3D BiOI–GO composite with enhanced photocatalytic performance for phenol degradation under visible-light

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Abstract

Coupling semiconductors with graphene-based materials could enable better photocatalytic performance as compared to that of pristine semiconductors. In this work, a three-dimensional BiOI–GO composite was fabricated by a simple self-assembly approach. The resultant BiOI–GO composite showed a higher photocatalytic activity than that of pure BiOI and P25 towards the degradation of phenol under visible-light irradiation, which could be attributed to the more effective separation of photogenerated electrons and holes between BiOI and GO, and the better adsorption capacity of phenol.

Keywords: BiOI-based photocatalyst; Graphene oxide; Visible light

1. Introduction

The photocatalytic degradation of organic pollutants over semiconductor photocatalysts has attracted considerable interest for its potential applications in environment purification. In the past several decades, much attention was paid to TiO2-based photocatalysts, due to their high photoreactivity, non-toxicity, low cost and stability [1–3]. However, TiO2 can only be excited under UV light irradiation due to its large band gap of ~3.2 eV, which limits its practical application. Consequently, developing photocatalysts that could be excited under visible-light which is abundant in solar spectrum has become an imperative research topic in recent years [4–7]. As an alternative, the family of bismuth oxyhalides has showing promising potential, owing to their unique layered structures and narrow band gaps, which generally can favor the separation of photoinduced electron–hole pairs and assure them a relatively high visible-light-driven photocatalytic performance on the degradation of organic pollutants [8–11]. Among them, BiOI has the smallest band gap (~1.8 eV) with strong absorption in the visible-light region [11–13]. Moreover, BiOI with three-dimensional (3D) hierarchical structures have been proved to be more photoactive than irregular ones due to the better light harvesting ability and more effective utilization of charge carriers [12–14]. However, the visible-light-driven photocatalytic activity of pure BiOI is usually not as ideal as expected due to the quick recombination of photoinduced electrons and holes [15–17]. Therefore, various BiOI-based composite materials, such as BiOI/TiO2, BiOI/multi-walled carbon nanotubes and BiOI,R1−x (R=Cl, Br) solid solutions [18,19], have been developed to enhance the photocatalytic activity of BiOI via promoting the separation of photoinduced charge carriers.

Graphene and its derivatives, are excellent electron media-

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superior conductivity, and have attracted numerous attentions recently [20–27]. Many studies have been devoted to enhancing the photocatalytic properties of semiconductor photocatalysts by coupling with reduced graphene oxide (RGO) [20–22] or graphene oxide (GO) [23,25]. Herein, we firstly synthesized 3D BiOI microspheres via a hydrolysis process, and then coupled the BiOI microspheres with GO through a simple self-assembly route. The obtained BiOI–GO composite showed a highly efficient photocatalytic activity towards the degradation of phenol under visible-light irradiation, which could be attributed to the effective charge separation between BiOI and GO.

2. Experimental

2.1. Synthesis of 3D BiOI microspheres and BiOI–GO composite

All reagents such as bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, Guangdong Chemical Reagent Engineering-technological Research and Development Center), potassium iodide (KI, Guangdong Guanghua chemical factory Co. Ltd.), phenol (AR, 99.0%, Tianjin Guangcheng Chemical Reagent Co. Ltd.) and polyvinylpyrrolidone (PVP-K30, Mn=58,000, Shanghai bopu Co., Ltd.), were used as received without further purification. Graphene oxide (GO) was prepared from natural graphite powder (> 99.8%, Alfa Aesar) by a modified Hummers’ method [27].

Hierarchical BiOI microspheres were synthesized according to a reported approach [11]. Briefly, 1.51 g Bi(NO₃)₃·5H₂O, 0.40 g PVP-K30 and 5 mL HNO₃ (1.0 M) were added into 50 mL distilled water to form solution A; 0.50 g KI, 0.40 g PVP-K30 were added into 60 mL distilled water to form solution B. Then solution B was added dropwise into solution A under magnetic stirring. The resultant mixture was kept under stirring at ambient temperature for 2 h. After that, the formed yellow precipitate was collected by centrifugation, and washed several times with distilled water and absolute ethanol in sequence, and then dried at 80 °C for 3 h.

To prepare BiOI–GO composite, a well-dispersed GO suspension was firstly prepared by adding 4.5 mg GO into a mixture of 20 mL distilled water and 10 mL ethanol under magnetic stirring, followed by ultrasonic treatment for 0.5 h. Then, 12 mL GO suspension was extracted and mixed with another suspension composed of 0.36 g as-prepared BiOI microspheres, 20 mL distilled water and 10 mL ethanol under continuous stirring till a dark-orange precipitate formed after 1 h. The obtained dark-orange precipitate was collected by centrifugation, and washed thoroughly with distilled water and absolute ethanol for several times, and then dried at 80 °C overnight.

2.2. Characterization of samples

The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer, using monochromatic Cu-Kα irradiation source (λ=0.1542 nm) at a scan rate (2θ) of 0.05° s⁻¹. The average crystallite size was calculated according to Scherrer equation. Morphology analysis was conducted on an S-4800 field emission scanning electron microscope (FESEM, Hitachi, Japan) at an accelerating voltage of 10 kV. The nitrogen adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 gas adsorption apparatus. All the obtained samples were degassed at 180 °C before measurement. The Brunauer–Emmett–Teller surface area (S BET) was obtained using the adsorption isotherm data in the relative pressure (P/P0) range 0.05–0.3, and the pore size distribution was obtained using desorption isotherm via the Barrett–Joyner–Halender (BJH) method based on a cylindrical pore model. The total pore volume and the average pore size were estimated from the nitrogen adsorption volume at P/P0 of 0.994. UV–visible diffuse reflectance spectra (DRS) were measured on a UV–visible spectrophotometer (UV-2550, Shimadzu, Japan), using BaSO₄ powder as a standard. Raman spectra were recorded on a micro-Raman spectrometer (Renishaw InVia, UK) at room temperature, in the back scattering geometry with a 633 nm Ar⁺ laser as an excitation source. Photoluminescence (PL) spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer.

2.3. Photocatalytic activity test

Photocatalytic activities of the samples were evaluated by degradation of phenol in aqueous solution under visible-light irradiation at ambient temperature. Typically, 100 mg of photocatalyst was dispersed in 10 mL ethanol and then the suspension was transferred into a dish with a nominal diameter of 8.0 cm, which was then dried in an oven at 80 °C for about 3 h to evaporate the ethanol and consequently coat the sample evenly onto the dish. Then 20 mL aqueous solution of phenol with a concentration of 100 mg/L was added into the above-mentioned dish coated with the photocatalyst. Finally, the dish was placed under a 350 W Xeon lamp with a UV-cutoff filter (λ > 420 nm, Shanghai Lansheng Electronic Co., China), which was placed 20 cm above the dish. At given time intervals, the concentration of phenol solution was estimated by a UV–vis spectrophotometer (UVmini-1240, Shimadzu, Japan) at the wavelength of 269 nm. For comparison, P25 and blank samples were also tested under the same condition.

3. Results and discussion

3.1. Morphology analysis

The SEM images of as-prepared BiOI microspheres and BiOI–GO composite are presented in Fig. 1. It can be seen that pure BiOI sample is composed by hierarchical flower-like microspheres assembled by nanolamellas (Fig. 1a and b). This may be attributed to the crystal face inhibition effect of PVP, benefiting the formation of 3D spherical architectures [11]. The diameter of the microspheres varies from about 0.5–1.0 μm. Fig. 1c and d shows that in the BiOI–GO composite, the BiOI microspheres are enwrapped by GO nanosheets (marked in arrow in Fig. 1d) with desirable affinity between each other.
The results indicate that the BiOI–GO composite can be easily prepared through the simple self-assembly process of GO nanosheets onto the surface of BiOI microspheres. Scheme 1 illustrates the formation process of the BiOI–GO composite, during which no additional surfactant or linker was added. Owning to the high specific surface area, GO possesses high surface free energy. When BiOI microspheres and GO nanosheets were mixed together in solvent, the GO nanosheets trended to enwrap onto the surface of BiOI microspheres to minimize the total energy of the system. This thermodynamic spontaneous process along with the subsequent drying treatment could strengthen the interconnection between GO and BiOI to form a stable structure. Similar methods have also been used for the preparation of BiPO₄–GO, WO₃–RGO, BiVO₄–RGO and TiO₂–RGO composites [28–31].

3.2. BET surface area and pore structure

Nitrogen adsorption–desorption isotherms of both BiOI and BiOI–GO samples are of typical type IV (BDDT classification) with H3 hysteresis loops, as shown in Fig. 2, indicating the presence of mesopores and the formation of slit-like pores due to the aggregation of the sheet-like particles [32,33]. The pore size distribution curves (inset of Fig. 2) are broad from 2 to 110 nm, with two peaks centered at 3.9 and 80/90 nm, respectively. The former indicates the existence of small mesopores, which are caused by the intra-aggregation of BiOI crystallites within BiOI nanolamellas. The latter suggests the formation of macropores due to the inter-aggregation of BiOI nanolamellas. The BET surface area, average pore size and pore volume of BiOI microspheres and BiOI–GO composite are listed in Table 1. The results indicate that the introduction of GO did not affect obviously on the surface area and pore structure of BiOI, excluding the related effect on the enhancement of photocatalytic activity to be discussed.
3.3. Crystal structure

The XRD patterns of as-synthesized BiOI microspheres and BiOI–GO composite are shown in Fig. 3. All the diffraction peaks of both samples can be readily indexed as the tetragonal phase of BiOI (JCPDS 73-2062). The average crystallite size of BiOI is estimated to be about 19.5 nm using Scherrer's equation, based on the main (110) diffraction peak. No obvious diffraction peaks for carbon species are observed in the composite, due to the low amount (1.0 wt%) and poor crystallinity of GO.

3.4. Optical property

Fig. 4 shows the UV–vis DRS of BiOI microspheres and BiOI–GO composite. Both samples show strong photoabsorption from UV to visible light, with absorption edges at ~630 nm. The steep absorption edge in the visible range indicates that the absorption is from the intrinsic band-gap transition rather than from the impurity levels [5,34]. The band gap ($E_g$) of BiOI microspheres is estimated to be 1.97 eV. The introduction of GO does not change the absorption edge of BiOI, but induces stronger adsorption in visible light region ($\lambda > 600$ nm), which can be attributed to the dark color of GO. The valence band maximum (VBM) and the conduction band minimum (CBM) of BiOI are calculated to be 2.45 eV and 0.48 eV respectively using the reported method [35].

3.5. Raman spectra

Raman spectra of BiOI microspheres and BiOI–GO composite are shown in Fig. 5. Two peaks at 1340 and 1595 cm$^{-1}$, corresponding to D band and G band of GO, are observed in the spectrum of BiOI–GO composite, which reflects the degree of edge chirality and the relative degree of graphitization, respectively [22,36]. Nevertheless, such peaks do not appear in the spectrum of BiOI microspheres. This indicates the successful enwrapping of GO onto BiOI microspheres, which is consistent with SEM images shown in Fig. 1c and d.

3.6. Photoluminescence spectra

PL spectra are usually used to estimate the separation efficiency of photoinduced charge carriers for semiconductors. A higher intensity of PL indicates a faster recombination of charge carriers [21,37]. The PL spectra of BiOI and BiOI–GO were measured under the excitation of a 450 nm laser. As shown in Fig. 6, pure BiOI sample exhibits a strong emission at 677 nm. While for BiOI–GO composite, the peak intensity decrease obviously, indicating that the presence of GO can effectively suppress the recombination of the photogenerated electron–hole pairs, and thus prolong their lifetime.

3.7. Photocatalytic performances

Phenolic compounds in wastewater, mainly from the coal gasification, petroleum industry, resin plants, and some pharmaceutical processes, are toxic and cause serious problems to human and aquatic species [38]. The removal of phenolic compounds is highly desirable. Here we evaluate the photocatalytic activities of the as-prepared BiOI–GO photocatalyst by the degradation of phenol with initial concentration of...
100 mg/L under visible-light irradiation (λ > 420 nm). P25 and pure BiOI microspheres are also investigated.

As shown in Fig. 7a, blank test under visible light indicated that no noticeable degradation of phenol was observed in the absence of any photocatalyst. BiOI microspheres and BiOI–GO composite exhibited much higher photocatalytic activity than P25, which could be mainly attributed to the narrower band gap of BiOI (1.97 eV) than TiO2 (3.2 eV). Moreover, the photocatalytic activity of BiOI–GO composite was higher than that of BiOI microspheres, suggesting the positive effect of GO for the enhancement of photocatalytic activity of BiOI. The temporal evolution of the absorption spectra of phenol solution over BiOI–GO was shown in Fig. 7b, in which the gradual decrease of the intensity indicates the effective decomposition of phenol.

The enhancement of photocatalytic performance over BiOI–GO composite could be ascribed to two main reasons. On one hand, as an excellent electron mediator, the GO could trap the photoinduced electrons from the CB of BiOI to facilitate the separation of charge carries, which is quite beneficial for the photocatalytic reaction. On the other hand, the adsorption of phenol molecules onto the surface of the photocatalyst could be improved by the interaction of π–π conjugations between GO and phenol molecules, as well as the hydrogen bonding between the oxygen functional groups of GO and the phenolic hydroxyl groups [39], which could further promote the photocatalytic process.

3.8. Photocatalytic mechanism

The active species during the photocatalytic process were studied by introducing different trapping agents before light irradiations, including 1 mM p-benzoquinone (BQ) as a quencher of •O2, 0.01 M triethanolamine (TEOA) as a quencher of holes (h+) and 0.01 M isopropanol (IPA) as a quencher of •OH respectively [40]. Fig. 8 displayed the results of the trapping experiments for both BiOI and BiOI–GO samples under xenon lamp irradiation (λ > 420 nm).

It can be seen that the photodegradation was almost not affected by IPA for both samples, indicating that •OH is not the main active specie. While when BQ was added, the photodegradation of phenol showed modest decrease, suggesting that •O2 participated in the photocatalytic reaction. More importantly, the photodegradation of phenol showed significant decrease after the addition of TEOA. This reveals that h+ was the major active specie for the BiOI-based photocatalysts in this work. It is known that the standard redox potential of •OH/H2O (E° = 2.27 V at pH 7) [2,41] is less positive than the VBM of BiOI (2.45 eV), implying the possible •OH generation. However, it was deemed that using the standard redox potential of Bi4+/Bi3+ (E° = 1.59 V vs NHE) for comparison is more suitable to estimate the possibility [4,11,42]. As expected, there are no obvious production of •OH during the photocatalytic reactions. Instead, phenol preferred to be directly oxidized by h+ on the surface of the photocatalyst. It seems unlikely that •O2 was generated by reduction of the dissolved O2, because the CBM of BiOI (0.48 eV) is less negative than the reduction potential E°(O2/O2•−) (−0.28 eV vs NHE, pH=7) [2,41]. However, here the results indicate that •O2 was one of the active species. Similar results were also reported in other studies related to BiOI photocatalysts [40,43,44], while the calculated conduction band minimum of these materials are all less negative than E°(O2/O2•−). The possible reason is because the electrons on BiOI could be excited to a higher energy level to form a temporary CBM by the incident light with higher energy, and the temporary CBM is more negative than E°(O2/O2•−). Hence the electrons on the temporary CBM can react with O2 to produce •O2 [44,45].

A possible mechanism of the photocatalytic phenol degradation by BiOI–GO composite is proposed in scheme 2.
the photocatalyst was irradiated by visible light, photoinduced electrons and holes were generated on BiOI. Then the electrons were trapped by GO, thus the charge carriers were separated effectively [46]. At the same time, phenol molecules adsorbed on the surface of the photocatalyst were directly oxidized to decomposed products by photogenerated holes. Besides, a small amount of phenol molecules were eliminated by super-oxide radical generated by the reduction of dissolved O2. In addition, the longer-wavelength light absorbed by GO may cause a positive photo-thermal effect to promote the migration of charge carriers, which favors the photocatalytic reaction.

4. Conclusions

BiOI–GO composite consisting of BiOI microspheres enwrapped by GO nanosheets is fabricated via simple hydrolysis preparation of BiOI combined with subsequent self-assembly of GO. This BiOI–GO composite exhibits improved visible-light photocatalytic performance on the degradation of phenol as compared to pure BiOI microspheres and P25, which is due to the enhancement of the separation efficiency of photoinduced charge carriers and the adsorption capacity of phenol molecules. This work may provide a simple route for the preparation of semiconductor–GO composite for efficient photocatalytic application.

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References


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