A highly efficient visible-light driven photocatalyst: two dimensional square-like bismuth oxyiodine nanosheets

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Two dimensional (2D) square-like bismuth oxyiodine (BiOI) nanosheets with a thickness of about 10 nm and exposed (001) facets are obtained by a facile hydrothermal route without any surfactant and special solvent. The photocatalytic performance of as-prepared 2D square-like BiOI nanosheets is evaluated by the photodegradation of rhodamine-B (RhB), methyl orange (MO) and phenol under visible-light irradiation. The products show highly efficient photocatalytic performance and good photostability and recyclability under visible light irradiation. The efficient visible-light driven photocatalytic activity can be ascribed to the thin 2D square shape nanosheet with exposed (001) facets, which provides an appropriate diffusion length and self-induced internal static electric field direction of BiOI, and improves the separation efficiency of photoinduced electron–hole pairs in BiOI nanosheets. Furthermore, the thin nanosheets that have a greater percentage of (001) facet exposure could induce stronger internal static electric fields, and improve the photocatalytic activity.

1. Introduction

Since the discovery of photocatalytic splitting of water on TiO2 electrodes in 1972 by Honda and Fujishima,1 efficient utilization of solar energy for photocatalysis towards environmental purification and solar energy conversion has been attracting massive research interest.2,3 Various photocatalysts have been prepared and used in photocatalytic water splitting and photodegradation of organic pollutants.4–10 However, the photocatalysis of many photocatalysts is limited only under ultraviolet irradiation (λ < 380 nm). Therefore, it is still of great significance to develop visible-light driven photocatalysts for highly efficient solar utilization.

Recently, as a series of novel layered ternary oxide semiconductors, bismuth oxyhalides (BiOX, X = Cl, Br, and I) have received much attention because of their excellent photocatalytic performances.11–18 Bismuth oxyhalides possess a layered structure (as shown in Fig. 1), which is consisting of [Bi2O2]X2− slabs separated by double slabs of halogen atoms. The space of layered structures is large enough to increase for polarizing the related atoms and orbitals. The induced dipole could then improve the separation efficiency of the hole–electron pairs. With the benefits from their open and layered crystalline structures, the bismuth oxyhalides show outstanding photocatalytic performances. BiOCl shows better photocatalytic activity than TiO2 under ultraviolet irradiation. Furthermore, bismuth oxyhalides can extend light absorption to the visible light range. It is highly important for the direct use of sunlight.

As is known, the properties of materials are determined by their crystalline structures. Meanwhile, the morphology of structures also plays important roles. Profiting from high specific surface areas and the large fraction of uncoordinated surface atoms, quasi-two-dimensional (quasi-2D) materials have attracted high research interest.12,16,19–21 For photocatalytic applications, the exposed surface atoms of quasi-2D materials could easily escape from a lattice to form vacancies.

Fig. 1 Schematic representation of the crystal structure of BiOX: (a) crystal structure of BiOX; (b) (001) facets of BiOX; and (c) [Bi2O2]X2− layers of BiOX.
that could have a strong advantageous effect on the photocatalytic performance.\textsuperscript{12} Especially quasi-2D structures of bismuth oxyhalide shall have largely improved photocatalytic performance, which has been partially approved recently by the excellent visible light photoactivity of BiOCl nanosheets.\textsuperscript{11,12,16} For even better visible light absorption compared with BiOCl, various morphologies of BiOI ($E_g = 1.77–1.92$ $\text{eV}$) photocatalysts have also been fabricated.\textsuperscript{14,22–27} However, so far the quasi-2D nanostructure of BiOI has rarely been realized and reported. Therefore, nowadays, how to achieve quasi-2D nanostructure of BiOI represents a timely research topic within the field of photocatalytic application of BiOX. In this paper, using a cost-effective and environmentally friendly hydrothermal process, 2D square-like BiOI nanosheets with a high percentage of exposed {001} facets were achieved. Different from most of the conventional hydrothermal processes using surfactants or special solvents that incur high experimental costs, our non-surfactant process and aqueous system are highly desirable for reducing the cost. More importantly, these quasi-2D nanosheets show superior visible-light photocatalytic performance, which originates from the highly exposed active facets and several-nanometer thickness of the quasi-2D nanosheets. It is found that after only 15 min of visible light irradiation, the decolouration ratio of RhB and MO reaches 90% and 94%, respectively.

2. Experimental

2.1. Materials

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) was obtained from Sigma-Aldrich Co. LLC. All other chemicals were of analytical grade purity, obtained from Alfa Aesar GmbH & Co KG, and used as received without further purification.

2.2. Synthesis of 2D square-like BiOI nanosheets

The 2D square-like BiOI nanosheets were synthesized using a simple hydrothermal process. In a typical synthesis, 0.485 g of Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 20 mL of 0.1 M HNO$_3$ solution with vigorous stirring for 20 min. Next, 20 mL of 0.02 M KI solution was added dropwise into the above solution. Then, the pH value was adjusted to 5 using 5 M KOH solution, yielding a uniform light-yellow suspension. After another 20 min of agitation, the mixture was transferred into a 50 mL capacity Teflon-lined stainless steel autoclave, and this autoclave was heated at a temperature of 120 $^\circ$C for 6 h and then cooled to room temperature naturally. The resulting brick-red solid powder was collected by centrifugation and washed with deionized water several times to remove residual ions. The final products were then dried at 30 $^\circ$C for 4 h for further characterization.

2.3. Synthesis of BiOI microplates

For the BiOI microplates, 2.425 g of Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 20 mL of 0.1 M HNO$_3$ solution with vigorous stirring for 20 min. Next, 20 mL of a 0.1 M KI solution was added dropwise into the above solution, which yielded a uniform brick-red suspension. After another 20 min of agitation, the mixture was transferred into a 50 mL capacity Teflon-lined stainless steel autoclave, and this autoclave was heated at a temperature of 120 $^\circ$C for 6 h and then cooled to room temperature naturally. The resulting brick-red solid powder was collected by centrifugation and washed with deionized water several times to remove residual ions. The final products were then dried at 30 $^\circ$C for 4 h for further characterization.

2.4. Characterization

Powder X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance equipped with graphite monochromatized high-intensity Cu Kα radiation ($\lambda = 1.54178$ Å). The scanning electron microscopy (SEM) images were obtained using a HITACHI S4800 scanning electron microscope. The transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010F operated at an acceleration voltage of 100 kV. High-resolution transmission electron microscopy (HRTEM) and the corresponding selected area electron diffraction (SAED) analyses were performed at an acceleration voltage of 200 kV. Room-temperature UV-Vis absorption spectroscopy was carried out on a Varian Cary 5000 UV-VIS-NIR spectrophotometer. The Brunauer–Emmett–Teller (BET) surface areas were measured by nitrogen adsorption on an ASAP2020M accelerated surface area and porosimetry system.

2.5. Photocatalytic measurement

Visible light photocatalytic activities of the as-prepared products were evaluated by examining the photodegradation of RhB, MO and phenol under visible light irradiation from a 300 W Xe lamp with a 420 nm cut-off filter simulating the AM1.5 spectrum (Newport solar simulator). Typically, 10 mg of the as-prepared product was added into 50 mL of 2.0 $\times$ 10$^{-5}$ M RhB, 50 mL of 2.0 $\times$ 10$^{-5}$ M MO and 50 mL of 2.0 $\times$ 10$^{-4}$ M phenol aqueous solution, separately. Before illumination, the suspension was placed in the dark under constant stirring for 90 min to reach adsorption/desorption equilibrium. Five millilitres of the suspension were taken out every 5 min for RhB and MO, every 10 min for phenol and centrifuged to remove the photocatalyst for UV-Vis absorption spectrum measurements. The concentrations of RhB, MO and phenol were determined by monitoring their characteristic absorption at 553 nm, 462 nm and 270 nm, respectively. For the recycling experiments, first, five parallel experiments were performed; second, all the photocatalysts after the first cycle of photodegradation were collected, washed and dried; last, every 10 mg of the treated photocatalysts was used in photodegradation again. We repeated these processes five times.

2.6. Photoelectrochemical measurements

The photoelectrodes were prepared according to the literature.\textsuperscript{11,28,29} The indium doped oxide (ITO, Präzisions Glas & Optik GmbH, Germany) substrates were cleaned by ultrasonication in distilled water, ethanol, and isopropanol for
10 min sequentially. Both edges of the ITO substrates were covered with AB glue. Typically, the suspension was prepared by grinding 5 mg of the as-prepared products, 10 µL of PEDOT-PSS (Sigma-Aldrich, 1.3 wt%) aqueous solution and 50 µL of water, and the film was dried in air and annealed at 150 °C for 10 min. The photocurrents were measured by the Bio Logic potentiostats in a standard three-electrode system with the as-prepared samples as the working electrode, a Pt mesh as the counterelectrode, and an Ag/AgCl electrode as a reference electrode. The solar simulator equipped with a visible-light fibre-optical was used as a light source. The 0.15 M KI/acetonitrile solution was used as the electrolyte.

3. Results and discussion

In this work, we prepared free-standing 2D square-like BiOI nanosheets via a very simple one-step solvothermal method. The crystallinity and phase purity of the as-prepared products were confirmed by XRD analysis. As presented in Fig. 2, the XRD pattern could be well indexed to the tetragonal phase of BiOI with the lattice parameters of $a = b = 3.994$ Å and $c = 9.149$ Å, which is in good agreement with the standard card (JCPDF no. 10-0445). The strong and sharp peaks indicate that the as-prepared products are highly crystallized.
The morphological features of as-prepared 2D square-like BiOI nanosheets were characterized by SEM and TEM. The typical SEM and TEM images (as shown in Fig. 3a and c) reveal that the as-prepared samples consist of large-scale nanosheet shaped structures with widths of about 100–300 nm and thicknesses of around 10 nm. As shown in Fig. 3b and d, the SEM and TEM images of two individual nanosheets further confirmed the square-like shape of these nanosheets. The HRTEM (Fig. 3e) further indicated the highly crystalline nature of the nanosheets. The continuous clear lattice fringes with an interplanar lattice spacing of 0.282 nm and an angle of 90° correspond to the (110) atomic planes of the tetragonal BiOI. The spot SAED pattern (top right inset in Fig. 3e) revealed the single-crystalline characteristic of the square-like BiOI nanosheet. The angle of adjacent spots labeled in the SAED pattern is 45°, which is in agreement with the theoretical value of the angle between the (110) and (200) planes of tetragonal BiOI. It shows that the set of diffraction spots can be indexed as the [001] zone axis, as shown in the inset of Fig. 3d. The fast Fourier transform (FFT) image (bottom right inset in Fig. 3e) of the as-prepared square-like BiOI nanosheet shows a tetragonal structure, which agrees with the XRD result. Considering that the c parameter of BiOI is 9.149 Å, it can be inferred that each BiOI nanosheet consists of around 10 [I-Bi-O-Bi-I] units. As a comparison, BiOI microplate samples with micrometer-level side-widths were also prepared.

The SEM image (Fig. 4) shows that these BiOI microplates are also square-like in morphology, with a size of 0.5–1.5 µm and a thickness of more than 50 nm. The results of HRTEM and SAED of the as-prepared microplates are in accordance with those of the 2D square-like nanosheets. On the basis of the above structural information, the 2D square-like BiOI nanosheets have approximately 93% highly reactive {001} facets exposed, whereas the BiOI microplates have a lesser percentage of around 85%. But at the same volume space, 2D square-like BiOI nanosheets have 3 times greater percentage of exposed {001} facets than BiOI microplates. This was proved by the BET results. As shown in Fig. 5, the specific surface area of the nanosheet BiOI is 38.32 m² g⁻¹, which is three times more than that of the microplate BiOI (11.10 m² g⁻¹).

The energy band structure of a semiconductor is considered to be a key factor to determine its photocatalytic activity. Fig. 6 presents the UV-Vis absorption spectra of the 2D square-like
BiOI nanosheets and BiOI microplates, in which a noticeable shoulder was observed at 730 nm and 653 nm, respectively. The band gap value \( (E_g) \) could be evaluated using the equation 
\[
\alpha \nu = A (\nu - E_g)^{n/2}
\]
where \( \alpha \), \( \hbar \), \( \nu \), \( E_g \) and \( A \) are the absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. Among them, \( n \) depends on the characteristics of the transition in a semiconductor. For BiOI, the value of \( n \) is 4 for the indirect transition. The band gap value of BiOI can be estimated from the curve of \( (\alpha \nu^{1/2}) \) versus photon energy \( (\nu) \) plotted. According to these, the band gap value of BiOI nanosheets is around 1.70 eV, slightly smaller than that of BiOI microplates (1.90 eV).

The commonly used approach to characterize the activity of the photocatalysts is to investigate the photocatalytic degradation of organic dyes or toxic pollutants, which is of great significance in environmental pollutant treatment. In our work, the photocatalytic performance of the 2D square-like BiOI nanosheets is evaluated under simulated solar irradiation with a 420 nm cut-off filter using RhB as a probe molecule in aqueous solution. The relevant data for the BiOI microplate are also given for the sake of comparison. As shown in Fig. 7a, the characteristic absorbance at 553 nm of RhB in aqueous solution decreases very fast with time of visible-light irradiation for 2D BiOI nanosheets. In contrast, the characteristic absorbance of BiOI microplates decreases much more slowly under the same conditions (Fig. 7b). As presented in Fig. 7c, in the absence of photocatalysts and under black conditions with photocatalysts, decomposition of RhB is inappreciable, suggesting that the photolysis of RhB is negligible within the test period. The decolouration rate of RhB in the presence of 2D square-like BiOI nanosheets reaches 90% after 15 min of visible-light irradiation, but only around 25% of RhB molecules are decomposed within the same time. In order to clarify the stability of the high photocatalytic performance of the as-prepared 2D square-like BiOI nanosheets, a recycling experiment for the photodegradation of RhB under visible-light irradiation was performed. As shown in Fig. 7d, the photodegradation rate remains constant over six more cycles; such an excellent recyclability indicates that the 2D square-like BiOI nanosheet is stable under visible-light irradiation, which is very important for its industrial application.

MO is an acid–base model organic pollutant and its color is determined by the azo bonds and their associated chromophores and auxochromes. The photocatalytic activity of 2D square-like BiOI nanosheets under visible light irradiation is further authenticated by photodegradation of MO in water; the relevant data for the BiOI microplate are also given for com-

![Fig. 7](https://example.com/fig7.png)

**Fig. 7** Photocatalytic performance of the as-prepared 2D square-like BiOI nanosheets and BiOI microplates. (a) Visible light driven photodegradation of RhB with 2D square-like BiOI nanosheets; (b) visible light driven photodegradation of RhB with BiOI microplates; (c) comparison of decolouration efficiency under visible light irradiation; and (d) cycling curve of photodegradation of RhB with 2D square-like BiOI nanosheets.
parison. As shown in Fig. 8a, the characteristic absorbance of MO in water at 462 nm diminishes gradually as the exposure time under visible-light irradiation for 2D square-like BiOI nanosheets increases, and the absorption peak completely disappears after 15 min. However, the characteristic absorbance of BiOI microplates decreases extremely slowly under the same conditions (Fig. 8b). As shown in Fig. 8c, in the absence of photocatalysts and black conditions with photocatalysts, the decomposition of MO is negligible, which means that the photolysis of MO is insignificant during the test period. The decolouration rate of MO reaches up to 94% after 15 min visible-light irradiation in the presence of 2D square-like BiOI nanosheets. But for BiOI microplates, the decolouration rate is only less than 7% within the same time of visible-light irradiation. The recycling experiment for the photodegradation of MO under visible-light irradiation verified the excellent recyclability of as-prepared 2D square-like BiOI nanosheets. Over five more cycles, the photodegradation rate has no distinct difference (Fig. 8d), suggesting that the as-prepared 2D square-like BiOI nanosheets are stable for visible light photocatalysis.

The health threat of phenol and phenolic pollutants is well known; great attention has been paid to their degradation during the last few decades. However, all of their compounds have benzene rings, which present a strong inhibitive function for biological degradation. Here we performed a photocatalysis degradation process for phenol to investigate the photocatalytic performance of as-prepared products. As presented in Fig. 9a, along with the time prolonging, the characteristic absorbance of phenol in water at 270 nm decreases under visible-light irradiation in the presence of 2D square-like BiOI nanosheets, and the degradation rate of phenol in water runs up to 70% after 60 min of visible-light irradiation. With the same conditions, the contrastive BiOI microplates have lessened by only around 9%. As a comparison, direct photolysis of phenol and 2D square-like BiOI nanosheets was carried out in the absence of photocatalysts and black conditions with photocatalysts, respectively. The result exhibited in Fig. 9b clarifies that the direct photolysis of phenol and 2D square-like BiOI nanosheets is not appreciable.

It is well-known that the photocatalytic degradation of dyes on semiconductors originates from two kinds of pathways, namely, the direct semiconductor photoexcitation process and indirect dye self-photosensitization. In the RhB and MO photodegradation process, the characteristic absorbance peaks of RhB and MO are located at 553 nm and 462 nm, respectively. Both of them are in the visible-light region. Meanwhile, the photocatalyst has a narrow band gap; thus the two photo-
catalytic pathways could proceed. However, in the process of phenol photodegradation, the characteristic absorbance peak of phenol is located only at 270 nm and not in the visible-light region. Therefore, the degradation of phenol may mainly proceed in a direct semiconductor photoexcitation pathway under visible-light irradiation. Compared with BiOI microplates, as-prepared 2D square-like BiOI nanosheets have a smaller band gap, corresponding to higher utilization of solar light to generate more electron–hole pairs. On the basis of the unique layered structure of BiOI, the [Bi₂O₂] slab is interleaved with double slabs of halogen atoms; it could induce the presence of internal static electric fields that are perpendicular to the [Bi₂O₂] slab and halogen anionic slabs in BiOI. These induced internal static electric fields can improve the separation efficiency of the photoinduced electron–hole pairs. The BiOI nanosheets have higher percentage of exposed {001} facets, which could induce the generation of stronger internal static electric fields. Furthermore, the thin 2D BiOI nanosheets have a comparable shorter distance for photoinduced electron–hole pairs to be effectively separated. In addition, the square-shaped structures have many uncoordinated surface atoms on the thin BiOI nanosheets, which further promote their photocatalytic activity. As confirmed by the transient photocurrent responses of the 2D BiOI nanosheets and BiOI microplates under visible light irradiation (Fig. 10), both electrodes generate photocurrents with a reproducible response to on/off cycles, but the BiOI nanosheets present a higher photocurrent than the BiOI microplates, proving more efficient photoinduced charge separation and transfer of BiOI nanosheets. Accordingly, 2D square-like BiOI nanosheets present higher photocatalytic activity than BiOI microplates under visible light.

4. Conclusion

In summary, 2D square-like BiOI nanosheets have been synthesized via a low-cost and general hydrothermal process in the absence of a surfactant and a special solvent. The resulting BiOI nanosheets with a thickness of ~10 nm and exposure of {001} facets exhibited highly efficient photocatalytic activity by visible light. Based on the photodegradation of phenol under visible light, we proposed that the direct semiconductor photoexcitation pathway is dominant during the photocatalysis process. The efficient visible-light driven photocatalytic activity could be ascribed to the high percentage of exposed {001} facets and the thin 2D-square-shaped nanosheet. The high areas of {001} facets correspond to efficient photogeneration and electron–hole pair separation, based on appropriate self-induced internal static electric fields of BiOI. And the thin nanosheets further increased the separation efficiency of photoinduced electron–hole pairs. The as-prepared efficient 2D square-like BiOI nanosheet photocatalysts have potential for industrial application. And the cost-effective fabrication process of 2D BiOI nanosheets could be a general method for achieving other BiOX 2D nanostructures to realize high-performance photocatalysts.
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Notes and references