A one-step hydrothermal preparation strategy for layered BiO₄/Bi₂WO₆ heterojunctions with enhanced visible light photocatalytic activities†

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Through the introduction of a new Bi-based semiconductor BiO₄, the novel BiO₄/Bi₂WO₆ heterojunctions composed of two layered structures were successfully fabricated by a one-step hydrothermal method. The as-prepared samples were thoroughly characterized by XRD, SEM, TEM, HRTEM, XPS, ICP, DRS and PL spectra technologies. The photodegradation experiments indicated that the BiO₄/Bi₂WO₆ composites showed much higher visible-light-driven (VLD) photocatalytic activity than those of either individual BiO₄ and Bi₂WO₆ for rhodamine B (RhB) degradation, which are attributed to the high separation of photogenerated electron–hole pairs resulted by the BiO₄/Bi₂WO₆ heterojunctions. This is the first report of the photocatalytic activity of the new Bi-based compound BiO₄ and BiO₄/Bi₂WO₆ composites under visible light. Moreover, our research provided a new layered semiconductor, which can be applied in the future for heterojunction construction and energy band structure design.

Introduction

Photocatalytic technology has attracted much attention for offering great potential use in organic wastewater treatment for environmental remediation.1–3 Though TiO₂ is the most widely researched photocatalyst, it suffers from many problems, including the poor catalytic stability, high recombination of photogenerated electron–hole pairs and especially the low solar energy conversion efficiency due to its large energy bandgap.4–6 In order to cope with these problems, great efforts have been made on the development of new photocatalysts with visible light response and improvement of the photocatalytic activity.6 Among which, fabrication of heterojunction photocatalysts by coupling of two semiconductors with appropriate band edges has been a significant approach as a novel strategy.7–9 In the heterojunction composites, the recombination of photogenerated electron–hole pairs can be effectively suppressed through a charge transfer, thus resulting in high photocatalytic activity. Nevertheless, the construction of heterojunction system is not easy because the energy levels of the two semiconductors must be well-matched overlapping band-structures. Therefore, seeking for coupling photocatalysts with matched conduction band (CB) and valence band (VB) has been the most crucial problem.

Bismuth tungstate (Bi₂WO₆), with perovskite-like structure, is one of the simplest members and probably the most studied example of the Aurivillius oxide family. It possesses a layered structure composed of alternating bismuth oxide (Bi₂O₂)²⁺ layers and (WO₄)²⁻ octahedral layers,18 which is considered to promote the generation and the separation of the charge carriers, and thus, Bi₂WO₆ exhibits excellent photocatalytic activity under visible light irradiation.19–22 To further improve the photocatalytic activity of Bi₂WO₆, various strategies were adopted, including element doping (such as B, Fe, Eu, etc.),11–15 solid-solution design (such as BiₓWₓMo₁₋ₓO₆, BiₓY₁₋ₓWO₆ etc.),16,17 forming p–n heterojunction,18 as well as coupling with heterogeneous semiconductors.19–23 Up to now, several kinds of Bi₂WO₆ based heterojunctions have been developed, for instance, TiO₂/Bi₂WO₆,19 ZnWO₄/Bi₂WO₆,20 WO₃/Bi₂WO₆,21 BiOI/Bi₂WO₆ (ref. 22) and Ca₂N/Ca₂Bi₂WO₆,23 etc.

BiO₄ is a new bismuth iodate as a nonlinear optical material synthesized by Nguyen et al. recently.24 It also exhibits a layered structural topology. Instead of a perovskite-like anion block separating the (Bi₂O₂)²⁺ layers in Aurivillius phases, the locally polar iodate (IO₃)⁻ anions are observed between (Bi₂O₂)²⁺ layers in the structure of BiO₄. This layered configuration will also be favorable for charge transfer. By investigating the energy levels of BiO₄, it is fortunate to find that the energy levels of BiO₄ and Bi₂WO₆ are well-matched overlapping band-structures. Thus, they may be suitable to construct a heterojunction with a high visible light catalytic activity.

Herein, we successfully fabricated the BiO₄/Bi₂WO₆ heterojunctions containing two layered structures via a one-step hydrothermal method. The photocatalytic experiments under visible light irradiation showed that the present BiO₄/Bi₂WO₆
heterojunction possesses excellent photocatalytic activity for degrading rhodamine B (RhB) under visible light irradiation, which is much higher than those of either individual BiIO₄ or Bi₂WO₆. Accordingly, a reasonable model is proposed to illustrate the key roles of BiIO₄ in the photocatalytic process. It is noteworthy that this is the first report regarding the photocatalytic decomposition for organic compounds of BiIO₄ and BiIO₄/Bi₂WO₆ composite under visible light.

**Experimental section**

**Synthesis**

All the reagents used were AR grade and without further purification. BiIO₄/Bi₂WO₆ heterojunction was obtained by a hydrothermal method. In a typical procedure, 2.42 g Bi(NO₃)₃·5H₂O was added to 30 ml deionized water, and the breaker was placed in an ultrasonic bath for 10 min to dissolve raw materials. Meanwhile, a certain amount of I₂O₅ and Na₂WO₄·2H₂O were dissolved in 30 ml deionized water to obtain a clear solution. Then, the solution was added to the suspension and subsequently stirred for another 3 h at room temperature. The resulting white suspension was subsequently transferred into a 100 ml Teflon-lined stainless autoclave and heated at 180 °C for 24 h. After cooling, the products were collected by filtration and washed repeatedly with deionized water and ethanol and then dried at 60 °C for 12 h. According to this method, different molar ratios of BiIO₄/Bi₂WO₆ at 2%, 5%, 10% and 15% were prepared, respectively. The pure BiIO₄ and Bi₂WO₆ samples were also synthesized under the same conditions as references.

**Characterizations**

The crystal structures of the obtained samples were examined by X-ray diffraction (XRD) using a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu Kα radiation (λ = 1.5418 Å). The scanning step width of 0.02° and the scanning rate of 0.2° s⁻¹ were applied to record the patterns in the 2θ range of 10–70°. The morphology and microstructure were obtained by a S-4800 scanning electron microscope (SEM) and a transmission electron microscopy (TEM and HRTEM; JEM-2100F). X-ray photoelectron spectroscopy (XPS) analysis was performed on a VGMK II X-ray photoelectron spectrometer. A Varian 710-ES (Varian, Shanghai, China) inductively coupled plasma optical emission spectrometer (ICP-OES) with Sepex Certiprep standards was used to analyze the element of composition of the samples. UV-vis spectra were performed with sample powder from Perkin Elmer Lambda 35 UV-vis spectrometer. The spectra were collected at 200–1000 nm referenced to BaSO₄. Room temperature excitation and emission spectra were measured on a JOBIN 10 YVON FluoroMax-3 fluorescence spectrophotometer with a photomultiplier tube 11 operating at 400 V, and a 150 W Xe lamp was used as the excitation lamp.

**Photocatalytic evaluation**

Photocatalytic activities of BiIO₄/Bi₂WO₆ heterojunctions were evaluated by degradation of RhB under visible light irradiation of a 1000 W Xenon lamp with the 400 nm cutoff filter. Powder photocatalyst (50 mg) was dispersed into 50 ml of dye solution (10⁻⁵ mol l⁻¹). Before illumination, the photocatalyst powder and dye solution were vigorously stirred in dark for 1 h to achieve the adsorption–desorption equilibrium of suspensions. After that, the light was turned on, and 2 ml of the suspension was taken at certain intervals and separated through centrifugation. The UV-vis spectra of the centrifuged solution were recorded using a U-3010 spectrophotometer.

**Results and discussion**

**Characterization of BiIO₄/Bi₂WO₆ heterojunctions**

BiIO₄ crystallizes in orthorhombic space group Pca2. In the asymmetric units, there are only one crystallographically independent Bi atom, one independent I atom and four independent O atoms. The Bi–O and I–O distances range between 2.246(6)–2.581(3) Å and 1.813(4)–1.844(4) Å respectively. The structure may be described as containing layers of (Bi₂O₂)²⁺ cations that are connected to (IO₃)⁻ anions. The (Bi₂O₂)²⁺ layers are structurally analogous to that observed in Bi₂WO₆ with Aurivillius structure. The crystal structures of Bi₂WO₆ and BiIO₄ were shown in Fig. 1a and b, respectively. It can be seen that they possess very similar crystal structures, except the space between [Bi₂O₂]²⁺ layers were filled with WO₆ octahedra and IO₄ groups in Bi₂WO₆ and BiIO₄, respectively.

![Fig. 1 Crystal structures of (a) Bi₂WO₆ and (b) BiIO₄.](image-url)
The XRD patterns of Bi$_2$WO$_6$, BiIO$_4$ and BiIO$_4$/Bi$_2$WO$_6$ heterojunctions were presented in Fig. 2. Due to the low content of BiIO$_4$ and high intensity of Bi$_2$WO$_6$ diffraction peaks, only one diffraction peak of orthorhombic BiIO$_4$ (ICSD #262019) appeared when the molar ratio of BiIO$_4$/Bi$_2$WO$_6$ is from 0.1 to 0.15, and the strongest peak of BiIO$_4$ is attributed to (121) plane, which is in good agreement with the following HRTEM analyses. No impurity peak is found in BiIO$_4$/Bi$_2$WO$_6$ composites, suggesting that the heterojunction has a two-phase composition: BiIO$_4$ and Bi$_2$WO$_6$.

Fig. 3 shows the SEM images of BiIO$_4$, Bi$_2$WO$_6$, and BiIO$_4$/Bi$_2$WO$_6$ composite photocatalysts with different molar ratios, respectively. The pure Bi$_2$WO$_6$ products (Fig. 3a) were composed of a number of regular nanosheets with sizes of several hundred nanometers and thicknesses below 50 nm, and the pure BiIO$_4$ sample also displays flakelike morphologies with the size ranging from several hundred nanometers to tens of micrometers (Fig. 3f). After introducing BiIO$_4$ onto the surface of Bi$_2$WO$_6$, the BiIO$_4$/Bi$_2$WO$_6$ heterostructures were formed as shown in Fig. 3b–e. Though the size of Bi$_2$WO$_6$ in all these heterojunctions is similar to that of the pristine Bi$_2$WO$_6$, the morphologies of the composite became gradually irregular compared to pure Bi$_2$WO$_6$ nanosheets as the increase of the content of BiIO$_4$, which indicates the formation of BiIO$_4$/Bi$_2$WO$_6$ heterostructures.

The obtained 10% BiIO$_4$/Bi$_2$WO$_6$ heterojunction was further characterized by TEM and HRTEM. The low and high magnification TEM image in Fig. 4a and b confirmed that products were all composed of nano-flakes, but more irregular than pure Bi$_2$WO$_6$ (Fig. S1†). From Fig. 4b, it can be clearly seen that the thicknesses of these nano-flakes are estimated to be only several nanometers. The HRTEM image and fast Fourier transform (FFT) images (Fig. 4c–e) of BiIO$_4$/Bi$_2$WO$_6$ heterojunction confirm the two phases BiIO$_4$ and Bi$_2$WO$_6$ and their single crystal nature. The lattice resolved HRTEM image from inverse FFT indicates that the two sets of lattice fringes with spacings of 0.314 nm and 0.326 nm, which are consistent with the spacing of (131) and (121) planes of orthorhombic Bi$_2$WO$_6$ and BiIO$_4$, respectively.

To further confirm the BiIO$_4$/Bi$_2$WO$_6$ heterojunctions, we have carried out the XPS and ICP-OES measurements on the 10% BiIO$_4$/Bi$_2$WO$_6$ sample. The overall XPS spectra for the 10% BiIO$_4$/Bi$_2$WO$_6$ was shown in Fig. 5a, in which the Bi, W, O and I peaks could be detected for the 10% BiIO$_4$/Bi$_2$WO$_6$ composites. Fig. 5b–e are the high resolution XPS spectra of Bi 4f, W 4f, O 1s and I 3d respectively. It can be seen that, the binding energies of Bi 4f$_{7/2}$, Bi 4f$_{5/2}$, W 4f$_{7/2}$, W 4f$_{5/2}$, and O 1s were 159.4, 164.6, 35.6, 37.8, and 530.2 eV, respectively. The I 3d region exhibit the characteristic peaks at 619.5 and 631.4 eV, which
were ascribed to I 3d$_{3/2}$ and I 3d$_{5/2}$, respectively. Moreover, the ICP results indicated the molar ratio of Bi : I : W = 21.3 : 1 : 9.8, which is in agreement with the expected value in 10% BiIO$_4$/Bi$_2$WO$_6$ sample. These results all demonstrate the BiIO$_4$/Bi$_2$WO$_6$ heterojunction are well formed.

Fig. 6 displayed the UV-vis diffuse reflectance absorption spectra (DRS) of the as-prepared BiIO$_4$, Bi$_2$WO$_6$, and BiIO$_4$/Bi$_2$WO$_6$ photocatalysts. Compared with pure Bi$_2$WO$_6$, the BiIO$_4$/Bi$_2$WO$_6$ composites all exhibit blue-shifts on the absorption edges. Since the visible light absorption of Bi$_2$WO$_6$ was caused by band gap transition, the absorption vs. energy was plotted. As shown in the inset (a) of Fig. 6, the band gap of Bi$_2$WO$_6$ was estimated to be 2.7 eV. In semiconductors, the square of absorption coefficient is linear with energy for direct optical transitions in the absorption edge region; whereas the square root of absorption coefficient is linear with energy for indirect transitions. Data plots of absorption$^{1/2}$ versus energy in the absorption edge region for BiIO$_4$ shown in the inset (b) of Fig. 6 is nearly linear, which indicate the absorption edge of BiIO$_4$ is caused by indirect transitions. Band gap of BiIO$_4$ is determined...
by optical absorption near the band edge by the following equation:

$$a_{hv} = A(hv - E_g)^{n/2}$$  \(1\)

where \(a\), \(hv\), \(A\), and \(E_g\) are optical absorption coefficient, the photonic energy, proportionality constant, and band gap, respectively. In this equation, \(n\) decides the type of the transition in a semiconductor (\(n = 1\), direct absorption; \(n = 4\), indirect absorption). By applying \(n = 4\), the indirect band gap of BiO\(_4\) is determined from the plot of absorption \(1/2\) versus energy, as presented in the inset (b) of Fig. 6. By extrapolating the straight line to the \(x\)-axis in this plot, the \(E_g\) of BiO\(_4\) was estimated to be 2.99 eV.

**Photocatalytic study of BiO\(_4\)/Bi\(_2\)WO\(_6\) heterojunctions**

On the basis of the above results, the photodegradation of RhB has been investigated to evaluate the photocatalytic activity of as-synthesized BiO\(_4\)/Bi\(_2\)WO\(_6\) heterojunctions under visible light irradiation. The characteristic absorption peak at 554 nm was employed to determine the degradation degree of RhB. As displayed in Fig. 7a, the blank experiment (without photocatalysts) shows that RhB molecules are very stable and the photolysis is negligible. As for the pure BiO\(_4\) and Bi\(_2\)WO\(_6\), they show relatively poor activity, on which approximately 10% and 55% of MO are decomposed after irradiation for 3 h. When BiO\(_4\) and Bi\(_2\)WO\(_6\) were combined to construct BiO\(_4)/Bi\(_2\)WO\(_6\) heterostructures, it can be found that the content of BiO\(_4\) dramatically affects the photocatalytic activities of BiO\(_4)/Bi\(_2\)WO\(_6\) even though the content of BiO\(_4\) was very low. The photocatalytic activities of BiO\(_4)/Bi\(_2\)WO\(_6\) heterojunctions with molar ratio 2%, 5% and 10% is significantly improved compared with pure BiO\(_4\) and Bi\(_2\)WO\(_6\), while it decreases with the further increase of BiO\(_4\) content. When the theoretical molar ratio of BiO\(_4\) to Bi\(_2\)WO\(_6\) was 10%, the highest photocatalytic activity was obtained, resulting in the degradation efficiency of RhB 95.5% after 3 h irradiation. As shown in Fig. 7b, the main absorption peak of RhB molecules at 554 nm decreases with irradiation time, and almost disappears after about 3 h. In order to compare the degradation rate quantitatively, the first order kinetics curves (Fig. S2†) and RhB photodegradation apparent rate constants (Fig. 7c) were also plotted. The experimental data obviously showed the apparent rate constant \(k\) is 0.032 h\(^{-1}\), 0.38 h\(^{-1}\), 0.56 h\(^{-1}\), 1.10 h\(^{-1}\), 0.23 h\(^{-1}\) and 0.27 h\(^{-1}\) for pure BiO\(_4\), 2% BiO\(_4)/Bi\(_2\)WO\(_6\), 5% BiO\(_4)/Bi\(_2\)WO\(_6\), 10% BiO\(_4)/Bi\(_2\)WO\(_6\), 15% BiO\(_4)/Bi\(_2\)WO\(_6\) and pure Bi\(_2\)WO\(_6\), respectively. In other words, 10% BiO\(_4)/Bi\(_2\)WO\(_6\) exhibits the highest photocatalytic activity, which is almost 34.4 and 4.1 times higher than those of pure BiO\(_4\) and Bi\(_2\)WO\(_6\), respectively, which suggests that BiO\(_4)/Bi\(_2\)WO\(_6\) is an excellent composite photocatalyst under visible light.

Photoluminescence (PL) spectra are a useful technique to survey the separation efficiency of the photogenerated charge carriers in a semiconductor, because PL emission mainly results from the recombination of free carriers.\(^{21}\) In general, the lower the PL intensity, the lower the recombination rate of photogenerated electron–hole pairs, and the higher the photocatalytic activity of semiconductor photocatalysts. Fig. 8 shows the PL spectra of the BiO\(_4)/Bi\(_2\)WO\(_6\) composites at different molar ratios at room temperature compared with that of pure Bi\(_2\)WO\(_6\). It can be seen that 10% BiO\(_4)/Bi\(_2\)WO\(_6\) displays the lowest emission peaks, and thus possess the highest photocatalytic activity which is in good agreement with the result from photodegradation experiment.
According to the above experimental results, the enhanced photocatalytic activity of BiIO4/Bi2WO6 heterojunctions can be mainly attributed to the effective electron–hole separations at the interfaces of the two semiconductors. The photoinduced electron and hole could migrate to the surface to react with the adsorbed reactants, and the migration direction of the photo-generated charge carrier depends on the band edge positions of semiconductors. The band edge positions of the as-prepared semiconductors are theoretically predicted using electronegativity of the constituent atoms, which is defined as the geometric average of the absolute electronegativity of the constituent atoms, $\chi$ is the energy of free electrons on the hydrogen scale (4.5 eV), and $E_g$ is the band gap.

For BiIO4, the $X$ is calculated to be 6.84 eV, consequently. The $E_{CB}$ and $E_{VB}$ are estimated to be 0.85 eV and 3.84 eV, respectively. The $X$ of Bi2WO6 is calculated to be 6.39 eV, and the $E_{CB}$ and $E_{VB}$ are estimated to be 0.52 eV and 3.27 eV, respectively.

Under visible light illumination ($\lambda > 400$ nm), BiIO4 and Bi2WO6 could be excited and induce the generation of photoelectrons and holes. According to their energy band position in Fig. 9, the conduction band gap potential of Bi2WO6 is more negative than that of BiIO4. Therefore, photo-generated electrons on the surface of Bi2WO6 could easily transfer into the conduction band of BiIO4 under the inducement action of the internal electric field, leaving holes on the Bi2WO6 valence band. Meanwhile, the photo-induced holes in the valance band of BiIO4 could be transferred to valance band of Bi2WO6. Thus, the photo-generated electrons and holes in the BiIO4 and Bi2WO6 could be separated effectively in the BiIO4/Bi2WO6 heterojunctions and the recombination of electron–hole pairs can be reduced, resulting in an enhanced photocatalytic activity. In addition, the coupling of two layered structure may also enhance the photoinduced electron–hole separation and transfer. The oxidation and reduction sites in photocatalytic reaction locate at the surface and edge position of two-dimensional layered structure, respectively. Thus, the photogenerated-electrons only travel a very short distance (subnanometer) to reach the surface layer structure, and then were trapped by the hydroxyls in the layer gap. This rapid hole-trapping process allows more photogenerated-electrons more easily move to the edge of the layered structure, reducing the recombination probability of photogenerated-carriers. Thus, the presence of internal electric fields between [Bi2O2] and [WO6]/[IO3] are favorable for the efficient photoinduced electron–hole separation and transfer, which is also propitious to a high-photocatalytic efficiency of BiIO4/Bi2WO6 heterojunctions. However, due to the large band gap of BiIO4, the absorption of visible light will be decreased in BiIO4/Bi2WO6 composites with excess content of BiIO4, which will reduce the photocatalytic activity of the BiIO4/Bi2WO6 composite photocatalyst with more content of BiIO4.

Conclusions

In summary, we have successfully developed a novel BiIO4/Bi2WO6 heterojunction containing two layered structures by a facile hydrothermal method. The resulting composite catalysts were found to be composed of two kinds of nanosheets. The reasonable fabrication of BiIO4/Bi2WO6 heterojunctions is very beneficial for the separation and easy transfer of photogenerated electrons and holes at the intimate interface of heterojunctions, thus resulting in the enhanced visible-light-driven photocatalytic activity. The optimum photocatalytic activity of the 10% BiO4/Bi2WO6 heterojunction for the degradation of RbH was almost 34.4 and 4.1 times higher than those of individual BiIO4 and Bi2WO6, respectively. This result indicated BiIO4/Bi2WO6 heterojunction is an excellent composite photocatalyst under visible light. Moreover, our research provided a new semiconductor, BiIO4, with an Aurivillius-related structure, which can be used for heterojunction construction and energy band structure design.
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Notes and references