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Article

Construction of nitrogen and phosphorus co-doped graphene quantum dots/Bi₅O₇I composites for accelerated charge separation and enhanced photocatalytic degradation performance

Kai Li ^a, Mengxia Ji ^a, Rong Chen ^b, Qi Jiang ^b, Jiexiang Xia ^{a,*}, Huaming Li ^a^a School of Chemistry and Chemical Engineering, Institute for Energy Research, Jiangsu University, Zhenjiang 212013, Jiangsu, China^b School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China

ARTICLE INFO

Article history:

Received 2 November 2019

Accepted 18 December 2019

Published 5 August 2020

Keywords:

Bi₅O₇I

N,P co-doped graphene quantum dots

Photocatalysis

Ionic liquid

Charge separation

ABSTRACT

Nitrogen and phosphorus co-doped graphene quantum dot-modified Bi₅O₇I (NPG/Bi₅O₇I) nanorods were fabricated via a simple solvothermal method. The morphology, structure, and optical properties of the as-prepared samples were investigated by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), and diffused reflectance spectroscopy. The photocatalytic performance was estimated by degrading the broad-spectrum antibiotics tetracycline and enrofloxacin under visible light irradiation. The photo-degradation activity of Bi₅O₇I improved after its surface was modified with NPGs, which was attributed to an increase in the photogenerated charge transport rate and a decrease in the electron-hole pair recombination efficiency. From the electron spin resonance spectra, XPS valence band data, and free radical trapping experiment results, the main active substances involved in the photocatalytic degradation process were determined to be photogenerated holes and superoxide radicals. A possible photocatalytic degradation mechanism for NPG/Bi₅O₇I nanorods was proposed.

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1. Introduction

In recent years, a large number of antibiotics from medicine have been emitted into the ambient because of the fast socialization process [1]. Antibiotics are highly bio-toxic; therefore, the presence of excess antibiotics in the water environment has caused adverse effects and widespread concern around the world. The conventional treatments have limitations such as extremely difficult degradation process and high cost [2]. Since the first report of photocatalytic water splitting on a TiO₂ photochemical electrode under light irradiation in 1972, semiconductor photocatalysis has received wide attention as an effi-

cient and environmentally friendly technique for energy conversion and environmental protection [3–7]. To date, several photocatalysts have been reported, such as TiO₂, BiPO₄, Bi₂WO₆, Bi₂GeO₅, g-C₃N₄, and CdS [8–13].

Bismuth oxyhalides (BiOX, X = Cl, Br, I) have drawn extensive interest in the field of photocatalysis as prospective photocatalysts because they can efficiently and thoroughly remove organic pollutants under visible or UV light irradiation [14–17]. The advantages of BiOX include effective photogenerated electron-hole separation and outstanding photocatalytic performance, which are attributed to its unique layered structure that can induce the generation of internal static electric fields [18].

* Corresponding author. Tel/Fax: +86-511-88791108; E-mail: xjx@ujs.edu.cn

This work was supported by the National Natural Science Foundation of China (21676128 and 21576123), Jiangsu University Scientific Research Funding (11JDG0146), and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX17_1791).

DOI: 10.1016/S1872-2067(20)63531-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 8, August 2020

In particular, BiOI is interesting because of its strong ability to absorb visible light under sunlight irradiation [19]. However, the high photogenerated carrier recombination rate significantly limits its photocatalytic performance. So far, many measures have been implemented to enhance the photocatalytic activity of BiOI, such as nanoscaling [20], tailoring crystal facets [21], doping [22], surface modification [23], and compositing with other photocatalysts [24]. Recently, to raise the photocatalytic activity of BiOI, various materials have been applied, successfully yielding composite materials such as AgI-BiOI [25], Au-BiOCl-OV [26], and mesoporous g-C₃N₄/BiOI [27]. In addition, it has been found that the photocatalytic performance of BiOI can be enhanced by adjusting the proportion of halogen in BiOI, resulting in novel Bi-rich materials. Bi-rich BiOI materials with different halogen contents, such as Bi₅O₇I, Bi₄O₅I₂, and Bi₇O₉I₃, have been reported to exhibit high photocatalytic activity owing to narrow band gaps or the presence of hybridized I 5*p* orbitals in the valence band (VB) [28–30]. Bi₅O₇I has been used in the field of photocatalytic organic pollutant removal and nitrogen fixation. However, it has some intrinsic drawbacks, like inadequate absorption of visible light, and poor separation and high recombination rate of photoinduced electron-hole pairs [31]. To overcome these drawbacks, for the Bi₅O₇I material, metal element doping, crystal facet controlling, heterojunction construction, and other approaches have been explored [32–34]. Fang et al. synthesized a Ag/AgBr/Bi₅O₇I heterojunction with enhanced photogenerated electron-hole pair separation efficiency and excellent photo-generated electron mobility [35]. In 2018, Chen's group successfully prepared an Ag₂O/Bi₅O₇I heterojunction with improved charge separation rate and light capture capacity [36]. Thus, after being compounded with other materials, Bi₅O₇I exhibits enhanced photocatalytic activity, which is attributed to reduced photogenerated electron-hole pair recombination efficiency. However, Bi₅O₇I-based composites suffer from poor visible light absorption. Therefore, it is especially important to develop novel Bi₅O₇I-based composite photocatalysts for high utilization of visible light.

Graphene quantum dots (GQDs) have been widely used in bioimaging, optical sensing, and photocatalysis because of their quantum size effect [37–40]. However, their low quantum yield (QY) limits their application in the field of photocatalysis [41]. Recently, GQDs co-doped with elements (N, Cl or N, B) have received a lot of attention because of their enhanced QYs [42–44]. Li's group has developed a bottom-up method to prepare S, N co-doped GQDs with more than 70% QY [45]. Moreover, element-doped GQD-modified photocatalytic systems have been constructed [46,47]. Ding et al. [48] demonstrated that S, N-GQDs in (BiO)₂CO₃ composites accepted photogenerated electrons during the photocatalytic reaction, thus distinctly inhibiting the recombination of photoinduced charge carriers and enhancing the photocatalytic performance of the photocatalyst. Moreover, CeO₂ was modified with S, N co-doped GQDs, resulting in good visible light absorption [49]; the photocatalyst decorated with GQDs exhibited increased absorption in the visible light region. Lately, N, P co-doped GQD (NPG) were demonstrated to exhibit a high QY by Zhao's group [50].

Inspired by the previous content, the photocatalytic activity of NPG-modified Bi₅O₇I is very worthy of expectation. Furthermore, how NPG improve the photocatalytic activity of Bi₅O₇I needs to be studied clearly.

In this study, NPG/Bi₅O₇I composite materials were synthesized via a simple solvothermal method with the ionic liquid 1-ethyl-3-methylimidazolium iodide ([Emim]I). The results showed that the introduction of NPG significantly improved the visible light absorption capacity of Bi₅O₇I and the rate of separation of photogenerated electron-hole pairs in Bi₅O₇I, simultaneously. The NPG/Bi₅O₇I samples exhibited high photocatalytic activity for the degradation of colorless antibiotics tetracycline (TC) and enrofloxacin (ENR) under visible light irradiation. The primary active species involved in the photocatalytic reaction were determined to be O₂^{•−} and holes. Furthermore, a possible reaction mechanism for the enhanced photocatalytic activity was proposed.

2. Experimental

2.1. Materials and sample preparation

All reagents employed in this experiment were analytical grade and used as received with no extra purification. The ionic liquid 1-ethyl-3-methylimidazolium iodide ([Emim]I, 99%) was bought from Chengjie Chemical Co. Ltd., Shanghai.

2.2. Synthesis of NPG and NPG/Bi₅O₇I composite samples

NPG was synthesized according to the literature [50]. The detailed experimental process is as follows. 500 μL of tetrakis (hydroxymethyl) phosphonium Chloride (PEI-EC) and 1.5 mL of ethylenediamine endcapped polyethylenimine (THPC) were dissolved in 25 mL of distilled water. The resulting solution was agitated for 30 min, transferred into a Teflon-lined stainless steel autoclave (50 mL), and then, placed in a baking oven at 230 °C for 8 h. Then, the autoclave was naturally cooled down to room temperature, and the pH of the obtained yellow liquid was adjusted to 7.0 by adding NaOH solution under constant stirring. The above blend was dialyzed in distilled water for 24 h to remove small molecular substances. Finally, the obtained NPG solution was preserved in a glass bottle for further use.

NPG/Bi₅O₇I composites were synthesized via a solvothermal process. Typically, a certain volume of NPG and 1 mmol of Bi(NO₃)₃·5H₂O were dispersed in 10 mL of mannitol solution (0.1 mol L^{−1}) to obtain solution A. Separately, 8 mL of 0.1 mol L^{−1} mannitol solution was added into 1 mmol of [Emim]I with continuous magnetic stirring to obtain solution B. Then, solution B was poured into solution A and the pH of the mixed solution was regulated to 13 by adding 1 mol L^{−1} NaOH solution under continuous stirring for 30 min. Next, the resulting suspension was poured into a high-pressure reactor (25 mL) and heated at 140 °C for 24 h. The obtained precipitate was washed with water and ethanol for three times, and then, placed in a 60 °C oven for 12 h. During the synthesis process, 4, 6, and 8 mL of NPG were added to obtain NPG/Bi₅O₇I-1, NPG/Bi₅O₇I-2, and

NPG/Bi₅O₇I-3, respectively. In addition, pure Bi₅O₇I nanorods were synthesized by a similar process without adding NPGs.

2.3. Characterization

X-ray diffraction (XRD, Shimadzu XRD-6000) was performed to determine the crystalline structure and purity of the as-prepared samples at a 2θ scan rate of 7° min^{-1} with the Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The chemical composition and chemical states of elements were determined by X-ray photoelectron spectroscopy (XPS) measurements using a Mg $K\alpha$ excitation source with an ESCALAB MKII equipment. The morphology and microtexture of the as-prepared samples were observed with a scanning electron microscopy (SEM, JSM-7800F, JEOL) instrument equipped with an energy-dispersive X-ray spectroscope (EDS) using an acceleration voltage of 10 kV. Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) and high-resolution TEM (HRTEM, Tecnai G2 F30 S-TWIN) were performed at 200 kV. The UV-vis diffuse reflectance spectra were recorded on a UV-2450 diffuse reflectance spectrophotometer (DRS, Shimadzu Co.) with BaSO₄ powder as the standard reference. The structural information of the samples was obtained by performing Fourier-transform infrared (FT-IR) spectroscopy (Nicolet Model Nexus 470) with KBr as the background. The photoluminescence (PL) spectra were recorded on a Cary Eclipse fluorescence spectrometer with an excitation wavelength of 360 nm. A Raman spectrometer (Renishaw Invia) was used to collect the Raman spectra. A JES-FA200 ESR spectrometer was used to record different electron spin resonance (ESR) signals with a spin-trap reagent, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), in different environments (methanol for O₂^{•-} and water for •OH). N₂ adsorption-desorption measurements were performed to determine the specific surface areas of the samples using TriStar II3020 (Micromeritics Instrument Corporation, USA) according to the Brunauer-Emmett-Teller (BET) method.

2.4. Photocatalytic degradation performance evaluation

The photocatalytic activities of the as-prepared samples were determined by performing photocatalytic degradation of TC (20 mg L⁻¹) and ENR (10 mg L⁻¹) under visible light irradiation at 30 °C in a circulating water bath. A 300 W xenon lamp with a 400 nm UV filter was used to provide visible light. Typically, 50 mg of the photocatalyst was ultrasonically dispersed in 100 mL of TC or ENR solution. The mixture was continuously magnetic stirred; an air pump was used to provide oxygen. For 30 min, no light was supplied in order to achieve the adsorption-desorption equilibrium between the catalyst and the pollutant. After visible light irradiation, 4 mL of the reacted solution was taken out and centrifuged at regular intervals. The supernatant obtained by centrifugation was subjected to further detection. The concentrations of TC and ENR were determined using a UV-vis spectrophotometer; the characteristic absorption peaks of TC and ENR were detected at 356 nm and 273 nm, respectively.

2.5. Photoelectrochemical measurements

Photoelectrochemical analysis was performed on a standard three-electrode system (CHI 660B) using a platinum wire electrode as the counter electrode, a saturated Ag/AgCl as the reference electrode, and indium-tin oxide (ITO) glass ($1 \times 0.5 \text{ cm}^2$) coated with 0.1 mg of the sample as the working electrode. The electrolyte used for the photocurrent measurements was 0.1 mol L⁻¹ phosphate buffered saline solution with pH = 7 and the electrochemical impedance liquid used was 0.1 mol L⁻¹ KCl solution containing 5 mmol L⁻¹ Fe(CN)₆³⁻/Fe(CN)₆⁴⁻. A 300 W xenon lamp (current: 13 A) was used as the light source.

3. Results and discussion

XRD was performed to determine the crystalline structure and composition of pure Bi₅O₇I and NPG/Bi₅O₇I composite samples. The pure Bi₅O₇I characteristic peaks agreed well those of the standard XRD pattern (JCPDS No. 38-0669), which indicated the successful synthesis of the Bi₅O₇I photocatalyst. The characteristic peaks at 28.1° , 30.4° , 31.4° , 37.8° , 42.5° , and 49.5° in Fig. 1 corresponded to the (3 1 1), ($\bar{3}$ 1 3), ($\bar{6}$ 0 3), (6 0 2), (0 2 0), and ($\bar{9}$ 1 2) crystal planes of Bi₅O₇I, respectively. Notably, no additional peaks were observed in the XRD patterns of the NPG/Bi₅O₇I composites, which could be attributed to the low NPG content. Moreover, the patterns of different NPG/Bi₅O₇I composites were consistent with that of the standard sample, demonstrating that the addition of NPGs did not change the crystal phase of Bi₅O₇I.

XPS was performed to ascertain the chemical states and compositions of the NPG/Bi₅O₇I-2 and Bi₅O₇I photocatalysts. Fig. 2a shows the survey scan spectra of pure Bi₅O₇I and NPG/Bi₅O₇I-2, indicating that NPG was successfully introduced into Bi₅O₇I. The chemical states of the two samples were investigated by high-resolution XPS. As displayed in Fig. 2b, the peaks at binding energies of 164.0 and 158.7 eV were assigned to Bi 4f_{5/2} and Bi 4f_{7/2}, indicating that Bi existed in the form of Bi³⁺ [51]. In Fig. 2c, the peak at 529.8 eV was assigned to the oxygen of Bi₅O₇I [32]. The I 3d spectra (Fig. 2d) exhibited two peaks at 619.2 and 630.7 eV, which indicated the existence of I 3d_{3/2} and 3d_{5/2} components, respectively [52]. Compared to those for pure Bi₅O₇I, the Bi 4f and I 3d peaks for NPG/Bi₅O₇I

Fig. 1. XRD patterns of pure Bi₅O₇I and NPG/Bi₅O₇I samples with different NPG contents.

Fig. 2. XPS data for $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 samples. (a) Survey spectra of the samples; (b) Bi 4f, (c) O 1s, (d) I 3d, (e) C 1s, and (f) P 2p spectra.

were slightly shifted to lower binding energies, proving the occurrence of interaction between NPG and $\text{Bi}_5\text{O}_7\text{I}$. In the C 1s XPS profiles (Fig. 2e), the peaks at 288.1, 285.8, and 284.6 eV indicated the existence of C=C, oxygenated carbon, and carbon nitrite functional groups, respectively [53]. The peaks at 133.1 and 131.9 eV in Fig. 2f were assigned to the P–P bonds and P–O bonds, respectively. The C 1s and P 2p spectra verified that NPG was successfully introduced into $\text{Bi}_5\text{O}_7\text{I}$ and the XPS results were well consistent with the XRD results [54,55].

In order to further prove that NPGs were successfully introduced into $\text{Bi}_5\text{O}_7\text{I}$, the as-prepared samples were subjected to FT-IR spectroscopy and the data are presented in Fig. S1a. The absorption peak at 539 cm^{-1} was assigned to the Bi–O stretching mode [56]. After NPG addition, a weak band appeared at 959 cm^{-1} , corresponding to the stretching vibration of C–H; as the amount of NPGs increased, the peaks at this position became more intense, which indicated that NPG was successfully compounded with $\text{Bi}_5\text{O}_7\text{I}$ [57]. In the Raman spectra (Fig. S1b), the two distinct peaks at 100.2 and 150.2 cm^{-1} corresponded to the A_g and E_g inner Bi–I stretching modes, respec-

tively [25,58]. Compared to the pure $\text{Bi}_5\text{O}_7\text{I}$ nanorods, peaks of NPG/ $\text{Bi}_5\text{O}_7\text{I}$ existed two differences: (1) after the NPG introduced, the peak intensity dramatically increased, (2) peaks of NPG/ $\text{Bi}_5\text{O}_7\text{I}$ materials shifted to 99.6 and 150.8 cm^{-1} , respectively, indicating that the strong interactions between $\text{Bi}_5\text{O}_7\text{I}$ and NPG.

In general, the photocatalytic behavior of a semiconductor photocatalyst significantly depends on its optical response ability and energy band structure. The DRS data and calculated band gaps for the samples are displayed in Fig. 3. The intrinsic absorption edge of the as-prepared $\text{Bi}_5\text{O}_7\text{I}$ sample was confirmed to be 415 nm. With increasing amount of NPGs, the optical absorption capacity of the composite material in the 415–800 nm range distinctly increased, indicating that the NPG-modified $\text{Bi}_5\text{O}_7\text{I}$ material utilized more visible light, which boosted the photocatalytic activity [59]. In addition, the band gap of $\text{Bi}_5\text{O}_7\text{I}$ calculated according to the Tauc approach was 2.81 eV [60].

The morphology and microstructure of the $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 photocatalysts were investigated by SEM, TEM,

Fig. 3. (a) UV-vis diffuse reflectance spectra of $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ materials; (b) $(\alpha E_{\text{photon}})^{1/2}$ vs. E_{photon} curve of the as-prepared $\text{Bi}_5\text{O}_7\text{I}$ sample.

Fig. 4. TEM images of (a) Bi₅O₇I and (b) NPG/Bi₅O₇I-2 samples; (c) High-resolution TEM image of the NPG/Bi₅O₇I-2 material; (d) EDS profile of the NPG/Bi₅O₇I-2 material.

and HRTEM. As shown in Fig. 4a, the pure Bi₅O₇I sample exhibited a slender nanorod structure. As observed from Fig. 4b and Fig. 4c, after NPG addition, a lot of dark dots with an average size of around 4 nm uniformly distributed on the surface of Bi₅O₇I appeared, suggesting that NPG had been successfully combined with Bi₅O₇I. The 0.32 nm lattice spacing corresponded to the NPG (0 0 2) crystal planes [50]. Meanwhile, the lattice spacing values of 0.284 and 0.213 nm for NPG/Bi₅O₇I-2 corresponded to the (-0 6 3) and (0 2 0) crystal planes of Bi₅O₇I. The EDS pattern showed C, N, O, P, Bi, and I peaks, which well confirmed the above-mentioned analysis results. Moreover, elemental mapping was conducted to determine the elemental distribution in the as-synthesized NPG/Bi₅O₇I composite (Fig. S1). The above-mentioned results strongly testified that NPGs were anchored on the surface of Bi₅O₇I nanorods.

Nitrogen adsorption-desorption curves were recorded to calculate the specific surface areas of the as-prepared photocatalysts. As shown in Fig. 5a, the specific surface area of the original Bi₅O₇I sample was only 9.70 m² g⁻¹; however, with NPG introduction, the specific surface area increased, and the value reached 40.57 m² g⁻¹ for NPG/Bi₅O₇I-2. It was expected that the increased specific surface area could provide adequate reaction sites to adsorb more pollutants, which would probably improve the photocatalytic activity [61].

Colorless antibiotics TC and ENR were selected as the typical pollutants to study the photocatalytic activity of the prepared materials under visible light irradiation. The adsorption ability of Bi₅O₇I nanorods and NPG/Bi₅O₇I composites toward the two different model pollutants TC and ENR in the dark was evaluated and the adsorption curves are exhibited in Fig. S3. As observed, the adsorption-desorption equilibrium was reached

between the photocatalysts and pollutants after adsorption for 30 min in the dark. As displayed in Fig. 6a, Bi₅O₇I nanorods only degraded 24.1% of TC after irradiation for 120 min, indicating the low photocatalytic degradation efficiency of Bi₅O₇I toward TC. The NPG/Bi₅O₇I composites, exhibited significantly improved photocatalytic degradation performances. After irradiation for the same time, 42.7%, 78.5%, and 50.0% of TC were removed by NPG/Bi₅O₇I-1, NPG/Bi₅O₇I-2, and NPG/Bi₅O₇I-3, respectively, and NPG/Bi₅O₇I-2 exhibited the highest degradation rate for TC. ENR was used to further confirm the superior performances of the NPG/Bi₅O₇I composites and the photocatalytic degradation results are shown in Fig. 6b. Even after irradiation for 120 min, NPG/Bi₅O₇I-2 displayed the highest photocatalytic degradation rate; it could degrade 54.9% of ENR, while ENR hardly degraded over the pure Bi₅O₇I photocatalytic system. This result confirmed the high efficiency of the NPG/Bi₅O₇I photocatalyst for persistent antibiotic contaminant removal.

Electrochemical impedance spectroscopy (EIS) and photo-current measurements were performed to explore the separation and recombination efficiency of photogenerated electron-hole pairs. Usually, the smaller the Nyquist circle, the smaller is the resistance for charge transfer [62,63]. As can be seen from Fig. 7a, the Nyquist semicircle for NPG/Bi₅O₇I-2 was much smaller than that for pure Bi₅O₇I, indicating that the introduction of NPGs accelerated the transfer of photogenerated electrons. As is well known, the higher the photocurrent response, the higher separation efficiency of photoinduced electrons and holes, which contributes to enhanced photocatalytic activity [64]. The transient photocurrent responses of Bi₅O₇I and NPG/Bi₅O₇I were measured for several on-off cycles of

Fig. 5. Nitrogen adsorption-desorption isotherms of (a) pure Bi₅O₇I and (b) NPG/Bi₅O₇I-2 hybrid material.

Fig. 6. Photocatalytic degradation of (a) TC and (b) ENR in the presence of $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ composites with different NPG loading amounts under visible light irradiation.

Fig. 7. (a) Electrochemical impedance spectra, (b) transient photocurrent responses, (c) steady-state PL spectra, and (d) valence band XPS profiles of pure $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 materials.

xenon light irradiation (Fig. 7b). As can be seen, the current for NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 was about three times higher than that for pure $\text{Bi}_5\text{O}_7\text{I}$, indicating that the separation efficiency of electron-hole pairs in NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 was much higher than that in $\text{Bi}_5\text{O}_7\text{I}$. The results of photoelectrochemical measurements demonstrated that NPG introduction indeed boosted the separation and utilization efficiency of photogenerated electron-hole pairs in $\text{Bi}_5\text{O}_7\text{I}$ nanorods.

Steady-state PL spectroscopy was performed to determine the recombination efficiency of photogenerated charge carriers in $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2. Strong emission peaks located at about 470 nm can be observed in Fig. 7c. The PL intensity for the NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 composite was lower than that for pure $\text{Bi}_5\text{O}_7\text{I}$, which indicated that NPG inhibited the recombination of electrons and holes during the photodegradation process [65]. The results of EIS, photocurrent, and PL measurements con-

firmed that the introduction of NPG was an effective way to promote the separation and utilization efficiency of photogenerated charge carriers in $\text{Bi}_5\text{O}_7\text{I}$.

In order to determine the band structures of pure $\text{Bi}_5\text{O}_7\text{I}$ and NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2, the energy level of the VB maximum (VBM) was determined by XPS VB analysis (Fig. 7d). The VB positions for the NPG/ $\text{Bi}_5\text{O}_7\text{I}$ -2 composite and pure $\text{Bi}_5\text{O}_7\text{I}$ were the same (1.36 eV), indicating that the introduction of NPG did not change the electronic density of $\text{Bi}_5\text{O}_7\text{I}$ [66]. The VBM of $\text{Bi}_5\text{O}_7\text{I}$ was calculated to be 1.99 eV after including a correction of 0.63 eV. The E_g value was confirmed to be 2.81 eV from DRS analysis, and the energy of the conduction band (CB) minimum was calculated to be -0.91 eV using the formula $E_{\text{CB}} = E_{\text{VB}} - E_g$. As is well known, the $\cdot\text{OH}/\text{OH}^-$ and $\text{O}_2/\text{O}_2^{\cdot-}$ reduction potentials are 2.38 eV and -0.046 eV vs. NHE, respectively [67]. So, O_2 can be reduced to $\text{O}_2^{\cdot-}$ by the electrons in the CB of the as-prepared

Fig. 8. DMPO spin-trapping ESR spectra of (a,b) $\text{Bi}_5\text{O}_7\text{I}$ and (c,d) $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ in (a,c) methanol dispersion and (b,d) aqueous dispersion under visible light irradiation.

sample; however, OH^- cannot be oxidized to $\cdot\text{OH}$.

ESR was performed to verify the active species produced by $\text{Bi}_5\text{O}_7\text{I}$ and $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ materials in the presence or absence of visible light. As displayed in Fig. 8a, four peaks of $\text{DMPO-O}_2^{\cdot-}$ were observed for the pure $\text{Bi}_5\text{O}_7\text{I}$ nanorods, indicating that the excited electrons in the CB of $\text{Bi}_5\text{O}_7\text{I}$ were capable of reducing O_2 to $\text{O}_2^{\cdot-}$ under visible light irradiation. After NPG introduction, four stronger $\text{O}_2^{\cdot-}$ peaks were detected for $\text{NPG/Bi}_5\text{O}_7\text{I-2}$, demonstrating that more effective electrons participated in the O_2 reduction reaction (Fig. 8c). No characteristic peaks of $\cdot\text{OH}$ were noticed in Fig. 8b and 8d, indicating the insufficient redox potential of $\text{Bi}_5\text{O}_7\text{I}$ and $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ materials, which were consistent with the calculated energy band positions. The above results indicated that $\text{O}_2^{\cdot-}$ played a crucial role in the photodegradation of the antibiotic pollutants. Meanwhile, the introduction of NPG significantly improved the utilization of excited electrons toward abundant $\text{O}_2^{\cdot-}$ generation. Besides,

free radical trapping experiments were carried out on $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ to further determine the active species involved in the photocatalytic process. Distinct trapping agents (*tert*-butanol for $\cdot\text{OH}$, N_2 for $\text{O}_2^{\cdot-}$, and triethanolamine (TEOA) for holes) were added to the target TC solution. As revealed by Fig. S4, the photodegradation efficiency of $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ for TC was significantly reduced after the addition of TEOA and N_2 , indicating that holes and $\text{O}_2^{\cdot-}$ were the primary active species involved in the degradation process. The removal rate of TC did not change with the addition of *tert*-butanol, indicating that $\cdot\text{OH}$ was not the main active species. These experimental results were well consistent with the ESR analysis results.

Reusability of the semiconductor materials is also a vital factor to evaluate whether the photocatalysts can meet the requirements of industrial production. Fig. 9a shows the cycling curves for the degradation of TC over the $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ composite. After four cycles of photocatalysis, the degradation

Fig. 9. (a) Cycling runs for photodegradation of TC in the presence of $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ material under visible light irradiation; (b) XRD patterns of $\text{NPG/Bi}_5\text{O}_7\text{I-2}$ before and after the photocatalytic cycle experiments.

Fig. 10. Schematic diagram illustrating the separation and transfer of photogenerated electron-hole pairs in the NPG/Bi₅O₇I material under visible light irradiation and the possible reaction mechanism.

efficiency of the composite for TC remained at around 75%. Moreover, Fig. 9b exhibits the XRD patterns of the NPG/Bi₅O₇I-2 photocatalyst before and after four cycles. No apparent changes were observed in the pattern of the recycled NPG/Bi₅O₇I-2 sample as compared to that of the fresh NPG/Bi₅O₇I-2. Both experimental results confirmed the high structure-activity stability of the as-prepared NPG/Bi₅O₇I composite.

Summarizing the above conclusions, a possible photocatalytic mechanism for the fabrication of NPG/Bi₅O₇I composite system was determined. As displayed in Fig. 10, when irradiated with visible light, the electrons in the VB of Bi₅O₇I would be excited and jump to the CB. Thus, photogenerated holes would be formed in the VB. Then, the excited electrons would rapidly transfer from the surface of Bi₅O₇I nanorods to NPGs, radically inhibiting the recombination of electron-hole pairs in Bi₅O₇I. Increasingly, more transferred electrons would aggregate on the surface of the NPG, contributing to a strong reduction ability, thereby facilitating the reduction of O₂ to O₂^{•-} via a one-electron process. Thus, a large number of superoxide radicals would efficiently degrade organic pollutants into inorganic small molecules under visible light irradiation. Meanwhile, the photogenerated holes in the VB would directly oxidize the pollutants. Accordingly, the NPG/Bi₅O₇I composite system exhibited a significantly enhanced photocatalytic degradation performance toward colorless antibiotics.

4. Conclusions

NPG/Bi₅O₇I composites were successfully synthesized by a simple ionic liquid-assisted solvothermal method; the composites showed excellent stability and photocatalytic degradation performance for antibiotics TC and ENR. The introduction of NPGs greatly improved the visible light capture capability of Bi₅O₇I and the photogenerated carrier migration rate, and effectively suppressed the integration of electron-hole pairs, which were attributed to the close interfacial contact between the NPGs and Bi₅O₇I nanorods. The ESR spectra and free radical trapping experiment results indicated that O₂^{•-} and photogen-

erated holes were the primary active species involved in the photocatalytic degradation reaction. The study provides novel ideas for the design of NPG-modified semiconductor materials with enhanced visible light absorption capacity and abundant excited charge carriers for photocatalytic contaminant elimination, water decomposition, and carbon dioxide reduction.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1230–1239 doi: 10.1016/S1872-2067(20)63531-8

Construction of nitrogen and phosphorus co-doped graphene quantum dots/Bi₅O₇I composites for accelerated charge separation and enhanced photocatalytic degradation performance

Kai Li, Mengxia Ji, Rong Chen, Qi Jiang, Jiexiang Xia *, Huaming Li
Jiangsu University

N and P co-doped graphene quantum dot-modified Bi₅O₇I (NPG/Bi₅O₇I) nanorods were prepared via an ionic liquid-assisted solvothermal method. Holes and superoxide radicals were the main active species involved in the photocatalytic degradation reaction.

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氮磷共掺杂石墨烯量子点/Bi₅O₇I复合材料的构筑及增强的光催化降解性能

李 凯^a, 季梦夏^a, 陈 蓉^b, 姜 琪^b, 夏杰祥^{a,*}, 李华明^a

^a江苏大学化学化工学院, 能源研究院, 江苏镇江212013

^b江苏大学环境安全与工程学院, 江苏镇江212013

摘要: 碘氧铋(BiOI)半导体光催化剂具有独特的层状结构与宽的光吸收范围, 在光催化降解污染物方面表现出较好的催化活性。然而, 较窄的带隙加快了光生电子空穴对的复合, 大大限制了BiOI光催化剂的发展应用。研究表明, 通过富铋策略调控卤氧铋材料中的卤素含量, 可以实现对其能带结构的可控调控。本文通过构筑氮磷共掺杂石墨烯量子点/Bi₅O₇I(NPG/Bi₅O₇I)复合光催化材料, 不仅提高了Bi₅O₇I材料对可见光的吸收能力, 同时增大了光生电子空穴对的分离效率, 显著提升了NPG/Bi₅O₇I复合材料的光催化降解性能。

本实验通过简单的离子液体辅助溶剂热方法合成了NPG/Bi₅O₇I复合光催化材料。采用X射线衍射(XRD)、傅里叶变换红外光谱(FTIR)、拉曼光谱(Raman)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和高分辨率透射电子显微镜(HR-TEM)等表征手段证明已经成功地制备了NPG/Bi₅O₇I复合材料。同时, 以盐酸四环素(TC)和恩诺沙星(ENR)为目标污染物探究了所制备NPG/Bi₅O₇I材料的光催化活性。实验结果表明, 在相同的实验条件下, 相对于Bi₅O₇I纳米棒, NPG/Bi₅O₇I复合材料具有更高的光催化活性。光照120 min后, 相比于Bi₅O₇I单体材料, NPG/Bi₅O₇I复合材料对TC的去除率提高了54.4%, ENR的去除率则提高了约54.9%。紫外可见漫反射(DRS)、稳态荧光(FL)、光电流和阻抗(EIS)结果表明, NPG的引入能够显著拓宽Bi₅O₇I材料的光吸收范围, 提高材料光生载流子的分离效率, 抑制其重组, 大大提升材料的光催化降解活性。电子顺磁共振(ESR)、X射线光电子能谱分析(XPS)和自由基捕获实验结果进一步验证了NPG/Bi₅O₇I复合材料光催化性能提高的可能机制。当可见光照射时, Bi₅O₇I价带上的电子被激发跃迁至导带并在价带留下空穴; 跃迁至导带的光生电子则迅速从Bi₅O₇I转移到NPG, 从而有效地抑制了光生电子空穴对的重组。随着光照时间的延长, 聚集在NPG上的电子将O₂还原为•O₂⁻, 产生的•O₂⁻进一步将有机污染物降解为小分子无机物。与此同时, Bi₅O₇I价带上的空穴具有极强的氧化能力, 可以直接将目标污染物矿化降解。

关键词: Bi₅O₇I; 氮磷共掺杂石墨烯量子点; 光催化; 离子液体; 电荷分离

收稿日期: 2019-11-02. 接受日期: 2019-12-18. 出版日期: 2020-08-05.

*通讯联系人. 电话/传真: (0511)88791108; 电子信箱: xjx@ujs.edu.cn

基金来源: 国家自然科学基金(21676128和21576123); 江苏大学科研经费(11JDG0146); 江苏省研究生科研与实践创新计划项目(KYCX17_1791).

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