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Synthesis of one-dimensional Bi_2O_3 - Bi_5O_7I heterojunctions with high interface quality⁺

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One-dimensional Bi_2O_3 - Bi_5O_7I heterostructures with enhanced visible light photocatalytic performance were synthesized by high temperature calcination of BiOl-Bi(OHC₂O₄)·2H₂O precursors. The Bi₅O₇I nanosheets uniformly grew on the Bi₂O₃ porous rods. The photocatalytic performance of the obtained products was evaluated by degradation of methyl orange (MO) and phenol under visible light irradiation. The results show that the Bi₂O₃-Bi₅O₇I heterostructure displays higher photocatalytic activity than pure phase Bi₂O₃ and Bi₅O₇I, and MO and phenol with high concentration can be completely degraded in 60 min under visible light irradiation using the Bi₂O₃-Bi₅O₇I (DS-2) heterostructure as a photocatalyst. This enhanced photocatalytic performance is ascribed to the synergistic effect of the suitable band alignment of Bi₂O₃ and Bi₅O₇I, high interface quality and one-dimensionally ordered nanostructure. Radical scavenger experiments indicate that holes (h⁺) and superoxide radicals ('O₂⁻) were the main active species for MO and phenol degradation during the photocatalytic process. This work will offer a simple route to design and synthesize junction structures with high interface quality for photocatalytic applications.

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Introduction

Environmental pollution and energy shortage are the two key problems to be solved due to rising global population and fast-growing industry. Thus, it is urgent to develop renewable and environmentally friendly technologies for environmental remediation and green energy production. Compared with other proposed technologies, photocatalytic technology is considered as the most promising technology for environmental remediation due to its highly efficient, eco-friendly and lowcost approach.¹

A variety of strategies have been developed in the past decade in order to improve efficiencies of photocatalysts, such as doping, co-deposition of noble metals, formation of semiconductor heterojunctions and crystal facet engineering. Among the proposed strategies, the formation of semiconductor heterojunctions has been proved to be one of the most promising ways because of its feasibility and effectiveness for the spatial separation of electron-hole pairs.^{2–4} However, practical applications of semiconductor heterojunctions are still limited by their low photocatalytic activity and instability due to low interfacial quality. The interfacial charge transfer between semiconductor interfaces is performed in picoseconds, so the fast transfer rate requires the interface to provide the smallest energy barrier (large coupling area).^{5,6} Therefore, the interfacial quality plays a key role in improving photocatalytic activity.

Over the past decade, fabrication of a high interface quality in heterostructured catalysts has attracted increasing attention.7-15 For example, Rohrer et al. studied and compared the photocatalytic activity of AFeO3/TiO2 and ATiO3/ TiO₂ heterojunctions. It was found that ATiO₃/TiO₂ had a higher reactivity than AFeO3/TiO2 under the same conditions.¹⁵ The reason was that chemically strong Ti-O-Ti bonds could be formed between ATiO₃ and TiO₂ at the interface instead of AFeO₃ and TiO₂. Peng et al. synthesized Bi₂O₃-Bi₂O_{2.33} heterostructures through high temperature calcinations.10 The obtained Bi₂O₃-Bi₂O_{2.33} heterostructures exhibited outstanding photocatalytic performance to degrade phenol and MO dyes with high concentration in a short time under solar/visible light irradiation. The enhanced photocatalytic activity was ascribed to the small interfacial lattice mismatch between Bi2O3 and Bi2O2.33 which enhanced the interface quality. So, according to the reported results, it is believed that the similar composition (or structure) on both sides of the interface is beneficial to form heterostructures with high interfacial quality. Namely: low interfacial defects, chemically-strong bonds and large contact areas in the interface.

To date, most heterojunctions are obtained by a solutionphase method in which components of the heterojunction are prepared separately and then integrated with the other.

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This kind of operation was feasible and straight-forward, but may lead to the limited contact interface area between individual components and thus decreased the interface quality of semiconductor heterostructures.¹⁶ Recently, our group has proved that the high temperature calcining precursor method could effectively improve the interface quality.^{10,11,17-19} During the calcination process, precursors decompose to respective calcined-products. Simultaneously, these respective calcined-products and precursors involve a chemical reaction with each other, and then form new heterostructures via epitaxial growth at the interface. So, the high temperature calcining precursor method utilizes structural rearrangement at the atomic level, which is helpful to obtain chemicallystrong bonds across interfaces with large contact areas. Moreover, high temperature is beneficial to decrease the interface defect density of semiconductor heterostructures, and then improve the interface quality.

Bi₅O₇I is a newly found visible-light-driven photocatalyst, and its dispersed hybridized valence bands with a moderate band gap (~2.87 eV) endow Bi_5O_7I with efficient photocatalytic activity in the decomposition of pollutants under visible light.²⁰⁻²⁹ However, Some drawbacks in Bi₅O₇I still exist, such as deficient light absorption, low transfer efficiency of photogenerated charge carriers, and so forth. Therefore, construction of heterojunction structures by combining Bi₅O₇I with other appropriate semiconductors may be a constructive and instructive method to further improve the photocatalytic activity of Bi₅O₇I. Recently, some Bi₅O₇I-based heterostructures, such as Bi₅O₇I/BiOBr_xI_{1-x},³⁰ Ag₂O/Bi₅O₇I p-n junction,³¹ coreshell-like BiOCl_{0.5}I_{0.5}/Bi₅O₇I,³² Sr₂TiO₄-Bi₅O₇I,³³ AgI/Bi₅O₇-I,^{34,35} Ag/AgBr/Bi₅O₇I,³⁶ Bi₄O₅I₂/Bi₅O₇I,^{37,38} BiOI/Bi₅O₇I,³⁹ g-C₃N₄/Bi₅O₇I,⁴⁰ and Bi₅O₇I/Bi₂O₃,^{41,42} have been synthesized. However, most of the obtained Bi₅O₇I-based heterostructures still have low photocatalytic activity due to their low interface quality.

In this work, we synthesized one-dimensional Bi2O3-Bi₅O₇I heterostructures with high interface quality by high temperature calcination of BiOI-Bi(OHC₂O₄)·2H₂O precursors. Methylene orange (MO) and phenol with high concentration were used as model compounds to investigate the photocatalytic activities of the Bi₂O₃-Bi₅O₇I₁ heterostructure under visible light irradiation. The results demonstrated that the Bi₂O₃-Bi₅O₇I heterostructures exhibited more excellent photocatalytic activity than the recently reported Bi5O7I-based heterostructures for degrading high concentration MO dyes and phenol.^{28,30,33,38-40,43} The enhanced photocatalytic performance was attributed to the synergistic effect of the following three factors: (1) the formation of p-n junctions between Bi₂O₃ and Bi₅O₇I effectively drives the photogenerated electrons and holes to reach the most stable energy configuration and then leads to a spatial charge separation; (2) the high interface quality provides a small penetration barrier for the photogenerated carrier transfer across the interface of the Bi₂O₃-Bi₅O₇I heterojunction; and (3) a onedimensional ordered nanostructure is desirable for facilitating highly efficient and directional transport and separation

of electrons and holes. This work provided a simple route to design and synthesize Bi-based heterostructures with high interface quality for photocatalytic applications.

Experimental section

Sample preparation

All reagents were of analytical grade and used without any further purification in our experiment.

Bi(OHC₂O₄)·2H₂O nanorods were synthesized according to our earlier report.¹⁷ Afterwards, Bi(OHC₂O₄)·2H₂O-BOI composites were prepared by a hydrothermal method. Firstly, 0.35 g Bi(OHC2O4)·2H2O nanorods were dispersed in 25 ml ethylene glycol (EG) solution to be a homogeneous solution under magnetic stirring. Secondly, Bi(NO₃)₃·5H₂O was added to the above solution, followed by stirring for 30 min. Thirdly, 25 mL of KI mannitol solution (0.1 M) was slowly added into the above mixture, followed by stirring for 60 min. Finally, the mixture was sealed into a Teflon-lined stainless steel autoclave and treated at 100 °C for 10 h. After being cooled down to room temperature naturally, the products were collected and washed several times with deionized water and absolute ethanol, and dried at 60 °C for 4 h. The asobtained samples were labeled S-1, S-2 S-3 and S-4 when the molar ratio of Bi(OHC2O4)·2H2O:BiOI is 100:1.5, 100:2.5, 100:5 and 100:15, respectively.

 Bi_2O_3 - Bi_5O_7I heterojunctions were obtained by calcining S-1, S-2, S-3 and S-4 precursors at 350 °C for 3 h in air, and the corresponding calcined-products were labeled DS-1, DS-2, DS-3 and DS-4, respectively.

 Bi_2O_3 rods were obtained by calcining $Bi(OHC_2O_4) \cdot 2H_2O$ precursors at 350 °C for 4 h in air.

Test of photocatalytic activity

Photocatalytic performance of the obtained Bi2O3-Bi5O7I heterostructures was tested by degrading MO dye and toxic phenol under visible light irradiation. A 300 W Xe lamp (CEL-HXF300F, Beijing China Education Au-light Co., Ltd) with a 400 nm cut off filter was used as a visible light source. In a typical photocatalytic experiment, 50 mg of photocatalyst and 50 mL MO (30 mg L^{-1}) or phenol (20 mg L^{-1}) solution were mixed together under magnetic stirring. Prior to illumination, the suspension was stirred for 30 min in the dark to reach an adsorption-desorption equilibrium between MO (or phenol) and the photocatalyst. At each irradiation time intervals, the above suspension (3 mL) was collected and centrifuged, then the supernatant was monitored by UV-vis absorption spectroscopy. All the photocatalytic reactions were carried out at room temperature by cooling water circulation. Additionally, in order to test the durability, the photocatalyst was reused five times to degrade MO dye molecules. The experiments of trapping active species were similar to the photocatalytic tests. Ammonium oxalate (AO), *p*-benzoquinone (BQ) and *t*-butanol acted as the scavengers of hole (h^+), the superoxide radicals (O_2^-) and hydroxyl radicals ('OH), respectively.

Photocatalyst characterization

Field emission scanning electron microscopy (FE-SEM) images were recorded on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images were performed using a JEOL-2010 microscope with an accelerating voltage of 200 kV. X-Ray powder diffraction (XRD) was carried out using a Rigaku (Japan) D/max- γ A X-ray diffractometer with Cu-K α radiation ($\lambda = 0.154178$ nm). UV-vis diffusereflectance spectrum was recorded with a UV-2450 spectrophotometer in the wavelength range of 200–800 nm at room temperature. BaSO₄ was used as the reflectance standard material. X-Ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer RBD upgraded PHI-5000C ESCA system. FT-IR spectroscopy was performed with a FT-IR spectrometer using KBr disks.

Electrochemical impedance spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy (EIS) measurements were conducted at a frequency between 0.1 Hz and 100 kHz using a CHI660D instrument. A three-electrode system was used, in which a Bi_2O_3 - Bi_5O_7I electrode, a saturated calomel electrode and a platinum sheet were employed as the working electrode, the reference electrode and the auxiliary electrode, respectively. The working electrode was prepared by pasting a slurry mixture of the as-prepared Bi_2O_3 - Bi_5O_7I sample (80 wt%), acetylene black (15 wt%) and polytetrafluoroethylene binder (5 wt%) using ethanol as a solvent onto a piece of nickel foam and dried under vacuum at 50 °C for 6 h. 0.5 M Na_2SO_4 was used as the detecting electrolyte.

Results and discussion

BiOI–Bi(OHC₂O₄)·2H₂O heterostructures were synthesized by a hydrothermal method at 100 °C for 10 h using Bi(OHC₂O₄) ·2H₂O rods as precursors. Fig. S1† shows the XRD patterns of the BiOI–Bi(OHC₂O₄)·2H₂O heterostructures, pure BiOI and Bi(OHC₂O₄)·2H₂O. From Fig. S1a,† it can be found that all the diffraction peaks can be indexed to the bismuth oxalate Bi(OHC₂O₄)·2H₂O precursor.⁴⁴ When the molar ratio of Bi(OHC₂O₄)·2H₂O:BiOI is 100:15 (S4 sample), a new diffraction peak (Fig. S1d†) appears which can be indexed to tetragonal BiOI (Fig. S1g,† JCPDS No. 10-0445).

BiOI–Bi(OHC₂O₄)·2H₂O precursors (S-1, S-2, S-3 and S-4) were calcined at 350 °C for 3 h in air and the respective calcined-products were obtained which were labeled DS-1, DS-2 and DS-3, respectively. Fig. 1 shows their XRD patterns. It can be found that two sets of XRD peaks exist in the DS-4 samples, which are indexed to tetragonal Bi₂O₃ (JCPDS No. 27-0050) and orthorhombic Bi₅O₇I (JCPDS No. 40-0548). However, no BiOI XRD peaks are discovered, implying the change of BiOI into Bi₅O₇I during the calcination process. No Bi₅O₇I peaks are found in the DS-1, DS-2 and DS-3 samples, which are due to the low loaded-BiOI content according to Fig. S1.†



Fig. 1 The XRD patterns of Bi_2O_3 , Bi_5O_7I , Bi_2O_3 - Bi_5O_7I heterostructures and standard card of Bi_2O_3 and Bi_5O_7I .

Fig. 2 displays the SEM images of the $Bi_2O_3-Bi_5O_7I$ heterojunctions and their precursors. $Bi(OHC_2O_4)\cdot 2H_2O$ is a rod-like structure with a smooth surface (Fig. S2a†). After calcinations at 320 °C for 4 h, $Bi(OHC_2O_4)\cdot 2H_2O$ transformed into porous Bi_2O_3 rods due to gas removal (Fig. S2b† and 1b). The BiOI- $Bi(OHC_2O_4)\cdot 2H_2O$ precursors are also 1D rod-like structures, and the BiOI nanosheets grow dispersedly on the $Bi(OHC_2O_4)$ $\cdot 2H_2O$ nanorod (Fig. 2a). Meanwhile, with the increase of the loaded-BiOI content, more and more BiOI nanosheets grow on the $Bi(OHC_2O_4)\cdot 2H_2O$ rods (Fig. 2c, e and g). After calcining $BiOI-Bi(OHC_2O_4)\cdot 2H_2O$ precursors at 350 °C for 3 h, the shape of the obtained $Bi_2O_3-Bi_5O_7I$ heterostructures were similar to the Bi_2O_3 porous rods (Fig. 2b, d, f and h), and Bi_5O_7I not BiOI nanosheets grow on the Bi_2O_3 porous rods according to the result of the XRD patterns.

As we know, BiOI can't decompose at low-temperature (less than 400 °C).⁴⁵ So, the above results clearly reveal that chemical reaction occur between Bi(OHC₂O₄)·2H₂O and BiOI during calcinations. The Bi₂O₃ could be obtained directly by calcining Bi(OHC₂O₄)·2H₂O nanorods (reaction eqn (1)). At the same time, Bi₂O₃ would react with the loaded-BiOI to obtain the Bi₅O₇I phase at 350 °C.

$$m\mathrm{Bi}(\mathrm{OHC}_{2}\mathrm{O}_{4})\cdot 2\mathrm{H}_{2}\mathrm{O} + \frac{m}{2}\mathrm{O}_{2} \rightarrow \frac{m}{2}\mathrm{Bi}_{2}\mathrm{O}_{3} + 2m\,\mathrm{CO}_{2} + \frac{3}{2}m\,\mathrm{H}_{2}\mathrm{O}$$
(1)

$$\frac{m}{2}\operatorname{Bi}_{2}\operatorname{O}_{3} + \frac{n-m}{2}\operatorname{BiOI} \to \operatorname{Bi}_{n}\operatorname{O}\frac{3n-m}{2}\operatorname{I}_{m}$$
(2)

where *n* is the initial molar amount of Bi^{3+} , *m* is the molar amount of $Bi(OHC_2O_4)\cdot 2H_2O$ added. Consequently, the O-rich BiOI compounds can be formed when n > m.⁴⁶ According to the reported result, Bi_5O_7I can't be obtained until the reaction temperature reaches 500 °C if the BiOI precursor is calcined.⁴⁵ Thus, we supply a simple and low-temperature method to obtain Bi_5O_7I .



Fig. 2 FE-SEM images of the precursors and their respective calcined products, S-1 (a), DS-1 (b), S-2 (c), DS-2 (d), S-3 (e), DS-3 (f), S-4 (g) and DS-4 (h).

Surface compositions and chemical states in the Bi_2O_3 , DS-2 and Bi₅O₇I samples were measured by XPS. A type full XPS spectrum of the above samples is shown in Fig. 3a. It can be seen that Bi and O elements exist in all the samples, but I element only exists in DS-2 and Bi₅O₇I. The high resolution XPS spectra of Bi, I and O are shown in Fig. 3b-d. The two peaks of DS-2 located at 164.2 and 158.9 eV are ascribed to Bi 4f5/2 and Bi 4f7/2 (Fig. 3b), respectively, which prove that the Bi ions in the DS-2 sample are in form of Bi³⁺. More importantly, after Bi2O3 and Bi5O7I are in contact with each other, the peaks of Bi 4f in the DS-2 sample slightly shift to higher (or lower) binding energies compared to the Bi₂O₃ (or Bi₅O₇I) sample, indicating the strong chemical interaction between Bi₂O₃ and Bi₅O₇I in the interface. A similar phenomenon is discovered in the O1s spectrum (Fig. 3d). The high resolution XPS spectrum of I 3d is displayed in Fig. 3c, and the peaks at 630.7 and 619.3 eV are assigned to I 3d3/2 and I 3d5/2, respectively. In the DS-2 sample, the peaks of I 3d3/2 and I 3d5/2 also appear, but the intensity of the peaks are weaker and the position of the peaks shifts to the lower binding energy than that in Bi₅O₇I (Fig. 3c). This result not only proves that small Bi₅O₇I exists in the DS-2 sample, but also shows that the strong chemical interaction is formed between Bi₂O₃ and Bi₅O₇I in the interface. Furthermore, according to the XPS result of DS-2, the molar ratio of Bi and I in the DS-2 sample is 19.02:0.69 (27.57:1), more than the molar ratio of Bi and I in the Bi₅O₇I sample, implying only few Bi₅O₇I existences in the DS-2 sample, in good accordance with the XRD and SEM results.

In order to prove the formation of the Bi_5O_7I - Bi_2O_3 heterostructure, the IR spectra of pure Bi_2O_3 , Bi_5O_7I and DS-4 samples are measured (Fig. 4). We can see that the peaks at

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Fig. 3 Survey XPS spectra of Bi₂O₃, DS-2, and Bi₅O₇I samples (a) and their high-resolution XPS spectra of (b) Bi 4f, (c) I 3d and (d) O 1s.

419.0, 508.1, 572.1 and 615.2 cm⁻¹ can be observed in the IR spectrum of Bi₅O₇I,⁴⁰ which can be ascribed to the vibration of Bi–O bonds. In the IR spectrum of pure Bi₂O₃, 419.0, 520 and 631 cm⁻¹ are assigned to the vibration of Bi–O bonds.⁴⁷ After Bi₂O₃ and Bi₅O₇I are combined with each other, the main characteristic peaks ascribed to Bi₂O₃ (419.0 cm⁻¹) and Bi₅O₇I (615.2 cm⁻¹) appear in the Bi₅O₇I–Bi₂O₃ heterostructure. However, the characteristic peaks centered at 572.1 cm⁻¹ (Bi₅O₇I) shift to the higher wavenumber (574.9 cm⁻¹), while the characteristic peak at 520 cm⁻¹ (Bi₂O₃) shifts to the lower wavenumbers. This result implies the formation of the

strong interfaces *via* strong chemical interaction in the Bi_5O_7I - Bi_2O_3 heterostructures.¹¹ This conclusion is consistent with the result of XPS analysis.

TEM technology was used to obtain structural information of the obtained DS-2 sample in detail. The TEM and HRTEM images of DS-2 are shown in Fig. 5. It is clearly noted that the Bi_5O_7I nanosheets grow onto the surface of the Bi_2O_3 porous rod, which is consistent with the SEM and XRD results. Fig. 5b shows the HRTEM image of DS-2. The lattice spacing of 0.347 nm corresponds to (210) planes of Bi_2O_3 , and 0.318 nm corresponds to the (312) plane of Bi_5O_7I , respectively. The



Fig. 4 IR spectra of pure Bi₂O₃, Bi₅O₇I and DS-4 heterostructures.



Fig. 5 TEM (a) and HRTEM (b) images of the DS-2 heterostructure.

interfacial crystal lattice matches well (see the red ring in Fig. 5b) between Bi_2O_3 and Bi_5O_7I , indicating the crystallographic-oriented growth of Bi_5O_7I from the Bi_2O_3 surface, which favors the formation of chemically strong bonds across the large contact interfaces.

The photocatalytic activity of the obtained heterostructures was evaluated by degrading MO and phenol. Fig. 6a and c display the degradation curve of MO and phenol in the presence of photocatalysts. It can be found that DS-2 displays excellent photocatalytic performance among all the samples. When using DS-2, Bi_2O_3 and Bi_5O_7I as photocatalysts, the degradation efficiencies of MO (30 mg L⁻¹) are 98%, 80% and 48% in 60 min under visible light irradiation (Fig. 6a and b), respectively. In addition, 99%, 62% and 33% of phenol (20 mg L⁻¹) can be degraded in 60 min (Fig. 6c). Moreover, the absorption peaks of phenol at 208 nm almost disappear in 60 min (Fig. 6d) using the DS-2 sample as the photocatalyst. This indicates that all the phenol molecules are completely degraded to small molecular compounds, such as CO₂ and H₂O. Compared with the reported Bi-based



Fig. 6 Photocatalytic degradation curves of MO (30 mg L^{-1}) (a) and phenol (20 mg L^{-1}) (c) using different photocatalysts; UV-vis absorption spectra of MO (b) and phenol (d) using DS-2 as the photocatalyst under visible light irradiation.

photocatalysts for degradation of phenol with the similar photocatalytic conditions, the DS-2 sample shows excellent photocatalytic activity. This enhanced photocatalytic activity is ascribed to the formation of high interface quality in the DS-2 sample, which can be seen from the SEM and HRTEM images (Fig. 2 and 5).

In addition, the photocatalytic activity of Bi_2O_3 - Bi_5O_7I photocatalysts was also investigated by degrading RhB and MB solutions under visible light irradiation (Fig. S3†). It is found that RhB (10 mg L⁻¹) and MB (10 mg L⁻¹) can be degraded completely within 100 and 60 min, respectively, using the DS-2 sample as the photocatalyst. This result shows that the obtained DS-2 selectively degrades MO and phenol.

To investigate the stability of photocatalytic performance in the visible light region, the DS-2 sample was used to degrade MO in five repeated cycles, and the results are shown in Fig. 7. The DS-2 photocatalyst retains its excellent photocatalytic activity after 5 repeated cycles (Fig. 7), implying that the DS-2 photocatalyst possesses favorable stability. Small amounts of $Bi_2O_2CO_3$ are found to be present in the XRD pattern of DS-2 after recycling the photocatalyst (Fig. 7b, see the red arrows). This may be due to the Bi_2O_3 reaction with CO_2 which comes from the decomposition of MO in the process of photocatalysis.

UV-vis diffuse-reflectance spectroscopy (DRS) was used to measure the optical properties of Bi_2O_3 , Bi_5O_7I and Bi_2O_3 - Bi_5O_7I samples. As shown in Fig. 8a, Bi_2O_3 - Bi_5O_7I heterojunctions show good visible light absorption. The optical band gaps of Bi_2O_3 and Bi_5O_7I (Fig. 8b) can be determined by the following equation:

$$\alpha h v = A (h v - \mathrm{Eg})^{n/2}$$

in which α , *h*, *v*, *A* and Eg are the absorption coefficient, Planck constant, light frequency, a constant and band gap, respectively. Also, *n* is equal to 4 for the indirect band gap and 1 for the direct band gap. Here n = 4 for both Bi₂O₃ and Bi₅O₇I. Fig. 8b shows the plots of $(\alpha hv)^{n/2}$ versus *hv* for Bi₂O₃ and Bi₅O₇I. The band gap (Δ Eg) is estimated by extrapolating the straight line to the abscissa axis; therefore, Δ Eg (Bi₂O₃) and Δ Eg (Bi₅O₇I) are estimated to be 2.26 eV and 2.86 eV, respectively.



Fig. 7 Cycling times of the photocatalytic degradation of MO (30 mg L^{-1}) in the presence of DS-2 under visible light irradiation after five repeated cycles and (b) the XRD pattern of DS-2 before and after five repeated cycles.



Fig. 8 (a) UV-vis diffuse reflectance spectra of Bi_2O_3 , Bi_5O_7I and Bi_2O_3 - Bi_5O_7I samples, and (b) the plots of $(\alpha hv)^{1/2}$ vs. hv of Bi_2O_3 , Bi_5O_7I .



Fig. 9 VB-XPS spectra of Bi₂O₃, Bi₅O₇I and DS-2.

To determine the relative positions of the conduction band (CB) and VB edges, the VB-XPS spectra for Bi₂O₃, Bi₅O₇I and DS-2 were measured, as shown in Fig. 9. In contrast to Bi₅O₇I, the VB maximum of DS-2 is down-shifted from 1.69 to 1.53 eV. Compared to Bi₂O₃, the VB maximum of DS-2 is upshifted from 1.32 to 1.53 eV. The shift of the VB maximum position for DS-2 can be attributed to the formation of the heterojunction, as confirmed by XRD and TEM results. The VB edges of Bi₂O₃ and Bi₅O₇I are 1.32 eV and 1.69 eV, respectively. According to the VB edges, combining with band gaps of Bi₂O₃ (2.26 eV) and Bi₅O₇I (2.80 eV), the CB edge potential of Bi₂O₃ and Bi₅O₇I is -0.94 eV and -1.11 eV, respectively, calculated from the equation of $E_{CB} = E_{VB} - Eg$.

Trapping experiments were performed to detect the active species generated in the photodegradation process. *tert*-Butyl alcohol (TBA), ammonium oxalate (AO) and 1,4-benzoquinone (BQ) were used as scavengers to trap hydroxyl radicals ('OH), holes (h^+) and superoxide radicals ('O₂⁻). It can be observed from Fig. 10 that the photocatalytic degradation of MO and phenol molecules is remarkably inhibited with the addition of AO and BQ. However, the addition of TBA did not cause significant deactivation of the DS-2 photocatalyst, illustrating that 'OH has little contribution to MO and phenol photo-



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degradation. These results demonstrate that O_2^- and h^+ are the main active species in the photocatalytic process under visible light irradiation.

The typical EIS spectra of pure Bi₂O₃, Bi₂O₃-Bi₅O₇I heterostructures and pure Bi5O7I are shown in Fig. 11. As is wellknown, the arc radius in the impedance spectrum can reflect the reaction rate on the photocatalyst surface, and the smaller arc radius implies a more efficient separation of photogenerated electron-hole pairs and a higher efficiency of charge transfer. The arc radii of the prepared DS-2 sample is smaller than that of pure Bi₂O₃ and Bi₅O₇I, suggesting that the Bi₂O₃-Bi₅O₇I heterostructure could facilitate the separation and migration of photogenerated electron-hole pairs in comparison with pure Bi₂O₃ and Bi₅O₇I. Therefore, the EIS measurements demonstrate that the Bi2O3-Bi5O7I heterostructure can significantly promote the separation of photogenerated electron-hole pairs and suppress the recombination of photogenerated electron-hole pairs in the DS-2 samples, thus improving the photocatalytic activities.

Based on the results of the trapping experiments and the VB-XPS data, we readily illustrate the schematic diagram for the photocatalytic reaction mechanism and charge transfer of the Bi_2O_3 - Bi_5O_7I heterostructures under visible light



Fig. 10 Active species trapping experiments using DS-2 as the photocatalyst under visible light irradiation, (a) MO (30 mg L^{-1}) and (b) phenol (20 mg L^{-1}).



Fig. 12 Schematic of (a) the energy bands of Bi_2O_3 and Bi_5O_7I , and (b) the formation of Bi_2O_3 - Bi_5O_7I heterostructures and the possible charge separation.

irradiation, as shown in Fig. 12. For the p-type Bi₂O₃, the Fermi energy level is close to the VB edge, whereas for the n-type Bi₅O₇I, the Fermi energy level is close to the CB band. When the two semiconductors are in contact to form a p-n junction, there is a diffusion of electrons from Bi₅O₇I to Bi₂O₃ due to their different Fermi energy levels, resulting in accumulation of negative charges in Bi₂O₃ close to the junction. At the same time, the holes transfer from Bi₂O₃ to Bi₅O₇I, leaving a positive section in Bi₅O₇I near the junction. Moreover, the energy bands of Bi₂O₃ shift upward along the Fermi level and those of the Bi₅O₇I shift downward along its Fermi level (Fig. 12b). With equilibration of Bi₂O₃ and Bi₅O₇I Fermi levels, the diffusion of electrons from Bi₅O₇I to Bi₂O₃ stops. Therefore, an equilibrium state is formed and an interbuilt electric field will also be generated at the interface. The narrow bandgap Bi₂O₃ is excited to generate photogenerated electron-hole pairs under visible light irradiation. Due to the potential difference, the electrons migrate from the conduction band of Bi₂O₃ to that of Bi₅O₇I, and the holes remain on the valence band of Bi2O3. Similarly, the photogenerated holes migrate from the valence band of Bi₅O₇I to that of Bi₂O₃. The internal electric field and high interface quality at the junction will enhance the photogenerated electron and hole mobility, increasing the photocatalytic activity of the Bi₂O₃-Bi₅O₇I p-n heterojunction.

Conclusions

In summary, one-dimensional (1D) $Bi_2O_3-Bi_5O_7I$ heterostructured photocatalysts with high interface quality have been synthesized by calcining $Bi(OHC_2O_4)\cdot 2H_2O$ -BiOI precursors in air at 350 °C for 3 h. Bi_5O_7I nanosheets grow on the Bi_2O_3 nanorods. The obtained $Bi_2O_3-Bi_5O_7I$ heterojunctions exhibit higher photocatalytic activity than pure Bi_2O_3 and Bi_5O_7I for the degradation of MO and phenol with high concentration under visible light irradiation. This enhanced photocatalytic activity is due to the formation of a high quality interface between Bi_2O_3 and Bi_5O_7I . Moreover, a 1D ordered nanostructure is favorable for highly efficient and directional transport and separation of electrons and holes. The h^+ and O_2^- radicals are the main active species for photocatalytic degradation of phenol and MO over Bi_2O_3 - Bi_5O_7I . This work provides a facile and versatile strategy to fabricate heterojunctions with a high quality interface on a large scale.

Conflicts of interest

The authors declare that they have no conflict of interest.

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