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Novel carbon and defects co-modified g-C₃N₄ for highly efficient photocatalytic degradation of bisphenol A under visible light



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GRAPHICAL ABSTRACT

Carbon and defects co-modified carbon nitride (C_x CN) was synthesized by a novel and facile method, shows porous structure, a lower bandgap and longer life of photogenerated electron-hole pairs for more fully use of solar-energy, and thus its photocatalytic degradation activity is about 22 times higher than that of pristine g- C_3N_4 .



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ABSTRACT

Graphite carbon nitride (g-C₃N₄, CN) is considered as a promising semiconductor for environmental catalysis. However, pure CN can not meet the requirements for actual applications due to its high recombination rate of photogenerated electron-hole pairs and a relatively large band gap preventing full utilization of solar energy. In this work, we report synthesis of a novel carbon and defects co-modified g-C₃N₄ (C_xCN) by calcination of melamine activated by oxalic. This new catalyst C_xCN has porous structure with much higher surface areas compared with pristine CN. UV–vis analysis and DFT calculations show that C_xCN has a lower bandgap for enhancing visible light adsorption compared with CN. Photoluminescence (PL) and photoelectrochemical analyses show that C_xCN has a low recombination rate of photogenerated electron-hole pairs, which improves the utilization of solar energy. As a result, C_xCN samples show high efficiency for the degradation of bisphenol A (BPA) under visible light irradiation, where the best catalyst of C_xCN (C_{1.0}CN) samples shows about 22 times higher photocatalytic degradation rate than that of CN. Moreover, C_{1.0}CN shows high mineralization rate and

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1. Introduction

Photocatalytic degradation of pollutants by sunlight is one of promising processes to solve current worldwide environmental problems (Wang et al., 2014; Hisatomi et al., 2014; Cao et al., 2015; Zhou et al., 2019; Hou et al., 2018; Xu et al., 2018; Feng et al., 2018, 2017a; Feng et al., 2017b). As majority of solar energy is from visible light, developing semiconductors with visible light response is an important and challenging research topic (Xu et al., 2019). Metallic based semiconductors like CdS (Han et al., 2014a; Min et al., 2014), WO₃ (Grilla et al., 2018; Fernández-Domene et al., 2018) and α-Fe₂O₃ (Mishra and Chun, 2015; Han et al., 2014b) have been widely used for visible light photo-degradation of pollutants. However, metal ions leaching from these semiconductors may cause secondary environmental contamination. Thus, metal-free semiconductors, such as graphitic carbon nitride (g-C₃N₄), are considered as good candidates for photocatalytic degradation of pollutants (Wu et al., 2018a; Li et al., 2016; Wang et al., 2018). In addition, g-C₃N₄ has advantages of high thermal and chemical stability, easy synthesis, and proper optical features (Yan et al., 2009; Wu et al., 2015; Bai et al., 2015; Wang et al., 2009; Hong et al., 2013; Liu et al., 2018a; Li et al., 2015). As a result, g-C₃N₄ has been widely used for photo-degradation in recent years. However, pure g-C3N4 cannot fully meet the requirements for actual applications due to its low survival life of photogenerated electron-hole pairs and a large band gap preventing full use of solar energy (Li et al., 2012; Niu et al., 2014; Wang et al., 2012; Liu et al., 2018b; Fan et al., 2019).

Modification of g-C₃N₄ with different elementals, such as Ag, K, Au, C, N, O etc., (Wu et al., 2014; Liu et al., 2018c; Zhou et al., 2018; Wu et al., 2017; Sun et al., 2017; Liu et al., 2015; Xue et al., 2015) is considered as a good choice. In particularly, carbon modification is considered to be a better pathway due to no recombination center formation compared with foreign atom doping (Fang et al., 2015). For examples, Dong et al. synthesized g-C₃N₄ with carbon self-doping for improving photodegradation of RhB (Dong et al., 2012). Bian et al. synthesized C==C π bond modified g-C₃N₄ for enhancing photo-electrochemical cell performance. (Bian et al., 2017). Ran et al. synthesized carbon self-doped g-C₃N₄ for photocatalytic NO removal (Ran et al., 2018) Meanwhile, creating defects is also a good strategy to enhance the photocatalytic activity of g-C₃N₄. For examples, Niu et al. synthesized g-C₃N₄ with distinctive defects to improve photocatalytic hydrogen evolution (Niu et al., 2018). Shi et al. synthesized holey defective g-C₃N₄ for efficient visible-light-driven H₂O₂ production (Shi et al., 2018a). Che et al. synthesized vacancy defect of g-C₃N₄ to improve photodegradation of 2-mercaptobenthiazole (Che et al., 2019). Therefore, g-C₃N₄ modified by both carbon and defects is expected to have superior performance in photocatalytic degradation.

In this paper, we firstly synthesized carbon and defects co-modified g-C₃N₄ (C_xCN) with a facile calcination process of new precursors, which were obtained from melamine activated by oxalic acid at low temperature reaction. Comparing with pure g-C₃N₄ (CN), C_xCN has a lower bandgap and shows lower combination rates of photogenerated electron-holes. As a result, C_xCN samples demonstrate high efficiencies for the degradation of bisphenol A (BPA) under visible light irradiation, while the best sample (C_{1.0}CN) shows the highest photocatalytic degradation activity, with 22 times higher than that of CN. Meanwhile, C_{1.0}CN can photodegarade BPA into CO₂ and H₂O with a high mineralization rate, where the generated active species are mainly superoxide radicals ($'O_2^-$) and holes (h⁺).

2. Experiments

2.1. Chemicals

Melamine (C₃H₆N₆, Aladdin Chemistry, \geq 99%), and oxalic acid (C₂H₂O₄, Aladdin Chemistry, \geq 99%) were used without any purification. Ultrapure water with the specific resistance of 18.2 MΩ cm was obtained by reversed osmosis followed by ion-exchange and filtration.

2.2. Preparation of carbon and defects co-modified $g-C_3N_4$

Pure CN powder was synthesized as follows: melamine (10 mmol, 1.274 g) was put into a covered crucible and heated at 550 °C in a furnace for 4 h in static air (ramp rate: 1° C min⁻¹), then the obtained powder was grinded with a mortar. C_xCN samples were synthesized using new precursors. Typically, C_{1.0}CN was prepared as below: oxalic acid (10 mmol, 0.99 g) and melamine (10 mmol, 1.27 g) were added into 100 mL ultrapure water, which was placed in a beaker (200 mL) with stirring at 50 °C for 5 h. Then the above precipitate was collected after water washing for 3 times and then freeze-dried for two days. Then, the obtained powder was put into a covered crucible and heated following the similar procedure of CN. Different oxalic acid: melamine molar ratios (0.5:1, 1.5:1, and 2.0:1) were used and the samples were calcined to obtain other C_{0.5}CN, C_{1.5}CN, and C_{2.0}CN, respectively.

2.3. Photocatalytic test

A photocatalyst (20 mg) was put into a 200 mL beaker containing 100 mL BPA solution (10 mg L^{-1}) , where a light source was placed 20 cm above the solution surface. The reaction started with magnetic stirring under a Xenon lamp (300 W, Microsolar 300) irradiation with a 420 nm cutoff filter. After a certain reaction interval, 3 mL of BPA reaction solution was collected for evaluating the photocatalytic degradation activities. Related adsorption experiment was operated under dark condition, and the test process is similar to photocatalytic reaction. Cycling experiment was conduct as follows: after degradation of BPA, the photocatalyst was collected with water washing for 2 times, and then used for the next cycle experiment. The trapping experiment was carried out to analyze main active species, where three types of scavengers [tert-butyl alcohol (TBA, 10 mM), disodium ethylenediaminetetraacetate (EDTA-2Na, 10 mM) and benzoquinone (BQ, 10 mM)] were used for the active species [hydroxyl radicals ('OH), holes (h⁺) and superoxide radicals ('O₂-), respectively] [Wu et al., 2018a; Liu et al., 2019] identification during photocatalytic degradation of BPA under visible light irradiation.

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were performed on a D/ Max-Ultima IV X-ray diffractometer with Cu $K\alpha$ irradiation ($\lambda = 1.5406$ Å) by a scan rate of 8°/min. Transmission electron microscopy (TEM) was operated by a Talos F200s with an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) data were obtained by an ESCALABMk 250Xi spectrometer with a C 1s reference peak at 284.6 eV. UV–vis diffuse reflection spectra of the samples were recorded on an Agilent 300 spectrophotometer. The photoluminescence (PL) spectra of the samples were tested on a PL-4500 fluorescence spectrophotometer. The Brunauer-Emmett-Teller (BET) surface areas were determined by N₂ sorption using a Micromeritics ASAP 2020 Plus HD88 analyzer. Mineralization rate of BPA after photocatalytic reaction was determined by total organic carbon (TOC), which was measured on a TOC-L CPH Total Organic Carbon Analyzer (SHIMADZU). The thermal analysis of samples was operated on Mettler Toledo TGA2 under N_2 atmosphere. An electrochemical workstation (CHI650E) equipped with a standard three-electrode system was used for testing the photoelectrochemical performance. Electron paramagnetic resonance (EPR) was operated on */EMXplus-10/12 (Bruker).

2.5. Density functional theory calculations

All the calculations were performed based on density functional theory (DFT), and the DMOL3 modulus was implemented for the calculations of geometry optimization and band structure. The exchange correlation interactions were described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function. Spin-polarization was included in all calculations, a damped van der Waals correction was incorporated using Grimme's scheme to describe the non-bonding interactions and 0.005 Ha smearing was used in the calculations. The Brillouin zone was sampled with the Monkhorst-Pack mesh with K-points of $6 \times 6 \times 1$ grid in reciprocal space during electronic structure calculations. CN of $4 \times 4 \times 1$ supercell containing one single atomic layer with a vacuum width of 15 Å was used in our simulation. The vacuum width is considered to be big enough to eliminate the interaction between the layers. All atoms are allowed to relax in all energy calculations.

3. Results and discussion

Morphology of catalysts is very important for catalytic reaction. Thus, TEM was used for microstructure characterization of CN and C1.0CN. As shown in Fig. 1a-b, C1.0CN has the similar nanosheet structure with CN, while C1.0CN nanosheet contains some irregular porous structures. These porous structures may be caused by CO₂ releasing during the synthesis process at high temperature calcination. As shown in Figure S1, precursors of $C_{1,0}CN$ have a much higher volume compared with that of CN (melamine) with the same weight. The C1.0CN precursors, mixture of oxalic acid and melamine, have new structure, as shown from XRD in Figure S2. Some $C_2 O_4{}^2^-$ or $HC_2 O_4{}^$ from oxalic acid (H₂C₂O₄) were added into C_{1.0}CN precursors. The $C_2 {O_4}^{2-}\text{, }HC_2 {O_4}^-$ or combined $H_2 C_2 O_4$ of $C_{1.0} CN$ precursors can be decomposed at high temperature to release CO₂ during the calcination process, making porous structures in $C_{1,0}$ CN. This phenomenon can be also explained by the TGA analysis on the two different precursors (precursors of CN and C_{1.0}CN, Figure S3). The polymerization temperature of C_{1.0}CN precursors (234 °C) is lower than that of CN precursors (289 °C), and there is slight weight loss before the polymerization of C1.0CN precursors, which may be caused by CO2 releasing. In addition, the surface area of $C_{1.0} \text{CN}~(32.1~\text{m}^2~\text{g}^{-1})$ is higher than that of CN $(12.0 \text{ m}^2 \text{g}^{-1})$ based on BET surface area analysis (Figure S4), which can provide more reactive sites for improving its



Fig. 2. XRD patterns of all the synthesized samples (C_xCN).

photocatalytic activity.

For the structure of C_xCN samples, XRD characterization was performed and the results are shown in Fig. 2. C_xCN samples present the same main XRD diffraction peaks as CN with 2-theta positions of 13.0° and 27.3°, which are known as the in-plane structure (Li et al., 2018; Lin and Wang, 2013) and interlayer reflection structure [Lin and Wang, 2013; Lu et al., 2018] of g-C₃N₄, respectively. Therefore, the in-plane and interlayer structures of C_xCN samples are almost the same as those of CN.

This phenomenon was confirmed by XPS analysis of CN and C₁₀CN. After analyzing the survey of XPS spectra (Figure S5), it is found that C_{1.0}CN has the same signals of C 1s, N 1s and O 1s compared with CN. To further confirm these results, high resolution of C 1s and N 1s were analyzed. As shown in Fig. 3a, the C 1s high resolution XPS pattern of C1.0CN is similar to that of CN. The peak located at 284.6 eV denotes the C–C bond, and the highest peak at 288.0 eV indicates the sp²-bond carbon (N=C-N), and the peak at 286.3 eV is attributed to the C-NH₂ species on g-C₃N₄ (Li et al., 2012; Lin and Wang, 2013). With N 1s spectra shown in Fig. 3b, the highest peak of N 1s located at 398.5 eV indicates the sp²-hybridized nitrogen of N atom aromatic rings (C-N=C) (Li et al., 2015; Wu et al., 2018b), while the nearby peak at 400.0 eV is considered as the tertiary nitrogen N-(C)₃ groups (Dong et al., 2012). Then the weak peak at 401.1 eV is attributed as amino groups (C-N-H) (Li et al., 2012). Therefore, C_{1.0}CN possesses the similar chemical bonds with CN. However, after analyzing different chemical bond contents in CN and $C_{1.0}$ CN (Table S1), the C-C bond content in C_{1.0}CN is higher than that in CN, i.e., additional carbon atoms were added in C_{1.0}CN and new C-C bonds were formed, which can be also confirmed by the changes of carbon element contents in the two different samples (Table S2). The content of N-(C)₃ bond from



Fig. 1. TEM images of CN (a) and $C_{1.0}CN$ (b).



Fig. 3. (a) The C 1s XPS high-resolution and (b) the N 1s XPS high-resolution spectra of CN and $C_{1.0}$ CN.

 $C_{1.0}CN$ is lower than that of CN as shown in N 1s XPS high-resolution analysis, while C–N–H and C–NNH and C–NH₂ bonds are slightly increased in $C_{1.0}CN$ sample. Therefore, N–(C)₃ may be broken and some defects (as shown in DFT models) may be formed in $C_{1.0}CN$. The additional C–C bond and defects in $C_{1.0}CN$ may lead to promising effect on the optical properties, which will be discussed below.

For the band structures of the samples, UV-vis diffuse reflectance spectra were obtained. As shown in Fig. 4a, the UV-vis adsorption spectra of all C_xCN samples have a red shift compared with that of CN, which means a better visible light absorption of C_xCN. Meanwhile, the band gap energies of C1.0CN and CN were also determined to be 2.57 and 2.69 eV (Fig. 4b), respectively. For different properties of C_xCN and CN, DFT calculations were also performed. The atomic structure of CN and its related band structure are shown in Fig. 5a-b, where the bandgap energy of CN was calculated as 1.69 eV, which is different from the experimental result of 2.7 eV. This lower bandgap energy of CN from the calculation is due to the calculation method, which is caused by the neglected self-interaction of PBE functional in this work and this method is also demonstrated as a viable method for analyzing the band structure change trend of CN with different elemental or group modifying (Jing et al., 2018). The structure of defects modified CN (shown in Table S3) was configured by removing two melem (2,5,8triamino-tri-s-triazine) (Jürgens et al., 2003) blocks, and the related bandgap is calculated as 1.479 eV (Figure S6a). As shown in this model, the N-(C)₃ bond is reduced and the contents of C-N-H and C-NH₂ bonds are increased in C_xCN, which is consistent with the XPS results. With one carbon atom added into the defects modified CN, three types of C_xCN structure have been generated (shown in Table S3), and the calculated bandgap energies of all the three C_xCN (Fig. 5d and Figure S6bc) are lower than that of CN. As shown in Fig. 5c-d, the bandgap energy of C_xCN (type I) from DFT calculation is 1.43 eV, and the reduction of 0.26 eV compared with that of CN is close to the experimental value (0.12 eV). So C_xCN (type I) is considered as the most possible structure of C_{1.0}CN, which would induce a better photocatalytic degradation

activity under visible light irradiation.

The recombination rate of photo-generation electron-hole pairs is a key factor to determine photocatalytic activity of the samples. Therefore, photoluminescence spectra (PL) and photoelectrochemical test were operated to test the photocatalytic activity of the samples. Fig. 6a shows the PL spectra of C_{1.0}CN and CN (as a reference) at excited wavelength of 400 nm at room temperature. C1.0CN shows much lower emission peak compared with CN, indicating that photo-generated electron-hole's life of C1.0CN is much longer than that of CN (Tu et al., 2017; Nie et al., 2018). The intrinsic electronic structure and unpaired electrons of the samples were analyzed with electron paramagnetic resonance (EPR) spectra. As shown in Figure S7, the Lorentzian line center with a g factor of 2.0036, which is attributed to the unpaired electrons on sp²-carbon atoms of aromatic rings (Shi et al., 2018b). The higher signal of $C_{1.0}$ CN indicates the increase of the density state of conduction band, [Chen and Wang, 2018] which may be caused by the additional carbons or defects of $C_{1.0}$ CN. In addition, the photoelectrochemical tests under visible light irradiation (Fig. 6b) show that C_{1.0}CN has a much higher photocurrent density than that of CN. Thus, C_{1.0}CN is expected to have a better photocatalytic degradation activity (Liu et al., 2018d; Chen et al., 2017; Chen et al., 2019a).

The photocatalytic activities of different samples were evaluated under visible light irradiation ($\lambda > 420$ nm) for photocatalytic degradation of BPA. As shown in Fig. 7a, all C_xCN samples show much higher photocatalytic activities than that of CN, and the catalyst C_{1.0}CN can completely degrade BPA in solution within 90 min. However, ~22% BPA can be degraded by CN at the same conditions. C_{1.0}CN shows the best photocatalytic activity due to its better visible region adsorption ability compared with other samples (Fig. 4a). A first-order model can be used for this photocatalytic reaction as shown Eq. (1) (Ge et al., 2011; Zhao et al., 2018; Chen et al., 2019; Ling et al., 2019).

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \tag{1}$$



Fig. 4. (a) UV/vis adsorption spectra of all synthesized samples, (b) bandgap of CN and $C_{1.0}$ CN.



Fig. 5. (a) Theoretical model of CN and (b) its band structure; (c) theoretical model of CxCN and (d) its band structure from DFT calculation.



Fig. 6. (a) Photoluminescence (PL) spectra of CN and C_{1.0}CN under the 400 nm excitation, (b) photocurrent analysis of CN and C_{1.0}CN under the same conditions.

where C_0 and C_t denote the concentration of BPA solution at 0 and t min, respectively, while k is the apparent reaction rate constant. As shown in Fig. 7b, C_{1.0}CN shows the photo-degradation rate at about 22 times higher than that of CN based on the k values. As shown in Table S4, C1.0CN also shows a higher photocatalytic activity compared with other self-elemental (carbon or nitrogen) or defects modified g-C₃N₄, reported before. In addition, the BPA adsorption experiments of C_{1.0}CN and CN under dark condition were also investigated (Fig. 7c). The concentration of BPA solution did not decrease during 90 min adsorption experiment. Thus, the decrease of BPA concentration is only attributed to photo-degradation reaction. The stability of C_{1.0}CN was also tested with a recycling experiment (Fig. 7d). After 5 times recycling, about 54% BPA solution can be degraded during 90 min reaction, which is still much higher than that of CN (22%). The reduced photocatalytic activity of C1.0CN may be caused by the additional carbon from the decomposition of BPA. Comparing with XPS results (Figure S8) of C1.0CN after the photocatalytic reaction, the C-C bonds increased greatly and the contents of carbon in C1.0CN increased from 40.4 at.% ($C_{1,0}$ CN without reaction) to 50.5 at.%.

In addition, mineralization rate of BPA solution after photocatalytic reaction was determined by TOC analysis (Fig. 8a). The mineralization rate of BPA degraded by $C_{1.0}$ CN reaches 60.6% during 90 min, which is much higher than that of CN (4.5%), confirming again that $C_{1.0}$ CN

shows a highly efficient photocatalytic degradation of BPA under visible light irradiation.

To clarify the mechanism of photocatalytic degradation of BPA solution, we performed trapping experiments of $C_{1.0}$ CN to detect the active species during the photocatalytic degradation reaction (Fig. 8b). Three different scavengers including TBA, EDTA-2Na and BQ were used for quenching hydroxyl radicals (`OH), holes (h⁺) and superoxide radicals ('O₂⁻), respectively. After adding TBA, BPA photo-degradation rate of $C_{1.0}$ CN rarely changed during 90 min reaction. When adding EDTA-2Na, BPA photo-degradation rate of $C_{1.0}$ CN was reduced remarkably to 57% degradation of BPA solution within 90 min. After adding BQ, BPA solution concentration was not changed during the whole 90 min photo-degradation reaction. Therefore, the main active specie is possibly superoxide radicals ('O₂⁻), and holes (h⁺) also play a partial role in the photocatalytic degradation reaction.

Based on the discussion above, the corresponding photocatalytic degradation mechanism was presented in Fig. 9. The band structures of CN and $C_{1.0}$ CN are shown in Fig. 9a. The valence band (VB) was calculated from VB XPS spectra analysis shown in Figure S9. $C_{1.0}$ CN shows a higher VB (+1.79 eV) compared with that of CN (+1.70 eV), which indicated that the holes from $C_{1.0}$ CN have stronger oxidation capability for easier photo-degradation of BPA (Sun et al., 2014). The conduction band (CB) of $C_{1.0}$ CN is lower than that of CN, indicating that the



Fig. 7. (a) Photodegradation of BPA with the synthesized samples (C_x CN) under visible light irradiation, (b) photodegradation rate of related samples under visible light irradiation, (c) BPA solution adsorption tests of CN and $C_{1.0}$ CN under the dark conditions, (d) The recycling experiments of $C_{1.0}$ CN for degradation of BPA.

electrons from CN have a higher reduction potential for easier O₂ capture to form superoxide radicals ($^{\circ}O_2^{-}$). However, C_{1.0}CN has a lower bandgap compared with CN, which promotes electron-holes production under the same visible light irradiation. In addition, the recombination rate of photo-generated electron-hole pairs from C_{1.0}CN is much lower than that of CN. As a result, C_{1.0}CN has more superoxide radicals ($^{\circ}O_2^{-}$) production compared with CN under the same conditions. Therefore, C_{1.0}CN shows a higher photodegradation activity compared with CN. The photocatalytic reaction mechanism can be explained in Fig. 9b. With irradiation of visible light, C_xCN is excited, photogenerated electron combines with dissolved oxygen to form superoxide radicals ($^{\circ}O_2^{-}$). Therefore, generated superoxide radicals ($^{\circ}O_2^{-}$) and holes (h⁺) from C_{1.0}CN can effectively degrade BPA into CO₂ and H₂O during photocatalytic reaction.

4. Conclusions

We successfully synthesized carbon and defects co-modified g-C₃N₄

(C_xCN) using a novel and facile method. The carbon and defects comodification can tune the band structure to promote utilization of solar energy, C_xCN showing a higher photo-degradation of BPA and higher mineralization rate. $C_{1.0}CN$ has the best performance among C_xCN samples, which shows 22 times higher photocatalytic degradation rate compared with CN. Radical quenching tests demonstrated that generated superoxide radicals (' O_2^-) and holes (h⁺) are responsible for the photodegradation. This study provides a new design of carbon or defects modified photocatalyst for photocatalytic applications.

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Fig. 8. (a) TOC removal of BPA solution degraded by CN and $C_{1.0}$ CN after photocatalytic degradation reaction under visible light irradiation. (b) Trapping experiment of $C_{1.0}$ CN for degradation of BPA using different scavengers under visible light irradiation.



Fig. 9. (a) The band energy of CN and $C_{1,0}CN$, (b) the proposed mechanism of $C_{1,0}CN$ for degradation of BPA solution under visible light irradiation.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2019.121323.

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