**Bi$_5$O$_7$I/g-C$_3$N$_4$ Heterostructures With Enhanced Visible-Light Photocatalytic Performance for Degradation of Tetracycline Hydrochloride**

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Bi$_5$O$_7$I/g-C$_3$N$_4$ p-n junctioned photocatalysts were synthesized by alcohol-heating and calcination in air. The structures, morphologies and optical properties of as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–Vis diffuse reflectance spectroscopy (DRS). Photocatalytic activity of the heterojunctioned composites were evaluated by degradation of Rhodamine B (RhB) and tetracycline hydrochloride (TCH) under visible light illumination. The results indicated that the composites exhibited superior efficiencies for photodegradation of RhB and TCH in comparison with pure BiOI, Bi$_5$O$_7$I and g-C$_3$N$_4$. An effective built-in electric field was formed by the interface between p-type Bi$_5$O$_7$I and n-type g-C$_3$N$_4$, which promoted the efficient separation of photoinduced electron-hole pairs. In addition, 8% Bi$_5$O$_7$I/g-C$_3$N$_4$ composite showed excellent photostability in a five-cycle photocatalytic experiment. Experiments on scavenging active intermediates revealed the roles of active species.

**Keywords:** photocatalysis, heterostructures, visible light adsorption, charge carrier separation, tetracycline hydrochloride

**INTRODUCTION**

Tetracycline antibiotics have a wide range of applications as broad-spectrum antibiotics. TCH with a high water solubility is formed by combining tetracycline with hydrochloric acid, which is widely used for treatment of human and animal diseases owing to its low cost, broad antibacterial spectrum, high chemical stability and low side effects (Wang and Wang, 2015). However, TCH has been overused worldwide in animal husbandry and aquaculture production. It is difficult to achieve total removal of TCH in natural environment due to its benzene-containing skeleton, which results in its long-term existence in water environment and harm to ecological environment and human health. Among various treatment methods of TCH, photocatalytic oxidation technology exhibits advantage of environmental-friendly process, low-energy cost and easy operation (Chen and Liu, 2016).

In recent years, semiconductor-based photocatalysts have been developed intensively due to their potential applications in water splitting (Kudo and Miseki, 2003), degradation of organic pollutants (Carey et al., 1976), photocatalytic reduction of carbon dioxide (Roy et al., 2010), photocatalytic organic synthesis (Xiao et al., 2015), etc. Titanium dioxide as a traditional semiconducting
The TiO2/C3N4 (Yan et al., 2016), BiOBr/g-C3N4 (Ye et al., 2013), and Bi5O7I/g-C3N4 (Chang et al., 2019) photocatalysts have been developed to enhance catalytic performance in degradation of organic pollutants in the past decades. Among these methods, formation of heterostructures has shown a promising improvement in the efficiency of charge separation and transfer. BiOI is a p-type of photocatalytic material with a layered structure. It has attracted intense scientific interest due to its unique properties based on narrow band gap and excellent photocatalytic performance (Lei et al., 2010; Rong et al., 2012; Chang et al., 2019). Bi5O7I is an n-type semiconductor with a high thermodynamic stability. Due to the decrease in proportion of iodine atoms, the positions of conduction and valence bands of Bi5O7I vary from BiOI, which has been extensively studied as a photocatalyst in degradation of organic pollutants (Geng et al., 2018; Wang et al., 2018; Xia et al., 2018). Bi5O7I possesses a more negative valence potential, which enables it to generate more holes to degrade pollutants after photoactivation (Liang et al., 2019). However, pure Bi5O7I is limited for application in photocatalysis because of weak visible-light absorption and easy recombination of photo-generated charge carriers. Formation of a heterojunctioned structure by combining Bi5O7I with other suitable semiconductors is possibly a promising method to improve the photocatalytic activity.

Photocatalytic performance, pure Bi5O7I or g-C3N4 samples were synthesized according to the previous report (Xiang et al., 2016). Briefly, Bi(NO3)3·5H2O (AR, 99.0%) was added slowly into an ethylene glycol (EG) solution containing KI (AR, 99.0%) with the Bi/I molar ratio of 1. The mixture was stirred for 0.5 h at room temperature in air, and then poured into a 50 ml Teflon-lined stainless autoclave until 80% of the autoclave volume was filled. The autoclave was allowed to be heated at 160°C for 12 h under autogenous pressure, and then cooled to room temperature in air. The resulting precipitates were collected and washed with ethanol and deionized water and dried at 60°C in air for 12 h.

Bi5O7I/g-C3N4 heterojunctioned composites were synthesized by a calcination method. BiOI and urea powers were mixed and ground for 0.5 h with agate grinding bowl. The resulting solid was placed in a crucible covered with an alumina lid and was then heated to 500°C in a muffle furnace for 2 h with a heating rate of 15°C/min. After cooling naturally to room temperature, the pale yellow resultant was washed for three times with deionized water and ethyl alcohol, respectively, and dried at 60°C in air for 12 h. The product was labeled as BiOI/g-C3N4.

Efficient degradation of TCH remains a challenge for semiconductor-based photocatalysis (Chen and Liu, 2016). In this work, a facile synthesis of Bi5O7I/g-C3N4 heterojunctioned structures were developed to enhance absorption of visible light and separation of photoinduced electron-hole pairs. Bi5O7I/g-C3N4 heterostructures were formed by synthesis of BiOI via an alcohol-heating route followed by calcination with mixing with urea powder. Photocatalytic performance of the heterojunctioned composites were evaluated by degradation of RhB and TCH under visible light illumination.

MATERIALS AND METHODS

Synthesis of Bi5O7I/g-C3N4 Composites

All the chemicals were analytical grade and used as received without further purification. BiOI powders were synthesized according to the previous report (Xiang et al., 2016). Briefly, Bi(NO3)3·5H2O (AR, 99.0%) was added slowly into an ethylene glycol (EG) solution containing KI (AR, 99.0%) with the Bi/I molar ratio of 1. The mixture was stirred for 0.5 h at room temperature in air, and then poured into a 50 ml Teflon-lined stainless autoclave until 80% of the autoclave volume was filled. The autoclave was allowed to be heated at 160°C for 12 h under autogenous pressure, and then cooled to room temperature in air. The resulting precipitates were collected and washed with ethanol and deionized water and dried at 60°C in air for 12 h.

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Characterization

X-ray diffraction (XRD) patterns of the samples were carried out on a diffractometer XRD-6100 (Shimadzu, Japan) operating at 40 KV and 30 mA with Cu Kα radiation (λ = 0.154,056 nm). Morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM) SU-1510 (Hitachi, Japan) and a high-resolution transmission electron microscope (HRTEM) Tecnai G2 F20 (FEI Company, United States). Reflection spectra of the samples were measured on a UV-Visible-NIR spectrophotometer UV-3600 (Shimadzu, Japan) in the range of 260–750 nm and BaSO4 was employed as a reflectance.
Brunauer–Emmett–Teller (BET) specific surface areas of the samples were analyzed by Autosorb-IQ-C specific surface analyzer (Kanta Instruments, United States). Chemical oxygen demand (COD) was evaluated by COD Max II Chemical Oxygen Demand Velocity Tester (Hach Company, United States). A CHI 660E electrochemical workstation and a three-electrode system including a reference electrode (RE), a counter electrode (CE) and a working electrode (WE) were used in photocurrent tests. The counter and reference electrodes were a piece of Pt mesh and a saturated calomel electrode, respectively. The working voltage was a positive bias of 1 V, the light source was a 20 W LED lamp, and the illumination interval was 20 s.

**Photocatalytic Activity Tests**

Degradation of RhB and TCH under visible light was used to evaluate the photocatalytic activities of all as-prepared samples. A 300 W xenon lamp equipped with a 420 nm cutoff filter severed as a visible light source was placed 15 cm above the water bath. Water circulation system was used to keep reactant suspension at 20°C avoiding the influence of photo-thermal effect. In a typical
experiment, a suspension was prepared by mixing 0.1 g photocatalyst into 100 ml of 8 mgL$^{-1}$ RhB aqueous solution and 100 ml of 20 mgL$^{-1}$ TCH aqueous solution, respectively. Before illumination, the suspension was vigorously stirred in the dark for 1 h to reach adsorption-desorption equilibrium. At given irradiation time intervals of 15 min, 3 ml of suspensions were collected and centrifuged at 5,000 rpm for 3 min to remove the catalysts. The absorbance of the solution was analyzed at 554 nm for RhB and 357 nm for TCH by UV-Vis spectrophotometer to monitor photocatalytic degradation of RhB and TCH, respectively.

**RESULTS AND DISCUSSION**

**XRD Analysis**

XRD was performed to investigate the phase structures of as-prepared samples and the results of g-C$_3$N$_4$, BiOI, Bi$_5$O$_7$I, BiOI/g-C$_3$N$_4$ and Bi$_5$O$_7$I/g-C$_3$N$_4$ are shown in Figure 1. The strongest peak of pure g-C$_3$N$_4$ (JCPDS No.87-1,526) at 27.75° is assigned to its (002) crystal plane (Yang et al., 2013; Dong et al., 2015; Ho et al., 2015). The characteristic diffraction peaks at 2θ = 29.64° and 31.65° for pure BiOI, correspond to the (102) and (110) crystal planes of tetragonal BiOI, respectively (JCPDS, No.10-0445). The diffraction peaks at 28.06°, 31.08°, 33.02°, and 33.40° observed on pure Bi$_5$O$_7$I are indexed to crystal planes (312), (004), (204) and (020) of orthorhombic Bi$_5$O$_7$I, respectively, according to the XRD standard card (JCPDS No.40-0548), which suggested the formation of Bi$_5$O$_7$I after calcination for twice at 500°C. The XRD pattern of 8% BiOI/g-C$_3$N$_4$ presents characteristic diffraction peaks corresponding to BiOI and g-C$_3$N$_4$, indicating formation of composite including BiOI and g-C$_3$N$_4$ after the first calcination at 500°C. All the peaks in the XRD pattern of 8% Bi$_5$O$_7$I/g-C$_3$N$_4$ were indexed to the characteristic diffraction of crystal planes of orthorhombic Bi$_5$O$_7$I, suggesting that BiOI has been transformed into Bi$_5$O$_7$I after the second calcination at 500°C. No obvious characteristic diffraction peaks were identified for g-C$_3$N$_4$ in the sample, which can be ascribed to low crystallinity of g-C$_3$N$_4$ and overlap of the main peaks with Bi$_5$O$_7$I at 28.06° and g-C$_3$N$_4$ at 27.75°. In
addition, no impurity peaks are detected in these patterns, revealing that the composites are composed of g-C3N4 and Bi5O7I with a high purity.

**SEM and BET Analysis**

Figure 2 shows typical FE-SEM images of as-prepared photocatalysts. Microspherical structures with diameter of about 2.5 μm, composed of nanosheets, were observed in BiOI sample, as shown in Figure 2A. Figure 2B shows the aggregated particles of Bi5O7I photocatalyst which was formed by calcination of BiOI in air. Figures 2D,E show the aggregation of micrometer sized irregular particles of BiOI/g-C3N4 and Bi5O7I/g-C3N4 composites, respectively. In the specific surface analysis testing, the specific surface areas of Bi5O7I, g-C3N4 and 8% Bi5O7I/g-C3N4 were determined to be 17.6, 14.2 and 16.5 m²g⁻¹, respectively which indicated that specific surface area had a trivial effect on photocatalytic performance.

**TEM Analysis**

Sample 8% Bi5O7I/g-C3N4 was further characterized by TEM, as shown in Figure 3. Nanoparticles with diameter of several nanometers were distributed in the composite, suggesting that the as-synthesized Bi5O7I/g-C3N4 composite was possibly mixtures of two different components. In the HRTEM image (Figure 3B), the lattice fringes of 0.338, 0.249 and 0.316 nm coincide with the interplanar spacing of plane (002) of g-C3N4 and planes (114) and (312) of Bi5O7I, respectively, which is consistent with the results of XRD analysis. Furthermore, Bi5O7I nanospheres were distributed on the surface of g-C3N4, which implied a superior absorption of visible light. Based on the results of XRD, SEM, and TEM, the composites were successfully synthesized and formation of the interfaces between Bi5O7I and g-C3N4 confirmed a p-n junction structure in the composite.

**UV-Vis DRS Analysis**

Figure 4 exhibits the UV-Vis diffuse absorbance spectra of as-prepared photocatalysts. Apparently, BiOI absorbs light most effectively with an absorption edge at about 700 nm. Comparatively, the pure g-C3N4 sample exhibits a shorter absorption edge, which is located at about 450 nm. The light absorption threshold of samples extended to longer wavelength with the introduction of BiOI and Bi5O7I, which indicated that the visible light adsorption of as-prepared composites was contributed by the formation of BiOI and Bi5O7I. The band gap energies of as-prepared composites can be calculated using classical Tauc’s approach.
\[ ahv = A(hv - E_g)^{1/2} \]  

where \( \alpha \), \( h \), \( \nu \), \( A \) and \( E_g \) are absorption coefficient, Planck's constant, light frequency, proportionality constant and band gap energy, respectively (Huang et al., 2014). Among them, values of \( n \) are 4 for indirect transition and 1 for direct transition, respectively (Xu et al., 2015). Since both Bi\(_5\)O\(_7\)I and g-C\(_3\)N\(_4\) are indirect transition semiconductors (Yang et al., 2014; Liu et al., 2015), values of \( n \) are 4. Hence, values of \( E_g \) for Bi\(_5\)O\(_7\)I and g-C\(_3\)N\(_4\) can be estimated to be 2.59 and 2.71 eV respectively. These \( E_g \) values are in accordance with those in previous reports (Chen et al., 2015; Bai et al., 2016).

**Photocatalytic Properties**

The photocatalytic activities of as-synthesized samples were first characterized by degradation of RhB under visible light illumination (\( \geq 420 \) nm), as shown in Figure 5A. \( C \) was the concentration of RhB during the reaction and \( C_0 \) was the initial concentration of RhB. As for pure g-C\(_3\)N\(_4\) and BiOI, only 21 and 39% of RhB were photodegraded after visible-light irradiation for 120 min, respectively. Meanwhile, Bi\(_5\)O\(_7\)I achieved superior photocatalytic activity over BiOI. After formation of BiOI/g-C\(_3\)N\(_4\) and Bi\(_5\)O\(_7\)I/g-C\(_3\)N\(_4\), the composites show a significant increase in RhB degradation performance compared with the pure BiOI, Bi\(_5\)O\(_7\)I and g-C\(_3\)N\(_4\). The degradation of RhB was fitted for first-order kinetics with a Langmuir-Hinshelwood model (Sun et al., 2014): \( \ln \left( \frac{C_0}{C} \right) = \)
where $k$ is the reaction rate constant, which were presented in Figure 5B. The reaction rate constants of pure g-C$_3$N$_4$, pure BiOI and pure Bi$_2$O$_3$I were estimated to be $0.00370\text{ min}^{-1}$, $0.00820\text{ min}^{-1}$, $0.01456\text{ min}^{-1}$, respectively. With formation of composites, the $k$ values increased to $0.02095\text{ min}^{-1}$, $0.02843\text{ min}^{-1}$, $0.02028\text{ min}^{-1}$ and $0.03497\text{ min}^{-1}$ for 6% BiOI/g-C$_3$N$_4$, 8% BiOI/g-C$_3$N$_4$, 10% BiOI/g-C$_3$N$_4$ and 8% Bi$_2$O$_3$I/g-C$_3$N$_4$, respectively. The optimal degradation rate constant achieved by 8% Bi$_5$O$_7$I/g-C$_3$N$_4$ was approximately 9.45 times higher than that of pure g-C$_3$N$_4$, 4.26 times of pure BiOI and 2.40 times of pure Bi$_2$O$_3$I, respectively.

The photostability of 8% Bi$_5$O$_7$I/g-C$_3$N$_4$ was characterized through a five-cycle photocatalytic experiment, as shown in Figure 5C. No apparent deactivation was detected in five successive degradation reactions under visible light irradiation, suggesting the possibility for practical application in treatment of water pollution.

To investigate active species involved in the photocatalytic reaction, BQ, IPA and EDTA were used as scavengers to trap O$_2^-$, ·OH and h$^+$, respectively. The effects of different scavengers on the removal efficiency of RhB were shown in Figure 5D. The results indicated that the removal percentage of RhB was significantly decreased to approximate 57, 38, 31% after addition of EDTA, BQ and IPA, respectively. These results revealed that all the reactive species of h$^+$, ·OH, and O$_2^-$ participated in the photocatalytic degradation processes and all of them played important roles in the photocatalytic degradation reaction of RhB.

Figure 6 shows the photocatalytic activity of as-prepared samples in degradation of TCH under visible light illumination ($\geq420$ nm). Similarly, 8% Bi$_2$O$_3$I/g-C$_3$N$_4$ achieved the superior photocatalytic activity. Photocatalytic activity descended in the queue as 8% Bi$_2$O$_3$I/g-C$_3$N$_4$ > 8% BiOI/g-C$_3$N$_4$ > 10% BiOI/g-C$_3$N$_4$ > 6% BiOI/g-C$_3$N$_4$ > Bi$_2$O$_3$I > g-C$_3$N$_4$ > BiOI. Stability experiments indicated that sample 8% Bi$_2$O$_3$I/g-C$_3$N$_4$ showed a stable efficient photocatalytic performance in photodegradation of TCH. Scavengers experiments illustrated that h$^+$ played an important role in the photocatalytic degradation reaction of TCH.

To further confirm complete photodegradation of RhB and TCH, COD of the solutions were measured before and after degradation tests. The COD values of the solutions before degradation of RhB and TCH were evaluated to be 9.5 mg/L and 32.0 mg/L, respectively. Those after degradation of RhB and TCH were 1.2 mg/L and 2.8 mg/L, respectively, both of which were significantly lower than the WHO guideline value of 10 mg/L. It suggested very rare organic species in the solutions.

Testing on transient photocurrent response were performed to study the transfer and separation efficiency of photogenerated charge carriers under visible light irradiation. Stronger photocurrent intensity usually indicates higher separation efficiency of holes and electrons. Figure 7 illustrates the transient photocurrent response curves of pure BiOI, Bi$_2$O$_3$I, g-C$_3$N$_4$ and Bi$_2$O$_3$I/g-C$_3$N$_4$ composite. Once the light source was turned on and off, the sample electrode exhibited a rapid photocurrent change. Furthermore, the Bi$_2$O$_3$I/g-C$_3$N$_4$ composite showed a strongest photocurrent response. It suggests that more efficient separation efficiency of electrons and holes occurred in Bi$_5$O$_7$I/g-C$_3$N$_4$ heterojunction, thus an enhanced photocatalytic activity was achieved by Bi$_2$O$_3$I/g-C$_3$N$_4$ composite photocatalyst.

**Proposed Mechanism for Enhanced Photocatalytic Activity With Bi$_2$O$_3$I/g-C$_3$N$_4$ Composites**

Figure 8 shows the proposed photocatalytic mechanism of Bi$_2$O$_3$I/g-C$_3$N$_4$. The valence band edge potential and the conduction band edge potential of Bi$_2$O$_3$I and g-C$_3$N$_4$ were calculated using electronegativity with the following empirical equations (Li et al., 2015b)
visible valence band edge potential, $E_{CB}$ is the conduction band edge potential, $x$ is the electronegativity of chemical elements (a, b, and c are the atomic number of compounds), $E_g$ is the energy of free electrons on the hydrogen scale (about 4.5 eV), $E_f$ is the band-gap energy of semiconductor and $x$ is the electronegativity of the semiconductor. The $X$ value for Bi$_5$O$_7$I is about 6.22 eV. For g-C$_3$N$_4$, the $X$ value is 4.73 eV (An et al., 2018). Therefore, the valence of $E_{VB}$ and $E_{CB}$ of Bi$_5$O$_7$I and g-C$_3$N$_4$ were calculated to be 3.02, 0.43 eV and 1.59, −1.13 eV, respectively. The Fermi energy ($E_f$) level of Bi$_5$I as a p-type semiconductor is closed to the valence band, while that of g-C$_3$N$_4$ as a n-type semiconductor is closed to the valence band. After contact was made between Bi$_5$I and g-C$_3$N$_4$, electrons and holes migrated, i.e., electrons in g-C$_3$N$_4$ diffused to Bi$_5$I and holes in Bi$_5$I diffused to g-C$_3$N$_4$ which led to the formation of an electric field (Wang et al., 2014). The diffusion process continued until the Fermi levels of Bi$_5$I and g-C$_3$N$_4$ reached an equilibrium state. Simultaneously, the valence and conduction bands of heterojunctioned Bi$_5$I and g-C$_3$N$_4$ were bent to render a balanced state. After visible light illumination, the induced holes from the valence band of g-C$_3$N$_4$ transferred to the valence band of Bi$_5$I and the photoexcited electrons transferred from the conduction band of Bi$_5$I to the conduction band of g-C$_3$N$_4$ driven by built-in electric field. It allows more effective separation and longer lifetime of photoinduced electron-hole pairs. Electrons gathered on the surface of g-C$_3$N$_4$ reacted with O$_2$ in the water to form •OH (Lin et al., 2016), leading to the degradation of RhB. Simultaneously, holes on the valance band of Bi$_5$I possesses a higher oxidation capability on RhB and TCH. The formation of Bi$_5$I/g-C$_3$N$_4$ heterojunction not only expands the photoresponse region, but also suppresses the recombination of photogenerated electron-hole pairs and improves the photocatalytic activity.

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**CONCLUSION**

In summary, visible-light-driven heterostructured Bi$_5$I/g-C$_3$N$_4$ photocatalysts were designed and synthesized by alcohol-heating and calcination processes. Enhanced photodegradation performance of RhB and TCH under visible light (λ ≈ 420 nm) was achieved by the 8% Bi$_5$I/g-C$_3$N$_4$ composite compared with pure BiOI, g-C$_3$N$_4$ and Bi$_5$I. An effective built-in electric field was formed by the interface between p-type Bi$_5$I and n-type g-C$_3$N$_4$, which promoted the efficient separation of photogenerated electron-hole pairs. Furthermore, 8% Bi$_5$I/g-C$_3$N$_4$ composite showed excellent photoactivity in a five-cycle photocatalytic experiment. Experiments on scavenging active intermediates revealed that h$, \cdot$OH, and O$_2^−$ were all active species in photodegradation of RhB and h$^+$ was dominant in photodegradation of TCH.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

**AUTHOR CONTRIBUTIONS**

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

**FUNDING**

This paper is based on the research sponsored by the National Natural Science Foundation of China (NSFC, Grant Nos 41975172, 20907021).

**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: [https://www.frontiersin.org/articles/10.3389/fchem.2021.781991/full#supplementary-material](https://www.frontiersin.org/articles/10.3389/fchem.2021.781991/full#supplementary-material)
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