, L. Li, L. Wang, J. Huang, Q. Wang, *ACS Sustainable Chem. Eng.*, **2018**, 6, 11939–11948.
- [40] C. Lv, G. Chen, X. Zhou, C. Zhang, Z. Wang, B. Zhao, D. Li, *ACS Appl. Mater. Interfaces*, **2017**, 9, 23748–23755.
- [41] L. W. Shan, G. L. Wang, L. Z. Liu, Z. Wu, *J. Mol. Catal. A*, **2015**, 406, 145–151.
- [42] F. Deng, L. Zhao, X. Luo, S. Luo, D. D. Dionysiou, *Chem. Eng. J.*, **2018**, 333, 423–433.
- [43] S. Han, J. Li, K. Yang, J. Lin, *Chin. J. Catal.*, **2015**, 36, 2119–2126.

BiOCl_{0.9}I_{0.1}/β-Bi₂O₃复合材料在模拟太阳光下光催化降解盐酸四环素性能

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摘要: 盐酸四环素(TCH)是一种常见且广泛用于制药保健和兽医领域的抗生素, 水生环境中的TCH残留物可诱导抗生素抗性病原体的发展, 并对人类健康具有潜在的长期威胁。然而, 传统的物理吸附和生物降解方法很难实现对TCH的降解。光催化技术由于其高效, 简单的操作和低成本被认为是降解TCH的实用方法。BiOX (X = Cl, Br和I)是具有间接带隙的半导体, 其光生载流子的复合概率相对较低, 因而在光催化中有着广泛应用。但是, 当单独BiOX作为光催化材料时, 其电子-空穴对分离弱、载流子传输慢, 从而使BiOX不能很好的在光催化领域发挥作用。为了缓解或解决此限制性因素, 将卤氧化物BiOCl_{0.9}I_{0.1}与半导体β-Bi₂O₃复合, 通过在光照下降解20 mg·L⁻¹的TCH来评价复合材料的光催化性能。

基于此, 本文采用电子扫描电镜(SEM)、高分辨透射电镜(HRTEM)、X射线衍射(XRD)、和电流时间(*i-t*)等对其进行了表征和活性测试, 通过UV-vis漫反射光谱, Mott-Schottky图和XPS光谱, 分析样品的相对VB和CB边缘位置和元素价态; 通过能带评价, 探讨了BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃在TCH降解过程中光催化活性的可能机理。SEM分析表明, 纯BiOCl_{0.9}I_{0.1}样品是方形纳米片且尺寸约为100 nm, 其规则地成层并层层覆盖。将制备的BiOCl_{0.9}I_{0.1}/15%β-Bi₂O₃复合物的基本形态与纯BiOCl_{0.9}I_{0.1}和纯β-Bi₂O₃进行比较, 纯β-Bi₂O₃为块状结构, 形成复合物后, BiOCl_{0.9}I_{0.1}纳米片作为组分嵌入β-Bi₂O₃块中, BiOCl_{0.9}I_{0.1}纳米片在β-Bi₂O₃表面部分聚集成最终覆盖整个表面的小花状微结构。BiOCl_{0.9}I_{0.1}纳米片的存在极大地增加了复合物的比表面积, 并为反应提供了更多的活性位点。HRTEM表征结果进一步确认了上述结果。紫外漫反射吸收光谱表明,

β - Bi_2O_3 能有效增加 $\text{BiOCl}_{0.9}\text{I}_{0.1}$ 对可见光的吸收,增加了对光的利用率.

光催化性能测试表明在光照 120 min 后, $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ 复合材料的样品中 TCH 的降解率达到了 82.4%, 而 $\text{BiOCl}_{0.9}\text{I}_{0.1}$, $\beta\text{-Bi}_2\text{O}_3$, $\text{BiOCl}_{0.9}\text{I}_{0.1}/5\%\beta\text{-Bi}_2\text{O}_3$, $\text{BiOCl}_{0.9}\text{I}_{0.1}/10\%\beta\text{-Bi}_2\text{O}_3$ 和 $\text{BiOCl}_{0.9}\text{I}_{0.1}/20\%\beta\text{-Bi}_2\text{O}_3$ 等复合样品的 TCH 的降解率分别为 54.8%, 21.0%, 70.0%, 73.2% 和 79.9%, 说明 $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ 对水中的盐酸四环素有很好的降解作用. 为了探索 TCH 光降解中涉及的活性物质, 我们进行了一系列清除试验, 得出 TCH 光降解的主要活性物质是 $\cdot\text{O}_2^-$ 和 $\cdot\text{OH}$. 为了研究 $\text{BiOCl}_{0.9}\text{I}_{0.1}/x\%\beta\text{-Bi}_2\text{O}_3$ 复合催化剂的重复使用性能, 将反应后的样品粉末收集, 并在相同条件下重复使用三次. 结果发现, $\text{BiOCl}_{0.9}\text{I}_{0.1}/15\%\beta\text{-Bi}_2\text{O}_3$ 的光催化活性未见显著降低, 表明它具有优异的稳定性和可再利用性.

关键词: $\text{BiOCl}_{0.9}\text{I}_{0.1}/\beta\text{-Bi}_2\text{O}_3$; 光降解; 盐酸四环素; 光催化; 模拟太阳光

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