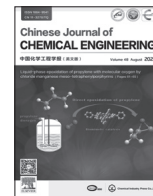




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Full Length Article

Pomelo biochar as an electron acceptor to modify graphitic carbon nitride for boosting visible-light-driven photocatalytic degradation of tetracycline

Feng Guo^{1,2,#}, Chunli Shi^{1,#}, Wei Sun¹, Yanan Liu¹, Xue Lin^{1,*}, Weilong Shi^{3,4,*}¹ School of Material Science and Engineering, Beihua University, Jilin 132013, China² School of Energy and Power, Jiangsu University of Science and Technology, Zhenjiang 212003, China³ School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China⁴ College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

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ABSTRACT

In this study, biochar (BC) derived from pomelo was prepared via a high-temperature calcination method to modify the graphitic carbon nitride (g-C₃N₄) to synthesize the BC/g-C₃N₄ composite for the degradation of the tetracycline (TC) antibiotic under visible light irradiation. The experimental results exhibit that the optimal feeding weight ratio of biochar/urea is 0.03:1 in BC/g-C₃N₄ composite could show the best photocatalytic activity with the degradation rate of tetracycline is 83% in 100 min irradiation. The improvement of photocatalytic activity is mainly attributed to the following two points: (i) the strong bonding with π - π stacking between BC and g-C₃N₄ make the photogenerated electrons of light-excited g-C₃N₄ transfer to BC, quickly and improve the separation efficiency of carriers; (ii) the introduction of BC reduces the distance for photogenerated electrons to migrate to the surface and increases the specific surface area for providing more active sites. This study provides a sustainable, economical and promising method for the synthesis of photocatalytic materials their application to wastewater treatment.

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1. Introduction

The use of antibiotics has peaked in recent decades. Among them, tetracycline (TC) is the most widely used, and their consumption has ranked second in the world [1,2]. This is because TC is not only used in clinical medicine in some countries, but are often used as growth promoters to raise livestock and increase the yield of aquaculture [3,4]. Nevertheless, due to overuse or even abuse, TC cannot be effectively decomposed and absorbed in the organism, resulting in a large amount of TC being discharged into the water environment [5,6]. A large number of experiments have confirmed that TC derivatives and incompletely degraded products can induce bacterial resistance [7–9], which seriously threatens ecosystems and human health [10–12]. In order to solve the above problems, the researchers used adsorption, biodegradation, electrochemical oxidation and other treatment methods [13–15].

However, the adsorption method may be troubled by secondary pollution because it is only the transfer of pollutants, not the elimination of pollutants. The period of biodegradation method is long and the treatment effect is weak. Electrochemical oxidation requires additional use of electricity and increased water treatment costs. Consequently, how to remove TC from water environment quickly and effectively by using a green technology is one of the hot spots in the field of environment.

Photocatalysis has been used as a low-cost and environmentally friendly technology for the treatment of antibiotic contamination in wastewater due to the combination of heterogeneous catalysis and solar technology [16–22]. Over the past decades, various efficient photocatalysts have been designed worldwide, such as Ag-based photocatalysts (e.g. Ag₃PO₄ [23], AgBr [24]), metal oxides (e.g. TiO₂ [25], ZnO [26]), metal sulfides (e.g. CdS [27,28], MoS₂ [29,30]), etc. However, most of these photocatalysts involve noble metal-based systems or can only use ultraviolet light (about 4% of the solar spectrum) or release toxic ions, resulting in secondary pollution [31]. Thus, the development of metal-free visible-light photocatalyst has received more and more attention.

* Corresponding authors at: School of Material Science and Engineering, Beihua University, Jilin 132013, China (X. Lin); School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China (W. Shi).

E-mail addresses: jlsdlinxue@126.com (X. Lin), shiwl@just.edu.cn (W. Shi).

The authors contributed equally to this work.

Carbon nitride ($g\text{-C}_3\text{N}_4$) with a relatively moderate band gap (~ 2.7 eV), visible-light response ($\sim 43\%$ of solar spectrum), low toxicity and cost raw materials has been shown to be promising visible-light photocatalysts for photocatalytic applications in hydrogen production and environmental purification [32–38]. However, the inherent defects, such as small specific surface area and the rapid recombination rate of photogenerated electron-hole pairs, lead to the low photocatalytic activity of pristine $g\text{-C}_3\text{N}_4$, which limits its application in the field of photocatalysis [39–43]. Recently, various strategies have been adopted to improve the photocatalytic efficiency of $g\text{-C}_3\text{N}_4$, including doping transition metals or coating noble metals [17,44], constructing heterostructures [45–47], and modified carbon materials [48–51]. Among them, carbon material modification is a simpler method to inhibit photoinduced carrier recombination and improve visible light response of semiconductors.

Biochar (BC) is a solid carbon material produced by high-temperature pyrolysis of various solid wastes such as wood, leaves, grass, sludge, fertilizer and microalgae, etc., and its production cost is lower than that of ordinary carbon materials, which has the advantages of economy and application [52–54]. According to statistics, China produces about 3×10^6 tons of pomelo per year, and its by-product pomelo peel is about 1×10^6 tons [55]. A large amount of pomelo peel (such as 40% of pomelo weight) is discarded to landfills, which will pose a threat to the environment of our country [56]. In fact, using pomelo peel as a porous biochar has shown a broader prospect in various applications, such energy conversion and storage [57]. In addition, pomelo peel is composed of cellulose, hemicellulose and lignin and is rich in functional groups including hydroxyl, carbonate, carboxyl, phenol and ether groups. because pomelo peel also has a porous structure, it is a promising carbon-based wastewater treatment material [58]. Consequently, the combination of BC derived from pomelo peel and $g\text{-C}_3\text{N}_4$ may be an effective way to accelerate the charge separation efficiency and optical absorption of $g\text{-C}_3\text{N}_4$. In particular, it is more conducive to the reuse and green disposal of biomass waste based on the concept of “recycled waste”.

In this work, BC derived from pomelo peel was used as a carbon-based material to modify $g\text{-C}_3\text{N}_4$ for photocatalytic remove TC in water under visible light irradiation. The focus of this experiment is to design a non-toxic, simple synthesis and non-metal composite photocatalytic material with high photocatalytic activity. Several characterization methods were used to explore its structure and applicability. By using pomelo peel carbon materials to overcome the limitations of $g\text{-C}_3\text{N}_4$ to prepare composite materials, thereby improving spectral capture and reducing recombination of photo-induced charges, improving the photocatalytic activity of $g\text{-C}_3\text{N}_4$, and also competing with highly efficient metal-based photocatalysts.

2. Experimental

2.1. Materials

Pomelo peel was obtained for free from the fruit shop of Beihua University in Jilin City, of China. Tetracycline hydrochloride ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 \cdot \text{HCl}$), triethanolamine (TEOA) and isopropyl alcohol (IPA) were purchased from Macklin Reagent Co., Ltd. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) was supported from Tianjin Damao Chemical Reagent Factory. Urea ($\text{CH}_4\text{N}_2\text{O}$) was purchased from Sinopharm Chemical Reagent Co., Ltd, and distilled water was provided by UPT-A (Shanghai Shenfen Analytical Instruments Co., Ltd.). All chemicals were analytical pure reagents and used without further purification.

2.2. Preparation of biochar carbon derived from pomelo

The whole pomelo peel was cut into small pieces with a knife then washed with distilled water and ethanol to remove impurities. After completely drying at 120°C , it was put into a tube furnace. At the N_2 atmosphere, it was first heated at $3^\circ\text{C} \cdot \text{min}^{-1}$ to 400°C for 1 h and then at $2^\circ\text{C} \cdot \text{min}^{-1}$ to 800°C for 1 h. Finally, biochar carbon derived from pomelo was ground to a fine powder by using an agate mortar and denoted as the BC.

2.3. Preparation of BC/ $g\text{-C}_3\text{N}_4$ photocatalyst

The BC/ $g\text{-C}_3\text{N}_4$ composite photocatalysts were prepared according to the Fig. 1. First, dissolve 10 g of urea in 30 ml of distilled water was stirred for 30 min. Moreover, the above solution was added different proportions of BC and then stirred for another 30 min. The mixture was then placed in a crucible and finally heated to 550°C at a rate of $5^\circ\text{C} \cdot \text{min}^{-1}$ in a muffle furnace and maintained for 2 h. After natural cooling to room temperature, the yellow powder was obtained. The as-prepared photocatalysts were labeled as BC/ $g\text{-C}_3\text{N}_4$ -X ($X = 0.01, 0.03, 0.05, 0.1$ and 0.3 g), which represents the introduction of BC weight in composite and the following discussion of BC/ $g\text{-C}_3\text{N}_4$ will focus on the sample with the highest photocatalytic activity (e.g., BC/ $g\text{-C}_3\text{N}_4$ -0.03). The preparation of pure $g\text{-C}_3\text{N}_4$ is done in the same process without the addition of BC.

2.4. Photocatalytic activity and trapping active species experiments

The photocatalytic activity of as-prepared products was tested by decreasing TC in visible light at room temperature in the photochemical reactor (CEL-LB70-5, Beijing Zhongjiao Jinyuan Co. Ltd.). The built-in 500 W Xe lamp with a UV cutoff filter was used as the visible-light source. Specific steps were given as follows. First, 50 mg of photocatalyst was added to 100 ml TC solution ($10 \text{ mg} \cdot \text{L}^{-1}$) and stirred for 30 min in dark to achieve the adsorption-desorption equilibrium. During the experiment, 3 ml suspension was collected at given time intervals and the photocatalyst powders were removed by the centrifugation. Finally, the obtained supernatant was analyzed by UV-visible spectrophotometer at 357 nm. In addition, the operation of the trapping active species experiments is similar to that of the photocatalytic degradation experiment except for the addition of triethanolamine (TEOA, $2 \text{ mmol} \cdot \text{L}^{-1}$), isopropanol (IPA, $2 \text{ mmol} \cdot \text{L}^{-1}$) and nitrogen (N_2 , bubbling for 1 h) before photocatalytic degradation process. The details of specific characterizations are given in the Supporting Information.

3. Results and Discussion

Further information about morphology and microstructure of the as-prepared sample can be obtained from the scanning electron microscope (SEM) and transmission electron microscope (TEM) images. The SEM images of BC and as-prepared BC/ $g\text{-C}_3\text{N}_4$ samples were provided in Fig. S1. As can be seen that BC shows the bulk structure, while BC/ $g\text{-C}_3\text{N}_4$ composites become more loose and porous with the introduction of BC. It can be clearly seen that pure $g\text{-C}_3\text{N}_4$ presents the thin nanosheet morphology with several porous structure (Fig. 2(a)). After coating BC on the $g\text{-C}_3\text{N}_4$ nanosheets, the lamellar structure of $g\text{-C}_3\text{N}_4$ nanosheets itself did not change (Fig. 2(b)). The dark part in the picture indicates that the BC particles are tightly attached to the layers of the $g\text{-C}_3\text{N}_4$ nanosheets, which was also further verified by the energy dispersive X-ray (EDX) spectrum of BC/ $g\text{-C}_3\text{N}_4$. Compared with the $g\text{-C}_3\text{N}_4$ (Fig. S2 and Table S1), the results showed that the three main

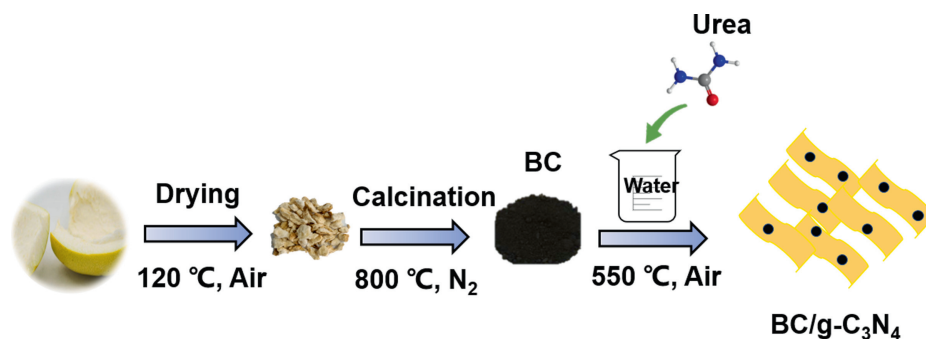


Fig. 1. Specific synthesis steps of BC/g-C₃N₄ composite.

elements of the g-C₃N₄ composites are C (49.8%), N (48.2%) and O (2.01%). And the main elements of C, N and O in BC/g-C₃N₄ composites are 54.7%, 33.8% and 12.2%, respectively (Fig. 2(c)), the increase in the proportion of C element shows the successful preparation of composite material. The existence of O element in BC/g-C₃N₄ will be further explained in the XPS characterization. Fig. 2(d) shows the N₂ adsorption-desorption isotherms and pore size distribution curves (inset) of g-C₃N₄ and BC/g-C₃N₄, respectively. In the range of 0.6–1.0 P/P_0 , the isotherms display the typical IV with an obvious H3 hysteresis loops, confirming the existence of typical mesoporous structure [5,59], which are agreement with the TEM images. According to the computing results of N₂ adsorption/desorption measurement, the Brunauer-Emmett-Teller (BET) surface area of BC/g-C₃N₄ is as high as 141.56 m²·g⁻¹, which is higher than that of urea-derived g-C₃N₄ (88.69 m²·g⁻¹). When BC and g-C₃N₄ are combined together, the composite material will inevitably increase the surface area and adsorption performance. Based on

the pore size distribution curve (inset), it can clearly observe that the pore size of the composite photocatalytic material is mainly less than 15 nm. These pores may be caused by the space between the BC and g-C₃N₄ nanolayers, further proving that BC can affect the structure of g-C₃N₄.

X-ray diffraction (XRD) is a rapid analytical technique that can be used to identify the phases of any crystalline material, thus providing information about crystal face and size. Fig. 3(a) shows the XRD patterns of g-C₃N₄ and BC/g-C₃N₄. From the pattern of pristine g-C₃N₄, two distinct diffraction peaks at 13.1° and 27.4°, which belong to the (1 0 0) and (0 0 2) planes of graphitic carbon nitride [60]. The one peak at 13.1° is a typical in-plane stacking peak in conjugated aromatic systems, and the other one peak at 27.4° is related to the in-plane structure stacking pattern, consistent with the diffraction surface reported in other literature (JCPDS 87-1526) [61–63]. For the BC/g-C₃N₄ composite, an XRD diffraction peak similar to that of g-C₃N₄ was exhibited. However, it is note-

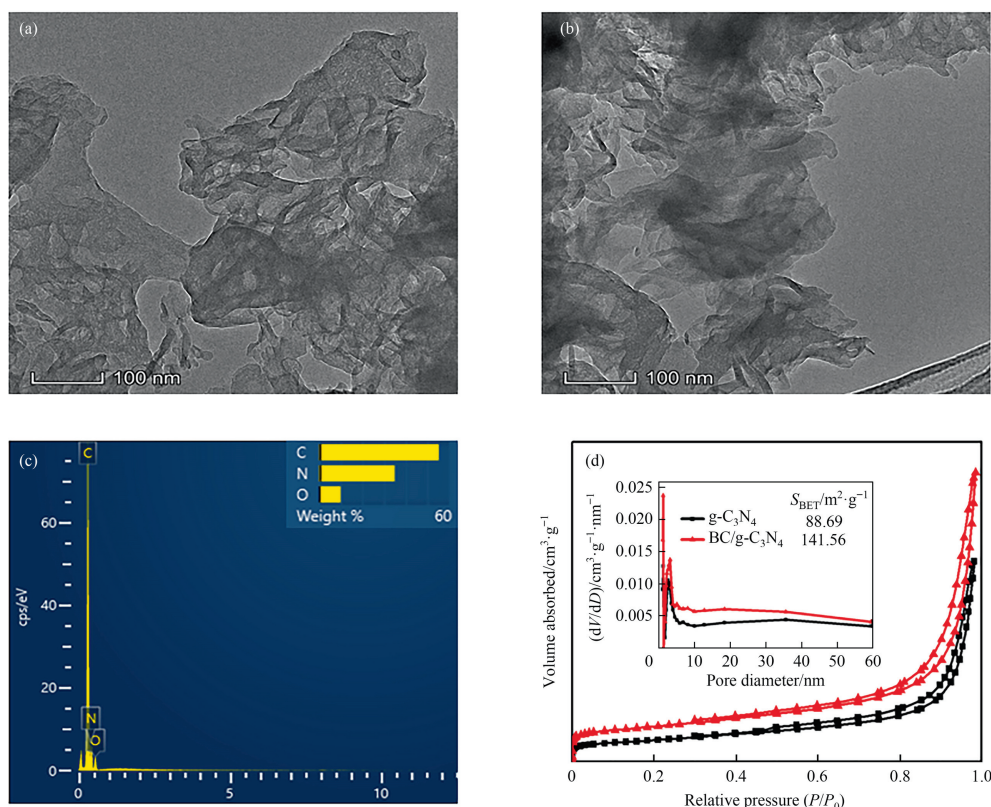


Fig. 2. TEM images of the (a), (b) g-C₃N₄ and BC/g-C₃N₄ composite; (c) EDX spectra of the BC/g-C₃N₄ sample; (d) N₂ adsorption-desorption isotherms and inset shows pore-size distribution curves for g-C₃N₄ and BC/g-C₃N₄ samples at 77 K.

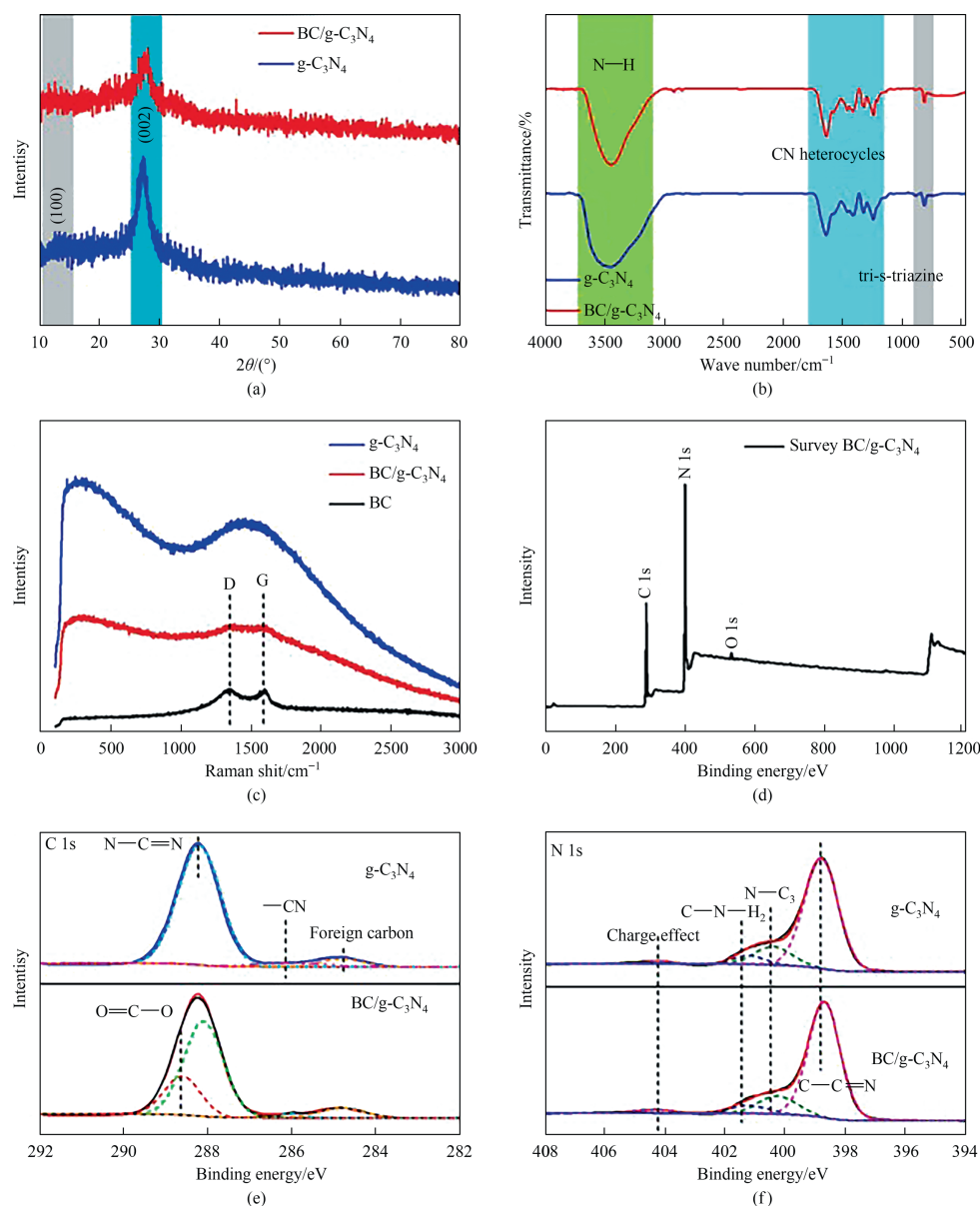


Fig. 3. (a) XRD patterns and (b) FT-IR spectra of g-C₃N₄ and BC/g-C₃N₄ composite. (c) Raman spectra of BC, g-C₃N₄ and BC/g-C₃N₄ composites. XPS spectra of the g-C₃N₄ and BC/g-C₃N₄ samples: (d) survey spectra, (e) C 1s region and (f) N 1s region.

worthy that the intensity of the (1 0 0) and (0 0 2) diffraction peaks of the composites is reduced, which is due to the fact that the introduction of BC covers the spatial positions of layers and the interplane over g-C₃N₄ nanosheets. In addition, the (0 0 2) peak shows a small change, a red shift from 27.4° to 27.8°, and the reason for this difference may be the close contact between BC and g-C₃N₄ layers through the intercalation effect, which further proves that BC has been incorporated into g-C₃N₄. Fourier infrared (FT-IR) spectroscopy can be used to determine the presence of functional groups in the as-prepared composite materials. In Fig. 3(b), a stronger adsorption area is observed for the g-C₃N₄ sample between 3000–3640 cm⁻¹, which is caused by the tensile vibration of N–H [64,65]. Moreover, a series of typical stretching vibration modes of C–N heterocycles (between 1683–1399 cm⁻¹) and strong bending vibration modes of tri-s-triazine units (812 cm⁻¹) can be observed [66,67]. The stretching vibration modes of C–N(–C)C and C–NH–C are at 1326 and 1241 cm⁻¹, respectively. More importantly, there are no absorption peaks at 2980 and

2200 cm⁻¹, which excludes the formation of CN triple bonds [68]. Compared with the pristine g-C₃N₄, the bands at 2920 and 2851 cm⁻¹ in the BC/g-C₃N₄ sample are attributed to the C–H interaction on the carbon surface, while the bands at 2361 cm⁻¹ is attributed to the C–O vibration in the composite [69]. These findings means the introduction of additional carbon in the composite has not changed the CN skeleton structure during the polymerization reaction of urea. To further identify the as-synthesized product, the Raman spectrometer was carried out (Fig. 3(c)). Pure BC presents two obvious peaks at 1350 and 1583 cm⁻¹ that corresponding to the D-band and G-band, respectively [70]. Usually, the D-band is attributed to the defect centers or disordered structure in the carbon-containing materials, while the G-band is caused by the tensile vibration of graphite sp² hybrid carbon [71]. A broader Raman characteristic peak of carbon nitride is shown at the range of 1400–3000 cm⁻¹, which results from the overlap of the peaks N-(C)₃ (1400 cm⁻¹), C–N=C (1600 cm⁻¹), C (sp²) (1380 cm⁻¹), and C (sp³) (1600 cm⁻¹), respectively [72,73]. Com-

pared with the BC and g-C₃N₄ samples, the Raman spectrum of the BC/g-C₃N₄ composite material not only has the diffraction peak similar to pure BC, but also retains the diffraction peak of pure g-C₃N₄, which implies that BC is successfully combined with g-C₃N₄ photocatalyst. X-ray photoelectron spectroscopy (XPS) was further utilized to investigate the chemical composition of the as-prepared BC/g-C₃N₄ composite. The XPS survey scan spectra of BC/g-C₃N₄, as shown in Fig. 3(d), it can be seen that the composite material mainly contains the binding energy of C and N elements. The high-resolution C 1s spectrum (Fig. 3(e)) shows that the peaks at 284.9, 288.2, and 285.9 eV in g-C₃N₄ and BC/g-C₃N₄ belong to the foreign carbon, N=C=N and —CN in the typical aromatic C₃N₄ unit, respectively [74,75]. The O=C—O associated with 288.4 eV was detected from BC/g-C₃N₄, further confirming that biomass carbon affects the skeleton of g-C₃N₄ [76,77]. The formation of the O=C—O bond also reflects that biomass carbon may affect the polymerization of the triziny end group, indicating that the end group of the original g-C₃N₄ has changed [78]. In Fig. 3(f), high-resolution N 1s XPS spectra can be deconvoluted into four peaks centered at 398.7, 400.5, 401.3, 404.3 eV by the Gaussian curve fitting. The peak at

398.7 eV corresponded to the sp²-hybridized nitrogen (C=N=C), whereas the peak at 400.5 eV was regarded as the tertiary nitrogen N-(C)₃ groups [79,80]. The peak occurring at 401.3 eV indicated the presence of amino functions (C—N—H), originating from the incomplete thermal condensation of the tri-s-triazine-based structure [81], and the last peak at 404.3 eV might be ascribed to the π -excitation [82].

To study the optical properties of the samples, the UV–vis diffuse reflectance spectra were employed and shown in Fig. 4(a). As can be seen, the absorption edge of g-C₃N₄ at about 450 nm indicates a band gap of 2.86 eV, calculated by the Kubelka-Munk function (Fig. 4(b)). When the g-C₃N₄ sample was combined with carbon carbide in waste biomass, it was found that the absorption edge shifted to a longer wavelength, which increased the absorption efficiency of the BC/g-C₃N₄ sample in the whole wavelength range, resulting in a narrow band gap (2.84 eV). The absorption spectra of BC/g-C₃N₄ composites with different loadings and digital pictures of sample powder are also shown in Fig. S3 and Fig. S4. This means that the BC/g-C₃N₄ composite photocatalyst can absorb more visible light to excite the photogenerated charge and

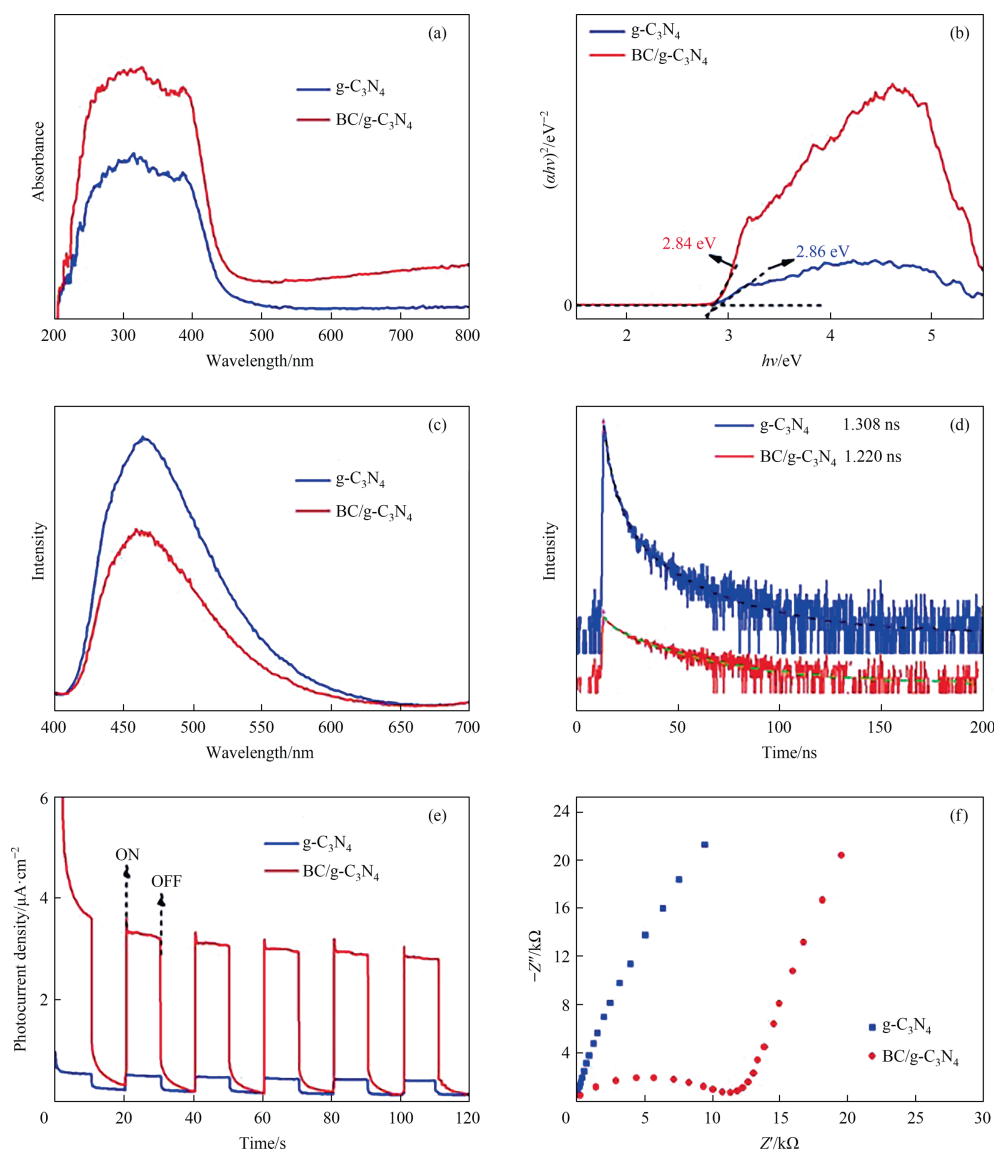


Fig. 4. (a) UV–vis diffuse reflectance spectra, (b) band gap energies, (c) PL spectra, (d) time-resolved fluorescence decay curves, (e) photocurrent response and (f) EIS spectra plots of g-C₃N₄ and BC/g-C₃N₄ composite.

thus exhibit excellent photocatalytic activity. The steady-state photoluminescence (PL) emission spectrum was used to investigate the charge carrier transfer and recombination efficiency of as-prepared photocatalytic materials. Fig. 4(c) show that $g-C_3N_4$ has a strong emission peak around 460 nm at the excitation wavelength of 350 nm. Compared with pristine $g-C_3N_4$, the PL emission peak intensity of the BC/ $g-C_3N_4$ composite decreases and the PL signal intensity is suppressed, which indicates that the introduced BC can act as an electron trap, enabling the electrons of $g-C_3N_4$ to be captured and transferred to the BC under visible light irradiation, thus effectively accelerating the transfer and separation of electron-hole pairs, and thus further improving the efficiency of the degradation TC [83–85]. In addition, the lifetime of the carrier was detected by time-resolved fluorescence attenuation spectroscopy. By fitting the attenuation spectrum (Fig. 4(d)), the singlet lifetime of pristine $g-C_3N_4$ is 1.308 ns, and that of BC/ $g-C_3N_4$ composite is 1.220 ns. The decrease in singlet lifetime indicates the enhancement of exciton dissociation, which helps the charge transfer from the bulk phase to the photocatalyst surface in BC/ $g-C_3N_4$ composite [86,87]. It is further proved that the introduction of BC can effectively prevent the recombination of carriers and improve the photocatalytic activity. While the tight interface between BC and $g-C_3N_4$ facilitates the separation of charge carriers because BC has a high electron storage capacity and is considered a useful electron acceptor. To better study the electron transfer mechanism of composite photocatalytic materials, the photo-induced charge separation efficiency of $g-C_3N_4$ and BC/ $g-C_3N_4$

composites was qualitatively studied by instantaneous photocurrent response experiments under periodic visible light switching on/off conditions (Fig. 4(e)). Compared with pure $g-C_3N_4$, the transient photocurrent of BC/ $g-C_3N_4$ is greatly increased, which is more than 4 times that of pure $g-C_3N_4$, improving the inhibition of photo-induced electron-hole recombination of $g-C_3N_4$. It also shows that the BC/ $g-C_3N_4$ composite photocatalyst interface promotes the separation of electron-hole pairs and produces good photocatalytic performance. Meanwhile, the surface resistance of the semiconductor also affects the photocatalytic performance of the catalyst, which can be derived from the electrochemical impedance spectra (EIS) measurement based on the semicircle diameter corresponding to the carrier transfer resistance [88–90]. Generally speaking, the diameter of the half arc in the EIS Nyquist diagram is smaller, which means that the interface electron transfer resistance is lower [83,91]. This also obviously implies that the charge transfer efficiency on the photocatalyst surface is higher [39]. Fig. 4(f) shows that the arc radius of the BC/ $g-C_3N_4$ electrode is smaller than that of pristine $g-C_3N_4$ electrode, indicating that the separation and transfer of photo-generated charge carriers is faster in composite during the photocatalytic reaction. These results again confirm that BC, as electron acceptor, promotes carrier transfer based on its close contact with $g-C_3N_4$ at the contact interface and good conductivity, thus achieving effective separation of electron-hole pairs [52]. The above results are very consistent with the observation of photocatalytic activity.

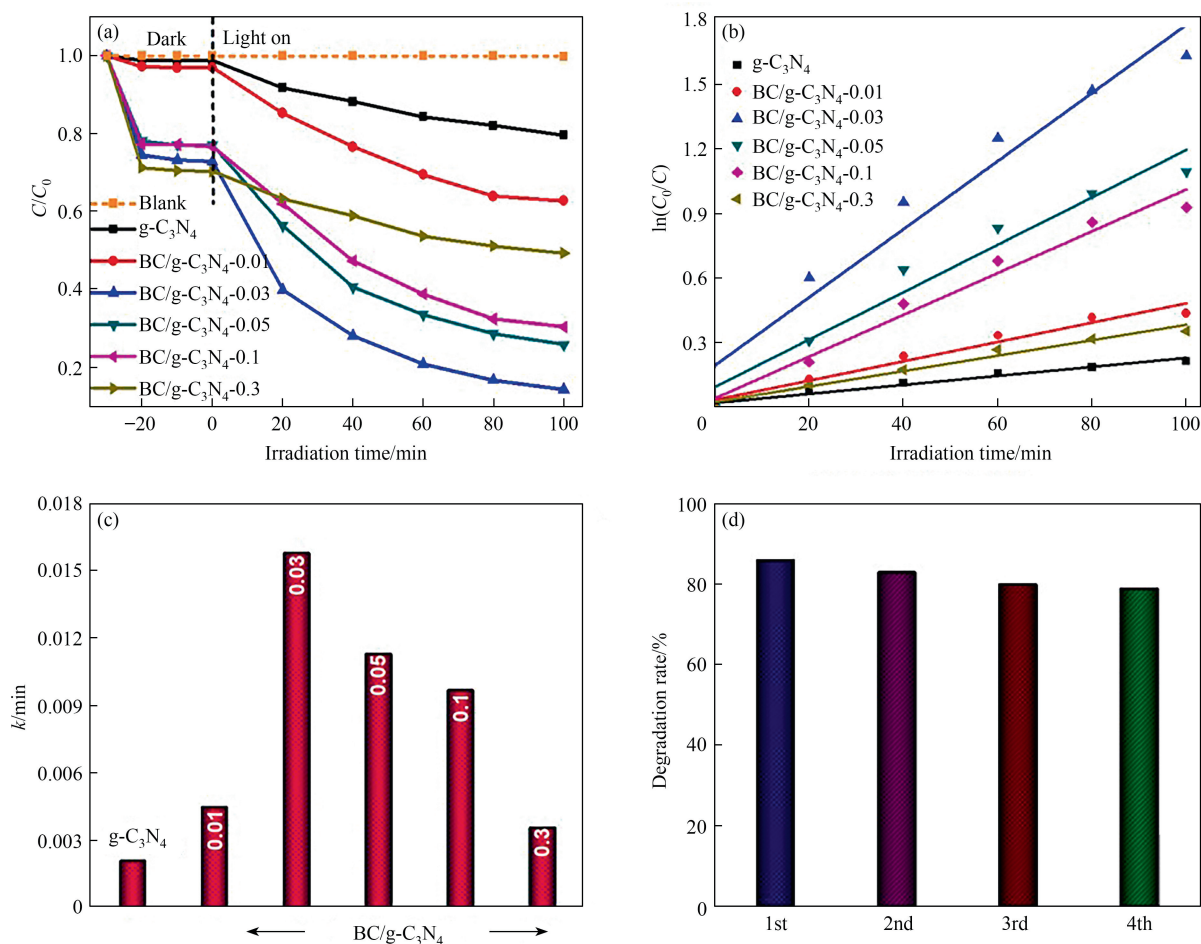


Fig. 5. (a) Photocatalytic degradation of TC over composite photocatalyst (BC/ $g-C_3N_4$ -x) under visible light irradiation. (b) Quasi-first order kinetic study and (c) kinetic constants for photocatalytic degradation of TC over different samples under visible light irradiation. (d) Cycling tests of optimal BC/ $g-C_3N_4$ -0.03 for TC degradation.

The photocatalytic performance of as-prepared $g\text{-C}_3\text{N}_4$ and $\text{BC}/g\text{-C}_3\text{N}_4$ composite materials was evaluated by the photodegradation of antibiotic contamination tetracycline (TC) under visible light (500 W xenon lamp, $\lambda > 420 \text{ nm}$). From the Fig. 5(a), on the one hand, in the absence of photocatalysts, the TC photodegradation curve clearly shows that it is very stable under dark and visible light irradiation conditions and can resist photodegradation. On the other hand, the photodegradation efficiency of pure $g\text{-C}_3\text{N}_4$ is very poor. The reasons for the low photocatalytic activity of pure $g\text{-C}_3\text{N}_4$ are its rapid electron-hole recombination rate and weak visible light absorption [68]. Notably, the as-prepared $\text{BC}/g\text{-C}_3\text{N}_4$ composite photocatalysts exhibit high photocatalytic activity. In addition, when the adsorption-desorption equilibrium is reached, the adsorption capacity of TC by $\text{BC}/g\text{-C}_3\text{N}_4$ composites is higher than that of $g\text{-C}_3\text{N}_4$, which is due to the super adsorption capacity of BC. By the comparison, the best sample for degradation is $\text{BC}/g\text{-C}_3\text{N}_4\text{-0.03}$, and the degradation efficiency of $\text{BC}/g\text{-C}_3\text{N}_4\text{-0.03}$ was 88.2% within the 100 min of continuous irradiation under visible light. Nevertheless, the photodegradation of the composites decreased with increasing BC content (over 0.03) for TC. It can be found that excessive BC can reduce the photocatalytic performance of photocatalyst to TC, which may be because the surface of $g\text{-C}_3\text{N}_4$ is covered by BC, which hinders the utilization of visible light at the active site of photocatalyst [92]. The corresponding pseudo-first-order kinetic diagram of the prepared photocatalyst is given in Fig. 5(b). As can be seen, all samples display good linearity, which indicates that all photocatalysts follow the first order kinetics during the photodegradation of TC, and the slope of $\text{BC}/g\text{-C}_3\text{N}_4\text{-0.03}$ samples is higher than that of pristine $g\text{-C}_3\text{N}_4$ and other samples. Based on the corresponding kinetic constants (k) of TC over as-prepared samples (Fig. 5(c)), it is obviously found that the kinetic constants of optimal $\text{BC}/g\text{-C}_3\text{N}_4\text{-0.03}$ is about 6 times higher than that of $g\text{-C}_3\text{N}_4$. Notably, the as-prepared $\text{BC}/g\text{-C}_3\text{N}_4$ composite photocatalyst exhibited excellent activity among the $g\text{-C}_3\text{N}_4$ -based

materials reported in recent years for degradation of TC (see Table S2). In order to study the stability and recyclability of the $\text{BC}/g\text{-C}_3\text{N}_4$ composite material, a cycle experiment on the photodegradation of TC by the $\text{BC}/g\text{-C}_3\text{N}_4\text{-0.03}$ photocatalyst was carried out (Fig. 5(d)). After four consecutive cycles, the photocatalytic activity of $\text{BC}/g\text{-C}_3\text{N}_4\text{-0.03}$ is basically stable, which also shows that the $\text{BC}/g\text{-C}_3\text{N}_4$ composite material is very stable during the photocatalytic reaction. Furthermore, the FT-IR spectra (Fig. S5) of $\text{BC}/g\text{-C}_3\text{N}_4$ composite before and after photocatalysis were tested, and the vibration peaks were found to be basically unchanged, the excellent stability of $\text{BC}/g\text{-C}_3\text{N}_4$ material was further verified.

The capture experiment was tested to determine the $\text{BC}/g\text{-C}_3\text{N}_4$ to confirm the active substance during the photocatalytic degradation TC process. Three kinds of scavenger agents (N_2 , TEOA, IPA) were selected to capture superoxide radical $\cdot\text{O}_2^-$, h^+ and $\cdot\text{OH}$, respectively. As shown in Fig. 6(a) and (b), with the introduction of three sacrificial agents, the activity of the two samples decreased to varying degrees, and the trend was basically no scavenger > TEOA > IPA > N_2 , which demonstrates both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ are important active substances that degrade TC over pristine $g\text{-C}_3\text{N}_4$ and $\text{BC}/g\text{-C}_3\text{N}_4$. In addition, electron spin resonance (ESR) spectroscopy analysis further tested to detect active species. From Fig. 6c and d, in dark conditions, no ESR signals were observed for pure $g\text{-C}_3\text{N}_4$ and $\text{BC}/g\text{-C}_3\text{N}_4$ composite materials, which indicates that no active species were generated in the dark. Significantly, under visible light irradiation for 10 min, six and four relatively strong characteristic signals corresponding to $\text{DMPO}\cdot\text{O}_2^-$ and $\text{DMPO}\cdot\text{OH}$ were observed. Furthermore, the signal intensities of $\text{BC}/g\text{-C}_3\text{N}_4$ are obviously higher than that of $g\text{-C}_3\text{N}_4$, suggesting that the introduction of BC can effectively increase the content of active species produced in the unit time of the composite, and then accelerate the forward progress of photocatalytic reaction.

The presence of intermediate products was checked *via* liquid chromatography-mass spectrometry (LC-MS) technique, and the

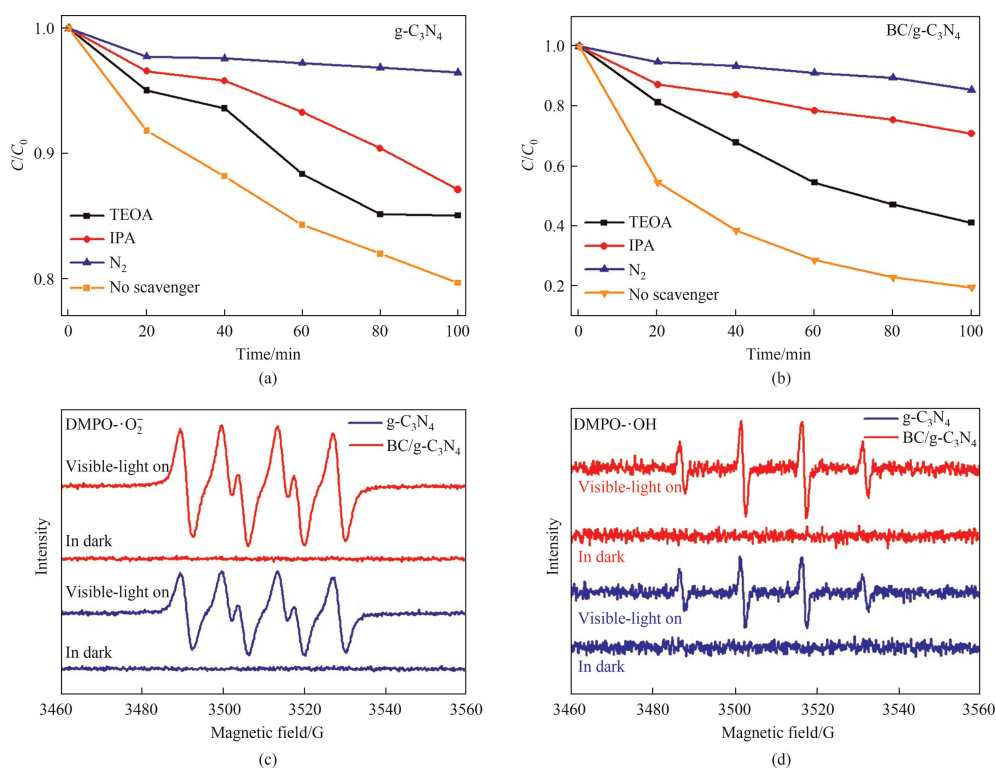


Fig. 6. Species trapping experiments for degradation of TC over (a) $g\text{-C}_3\text{N}_4$ and (b) $\text{BC}/g\text{-C}_3\text{N}_4$. ESR spectra of (c) $\text{DMPO}\cdot\text{O}_2^-$ and (d) $\text{DMPO}\cdot\text{OH}$ for $g\text{-C}_3\text{N}_4$ and $\text{BC}/g\text{-C}_3\text{N}_4$.

corresponding spectra are exhibited in Fig. S6. Based on this, the possible TC degradation pathway of as-prepared BC/g-C₃N₄ was inferred and shown in Fig. 7. It is well known that the molecular weight of TC is 445, and TC can be attacked by main reactive species to produce many intermediate products. The P1 was formed via adding hydrogen to the carbonyl [93]. Then, due to the ring opening and bond breaking reactions, P1 can be further degraded to form P2 and P3 via bond breaking and addition reaction [94]. Next, P3 was decomposes to form P4, P5 and P9 by the loss of hydroxyl group or N-methyl [95]. Moreover, P6 can be formed into P9 through dehydroxylation, deamination, addition reaction and ring opening reaction [96]. Finally, some products with small molecular weight, such as P10, P11, P12, CO₂ and H₂O can be formed from the subsequent reactions [97].

Through the above experimental conclusions, the possible photocatalytic mechanism of BC/g-C₃N₄ composite degradation of TC under visible light irradiation was proposed, as shown in Fig. 8. At first, the composite material was excited under visible light irradiation due to its suitable band gap energy (about 2.84 eV). As a result, the photogenerated electrons are transferred to the CB of g-C₃N₄, and the holes (h⁺) are left in the VB (Eq. (1)). Afterwards, due to the electron acceptor properties of BC, the electrons (e⁻) are captured rapidly by the BC and diffuse to the surface of the photocatalyst, thereby reacting with O₂ to generate ·O₂⁻ (Eqs. (2) and (3)). Meanwhile, h⁺ in VB of g-C₃N₄ cannot directly capture H₂O to generate ·OH because of the more negative valence band edge, so ·OH is generated through the route described in Eqs. (4)–(6) [98,99]. According to the above-mentioned active material trapping experiment results, ·OH and ·O₂⁻ are important active materials, and h⁺ is also the main active material. Therefore, ·O₂⁻ or ·OH further directly reacts with TC to produce non-toxic and harmless small molecules such as CO₂ and H₂O (Eq. (7)), and h⁺ can directly oxidize pollutants [83,100]. Based on the above analysis, the degradation reaction process of BC/g-C₃N₄ to TC was given as follows:

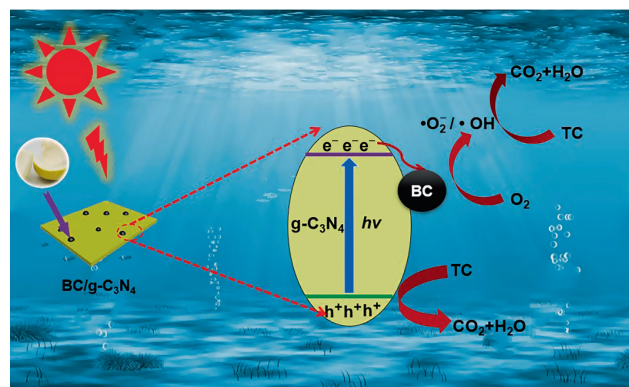
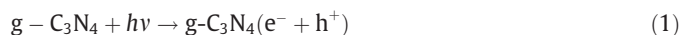


Fig. 8. Possible photocatalytic mechanism for photodegradation of TC over BC/g-C₃N₄ composite photocatalyst.



4. Conclusions

In summary, the BC/g-C₃N₄ photocatalytic material was successfully prepared by a simple one-step calcination method. The above characterization results show that the BC/g-C₃N₄ composite photocatalyst has high photocatalytic activity, excellent stability and recyclability. The optimum BC/g-C₃N₄-0.03 sample showed the best removal TC efficiency (83%) within the 120 min irradiation. The increase in photocatalytic activity is attributed to the fact that the prepared biomass carbon with the π-conjugated structure, which promotes the high separation efficiency of electron-hole pairs. In addition, ESR technique and active species capture experiments also show that ·O₂⁻ and ·OH are important active species in the photodegradation process. This research not only provides examples of environmentally friendly and cost-effective photocatalysts, but also suggests potential enlightenment for the

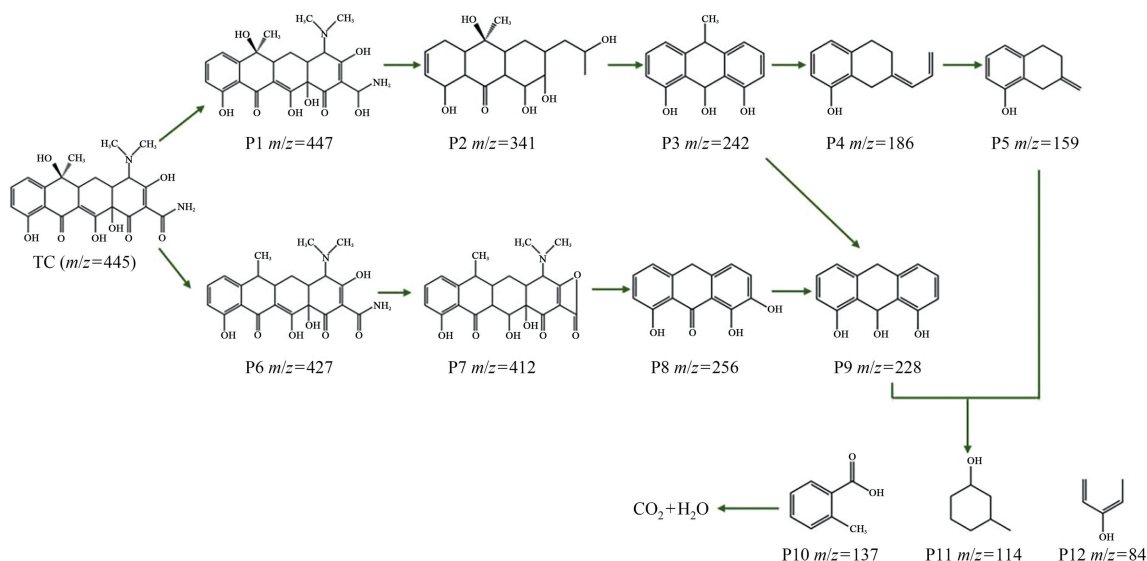


Fig. 7. The possible degradation pathway of TC over BC/g-C₃N₄ photocatalyst.

preparation of biomass carbon modified photocatalyst system using other biomass precursors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.06.027>.

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