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1.5% Bi₂WO₆:Er⁺³ exhibited highest photocatalytic activity as the separation efficiency of the photogenerated electron–hole pairs is enhanced.
Synthesis of Er-doped Bi$_2$WO$_6$ and enhancement in photocatalytic activity induced by visible light

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Bi$_2$WO$_6$:Er$^{3+}$ with hierarchical flower-like microstructures were synthesized by a one-step hydrothermal method. The photocatalysts thus obtained were characterized in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), X-ray photoelectron spectroscopy (XPS) as well as photoluminescence (PL) measurements. Results obtained by XPS confirmed the presence of Er$^{3+}$ dopants in Bi$_2$WO$_6$. Moreover, the results obtained from SEM have shown that doping with Er ions results in hierarchical flower-like microstructures of Bi$_2$WO$_6$. Under visible light irradiation, with an appropriate doping content, the photocatalysts exhibit significant improvement in the photocatalytic activity as the separation efficiency of the photogenerated electron–hole pairs is enhanced. Notably, the photocatalytic activity of 1.5% Bi$_2$WO$_6$:Er$^{3+}$ is 3.69 times that of undoped Bi$_2$WO$_6$. The results indicate that an appropriate doping content can improve photocatalytic activity, caused by wider band gap, hierarchical flower-like microstructures, and defects generated by doping with Er$^{3+}$, which in turn increase the separation efficiency of the photogenerated electron–hole pairs.

For improving the photocatalytic activity of Bi$_2$WO$_6$, doping metal or non-metal elements into Bi$_2$WO$_6$ is an efficient method for decreasing the recombination rate of the photogenerated electron–hole pairs and enhancing the visible light absorption. Thus far, the doping of metal and non-metal elements such as Fe$^{2+}$, Ag$^{2+}$, and F$^{−}$ into Bi$_2$WO$_6$ has already been reported to improve the photocatalytic activity for the degradation of some dyes under visible light. In recent years, the replacement of Bi$^{3+}$ by rare-earth ions such as Y$^{3+}$ and Gd$^{3+}$ has been reported to improve the photocatalytic activity of Bi$_2$WO$_6$. Notably, Y$^{3+}$ and Gd$^{3+}$ are not luminescent active ions, but Er$^{3+}$ is a type of a luminescent active ion. Very few studies have focused on the modification of Bi$_2$WO$_6$ by doping with luminescent active ions. Under the circumstances, the improvement is reached by increasing the number of incoming radiation photons absorbed by the photocatalyst. The luminescent active ions could handle and transform the not absorbed photons into appropriate energy ones.

Er was selected because the electronic structure and light absorption of Er$^{3+}$ are very different from those of Bi$^{3+}$; besides, the ionic radius of Er$^{3+}$ (89 pm) is smaller than that of Bi$^{3+}$ (103 pm), and the lattice parameters of Bi$_2$WO$_6$ may decrease after the substitution of for Bi$^{3+}$ with Er$^{3+}$, thereby resulting in a reduced lattice spacing d. This reduction will significantly affect the optical and surface properties. To the best of our knowledge, a recent paper has explored a TiO$_2$/Bi$_2$WO$_6$-Er with plate-like structure, obtain a conclusion the higher band-gap values in lower Er doped systems would be the cause of a better electron hole separation under UV irradiation. In this paper, Er$^{3+}$-doped Bi$_2$WO$_6$ photocatalysts were synthesized by a one-step hydrothermal method. The samples showing flower-like hierarchical organization...
and were tested under visible irradiation (λ > 420 nm). To investigate the effects and mechanism of Er$^{3+}$ in Bi$_2$WO$_6$, the photocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS), as well as photoluminescence (PL) measurements. With respect of the degradation of rhodamine B (RhB) under visible light (λ > 420 nm), as compared with undoped Bi$_2$WO$_6$, Er$^{3+}$-doped Bi$_2$WO$_6$ exhibited significant enhancement in photocatalytic activity toward the degradation of rhodamine B.

**Result and discussion**

**Characterization of photocatalysts**

Fig 1 shows the XRD results of the samples. As can be observed, obvious diffraction peaks were observed for Bi$_2$WO$_6$, matching those of Bi$_2$WO$_6$ (ICPDS 39-256); peaks were observed at 28.2°, 32.7°, 47.1°, and 55.9°, which correspond to the diffraction peaks of (131), (200), (202), and (133) crystal planes of Bi$_2$WO$_6$, respectively. The strongest peak of Bi$_2$WO$_6$ was attributed to (131) plane, which is in good agreement with the following high-resolution transmission electron microscopy (HRTEM) analyses. Notably, there were no characteristics of the erbium oxide phase in all samples. The Er$^{3+}$ dopant is hypothesized not to affect the crystal structure of Bi$_2$WO$_6$. Nevertheless, because the ionic radius of Bi$^{3+}$ (103 pm) is greater than that of Er$^{3+}$ (89 pm), the lattice parameters of Bi$_2$WO$_6$ decrease when Bi$_2$WO$_6$ is substituted by Er$^{3+}$; therefore, the lattice spacing d decreases.

As shown in the inset in Fig 1, the peaks of Bi$_2$WO$_6$ clearly shifted to higher 2θ angles. Moreover, the cell parameters of undoped Bi$_2$WO$_6$ and 1.5% Bi$_2$WO$_6$:Er$^{3+}$ were determined from XRD data and were found to be a = 5.459 Å, b = 16.454 Å, and c = 5.445 Å for undoped Bi$_2$WO$_6$ and a = 5.452 Å, b = 16.439 Å, and c = 5.441 Å for Bi$_2$WO$_6$:Er$^{3+}$. The decrease of lattice parameters also corresponds to the result of the shift. The result suggests that Er$^{3+}$ is substituted for Bi$^{3+}$ and is successfully doped into the crystal lattice of Bi$_2$WO$_6$.

The morphologies and particle sizes of Bi$_2$WO$_6$:Er$^{3+}$ with different contents of Er$^{3+}$ were investigated by SEM, as shown in Fig 2. Fig 2 a–f shows typical SEM images of undoped Bi$_2$WO$_6$, 0.5% Bi$_2$WO$_6$:Er$^{3+}$, 1% Bi$_2$WO$_6$:Er$^{3+}$, 1.5% Bi$_2$WO$_6$:Er$^{3+}$, 2% Bi$_2$WO$_6$:Er$^{3+}$, and 3% Bi$_2$WO$_6$:Er$^{3+}$, respectively. From Fig 2a, undoped Bi$_2$WO$_6$ exhibited a sheet-like microstructure, with the size of the Bi$_2$WO$_6$ nanosheet being approximately 100–200 nm. On the other hand, Bi$_2$WO$_6$:Er$^{3+}$ (Fig 2b–f) exhibited a hierarchical flower-like microstructure composed of extensive nanosheets with diameters of approximately 4–5 μm. Clearly, Er$^{3+}$ markedly affected the morphology of Bi$_2$WO$_6$. As compared to undoped Bi$_2$WO$_6$, these hierarchical flower-like microstructures, composed of extensive nanosheets, exhibited several advantages. On the one hand, these hierarchical flower-like microstructures can absorb more photon energy because of multiple scattering. On the other hand, because of their large surface area, the photogenerated charge carriers can transport electrons to the interface of Bi$_2$WO$_6$. Besides, several mesopores serve as transport tracers for improving the transfer rate of small organic molecules. Because of the above-mentioned reasons, there is enhancement in the photocatalytic activity of Bi$_2$WO$_6$:Er$^{3+}$ with hierarchical flower-like microstructures.

Fig. 3 shows the TEM and HRTEM images of 1.5% Bi$_2$WO$_6$:Er$^{3+}$. As shown in Fig 3a, hierarchical flower-like microstructures were clearly observed for 1.5% Bi$_2$WO$_6$:Er$^{3+}$. As shown in Fig 3b, after the dispersion of 1.5% Bi$_2$WO$_6$:Er$^{3+}$ in an ultrasonic bath, nanosheets were observed. Fig 3c, d shows HRTEM images of 1.5% Bi$_2$WO$_6$:Er$^{3+}$. As can be observed in the HRTEM images, two sets of lattice fringes were observed with an interplanar spacing of 0.315 nm and 0.273 nm, respectively, which correspond to spacings of (131) and (200) facets of Bi$_2$WO$_6$, respectively.
The chemical states and surface compositions of 3% Bi$_2$WO$_6$:Er$^{3+}$ (Fig. 4) and 1.5% Bi$_2$WO$_6$:Er$^{3+}$ (Fig. S1) were investigated by XPS surface measurements. Fig. 4a shows the full scan XPS spectra of 3% Bi$_2$WO$_6$:Er$^{3+}$; Bi, W, O, and Er were detected. Fig. 4b–e show high-resolution XPS spectra of four primary elements: Bi 4f, W 4f, O 1s, and Er 4d, respectively. Fig. 4b shows the XPS spectra of Bi 4f. The major peaks at 159.42 eV and 164.72 eV were assigned to Bi 4f 7/2 and Bi 4f 5/2, respectively. As shown in Fig. 4c, in the XPS spectra of Bi 4f, peaks were observed at 35.67 eV and 37.82 eV, corresponding to W 4f 7/2 and W 4f 5/2, respectively. Fig 4d shows the XPS spectrum of O 1s. A peak was observed at 530.34 eV, assigned to O 1s. Two others were observed at 531.15 eV and 532.15 eV, attributed to the surface hydroxyl groups. As shown in Fig. 4e, the binding energy (BE) of Er 4d 5/2 increased to 169.8 eV; however, the BE of Er 4d 3/2 in erbium oxide has been reported to be 168.0 eV (32), attributed to the Bi–O bonds in the (Bi$_2$O$_3$)$^{2+}$ sheets of the Bi$_2$WO$_6$ layered structure. Besides, another peak was observed at 532.15 eV, attributed to the surface hydroxyl groups. As shown in Fig. 4e, the binding energy (BE) of Er 4d 5/2 increased to 169.8 eV; however, the BE of Er 4d 3/2 in erbium oxide has been reported to be 168.0 eV (32), attributed to the Bi–O bonds in the (Bi$_2$O$_3$)$^{2+}$ sheets of the Bi$_2$WO$_6$ layered structure.

**Photocatalytic activity**

The photocatalytic activities of P25, undoped Bi$_2$WO$_6$ and Bi$_2$WO$_6$:Er$^{3+}$ were evaluated by the degradation of RhB dye in water under visible light irradiation. Fig. 5a shows the efficiencies of photocatalytic degradation under visible light irradiation. The photolysis of RhB dye was negligible in the absence of the samples, indicating that RhB dye is stable under visible light. Er-doped Bi$_2$WO$_6$ exhibited photocatalytic activity significantly better than that exhibited by undoped Bi$_2$WO$_6$ and P25. Among these photocatalysts, 1.5% Bi$_2$WO$_6$:Er$^{3+}$ exhibited the highest photocatalytic activity, and the photocatalytic degradation of RhB reached 99% within 4 h. As compared to undoped Bi$_2$WO$_6$, 1.5% Bi$_2$WO$_6$:Er$^{3+}$ exhibited an obviously enhancement in photocatalytic activity. The strongest absorption of the RhB solution in the visible region shifted from 554 to 500 nm after 4 h of visible irradiation (Fig. 5b), reflecting the emergence of N-demethylation and de-ethylation in the photodegradation processes. We research what happens to the total organic content. In the photodegradation process, the major absorption band shifted to 500 nm step by step. Under visible irradiation, deethylation of the fully N,N,N′,N′-tetraethylated rhodamine molecule (i.e., RhB) has the wavelength position of its major absorption band moved toward the blue region, λ$_{max}$, RhB, shown in the following equations:

$$-\frac{d[C]}{dt} = k[C].$$

$$-\ln(C/C_0) = kt.$$  

Here, k is the apparent pseudo-first-order rate constant, $C_0$ is the initial concentration after the adsorption–desorption equilibrium, C is the RhB concentration during the irradiation time. As shown in Fig 5c, from experimental data, the apparent rate constants k of undoped Bi$_2$WO$_6$, 0.5% Bi$_2$WO$_6$:Er$^{3+}$, 1.0% Bi$_2$WO$_6$:Er$^{3+}$, 1.5% Bi$_2$WO$_6$:Er$^{3+}$, 2.0% Bi$_2$WO$_6$:Er$^{3+}$, and 3.0% Bi$_2$WO$_6$:Er$^{3+}$ were 0.229, 0.565, 0.783, 0.846, 0.458, and 0.413 h$^{-1}$, respectively. Notably, the photocatalytic activity of 1.5% Bi$_2$WO$_6$:Er$^{3+}$ was 3.69 times that of undoped Bi$_2$WO$_6$.
To further investigate the photocatalytic properties of the Bi$_2$WO$_6$ and Bi$_2$WO$_6$:Er$^{3+}$ catalyst, methyl orange (MO) and methylene blue (MB) dye was also selected to evaluate the photocatalytic activity$^{33}$ (Fig. S2). The 1.5% Bi$_2$WO$_6$:Er$^{3+}$ catalyst exhibited better photodegraded efficiency for the photocatalytic decomposition of RhB, MO and MB dye under visible-light irradiation. Thus, Er$^{3+}$ doping is an effect way to enhance the photocatalytic activity of Bi$_2$WO$_6$.

In order to further confirm the proposed role of O$_2$, we do the photocatalytic study under reduced pressure (10 Pa) (Fig. S3). The result is in agreement with the conclusion above.

**Mechanism of photocatalytic activity enhancement**

Fig. 8a shows UV–vis DRS of synthesized samples. As can be observed, the substitution of Bi$^{3+}$ with Er$^{3+}$ resulted in the blue-shift of the absorption edge. For a semiconductor, UV–vis absorption near the band edge follows the equation.

$$A_{hv} = (\frac{\alpha hv - E_g}{n})^{1/2}$$
Here, $\alpha$, $\nu$, $E_g$, and $h$ represent the absorption, light frequency, band gap, and Planck’s constant, respectively. The $n$ value is associated with different types of transitions, $n = 4$ and 1, which correspond to indirect and direct absorption, respectively. $\text{Bi}_2\text{WO}_6$ is an indirect band gap-type semiconductor. The band gaps of undoped $\text{Bi}_2\text{WO}_6$ and 1.5% Er-$\text{Bi}_2\text{WO}_6$ were determined to be 2.67 eV and 2.72 eV, respectively, as shown in Fig 8b. The band gap of 1.5% Er-$\text{Bi}_2\text{WO}_6$ was wider than that of $\text{Bi}_2\text{WO}_6$, which is favorable for visible-light-driven photocatalytic activity.

The generation and transfer of the photogenerated charge carriers in the photocatalytic process can be indirectly monitored by the generation of photocurrent. Typically, the higher the photocurrent, the higher the separation efficiency of the photogenerated electron–holes. Fig 9a shows the photocurrent–time testing curves of undoped $\text{Bi}_2\text{WO}_6$ and 1.5% Er-$\text{Bi}_2\text{WO}_6$ in the presence or absence of visible light irradiation. As compared to undoped $\text{Bi}_2\text{WO}_6$, 1.5% Er-$\text{Bi}_2\text{WO}_6$ exhibited a distinctly enhanced photocurrent response. The results indicate that the photogenerated electron–hole pairs of 1.5% Er-$\text{Bi}_2\text{WO}_6$ could be separated more effectively than those of undoped $\text{Bi}_2\text{WO}_6$. Hence, Er$^{3+}$ improves the photoelectrochemical property of $\text{Bi}_2\text{WO}_6$. 

Please see the figure captions for detailed explanations of the figures.


Fig. 10 Photoluminescence spectra of Bi$_2$WO$_6$:Er$^{3+}$ (0%, 0.5%, 1%, 1.5%, 2%, and 3%)

Electrochemical impedance spectroscopy (EIS) is an available method for representing the transfer processes of photogenerated electron–holes in the photocatalyst. A small arc radius was observed for the electrode, indicative of low transfer resistance for the interfacial charge carriers. The lower the transfer resistance of the charge carrier, the higher the charge-transfer efficiency. Fig. 9b shows the EIS Nyquist plots of undoped Bi$_2$WO$_6$ and 1.5% Bi$_2$WO$_6$:Er$^{3+}$ in the presence or absence of visible light irradiation. As compared to undoped Bi$_2$WO$_6$, 1.5% Bi$_2$WO$_6$:Er$^{3+}$ exhibited a smaller charge-transfer resistance.

PL measurements are a useful technique for investigating the recombination rate of the photogenerated electron–hole pairs in a semiconductor, because PL emission mainly results from the recombination of photogenerated electron–hole pairs.$^{39}$ In general, a lower PL intensity indicates a lower recombination rate of photogenerated electron–hole pairs, and thus higher photocatalytic activity for semiconductor photocatalysts. Fig. 10 shows the PL spectra of the Bi$_2$WO$_6$:Er$^{3+}$ photocatalysts at different molar ratios as compared to those of undoped Bi$_2$WO$_6$. By contrast, 1.5% Bi$_2$WO$_6$:Er$^{3+}$ exhibited the lowest emission intensity, suggesting that it exhibits the highest photocatalytic activity; this result is in agreement with that obtained for the degradation of RhB under visible light.

In the light of the optical property analysis and active species trapping experiments, the possible photocatalytic mechanism of Bi$_2$WO$_6$:Er$^{3+}$ under visible light irradiation was clarified in Fig. 11. Under visible light irradiation, the photogenerated electrons were excited to the conduction band (CB), and the photogenerated holes were left in the valence band (VB) in the photocatalytic process. The blue-shift of the optical absorption edge occurred after the substitution of Bi$^{3+}$ with Er$^{3+}$, indicating that some energy levels are formed under the VB. The doping of Er$^{3+}$ induces a slight modification of band positions. Such small shift, denoted by the band gap value enlargement, clearly affects the photogenerated charge pairs, causing a better electron hole separation. Besides, under visible light irradiation, the photogenerated electrons were Er$^{3+}$ at the defects sites. Then, the trapped electrons are transferred to the oxygen molecules adsorbed on the surface of Bi$_2$WO$_6$. Those processes can significantly decrease the recombination rate of the photogenerated electron–hole pairs, contributing to the enhanced degradation of RhB by the active hole species. Meanwhile, oxygen molecules adsorbed on the surface of Bi$_2$WO$_6$:Er$^{3+}$ can react with the released electrons to generate another active species, ·O$_2^-$, for the degradation of RhB. However, those processes can effectively enhance the photocatalytic activity of Bi$_2$WO$_6$:Er$^{3+}$. The possible photocatalytic mechanism was in agreement with the result obtained from the active species trapping experiments. Nevertheless, excess Er$^{3+}$ would cover the active sites or operate as the recombination center on Bi$_2$WO$_6$ decreasing the separation efficiency of the photogenerated electron–hole pairs. Hence, the optimum doping concentration of Er$^{3+}$ is 1.5%.

Conclusions

Bi$_2$WO$_6$:Er$^{3+}$ with hierarchical flower-like microstructures was successfully synthesized by a one-step hydrothermal method. The result showed that doping with Er$^{3+}$ led to the hierarchical flower-like microstructures of Bi$_2$WO$_6$. Under visible light irradiation, 1.5% Bi$_2$WO$_6$:Er$^{3+}$ exhibited the highest photocatalytic activity, and the photocatalytic degradation of RhB reached 99% within 4 h. As compared to undoped Bi$_2$WO$_6$, 1.5% Bi$_2$WO$_6$:Er$^{3+}$ exhibited approximately 3.69 times enhancement in photocatalytic activity as the separation efficiency of the photogenerated electron–hole pairs is enhanced. This study suggests that the use of doping ions into Bi$_2$WO$_6$ could be a simple method for the enhancement in photocatalytic activity.

Acknowledgements

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Notes and references

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