Hydrothermal synthesis, characterisation and photocatalytic properties of BiOIO₃ nanoplatelets

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ABSTRACT
In this work, BiOIO₃ nanoplatelets were successfully prepared by a simple hydrothermal method. The as-prepared samples were characterised by energy-dispersive spectroscopy, scanning electron microscopy, high-resolution transmission electron microscopy, X-ray powder diffraction and ultraviolet-visible diffuse reflectance spectroscopy. The photocatalytic activities of the as-prepared BiOIO₃ nanoplatelets were evaluated by photodegradation of rhodamine B (RhB) under simulated solar light. The results showed that the change of temperature within a certain range has almost no influence on the morphology and size of BiOIO₃ nanoplatelets. However, it had an obvious effect on the photocatalytic performance of BiOIO₃ nanoplatelets. The results showed that the BiOIO₃ sample synthesised at 130°C exhibited the highest photocatalytic activities compared to others, with RhB completely decomposed in 80 min. The products with proper crystallinity formed at 130°C have the optimal rate of RhB photodegradation. It indicated that the most favourable crystallinity made it beneficial to improve the photocatalytic activity. The possible mechanism of the photocatalytic reaction based on deep analysis and the experimental results was discussed in detail.

1. Introduction
Photocatalysis has been recognised as a great potential on saving energy and solving water environmental issues, such as solar energy conversion, pollutants decomposition or carbon dioxide reduction.[1–5] Especially, semiconductor photocatalysts have been the focus of researchers for solving the energy crisis and environmental remediation with an easy way of utilising the energy of either natural sunlight or artificial indoor illumination, which is amply available everywhere in the world, on account of ultraviolet light only occupying about 5% of the solar light, less than others. In order to make better use of natural sunlight, it is crucial to develop photocatalysts which can be activated by solar light. In view of the above particular significance, it is also necessary to contain the functional applications that semiconductor material photocatalysts can photodecompose organic pollutants employing the conversion of luminous energy into chemical energy in reactions.

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under solar light. During the past 40 years, a lot of endeavour has been devoted to developing new and optimal photocatalyst systems, including photocatalysts with narrow band gap (BiOBr, Bi₂WO₆), plasmonic photocatalysts (Ag/AgX (X=Cl, Br), Ag/AgCl-AgI and Au), organic photocatalysts (g-C₃N₄) and elemental photocatalysts (B, Si, P and S). [6–19] The semiconductor of bismuth compound is a typical photocatalyst which has attracted extensive attention because of their interesting physical and chemical properties, such as band gaps, electrical and optical properties.[20–22] However, its photocatalytic activity has also been limited by the high recombination rate of the photogenerated electron–hole pairs in the course of photocatalytic reaction.

Recently, a novel semiconductor BiOIO₃ has attracted more interest because of its unique photoelectric properties and excellent photocatalytic performance. The BiOIO₃ sample is constructed by B₂O₄ layers interleaved by slabs comprised of IO₃ pyramids.[23] The superposition of the dipole moments of IO₃ pyramids gives rise to a pyroelectric polarisation in cells, which has been proven to possess the ability to effectively inhibit the recombination of electron–hole pairs.[24] Hence, we developed a hydrothermal method to prepared BiOIO₃ nanoplatelets, and the effect of reaction temperature on its morphology, structure and catalytic activity was studied. The possible mechanisms of photocatalytic degradation were also investigated by adding the corresponding scavengers of the reactive species. The results showed that the proposed synthesis method was a simple, inexpensive route for synthesising the promising BiOIO₃ photocatalyst.

2. Experimental section

2.1. Sample preparation

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 485.07, AR) and potassium iodate (KIO₃, 214.00, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Rhodamine B (RhB) (C₂₈H₃₁ClN₂O₃, 479.01, P95%) was purchased from Sigma-Aldrich. All the chemicals were used without further purification. The BiOIO₃ sample was synthesised as follows: 0.4851 g of Bi(NO₃)₃·5H₂O as the sources of Bi was dispersed in 15 mL aqueous solution. Then, 0.6420 g of KIO₃ dissolved by 25 mL aqueous solution as the sources of IO₃ was added to the earlier suspension and kept continuously stirring for 30 min at room temperature. Then, the mixture was transferred into 50 mL Teflon-lined stainless steel autoclaves. The aqueous suspension was hydrothermally heated at temperature of 110, 120, 130 and 140 °C. After heating for 12 h, the samples naturally cooled down to room temperature. Afterwards, all generated samples were obtained by centrifuging, filtering and rinsing with deionised water and ethanol for three times. Finally, the samples were dried at 60 °C for 12 h.

2.2. Characterisation

The morphologies and microstructures of the obtained products were observed by a scanning electron microscopy (SEM) (Hitachi S-4700) at scanning voltages 15 kV and high-resolution transmission electron microscopy (HRTEM) analyses at an accelerating voltage of 200 kV were conducted by Tecnai G2 F30 microscopy. Chemical compositions of as-prepared samples were explored by energy-dispersive X-ray detector (EDS, Thermo
Noran VANTAG-ESI). The crystal phases of the samples were characterised by X-ray diffraction (XRD) on an X-ray diffractometer (Thermo ARL SCINTAG X’TRA) using CuKα radiation (λ = 0.154056 nm). Ultraviolet visible (UV-Vis) diffuse reflectance spectrum (DRS) of the products was measured at room temperature in the range of 200–800 nm on an UV-Vis spectrophotometer (Lambda 850) equipped with an integrating sphere, and BaSO₄ was used as a reference. X-ray photoelectron spectroscopy (XPS) equipped with Al Kα X-rays (hv = 1486.6 eV) radiation (Thermo ESCALAB 250) was used to study the surface properties.

2.3. Photocatalytic experiments

The photocatalytic activity of the BiOIO₃ samples was evaluated by photodegradation of RhB solution at room temperature under simulated solar light. The light source was equipped with a 300 W Xe lamp and was focused on the beaker. In each experiment, 0.1 g of the as-prepared photocatalyst was dispersed into 200 mL of RhB solution (10 mg/L). Prior to irradiation, the suspension was placed in dark and continuously stirred by a magnetic stirrer for 30 min in order to reach the equilibrium of adsorption–desorption between the catalyst and RhB. Subsequently, at regular intervals of every 10 min, about 3 mL of suspension was sampled and centrifuged to separate the solution from the BiOIO₃ photocatalyst particles. The concentration of RhB was determined by measuring the characteristic absorption at 553 nm using a UV759S UV-Vis spectrophotometer.

3. Results and discussion

The morphologies and microstructures of as-prepared BiOIO₃ at different temperatures (110, 120, 130 and 140 °C) were investigated by SEM and HRTEM, and the results are shown in Figure 1. Figure 1(a–d) reveal that these samples have uniformly platelet-like morphologies with an average size ranging from 50 to 300 nm. HRTEM observation of the nanoplatelets (Figure 1(e)) shows the ordered lattice fringes with inter-planar spacing of 0.325 nm, matching well with the (121) diffraction plane of BiOIO₃. Meanwhile, chemical composition of BiOIO₃ was detected by EDS, and the results of EDS were reasonably agreed with the nominal element composition of Bi, I and O (Figure 1(f)).

XRD analysis was used to check the purity and crystal phase of the as-prepared samples. Figure 2 shows the XRD patterns of the as-prepared BiOIO₃ at different temperatures. All the diffraction peaks can be indexed to orthorhombic BiOIO₃ (space group Pca2₁; a = 506584(4), b = 11.0386(8), c = 5.7476(4) Å) from the database of ICSD (no. 262019) and no other phases can be found, which agree with the phase-pure of BiOIO₃. As can be investigated, the diffraction peaks are getting stronger with the increase of temperature, indicating that the crystallinity of the as-prepared products gets better.

To determine the composition of surface and the electronic state of the BiOIO₃ sample, XPS analysis was further carried out. Figure 3 shows the XPS spectrum of the BiOIO₃ synthesised at 130 °C. It can be observed that two strong peaks at the binding energies of 158.65 and 163.98 eV ascribe to Bi 4f⁷/₂ and Bi 4f⁵/₂, respectively, which indicates the existence of the Bi³⁺ in BiOIO₃ (Figure 3(a)). The two strong peaks around 635.4 and 623.7 eV are attributed to I 3d⁵/₂ and I 3d⁷/₂ states of I⁻⁺ (Figure 3(b)). The O 1s core level
spectra could be deconvoluted into two peaks at binding energies of around 529.1 and 529.8 eV (Figure 3(c)), which can be assigned to the Bi–O and I–O bonds, respectively.

It is well known that the light absorption and the migration of the light-induced electrons and holes play an important role in determining photocatalytic activity. Diffuse reflectance spectrum (DRS) is a useful tool for characterising absorption properties in optical materials. The as-prepared BiOIO₃ nanoplates at 110, 120, 130 and 140 °C were measured by DRS, as shown in Figure 4(a). The series of BiOIO₃ shows the similar absorption edge lack of 400 nm. There are no obvious variations or shifts of the absorption edges. In view of that, the variation of temperature makes no significant difference. It can be seen from Figure 4(b) that the band gaps of these products are calculated to be
following the equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where $\alpha$, $h$, $m$, $A$ and $E_g$ are absorption coefficient, plank constant, light frequency, proportional constant and band gap energy, respectively.\textsuperscript{[25]}

The photocatalytic activity of BiOIO$_3$ nanoplates was evaluated by testing the degradation of RhB under simulated solar light. Figure 5(a) shows that the as-prepared BiOIO$_3$ product at 130 °C has better photocatalytic activity than other products. The degradation rate reached 100% in the presence of BiOIO$_3$ after 80 min under simulated solar light. The corresponding dark adsorption abilities for RhB over as-prepared BiOIO$_3$ nanoplates at 110, 120, 130 and 140 °C were 14.4%, 12.3%, 14.3% and 15.4%, respectively. It is worth noting that the photocatalytic activity of the BiOIO$_3$ can be enhanced with the temperature rising. However, when temperature reached 130 °C, further increasing of temperature leaded to the decline of photocatalytic activity.\textit{According to} the result of XRD analysis, it can be found that the increase of crystallinity can be obtained with increasing the temperature. The results may suggest that crystallinity plays an important role in the improvement of the photocatalytic activity, and the proper degree of crystallinity of the as-prepared BiOIO$_3$ product can be obtained at 130 °C. This is may be due to the fact that the high crystallinity means less defects on the surface of BiOIO$_3$. During the process of photocatalytic reaction, defects can become centres to capture photo-induced electrons.\textsuperscript{[26]} The suitable amount of defects can be the capture centre of photogenerated carriers and the separation of photogenerated electron—hole pairs which contributes to the enhancement of photocatalytic activity. Nevertheless, when the defect existing excessively, it may become the recombination centre of photogenerated electron—hole pairs. The major absorption peak corresponding to RhB gradually shifts from 553 to 505 nm (Figure 5(b)). As can be seen, the characteristic absorption band of RhB diminished quickly. These shifts derived from formation of a sequence of $N$-deethylated intermediates of rhodamine molecule, which will be identified and shown in the following results. The obvious decrease in the maximum absorption indicates that RhB suffered from a destruction of the whole conjugated chromophore. In the previous stage under irradiation, due to the high concentration of RhB and the small quantity of $N$-deethylated intermediates, the shift of absorption band can be omitted. However, with further degradation of RhB...
Figure 3. XPS spectra of the as-prepared BiOIO₃ sample: the spectra in the energy regions of (a) the Bi 4f, (b) the I 3d and (c) the O 1s states.
and the gradual increase of the intermediates in the later stage, the blue shift of spectral got more conspicuous.[27] The stability of the as-prepared BiOIO₃ sample at 130 °C was also evaluated through the recycle of the used catalyst. As shown in Figure 5(c), the photocatalytic efficiency of BiOIO₃ nanoplates for RhB degradation still reached 85% after three cycling runs.

To further ascertain the roles of possible primary active species (such as holes and ⋅OH) existing in the BiOIO₃ photocatalytic degradation process of RhB, the corresponding effective scavengers were added to the reaction system, namely, benzoquinone (as O₂⋅− radical scavenger), ammonium oxalate (as hole scavenger) and isopropanol (as ⋅OH scavenger), respectively. The results show that the addition of holes scavenger, ammonium oxalate into the solutions leads to the depression of the degradation rate of RhB (Figure 6). Meanwhile, the addition of ⋅OH scavenger, isopropanol also weakens the degradation rate of RhB to a lesser extent. These results indicate that h⁺ and O₂⋅− play major parts in the photo-oxidation process, and ⋅OH also has the weak effect.

Figure 4. (Colour online). (a) UV-Vis diffuse reflectance spectra of BiOIO₃ with the synthesised temperature at 110, 120, 130 and 140 °C, and (b) band gap of photocatalysts.
Figure 5. (Colour online). (a) Photodegradation of RhB over the BiOIO₃ at 110, 120, 130 and 140 °C. (b) Absorption spectrum of the RhB solution in the presence of the as-prepared BiOIO₃ at 130 °C. (c) Cycling runs in the photodegradation of RhB in the presence of BiOIO₃ samples.
In fact, the conductance band (CB) and valence band (VB) edge electrochemical potentials of BiOIO₃ semiconductor were the key factors to understanding the photodegradation mechanism of contaminants over BiOIO₃. The flat-band potential of BiOIO₃ was calculated by the Mulliken electronegativity of an atom [28]:

\[
E_{\text{CB}} = X - E_c - 0.5E_g \quad \text{(1)}
\]

\[
E_{\text{VB}} = E_{\text{CB}} + E_g \quad \text{(2)}
\]

where \(E_{\text{VB}}\) is the VB top potential; \(E_{\text{CB}}\) is the CB bottom potential; \(E_g\) is the band gap energy of BiOIO₃; \(X\) is the electronegativity of BiOIO₃, which is the geometric mean of the electronegativity of constituent atoms and \(E_c\) is the energy of free electrons on the hydrogen scale (4.5 eV). The band edge potentials of the CB and VB of BiOIO₃ semiconductor were speculated to be 0.64 and 3.75 eV, respectively. Scheme 1 shows a schematic band structure of BiOIO₃ semiconductor based on the earlier calculation. During the

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**Figure 6.** (Colour online). The effects of ammonium oxalate and isopropanol on the degradation of RhB in the presence of the as-prepared BiOIO₃ at 130 °C.

**Scheme 1.** Photocatalytic mechanism scheme of the BiOIO₃ semiconductor under simulated solar light.
process of photocatalytic degradation, the target compound was first adsorbed by the BiOIO₃ samples. The photogenerated electrons on the CB of BiOIO₃ were captured by oxygen molecules by generating reactive •O₂⁻. As a very efficient oxidising agent, the resulting •O₂⁻ and holes can oxidise most organic compounds into their mineral end products.

4. Conclusion

In summary, BiOIO₃ nanoplates were successfully prepared by a hydrothermal process. The results show that the change of synthesis temperature has almost no obvious effect on the morphologies and particle size of BiOIO₃. In addition, it also makes no difference to the results of DRS. However, the crystallinity and photocatalytic activity of the samples were distinctly affected by the temperature, and the as-prepared BiOIO₃ at 130 °C showed the highest photocatalytic activities with almost all RhB decomposed in 80 min. The results suggest that the proper degree of crystallinity can be obtained at 130 °C and the appropriate amount of defects can act as the capture centre of photogenerated carriers and the effective separation of photogenerated electron–hole pairs. The possible mechanisms are proposed according to the experimental results. The present work suggests that the BiOIO₃ is a promising photocatalyst for the degradation of organic pollutants and environmental remediation.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work is financially supported by the National Nature Science Foundation of China [grant number 21273034].

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