Fabrication of 3D Bi₂O₃-BiOI heterojunction by a simple dipping method: highly enhanced visible-light photoelectrocatalytic activity

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Abstract

Three-dimensional (3D) Bi₂O₃-BiOI heterojunction was fabricated on the basis of Bi₂O₃ film by a simple dipping method at room temperature. The as-prepared film samples were characterized by scanning electron microscope (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-Vis DRS spectra. Results indicated that BiOI nanosheets with cross-flake arrays were formed via in situ etching and exchanging of Bi₂O₃ layer by I⁻ in KI aqueous solution, which grow around the residual Bi₂O₃ particles to form 3D Bi₂O₃-BiOI heterojunction. Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) Nyquist plots and incident monochromatic photon-to-current conversion efficiency (IPCE) indicated that easier generation, separation and transfer of photogenerated charges were achieved on the special 3D heterojunction. The photocurrent density of the 3D Bi₂O₃-BiOI composite increased by 8.4 times relative to pure Bi₂O₃ at 0.35 V vs. Ag/AgCl in 0.2 M Na₂SO₄ aqueous solution under visible light irradiation. For the PEC degradation of phenol, the composite film also exhibited greatly enhanced activity. The calculated rate constant was 3.8 times that on pure Bi₂O₃. Furthermore, good stability in long-time photocurrent and cyclic degradation of phenol can both be observed, indicating that the 3D Bi₂O₃-BiOI film can be potentially applied in water oxidation and environmental remediation.

Keywords: Photoelectrocatalytic; 3D Bi₂O₃-BiOI; Visible light; Water oxidation; Phenol degradation

1. Introduction

With increasing concerns on the compelling environmental and energy crises, more researches have been performed on the utilization of clean and abundant solar energy [1]. Photocatalysis, which is green and energy saving, can be adopted to cope with these crises. Moreover, a great deal of photocatalytic materials have been explored and studied, including TiO_2 [2-5], Fe_2O_3 [6-8], BiVO_4 [9-11], and $\text{g-C}_3\text{N}_4$ [12-14]. Typically, TiO_2 has attracted more attention due to high chemical stability, large availability, low cost and low toxicity [15]. However, low quantum efficiency and wide band gap limit the wide practical application of TiO_2 . It is urgent to develop efficient and stable photocatalysts that can utilize sunlight or visible light [16-20].

Recently, Bi (III)-based photocatalysts have emerged as an attractive photocatalytic material. Especially, Bi_2O_3 is considered as a potential candidate due to its high electrochemical stability, small band gap (2.6 eV-2.8 eV), as well as high redox reversibility [21,22]. However, the wide application of pure Bi_2O_3 was still constrained due to low photocatalytic activity. Thus, considerable efforts have been made to improve its photocatalytic performance by incorporating/coupling Bi_2O_3 with other substance. For example, $\text{SiO}_2@\text{Bi}_2\text{O}_3$ [23], $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ [24], $\text{Bi}_2\text{O}_3\text{-Bi}_2\text{S}_3$ [25], $\text{AC-Bi}_2\text{O}_3$ [26], $\text{beta-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ [27] and $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ [28] were reported. Hameed et al. reported that the yellow Bi_2O_3 can be slowly transformed into the brown $\text{Bi}_2\text{O}_{4-x}$ with remarkable changes in the photoactivity under UV or solar irradiation, and the extent of transformation might be reduced by the formation of nanocomposites [29-32]. Besides, bismuth oxyhalide, such as BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) also draw special attentions due to their unique layered structure, high electrochemical stability and activity [33-35]. Ji and Tong's group boosted the photocatalytic performance of BiOX nanosheets by improving the charge separation, transfer, and optical absorption [36-39]. The formation of heterojunction structure by coupling Bi_2O_3 with BiOX can be an efficient method to improve the photocatalytic activity [40,41]. For example, $\text{BiOCl/Bi}_2\text{O}_3$ shows unexpectedly high efficiency in decomposing organic compounds compared to the individual BiOCl or Bi_2O_3 [42]. Han et al.

coupled β - Bi_2O_3 with BiOI through an in-situ treatment with hydriodic acid and achieved much higher photocatalytic activity for the degradation of methyl orange [41]. Comparing to BiOCl or BiOBr, BiOI displays the narrowest band gap (1.77 eV-1.92 eV), largest BET surface area and strongest visible light absorption [40]. However, its visible-light photocatalytic activity was still low for environment remediation due to easily combined electron-hole pairs. Moreover, the preparation of BiOI usually involved heat treatment and use of organic surfactants or additives [43-46].

PEC process has been confirmed to be superior to single photocatalytic (PC) one in energy conversion and environment remediation [47-50]. The bias potential applied to the working electrode can further promote the separation of photogenerated electron-hole pairs and increase the efficiency of photocatalysis. Moreover, the film photocatalysts immobilized on the conductive electrodes in PEC process are more easily reused and can avoid secondary pollution of powdered photocatalysts. Furthermore, nanostructure engineering could also improve the PC performance since well-designed structures, interfaces and large surface area led to more efficient light absorption, faster charge transfer and electron-hole separation [51, 52]. Thus, the proper combination of applied bias potential and nanostructure heterojunction was anticipated to achieve better PEC performance.

In this study, we report the fabrication of visible-light-driven 3D Bi_2O_3 -BiOI on FTO by a simple dipping method at room temperature. Via in situ etching and exchanging of Bi_2O_3 layer by I⁻ in KI aqueous solution, BiOI nanosheets with cross-flake arrays were grown around residual Bi_2O_3 particles to form 3D Bi_2O_3 -BiOI films (Scheme 1). Photoelectrochemical techniques (LSV, EIS, IPCE and I-V characteristics) were applied to investigate possible changes in generation, separation and transfer of photogenerated charges. The visible-light-induced PEC degradation of phenol using the as-prepared films as anodes was also tested. Furthermore, the stability in long-time photocurrent and cyclic degradation of phenol were both evaluated, which were vital for future practical application in either water oxidation or environment remediation.

2. Experimental

2.1 Chemicals

Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.0\%$), Potassium iodide (KI, $\geq 99.0\%$), Ethylene glycol and Nitric acid (HNO_3 , 65.0% ~ 68.0%) were all purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (Sichuan, China). All chemicals were of analytical grades and used without further purification.

2.2 Synthesis of Bi_2O_3 -BiOI, Bi_2O_3 and BiOI films

Bi_2O_3 films were prepared by a simple drop-coating method (Scheme 1). A 0.2 M precursor solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in ethylene glycol including 1 M HNO_3 was prepared, and 20 μL of the precursor solution was pipetted onto F-doped tin oxide (FTO, Nippon Sheet Glass, Japan) substrate (10 mm $\times$ 10 mm) and then dried in a vacuum at 80 $^\circ\text{C}$. Subsequently, the films were heated to 500 $^\circ\text{C}$ for 3 h to produce Bi_2O_3 films in a muffle furnace. Bi_2O_3 -BiOI films were fabricated by simply immersing the as-prepared Bi_2O_3 films in 0.2 M KI solution for a certain time (30 to 120 min) at pH 3. BiOI films were obtained at prolonged immersion time (360 min). After immersion, the obtained composite films were thoroughly washed with deionized water and dried in air at room temperature.

Scheme 1. Schematic processes for the fabrication of 3D Bi_2O_3 -BiOI and Bi_2O_3 films.

2.3 Characterization

Scanning electron microscope (SEM) surveys were collected by a S-4700 (II) (Hitachi) scanning electron microscope to image the surface morphology. High resolution transmission electron microscopy (HRTEM) (JEOL JEM-2010) was used to further confirm the surface structure. X-ray diffraction (XRD) patterns were obtained on a Phillips PANalytical X'PERT diffractometer with monochromatic Cu-K radiation at 40 kV and 40 mA to characterize the

crystal structure of the as-prepared photocatalytic films. The absorption spectra were recorded on a diffuse reflectance absorption spectra (UV-Vis-DRS, Purkinje General TU-1901). X-ray photoelectron spectroscopy (XPS, ESCA lab 220i-XL spectrometer with Al K α at 1486.6 eV) was tested to determine the atomic compositions and valance states.

2.4 Photoelectrochemical measurements

Photoelectrochemical measurements were carried out using conventional three electrodes setup including a working electrode, a platinum foil counter electrode and a Ag/AgCl reference electrode. An electrochemical station (CHI 660E, Shanghai Chenhua, China) was used to perform photoelectrochemical investigations. The experiments were conducted under visible light irradiation (≥ 420 nm) using a Xe lamp (500W, Shanghai lansheng, China) at an intensity of ca. 100 mW/cm². All films were back-illuminated through the FTO glass. The liner sweep voltammetry (LSV) measurements were carried out in 0.1 M Na₂SO₄ with or without 0.1 M Na₂SO₃ aqueous solution. The incident monochromatic photon-to-current conversion efficiency (IPCE) measurements were detected with a Xe lamp fitted with different monochromatic filters (400, 430, 450, 475, 500, 550, 600, or 633 nm) combined with a power meter (model FZ-A) in the same electrolyte mentioned above. Electrochemical impedance spectroscopy (EIS) analyses were measured in 0.2 M Na₂SO₄ (pH 6.2) aqueous solution under darkness and visible light irradiation.

2.5 PEC degradation of pollutants

To evaluate the PEC degradation efficiency and stability of the 3D Bi₂O₃-BiOI films, phenol (10 mg/L, 50 mL) was used as model pollutant. In the PEC degradation experiments, the as-prepared photoelectrode with an active area of 2 cm $\times$ 2 cm was used as working electrode, whereas titanium with the equal active area was used as counter electrode. The applied potential was 2.5 V unless otherwise mentioned. Typical PEC degradation was conducted under visible light irradiation (≥ 420 nm) in 0.2 M Na₂SO₄ solution (using Na₂SO₄ as electrolyte) containing phenol. After dark treatment for 30 min to establish an absorption/desorption equilibrium, reactions were initiated under illumination. The concentrations of phenol and its degradation intermediates were determined by

high-performance liquid chromatography (HPLC, Agilent 1200) with Diamonsil Model C18 column (150 nm $\times$ 4.6 mm, 5 μ m). 254 nm was selected as detecting wavelength and methanol/water (30/70, V/V) with a flow rate of 1 mL/min was used as mobile phase. Conversion of phenol was calculated by the formula: Conversion ($\eta\%$) = $(1 - C_t/C_0) \times 100$, where C_0 and C_t represented the original and residual phenol concentration in the degradation process, respectively.

3. Results and discussion

3.1 Morphology and structure

In the present study, Bi_2O_3 films were dipped in KI solution with variable immersion time. In order to observe possible morphological change induced by dipping, the as-prepared films were first investigated by SEM. As illustrated in Fig. 1, the transformation of Bi_2O_3 to BiOI can be clearly observed. Comparing to pure Bi_2O_3 before the dipping step (Fig. 1a), nanosheet structure emerged after 30 min immersion (Fig. 1b). With prolonged immersion time (Fig. 1c), more nanosheets with cross-flake arrays can be observed, which surrounded the particle-shaped Bi_2O_3 to form heterojunctions. After 360 min immersion (Fig. 1d), the particles disappeared, leaving uniform nanosheets with interleaving distribution. TEM and HRTEM were further performed to obtain the lattice structure information of Bi_2O_3 film with 90 min immersion. As shown in Fig. 1f, clear lattice fringes of $\alpha\text{-Bi}_2\text{O}_3$ and BiOI can both be observed after fast Fourier transform. For example, the largest portion with 0.28 nm lattice fringe was ascribed to (110) planes of BiOI nanosheets [53]. Meanwhile, 0.33 nm lattice fringe was ascribed to the (111) planes of $\alpha\text{-Bi}_2\text{O}_3$ [54]. Thus, for simplicity in the following study, Bi_2O_3 (90 min immersion) and Bi_2O_3 (360 min immersion) were denoted as $\text{Bi}_2\text{O}_3\text{-BiOI}$ and BiOI, respectively.

Fig. 1. SEM images of Bi_2O_3 films with variable immersion time in KI solution: (a) 0 min, (b) 30 min, (c) 90 min, (d) 360 min; (e) TEM and (f) HRTEM of Bi_2O_3 film with 90 min immersion.

XRD analysis was further carried out to investigate the crystal structures and phases of the as-prepared films, and the results were displayed in Fig. 2. As for Bi_2O_3 , peaks at 27.3° , 29.2° , 33.2° , 35.4° , 46.3° and 54.8° were observed, which corresponded to (1 2 0), (0 1 2), (2 0 0), (0 3 1), (2 2 1) and (3 0 4) planes of monoclinic $\alpha\text{-Bi}_2\text{O}_3$ (PDF 01-071-0465). As for $\text{Bi}_2\text{O}_3\text{-BiOI}$, new peaks appeared, which were ascribed to BiOI. For example, peaks at 29.8° and 31.7° belonged to the (0 1 2) and (1 1 0) crystal planes of BiOI with a tetragonal crystal structure. Since the films were prepared using FTO as substrate, signals of FTO can also be observed. In a word, combined with the results in SEM, BiOI nanosheets with cross-flake arrays were successfully grown around Bi_2O_3 particles to form 3D $\text{Bi}_2\text{O}_3\text{-BiOI}$ structure.

Fig. 2. XRD patterns of different films.

Since PEC reactions predominantly take place on/near the catalyst surface, XPS measurements were further carried out to investigate the surface properties. Survey spectra of the 3D $\text{Bi}_2\text{O}_3\text{-BiOI}$ film was displayed in Fig. 3a, which revealed obvious signals of Bi, O and I elements. According to the atomic percentage of each element, the molar ratio of BiOI to Bi_2O_3 on the surface layer was calculated to be 1.1 : 1. As for Bi 4f, Fig. 3b illustrates that there are two couple of peaks corresponding to Bi_2O_3 (163.6 eV for Bi $4f_{5/2}$ and 158.3 eV for Bi $4f_{7/2}$) and BiOI (164.3 eV for Bi $4f_{5/2}$ and 159.0 eV for Bi $4f_{7/2}$), respectively. Moreover, the separation between Bi $4f_{7/2}$ and Bi $4f_{5/2}$ was 5.3 eV, indicating characteristic Bi^{3+} state [46]. Consistent with Bi 4f, the presence of lattice I⁻ in BiOI (618.4 eV and 629.9 eV) can also be observed in I 3d spectra (Fig. 3c) [55]. As for O 1s (Fig. 3d), peaks corresponding to O^{2-} in Bi-O, surface hydroxyl groups and H_2O can all be observed [56, 57]. Therefore, the presence of BiOI and Bi_2O_3 can be further confirmed by XPS analysis.

To clarify the interaction between Bi_2O_3 and BiOI in Bi_2O_3 - BiOI film, the binding energies of I species in BiOI before and after the formation of the heterojunction were compared, and the results were shown in Fig. S1. The XPS peaks for I $3d_{5/2}$ and I $3d_{3/2}$ in BiOI located at 618.6 eV and 630.1 eV, respectively. A 0.2 eV negative shift of binding energy (BE) for I $3d$ (618.4 eV and 629.9 eV) can be observed after introduction of Bi_2O_3 . According to the principle of XPS technique, negative shift of binding energy indicated that the outer electron cloud density around I atom increased after the formation of Bi_2O_3 - BiOI heterojunction. Thus, a strong interaction between Bi_2O_3 and BiOI can be inferred.

Fig. 3. XPS spectra of 3D Bi_2O_3 - BiOI film. (a) survey spectrum and high-resolution core spectrum for (b) Bi 4f , (c) I 3d , (d) O 1s .

3.2 Photoelectrochemical characterizations

LSV measurements were performed to compare the PEC performance of the as-prepared

film samples. As illustrated in Fig. 4a, the photocurrent density of Bi_2O_3 (0 min immersion) was greatly enhanced after its immersion in KI solution ranging from 30 to 360 min. The optimum performance was observed at 90 min immersion time (denoted as $\text{Bi}_2\text{O}_3\text{-BiOI}$). With prolonged immersion time at 360 min (BiOI), the LSV photocurrent density decreased drastically. In order to reveal the improvement of PEC performance caused by BiOI formation on Bi_2O_3 , LSVs of $\text{Bi}_2\text{O}_3\text{-BiOI}$, Bi_2O_3 and BiOI films in 0.1 M Na_2SO_4 with 0.1 M Na_2SO_3 (pH 9.3) aqueous solution under both visible and UV-vis light irradiation were compared. As shown in Fig. 4b and Fig. 4c, the photocurrent response of $\text{Bi}_2\text{O}_3\text{-BiOI}$ heterojunction was ca. 5 times and 6 times higher than that of Bi_2O_3 at 0.35 V (vs. Ag/AgCl) under visible and UV-vis light irradiation, respectively.

Fig. 4. (a) LSVs of different Bi_2O_3 -based films in 0.1 M Na_2SO_4 with 0.1 M Na_2SO_3 aqueous solution (pH 9.3); LSVs of $\text{Bi}_2\text{O}_3\text{-BiOI}$, Bi_2O_3 and BiOI films under (b) visible light ($\lambda > 420$ nm) and (c) UV-vis light irradiation. (d) LSVs of $\text{Bi}_2\text{O}_3\text{-BiOI}$, Bi_2O_3 and BiOI films in 0.2 M Na_2SO_4 (pH 6.2) aqueous solution

under visible light ($\lambda > 420$ nm) irradiation.

When Na_2SO_4 and Na_2SO_3 coexist in the same aqueous solution, Na_2SO_4 serves as the electrolyte and Na_2SO_3 serves as a sacrificial electron donor, so that the photogenerated holes can be consumed immediately [6]. To investigate the PEC activities of Bi_2O_3 -BiOI films for water oxidation, the LSVs of Bi_2O_3 -BiOI and Bi_2O_3 films in 0.2 M Na_2SO_4 (pH 6.2) aqueous solution without a sacrificial electron donor were also performed. As illustrated in Fig. 4d, the photocurrent response of Bi_2O_3 -BiOI heterojunction was 8.4 times that of Bi_2O_3 at 0.35 V (vs. Ag/AgCl) under visible light irradiation.

Fig. 5. (a) The UV-Vis DRS of different film samples and (b) Estimated corresponding band gaps; I-V characteristics of different film electrodes measured for H_2O_2 oxidation (0.5 M) under (c) darkness and (d) visible light irradiation.

For the enhanced photocatalytic performance of Bi_2O_3 -BiOI heterojunction, there are several possible reasons [47]: (a) more easily generated electron-hole pairs, (b) faster surface reaction kinetics on BiOI surface, and (c) enhanced charge separation or inhibited charge

recombination. It is generally accepted that formation of heterojunction will lead to enhanced charge separation. To rule out any other possibilities, the UV-Vis DRS of the as-prepared film samples were first performed to investigate the changes in optical absorption and band gap. As shown in Fig. 5a, all the films exhibit strong optical absorption in visible light region in the order of $\text{Bi}_2\text{O}_3 < \text{Bi}_2\text{O}_3\text{-BiOI} < \text{BiOI}$. According to transformed Kubelka-Munk function (Fig. 5b), the corresponding band gaps for Bi_2O_3 , BiOI and $\text{Bi}_2\text{O}_3\text{-BiOI}$ were estimated to be 2.41 eV, 1.86 eV and 2.12 eV, respectively. Since electron-hole pairs can be more easily generated on photocatalyst with smaller band gap, and it is BiOI not $\text{Bi}_2\text{O}_3\text{-BiOI}$ behaved the smallest band gap, reason (a) can be ruled out. For reason (b), H_2O_2 was added into Na_2SO_4 electrolyte as a hole scavenger (Fig. 5c and 5d). Negligible difference was observed for the dark currents between $\text{Bi}_2\text{O}_3\text{-BiOI}$ and BiOI, indicating almost equally fast reaction kinetics. Whereas, the dark currents of Bi_2O_3 was much smaller, indicating slow reaction kinetic on the surface of Bi_2O_3 . Under visible light irradiation (Fig. 5d), distinct difference was observed. Thus, the significantly enhanced photocatalytic performance of $\text{Bi}_2\text{O}_3\text{-BiOI}$ relative to BiOI should be due to the interface of the heterojunction, which led to enhanced charge separation. Whereas, comparing to pure Bi_2O_3 , the photocatalytic performance improvement on $\text{Bi}_2\text{O}_3\text{-BiOI}$ may be ascribed to the above mixed effects.

Fig. 6. Normalized plots of photocurrent as a function of time for different as-prepared films. Inset: typical photocurrent transient response curve at 0.35 V (vs. Ag/AgCl).

For further determination of charge separation properties, the charge recombination process in the as-prepared film electrodes was compared by testing the transient photocurrent

according to Eq. (1):

$$D = \frac{I_t - I_{st}}{I_{in} - I_{st}} \quad (1)$$

where D represents transient photocurrent, I_{st} is photocurrent obtained at steady state, I_{in} and I_t photocurrent were measured at irradiation time of 0 and t , respectively [58]. As shown in Fig. 6, the transient photocurrents of Bi_2O_3 , BiOI and $\text{Bi}_2\text{O}_3\text{-BiOI}$ films were compared at 0.35 V (vs. Ag/AgCl) under visible light irradiation. Among the tested samples, $\text{Bi}_2\text{O}_3\text{-BiOI}$ exhibited the largest t value at the same $\ln D$ value. For example, at $\ln D = -1$, the t value was estimated to be ca. 5.4 s for $\text{Bi}_2\text{O}_3\text{-BiOI}$. Whereas, for Bi_2O_3 and BiOI , it was 1.5 s and 2.4 s, respectively. Thus, the slowest recombination rate can be speculated in $\text{Bi}_2\text{O}_3\text{-BiOI}$ composite.

In addition to charge separation, the charge transfer properties were also important for PEC performance. Thus, EIS Nyquist plots were further performed to investigate the charge transfer process. As shown in Fig. 7, among the three tested films, the smallest radius of arc was observed on 3D $\text{Bi}_2\text{O}_3\text{-BiOI}$ under both dark and visible light conditions, indicating the smallest charge transfer resistance [59]. Thus, comparing to individual Bi_2O_3 or BiOI , the fabrication of 3D $\text{Bi}_2\text{O}_3\text{-BiOI}$ heterojunction contributes to the enhancement of generation, separation and transfer of electron-hole pairs.

Fig. 7. EIS Nyquist plots of $\text{Bi}_2\text{O}_3\text{-BiOI}$, Bi_2O_3 and BiOI films in 0.2 M Na_2SO_4 (pH 6.2) aqueous solution under (a) dark and (b) bright (visible light $\lambda > 420$ nm) conditions with a frequency range of 10^6 Hz to 0.01 Hz. Scan rate: 5 mV s^{-1} . Light intensity: 100 mW cm^{-2} .

To further demonstrate the high PEC activity of Bi₂O₃-BiOI heterojunction, IPCE was conducted in 0.1 M Na₂SO₄ with 0.1 M Na₂SO₃ aqueous solution at an applied potential of 0.35 V vs. Ag/AgCl (Fig. 8). The following equation is used to calculate the value of IPCE:

$$\text{IPCE (\%)} = 1240 \times \frac{i_{\text{ph}}}{\lambda \times P_{\text{in}}} \times 100\% \quad (2)$$

Where i_{ph} and P_{in} represent photocurrent (mA) and incident light power intensity (mW) at certain wavelength (λ , nm) on the semiconductor electrode, respectively. Bi₂O₃-BiOI, BiOI and Bi₂O₃ films exhibit similar photocurrent response tendency throughout the whole tested wavelength range: as the wavelength increases, the IPCE values decrease. Besides, it is obvious that the photocurrent response of Bi₂O₃-BiOI film is much stronger than that of Bi₂O₃ film.

Fig. 8. IPCE plots of Bi₂O₃, BiOI and Bi₂O₃-BiOI films calculated from the photocurrent in 0.1 M Na₂SO₄ with 0.1 M Na₂SO₃ aqueous solution (pH 9.3). Applied potential: 0.35 V vs. Ag/AgCl. Light intensity: 100 mW cm⁻².

3.3. PEC degradation of phenol

Fig. 9. (a) PEC degradation efficiency and (b) fitted rate constant of phenol on different film electrodes under visible light irradiation; Comparison of (c) phenol degradation efficiency and (d) fitted rate constants using Bi₂O₃-BiOI electrode under different processes. Reaction condition: 2.5 V, 0.2 M Na₂SO₄, pH unadjusted (6.2), 10 mg/L phenol.

To further investigate the PEC performance of the as-prepared films, PEC degradation of phenol was performed. As shown in Fig. 9a, among the tested films, 3D Bi₂O₃-BiOI film exhibited the highest PEC activity for phenol degradation. After pseudo-first-order kinetic fitting (Fig. 9b), the estimated rate constant (k) on the optimal film was 0.577 h^{-1} , which was 3.8 and 1.6 times that on Bi₂O₃ and BiOI, respectively. Furthermore, the performance of 3D Bi₂O₃-BiOI film was compared in PEC, PC, electrocatalytic (EC) processes and phenol photolysis (in the absence of any catalysts under visible light irradiation), respectively. As shown in Fig. 9c-d, significantly enhanced degradation dynamic and distinct synergistic effect can be observed in the PEC process. The evaporation and photolysis of phenol in the

reaction system is negligible. The main intermediates of phenol degradation were benzoquinone and hydroquinone according to the HPLC analysis (Fig. S2) and relevant works [16,50]. Moreover, a synergistic factor (SF) of 2.9 can be obtained according to the following equation [60, 61]:

$$SF = \frac{k_{PEC}}{k_{PC} + k_{EC}} \quad (3)$$

Where k_{PC} , k_{EC} and k_{PEC} were estimated rate constants for the PC, EC and PEC degradation of phenol, respectively. Since applied potential can significantly enhance the photocatalytic performance of 3D Bi₂O₃-BiOI film, different potentials were further applied in the PEC degradation of phenol.

Fig. 10. Effect of applied potential on rate constants (left) and E value (right) for the PEC degradation of phenol under visible light irradiation. Reaction condition: 0.2 M Na₂SO₄, 10 mg/L phenol.

As shown in Fig. 10 (left), the degradation rate of phenol increased from 1.0 V to 2.5 V, and then decreased slightly at 3.0 V. The highest rate constant was observed at 2.5 V. To further clarify the effect of applied potential, electrochemical enhancement (E , in %) was evaluated by equation (4). As shown in Fig. 10 (right), the E value was calculated to be 91.9% at 2.5 V.

$$E = \frac{k_{PEC} - k_{PC}}{k_{PEC}} \times 100\% \quad (4)$$

3.4. Stability of the 3D Bi₂O₃-BiOI film

In addition to enhanced PEC activity, stability of the optimal 3D Bi₂O₃-BiOI film was another factor associated with future practical applications. Thus, long-time photocurrent decay curves were carried out using Bi₂O₃ as comparison in 0.1 M Na₂SO₄ with 0.1 M Na₂SO₃ aqueous solution at 0.35 V vs. Ag/AgCl. As shown in Fig. 11a, the photocurrent response of Bi₂O₃-BiOI heterojunction was very stable with negligible attenuation after 21600 s (6 h) irradiation. Whereas, the photocurrent dropped distinctly on Bi₂O₃ film. Furthermore, the stability of the 3D Bi₂O₃-BiOI film was also evaluated in the cyclic PEC degradation of phenol. Herein, four cyclic runs were conducted. After each cycle, the film was simply taken out and rinsed with double distilled water and dried for the next cycle. As presented in Fig. 11b, negligible loss of activity was observed after 4 successive cyclic runs. Therefore, due to high PEC activity and stability, the present 3D Bi₂O₃-BiOI film demonstrated superior potential as photoanode for PEC applications, such as water oxidation and pollutant degradation.

Fig. 11. (a) Photocurrent decay curves of 3D Bi₂O₃-BiOI and Bi₂O₃ films in 0.1 M Na₂SO₄ with 0.1 M Na₂SO₃ aqueous solution (pH 9.3) at 0.35 V vs. Ag/AgCl; (b) Cyclic degradation of phenol using 3D Bi₂O₃-BiOI film under visible light irradiation at 2.5 V applied potential. Reaction condition: 0.2 M Na₂SO₄, pH unadjusted (6.2), 10 mg/L phenol.

3.5 Possible mechanism

Fig. 12. (a) Proposed mechanism of charge transfer and electron transport in 3D Bi₂O₃-BiOI under visible light; (b) Effect of different trapping agents on degradation efficiencies of phenol.

In the present study, it has been verified that the generation, separation and transfer of photogenerated charges were greatly accelerated in 3D Bi₂O₃-BiOI heterojunction, which subsequently led to enhanced PEC activity for phenol degradation. A tentative mechanism concerning charge transfer and electron transport in 3D Bi₂O₃-BiOI was displayed in Fig. 12a. The conduction band (CB) and valence band (VB) edges of Bi₂O₃ were reported to be +0.13 and +2.84 V (vs NHE), and those of BiOI were +0.56 and +2.42 V (vs NHE) [62], respectively. Thus, the photogenerated VB holes can be easily transferred from Bi₂O₃ to BiOI. Meanwhile, though the CB of pure BiOI was more positive than Bi₂O₃, when Bi₂O₃-BiOI heterojunction was formed, electrons in the CB of BiOI could be excited by the photon energy up to a higher potential edge (-0.68 eV) under visible light irradiation [62]. Thus, the photogenerated electrons can be transferred from BiOI to Bi₂O₃. Then, the photogenerated electrons can be continuously transferred to FTO substrate and driven to the cathode by an external applied potential. In this way, more efficient separation and reduced recombination of photogenerated electron-hole pairs can be achieved on the Bi₂O₃-BiOI interface. Therefore, Bi₂O₃-BiOI composite could exhibit better PEC activity than pure BiOI or Bi₂O₃ film. Moreover, to investigate the formation of possible active species (HO•, O₂^{•-} and h⁺) in the degradation process [63, 64], trapping experiments using different scavengers were also investigated. As shown in Fig. 12b, the scavenger of h⁺ (oxalic acid) can greatly inhibit the degradation of phenol, while the scavenger of O₂^{•-} (benzoquinone) has negligible effect. Besides, slight effect was also observed using HO• scavenger. Thus, the photogenerated

holes were considered as main active species, which is consistent with the description in Fig. 12a.

4. Conclusions

In this study, 3D Bi₂O₃-BiOI heterojunction photocatalyst was synthesized by a simple dipping method. The BiOI films could successfully grow on the basis of Bi₂O₃ at room temperature and showed the morphology of cross-flake arrays. Due to the formation of special 3D heterojunction between Bi₂O₃ and BiOI, the photogenerated charges can be more easily generated, separated and transferred. For the PEC performance in water oxidation, the photocurrent response of Bi₂O₃-BiOI was 8.4 times that of Bi₂O₃ at 0.35 V (vs. Ag/AgCl) in 0.2 M Na₂SO₄ aqueous solution under visible light irradiation. Besides, greatly enhanced activity of Bi₂O₃-BiOI was also observed for the PEC degradation of phenol. The estimated rate constant (*k*) on Bi₂O₃-BiOI (0.577 h⁻¹) was 3.8 times that on Bi₂O₃ (0.152 h⁻¹). Moreover, good stability was also observed in long-time photocurrent curve and cyclic runs. Therefore, this study provides a low-cost and efficient way for water oxidation and environmental remediation.

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