Novel p–n junction UiO-66/BiOI photocatalysts with efficient visible-light-induced photocatalytic activity

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ABSTRACT

Novel visible-light-induced UiO-66/BiOI photocatalysts with a p–n junction structure have been prepared for the first time through a facile hydrothermal method. The prepared photocatalysts were characterized using the powder X-ray diffraction, high resolution transmission electron microscopy, scanning electron microscopy, UV–visible diffuse reflectance spectra, and N₂ adsorption–desorption (Brunauer–Emmett–Teller) techniques respectively. The photodegradation performances of UiO-66/BiOI photocatalysts were evaluated by photodegrading salicylic acid under visible-light irradiation. The UiO-66/BiOI composites displayed much higher photocatalytic efficiencies than pure BiOI under visible light. When the content of UiO-66 was 5.2 wt%, the composite (UiO-66/BiOI-2) has the best photocatalytic activity. Most of the salicylic acid molecules can be degraded in 100 min. The degradation rate of UiO-66/BiOI-2 samples is higher than single BiOI and UiO-66. The enhanced photocatalytic performance of UiO-66/BiOI may be ascribed to the formation of p–n heterojunctions between BiOI and UiO-66, which facilitates the transfer and separation of the photogenerated charge carriers. After recycling of the photocatalyst for five times for the photodegradation of salicylic acid, more than 85% of salicylic acid could still be degraded in the fifth cycle, implying that the as-prepared photocatalysts are highly stable.

Key words | composites, p–n heterojunctions, photocatalysts

INTRODUCTION

Industrial plants generate large quantities of wastewater, which is a serious environmental problem for human society. Among various technologies used in wastewater treatment, photocatalysis is considered a promising method due to its low-cost and efficiency. Recently, visible-light-driven semiconductors have attracted lots of attention and efforts because they can effectively exploit visible-light absorption for photoexcitation, comparing with traditional photocatalysts (e.g. TiO₂ and ZnO) (He et al. 2013a, 2013b; Jiao et al. 2016; Shang et al. 2016; Zhou et al. 2016; Zheng & Jiao 2017). Among them, bismuth oxyiodide (BiOI) has a layered structure consisting of \( \text{Bi}_2\text{O}_2 \) \(^{2-} \) layers interleaved with slabs comprised of iodine atoms, and is a p-type semiconductor with narrow band gaps of about 1.78 eV, which makes it exhibit strong photoresponse in the visible-light region (Cao et al. 2014; Cheng et al. 2014; He et al. 2015; Han et al. 2015; Mehraj et al. 2016). Nevertheless, BiOI on its own shows poor photocatalytic activity owing to fast recombination of photo-excited electrons and holes (Xiao & Zhang 2010). The p–n junction is an essential heterojunction in the semiconductor industry which has been proven to be an efficient way to separate electron–hole pairs as the result of the generation of an internal electric field (Chang et al. 2015; Kim et al. 2005; Zhong et al. 2015). Since BiOI is an intrinsic p-type semiconductor, to construct a p–n junction coupling BiOI with an n-type semiconductor is a more effective way to increase the separation efficiency of photoinduced charge carriers, which has been confirmed in BiOI/BiVO₄ (Ye et al. 2015)], \( \text{Bi}_2\text{WO}_6/\text{BiOI} \) (Xiang et al. 2016), BiOI/TiO₂ (Dai et al. 2011), BiOI/ZnO (Jiang et al. 2011), BiOI/Bi₁₂O₁₇C₁₂ (Huang et al. 2016), and BiOI/Bi₁ₓTi₁₋ₓO₁₂ (Hou et al. 2013).

Metal-organic frameworks (MOFs) are a class of crystalline porous materials, in which metal centers are cross-linked by molecular organic linkers. MOFs can behave as semiconductors and will be excited to produce electron–hole pairs under light illumination (Horiuchi et al. 2012; Ai et al. 2014; Gao et al. 2014). Compared with the ordinary
photocatalysts, photoactive MOFs exhibit large surface area and intrinsic porosity, which facilitates the mass transport in photocatalytic reactions (He et al. 2013a, 2013b; Peng et al. 2013; Shen et al. 2015), so photoactive MOFs attract increasing amounts of attention in the photocatalysis field (Shen et al. 2015; Li et al. 2016; Wang et al. 2016; Liang et al. 2017). Among various types of photoactive MOFs, Zr-containing MOFs of UiO-66 demonstrate higher thermocrystalinity and chemical stability as well as the excellent properties as other MOFs. Moreover, UiO-66 shows an n-type semiconductor feature and exhibits excellent structural stability in water (Luo et al. 2012; Yuan et al. 2015). Therefore, UiO-66 is a promising photocatalyst used in aqueous medium, such as water treatment and water splitting. However, to the best of our knowledge, there are very few reports on UiO-66-based photocatalysts for water treatment up to now (Sha et al. 2015; Li et al. 2016) and combining p-type BiOI with n-type UiO-66 as a photocatalyst for water treatment has not been studied yet. Therefore, we prepared novel p–n junction photocatalysts by growing BiOI nanoparticles on presynthesized UiO-66 nanocrystals through a solvothermal method. A series of UiO-66/BiOI composite photocatalysts with different content of UiO-66 were prepared for comparison. Our results clearly show that all UiO-66/BiOI p–n junctions exhibit remarkable photocatalytic activity that is better than for pure BiOI and UiO-66. Among the prepared samples, the UiO-66/BiOI-2 nanocomposite has the best photocatalytic activity. The enhanced photocatalytic performance may be the result of the formation of the p–n junction, which causes the effective separation of electron–hole pairs. The recycle experiment shows that UiO-66/BiOI nanocomposites possess extremely good photocatalytic stability.

**EXPERIMENTAL SECTION**

**Materials**

All chemicals were analytical grade and used as received without any further purification. 1,4-benzenedicarboxylic acid (BDC), ZrCl4 and Bi(NO3)3.5H2O were purchased from Sinopharm Chemical Reagent Co. Ltd, China. KI (99%) was supplied by Aladdin.

**Synthesis of UiO-66**

According to the literature (Cavka et al. 2008), UiO-66 octahedrons were synthesized through a solvothermal route. In a typical synthesis, ZrCl4 (298.4 mg) and BDC (212.8 mg) were dissolved in 150 mL N,N-dimethylformamide (DMF). The acetic acid (30.0 mL, 31.47 mg) was then added into the solution to tune the morphology of UiO-66, following the ultrasonic treatment for 20 min. The obtained homogeneous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was kept in the furnace at 120 °C for 24 h, and then cooled to room temperature naturally. The products were collected by centrifugation, washed three times with DMF, and then soaked in methanol at 60 °C for 3 days, replacing the methanol every 24 h to exchange the DMF solvent.

**Preparation of a series of UiO-66/BiOI composites**

The UiO-66/BiOI composites were prepared through a facile precipitation method with the presence of UiO-66. Typically, 0.3 mmol Bi(NO3)3.5H2O was dissolved in 40 mL demonized water with pH = 2.0 adjusted by 0.5 M nitric acid (HNO3) under vigorous stirring for 60 min to obtain a transparent solution A. Meanwhile, different amounts of as-synthesized UiO-66 and 0.3 mmol KI were dispersed in 30 mL deionized water with ultrasonic dispersion to obtain a homogeneous dispersion B. Then, the mixture B was added dropwise into solution A under stirring. Subsequently, the pH value of the final suspension was adjusted to 5.0 by 2.0 M NH3·H2O and transferred into a 100 mL Teflon-lined autoclave and maintained at 85 °C for 24 h with continuous stirring. The formed red precipitates were collected and washed several times with deionized water and ethanol respectively. Then the samples were dried in a vacuum oven for 24 h at room temperature. For comparison, the pure BiOI nanosheets were also prepared through the same procedures without introducing the UiO-66.

**Characterization**

The powder X-ray diffraction (XRD) patterns of the samples were recorded by a Bruker AXS D8 Advance powder diffractometer with CuKα X-ray radiation (λ = 0.15406 nm). The morphologies of the synthesized samples were observed on a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). High resolution transmission electron microscopy (HRTEM) mages were taken on a JOEL JEM-2100 microscope. UV–visible diffuse reflectance spectra of the samples were taken on a UV–visible–near-infrared spectrophotometer (Cary 5000, Varian) with BaSO4 as a reference. The surface area of samples was calculated using the Brunauer–Emmett–Teller (BET) method using the Micromeritics ASAP2020 measurement instrument.
Photocatalytic activity measurement

In the experimental setup, a 300 W Xe lamp with a light intensity of 300 mW cm$^{-2}$ was employed as a light source and a 420 nm cut-off filter (Xujiang Electromechanical Plant, China) was used to provide only visible-light irradiation. About 100 mg photocatalyst was added to 100 mL of salicylic acid solution ($C_0 = 10$ mg/L). Before being irradiated, the suspensions were magnetically stirred in the dark for 3 h to reach the adsorption–desorption equilibrium between photocatalysts and salicylic acid. Then the solution was exposed to visible-light irradiation under magnetic stirring. About 5 mL aliquots were collected from the suspension and centrifuged immediately every 10 min. The degradation of salicylic acid was monitored by checking the absorbance at 296 nm using a Shimadzu UV-2550UV-Vis spectrometer. All photocatalysis experiments were performed five times for reproducibility. Graphical results are presented as means and standard deviations after calculation.

RESULTS AND DISCUSSION

Material characterization

A series of composite UiO-66/BiOI samples with different contents of UiO-66 were synthesized by a simple hydrothermal–co-precipitation method. In general, UiO-66 was firstly fabricated through a typical hydrothermal method, and then 30, 60 and 90 mg of UiO-66 were added in the growth solution of BiOI. The samples were named as UiO-66/BiOI-1, UiO-66/BiOI-2 and UiO-66/BiOI-3 and the weight contents of UiO-66/BiOI-1, UiO-66/BiOI-2 and UiO-66/BiOI-3 are 2.6, 5.2 and 7.8 wt% respectively. The XRD patterns of pure BiOI, UiO-66 and UiO-66/BiOI composites with different weight contents of UiO-66 are shown in Figure 1. The XRD pattern of as-synthesized UiO-66 can be well matched with the previous report (Shen et al. 2013), indicating that UiO-66 has been successfully synthesized. The XRD peaks of pure BiOI could be indexed to pure tetragonal phase (JCPDS No. 10-0445) (Ye et al. 2015). For the UiO-66/BiOI composites, characteristic peaks of BiOI and UiO-66 were both observed and the characteristic peak for UiO-66 became stronger with the increase of the content of UiO-66, reflecting a two-phase composition of UiO-66 and BiOI in these composites.

The morphologies and microstructures of UiO-66, BiOI and UiO-66/BiOI-2 were observed by SEM, TEM and HRTEM. As shown in Figure 2(a), the UiO-66 displays a cube morphology with an average edge length of about 500 nm. Figure 2(b) shows that the BiOI is composed of irregular smooth sheets, and the size of these sheets is about 1 μm. Figure 2(c) and 2(d) are the SEM and TEM images of UiO-66/BiOI-2 composites respectively. It is obvious that the UiO-66 cubes are present on the surface of BiOI sheets. The attached small irregular smooth sheets have a lattice fringe spacing of 0.298 nm, corresponding to the (102) crystallographic planes of the tetragonal BiOI (Figure 2(e)). However, HRTEM images of UiO-66 could not be obtained, as the UiO-66 microcrystals tend to be damaged under high energy electron beam irradiation.

The BET surface areas of the samples were investigated using N$_2$ adsorption–desorption measurements. As shown in Table 1, the BET surface area of UiO-66 and BiOI were 527.4072 and 16.1617 m$^2$ g$^{-1}$, respectively. It is noted that the content of UiO-66 greatly affects the BET surface area of the UiO-66/BiOI composites. Compared with the pure BiOI, the BET surface area of the UiO-66/BiOI composites gradually increases with increasing UiO-66 content, from 68.4469 to 300.5957 m$^2$ g$^{-1}$. The porous UiO-66 has large specific surface area, so the BET surface area of UiO-66/BiOI composites is increased gradually with the increase of UiO-66 content in hybrids. Larger surface area of the photocatalysts can supply more surface-active sites and facilitate the charge-carrier transport, leading to the enhancement of the photocatalytic performance (Zheng & Jiao 2017).

The absorption abilities of as-prepared samples at different wavelengths were investigated by diffuse reflectance spectroscopy (Figure 3). It can be seen that the
UiO-66 shows its fundamental absorption edge at about 320 nm, indicating that UiO-66 does not possess the ability to utilize photo-energy in the visible-light range. The absorption edge of pure BiOI is around 620 nm, possessing a strong absorption in the visible-light range. The UiO-66/BiOI composites with different UiO-66 contents show a mixed absorption feature of pure UiO-66 and BiOI. The absorption feature of UiO-66/BiOI-1 and UiO-66/BiOI-2 and UiO-66/BiOI-3 were similar to the

Table 1 | Porous structure parameters of UiO-66, BiOI and the UiO-66/BiOI composites with different weight ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>527.4072</td>
<td>0.280551</td>
</tr>
<tr>
<td>BiOI</td>
<td>16.1617</td>
<td>0.124270</td>
</tr>
<tr>
<td>UiO-66/BiOI-1</td>
<td>68.4469</td>
<td>0.050094</td>
</tr>
<tr>
<td>UiO-66/BiOI-2</td>
<td>138.7424</td>
<td>0.117471</td>
</tr>
<tr>
<td>UiO-66/BiOI-3</td>
<td>300.5957</td>
<td>0.176943</td>
</tr>
</tbody>
</table>
pure BiOI and the absorption edge of UiO-66 becomes more evident with the increase of UiO-66 content in hybrids.

Photocatalytic activity

In this study, the photocatalytic activities of BiOI, UiO-66 and UiO-66/BiOI composites were evaluated using the degradation of salicylic acid under the visible-light irradiation. As illustrated in Figure 4, the salicylic acid self-photodegradation is almost unobserved within 120 min without the photocatalyst, indicating that salicylic acid is quite stable toward incident light. Within the Figure 4, it can be seen that the concentration of salicylic acid is decreased gradually with the increase of UiO-66 content in hybrids without visible-light irradiation, which is owing to the adsorption of the photocatalyst. The porous UiO-66 has large specific surface, which can enhance the adsorption of salicylic acid. It is believed that an appropriate amount of UiO-66 could effectively enhance the adsorption ability of UiO-66/BiOI nanocomposites owing to the enlarged specific surface area. However, with the weight ratios of UiO-66 further increased, the effective surface of the BiOI nanoparticles would reduce due to the excess coverage of UiO-66, which thus causes the rapid decrease of the photocatalytic activity under visible-light irradiation. Therefore, only when the appropriate content (5.2 wt%) of UiO-66 is coupled with BiOI does the photocatalytic efficiency of UiO-66/BiOI-2 nanocomposites reach maximum. So most of the salicylic acid molecules can be degraded in 120 min for all UiO-66/BiOI composites and the UiO-66/BiOI-2 sample shows the fastest degradation rate. By comparison, salicylic acid is degraded at a lower rate for the pure BiOI than for UiO-66/BiOI composites.

Photocatalyst stability

The stability of photocatalysts is very important for their practical utility in real applications. So the stability of UiO-66/BiOI composites in photocatalytic degradation of salicylic acid under visible-light irradiation was studied using UiO-66/BiOI-2. The photocatalyst was separated from solution by a centrifuge after each photodegradation and reused after washing by ultrasonic cleaning with deionized water; other factors were kept identical. As shown in Figure 5, although there is a minor decrease in the photocatalytic efficiency for each cycle, more than 85% of salicylic acid could still be degraded in the fifth cycle, which indicated that UiO-66/BiOI composite has good stability in the photocatalytic reaction under visible-light irradiation.

Photocatalytic mechanism

According to the above results and some previous literature (Sha et al. 2015; Ye et al. 2015), the enhanced photocatalytic activity of UiO-66/BiOI can be attributed to the following reasons. First, for the photocatalytic degradation process, the preliminary adsorption of the reactants is very important for efficient degradation. The UiO-66/BiOI composites have relative large surface area comparing with pure BiOI. So the UiO-66/BiOI composites can absorb more reactants on their surfaces, leading to the chemical reaction more easily. Second, the formation of the UiO-66/BiOI p-n junction plays a profound role in the photocatalytic degradation.
of salicylic acid over UiO-66/BiOI composites and a possible mechanism is proposed, as is shown in Figure 6. The BiOI is a p-type semiconductor; the valence band (VB) top and the conduction band (CB) bottom of BiOI are 2.30 and 0.58 eV according to the previous report (Li et al. 2014). The reformed CB potential of BiOI (−0.68 eV) is more negative than that of UiO-66 (−0.60 eV), and the VB potential of BiOI (2.30 eV) is less positive than that of UiO-66 (2.90 eV). So the UiO-66/BiOI p–n junction belongs to the ‘B-type hetero-junction’ class (Shamaila et al. 2011). Consequently, the photoinduced electrons on the CB of BiOI can easily migrate to the CB of UiO-66, as the photogenerated holes on the VB of UiO-66 will transfer to the VB of BiOI. The electric field created by the B-type heterojunction between BiOI and UiO-66 at the interface facilitates the migration of electrons from the VB of the p-type to that of the n-type semiconductor. These would largely reduce the recombination rate of the photogenerated electrons and holes. The holes can directly oxidize organic molecules. The new CB potential of UiO-66/BiOI is more negative than that of that of E(O₂/−O₂) (−0.33 eV) (Mousavi & Habibi 2016), so photogenerated electrons in the new CB of UiO-66/BiOI can react with O₂ to form ·O₂⁻, which then reacted with organic molecules to make them degradable. Therefore, it is obvious that UiO-66/BiOI composites possess higher photocatalytic activity than pure BiOI and UiO-66.

**CONCLUSIONS**

In summary, a series of UiO-66/BiOI heterojunction photocatalysts with different UiO-66 content were prepared through a facile hydrothermal method. The obtained UiO-66/BiOI composites have optimal photoactivity for the degradation of salicylic acid under visible-light irradiation when the content of UiO-66 was 5.2 wt%. Moreover, we proposed the photocatalytic mechanisms of the UiO-66/BiOI heterojunction photocatalysts. The enhanced photocatalytic activity of UiO-66/BiOI composites can be the result of the formation of p–n junctions between BiOI and UiO-66, which could facilitate the separation of photo-excited electron–hole pairs. The UiO-66/BiOI composites exhibit high photostability in the recycling experiment. These results indicate that the obtained UiO-66/BiOI composites are potential visible light photocatalysts.

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The authors declare no competing financial interest.

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