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Article

Preparation of a p-n heterojunction 2D BiOI nanosheet/1DBiPO₄ nanorod composite electrode for enhanced visible light photoelectrocatalysis

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ABSTRACT

In this study, a 2D BiOI nanosheet/1D BiPO₄ nanorod/fluorine-doped tin oxide (FTO) composite electrode with a p-n heterojunction structure was prepared by a two-step electrodeposition method. Field-emission scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, UV-visible diffuse reflectance spectroscopy, and electrochemical testing were used to characterize its composition, crystal morphology, and optical properties. The BiOI/BiPO₄/FTO composite electrode has higher photoelectrocatalytic (PEC) activity for the degradation of tetracycline than pure BiPO₄ and BiOI. The PEC activity of the composite was 1.98 times and 2.46 times higher than those of the BiOI/FTO and BiPO₄/FTO electrodes, respectively. The effects of the working voltage and BiOI deposition time on the degradation of tetracycline were investigated. The optimum BiOI deposition time was found to be 150 s and the optimum working voltage is 1.2 V. Trapping experiments showed that hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) are the major reactive species in the PEC degradation process. The BiOI/BiPO₄/FTO composite electrode has good stability, and the tetracycline removal efficiency remains substantially unchanged after four cycles in a static system. The reason for the PEC efficiency enhancement in the BiOI/BiPO₄/FTO composite electrode is the increased visible light absorption range and the p-n heterojunction structure, which promotes the separation and migration of the photogenerated electrons and holes.

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1. Introduction

The pollution of water with toxic substances has drawn significant attention because of the risks to the environment and public health. Many traditional methods of water treatment, such as adsorption [1], biological oxidation [2], flocculation-precipitation [3], electrochemical catalytic oxidation, and photocatalysis [4–7], have been investigated for the removal of organic compounds from wastewater. Among them, photoca-

talysis is regarded as a promising and “green” sewage treatment technology because of its strong oxidation ability, low cost, and environmental friendliness [8–10]. However, photocatalyst technology is far from practical application because of the high recombination efficiency of the electron-hole pairs and low quantum efficiency [11,12]. In addition, the separation and recovery of the photocatalyst powder from treated water is challenging, which limits the efficiency and stability of the catalyst [13–15]. Compared with separate photocatalysis and

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electrooxidation processes, the combination of semiconductor photocatalysis and electrochemical oxidation (photoelectrocatalysis, PEC) for the degradation of organic contaminants in water has shown great potential. In the PEC process, the application of a small external bias not only increases the separation and transfer efficiency of the photogenerated electron-hole pairs but also oxidizes the organic compounds electrochemically [16–18]. Therefore, PEC has been widely applied for the removal of organic compounds because of the synergism between photocatalysis and electrocatalysis.

BiPO_4 was first reported as a photocatalyst in 2010 [19,20]. This compound has a higher photocatalytic activity than TiO_2 and is a promising UV-responsive photocatalyst. However, the BiPO_4 photocatalyst powder prepared by the conventional method has a low surface area [21], and the photocatalytic efficiency is limited in practice. In addition, the separation of the powdered photocatalyst after use is difficult, and its recyclability is poor. Zhang's group deposited BiPO_4 on fluorine-doped tin oxide (FTO) glass, which increased the contact area between the catalyst and liquid pollutants [22,23]. Thus, the PEC degradation of the organic compounds was increased compared with photocatalytic oxidation using the components separately. Furthermore, the BiPO_4/FTO electrode is more stable and solid-liquid separation is easier. However, BiPO_4 has a large band gap (3.8 eV), meaning that is responsive to ultraviolet light [19,24]. Thus, the utilization of solar energy is relatively low, limiting the catalytic efficiency. The combination of BiPO_4 with a visible-light-responsive semiconductor to form a heterojunction is an efficient method to increase the light absorption range and improve the photocatalytic activity. To date, the coupling of BiPO_4 with compounds such as BiVO_4 [25], AgBr [26], BiOBr [27], and $\text{g-C}_3\text{N}_4$ [28] has been reported to result in excellent photocatalytic activity in the visible region.

BiOI is a typical visible light catalyst with a narrow band gap and a large light absorption range [29–33]. Many researchers have used the light absorption properties of BiOI to modify TiO_2 [34, 35], BiOCl [36,37], ZnO [38], and other catalysts to form p-n heterojunctions, thus improving their light absorption properties and photocatalytic performance [39–42]. Powdered p-n $\text{BiPO}_4/\text{BiOI}$ composite catalysts with excellent visible light photocatalytic activity have been reported [43–45]. Considering the shortcomings of powdered photocatalysts, a composite electrode might be a more successful wastewater treatment method. To date, a $\text{BiOI}/\text{BiPO}_4$ film electrode for the PEC-based degradation of organic compounds has not been reported. Thus, the method of fabrication and the properties of the composite electrode should be studied in detail.

In this work, we used a simple two-step electrodeposition method to fabricate a $\text{BiOI}/\text{BiPO}_4$ film electrode. The prepared $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite film electrode has a p-n junction structure, which enhances visible light absorption and improves the electron-hole transfer efficiency. The $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite film electrode exhibits higher PEC oxidation ability than the pure BiOI/FTO and BiPO_4/FTO film electrodes. The effects of the working voltage and electrode deposition time, as well as other factors, on the removal of tetracycline were studied systematically. Finally, the mechanism

for the PEC oxidation of organic compounds by the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite film electrode is discussed.

2. Experimental

2.1. Preparation of materials

All chemicals were of analytical grade. The electrochemical deposition experiment was carried out using a CHI760e electrochemical workstation. The resistance of the FTO glass was 15 Ω . The FTO glass was washed in ethanol and 10% nitric acid for 30 min with ultrasonication. Then, the glass was thoroughly washed with ethanol and distilled water several times. Subsequently, it was dried at 60 $^\circ\text{C}$ for 12 h. The BiPO_4 precursor electrolyte solution was prepared as follows. 10 mmol/L of ethylenediaminetetraacetic acid (EDTA) was dissolved in 100 mL distilled water. Then, 10 mM of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added dropwise to the EDTA solution, and the pH was adjusted to 1 using concentrated HNO_3 . Subsequently, 100 mmol/L of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 50 mL of 30% H_2O_2 were added dropwise to the above solution (pH = 1), which was then stirred for about 30 min to obtain a homogeneous solution. The electrodeposition method was used to prepare BiPO_4/FTO electrode in a three-electrode system. The modified FTO glass was the working electrode and was rinsed with distilled water before electrodeposition. A Pt wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The BiPO_4/FTO electrode material was obtained by electrodeposition at a bias of -0.15 V for 45 min.

The BiOI precursor electrolyte solution was prepared as follows. 0.04 mol/L $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.4 mol/L KI were dissolved in 50 mL of distilled water, and the pH was adjusted to 1.7 by adding HNO_3 . Then, the solution was mixed with 20 mL of absolute ethanol (100%) containing 0.23 mol/L *p*-benzoquinone. A Pt wire was used as the counter electrode, and an SCE was used as the reference electrode. The prepared BiPO_4/FTO electrode was the working electrode. A series of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode materials were obtained by controlling the electrodeposition time of BiOI (30–180 s) at a bias voltage of -0.6 V. These samples are denoted $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-30\text{s}}$, $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-60\text{s}}$, $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-90\text{s}}$, $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-120\text{s}}$, $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$, and $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-180\text{s}}$. The BiOI/FTO electrode was fabricated under the same conditions using FTO as the substrate.

2.2. Characterization

X-ray diffractometry (XRD, Bruker D8 Advance, $\text{Cu K}\alpha$, $\lambda = 1.5406$ Å, 40 kV, 40 mA) analysis of the electrode material was carried out at room temperature in a scanning range of 10° – 70° . Morphological characterization of the catalytic material was carried out using field-emission scanning electron microscopy (FE-SEM, SU8010) at an acceleration voltage of 100 kV. Transmission electron microscopy (TEM, JEM 2100F) images were obtained at an acceleration voltage of 200 kV. The UV-vis diffuse reflectance spectra (DRS) of the electrodes were recorded on an UV-vis spectrophotometer (U-3010, Hitachi)

equipped with an integrating sphere, and BaSO_4 was used as the reference. Photoluminescence (PL) spectra of the electrodes were obtained by fluorescence spectrometry (FLS980, Edinburgh Instruments, UK) with an excitation wavelength of 245 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out using an XPS spectrometer (PHI XPS Quantera II) equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV).

2.3. Performance tests

The PEC performance of the materials was analyzed using an electrochemical workstation (CHI760E, Shanghai, China) with a Pt wire as the counter electrode and a SCE as the reference electrode. The $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode was the working electrode in the three-electrode system. The model organic pollutant was tetracycline (100 mL). The light source was a xenon lamp (Perfect Light) with an output intensity of 500 W. The area of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode material was 5 cm^2 . The concentration of tetracycline solution was determined at an absorption wavelength of 375 nm using a UV-visible spectrophotometer (U-3900, Hitachi). Photocurrent transient responses and electrochemical impedance spectroscopy (EIS) measurements were carried out on the same three-electrode electrochemical workstation with a Na_2SO_4 electrolyte solution (0.1 mol/L).

3. Results and discussion

3.1. Structural and properties analysis

The SEM images of the BiPO_4/FTO , BiOI/FTO , and $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrodes are shown in Fig. 1. As shown in Fig. 1(a), a large number of BiPO_4 nanorods with lengths of 1–2 μm and diameters of 400–600 nm were deposited on the FTO glass substrate. As shown by the image of the pure deposited BiOI in Fig. 1(b), the uniform BiOI nanosheets were directly electrodeposited on the FTO glass substrate. The images of $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite electrode (Figs. 1(c)–(f)) show that 2D BiOI nanosheets grew on the surface of the 1D BiPO_4 nanorods. When the BiOI deposition time was 90 s (Fig. 1(c)), the BiOI nanosheets aggregated together, forming flower-like BiOI structures. As the deposition time increased from 90 to 150 s, the flower structures gradually disappeared and nanosheets

Fig. 1. SEM images of the BiPO_4 (a), BiOI (b), and $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ (c–f) electrodes prepared with different BiOI deposition times. (c) 90 s; (d) 120 s; (e, f) 150 s.

appeared (Figs. 1(e) and (f)).

Powder XRD patterns of the prepared $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrodes were obtained to identify the crystal phases. As shown in Fig. 2, the (100), (101), (110), (111), (200), and (102) Bragg peaks of BiPO_4 were observed, corresponding to hexagonal BiPO_4 (JCPDS 15-0766). The characteristic (002), (102), (110), and (004) peaks are consistent with tetragonal BiOI (JCPDS 00-010-0445). These characteristic peaks of BiPO_4 and BiOI were observed in the XRD pattern of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite electrode, suggesting the successful preparation of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite electrode.

TEM was used to investigate the crystal structure and morphologies of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode material further (Fig. 3). Figs. 3(a) and (b) show that the BiOI nanosheets were successfully loaded onto the BiPO_4 nanorods. In Figs. 3(c) and (d), several lattice stripes with lattice distances of 0.349, 0.606, 0.267, and 0.282 nm can be clearly seen, and these can be attributed to the (110) and (100) crystal planes of hexagonal BiPO_4 and the (111) and (110) crystal planes of tetragonal BiOI , respectively. The results suggest that the p-n heterojunction of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite electrode had been successfully prepared by the two-step electrodeposition method, which is consistent with the XRD characterization of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode materials. Energy dispersive X-ray (EDX) spectroscopy measurements of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ composite electrode and the corresponding EDX mappings are shown in Fig. 3. Only Bi, O, I, and P are present in the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ composite electrode, and these elements are uniformly distributed.

XPS measurements were used to investigate the surface chemical states of the BiPO_4/FTO , BiOI/FTO , and $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite electrode.

Fig. 2. XRD patterns of the pure BiPO_4/FTO , BiOI/FTO , and $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ composite electrode.

Fig. 3. TEM images of BiOI/BiPO₄/FTO-150s (a–d) and EDX elemental maps of P, Bi, O, and I.

OI/BiPO₄/FTO electrodes. As shown in the XPS survey spectra (Fig. 4(a)), I and P were both present in the BiOI/BiPO₄/FTO electrode. The P 2p peak is located at 132.25 eV in the spectrum of the BiOI/BiPO₄/FTO electrode and at 131.87 eV in the spectrum of the BiPO₄/FTO electrode (Fig. 4(b)), indicating that P is present as P⁵⁺. The small shift to a higher binding energy of P⁵⁺ in the BiOI/BiPO₄/FTO electrode indicates that there is some interaction between BiOI and BiPO₄. The binding energies of I 3d_{5/2} (618.24 eV) and I 3d_{3/2} (629.84 eV) in the spectrum of the BiOI/BiPO₄/FTO electrode are a little lower than those of the BiOI/FTO electrode (618.36 and 630.01 eV) and are characteristic of I⁺ [46]. As shown in Fig. 4(d), the binding energies of 157.99 and 163.32 eV in the spectrum of the BiOI/BiPO₄/FTO electrode correspond to Bi 4f_{7/2} and Bi 4f_{5/2} of

Bi³⁺. The binding energies of the Bi³⁺ peak in the spectra of the BiOI/FTO and BiOI/BiPO₄/FTO electrodes are lower than those in the spectrum of the BiPO₄/FTO electrode. The decrease in the binding energy of Bi³⁺ in BiPO₄ might be due to electron transfer from BiOI to BiPO₄, which would increase the electron cloud density in the outer layer of BiPO₄. Correspondingly, the electron cloud density of BiOI would decrease, resulting in an increase in the band energy of Bi³⁺ in BiOI. The XPS results further demonstrate the coexistence of BiPO₄ and BiOI in the as-prepared p-n heterojunction electrode.

Fig. 5 shows the UV-vis DRS of BiOI/FTO, BiPO₄/FTO, and BiOI/BiPO₄/FTO electrodes. BiPO₄ shows absorption in the ultraviolet region with an absorption edge at about 360 nm. Although pure BiOI exhibits strong visible light absorption with

Fig. 4. XPS spectra of BiPO_4/FTO , pure BiOI/FTO , and $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrodes. (a) Survey; (b) P 2p; (c) I 3d; (d) Bi 4f.

an absorption edge at about 635 nm. Compared with the pure BiPO_4 nanorods and BiOI nanosheets, the light absorption ability of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode from 250 to 600 nm was increased, which improved the PEC performance.

3.2. Photoelectrocatalytic performance

Fig. 6 shows the PEC degradation performance of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrodes prepared at different BiOI deposition times. The target pollutant was a tetracycline solution (10 ppm) containing 0.1 mol/L Na_2SO_4 . In the static system, the tetracycline solution did not undergo self-degradation under illumination, so the effects of self-degradation can be excluded. The PEC degradation efficiency of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ elec-

trode increased initially and then decreased with increasing BiOI deposition time (Fig. 6(a)). When the BiOI deposition time was 150 s, $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ had the maximum PEC degradation efficiency. The corresponding reaction rate constants for tetracycline degradation using the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrodes are shown in Fig. 6(b). For samples prepared at deposition times of less than BiOI 150 s, the photocatalytic degradation rate of tetracycline increased gradually and subsequently began to decrease. The $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ -150s electrode, which was prepared at a deposition time of 150 s, has the best reaction rate constant ($k = 0.35 \text{ h}^{-1}$), indicating that abundant BiOI inhibits the photoelectrocatalytic degradation efficiency.

Fig. 7 shows a comparison of the PEC degradation of tetracycline of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ -150s, BiPO_4/FTO , and BiOI/FTO

Fig. 5. The UV-vis DRS of the bare BiPO_4/FTO , pure BiOI/FTO , and $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrodes.

electrodes. As shown in Fig. 7(a), the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode has a higher PEC activity than the BiOI/FTO and BiPO_4/FTO electrodes at an applied working bias (E) of 1.2 eV, the PEC degradation efficiency of which reached nearly 80% in 4 h. The reaction rate constant (k) of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode is 0.386 h^{-1} , which is 1.98 times and 2.46 times higher than those of the BiOI/FTO and BiPO_4/FTO electrodes, respectively. The experimental results show that the formation of the $\text{BiOI}/\text{BiPO}_4$ composite film greatly improved the photoelectrocatalytic activity of the BiPO_4/FTO electrode.

The photocatalytic, electrocatalytic, and photoelectrocata-

lytic degradation performances of tetracycline by the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode were compared to verify the synergistic effect of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode. As shown in Fig. 8(a), the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode had photocatalytic and electrocatalytic degradation efficiencies of only 25% and 26%, respectively, for tetracycline after 4 h. In contrast, the PEC removal rate of tetracycline over the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode reached 77%, which is much greater than the electrocatalytic and photocatalytic removal rates. As shown in Fig. 8(b), the photoelectrocatalytic rate constant (k) of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode is 0.35 h^{-1} , which is 4.38 times and 4.12 times higher than the photocatalytic and electrocatalytic degradation rate constants, respectively. The kinetic study also shows that the pollutant removal rate for the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode is significantly higher in the photoelectrocatalytic process compared to the photocatalytic and electrocatalytic processes, suggesting that the catalyst benefits from the synergism of the photocatalytic and electrocatalytic degradation processes for the removal of organic compounds.

The applied bias potential can improve the separation of the photogenerated electron-hole pairs and enhance the PEC efficiency significantly. The effect of the working voltage (0.8–1.4 V) on the PEC efficiency of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode was investigated, and the results are shown in Fig. 9. With increasing voltage, the removal rate and reaction rate constant (k) of tetracycline initially increased and then decreased. At an applied voltage of 1.2 V, the $\text{BiOI}/\text{BiPO}_4/\text{FTO}_{-150\text{s}}$ electrode had the highest tetracycline removal rate, indicating that 1.2 V is the optimum applied working voltage.

Fig. 6. (a) Photoelectron synergistic catalytic efficiency of the $\text{BiOI}/\text{BiPO}_4/\text{FTO}$ electrode prepared at different BiOI deposition times; (b) the corresponding kinetic plots.

Fig. 7. (a) The photoelectrocatalytic activity of BiPO₄/FTO, BiOI/FTO, and BiOI/BiPO₄/FTO; (b) the corresponding reaction rate constants under an applied operating bias of 1.2 eV.

Fig. 8. (a) Photocatalytic, electrocatalytic, and photoelectrocatalytic degradation of tetracycline by the BiOI/BiPO₄/FTO-150s electrode; (b) kinetic plots and reaction rate constants.

3.3. Mechanism of photoelectrocatalytic performance enhancement

The transient photocurrent responses and EIS Nyquist plots of the BiOI/BiPO₄/FTO, BiOI/FTO, and BiPO₄/FTO electrodes are shown in Fig. 10. The BiOI/BiPO₄/FTO electrode exhibited the strongest photocurrent response: 2.5×10^{-5} A, which is twice that of the bare BiOI electrode and nearly 20 times that of the BiPO₄ electrode alone. This result indicates that the electron-hole separation efficiency was greatly improved. The Nyquist plots in Fig. 10(b) show that the BiOI/BiPO₄/FTO electrode has a smaller arc than those of the BiOI/FTO and BiPO₄/FTO electrodes. This means that the BiOI/BiPO₄/FTO electrode has better electron-hole separation because of the formation of the p-n heterojunction between p-BiOI and n-BiPO₄. The results are consistent with the comparative photoelectrocatalytic degradation experiments for the BiPO₄/FTO, BiOI/FTO, and BiOI/BiPO₄/FTO electrodes (Fig. 7).

Fig. 11 shows the transient photocurrent responses and

Nyquist plots of the BiOI/BiPO₄/FTO electrodes prepared at different deposition times. As shown in Fig. 11(a), with increasing BiOI deposition time, the photocurrent increased initially and then decreased, reaching a maximum at a deposition time of 150 s. In addition, the Nyquist plot of the BiOI/BiPO₄/FTO-150s electrode has the smallest radius (Fig. 11(b)). These results show that the BiOI/BiPO₄/FTO-150s electrode has the highest separation efficiency of the tested samples. The photocurrent and electrochemical impedance trends for the BiOI/BiPO₄/FTO electrodes are consistent with the trend in photoelectrocatalytic degradation activity shown in Fig. 6. Thus, the Nyquist plots of the different BiOI/BiPO₄/FTO electrodes further confirm their good photoelectrocatalytic activities.

Fig. 12 shows the PL of the BiPO₄/FTO, BiOI/FTO, and BiOI/BiPO₄/FTO electrodes. A higher PL intensity indicates a higher recombination of photogenerated electron-hole pairs. The BiOI/BiPO₄/FTO electrode yielded a lower PL intensity than those of the BiOI/FTO and BiPO₄/FTO electrodes, showing that the recombination of photogenerated electron-hole pairs

Fig. 9. (a) Photoelectrocatalytic degradation of tetracycline using the BiOI/BiPO₄/FTO-150s electrode at different applied voltages; (b) kinetic plots and reaction rate constants.

Fig. 10. (a) Transient photocurrent responses of the BiPO₄/FTO, BiOI/FTO, and BiOI/BiPO₄/FTO electrodes; (b) corresponding EIS Nyquist plots.

Fig. 11. (a) Transient photocurrent responses of different BiOI/BiPO₄/FTO electrodes; (b) the corresponding Nyquist plots.

was reduced in the BiOI/BiPO₄/FTO electrode.

Trapping experiments were carried out to identify the main active species in the PEC degradation process, and a possible mechanism of action was formulated. As shown in Fig. 13, when KI was used as a trapping agent for holes (h⁺), the PEC

removal efficiency of tetracycline over the BiOI/BiPO₄/FTO-150s electrode decreased only slightly, indicating that the holes (h⁺) have little effect on the PEC degradation. In contrast, when ascorbic acid (vitamin C, VC) was used as a scavenger for the superoxide radical (•O₂⁻), the PEC removal efficiency of the

Fig. 12. PL spectra of the BiOI/BiPO₄/FTO, BiOI/FTO, and BiPO₄/FTO electrodes.

Fig. 13. Active species trapping experiments in the degradation of tetracycline using the BiOI/BiPO₄/FTO-150s electrode.

BiOI/BiPO₄/FTO-150s electrode decreased significantly, indicating that the superoxide radical ($\bullet\text{O}_2^-$) is an important active species and plays an crucial role in the photoelectrocatalytic reaction. In addition, when isopropanol (IPA) was used to trap hydroxyl radicals ($\bullet\text{OH}$), the PEC removal efficiency also decreased significantly, indicating that the hydroxyl radical ($\bullet\text{OH}$) is another important active species in the photoelectrocatalytic reaction. Thus, holes (h^+) did not directly participate in the PEC degradation of tetracycline, and hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) are the dominant species in the photoelectrocatalytic reaction.

The light absorption, surface reactions, and the separation of electron-hole pairs are the main determinants of the photoelectrocatalytic activity of a photocatalyst. In this paper, the p-n het-

Fig. 14. Schematic of the degradation mechanism of the BiOI/BiPO₄/FTO-150s electrode.

erojunctions formed by the 2D BiOI nanosheet and 1D BiPO₄ nanorod semiconductor play a leading role in the efficient separation of the photogenerated electron-hole pairs. For the BiOI/BiPO₄/FTO composite electrode (Fig. 14), the conduction band of the p-type semiconductor (BiOI) moved up, whereas the conduction band of the n-type semiconductor BiPO₄ moved down until the Fermi level reached equilibrium [43,47,48]. In addition, the conduction band of BiOI was higher than that of BiPO₄. Thus, the transfer path of the electron-hole pairs was improved. On photoexcitation, the photogenerated electrons in the conduction band of p-BiOI were transferred to that of n-BiPO₄ effectively, subsequently rapidly moving to the platinum wire electrode through the external circuit under the action of the external bias. Finally, the photogenerated electrons transferred to the surface of the platinum wire reacted with oxygen and produced superoxide radicals ($\bullet\text{O}_2^-$), which degraded the organic pollutants. At the same time, the corresponding holes transferred from the valence band of n-BiPO₄ to that of p-BiOI and reacted with water to produce hydroxyl radicals ($\bullet\text{OH}$), which are the main active species in the photoelectrocatalytic reaction. Therefore, the fabrication of the p-n heterojunction structure promoted the separation and migration of the photogenerated charges, leading to the enhanced photoelectrocatalytic efficiency of the BiPO₄/FTO electrode. Furthermore, the addition of the BiOI nanosheets greatly improved the visible light absorption and increased the light utilization of the photoelectrode, enhancing the photoelectrocatalytic activity.

3.4. Stability of the BiOI/BiPO₄/FTO-150s electrode

The BiOI/BiPO₄/FTO-150s electrode stability was evaluated by XRD measurements before and after photoelectrocatalytic and cycling experiments. The BiOI/BiPO₄/FTO-150s electrode showed excellent cycling stability for the PEC degradation of tetracycline (Fig. 15(a)). The photoelectrocatalytic degradation rate did not change after four 16-h degradation cycles. As

Fig. 15. (a) Tetracycline degradation cycling tests using the BiOI/BiPO₄/FTO-150s electrode; (b) XRD patterns of BiOI/BiPO₄/FTO-150s electrode before and after four reaction cycles.

shown in Fig. 15(b), no changes in the phase or composition of the BiOI/BiPO₄/FTO-150s electrode occurred. This result indicates that BiOI/BiPO₄/FTO-150s remains stable throughout the

photoelectrocatalytic reaction.

4. Conclusions

A BiOI/BiPO₄ composite film electrode was fixed to FTO glass by a simple and rapid two-step electrodeposition method. The 2D BiOI nanosheets were successfully deposited on the 1D BiPO₄ nanorods to form a p-n heterojunction structure composite electrode. The composite electrode has excellent photoelectrocatalytic efficiency compared with pure BiOI/FTO electrodes and pure BiPO₄/FTO electrodes because of its broader light absorption range and greater migration and separation efficiency of the electron-hole pairs. Trapping experiments suggest that hydroxyl ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) are the main reactive species in the PEC degradation process. The composite electrode material was extremely stable and is a promising material for PEC-based oxidative water purification.

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Graphical Abstract

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Preparation of a p-n heterojunction 2D BiOI nanosheet/1DBiPO₄ nanorod composite electrode for enhanced visible light photoelectrocatalysis

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The p-n heterojunction structure promotes the separation and migration of photogenerated charges leading to enhanced photoelectrocatalytic efficiency in the BiOI/BiPO₄/FTO electrode.

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增强可见光光电催化活性的二维BiOI纳米片/一维BiPO₄纳米棒p-n异质结复合电极的制备

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摘要: 光电催化是一种新型催化技术, 在去除水中有机物方面具有独特的优势. 在光电协同作用下具有较高的量子效率, 电子-空穴负电荷率低, 稳定性好等优势. BiPO₄具有较宽的禁带宽度, 只能响应有限的紫外光区域, 极大限制了其光电催化效率. 因此, 本文在电化学三电极体系下, 通过简单的两步电沉积法将BiPO₄纳米棒/BiOI纳米片复合薄膜沉积固定在FTO玻璃上, 制备了BiPO₄/BiOI/FTO复合光电极材料. 通过场发射扫描电镜, 透射电子电镜, X射线光电子能谱、紫外可见漫反射光谱以及电化学测试对其组成、晶体形貌结构和光学性质进行表征. 考察了外加工作电压、碘氧铋电极沉积时间等因素对四环素去除效果的影响. 结果表明, BiOI纳米片生长在BiPO₄纳米棒上, 形成了异质结结构, BiPO₄/BiOI/FTO复合薄膜电极具有良好的光吸收性能和优异的电荷转移特性. 当碘氧铋沉积时间为150 s, 外加偏压为1.2 V时, 复合薄膜电极具有最佳的四环素去除效率, 4 h达到80%. 在相同的实验条件下, BiPO₄/BiOI/FTO复合薄膜电极对四环素的去除效率分别是BiPO₄/FTO电极和BiOI/FTO电极的1.6倍和1.4倍. 在光电协同作用下, BiPO₄/BiOI/FTO复合光电极对污染物的去除效率是单纯光催化和电催化对污染物去除效率的2.8倍和2.5倍. 同时该复合光电极具有好的稳定性, 经过四次16 h的循环实验, 光电极对四环素的去除效果基本保持不变.

根据一系列表征结果和p-n异质结形成的方式, 推测了p-n异质结的结构和反应过程. 在光激发作用下, BiOI导带上的

光生电子有效的转移到 BiPO_4 导带上, 然后在外加偏压的作用下通过外电路转移到铂丝电极上, 光生电子与氧气反应生产超氧自由基降解有机污染物. 另一方面, 光生空穴从 BiPO_4 价带上转移到 BiOI 价带上, 与水反应生产羟基自由基, 作为光电催化反应过程中的主要活性物种. 总之, 增强的光电催化活性 BiOI/BiPO_4 异质结构可能主要归因于p-n异质结结构改善催化剂的光吸收能力和有效的电子-空穴转移过程.

关键词: 电沉积; 光电催化; $\text{BiOI/BiPO}_4/\text{FTO}$; 四环素

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