Simple and Facile Ultrasound-assisted Fabrication of Bi₂O₂/g-C₃N₄ Composites with Excellent Photoactivity

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Abstract

$\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ (BOC/CN) composites photocatalyst was fabricated via a facile ultrasonic-assisted method. The crystal structure, morphology, optical and photocatalytic properties of the as-prepared samples were characterized by various analytical techniques. The results indicated that the $\text{Bi}_2\text{O}_2\text{CO}_3$ nanoflakes grew on the surface of the $\text{g-C}_3\text{N}_4$ nanosheets, forming closely contacted interfaces between the $\text{Bi}_2\text{O}_2\text{CO}_3$ and the $\text{g-C}_3\text{N}_4$ component. BOC/CN composites with 50 wt% of $\text{g-C}_3\text{N}_4$ showed the optimal photoactivity for the degradation of RhB under visible light, which was approximately 2.2 times higher than that of pure $\text{g-C}_3\text{N}_4$ and 7 times of pure $\text{Bi}_2\text{O}_2\text{CO}_3$, respectively. The enhanced performance of the BOC/CN composites was mainly attributed to a synergistic effect including the accelerated separation and migration of photogenerated charge carriers, demonstrated by Photoluminescence (PL), electrochemical impedance spectra (EIS) and photocurrent density. Finally, a possible photocatalytic mechanism was proposed based on the experimental results. It is expected that such a facile route method could provide new insights into fabricating other $\text{g-C}_3\text{N}_4$ -based composite photocatalysts for environmental remediation.

Keywords: ultrasonic assisted method, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites photocatalyst, visible light, photodegradation, photocurrent density.

1. Introduction

The semiconductor photocatalysis has received considerable attention owing to its potential application in organic pollutants elimination, water splitting and dye-sensitized solar cells [1-5]. In various semiconductor photocatalysis, two-dimensional (2D) layer materials have attracted extensive attention due to their unique structural and photocatalytic properties [6-10]. Nowadays, graphite-like carbon nitride (g-C₃N₄) nanosheets, one of 2D layer materials, have been explored as a promising photocatalyst for hydrogen evolution and environment purification under visible-light irradiation because of its chemical stability, moderate band gap (2.7 eV) and low-cost [11-18]. However, g-C₃N₄ also suffered from some tough problems including the inefficient energy conversion and high rate recombination of photogenerated carriers, which seriously limited its practical applications [19-27]. Therefore, many projects have been carried out to conquer these problems, including metal or non-metal doping, morphology control and coupling with other semiconductors [28-31]. Among them, constructing composites structures through coupling g-C₃N₄ with other semiconductors have been regarded as an effective approach for suppressing the recombination of photoinduced electrons-holes pairs and improving photocatalytic performance.

Recently, the bismuth-containing semiconductors coupling with g-C₃N₄ have been attracted extensive attention due to the low-cost and abundant source on Earth , such as Bi₂WO₆, BiXO (X=Cl, Br, I), BiVO₄, Bi₂MoO₆ [32-35]. It's remarkable that with the coupling of g-C₃N₄ and bismuth-containing composites would enhance the

separation and transportation of photoinduced carriers, thus resulting in the enhancement of visible-light-driven photocatalytic activity. Recently, increased efforts have been carried out the synthesis of bismuth-containing semiconductors, such as mixed-calcinations, situ preparation solvothermal techniques [36-41]. The photocatalytic technology for environmental remediation is inevitable demand of the times. Moreover, it is vital to investigate a simple and facile strategy for fabrication photocatalyst with dramatic photoactivity. And the ultrasonic-assisted gradually becomes an important tool for its applications in the synthesis and modification of semiconductor materials [42]. That makes them possible for synthesis of stable, high efficient and low cost photocatalysts. Hence, we attempted to synthesize $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites photocatalyst via a facile ultrasonic-assisted method. To the best of our knowledge, there are no published reports on such method for the synthesis of BOC/CN photocatalyst.

In this paper, we reported a novel route for the synthesis of BOC/CN photocatalyst via a facile ultrasonic-assisted method at low temperature for the first time. We investigated the structural and optical properties of BOC/CN composites. Importantly, was studied systematically the photocatalytic activity of BOC/CN composites under visible light irradiation and attempted to present a clear portrait of the key factor in determining the photocatalytic efficiency. According to the experimental result, a possible photocatalytic mechanism is investigated systematically.

2. Experimental

2.1 Preparation of $\text{Bi}_2\text{O}_2\text{CO}_3$ /g- C_3N_4 composites

2.1.1 Materials

All chemicals were analytical reagents without further purification. Melamine, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), sodium carbonate (Na_2CO_3), Rhodamine B (Rh-B), sodium sulfate (Na_2SO_4), isopropanol (IPA), disodium ethylenediamine tetraacetic acid (EDTA-2Na) and 1,4-benzoquinone (BQ) were purchased from Aladdin. Ethyl alcohol and nitric acid were purchased from Sinopharm.

2.1.2 Synthesis of the g- C_3N_4 nanosheets

The bulk g- C_3N_4 was prepared according to a previous method [43]. In details, 6 g of melamine was put into a corundum crucible and heated to 550 °C for 4h with the rate of 2.3 °C/min under atmospheric pressure. After calcination, as-obtained samples were washed with nitric acid, deionized water and ethyl alcohol for three times, respectively. Dried at 60 °C overnight. Then, 1 g of the collected bulk g- C_3N_4 powder was put into another corundum crucible for oxidation erosion, which was heated to 410 °C for 2 h and to 510 °C for another 2 h with the rate of 5 °C/min, the target g- C_3N_4 nanosheets were obtained eventually.

2.1.3 Synthesis of the BOC/CN composites

Taking the synthesis procedure of $\text{Bi}_2\text{O}_2\text{CO}_3$ /g- C_3N_4 composites with 50 wt% of g- C_3N_4 as an example: First, 95 mg of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 40 ml deionized water containing nitric acid ($1 \text{ mol} \cdot \text{L}^{-1}$) and ultrasonic for 30 min to obtain a

clarify solution as A. At the same time 50 mg of g-C₃N₄ nanosheets and 52 mg of Na₂CO₃ were dissolved in 100ml deionized water and ultrasonic for 30min to acquire a light yellow suspension solution as B. After that, A was added to B dropwise and then the suspension solution was highly disperse for 2 h by ultrasonic in ice-bath. Next, the suspension was filtrated and washed with ethyl alcohol and deionized water for three times, respectively. Finally, the BOC/CN composites were dried at 60 °C for 12 h. To synthesis different mass ratios of the BOC/CN composites, took the mass of g-C₃N₄ nanosheets as a constant and controlled the mass of bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and sodium carbonate (Na₂CO₃) to obtain the Bi₂O₂CO₃ mass ratios of 40%、50% and 60%, which were denoted as BOC/CN-1、BOC/CN-2 and BOC/CN-3. The possible synthesis procedure of BOC/CN composites was illustrated on scheme 1. In order to make a comparison, pure Bi₂O₂CO₃ was also prepared using the above-mentioned procedure without the addition of g-C₃N₄. In the supporting information, the direct stirring samples and mechanical mixed samples of Bi₂O₂CO₃ and g-C₃N₄ were prepared.

2.2 Characterization

The crystal structure of the above samples were detected by X-ray diffraction (D/max 2550, Rigaku Corporation) in the $2\theta = 10^\circ\text{-}80^\circ$ range. The morphology and microstructure of the prepared samples were observed with a scanning electron microscope (Nova Nano SEM 230, FEI Electron Optics B.V) and field emission transmission electron microscope (JEM-2100F, Japanese electronics co. LTD). The infrared spectrum of absorption was obtained by fourier transform infrared

spectroscopy (Nicolet 6700, Thermo Nicolet Corporation). Surface chemical compositions and chemical status were analyzed by X-ray photoelectron spectroscopy (K-Alpha 1063, Thermo Fisher). Photoluminescence spectra of the photocatalysts were measured on a fluorescence spectrophotometer (F-4600, Japan's Hitachi LTD) at an excited wavelength of 370nm. The UV-Vis spectra of the catalysts were obtained on a UV-Vis spectrometer (Evolution 220, Thermo Fisher Scientific) to characterize the light response range of the above samples.

2.3 Photocatalytic activity

Photocatalytic activity of the above samples were measured through the degradation of $10 \text{ mg}\cdot\text{L}^{-1}$ of RhB under the irradiation of visible light ($\lambda \geq 420 \text{ nm}$). RhB is a steady cationic dye, which has been widely used for assessing the property of various semiconductor photocatalysts. The procedure of the photocatalytic degradation was just as follows [44] : First, 10 mg of the as-prepared sample was added to 15 ml deionized water containing RhB of $10 \text{ mg}\cdot\text{L}^{-1}$, which was dispersed for 2 min by ultrasonic to obtain a suspension solution. Then, above suspension solution was transferred to the photochemical reaction instrument (BL-GHX-I) magnetic stirring 30 min in darkness to reach the adsorption-desorption equilibrium. Next, the suspension solution was exposed to visible light at given time intervals. Then, took 4 ml of the suspension solution immediately centrifuged at 12000 rpm for 3 min in order to attain a supernatant for further identification on the UV-Vis spectrophotometer.

To further understand the photocatalytic mechanism of the BOC/CN composites,

which had the outstanding photocatalytic performance during the photocatalytic degradation reaction, suitable sacrificial agents were used to perform the trapping experiments. Disodium ethylenediamine tetraacetic acid (EDTA-2Na), Isopropanol (IPA) and 1,4-benzoquinone (BQ) were used as the scavenger for photogenerated hole (h^+), hydroxyl radical ($\cdot OH$) and superoxide radical ($\cdot O_2^-$), respectively. The process of the trapping experiment was similar to the photocatalytic degradation process except for the presence of different scavenger ($10\text{ mmol}\cdot\text{L}^{-1}$) in RhB solution.

3. Results and discussion

3.1 Characterization of the crystal structure

Fig. 1 depicted the XRD patterns of as prepared samples. Two obvious peaks at the degree of 13.3° and 27.7° could be indexed to the (100) and (002) diffraction planes of g- C_3N_4 , corresponding to the periodic array of the in-planar tri-s-triazine and the inter-planar stacking of aromatic systems, respectively [35]. XRD patterns of the tetragonal phase $Bi_2O_2CO_3$ (PDF#41-1488, $a=3.865\text{\AA}$, $b=3.865\text{\AA}$, $c=13.675\text{\AA}$) exhibited excellent crystalline and purity, the peaks at the degree of 23.8° , 30.25° and 32.7° could be indexed to the (011), (013) and (110) planes, respectively. As for the different mass ratios of BOC/CN composites, their peaks' shape were similar to the pure $Bi_2O_2CO_3$, which indicated that the present of g- C_3N_4 nanosheets didn't change the components and crystal structure of $Bi_2O_2CO_3$ and these composites possessed remarkable crystalline. Apparently, the XRD peak intensity around 13.1° of $Bi_2O_2CO_3$ reduced as amount of g- C_3N_4 input was increased, but the BOC/CN-2 displayed the

lowest diffraction intensity in all the composites. As far as I am concerned, it was possible that the (002) plane of $\text{Bi}_2\text{O}_2\text{CO}_3$ was highly coupled growth over (100) plane of $\text{g-C}_3\text{N}_4$, which resulting to the low diffraction intensity of (002) plane of $\text{Bi}_2\text{O}_2\text{CO}_3$. Meanwhile, the peak at 13.3° of $\text{g-C}_3\text{N}_4$ couldn't be observed apparently yet the peak at 27.7° of $\text{g-C}_3\text{N}_4$ appeared in BOC/CN composites. For comparied, magnetic stirring and self-assembly were carried out (Supplementary Information Fig. S1 and S2). These results indicated that the $\text{Bi}_2\text{O}_2\text{CO}_3$ was successfully hybridized with $\text{g-C}_3\text{N}_4$ by the ultrasonic assisted method at low temperature.

3.2 FTIR and morphology structure analysis

In this work, to investigate the formation of hybrid composites and the molecular structures of the BOC/CN composites, FTIR was implemented and the corresponding results were shown in Fig. 2, which revealed the strong absorption mainly located in the $500\text{--}4000\text{ cm}^{-1}$. In the FTIR spectra of pure $\text{g-C}_3\text{N}_4$, a series of peaks located from 1200 cm^{-1} to 1500 cm^{-1} could be accounted for the typical stretching vibration of C-N heterocycles. The peaks at 1630 and 3162 cm^{-1} could be attributed to C=N stretching vibration modes and N-H stretching vibration modes, respectively. Besides, the peak at 808 cm^{-1} was belonging to the s-triazine ring modes. As for the $\text{Bi}_2\text{O}_2\text{CO}_3$, the intensive peaks at about 543 and 840 cm^{-1} were attributed to the stretching vibrations of the Bi-O in $\text{Bi}_2\text{O}_2\text{CO}_3$. All the FTIR spectra exhibited the characteristic peaks of both $\text{g-C}_3\text{N}_4$ and $\text{Bi}_2\text{O}_2\text{CO}_3$, and no impurity or solvent residue absorption peaks were detected. These peaks were also present in the BOC/CN-2 composites suggesting that $\text{g-C}_3\text{N}_4$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ existed in the composites, which was well in

accordance with the XRD analysis and indicated that there was no structural change of g-C₃N₄ and Bi₂O₂CO₃ in the preparation process.

Fig. 3 showed the morphology and nanostructure of pure g-C₃N₄, pure Bi₂O₂CO₃ and BOC/CN-2 composites characterized by SEM and TEM. As can be seen from the images of Fig. 3a and b, the bulk g-C₃N₄ turned into two-dimension irregular foliated nanosheets after the oxidation erosion, which was almost 30 nm in thickness. Consequently, it could easily provide large specific surface area for further assembly with Bi₂O₂CO₃. Obviously, Bi₂O₂CO₃ nanoplate was approximately 100 nm (Fig. 3c) in length, which was quite smaller and more regular than g-C₃N₄ and generated from the agglomeration of abundant Bi₂O₂CO₃ nanoparticles that each particle is about 2-5 nm in length as is vividly displayed in TEM images (Fig. 3d). The BOC/CN-2 composites prepared by ultrasonic assisted treatment exhibited nanosheets morphology as well (Fig. 3e and f). By reason of the huge mechanical energy in the ultrasonic-assisted treatment, the g-C₃N₄ nanosheets in the BOC/CN were a little bit smaller than the pure g-C₃N₄ (Fig. 3a and e). Obviously, Bi₂O₂CO₃ and g-C₃N₄ were composited preferably as shown in inset image of the Fig. 3e. The obvious lattice fringe spacing *d* of 0.291 nm, 0.272 nm and 0.372 nm in HRTEM image could be indexed to the (013), (110) and (011) planes, respectively, which well identified with the XRD phase analysis and confirmed successfully synthesis of the BOC/CN composites by the ultrasonic-assisted method

3.3 XPS analysis

To investigate the chemical valence state and bonding configuration of BOC/CN composites, X-ray photoelectron (XPS) was performed as shown in Fig. 4. The survey spectrum revealed the predominant presence of C, N, Bi and O in the sample of BOC/CN. Besides, the Bi and N were not detected in the spectra of g-C₃N₄ and Bi₂O₂CO₃, respectively, while the O on the surface of the g-C₃N₄ was came from the adsorption of oxygen from the atmosphere. These results were well in accordance with the XRD and FTIR analysis results. The binding energy for C1s peak at 284.8 eV was used as a reference , which could be assigned to the external hydrocarbon contamination. While the spectra of g-C₃N₄ and Bi₂O₂CO₃/g-C₃N₄ had the other peak at around 288.1 eV and 288.2 eV were came from the N-C=N in its chemical bone structure, which affirmed the existence of g-C₃N₄. Besides, the C 1s binding energy of BOC/CN-2 was slightly lower than that of g-C₃N₄. In the N 1s high resolution XPS spectra of g-C₃N₄, several peak at 398.5eV, 399.0 eV and 400.5 eV which could be ascribed to N (C-N=C) groups (sp² bonded), tertiary nitrogen N-(C)₃ groups and C-N-H amino groups, respectively. Notably, the N 1s binding energy of Bi₂O₂CO₃/g-C₃N₄ was slightly lower than that of g-C₃N₄, which is similar to the C 1s peak of N-C=N groups at 288.2 eV. Meanwhile, combined with the C 1s and N 1s spectra of Bi₂O₂CO₃ and g-C₃N₄, BOC/CN-2 had slight shift. The peaks at 164.6 and 159.3 eV were attributed to Bi4f_{5/2} and Bi4f_{7/2} of Bi₂O₂CO₃ [45]. Similarly, the peaks of O 1s were also changed, and the binding energy was changed from 529.7 eV to 530.3 eV, which is attributed to the [Bi₂O₂]²⁺ in Bi₂O₂CO₃. The peak at 531.2 eV is characteristic of Bi-O binding energy in Bi₂O₂CO₃, and the peak at 532 eV is

attributed to Bi-O in Bi₂O₂CO₃/g-C₃N₄. These results showed that the Bi₂O₂CO₃ was formed in the composites. Interestingly, the O and Bi peaks at Bi₂O₂CO₃ and Bi₂O₂CO₃/g-C₃N₄ composites had the same shift tendency. According to the discussion of XPS analysis above, further confirmed the BOC/CN-2 exhibited the presence of Bi₂O₂CO₃ and g-C₃N₄, which proven by XRD and FTIR.

3.4 UV–vis diffuse reflectance spectra

To investigate the optical response of novel BOC/CN-2 composites, the UV-Vis absorption spectra was carried out as shown in Fig. 5a. The pure g-C₃N₄ and Bi₂O₂CO₃ exhibited a strong absorption edge at 454 and 370 nm, respectively. And after hybridized by Bi₂O₂CO₃, the absorption intensity remained unchanged, but the absorption wavelengths of BOC/CN-2 red shift contrasting to g-C₃N₄ and Bi₂O₂CO₃. The band gap energies of semiconductors were estimated by kubelka-munk transformation [46]:

$$\alpha h\nu = A (h\nu - E_g)^{n/2} \quad (1)$$

Where α , h , ν , and A are the absorption coefficient, planck constant, light frequency, and a constant. Besides, the n depends on the characteristics of the transition in a semiconductor. As previous report, the n values of g-C₃N₄ and Bi₂O₂CO₃ was 4 and 1 [47]. Thus, as shown in Fig. 5b, c the band gap values of g-C₃N₄ and Bi₂O₂CO₃ were estimated to 2.73 eV and 3.36 eV, respectively. Besides, the potentials of valance band (E_{VB}) and conduction band (E_{CB}) of a semiconductor material could be calculated via the following empirical equations [14, 48]:

$$E_{VB} = X - E^e + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

Where E_{VB} is the valence band edge potential, X is the electronegativity of the semiconductor, E^e is the energy of free electrons vs. hydrogen (about 4.5 eV. NHE) and E_{CB} is the conduction band edge potential. The bandgap of g-C₃N₄ and Bi₂O₂CO₃ was estimated at 2.73eV and 3.36 eV, respectively. The X values of g-C₃N₄ and Bi₂O₂CO₃ are 4.67 eV and 6.54 eV, respectively. The E_{VB} and E_{CB} potential s of g-C₃N₄ and Bi₂O₂CO₃ could be calculated using eqn (2)-(3), which the E_{VB} , E_{CB} of g-C₃N₄ and Bi₂O₂CO₃ are 1.54 eV/NHE, -1.19 eV/NHE and 3.72 eV/NHE, 0.36 eV/NHE, respectively. Meanwhile, the valance band XPS spectra near the Fermi level were provided to explore the electronic structure of the g-C₃N₄ and Bi₂O₂CO₃. The valance band maximum edge potentials of cuprous ion were measured by the VB-XPS spectra to demonstrate the band alignment occurred for g-C₃N₄ and Bi₂O₂CO₃. As shown in Fig. 5d, the valance band maximum energy levels of g-C₃N₄ and Bi₂O₂CO₃ were determined to be about 1.65 and 3.67 eV. Therefore, combined with the UV-Vis data above, the conduction band maximum of g-C₃N₄ and Bi₂O₂CO₃ were -1.08 and 0.31 eV. It's receivable that experiment value had a little difference with theoretical value.

3.5 Photocatalytic activity

The degradation capacity for organic dyes under visible light irradiation is vital standard to evaluate the activity of catalysts. The visible light photocatalytic activity of the as-obtained samples were also evaluated by degradation of RhB and k , calculated from the fitted curve, as shown in Fig. 6. Bi₂O₂CO₃ possessed band gap of

3.6 eV but had photoactivity for RhB, which suggested that the excitation of RhB dye could sensitize the $\text{Bi}_2\text{O}_2\text{CO}_3$ catalysts. As vividly depicted on Fig. 6a and b, under visible light irradiation ($\lambda > 420 \text{ nm}$), pure $\text{g-C}_3\text{N}_4$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ had no notable effect on RhB degradation, which decomposed about 50% and 13% RhB in 45 min. While the samples BOC/CN-2 exhibited excellent visible light photocatalytic activity, which could be completely degraded in nearly 45 min under visible light irradiation and were almost 2.2 times of pure $\text{g-C}_3\text{N}_4$ nanosheets and 7 times of $\text{Bi}_2\text{O}_2\text{CO}_3$. Apparently, the proper amount of $\text{g-C}_3\text{N}_4$ nanosheets played an important role in degradation. What's more, the above results matched the following pseudo-first order kinetic equation well as shown in Fig.6c [37].

$$-\ln(C/C_0) = kt \quad (4)$$

Where C_0 and C are the initial concentration and the concentration at any time, k and t are the rate constant and degradation time, respectively. It is intuitionistic that the apparent k of the photodegradation in the presence of pure $\text{g-C}_3\text{N}_4$, $\text{Bi}_2\text{O}_2\text{CO}_3$, BOC/CN-1, BOC/CN-2 and BOC/CN-3 were 1.285, 0.314, 2.068, 6.317 and 1.726 $\text{min}^{-1} \cdot 10^{-2}$, respectively. These data gave kinetics proof that BOC/CN composites at a weight ratio of 50% performed the fast reaction rate (Supplementary Information Fig. S3), which was in accordance with the PL spectrum denoted in Fig.7. The total organic carbon (TOC) removal curve of RhB was shown in Supplementary Information Fig.S4, which indicated photocatalytic degradation capacity of BOC/CN-2 composites for organic dye.

3.6 photoluminescence and charge separation analysis

As we all known, the recombination of photo-induced charge carriers were characterized by photoluminescence emission spectra [49, 50]. For the reason that the intensity of PL is relative to the rate of free carrier recombination in semiconductor photocatalysis. The higher PL intensity accounts for higher recombination existing in the photocatalysts [51, 52]. In order to study the migration, transfer and separation of photogenerated charge carriers of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites, the photoluminescence were performed as shown in Fig. 7. For the BOC/CN composites, if the excited electrons in CB of $\text{g-C}_3\text{N}_4$ transfer to $\text{Bi}_2\text{O}_2\text{CO}_3$, the intensity of PL spectra of the composite would be lower than that of pure $\text{g-C}_3\text{N}_4$. As expected, it was found that the PL intensity of BOC/CN-2 decreased compared to pure $\text{g-C}_3\text{N}_4$. This result indicates that fewer $\cdot\text{OH}$ radicals were formed in the BOC/CN-2 composites and the excited electrons in CB of $\text{g-C}_3\text{N}_4$ transferred to the CB of $\text{Bi}_2\text{O}_2\text{CO}_3$ based on the principle of thermodynamics, since the CB potential of $\text{g-C}_3\text{N}_4$ (-1.08 eV) is more negative than that of $\text{Bi}_2\text{O}_2\text{CO}_3$ (0.31 eV) [37]. Besides, BOC/CN-2 possessed the lowest intensity out of 40%, 50% and 60% BOC/CN composites. Based on the above results, it could be concluded that the efficient transfer of photoinduced electrons between $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{g-C}_3\text{N}_4$ facilitated the electron-hole pair separation.

It is well known that the photocatalytic activity is closely related to the transfer rate of photo-generated charge pairs. The charge separation behavior of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites was investigated through the transient photocurrent measurements in Fig. 8. Obviously, the photocurrent density of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites rapidly reaches a steady-state value $0.8 \mu\text{A}/\text{cm}^2$ and completely reverts to

zero once the light is switched off, which was about 4 times higher than pure g-C₃N₄. Such fast rise and fall of the photocurrents indicates that carrier transport in the Bi₂O₂CO₃/g-C₃N₄ composites material proceeds very quickly. Furthermore, it can be seen clearly that the stability of the Bi₂O₂CO₃/g-C₃N₄ composites photoelectrode was stable in 800s. Therefore, it confirmed the intrinsic advantages of this structure in facilitating the separation of the photogenerated carriers and the high transfer rate of carriers.

In order to furtherly estimate the photogenerated charge carried behaviors, the electrochemical impedance spectroscopies (EIS) were carried out. The EIS was measured at the same condition with photocurrent experiment. As we all know, the arc radius on EIS Nyquist plot revealed the reaction rate occurring at the surface of the electrodes [53]. From Fig. 9, the arc radius diameter of BOC/CN-2 is smaller than Bi₂O₂CO₃ and g-C₃N₄, which revealing that the effective separation of photogenerated carriers over BOC/CN-2 composites. To confirm the stability of BOC/CN-2, the recycling measurements were carried out as shown in Fig. 10. After three cycles, the photodegradation performance is no obvious decay.

3.7 Active species trapping experiments and proposed photocatalytic mechanism

To the best of our knowledge, the photogenerated electrons and holes played a catalytic role in photodegradation. When the incident energy was larger than the E_g of a semiconductor photocatalyst, the electrons of VB would be excited, which would

spontaneously transited to CB and leaved holes in VB. The separated electrons and holes would migrate to surface and interface of the catalyst and combined with O_2 and H_2O to generate strong oxidizing species including hole (h^+), hydroxyl radical ($\cdot OH$) and superoxide radical ($\cdot O_2^-$) for further reaction. In order to identify the mechanism of photocatalytic of BOC/CN composites, the trapping experiments were carried out using EDTA-2Na, IPA and BQ as the scavenger for photogenerated h^+ , $\cdot OH$ and $\cdot O_2^-$, respectively [54]. As shown in Fig. 11a and b, the degradation rate for BOC/CN-2 composites structure was significantly decreased with the addition of different scavengers, especially with EDTA-2Na and IPA. It revealed that photogenerated h^+ and $\cdot OH$ held the dominated roles while $\cdot O_2^-$ took the second place. The trapping experiments also matched the pseudo-first order kinetic equation well as Fig. 11c and d shown, thus a possible mechanism of photocatalytic degradation based on the above results was proposed in this work (scheme 2). When the RhB suspensions containing certain amount of BOC/CN catalysts exposed to visible light ($\lambda \geq 420$ nm), the VB of g- C_3N_4 nanosheets with proper E_g (2.73 eV) could be excited to release electrons to its CB while there was no response about the VB of $Bi_2O_2CO_3$ in the heterostructure because of its wide E_g (3.36 eV). However, in the BOC/CN composites, the energy band structure of g- C_3N_4 and $Bi_2O_2CO_3$ matched well that the E_{CB} of g- C_3N_4 (-1.19 eV/NHE) is more negative than that of $Bi_2O_2CO_3$ (0.36 eV/NHE), thus $Bi_2O_2CO_3$ could act as an electrons receptor to accept the photogenerated electrons from the CB of g- C_3N_4 efficiently. Compared with the standard reduction potential of -0.33 eV/NHE ($O_2/\cdot O_2^-$), the e^- of g- C_3N_4 (-1.19 eV/NHE) E_{CB} transform into strong

oxidizing $\cdot\text{O}_2^-$ by the adsorption of O_2 . Moreover, $\cdot\text{OH}$ was produced after the reduction of $\cdot\text{O}_2^-$ and the photo-induced holes in $\text{g-C}_3\text{N}_4$ reacted with H_2O to produce $\cdot\text{OH}$ [55]. Finally, the RhB molecule were broken down by the oxidizing $\cdot\text{O}_2^-$ and $\cdot\text{OH}$, the possible procedure were just as the following equations:

Conclusion

In summary, the BOC/CN composites were successfully prepared via a facile one-pot ultrasonic-assisted process for the first time. The results indicated that the $\text{Bi}_2\text{O}_2\text{CO}_3$ nanoflakes grow on the $\text{g-C}_3\text{N}_4$ nanosheets producing closely contacted interfaces between those two components. In particular, the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites with 50 wt% of $\text{g-C}_3\text{N}_4$ showed the highest photodegradation efficiency for RhB, which was 2.2 and 7 times higher than pure $\text{g-C}_3\text{N}_4$ and $\text{Bi}_2\text{O}_2\text{CO}_3$, respectively. $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites with 50 wt% of $\text{g-C}_3\text{N}_4$ possesses the lower the PL intensity, the bigger photocurrent density and the smaller arc radius

diameter, which indicates this structure facilitates the separation and transfer of the photogenerated carriers. Based on the obtained results, the possible RhB degradation mechanism was rationally proposed to explain the enhanced photocatalytic performance. This work may provide an idea to design or fabricate efficient photodegradation efficiency that can find potential applications in environmental pollution remediation.

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Figure Captions

Figure 1 XRD patterns of pure g-C₃N₄, pure Bi₂O₂CO₃, BOC/CN-1, BOC/CN-2 and BOC/CN-3 composites.

Figure 2 FT-IR spectra of g-C₃N₄, Bi₂O₂CO₃, BOC/CN-2 composites.

Figure 3 SEM and TEM images of (a and b) g-C₃N₄, (c and d) Bi₂O₂CO₃ and (e and f) BOC/CN-2 composites.

Figure 4 (a) Survey spectra of g-C₃N₄, Bi₂O₂CO₃ and BOC/CN-2, high-resolution XPS spectra of (b) C 1s; (c) N 1s; (d) O 1s; (e) Bi 4f.

Figure 5 Fig. 5 (a) The UV-Vis DRS of pure g-C₃N₄ nanosheets, Bi₂O₂CO₃ and BOC/CN-2; plot of (Ahv)^{1/2} versus energy (hv) for the band gap energy of (b) g-C₃N₄ and (c) Bi₂O₂CO₃. (d) The VB-XPS of as-prepared g-C₃N₄ and Bi₂O₂CO₃.

Figure 6 (a) Photocatalytic degradation rate of Rh-B under visible-light irradiation (> 420 nm) of the synthesized samples; (b) the degradation capacity of the synthesized samples under visible-light irradiation in 45min; (c) a natural logarithm C/C₀ fitting curves of all samples; (d) the value of the rate constant *k* of the photodegradation of RhB in the presence of as-prepared samples.

Figure 7 PL spectra of pure g-C₃N₄ and Bi₂O₂CO₃/g-C₃N₄ nanosheets excited by wavelength of 370nm , emission wavelength was 437nm at room temperature.

Figure 8 Amperometric I–t curves of pure g-C₃N₄ and BOC/CN-2 samples under visible light (λ≥420 nm) at open circuit potential with on/off cycles.

Figure 9 The Nyquist plots of the pure Bi₂O₂CO₃, g-C₃N₄ and BOC/CN-2 samples at 365 nm.

Figure 10 Cycle runs of BOC/CN-2 for degradation of RhB under visible light irradiation ($\lambda > 420$ nm).

Figure 11 (a) Effects of different scavengers on degradation of Rh-B under visible-light irradiation (>420 nm) of BOC/CN-2; (b) the degradation capacity of the above samples under visible-light irradiation in 45min.

Scheme 1 Schematic illustration of the ultrasonic-assisted synthesis procedure.

Scheme 2 Schematic illustration of the possible photocatalytic mechanism in the heterostructured $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites under visible light irradiation.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig.9

Fig. 10

Fig. 11

Scheme 1

Scheme 2

Graphical Abstract

$\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ (BOC/CN) nanosheets were facilely fabricated via an ultrasonic-assisted method for the first time. The synthesized $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$ composites when contained 50 wt% of $\text{g-C}_3\text{N}_4$ showed the optimal photoactivity for the degradation of RhB under visible light irradiation, which shown great potential to the widely application in environmental remediation.