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Novel one-dimensional \( \text{Bi}_2\text{O}_3\)-\( \text{Bi}_2\text{WO}_6 \) p-n hierarchical heterojunction with enhanced photocatalytic activity

Yin Peng\(^a\), Mei Yan\(^a\), Qing-Guo Chen\(^a\), Cong-Min Fan\(^b\), Hai-Yan Zhou\(^a\) and An-Wu Xu\(^b\)

A novel one-dimensional (1D) \( \text{Bi}_2\text{O}_3 \) nanorods-\( \text{Bi}_2\text{WO}_6 \) nanosheets p-n junction photocatalyst was prepared by three steps synthetic route. The obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron mic-roscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), \( \text{N}_2 \)-sorption/desorption and Brunauer-Emmett-Teller surface area (BET). \( \text{Bi}_2\text{O}_3 \) rods with the diameter of about 200 nm were obtained by calcining \( \text{Bi}(\text{OHC})\text{O}_2\cdot2\text{H}_2\text{O} \) precursor. \( \text{Bi}_2\text{WO}_6 \) nanosheets vertically grown onto the \( \text{Bi}_2\text{O}_3 \) rods along the long axial direction. The photocatalytic activity to degrade Rhodamine B (RhB) and phenol under solar/visible light by p-n junction \( \text{Bi}_2\text{O}_3\)-\( \text{Bi}_2\text{WO}_6 \) nanorods was investigated. The result demonstrates that the novel \( \text{Bi}_2\text{O}_3\)-\( \text{Bi}_2\text{WO}_6 \) p-n heterostructures display higher photocatalytic activity than single \( \text{Bi}_2\text{O}_3 \) nanorods or \( \text{Bi}_2\text{WO}_6 \) flowers. The photogenerated carriers of \( \text{Bi}_2\text{O}_3 \) have been synthesized and \( \text{Bi}_2\text{WO}_6 \) have been used to identify a deep insight into the design and fabrication of advanced materials with heterojunction structures for photocatalytic applications and optoelectronic devices.

Introduction

With the environmental pollution increase, green chemistry has become a necessary requirement for the sustainable development of human society. Among the various green chemical techniques, semiconductor photocatalysis has been considered an cost-effective, sustainable and the most promising green chemical technology because it represents an easy way to complete degradation of organic pollutants by utilizing the solar energy.\(^1,^3\) However, some traditional photocatalysts (such as \( \text{TiO}_2 \), \( \text{ZnO} \), \( \text{SnO}_2 \)) can absorb only ultraviolet light due to their wide band gap and have moderate photocatalytic activity due to the high recombination rate of photogenerated carriers.\(^4,^6\) So, the development of photocatalysts performance under visible light constitutes the key point. A significant number of new photocatalysts do perform adequately under visible light but typically display poor performance with respect to \( \text{TiO}_2 \) commercial references (e.g., Degussa P25) under sunlight because the enhanced visible light absorption and fast recombination of charge recombination occurs simultaneously.\(^7\)

For that reason, instead of using a single semiconductor, combining two or more semiconductors with appropriate band positions to improve the photocatalytic performance is an established idea because it can lead to an enhanced charge separation and interfacial charge-transfer efficiency.\(^6,^{10}\)

Especially, it is noted that the fabrication of a p-n junction photocatalyst is believed to be the very effective because of the existence of an internal electric field.\(^11,^{12}\)

As one of the simplest Aurivillius oxides with layered structure, \( \text{Bi}_2\text{WO}_6 \) is special for its good photocatalytic performance under visible light irradiation.\(^13-15\) Bare \( \text{Bi}_2\text{WO}_6 \) presents photoabsorption properties from UV light to visible light with wavelength of shorter than ca. 450 nm,\(^16,^{17}\) which overlaps a small part of the solar spectrum. Moreover, the rapid recombination of photoinduced electron-hole pairs seriously limits the energy-conversion efficiency. To broaden the range of visible-light photosresponse and promote the separation of photogenerated carriers of \( \text{Bi}_2\text{WO}_6 \), we intend to design a composite photocatalyst by coupling \( \text{Bi}_2\text{WO}_6 \) with a narrow bandgap semiconductor \( \text{Bi}_2\text{O}_3 \) with matched band potentials. The well-established heterojunction structure could be employed to restrict the recombination of the charge carriers and enhance the quantum yield.\(^18\) The electrons excited by visible light can be transferred to \( \text{Bi}_2\text{WO}_6 \) from the narrow bandgap semiconductor, which favors the charge separation and also improves the visible-light photocatalytic activity of the heterostructure dramatically.\(^19\) \( \text{Bi}_2\text{O}_3 \) is a p-type semiconductor with a band gap of 2.8 eV and has proved to be a photocatalyst for water splitting and pollutant decomposition under visible-light irradiation. However, the photocatalytic activity of pure \( \text{Bi}_2\text{O}_3 \) is also low because of the high recombination probability of photogenerated electrons and holes.\(^16-21\) It is expected that the formation of p-n junction structure between n-type \( \text{Bi}_2\text{WO}_6 \) and p-type \( \text{Bi}_2\text{O}_3 \) will greatly enhance the photocatalytic activity. Recently, \( \text{Bi}_2\text{O}_3\)-\( \text{Bi}_2\text{WO}_6 \) p-n junction structures with microspheres,\(^22\) hollow microspheres,\(^23,^{24}\) and flowers,\(^25,^{26}\) have been synthesized and exhibit better photocatalytic activities than pure \( \text{Bi}_2\text{O}_3 \) or \( \text{Bi}_2\text{WO}_6 \) samples. However, \( \text{Bi}_2\text{O}_3\)-\( \text{Bi}_2\text{WO}_6 \) p-n heterojunction with highly ordered \( \text{Bi}_2\text{WO}_6 \) nanosheets grown on one-dimensional (1D) \( \text{Bi}_2\text{O}_3 \) nanorods have not been reported. Compare with above mentioned heterostructures, 1D p-n heterojunction photocatalysts have aroused great concern because of their high surface areas.
remarkable and directional transport characteristics of electrons and holes, and thus their enhanced photocatalytic activities. Here, we report for the first time the synthesis of a novel Bi$_3$O$_2$ nanorods-Bi$_2$WO$_6$ ordered nanosheets p-n junction via a simple method. This 1D heterostructure displays superior photocatalytic activity for degradation of the phenol and RhB under solar/visible light irradiation.

**Experimental Section**

**Photocatalyst preparation**

All the reagents used in our experiment were analytical grade and used as received without further purification.

Bi(OHC$_2$O)$_2$•2H$_2$O nanorods were first synthesized via a hydrothermal method. Bi(NO$_3$)$_3$•5H$_2$O (2.911 g) and Na$_2$C$_2$O$_4$ (1.206 g) were dissolved separately in 20 mL distilled water. Then the Na$_2$C$_2$O$_4$ solution was added into the Bi(NO$_3$)$_3$ suspension solution with vigorous magnetic stirring. The mixed suspension solution was poured into a stainless steel autoclave with a Teflon liner and heated at 120 °C for 40 h. The obtained solid sample was washed with deionized water and anhydrous ethanol, and then dried at 60 °C for 6 h.

Then, Bi$_2$WO$_6$•Bi(OHC$_2$O)$_2$•2H$_2$O samples were synthesized via a solvothermal process. 0.341 g of Bi(OHC$_2$O)$_2$•2H$_2$O nanorods were added into the 15 mL of Bi(NO$_3$)$_3$•5H$_2$O ethylene glycol (EG) solution under magnetic stirring, and then 15 mL of Na$_2$WO$_4$•2H$_2$O aqueous solution was added drop-wise and stirred for another 30 min. The mixture was sealed into a Teflon-lined stainless steel autoclave and treated at 160 °C for 2 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. Bi$_2$WO$_6$ flowers were obtained in the absence of Bi(OHC$_2$O)$_2$•2H$_2$O nanorods in above reactive system.

Finally, the Bi$_2$O$_3$-Bi$_2$WO$_6$ heterojunctions were obtained by calcining Bi$_2$WO$_6$•Bi(OHC$_2$O)$_2$•2H$_2$O composites at 400 °C for 2 h in air. The as-obtained samples with the molar ratio of Bi(OHC$_2$O)$_2$•2H$_2$O:Bi$_2$WO$_6$ 2:1.5, 2:3, 2:10, 2:2 and 2:4, were labelled WBP1, WBP2, WBP3, WBP4 and WBP5 respectively. And the corresponding calcined products Bi$_2$O$_3$-Bi$_2$WO$_6$ were labelled WB1, WB2, WB3, WB4 and WB5, respectively. Bi$_2$O$_3$ rods were obtained by calcinations of Bi(OHC$_2$O)$_2$•2H$_2$O precursors at 400 °C for 2 h in air.

**Photocatalytic activity measurements**

Photocatalytic activity of the prepared Bi$_3$O$_2$-Bi$_2$WO$_6$ samples was tested by decomposing phenol and RhB under solar/visible light irradiation. The light source was a 300 W Xe lamp (PLS-SXE300/300UV, Trusttech Co., Ltd. Beijing). In a typical experiment, the photocatalyst (100 mg) was added into 100 mL of phenol (or RhB) (10 mg/L) to produce a suspension for the degradation reaction at room temperature under air. Before the solar/visible light irradiation, the suspension was stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium of phenol (or RhB) on the surface of the photocatalyst. Then, the suspension was illuminated by the Xe lamp combined with a UV cutoff filter (λ ≥ 400 nm) under stirring. At given time intervals, above 4 mL suspension was withdrawn, and centrifuged to remove the precipitate. The degradation reaction process was monitored by measuring the concentration of phenol (or RhB) as a function of irradiation time in the solution with UV-Vis absorption spectra. Additionally, the recycling experiments were performed for six recycles to test the durability. After each cycle, the photocatalyst was centrifugation and used directly for the next test.

**Photocatalytic water splitting**

In a typical photocatalytic experiment, the prepared Bi$_3$O$_2$-Bi$_2$WO$_6$ sample (50 mg) was dispersed in an aqueous solution (100 mL) of Fe$_2$(SO$_4$)$_3$ (2.1 mM L$^{-1}$). The suspension was sealed in a quartz flask and purged with argon for 1 h to drive away the residual air. The photocatalytic oxygen production was initiated by irradiating the suspension with a 300 W Xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter (λ > 420 nm). The gas product was analyzed periodically through a gas chromatograph (Agilent 7890A) with a thermal conductivity detector (TCD).

**Characterization**

Field emission scanning electron microscopy (FE-SEM) images were recorded on a Hitachi S-4800 microscope. Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopic (HRTEM) images and the selected area electron diffraction (SAED) patterns were performed on a JEO-L2010 microscope with an accelerating voltage of 200 kV, and energy-dispersive X-ray spectroscopy (EDS) analysis was performed. X-Ray powder diffraction (XRD) was carried out on a Rigaku (Japan) D/max-γ A X-ray diffractometer with Cu-Kα radiation (λ = 0.154178 nm). UV-vis diffuse-reflectance spectrum was recorded with a UV-2450 spectrophotometer in the wavelength range of 200-800 nm at room temperature. Bi$_2$SO$_4$ was used as the reflectance standard material. The X-Ray photoelectron spectroscopy (XPS) was performed on a PerkinElmer RBD upgraded PHI-5000C ESCA system. Nitrogen adsorption/desorption measurements were performed at 77 K using a Micromeritics TriStar II 3020 M analyzer after the samples were degassed at 180 °C for 6 h. The Brunauer-Emmett-Teller (BET) surface area was estimated by using adsorption data in a relative pressure range from 0.05 to 0.3.

**Results and discussion**

In this study, Bi(OHC$_2$O)$_2$•2H$_2$O rods were first synthesized, then Bi$_2$WO$_6$•Bi(OHC$_2$O)$_2$•2H$_2$O nanosheet-rod heterostructures were obtained by hydrothermal treatment using Bi(OHC$_2$O)$_2$•2H$_2$O rods as support. Finally, Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n junction nanostructures wit nanosheets standing on rods were prepared by calcinations of Bi$_2$WO$_6$•Bi(OHC$_2$O)$_2$•2H$_2$O. The Bi(OHC$_2$O)$_2$•2H$_2$O-Bi$_2$WO$_6$ heterostructures with different Bi(OHC$_2$O)$_2$•2H$_2$O/Bi$_2$WO$_6$ molar ratio of 2:1.5, 2:3 and 2:10, were labelled as WBP1, WBP2 and WBP3, respectively. And the corresponding calcined products Bi$_2$O$_3$-Bi$_2$WO$_6$ was denoted as WB1, WB2 and WB3, respectively (see experimental section).

The X-ray powder diffraction (XRD) patterns of the obtained products are shown in Fig. S1. All of the diffraction peaks in the Fig. S1a could be indexed to bismuth oxalate (Bi(OHC$_2$O)$_2$•2H$_2$O) precursor reported by Monnereau et al. With the loaded-Bi$_2$WO$_6$ content increasing, the new diffraction peaks appear and their intensities increase gradually (Fig. S1b-d) and these new peaks can be indexed to orthorhombic Bi$_2$WO$_6$ (Fig. S1e). These results show that the heterostructure between Bi(OHC$_2$O)$_2$•2H$_2$O and Bi$_2$WO$_6$ is formed.

Fig. 1 shows the XRD patterns of obtained Bi$_3$O$_2$ rods, Bi$_3$O$_2$-Bi$_2$WO$_6$ p-n heterojunctions and Bi$_2$WO$_6$. All of the diffraction peaks shown in Fig. 1b and c can be well-indexed to the monoclinic structure of Bi$_2$WO$_6$ (JCPDS No. 76-1730) and
orthorhombic Bi$_2$WO$_6$ (JCPDS No. 39-0256), respectively. The sharp diffraction peaks of both Bi$_2$O$_3$ and Bi$_2$WO$_6$ indicate their good crystallinity. No traces of other phases are detected, confirming the high purity of the samples. Fig. 1c-e obviously show two sets of XRD peaks of monoclinic Bi$_2$O$_3$ and orthorhombic Bi$_2$WO$_6$, indicating that the as-synthesized products are composite materials. Moreover, it is noted that the diffraction peaks of Bi$_2$O$_3$ are weakened with increasing Bi$_2$WO$_6$/Bi$_2$O$_3$ molar ratio (see red labels in Fig. 1b-e), while the peak intensities of Bi$_2$WO$_6$ increase gradually.

![Fig. 1 The XRD patterns of (a) Standard Card of Bi$_2$O$_3$, (b) Bi$_2$O$_3$, (c) WB1, (d) WB2, (e) WB3 and (f) Bi$_2$WO$_6$.](image)

Fig. 2 displayed the SEM images of these Bi$_2$O$_3$-Bi$_2$WO$_6$ heterojunctions and their precursors. Bi(OHC$_2$O)$_6$•2H$_2$O is 1D rods with a mean diameter of 450 ± 50 nm and length of 5±1 µm. Each rod has smooth surface (Fig. 2a). After calcinations at 400 °C for 2 h, Bi(OHC$_2$O)$_6$•2H$_2$O transformed to Bi$_2$O$_3$ rods with rough surface and porosity due to gas removal (Fig. 2b). The obtained Bi$_2$WO$_6$-Bi(OHC$_2$O)$_6$•2H$_2$O precursors are also 1D rod-like structures, and the thin Bi$_2$WO$_6$ nanosheets grow vertically onto the surface of Bi(OHC$_2$O)$_6$•2H$_2$O nanorod (Fig. 2c). Meanwhile, the more the loaded-Bi$_2$WO$_6$ content is used, the more Bi$_2$WO$_6$ nanosheets orderly grow onto the Bi(OHC$_2$O)$_6$•2H$_2$O rods along the long axial direction (Fig. 2e, g), and the gap between Bi$_2$WO$_6$ nanosheets becomes narrower and narrower, finally each Bi(OHC$_2$O)$_6$•2H$_2$O rod is completely covered by Bi$_2$WO$_6$ nanosheets. During the formation of Bi(OHC$_2$O)$_6$•2H$_2$O-Bi$_2$WO$_6$ composite, the preferred outward diffusion of Bi ions from Bi(OHC$_2$O)$_6$•2H$_2$O precursor to Bi$_2$WO$_6$ leads to a net material flux across the composite interface. Therefore, some hollow structures (see red arrows in Fig. 2e, g) are formed based on the Kirkendall effect. From Fig. 2d, f, h, it can be clearly seen that the morphologies of the obtained Bi$_2$WO$_6$-Bi$_2$O$_3$ heterostructures were kept unchanged after calcining Bi$_2$WO$_6$-Bi(OHC$_2$O)$_6$•2H$_2$O precursors at 400 °C for 2 h.

To further obtain information about the structure of the sample, the WB2 p-n heterojunction was characterized by transmission electron microscopy (TEM). As shown in Fig. 3a, it can clearly see the Bi$_2$WO$_6$ nanosheets vertically grow onto the surface of the Bi$_2$O$_3$ nanorods, which is consistent with the result of the SEM measurements. Fig. 3b shows the high-resolution transmission electron microscopic (HRTEM) image taken from the tip of the Bi$_2$WO$_6$ nanosheet (red square highlighted in Fig. 3a). It is found that two sets of lattice fringes with interplanar spacing of 0.82 nm and 0.27 nm, well correspond to (020) and (002) planes of orthorhombic Bi$_2$WO$_6$. The selected area electron diffraction (SAED) pattern (inset in Fig. 3b) taken from the nanoparticles can be indexed as a Bi$_2$WO$_6$ single crystal recorded along the [100] zone axis. The energy dispersive spectroscopy (EDS) analysis further confirms that nanosheets only contain O, Bi and W elements, and the atomic ratio of Bi/W is calculated to be about 1.85:1, close to 2:1 in Bi$_2$WO$_6$ (Fig. S2).

![Fig. 2 The FE-SEM images of the Bi$_2$O$_3$-Bi$_2$WO$_6$ and their precursors (a) Bi(OHC$_2$O)$_6$•2H$_2$O, (b) pure Bi$_2$O$_3$, (c) WBP1, (d) WB1, (e) WBP2, (f) WB2, (g) WB3 and (h) WB3.](image)

Fig. 3 (a) The TEM and (b) HRTEM images of the WB2 heterojunction.

Quantitative X-ray photoelectron spectroscopy (XPS) analysis was carried out on the obtained WB2 heterostructures. The typical
full survey and high-resolution spectra for Bi 4f, W 4f, and O 1s region were showed in Fig. 4. It can be seen that only O, Bi and W elements exist in the sample (Fig. 4a, i). High resolution XPS spectrum of W 4f region shows a binding energy at 35.5 eV for W 4f5/2 and at 37.6 eV for W 4f3/2, suggesting that W exists in the chemical state of W6+ (Fig. 5b, i)22,36. The binding energy for Bi 4f5/2 and Bi 4f3/2 are 164.5 and 159.2 eV (Fig. 5c, ii) respectively, which prove all the Bi species in the WB2 sample are in the form of Bi3+. However, it is worth noting that these binding energy values are not exactly the same as those obtained from pure Bi2O3 or Bi2WO6.30,31 which reveal that interfacial structure is formed and the local environment and electron density of the elements is changed in some degree. The XPS spectrum for O1s can be deconvoluted to three peaks at 529.6, 530.5 and 531.9 eV, which can be assigned to Bi-O and W-O in Bi2WO6 (Fig. 4d (i)) and Bi-O in Bi2O3, respectively.23,25,33,32 On the other hand, according to the XPS result of sample WB2, the concentration of the surface Bi3+ is 20.66 atom%, whereas that of W6+ is 5.82 atom%. The atomic ratio of Bi and W is about 3.55, which is larger than the stoichiometric ratio in Bi2WO6. This result reveals the co-existence of Bi2O3 and Bi2WO6 species in the WB2 sample, in good accordance with the XRD, TEM and SEM results.

Adsorption and desorption experiments using N2 were carried out at 77 K. Fig. 5a displays the nitrogen sorption isotherms of the Bi2O3-Bi2WO6 heterostructures, pure Bi2O3 and Bi2WO6 samples. The shape of the isotherm is a type IV isotherm with a type H3 hysteresis loop at high relative pressures according to the IUPAC classification, which indicates that these samples are mesoporous structures in the pore diameter range of 2−50 nm.33,34 This result can be further confirmed by the corresponding pore size distribution, as shown in Fig. 5b. Considering the observed morphology of the samples, the smaller pores with a sharp peak at about 2.6 nm may be generated during the crystal growth process, whereas the larger pores (20−30 nm) could be generated during thermal treatment process. Table 1 gives the BET surface area and porous volume of different samples. It can be found that the BET specific surface areas of the Bi2O3-Bi2WO6 p-n junction structures are all higher than that of pure Bi2O3 nanorods (1.9 m2g−1), but lower than that of Bi2WO6 flowers (15.4 m2g−1). WB2 and Bi2WO6 have much larger pore volume than that of other samples, and Bi2O3 nanorods have the smallest pore volume.

Previous studies show that a suitable conformation of pores allows light waves to penetrate deep inside the photocatalysts and leads to high mobility of charge.35-38 It is speculated that the pores in the WB2 heterostructures and Bi2WO6 flowers allow the penetration of light waves and phenol or RhB molecules in solution deep into the photocatalysts, which may greatly promote the photocatalytic activity.

![Fig. 5](image-url) (a) Nitrogen adsorption-desorption isotherm and (b) the corresponding pore size distribution of the different samples.

Table 1 The surface area and pore volume of different samples.

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<td>WB1</td>
<td>14.247</td>
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<td>WB3</td>
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<td>Bi2O3</td>
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<tr>
<td>Bi2WO6</td>
<td>15.426</td>
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The optical property of Bi2O3-Bi2WO6 heterojunctions was examined using UV-vis diffuse-reflectance spectrum (DRS). As shown in Fig. 6, The absorption edge of the pure Bi2O3 and Bi2WO6 is ~437 and 428 nm, which shows their visible light absorption. After combining the two semiconductors, Bi2O3-Bi2WO6 heterojunctions show more intensive absorption within the visible light range in comparison with pure Bi2O3 or Bi2WO6, and the visible light absorption ability of the composite is gradually enhanced with loaded-Bi2WO6 increase. However, too much loaded-Bi2WO6 (such as sample WB3) will decrease the visible light absorption. For semiconductors, their optical band gap can be calculated from the absorption spectra using the equation αhν = A(hν − Eg)n, in which α, h, ν, A, and Eg are the absorption coefficient, Planck constant, light frequency, a constant and band gap, respectively.39 In the equation, n decides the characteristics of the transition in a semiconductor, here n = 2 for Bi2WO6 and n = 4 for Bi2O3.31 The energy of the band gap is calculated by extrapolating the straight line to the abcissa axis. The band gap of pure Bi2WO6 and Bi2O3 was estimated to be 2.89 and 2.71 eV, respectively.
junctions are formed, thus resulting in the highest photocatalytic capacity and can be used in environmental phenol using different samples as photocatalysts are shown in Fig. 2. Obviously, the photocatalytic activity of the samples is significantly affected by the Bi$_2$WO$_6$ content in Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n junction photocatalysts sequentially decreases. According to the SEM images (Fig. 2) of Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n heterojunctions, for low Bi$_2$WO$_6$ content in WB1 sample, sparse Bi$_2$WO$_6$ nanosheets grown on Bi$_2$O$_3$ rods are observed, so only a small number of p-n junctions are generated, leading to a low photocatalytic activity. When the Bi$_2$WO$_6$ content is increased in the WB2 sample, a large number of p-n junctions are formed, thus resulting in the highest photocatalytic activity for the optimal WB2 sample. With the Bi$_2$WO$_6$ content further increasing dense Bi$_2$WO$_6$ nanosheets almost cover the Bi$_2$O$_3$ rods, as observed in WB3 sample (Fig. 2h), which decreases the light irradiation on Bi$_2$O$_3$ rods and the p-n junction interfaces. This shielding effect of dense Bi$_2$WO$_6$ nanosheets coating on the Bi$_2$O$_3$ rods makes the photocatalytic activity of WB3 sample decrease. When WB2, Bi$_2$O$_3$, Bi$_2$WO$_6$ and P25 are used as photocatalysts, the degradation efficiencies of phenol are 100%, 44%, 13% and 2% in 60 min under solar light irradiation, respectively. Moreover, when WB2 was used as photocatalyst, the absorption peaks at 270 nm and 208 nm disappeared completely in 120 min (Fig. 7b). The total organic carbon (TOC) was measured, and results show that the phenol molecules can be thoroughly mineralized. Above facts clearly show that the as-obtained WB2 p-n junction structure owns outstanding photocatalytic capacity and can be used in environmental treatment and protection. The UV-vis absorbance spectra of phenol using different samples as photocatalysts are shown in Fig. S3.

In order to further evaluate the photodegradation capacity of Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n junction structures, the degradation of RhB aqueous solution under solar light irradiation was carried out. As shown in Fig. 5a, Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n junction photocatalysts display better degradation efficiency for RhB than pure Bi$_2$O$_3$ and Bi$_2$WO$_6$, and WB2 sample displays the best photocatalytical activity which can degrade 100% RhB in 60 min. Moreover, the absorption peaks of the RhB at 554 nm and 200 nm disappear completely after 60 min reaction, and no new peaks appear (Fig. 8b) using WB2 as photocatalyst. This lies in two facts: i) the removal of the ethyl groups and cleavage of the whole chromophore structure (cycloreversion) occurs simultaneously for RhB molecules during the photocatalytic process; ii) all RhB molecules are completely degraded. The comparison of the degradation of RhB using Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n heterojunctions (WB1–WB5) as photocatalysts is given in Fig. S4. It can be found that with the Bi$_2$WO$_6$ content increase (WB1 < WB4 < WB2), more and more p-n junctions are formed, which results in the highest photocatalytic activity for the optimal WB2 sample. However, with further increasing the Bi$_2$WO$_6$ content (WB2 < WB5 < WB3), dense Bi$_2$WO$_6$ nanosheets shield the light irradiation on Bi$_2$O$_3$ rods and the p-n junction interfaces and then result in the lowest photocatalytic activity for WB3 sample.

WB2 has also good photocatalytic performance for the degradation of RhB aqueous solution under visible light irradiation ($\lambda > 400$ nm) (Fig. S5a), and displays higher photocatalytic activity than Bi$_2$O$_3$-Bi$_2$WO$_6$ heterostructures reported in ref 24 and 25. However, the degradation mechanism of RhB molecules is different from that under solar light irradiation. The UV-Vis absorbance spectra of RhB molecules (Fig. S5b) after photocatalytic reaction indicate that the removal of the ethyl groups is the first stage and then cleavage of the whole chromophore structure (cycloreversion) occurs in RhB molecules by the visible light irradiation. 

To investigate the stability of photocatalytic performance in solar light region, the WB2 sample was used to degrade RhB dye in six repeated cycles, and the results are shown in Fig. 9. It is noteworthy that WB2 photocatalyst exhibits good photocatalytic performance under solar light irradiation (Fig. 9a), and its photocatalytic efficiency only reduces 2% after six repeated cycles. From the SEM image, we also find that WB2 still retained the original structure (Fig. 9b) after six repeated cycles. The XPS spectrum of the WB2 after being reused for six times to degrade RhB dye is also carried out to prove the photocatalytic stability of WB2 sample under solar light irradiation. As shown in Fig. 4 (ii), Bi species are still in the form of Bi$^{3+}$, and W exists in the form of W$^6$, demonstrating its high stability in the process of photocatalysis.
To determine the relative positions of conduction band (CB) and VB edges, the total densities of states of VB for Bi$_2$O$_3$, Bi$_2$WO$_6$ and WB2 were measured, as shown in Fig. 10. In contrast to Bi$_2$O$_3$, the VB maximum of WB2 is down-shifted from 1.30 to 1.71 eV. Compared to Bi$_2$WO$_6$, the VB maximum of WB2 is up-shifted from 2.24 to 1.71 eV. The shift of VB maximum position for WB2 can be attributed to the formation of heterojunction, as confirmed by XRD and TEM results.

According to the VB edges of Bi$_2$WO$_6$ and Bi$_2$O$_3$, and combined with band gap derived from DRS, the CB edge potentials of the two semiconductors can thus be obtained by using the equation of $E_{CB} = E_{CB} - E_F$. So, the energy band structures of Bi$_2$O$_3$ and Bi$_2$WO$_6$ is easy to be generated (Fig. 11a). For p-type Bi$_2$O$_3$, its Fermi energy level is close to the valence band, while for n-type Bi$_2$WO$_6$ its Fermi energy level is close to the conduction band. When the two semiconductors are in contact to form p-n junction (Fig. 11b), there is diffusion of electrons from Bi$_2$WO$_6$ to Bi$_2$O$_3$ due to their different Fermi energy level, resulting in accumulation of negative charges in Bi$_2$O$_3$ close to the junction. At the same time, the holes transfer from Bi$_2$O$_3$ to Bi$_2$WO$_6$, leaving a positive section in Bi$_2$WO$_6$ near the junction. Meanwhile, the energy bands of Bi$_2$O$_3$ shift upward along the Fermi level and those of the Bi$_2$WO$_6$ shift downward along its Fermi level (Fig. 11b). With equilibration of Bi$_2$O$_3$ and Bi$_2$WO$_6$, Fermi levels, the diffusion of electrons from Bi$_2$WO$_6$ to Bi$_2$O$_3$ stops. Therefore, an equilibrium state is formed and an inner electric field will also be generated at the interface. Under the solar/visible light irradiation, Bi$_2$O$_3$ with narrow band gap is excited and photocarriers and holes are generated. The excited electrons on the conduction band of p-type Bi$_2$O$_3$ transfer to that of n-type Bi$_2$WO$_6$, while the holes remain in the valence band of p-type Bi$_2$O$_3$. Furthermore, the migration rate of the photogenerated electrons and holes could be promoted by the internal electric field in the Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n heterojunctions and the photocatalytic activity is largely enhanced.

According to Fig. 10 and Fig. 11, it can be seen that the electronic structure of Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n junction structure matches well with the redox potential of hydrogen and oxygen molecules, namely, the bottom level of the conduct band has to be more negative than the redox potential of H$^+/\text{H}_2$ (0 eV vs normal hydrogen electrode (NHE)); the top level of the valence band has to be more positive than the oxidation potential of O$_2$/H$_2$O (1.23 eV). The experiments of photocatalytic water splitting into O$_2$ were performed (Fig. S6) using Bi$_2$O$_3$-Bi$_2$WO$_6$ as a photocatalyst. It can be found O$_2$ production is about 70 mL g$^{-1}$ in 4 h under 300 W Xe light irradiation.

As well known, many factors influence the photocatalytic activity of a photocatalyst, such as BET surface area, size of particles, etc. Prepared Bi$_2$WO$_6$ flower owns larger BET surface area than that of WB2, but its photocatalytic activity is much poorer than that of WB2 (Fig. 7, 8). This is mainly attributed to the formation of p-n junction in the WB2 sample.

**Conclusions**

In summary, the novel p-n junction photocatalysts of Bi$_2$O$_3$ rods-Bi$_2$WO$_6$ nanosheets have been prepared for the first time. Bi$_2$WO$_6$ nanosheets vertically grow on the Bi$_2$O$_3$ nanorods along the axial direction. The obtained Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n heterojunctions exhibit higher photocatalytic activity than pure Bi$_2$WO$_6$ and Bi$_2$O$_3$ for the degradation of phenol and RhB under solar/visible light irradiation. Phenol and RhB can be completely degraded in 60 min under solar light irradiation using Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n heterojunction as photocatalyst. This good photocatalytic activity is ascribed to the synergistic effects: (a) extended absorption in the visible light region; (b) formation of p-n junction enhancing the separation of photogenerated carriers; (c) 1D ordered nanostructure is favourable for high efficient and directional transport and separation of electrons and holes. This study provides a general and effective method to fabricate unique 1D Bi$_2$O$_3$-Bi$_2$WO$_6$ p-n junction photocatalyst on a large scale. Moreover, this route would offer new insight into the design and fabrication of other advanced materials with heterojunction structures for photocatalytic applications.

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**Notes and references**

A novel one-dimensional Bi$_2$O$_3$ nanorods-Bi$_2$WO$_6$ nanosheets p-n junction photocatalyst was prepared. This Bi$_2$O$_3$-Bi$_2$WO$_6$ heterostructure exhibits high photocatalytic activity for the degradation of phenol and Rhodamine B (RhB) under solar/light light irradiation, which is ascribed to the extended absorption in the visible light region and the effective separation of photogenerated electrons and holes by the internal electrostatic field in the junction region.