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Formation of BiOI/g-C₃N₄ nanosheet composites with high visible-light-driven photocatalytic activity

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ABSTRACT

Constructing binary heterojunctions is an important strategy to improve the photocatalytic performance of graphitic carbon nitride (g-C₃N₄). In this paper, a novel g-C₃N₄ nanosheet-based composite was constructed via in situ growth of bismuth oxyiodide (BiOI) nanoplates on the surface of g-C₃N₄ nanosheets. The crystal phase, microstructure, optical absorption and textural properties of the synthesized photocatalysts were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS), and nitrogen adsorption-desorption isotherm measurements. The BiOI/g-C₃N₄ nanosheet composite showed high activity and recyclability for the photodegradation of the target pollutant rhodamine B (RhB). The conversion of RhB (20 mg L⁻¹) by the photocatalyst was nearly 100% after 50 min under visible-light irradiation. The high photoactivity of the BiOI/g-C₃N₄ nanosheet composite can be attributed to the enhanced visible-light absorption of the g-C₃N₄ nanosheets sensitized by BiOI nanoplates as well as the high charge separation efficiency obtained by the establishment of an internal electric field between the n-type g-C₃N₄ and p-type BiOI. Based on the characterization and experimental results, a double-transfer mechanism of the photoinduced electrons in the BiOI/g-C₃N₄ nanosheet composite was proposed to explain its activity. This work represents a new strategy to understand and realize the design and synthesis of g-C₃N₄ nanosheet-based heterojunctions that display highly efficient charge separation and transfer.

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1. Introduction

Recently, graphitic carbon nitride (g-C₃N₄) has attracted intense attention as a visible-light-driven metal-free n-type semiconductor because of its high chemical and thermal stability (up to 600 °C in air), adjustable band-gap energy, and desirable

electronic and optical properties [1–6]. Although g-C₃N₄ has a lot of advantageous features, it still has some limitations, such as relatively low solar energy conversion efficiency, low visible light utilization, and poor quantum efficiency caused by the fast recombination of photogenerated electron-hole pairs [7–10], all of which restrict the widespread use of g-C₃N₄ in photoca-

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talysis. Many strategies have been employed to overcome the inherent disadvantages of g-C₃N₄, including non-metal doping [11], metal doping [12], and constructing three-dimensionally ordered macroporous [13] and heterojunction [14] structures. Among these methods, the construction of g-C₃N₄ nanosheet-based heterojunctions is considered to be the most promising approach to greatly improve the overall performance of g-C₃N₄. This is because the nanosheet structure of g-C₃N₄ possesses large surface area, numerous surface defects, and high charge separation efficiency compared with the properties of traditional bulk g-C₃N₄ [15–19], which can considerably enhance its photocatalytic activity. To date, various g-C₃N₄ nanosheet-based heterostructures with high quantum efficiency and photocatalytic activity have been synthesized, such as NaNbO₃/g-C₃N₄ [20], MoS₂/g-C₃N₄ [21], TiO₂/g-C₃N₄ [22], ZnIn₂S₄/g-C₃N₄ [23], BiOBr/g-C₃N₄ [24], CaIn₂S₄/g-C₃N₄ [25], and WO₃/g-C₃N₄ [26].

Bismuth oxyiodide (BiOI) is a typical p-type semiconductor that has been extensively investigated recently because of its narrow adjustable band gap (1.78 eV) and strong absorption capacity in the visible region. Additionally, BiOI is also a potential sensitizer for other wide-band-gap semiconductors [27–29]. BiOI is composed of interleaved [Bi₂O₂]²⁺ slabs and [I₂]²⁻ slabs, which can form an internal electric field, promoting the separation of photogenerated electron–hole pairs [30–32]. Considering the unique properties of BiOI, an attractive strategy is to couple g-C₃N₄ and BiOI to construct binary heterojunction composites, which could not only effectively improve the visible light utilization, but also establish an internal electric field at the phase interface of n-type g-C₃N₄ and p-type BiOI, benefitting the fast separation and hindering the recombination of photoinduced electron–hole pairs [33–35].

In this paper, a novel BiOI/g-C₃N₄ nanosheet composite is prepared via in situ growth of BiOI nanoplates on the surface of g-C₃N₄ nanosheets by the solvothermal method. The crystal phase, microstructure, textural properties, and optical absorption behavior of the synthesized composite photocatalyst are measured by a variety of characterization techniques. The potential application value of the BiOI/g-C₃N₄ composite is evaluated by its ability to photodegrade rhodamine B (RhB) under visible light. In addition, possible photocatalytic mechanisms are proposed to explain the transfer route of photogenerated charges and the origin of the catalytic activity of the composite.

2. Experimental

2.1. Materials synthesis

All reagents were of analytical grade and used without further treatment.

2.1.1. Synthesis of g-C₃N₄ nanosheets

A certain amount of melamine was directly calcined at 520 °C for 4 h in a tube furnace under a nitrogen atmosphere after heating at a rate of 2.5 °C min⁻¹ to give yellow bulk g-C₃N₄. Then, the bulk g-C₃N₄ (2 g) was directly calcined at 530 °C for 5 h in air in a muffle furnace. The resultant white g-C₃N₄ powder

was collected for use in further experiments.

2.1.2. Synthesis of the BiOI/g-C₃N₄ nanosheet composite

In a typical synthesis, a certain amount of Bi(NO₃)₃·5H₂O and g-C₃N₄ nanosheets (0.2 g) were added to ethylene glycol (EG; 20 mL) and vigorously stirred for 4 h to form solution A. An equimolar amount of KI was dissolved in deionized water (5 mL) and stirred for 30 min to form solution B. Solution B was added dropwise into solution A with continuous stirring, and then the resulting mixture was poured into a 50-mL Teflon-lined stainless-steel autoclave, which was subsequently heated at 160 °C for 45 min. After the autoclave was cooled to room temperature, the resultant precipitate was centrifuged and washed with water and ethanol several times, then dried at 60 °C for 12 h. The theoretic weight ratio of BiOI to g-C₃N₄ was 3:100. Pure BiOI without g-C₃N₄ nanosheets was synthesized under the same conditions. BiOI and pure g-C₃N₄ nanosheets were used as reference samples.

2.2. Characterization

The crystal phases of all samples were determined by X-ray diffraction (Shimadzu, Lab X XRD-6100). Fourier transform infrared (FT-IR) spectra were measured on a Nicolet Avatar 360 spectrometer (Thermo Fisher, Nicolet iS50). The microstructure and morphology of all samples were examined by transmission electron microscopy (TEM; JEOL, JEM-2100) and scanning electron microscopy (SEM; JEOL, JSM-6700F, 200 kV). UV-vis diffuse reflection spectra were recorded for dry-pressed disk samples on a Hitachi U-4100 UV-vis spectrometer (Shimadzu, UV-2600) using BaSO₄ as the reference. The textural properties of the photocatalysts were investigated using a Brunauer-Emmett-Teller (BET) analyzer (Quantachrome, Autosorb-iQ-TPX), and the specific surface area and pore size distribution of each sample were obtained using the BET equation.

2.3. Photocatalytic activity measurement

The photocatalytic activities of all catalyst samples were evaluated by their ability to degrade RhB solution (20 mg L⁻¹) using a 300-W Xe lamp (HSX-F300, Beijing NBeT) equipped with an optical cutoff filter (HSX-UV300) as the visible light source ($\lambda \geq 420$ nm). Before illumination, each as-prepared sample (0.03 g) was added to RhB aqueous solution (30 mL) and then stirred in the dark for 1 h to reach adsorption-desorption equilibrium. The stirred mixture was then exposed to visible light. At 10 min intervals, 1.5-mL aliquots of the mixture were removed and centrifuged to isolate the photocatalyst powder. The residual RhB concentration was then measured on a UV-vis spectrophotometer (UV-1900PPC, Shanghai, China). To investigate the repeatability and stability of the catalysts, recycling experiments were executed under the same reaction conditions. After reaction for 50 min, the residual concentration of the RhB solution was tested. The collected sample was washed with water, dried at 60 °C in air, and then put into the same volume of fresh RhB solution (20 mg L⁻¹) for the next photodegradation cycle.

2.4. Photocatalytic H_2 evolution

The photocatalytic H_2 evolution reaction of the composite was tested on in a Pyrex reaction cell at room temperature. First, 3 wt% of Pt was deposited on the surface of the composite as a co-catalyst. The sample (0.05 g) was dispersed in water (50 mL) containing triethanolamine (10 mL) as a sacrificial electron donor. The resulting suspension was bubbled with N_2 for 5 min to remove O_2 and then irradiated by a 300-W Xe lamp (HSX-F300, Beijing NBeT) with a UV filter ($\lambda \geq 420$ nm) to ensure the suspension was only irradiated with visible light. The amount of H_2 produced was analyzed by an online gas chromatograph (GC; Beifen-Ruili) with a thermal conductivity detector.

2.5. Photoelectrochemical measurements

The transient photocurrent responses of the as-prepared samples were recorded on an electrochemical workstation (CHI 660D, Chenhua, Shanghai, China) with a three-electrode system. Pt wire, Ag/AgCl, and a glassy carbon electrode (0.07065 cm^2) modified with an as-prepared sample served as the counter, reference, and working electrodes, respectively. The electrolyte was Na_2SO_4 aqueous solution (1 mol L^{-1}).

3. Results and discussion

The overall synthetic pathway to the BiOI/g- C_3N_4 composite is shown in Fig. 1. The g- C_3N_4 nanosheets were first synthesized via thermal exfoliation of bulk g- C_3N_4 at 530 $^{\circ}C$ for 5 h in air to break the hydrogen bonds between g- C_3N_4 layers [15]. Then, EG and $Bi(NO_3)_3 \cdot 5H_2O$ were mixed with the g- C_3N_4 nanosheets. EG was selected as the solvent because it can coordinate with Bi^{3+} to produce the alkoxide complex $Bi(OCH_2CH_2OH)_2^{2+}$ (hereafter denoted as $Bi(OR)^{2+}$) [36], which can prevent the premature reaction of Bi^{3+} . Additionally, the negative polarity of the g- C_3N_4 surface [37,38] means that it can readily adsorb $Bi(OR)^{2+}$ through electrostatic attraction without needing further surface modification. During the solvothermal procedure, BiOI nanoplates were controllably synthesized on the surface of

Fig. 1. Schematic diagram of the synthetic route to the BiOI/g- C_3N_4 nanosheet composites.

the g- C_3N_4 nanosheets by adding KI aqueous solution as an iodine source, finally providing the BiOI/g- C_3N_4 nanosheet composite.

Fig. 2(a) shows the XRD patterns of the as-prepared g- C_3N_4 nanosheets, BiOI/g- C_3N_4 composite, and pure BiOI. The g- C_3N_4 nanosheets exhibited two characteristic diffraction peaks at 13.02° (weak) and 27.48° (strong) in their XRD pattern. The strong and weak peaks correspond to the (002) and (100) diffraction planes, respectively, derived from the interplanar spacing and stacked in-plane repeating units in the aromatic system [4], consistent with the typical peaks for other reported g- C_3N_4 [17]. All peaks observed for BiOI are in accordance with tetragonal-phase BiOI (PDF #10-0445) [29,32]. The stronger peaks at 29.60° , 31.61° , 45.36° , 51.29° , and 55.12° are indexed to the (102), (110), (200), (114) and (212) diffraction planes of BiOI, respectively. The XRD pattern for the BiOI/g- C_3N_4 nanosheet composite contained the characteristic peaks of the two components, including the (002) diffraction peak of g- C_3N_4 and (102), (110), (200), (114), and (212) diffraction peaks of BiOI. This indicates that the BiOI nanoplates are well coupled with the g- C_3N_4 nanosheets. Note that the (002) diffraction peak from g- C_3N_4 in the composite shifted from 27.48° to 27.88° after solvothermal treatment. This is because the initial

Fig. 2. XRD patterns (a) and FT-IR spectra (b) of the as-prepared samples.

undulating structure of the g-C₃N₄ nanosheets in the BiOI/g-C₃N₄ composite changed to a planar structure during heat treatment, thus resulting in denser stacking and decreased gallery distance in the composite [15].

The FT-IR spectra of all samples are shown in Fig. 2(b). The absorption peak of pure BiOI at around 763 cm⁻¹ can be assigned to the symmetric stretching vibrations of Bi-O bonds [39,40]. The pure g-C₃N₄ displayed absorption peaks at around 806 and 1200–1700 cm⁻¹, which were attributed to the breathing modes of s-triazine and the stretching vibration of the CN heterocycles, respectively [5,37]. The absorption peak at 3165 cm⁻¹ is assigned to the residual N-H components from secondary and primary amines [13]. When BiOI grows in situ on the surface of g-C₃N₄ to form the heterostructured composite, the characteristic absorption peaks of both components are observed, revealing that BiOI has been introduced onto g-C₃N₄.

The microstructure and morphology of all samples were further examined by SEM and TEM. As illustrated in Fig. 3(a), the g-C₃N₄ nanosheets exhibited a crumpled and rough surface formed by stacking of a large number of g-C₃N₄ nanoparticles [14]. Thus, the g-C₃N₄ nanosheets can provide enough surface area to couple with BiOI nanoplates. Fig. 3(b) shows a TEM image of the pure g-C₃N₄, which clearly confirms that the g-C₃N₄ nanosheets possess smooth flat surfaces, similar to that of graphene nanosheets. The SAED pattern in the inset of Fig. 3(b) indicates that the g-C₃N₄ nanosheets possess a polycrystalline structure. As displayed in Fig. 3(c) and (d), the pure BiOI sample possesses its typical hierarchical structure of nano-

Fig. 3. SEM (a) and TEM (b) images of pure g-C₃N₄ nanosheets (inset: selected-area electron diffraction (SAED) pattern of g-C₃N₄). SEM (c) and TEM (d) images of pure BiOI (inset: SAED pattern of BiOI).

plates self-assembled to form flower-like motifs with a diameter of about 2–3 μm. The SAED pattern for a BiOI microflower shows that the pure BiOI is well crystallized; the diffraction spots indicate its single crystal nature and tetragonal phase.

An SEM image of the as-prepared nanosheet composite is presented in Fig. 4(a). Both g-C₃N₄ and BiOI are observed in this

Fig. 4. SEM image (a), energy-dispersive X-ray spectrum (b), TEM images (inset: SAED pattern) (c, d), and high-resolution TEM image (e) of the BiOI/g-C₃N₄ nanosheet composite.

SEM image, confirming that the BiOI nanoplates are well coupled with the g-C₃N₄ nanosheets. The energy-dispersive X-ray spectroscopy (EDX) results (Fig. 4(b)) revealed the co-existence of C, N, O, Bi, and I in the BiOI/g-C₃N₄ nanosheet composite. The TEM images in Fig. 4(c) and (d) clearly exhibit the microstructure and morphology of the nanosheet composites, revealing that BiOI nanoplates are irregularly dispersed on the surface of the g-C₃N₄ nanosheets. The BiOI nanoplates are approximately circular planar structures with a diameter of about 100–200 nm. The SAED pattern in the inset of Fig. 4(c) contains full diffraction circles related to polycrystalline g-C₃N₄ and diffraction spots corresponding to single-crystal BiOI, further proving the existence of both semiconductors in the composite. The high-resolution TEM image in Fig. 4(e) clearly shows the surface microstructure and interface boundary between BiOI and g-C₃N₄. The lattice fringes of 0.282 nm can be indexed to the (110) facet of tetragonal-phase BiOI (PDF #10-0445), while the lattice fringes of g-C₃N₄ were not clearly detected because of its low crystallinity [7,18].

The UV-vis diffuse reflectance spectra of all the as-prepared samples are shown in Fig. 5. The brick-red pure BiOI sample displayed the most extensive optical absorption of the samples with its absorption edge at about 671 nm, corresponding to band-gap energy of 1.85 eV, and indicating that pure BiOI strongly absorbs visible light. The pure g-C₃N₄ nanosheets were white and only weakly absorbed visible light. Their absorption edge was at about 460 nm, giving estimated band-gap energy of 2.70 eV, which fits with previously reported for g-C₃N₄ [23,27]. Compared with that of pure g-C₃N₄, the optical absorption of the pale yellow BiOI/g-C₃N₄ composite sample exhibits a red-shift and high intensity, which is caused by coupling with BiOI [39]. These results indicate that the BiOI nanoplates could capture visible light when deposited on the surface of g-C₃N₄ nanosheets. In addition, the band structure of BiOI and g-C₃N₄ can be calculated using the following equations:

$$E_{VB} = X - E_e + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

where X is the electronegativity of the semiconductor and has values of 4.73 for g-C₃N₄ [13] and 5.94 for BiOI [41]; E_e (4.5 eV) is the energy of free electrons on the hydrogen scale. The E_{VB}

values of BiOI and g-C₃N₄ were estimated to be 2.37 and 1.58 eV, respectively, and E_{CB} were 0.52 and –1.12 eV, respectively.

To investigate the excitation and transfer of photogenerated charge carriers of the samples, their photocurrent responses under visible-light irradiation were measured. Fig. 6 shows the transient photocurrent responses of the samples at a bias potential of 0.3 V. The pure BiOI electrode displayed the weakest photocurrent response, illustrating the poor separation and transfer efficiency of photoinduced charge carriers. This phenomenon is attributed to the thick-layer stacking structure of pure BiOI (Fig. 3(c)), which leads to the following results. The photoinduced electrons in the bulk phase are difficult to transfer to the surface phase before recombination, and the gradual decrease of photocurrent response shows the poor stability of pure BiOI under visible-light irradiation. The pure g-C₃N₄ nanosheets exhibited a relatively strong photocurrent response, which means they display efficient excitation and fast transfer of photogenerated charge carriers, which was attributed to their thin layer structure. The BiOI/g-C₃N₄ nanosheet composite exhibited the highest photocurrent response among the samples. This is caused by the formation of a p-n junction; the internal electric field established between the n-type g-C₃N₄ and p-type BiOI accelerated the separation of electron-hole pairs and suppressed their recombination.

The textural properties of the BiOI, BiOI/g-C₃N₄, and g-C₃N₄ samples were examined using the N₂ adsorption-desorption technique. As shown in Fig. 7(a), the adsorption-desorption isotherms for pure BiOI had no obvious hysteresis loop, suggesting this material contained almost no pores, consistent with the TEM observations. According to the IUPAC classification, the physisorption isotherms for the BiOI/g-C₃N₄ composite and g-C₃N₄ nanosheets are typical of type IV isotherms with an H3 hysteresis loop in the relative pressure (P/P_0) range of 0.45–1.0, indicating that the pore size distribution belongs to the mesoporous region [7,18]. The mesoporous structure of BiOI/g-C₃N₄ may originate from the stacking of g-C₃N₄ and BiOI particles [14]. The pore size distributions of all the samples determined by the Barrett-Joyner-Halenda (BJH) method are presented in Fig. 7(b). The main pore size for both BiOI/g-C₃N₄ and g-C₃N₄ was 1.96 nm, indicating the presence of some mi-

Fig. 5. UV-vis diffuse reflectance spectra of g-C₃N₄, BiOI/g-C₃N₄ nanosheet composite, and BiOI samples.

Fig. 6. Transient photocurrent responses of g-C₃N₄ nanosheets, the BiOI/g-C₃N₄ nanosheet composite, and pure BiOI.

Fig. 7. (a) N₂ adsorption-desorption isotherms of g-C₃N₄ nanosheets, the BiOI/g-C₃N₄ nanosheet composite, and pure BiOI. (b) Pore size distributions of the samples determined using the Barrett-Joyner-Halenda method.

coporous structure in both of the nanosheet samples. Pure BiOI did not exhibit a pore distribution because of its thick stacked layer structure, which agreed well with the physisorption isotherms. In addition, the g-C₃N₄ nanosheets show the largest BET surface area ($181.19 \text{ m}^2 \text{ g}^{-1}$) and smaller pore volume ($0.26 \text{ cm}^3 \text{ g}^{-1}$), while the BiOI/g-C₃N₄ composite possesses a relatively smaller surface area ($157.03 \text{ m}^2 \text{ g}^{-1}$) and the highest pore volume ($0.44 \text{ cm}^3 \text{ g}^{-1}$). This is because part of the surface of the g-C₃N₄ nanosheets in the composite was covered by BiOI nanoplates, which had a small surface area ($6.36 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.04 \text{ cm}^3 \text{ g}^{-1}$).

The photodegradation of RhB by the as-prepared catalysts in aqueous solution (20 mg L^{-1}) under visible-light irradiation was investigated. As shown in Fig. 8(a), RhB as a target pollutant is quite stable and its photodegradation under visible-light irradiation in the absence of a photocatalyst is negligible [13]. The pure BiOI sample exhibited the lowest photodegradation efficiency of the samples, with a residual RhB concentration of about 89% after 50 min of irradiation. This indicates that BiOI has poor photocatalytic activity, which was attributed to the rapid recombination of electron-hole pairs. The pure g-C₃N₄ nanosheets displayed high photocatalytic activity with a residual RhB concentration of about 10% under the same conditions. As expected, the BiOI/g-C₃N₄ nanosheet composite showed the highest photocatalytic activity of the samples with nearly 100% RhB conversion within 50 min of photoreaction, confirming that in situ growth of BiOI on g-C₃N₄ nanosheets can enhance the photocatalytic performance of g-C₃N₄.

To investigate the reaction dynamics of the RhB photodecomposition process over the different samples, the reaction kinetics of all the samples were quantitatively calculated using the Langmuir-Hinshelwood model [13,14]:

$$\ln(C_0/C) = Kt \quad (3)$$

where K is the pseudo-first-order rate constant, and C_0 and C represent the initial concentration of RhB solution and the concentration after irradiation time t , respectively. Fig. 8(b) shows the apparent linear relationship between $\ln(C_0/C)$ and t , which indicates that the photodegradation reaction obeys

pseudo-first-order dynamics. As illustrated in Fig. 8(c), K values for the g-C₃N₄, BiOI/g-C₃N₄, and BiOI samples were 0.04048, 0.06978 and 0.002 min^{-1} , respectively. The BiOI/g-C₃N₄ nanosheet composite has the highest K values of the samples; 1.72 times higher than that of pure g-C₃N₄ and 34.89 times higher than that of pure BiOI.

Recycling experiments for the photodegradation of RhB solution (20 mg L^{-1}) over BiOI/g-C₃N₄ were performed to investigate its stability and recyclability. As depicted in Fig. 8(d), the BiOI/g-C₃N₄ nanosheet composite showed excellent photocatalytic activity for the photodegradation of RhB (about 97.2% conversion after 50 min of irradiation) in the first cycle. In the second cycle test, the photocatalytic activity of BiOI/g-C₃N₄ decreased slightly; the RhB conversion lowered to 96.8% and then to 92.1% in the third cycle. In the fourth cycle, the RhB conversion declined to 90.9% after 50 min of photodegradation, but it was still higher than the conversions achieved in the first tests over pure BiOI (11.2%) and pure g-C₃N₄ (89.7%). In the fifth cycle, the conversion of RhB over BiOI/g-C₃N₄ was about 85%. The reasons for the slight decrease of photocatalytic activity could be the loss of the catalyst and/or structural damage.

To identify the main reactive species in the photocatalytic reaction, trapping experiments were performed for the BiOI/g-C₃N₄ nanosheet composite by adding different scavengers. Isopropyl alcohol (IPA), benzoquinone (BQ), and ethylenediaminetetraacetic acid disodium (EDTA-2Na) were used to scavenge hydroxyl radicals ($\cdot\text{OH}$), superoxide radical anions ($\cdot\text{O}_2^-$), and holes (h^+), respectively, generated in the photocatalytic reaction. The dosage of scavengers was determined from our previous studies [13,36]. As displayed in Fig. 9, the photocatalytic efficiency of RhB degradation by the BiOI/g-C₃N₄ composite was obviously inhibited by the addition of BQ (decreased to 60.6%) after 50 min of visible-light irradiation, indicating that $\cdot\text{O}_2^-$ plays an important role in the photodegradation process. Conversely, with the scavengers IPA and EDTA-2Na, the RhB degradation efficiency still remained high (89.2% and 90.6%, respectively), suggesting that $\cdot\text{OH}$ and h^+ are not the main reac-

Fig. 8. (a) Photodegradation efficiency of RhB solution (20 mg L⁻¹) by g-C₃N₄ nanosheets, the BiOI/g-C₃N₄ nanosheet composite, and BiOI; (b) Kinetic curves for photodegradation of RhB over the as-prepared samples; (c) Apparent constants for photodegradation of RhB by the samples; (d) Recycling experiments for the photodegradation of RhB solution using the BiOI/g-C₃N₄ nanosheet composite.

tive species involved in oxidation of RhB by the photocatalyst. The above analysis indicates that $\cdot\text{O}_2^-$ is the main reactive species in the decomposition of organic dye RhB over the BiOI/g-C₃N₄ heterojunction under visible-light irradiation, which means that photoinduced electrons dominate the overall reac-

tion process.

Based on the above findings, two possible reaction mechanisms for the photodegradation of RhB over the BiOI/g-C₃N₄ nanosheet composite were proposed as follows.

(1) The double-transfer mechanism. As shown in Fig. 10(a), under visible-light irradiation at energies below 2.95 eV ($\lambda > 420$ nm), the g-C₃N₄ nanosheets ($E_{\text{CB}} = -1.12$ eV vs. NHE, $E_{\text{VB}} = 1.58$ eV vs. NHE) can be excited to generate electron-hole pairs. The excited electrons transfer to the conduction band (CB), while the holes stay in the valence band (VB) of g-C₃N₄. Similarly, the BiOI ($E_{\text{CB}} = 0.52$ eV vs. NHE, $E_{\text{VB}} = 2.37$ eV vs. NHE) in this composite could be excited to generate a large number of high-energy electrons. These high-energy electrons can transfer thermodynamically from the VB of BiOI to the higher potential position of -0.58 eV in the CB of BiOI, which is more negative than $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV vs. NHE). Thus, the CB and VB positions of g-C₃N₄ are both more negative than those of BiOI. Therefore, in this case, a “staggered” p-n junction at the BiOI/g-C₃N₄ interface is formed, leading to the formation of an internal electric field in the direction from n-type g-C₃N₄ to p-type BiOI within the as-prepared nanosheet composite. This field is favorable for interfacial transfer of photoinduced charges and thus extends the lifetime of photoinduced elec-

Fig. 9. Photodegradation efficiency of RhB by the BiOI/g-C₃N₄ nanosheet composite with different scavengers under visible-light irradiation.

Fig. 10. Schematic diagram of the transfer of photoinduced electron-hole pairs. (a) The double-transfer mechanism; (b) The Z-scheme transfer mechanism.

trons (Fig. 10(a)). Previous studies [41,42,44,45] found that when the excited electrons rapidly transferred to the less negative CB of the surrounding BiOI, which still has strong reduction ability to react with dissolved oxygen or oxygen adsorbed on the catalyst surface to generate $\cdot\text{O}_2^-$ and hydrogen peroxide, both the active species could fully oxidize organic dye pollutants to CO_2 and H_2O , consistent with the results of trapping experiments.

(2) The Z-scheme transfer mechanism (Fig. 10(b)). Under visible-light irradiation at energies below 2.95 eV ($\lambda > 420$ nm), both BiOI and g-C₃N₄ are excited to generate electron-hole pairs. These excited electrons can quickly transfer to the CB of BiOI and g-C₃N₄, while the holes remain in the VB of BiOI and g-C₃N₄. A previous study [46] reported that I^- near the p-n junction was easily oxidized to I_3^- by the photoinduced holes; I_3^- could also be reduced by the photoinduced electrons. In this process, the photogenerated electrons on the side of BiOI and photogenerated holes on the side of g-C₃N₄ can be efficiently separated because of the extremely high reversibility of the intermediate I_3^-/I^- pairs achieved by Z-scheme transfer [46–48]. This may explain why the photoactivity of the composite is high under visible-light irradiation.

To determine which mechanism is closer to the true charge transfer path in RhB photodegradation by the samples, photocatalytic hydrogen (H_2) production tests over the samples were carried out. The above discussion revealed that the theoretical E_{CB} of the g-C₃N₄ nanosheets (about -1.12 eV vs. NHE) was more negative than the water reduction potential (0 eV vs. NHE). Therefore, if the charge transfer mode follows the Z-scheme transfer mode, the BiOI/g-C₃N₄ nanosheet composite should show much higher photoactivity for H_2 generation than that of pure g-C₃N₄. Fig. 11 shows the photocatalytic H_2 production efficiency of the g-C₃N₄ nanosheet, BiOI/g-C₃N₄ nanosheet composite, and BiOI samples. The g-C₃N₄ nanosheets display excellent performance in photocatalytic H_2 production; the rate of H_2 evolution reaches about $0.52 \text{ mmol g}^{-1} \text{ h}^{-1}$. In contrast, the pure BiOI sample has no photoactivity for H_2 production through water splitting. For the BiOI/g-C₃N₄ nanosheet composite, only $0.07 \text{ mmol g}^{-1} \text{ h}^{-1}$ of H_2 was generated after 2.5 h of photoreaction, indicating that most of the photogenerated electrons in the BiOI/g-C₃N₄ system do not take part in photocatalytic H_2 generation through water splitting. According to

Fig. 11. Photocatalytic H_2 evolution over g-C₃N₄ nanosheet, BiOI/g-C₃N₄ nanosheet composite, and BiOI samples.

these experimental results, we can infer that the charge transfer mode in the BiOI/g-C₃N₄ nanosheet composite should follow the double-transfer mechanism.

4. Conclusions

In this work, we demonstrated a facile solvothermal approach to grow BiOI nanoplates on the surface of the g-C₃N₄ nanosheets to construct a novel BiOI/g-C₃N₄ nanosheet composite. The obtained sample showed excellent activity and recyclability for the degradation of target pollutant RhB, with nearly 100% conversion of RhB after 50 min of visible-light irradiation. The high photoactivity of the composite may be derived from the synergistic effect of the effective separation of charges caused by the formation of an internal electric field at the interface between n-type g-C₃N₄ and p-type BiOI, strong visible-light absorption, and large surface area and pore volume.

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Graphical Abstract

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Formation of BiOI/g-C₃N₄ nanosheet composites with high visible-light-driven photocatalytic activity

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A BiOI/g-C₃N₄ nanosheet composite was constructed via in situ growth of BiOI nanoplates on the surface of g-C₃N₄ nanosheets. The composite showed excellent photocatalytic activity and recyclability under visible-light irradiation. A double-transfer mechanism of photoinduced electrons was proposed to explain the process of charge transfer and separation in the composite.

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新型BiOI/g-C₃N₄纳米片复合光催化剂的制备及其可见光催化活性增强

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摘要: 近年来, 石墨型氮化碳(g-C₃N₄)作为一种n型半导体光催化剂材料, 由于具有较好的热稳定性和化学稳定性, 同时具有可调的带隙结构和优异的表面性质而备受人们关注. 然而, 传统的g-C₃N₄块体材料存在比表面积小、光响应范围窄和光生载流子易复合等缺陷, 制约着其光催化活性的进一步提高. 因此, 人们开发了多种技术对块体状g-C₃N₄材料进行改性, 其中构建基于g-C₃N₄纳米薄片的异质结复合光催化材料被认为是强化g-C₃N₄载流子分离效率, 进而提高其可见光催化活性的重要手段. BiOI作为一种窄带隙的p型半导体光催化剂, 具有强的可见光吸收能力和较高的光催化活性, 同时它与g-C₃N₄纳米薄片具有能级匹配的带隙结构. 因此, 基于以上两种半导体材料的特性, 构建新型的BiOI/g-C₃N₄纳米片复合光催化剂材料不仅能够有效提高g-C₃N₄的可见光利用率, 而且还可以在n型g-C₃N₄和p型BiOI界面间形成内建电场, 极大促进光生电子-空穴对的分离与迁移效率.

为此, 本文通过简单的一步溶剂热法在g-C₃N₄纳米薄片表面原位生长BiOI纳米片材料, 成功制备了新型的BiOI/g-C₃N₄纳米片复合光催化剂. 利用X射线衍射仪(XRD), 场发射扫描电子显微镜(SEM)、透射电子显微镜(TEM)、紫外-可见漫反射光谱和瞬态光电流响应谱对所合成复合光催化剂的晶体结构、微观形貌、光吸收性能和电荷分离性能进行了表征测试. XRD, SEM和TEM结果显示, 结晶完好的BiOI呈小片状均匀分散在g-C₃N₄纳米薄片表面; 紫外漫反射光谱表明, 纳米片复合材料的吸光性能较g-C₃N₄薄片有显著提升; 瞬态光电流测试证明, 复合材料较单一材料有更好的电荷分离与迁移性能. 在可见光催化降解RhB的测试中, BiOI/g-C₃N₄纳米片复合光催化剂显示出了优异的催化活性和稳定性, 其光降解活性分别为纯BiOI和g-C₃N₄的34.89和1.72倍; 自由基捕获实验发现, 反应过程中的主要活性物种为超氧自由基(·O₂⁻), 即光生电子主导整个降解反应的发生. 由此可见, 强的可见光吸收能力和g-C₃N₄与BiOI界面处形成的内建电场协同促进了g-C₃N₄纳米薄片的电荷分离, 进而显著提高了该复合材料的可见光催化降解活性. 此外, 本文初步验证了在BiOI/g-C₃N₄纳米片复合光催化体系内光生电荷是依据“双向转移”机制进行分离和迁移的, 而非“Z型转移”机制.

关键词: g-C₃N₄; BiOI; 纳米片; 光降解; 双向转移; 可见光

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