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Fabrication of a β - Bi_2O_3 /BiOI heterojunction and its efficient photocatalysis for organic dye removal

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ABSTRACT

To improve β - Bi_2O_3 photocatalysis, we couple β - Bi_2O_3 with BiOI to form β - Bi_2O_3 /BiOI heterojunctions through an in-situ treatment with hydriodic acid. The prepared heterojunctions are characterized with X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, ultra violet-diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy. Upon visible-light irradiation ($\lambda > 420$ nm), the β - Bi_2O_3 /BiOI heterojunctions, especially with the molar ratio of HI to β - Bi_2O_3 at 0.4, exhibit much higher photocatalytic activity than pure β - Bi_2O_3 and BiOI for the degradation of methyl orange. The efficient separation of photogenerated electron-hole pairs across the interface of the heterojunction between β - Bi_2O_3 and BiOI would be responsible for the enhanced photocatalytic performances.

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1. Introduction

Environmental pollution and the energy shortage have become two of the biggest challenges currently facing humans. Semiconductor photocatalysis with a primary focus on TiO_2 is one of the most promising technologies for environmental remediation and energy conversion [1–4]. However, owing to its large band gap of 3.2 eV, TiO_2 can drive a catalytic reaction only under ultraviolet or near ultraviolet irradiation, which occupies less than 4% of the solar light spectrum on the earth. To make full use of solar light, therefore, the development of narrow band gap semiconductors as efficient visible-light photocatalytic materials has been of particular interest in recent years [5–10]. Bismuth trioxide (Bi_2O_3), which exhibits a narrow band gap that varies between 2.1–2.8 eV, is a promising candidate as a visible-light photocatalyst owing to its unique characteristics, such as strong absorption in visible region and non-toxic prop-

erty similar to TiO_2 . It is well-known that Bi_2O_3 has six polymorphic forms, including the α (monoclinic), β (tetragonal), γ (body-centered cubic), δ (face-centered cubic), ε (tetragonal), and ω (triclinic) phases, each with unique physical properties [11]. Among them, α - Bi_2O_3 , β - Bi_2O_3 and δ - Bi_2O_3 , with photocatalytic activities towards the degradation of organic pollutants, have been reported. β - Bi_2O_3 , with a relatively narrow band gap (less than ~ 2.50 eV), has been shown to be the most active form for photocatalytic application [12–14]. Nonetheless, their efficiencies are still insufficient for practical application.

The construction of a semiconductor heterojunction by coupling with a secondary substance (noble metal, other semiconductors, and so on) has been proven to be an effective and simple strategy to improve the photocatalytic activity of photocatalysts [15,16]. In the semiconductor heterojunction, several advantages can be achieved: (1) an improvement of the charge

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separation; (2) a long lifetime of the charge carriers; and (3) an enhancement of the charge transfer to the catalyst surface. All these features endow the semiconductor heterojunction with an enhanced photocatalytic performance. To date, many Bi₂O₃-based heterojunction photocatalysts have been successfully developed for the efficient degradation of organic pollutants [17–19]. In particular, the heterojunctions between α -Bi₂O₃ and bismuth oxyhalides (BiOX, X = Cl, Br, or I), formed through an in-situ treatment of α -Bi₂O₃ with HX, such as α -Bi₂O₃/BiOI and α -Bi₂O₃/BiOCl, exhibit unique advantages not only in photocatalytic performance but also in the fabrication method [20–22]. However, to the best of our knowledge, the heterojunctions between β -Bi₂O₃ and BiOX (X = Cl, Br, or I) are not yet to be reported. Among the BiOX family, bismuth oxyiodide (BiOI) possesses the smallest band gap (less than 1.8 eV) and strong absorption in the visible region [23]. With the aims of the full use of solar light, improvement in β -Bi₂O₃ photocatalysis for a practical application, and convenient fabrication features, in this work, we coupled β -Bi₂O₃ with BiOI to form β -Bi₂O₃/BiOI heterojunctions through an in-situ treatment with HI. The prepared β -Bi₂O₃-based heterojunctions have been shown to exhibit much higher photocatalytic activities than pure β -Bi₂O₃ and BiOI for the degradation of methyl orange (MO) upon visible-light irradiation. Furthermore, the mechanism of the enhanced photocatalytic performance over the heterojunctions was also investigated and discussed according to various characterization results.

2. Experimental

2.1. Sample preparation

β -Bi₂O₃ was synthesized by using Bi₂O₂CO₃ as a precursor, as reported in previous work [24]. Initially, 11.64 g of Bi(NO₃)₃·5H₂O was dissolved in 60 ml aqueous solution of HNO₃ (1 mol/L). Under constant stirring, 240 ml aqueous solution of Na₂CO₃ (0.6 mol/L) was slowly added into the solution to produce a large amount of white precipitate. The suspension was further stirred for 15 min and aged at 60 °C for 12 h. Finally, the precipitate was collected and washed several times with deionized water before being dried at 60 °C for 6 h to form the Bi₂O₂CO₃ precursor. β -Bi₂O₃ was obtained by annealing the prepared Bi₂O₂CO₃ at 350 °C for 30 min. The β -Bi₂O₃/BiOI heterojunctions were prepared by an in-situ treatment of β -Bi₂O₃ with HI. In detail, 0.7 g of the freshly prepared β -Bi₂O₃ was dispersed into 20 ml of an ethanol and water mixture with the desired amount of HI, which was prepared by changing the amount of the aqueous solution of HI (45%). To obtain the β -Bi₂O₃ based heterojunctions with different amount of BiOI, the molar ratios of HI to β -Bi₂O₃ (R_{HI}) in the dispersions were controlled at 0.2, 0.4, and 0.8, respectively. The dispersion was stirred and sonicated for 30 min at room temperature. After the treatment with HI, the precipitate was recovered by centrifugation, washed several times with ethanol, and finally dried at 80 °C in air for 10 h. By following this procedure, the pure BiOI was synthesized in the presence of HI in excess. For comparison, the pure β -Bi₂O₃ was also treated in the same manner in

the absence of HI.

2.2. Characterization

The polycrystalline X-ray diffraction (XRD) patterns of the prepared samples were recorded with an X-ray diffractometer (Shimadzu, XRD-7000) using Cu K_{α} ($\lambda = 1.5406 \text{ \AA}$) as X-ray radiation with an applied potential of 40 kV and electron beam current of 30 mA. Ultra violet-visible diffuse reflectance spectroscopy measurements were carried out on a UV-Vis spectrometer (Hitachi U-4100) equipped with a diffuse reflectance accessory. Field-emission scanning electron microscopy (FESEM) observations were performed with a JEOL 6701F microscope. High-resolution transmission images (HRTEM) were taken using a JEOL JEM-2010 electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a XPS system (ESCALAB 250Xi) with a 300 W Al K_{α} source. All binding energies were referenced to the C 1s peak (284.6 eV) of surface adventitious carbon. Photoluminescence (PL) spectra were obtained on a Hitachi F-4600 spectrophotometer with an excitation wavelength at 380 nm.

2.3. Evaluation of photocatalytic activity

MO was chosen as a model pollutant to evaluate the photocatalytic activities of the prepared pure Bi₂O₃, BiOI, and β -Bi₂O₃/BiOI heterojunctions under visible-light irradiation ($\lambda > 420 \text{ nm}$). In a typical photocatalytic experiment, 0.1 g of the catalyst was dispersed in 100 ml aqueous solution of MO ($4 \times 10^{-5} \text{ mol/L}$). The light source was a 300 W Xe-arc lamp (CHF-XM150, Beijing Trusttech. Co. Ltd.) equipped with a glass filter ($\lambda > 420 \text{ nm}$) to remove the UV wavelength light, and positioned about 8 cm above the aqueous suspension. Prior to irradiation, the suspension was magnetically stirred in the dark for 1 h to reach an adsorption-desorption equilibrium between the catalyst surface and MO molecules. At the given irradiation time intervals, 3 ml of the suspension was sampled and separated by centrifugation before analysis using a Hitachi U-3310 spectrophotometer. The intensity change in the characteristic absorption peak of MO at 461 nm was measured to evaluate the extent of MO degradation.

To investigate the photocatalytic degradation route of MO over these catalysts, triethanolamine (TEOA, 10 mmol/L), as an effective hole scavenger, and tert-butyl alcohol (TBA, 10 mmol/L), as $\bullet\text{OH}$ radical scavenger, were chosen to participate in the photocatalytic degradation of MO over these catalysts. Determination of MO concentration during the photocatalytic reaction in the presence of TEOA or TBA was also conducted by measuring the absorption of MO solution at 461 nm.

3. Results and discussion

3.1. Phase structure and morphology

Polycrystalline XRD was used to identify the phase structures and constitutions of the prepared samples. The XRD patterns of the prepared samples are illustrated in Fig. 1. It can be

Fig. 1. XRD patterns of β - Bi_2O_3 , BiOI, and β - Bi_2O_3 /BiOI heterojunctions with different R_{HI} values.

clearly observed that the prepared β - Bi_2O_3 exhibits a single tetragonal phase of well-crystalline β - Bi_2O_3 (JCPDS 27-0050). After the treatment with excess HI, the crystalline β - Bi_2O_3 was entirely transformed to the pure tetragonal BiOI phase (JCPDS 73-2062). In addition, with the increase in R_{HI} values in the β - Bi_2O_3 /BiOI heterojunctions, the intensity of the characteristic peaks for tetragonal BiOI are gradually increased, while those for tetragonal β - Bi_2O_3 are decreased simultaneously. These results reveal that the prepared β - Bi_2O_3 /BiOI heterojunctions

are composed of β - Bi_2O_3 and BiOI phases, and that β - Bi_2O_3 is the major phase.

The detailed morphology and microstructure of the prepared samples were inspected by FESEM and HRTEM. Fig. 2 presents the FESEM images of the β - Bi_2O_3 , BiOI, and β - Bi_2O_3 /BiOI heterojunctions ($R_{\text{HI}} = 0.4$). It is evident that the prepared pure β - Bi_2O_3 consists of aggregated short nanorods with lengths ranging from 200 to 300 nm and diameters of approximately 100 nm (Fig. 2(a)). The morphology of pure BiOI (Fig. 2(b)) appears to be irregular sheets with a thickness of less than 10 nm, which is similar to that reported in previous reports [25,26]. As for the β - Bi_2O_3 /BiOI heterojunction ($R_{\text{HI}} = 0.4$) sample (Fig. 2(c)), it can be found that the short nanorods became small, accompanying the formation of nanosheets after the treatment of β - Bi_2O_3 with HI. Fig. 3 displays the typical HRTEM images of pure β - Bi_2O_3 , BiOI, and β - Bi_2O_3 /BiOI heterojunction ($R_{\text{HI}} = 0.4$). All prepared samples were highly crystallized. The clear and uniform fringes with the measured lattice spacing of 0.34 nm (Fig. 3(a)) and 0.29 nm (Fig. 3(b)) matched well with the crystallographic planes of tetragonal β - Bi_2O_3 phase (210) and tetragonal BiOI phase (122), respectively [27,28]. Both of the fringes with the lattice spacing of 0.34 and 0.29 nm can also be clearly observed in Fig. 3(c), confirming the co-existence of the β - Bi_2O_3 and BiOI phases in the β - Bi_2O_3 /BiOI heterojunctions. The HRTEM observations are in good agreement with the XRD results. Moreover, it can also be seen in Fig. 3(c) that there is a well-contacted interface between the β - Bi_2O_3 and BiOI phases. The well-contacted interface is expected to be favorable for charge transfer between the two phases [15].

Fig. 2. FESEM images of β - Bi_2O_3 (a), BiOI (b), and β - Bi_2O_3 /BiOI heterojunctions ($R_{\text{HI}} = 0.4$) (c).

Fig. 3. HRTEM images of β - Bi_2O_3 (a), BiOI (b), and β - Bi_2O_3 /BiOI heterojunctions ($R_{\text{HI}} = 0.4$) (c).

Fig. 4. UV-diffuse reflectance spectra of β - Bi_2O_3 , BiOI, and β - $\text{Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions with different R_{HI} values.

3.2. Optical property and XPS analysis

The optical properties of the prepared samples were studied by UV-Vis diffuse reflectance spectroscopy, as illustrated in Fig. 4. All samples exhibited strong absorption in the visible light region. The pure β - Bi_2O_3 has an intense absorption starting at the wavelength near 535 nm, whereas the BiOI presents an absorption extending up to approximately 675 nm. Additionally, the absorption band edges of the β - $\text{Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions are between those of β - Bi_2O_3 and BiOI, and gradually shift to that of pure BiOI with the increase in the amount of BiOI (R_{HI}).

According to the absorption spectra, the band gap energy (E_g) of a semiconductor can be evaluated from the following formula [29]:

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

where α , $h\nu$, E_g , and A are the optical absorption coefficient, photo energy, band gap energy, and a constant, respectively. The value of n depends on the characteristic of the transition in a semiconductor (i.e., $n = 1$ for direct transition and $n = 4$ for

Fig. 5. (a) Plots of $(\alpha h\nu)^2$ versus $h\nu$ for β - Bi_2O_3 . (b) Plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for BiOI.

indirect transition). Here, n is 1 for β - Bi_2O_3 and is 4 for BiOI. In the plots of $(\alpha h\nu)^2$ versus $h\nu$ for β - Bi_2O_3 and $(\alpha h\nu)^{1/2}$ versus $h\nu$ for BiOI, as shown in Fig. 5, the band gap energies of β - Bi_2O_3 and BiOI are estimated from the tangent lines to be 2.28 and 1.77 eV, respectively. The band gap values for β - Bi_2O_3 and BiOI determined here are very similar to the values reported previously in the literature [25,30,31].

XPS was used to examine the surface chemical states and compositions of the elements in the samples. The XPS survey spectra, shown in Fig. 6(a), reveal no peaks of elements other than Bi, O, and C in the β - Bi_2O_3 , and Bi, O, I, and C in both BiOI and β - $\text{Bi}_2\text{O}_3/\text{BiOI}$ heterojunction ($R_{\text{HI}} = 0.4$) samples, evidencing the purity of our prepared samples. Fig. 6(b) displays the high resolution XPS spectra of Bi 4f regions of the pure β - Bi_2O_3 and BiOI samples. As observed in Fig. 6(b), the Bi 4f spectra of both samples consist of two individual symmetric peaks. In the Bi 4f core-level spectrum of the β - Bi_2O_3 , two peaks appearing at the binding energies of 158.53 and 163.83 eV, with a separation of 5.3 eV, are assigned to $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$, respectively, which is a characteristic of Bi^{3+} in β - Bi_2O_3 according to a previous report [11]. The positions and separation of two peaks in the Bi 4f core-level spectrum of the pure BiOI also support the presence of Bi^{3+} in the tetragonal BiOI phase [32].

Fig. 6. (a) XPS survey spectra of β - Bi_2O_3 , BiOI, and β - $\text{Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions ($R_{\text{HI}} = 0.4$). (b) High-resolution Bi 4f XPS spectra of β - Bi_2O_3 and BiOI. (c) High-resolution I 5d XPS spectra of BiOI and β - $\text{Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions ($R_{\text{HI}} = 0.4$).

Figure 6(c) presents the high resolution XPS spectra of I 5d regions of the pure BiOI and β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$). There are two individual symmetric peaks in the I 5d region. The two symmetric peaks of I 5d located at the binding energies of 619.08 and 630.58 eV in the I 5d core-level spectrum of the pure BiOI with a peak difference of 11.5 eV are ascribed to I 3d_{5/2} and I 3d_{3/2} of the I⁻ species in BiOI, respectively [25,33]. Notably, the binding energies of I 3d_{5/2} and I 3d_{3/2} obviously shift to lower values after the formation of β -Bi₂O₃/BiOI heterojunctions, whereas the peak separation value is still the same as that of the corresponding pure BiOI. This result suggests an interaction between β -Bi₂O₃ and BiOI in the heterojunctions. Earlier investigations indicated that when two semiconductors were in contact, electron migration between them occurs until a Fermi level equilibration of the composite is established [34]. In the present case, the observed shift of the binding energies of I 5d in BiOI to lower values suggests that the Fermi level of β -Bi₂O₃ is more negative than that of BiOI, so electron transfer from β -Bi₂O₃ to BiOI occurs when β -Bi₂O₃ and BiOI are in contact to form heterojunctions. The observed shift in binding energy also reflects the presence of a well-contacted interface between BiOI and β -Bi₂O₃ in the β -Bi₂O₃/BiOI heterojunctions, further confirming the above HRTEM observations.

3.3. Photocatalytic performance and mechanism

To investigate the photocatalytic efficiencies of the prepared β -Bi₂O₃/BiOI heterojunctions, the photocatalytic activities for the degradation of MO over pure β -Bi₂O₃, BiOI, and β -Bi₂O₃/BiOI heterojunctions with different R_{HI} values were evaluated under visible-light irradiation ($\lambda > 420$ nm), as shown in Fig. 7. The control experiment shows that the self-degradation of MO is negligible under visible-light irradiation in the presence of no catalysts. It is clear that all β -Bi₂O₃/BiOI heterojunctions with different R_{HI} values exhibit much higher photocatalytic activities than β -Bi₂O₃ or BiOI, demonstrating that the construction of the heterojunctions between β -Bi₂O₃ and BiOI is an efficient approach for enhancing the photocatalysis of β -Bi₂O₃ and BiOI. Moreover, the photocatalytic activity also depends on the amount of BiOI (R_{HI}) in

the β -Bi₂O₃-based heterojunctions. The highest activity is reached over the β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$). Approximately 95% of MO was degraded over the heterojunctions under visible-light irradiation for 2 h. The presence of excess BiOI ($R_{\text{HI}} \geq 0.8$) appears to be detrimental to the photocatalytic performance of the β -Bi₂O₃/BiOI heterojunctions. Clearly, changing the content of BiOI in the heterojunction has a significant influence on the heterojunction interface, β -Bi₂O₃ surface coverage, and surface morphologies of both components. Based on the results shown in Fig. 7, it could be concluded that an optimum combination of these factors has been achieved over the β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$), exhibiting the highest photocatalytic activity.

Figure 8 presents the degradation of MO over pure β -Bi₂O₃ and β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$) in the presence of different scavengers under visible-light irradiation. Almost no degradation of MO in two samples occurs when TEOA, as an effective hole scavenger, is added into the reaction solution, while the addition of TBA as $\bullet\text{OH}$ scavenger slightly influences the degradation of MO. These results reveal that the photogenerated hole is almost the sole active species involved in the degradation of MO over both samples. The hydroxyl radical $\bullet\text{OH}$ is regarded to be a very powerful oxidizing agent which can degrade most organic compounds. Almost no change in the degradation of MO in the presence of TBA infers the production of $\bullet\text{OH}$ is negligible in both systems. The effective production yield of the photogenerated holes in a semiconductor photocatalyst strongly depends on the separation degree of the photogenerated electron-hole pairs. According to the results shown in Fig. 7, therefore, an efficient separation of the photogenerated electron-hole pairs is achieved after β -Bi₂O₃ combines with BiOI to form the heterojunction, which is also supported by the PL spectra of pure β -Bi₂O₃ and β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$), as shown in Fig. 9. It can clearly be seen that a strong emission peak around 530 nm appears for the pure β -Bi₂O₃, which originates from the direct electron-hole recombination. The intensity of the PL emission peak of β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$) is dramatically decreased compared with that of pure β -Bi₂O₃, indicating an increase in the separation of the photogenerated electron-hole pairs after the for-

Fig. 7. Photocatalytic degradation of MO over β -Bi₂O₃, BiOI, and β -Bi₂O₃/BiOI heterojunctions with different R_{HI} values under visible-light irradiation for 2 h.

Fig. 8. Photocatalytic degradation of MO over β -Bi₂O₃ (a) and β -Bi₂O₃/BiOI heterojunctions ($R_{\text{HI}} = 0.4$) (b) in the presence of different scavengers under visible-light irradiation for 2 h.

Fig. 9. PL spectra of pure $\beta\text{-Bi}_2\text{O}_3$ and $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions ($R_{\text{HI}} = 0.4$).

mation of $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions. Moreover, the observed broadening and red-shift of the PL emission peak of $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions ($R_{\text{HI}} = 0.4$) are probably caused by the direct electron-hole recombination of both $\beta\text{-Bi}_2\text{O}_3$ and BiOI band transitions.

To understand the effects of the $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions on the separation of photo-generated electron-hole pairs, the band structures of $\beta\text{-Bi}_2\text{O}_3$ and BiOI before and after the formation of their heterojunctions were studied. The band positions of a semiconductor at the point of zero charge can be calculated through the following equations:

$$E_{\text{VB}} = \chi - E^e + 0.5E_{\text{g}} \quad (2)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (3)$$

where E_{VB} and E_{CB} are the valence band (VB) and conduction band (CB) potentials, respectively, χ is the absolute electronegativity of the semiconductor, and E^e is the energy of the free electron on the hydrogen scale (about 4.5 eV), and E_{g} is the band gap energy. The χ values for $\beta\text{-Bi}_2\text{O}_3$ and BiOI are approximately 5.95 and 5.94 eV, respectively. Given the band gap values from Fig. 5 and the equations above, the E_{VB} and E_{CB} of $\beta\text{-Bi}_2\text{O}_3$ can be calculated to be 2.59 and 0.31 V, respectively. Accordingly, the E_{VB} and E_{CB} of BiOI are 2.33 and 0.56 V, respectively.

According to the obtained band position data above, the $\beta\text{-Bi}_2\text{O}_3$ and BiOI appear to be in the nested architecture in their band structure before their contact to form the heterojunction, which seems to not be favorable for an efficient separation of photogenerated electron-hole pairs. Nevertheless, such nested architecture is completely changed after their contact. As has already been reported [35–37], $\beta\text{-Bi}_2\text{O}_3$ is a n-type semiconductor with the Fermi level close to its conduction band, whereas BiOI is a p-type semiconductor with the Fermi level close to its valence band. When $\beta\text{-Bi}_2\text{O}_3$ and BiOI are in contact to form a heterojunction, the electron migration from $\beta\text{-Bi}_2\text{O}_3$ to BiOI occurs, as evidenced by the XPS results in Fig. 6(c), until the Fermi levels of the two semiconductors reach equilibrium. As a result, the energy bands of $\beta\text{-Bi}_2\text{O}_3$ and BiOI shift downward and upward, respectively, and an electronic field is built at the interface of the heterojunction. Under visible-light irradiation, both $\beta\text{-Bi}_2\text{O}_3$ and BiOI are excited to generate electron-hole pairs. Driven by the electronic field at the interface,

Scheme 1. Schematic diagram of the photogenerated electron-hole pair separation and transfer over $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions under visible-light irradiation.

the electrons are transferred to the reformed CB of $\beta\text{-Bi}_2\text{O}_3$, probably to form H_2O_2 through two-electron reduction process according to the potential of the reformed CB of $\beta\text{-Bi}_2\text{O}_3$ [19], and the holes are transferred to the reformed VB of BiOI to degrade MO in the present case. Hence, the efficient separation of the photogenerated electron-hole pairs is successfully achieved across the interface of the heterojunction between $\beta\text{-Bi}_2\text{O}_3$ and BiOI, resulting in enhanced photocatalysis over the heterojunction. The above understanding of the enhanced photocatalysis over the $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions is schematically illustrated in Scheme 1.

4. Conclusions

We have successfully synthesized $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions through a precipitation method, followed by an in-situ treatment with HI. Compared with pure $\beta\text{-Bi}_2\text{O}_3$ and BiOI, the prepared $\beta\text{-Bi}_2\text{O}_3/\text{BiOI}$ heterojunctions, especially with the molar ratio of HI to $\beta\text{-Bi}_2\text{O}_3$ at 0.4, exhibit much higher photocatalytic activities for the degradation of MO under visible-light irradiation. The enhanced photocatalysis could be attributed to the efficient separation of the photogenerated electron-hole pairs achieved across the interface of the heterojunction between $\beta\text{-Bi}_2\text{O}_3$ and BiOI.

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Graphical Abstract

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The photogenerated electron-hole pairs are efficiently separated across the interface of the heterojunctions between β - Bi_2O_3 and BiOI, giving rise to the photocatalytic degradation of MO over the heterojunction.

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 β - Bi_2O_3 /BiOI异质结的制备及其有效去除有机染料的光催化作用

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摘要: 窄带半导体氧化铋(Bi_2O_3 , 带宽介于2.1–2.8 eV)因其强的可见光吸收和无毒性等特性而一直被认为是潜在的可见光催化材料。通常, Bi_2O_3 具有 α , β , γ , δ , ϵ 和 ω 等六种晶型, 其中, α , β 和 δ - Bi_2O_3 具有催化可见光降解有机物的活性。可是, 由于其光生电子-空穴复合较快, Bi_2O_3 的光催化活性还很低, 远不够实际应用。将半导体与另一种物质如贵金属或其他半导体复合形成异质结是一种有效控制光生电子-空穴复合, 提高光催化活性的方法。目前已成功开发了许多 Bi_2O_3 基的异质结光催化材料。尤其是通过用卤化氢酸与 α - Bi_2O_3 直接作用原位形成的 α - Bi_2O_3 与铋的卤氧化物 BiOX ($X = \text{Cl}, \text{Br}$ 或 I)的异质结在提高光催化活性和制备方面显示了优越性。然而, 具有更强可见光吸收的 β - Bi_2O_3 (带宽约2.3 eV)与卤氧化合物的异质结光催化性能却鲜有报道。本文通过用HI原位处理 β - Bi_2O_3 形成 β - Bi_2O_3 /BiOI异质结。该异质结表现较纯 β - Bi_2O_3 和BiOI更高的降解甲基橙(MO)可见光催化活性。通过多晶X射线衍射(XRD)、紫外漫散射(UV-DRS)、扫描电镜、透射电镜(TEM)、X光电子能谱(XPS)和荧光(PL)等手段研究了 β - Bi_2O_3 /BiOI异质结, 并提出其高催化活性的机理。

XRD结果显示, 用HI原位处理 β - Bi_2O_3 可形成BiOI相, 并且随着HI使用量增加, 混合物中的BiOI相逐渐增多。HRTEM结果进一步表明, 在混合物中的 β - Bi_2O_3 和BiOI都是高度结晶态, 且两相之间有很好的接触, 从而有利于两相之间的电荷移动。根据UV-DRS和 $\alpha h\nu = A(h\nu - E_g)^{n/2}$ 等公式, 计算出了 β - Bi_2O_3 和BiOI带隙分别为2.28和1.77 eV, 以及两种半导体的导带和价带位置。

$\beta\text{-Bi}_2\text{O}_3$ 的导带和价带位置分别为0.31和2.59 eV, 而BiOI的导带和价带位置分别为0.56和2.33 eV. 这样两种半导体能带结构呈蜂窝状, 显然不适合光生电子-空穴的分离. 然而, XPS测定结果显示, $\beta\text{-Bi}_2\text{O}_3$ 和BiOI相互接触形成异质结后, $\beta\text{-Bi}_2\text{O}_3$ 相的电子向BiOI相发生了明显的移动. 根据文献报道, 当两种费米能级不同的半导体接触时, 电子会从费米能级高的半导体移向费米能级低的半导体, 直至建立新的费米能级. $\beta\text{-Bi}_2\text{O}_3$ 被报道是典型的n型半导体, 其费米能级在上靠近其导带位置; 而BiOI是典型的p型半导体, 其费米能级在下靠近其价带位置. 基于此, 我们提出了 $\beta\text{-Bi}_2\text{O}_3$ /BiOI异质结高催化活性的机理. 当 $\beta\text{-Bi}_2\text{O}_3$ 与BiOI形成异质结时, 由于 $\beta\text{-Bi}_2\text{O}_3$ 的费米能级较BiOI的高, 因而电子从 $\beta\text{-Bi}_2\text{O}_3$ 转向BiOI, 直至新的费米能级形成. 因此电子在两相之间移动导致了 $\beta\text{-Bi}_2\text{O}_3$ 能带结构整体下移, 以及BiOI能带结构整体上移, 使得新形成的BiOI导带和价带位置高于 $\beta\text{-Bi}_2\text{O}_3$ 的. 当该异质结在可见光的照射下, 光生电子将移至 $\beta\text{-Bi}_2\text{O}_3$ 的导带, 而空穴会移至BiOI的价带, 最终达到了光生电子-空穴分离的效果, 产生高的光催化活性. PL测试也证实了 $\beta\text{-Bi}_2\text{O}_3$ /BiOI异质结具有更长的光生电子-空穴寿命.

关键词: 光催化; 异质结; 氧化铋; 铋的卤氧化合物; 甲基橙

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