Effective Photocatalytic H₂O₂ Production under Visible Light Irradiation at g-C₃N₄ Modulated by Carbon Vacancies

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Abstract

Hydrogen peroxide (H₂O₂) is of great significance in biological and environmental
processes as well as in chemical industry. Even though anthraquinone autoxidation
(AO) process has been the major artificial way to produce H₂O₂, its energy cost and
non-green nature have been motivating people to develop more efficient, economical
and green technologies as alternatives. Here we demonstrated that photocatalytic

H₂O₂ production at g-C₃N₄ could be improved by as much as 14 times in the absence of organic scavenger through a carbon vacancy-based strategy. Both the experimental and theoretical calculation results indicated that the creation of carbon vacancies could reduce the symmetry of g-C₃N₄ and produce the effect of electron delocalization. This will allow g-C₃N₄ to possess more excitable electrons and a narrower band gap. On the other hand, carbon vacancies provided more sites to adsorb molecular oxygen and thereby help electrons transfer from g-C₃N₄ to the surface adsorbed O₂. More interestingly, the presence of carbon vacancies changed the H₂O₂ generation pathway from a two-step single-electron indirect reduction to an one-step two-electron direct reduction. This study could not only develop a novel strategy to improve the H₂O₂ production activity of semiconductors, but also shed light on the deep understanding of the role played by surface defect structure on photocatalytic activity of semiconductor photocatalysts.

Key words: Photocatalysis, hydrogen peroxide, carbon vacancy, g-C₃N₄, oxygen reduction

1. Introduction

Hydrogen peroxide (H₂O₂) is an extremely versatile and useful agent. It is widely used in biological process, environmental remediation and chemical industry [1-3]. In the field of environmental remediation, H₂O₂ is a potent oxidant, which can directly or indirectly (in combination with other technology) oxidize a variety of organic or inorganic pollutants [4-6]. Since its reaction products are H₂O and O₂ only, H₂O₂ can also serve as an environmentally safe oxidant with numerous industrial applications

including chemical syntheses, paper bleaching, textile bleaching and detergents production [7-10]. At present, the main methods for large-scale production of H_2O_2 include anthraquinone autoxidation, oxidation of alcohols and electrochemical synthesis [11-13]. However, these methods can hardly be considered as green ones due to the consumption of a large amount of energy or organic solvent. In addition, H_2O_2 extracted from these systems may be contaminated by organic impurities. Therefore, it is highly desirable to develop efficient, economical and green technologies for the production of H_2O_2 .

Recently, H_2O_2 production from semiconductor photocatalytic process has attracted much attention because this procedure uses the sufficient and renewable sunlight as the driving force. Moreover, the photocatalytic approach does not need to use H_2 and can be a safe and green method. In the past decades, the H_2O_2 production photocatalysts were mainly focused on TiO_2 and modified TiO_2 [14-16]. For example, Maurino *et al.* reported that surface fluorination of TiO_2 could lead to an increase in the production rate of H_2O_2 [14]. Tsukamoto *et al.* found that the surface deposition with Au-Ag alloy could improve the H_2O_2 production rate of TiO_2 [16]. Although TiO_2 or modified TiO_2 in the presence of oxygen can effectively produce H_2O_2 under UV light irradiation, H_2O_2 also suffer self-decomposition induced by UV light [17]. Furthermore, UV light accounts for only ~4% of sunlight [18]. Therefore, it is essential to design and develop visible light active photocatalysts which could efficiently produce H_2O_2 while inhibit the decomposition process.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is a metal-free visible light photocatalyst very

promising for hydrogen evolution because of its desirable band gap of 2.7 eV [19-21]. Since its conduction band potential (-1.3 V) is more negative than the reduction potential of O₂/H₂O₂ (0.695 V), g-C₃N₄ could reduce O₂ to H₂O₂ under visible light thermodynamically [22, 23]. Shiraishi *et al.* found that H₂O₂ could be effectively produced by g-C₃N₄ in water/alcohol mixture under visible light irradiation [24]. However, in the absence of alcohol (organic scavenger), the efficacy of pure g-C₃N₄ was very low [25, 26]. This is due to the fact that pure g-C₃N₄ has two disadvantages: (1) the fast recombination of photogenerated electrons and holes; (2) low chemical adsorption capability of O₂ on its surface [27-29]. According to previous reports, vacancy defects have been found to be able to trap photogenerated electrons thus inhibiting the recombination of photogenerated electrons and holes [30-32]. Meanwhile, vacancy defects can also enhance the adsorption and activation of gas molecular because of their abundant localized electrons [33, 34]. In addition, amino nitrogen components can remarkably promote the interfacial electron transfer as recently observed by Zhang and his coworkers [35]. Considering the advantages of vacancy and amino nitrogen, it is reasonable to hypothesize that the coexistence of vacancy defects and amino nitrogen may improve the H₂O₂ production activity of g-C₃N₄ in absence of organic scavenger. Coincidentally, the formation of carbon vacancies in the structure of g-C₃N₄ is accompanied by the appearance of amino group (Scheme 1). Therefore, it is of great interest to systematically study the correlation between carbon vacancy and H₂O₂ production performance of g-C₃N₄. However, to the best of our knowledge, limited work has been presented in this

regard.

In this study, the effects of carbon vacancies on the oxygen reduction over g-C₃N₄ and the generation of H₂O₂ were systematically explored. Experimental results showed that carbon vacancy greatly improved the activity of g-C₃N₄ for H₂O₂ production in the absence of organic scavenger. A series of experiments were designed to identify the roles of carbon vacancies on the H₂O₂ production of g-C₃N₄ under visible light, and the mechanisms for the enhanced activity were analyzed in detail.

2. Experiments

2.1 Sample Preparation. g-C₃N₄ was synthesized by following the protocol developed in our previous work [36]. Melamine (4 g) in a covered crucible (30 mL) was heated in static air with a ramp rate of 20 °C/min up to 520 °C where it was held for 4 h. Carbon vacancy contained g-C₃N₄ (Cv-g-C₃N₄) was synthesized by calcining the as-prepared g-C₃N₄ in a tube furnace at 520 °C under high purity argon gas flow for 2 h. The resulted agglomerates were milled into powder in an agate mortar for further use.

2.2 Characterization. Power X-ray diffraction (XRD) patterns of the resulted samples were recorded on a Bruker D8 Advance diffractometer using Cu K_α irradiation ($\lambda = 1.5418 \text{ \AA}$). Element analysis was performed on Vario MICRO. Fourier transform infrared (FT-IR) spectra were obtained on an FT-IR spectrophotometer (Nicolet iS50, Thermo) with KBr as the reference. Chemical compositions of the samples were analyzed using X-ray photoelectronspectroscopy (XPS) (VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum chambers). All

the binding energies were calibrated to the C 1s peak (284.6 eV) arising from the adventitious carbon. Electron spin resonance (ESR) signals were recorded on a Bruker ESR A300 spectrometer at room temperature (298 K). The Brunauer-Emmett-Teller surface areas of the samples were determined by nitrogen adsorption-desorption isotherm measurements at 77 K, using a Micrometrics ASAP2020 system after samples were vacuum-dried at 180 °C overnight. Optical absorption spectra were obtained using a UV-visible spectrometer (Shimadzu UV-2550). Photoluminescence spectra (PL) were measured on a fluorescence spectrometer (Hitachi F-4500) at 293 K.

2.3 Photocatalytic experiments. The photocatalytic activities of the samples were evaluated by the activation of molecular oxygen under visible light irradiation ($\lambda > 420$ nm). A 300 W Xenon lamp with a 420 nm cutoff filter was chosen as visible light source. During each photocatalytic experiment, 0.1 g of a photocatalyst sample was dispersed into 100 mL of distilled water in a container with cooling water jacket outside. After that, the photocatalyst dispersion system was stirred in the dark for 2 h to ensure the adsorption-desorption equilibrium among the photocatalyst, dissolved oxygen and water before visible light irradiation. During the irradiation, about 4 mL of the suspensions was taken from the reaction cell at given time intervals, and then centrifuged to remove the photocatalyst particles. Subsequently, hydrogen peroxide (H_2O_2) was measured using a (p-hydroxyphenyl) acetic acid (POHPAA) analysis method [37]. Typically, a certain volume of fluorescence reagent (potassium hydrogen phthalate: 8.2 g/L, p-hydroxyphenylacetic acid: 270 mg/L, and type II horseradish

peroxidase: 30 mg/L) was pre-added into the reaction system. 1.0 mL of sample was then withdrawn at an interval time of 2 h and then mixed with 1.0 mL of 1.0 mol/L NaOH for 10 min for measuring the intensity of the fluorescence emission at 409 nm excited at 315 nm.

Superoxide radicals ($\cdot\text{O}_2^-$) were examined by electron spin resonance (ESR) spectral measurement. ESR spectra of the radicals were recorded on a Bruker EPR A300 spectrometer employing 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trapper. The spectra were collected with averages of 9 scans at 2 min after mixing the test sample in methanol solution. Methanol was used as the $\cdot\text{OH}$ radical scavenger to suppress the DMPO-OH signal.

2.4 Theoretical calculations. The band structures and electron density calculations were carried out using the program package CASTEP, working in a plane wave basis set. The Brillouin zones of the supercells were sampled by a grid of $3 \times 3 \times 1$ (g-C₃N₄ and Cv-g-C₃N₄) K-points. Electronic structures were calculated within the generalized gradient approximation from Perdew-Burke-Ernzerhof (GGA-PBE). The cutoff energy was 550 eV, and the Monkhorst-Pack k-point meshes were $5 \times 5 \times 3$ for all structures. In the process of calculation, the convergence tolerances were set as follows: $2.72\text{e-}5$ eV/atom for energy, 0.002 eV/Å for maximal force, 0.05 GPa for maximal stress, and 0.001 Å for max.

2.5 Photoelectrochemical experiments. Photoelectrochemical experiments were performed in a conventional three-electrode cell with a platinum plate ($1 \times 1 \text{ cm}^2$) as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference

electrode on a CHI 660C workstation. The photoelectrode (working electrode) was positioned in the middle of a 0.1 M KCl aqueous solution with the glass side facing the incident light. A 300W Xe lamp with a 420 nm cutoff filter was chosen as a visible light source.

The photoelectrodes were prepared by a spin coating method. Typically, the aqueous slurries of g-C₃N₄ and Cv-g-C₃N₄ were spin-coated on ITO glass substrate at a spin rate of 3000 rpm for 30 s under low vacuum. The films on ITO glass substrate were dried in air and annealed at 200 °C for 1 h as final photoelectrodes.

3. Results and Discussion

3.1 Structure Characterization for Samples. X-ray diffraction (XRD) is often used to characterize the phase structure of samples. As well known, g-C₃N₄ is featured with two XRD peaks: one at 13.0° corresponding to a d-spacing of 0.676 nm is arising from the in-plane structural packing motif, and the other at 27.4° is a characteristic interlayer stacking peak, corresponding to an interlayer distance of d=0.336 nm. As shown in Figure 1a, both samples show a typical g-C₃N₄ structure without any impurity phases, indicating that the heat treatment with argon gas did not affect the crystal structure of graphite-like carbon nitride. However, the peaks of Cv-g-C₃N₄ are weaker and shifted toward a higher 2θ value, suggesting that heat treatment with argon gas could destroy the crystallinity of g-C₃N₄ and could produce defects.

In order to identify the type of defects formed in the Cv-g-C₃N₄ framework, elemental analysis (EA) was used to determine the molar ratio of carbon to nitrogen (C/N) in the products. The C/N molar ratio of Cv-g-C₃N₄ is 0.6 (Figure 1b), lower

than that of g-C₃N₄ (0.7). This indicates that the defects formed in the Cv-g-C₃N₄ framework are carbon vacancies. Additionally, the content of H element in Cv-g-C₃N₄ is very plentiful, suggesting that more amino groups (-NH₂) were generated in Cv-g-C₃N₄ after the heat treatment with argon gas.

X-ray photoelectron spectroscopy (XPS) was further used to investigate the chemical compositions of the carbon nitride samples (Figures 2a and 2b). High-resolution XPS peaks of C 1s of the two samples can be fitted with two peaks at binding energies of 288.2 and 284.6 eV, which are ascribed to the tertiary carbon C-N₃ and C-C (arising from the adventitious carbon) groups, respectively. The area ratios of the two peaks at 288.2 and 284.6 eV were calculated to be 2.7 and 1.2 for g-C₃N₄ and Cv-g-C₃N₄, respectively. The decrease of tertiary carbon content percentage supports the assumption of carbon vacancy formation. In addition, the high-resolution XPS peaks of N 1s of g-C₃N₄ can be fitted with two peaks centered at 398.4 and 400.7 eV, which are ascribed to the tertiary carbon C-N-C and C-N₃ (arising from the adventitious carbon) groups, respectively. However, in addition to the N 1s peaks at 398.4 and 400.7 eV, a new peak at higher binding energy of 401.3 eV appeared in the high-resolution XPS spectra of Cv-g-C₃N₄ (Figure 2b). This peak is attributed to the amino groups (-NH₂) formed by the disappearance of tertiary carbon and further supports the formation of carbon vacancies.

Besides EA and XPS, Electron spin resonance (ESR) was also employed to verify the formation of carbon vacancies. Figure 2c shows that g-C₃N₄ exhibits a Lorentzian line centered at about 3512 G, which is arisen from the unpaired electrons on the

carbon atoms of the aromatic rings. Compare with pure g-C₃N₄, Cv-g-C₃N₄ possesses a much weaker ESR signal, suggesting the decrease of carbon content in Cv-g-C₃N₄. Therefore, it is concluded that carbon vacancies have been successfully formed in g-C₃N₄ after the heat treatment with argon gas.

Since surface and bulk defects play different roles in photocatalytic processes, it is crucial to identify the positions of carbon vacancies in the Cv-g-C₃N₄. In this prospect, high-resolution XPS depth profiles analysis was employed to monitor the -NH₂ change in the Cv-g-C₃N₄. It is found that the peak intensity of -NH₂ decreases continuously upon the etching time from 0 to 240 s, indicating the carbon vacancies mainly exist on the surface of Cv-g-C₃N₄ (Figure S1, in the supporting information). Figure 2d shows the possible formation mechanism of carbon vacancy. In the procedure of calcination, high temperature give the enormous energy to argon molecules. This makes a part of argon molecules do the irregular motion. Molecules which do irregular motion may hit the surface atoms. When argon molecule hit surface atom, it will impart energy to the targeted atom. If the imparted energy exceeds the binding energy of the targeted atom, targeted atom can be sputtered from the surface and form a vacancy simultaneously. As we know, carbon atom has a bigger surface area and smaller molecular weight than nitrogen atom. The bigger surface area makes carbon atom to accept more energy. Meanwhile, the smaller molecular weight and the bigger energy make carbon atom more likely to be sputtered from the surface.

3.2 Photocatalytic H₂O₂ production. H₂O₂ can be produced in both g-C₃N₄ and Cv-g-C₃N₄ systems (Figure 3). Control experiments show that H₂O₂ cannot be detected when oxygen is eliminated by argon gas, indicating oxygen is essential for the generation of H₂O₂ (Figure 3a). That means O₂ could be effectively reduced to H₂O₂ in the presence of water over both g-C₃N₄ and Cv-g-C₃N₄. However, in the absence of either photocatalyst or visible light, there is no H₂O₂ production (Figure 3a). This result unambiguously illustrates that the process of H₂O₂ production is accomplished by photocatalysis (Figure 3c). As shown in Figures 3a and 3d, the H₂O₂ production in g-C₃N₄ suspension slowly increases with extending the reaction time. Interestingly, the yield of produced H₂O₂ over Cv-g-C₃N₄ in the same visible light irradiation time is much higher than that over g-C₃N₄ (Figures 3b and 3d). Obviously, Cv-g-C₃N₄ is more active for the photoreduction of O₂ to H₂O₂, namely, 14 times more activity than g-C₃N₄. The influence of initial pH values on the H₂O₂ generation in the Cv-g-C₃N₄/H₂O/O₂ system was also investigated. We found that the pH value variation in the range of 5.0 to 7.0 did not affect the H₂O₂ production (Figure S2, in the supporting information), suggesting that Cv-g-C₃N₄ can efficiently produce H₂O₂ in a wide working pH range.

Niu and her co-workers revealed that nitrogen vacancy could also improve the photocatalytic activity of g-C₃N₄ [38]. To compare the improve effect of carbon vacancy and nitrogen vacancy, we synthesized the g-C₃N₄ with nitrogen vacancies (Nv-g-C₃N₄). The synthesis procedure of Nv-g-C₃N₄ was similar to that of Cv-g-C₃N₄ but changed the argon gas to hydrogen gas. The activity comparison in Figure S3 (In

supporting information) suggests that the activity of Cv-g-C₃N₄ is 6 times of that of Nv-g-C₃N₄. This result suggests that carbon vacancy is more effective for photocatalytic H₂O₂ generation than nitrogen vacancy.

3.3 The mechanism of activity enhancement. Since the production of H₂O₂ needs photogenerated electrons to reduce O₂, the generation of H₂O₂ relies on the amount of photogenerated electrons. As is well known, photocurrent also depends on the amount of photoelectrons transferred from semiconductor to the ITO glass substrate. The higher the photocurrent is, the more the photoelectrons are produced. Figure 4a shows that the photocurrent (The applied bias is 0 V vs SCE) generated over Cv-g-C₃N₄ reaches 8.12 $\mu\text{A cm}^{-2}$, 2.0 times that of g-C₃N₄ (4.05 $\mu\text{A cm}^{-2}$). The higher photocurrent in Cv-g-C₃N₄ implies that it could produce more photoelectrons to reduce O₂ molecule compared to g-C₃N₄.

Generally, the production of photoelectrons relates to three processes: visible light absorption, photoexcitation, and the separation of photoinduced charge carriers. UV-vis absorption spectra of g-C₃N₄ and Cv-g-C₃N₄ show the difference in absorption edges of the two samples. As seen in Figure 4b, the intrinsic absorption edge of Cv-g-C₃N₄ shows a red shift compared with that of g-C₃N₄. In addition, the absorption spectrum of Cv-g-C₃N₄ extends to the whole visible light region, even in the infrared region, thereby enhancing the absorption of light. This is consistent with the previous reports that vacancy defects can increase the visible light absorption of photocatalysts [33]. From the absorption spectra and simulation results (Figures 4d and 4g, both g-C₃N₄ and Cv-g-C₃N₄ are direct-gap semiconductors), the corresponding band gaps

of g-C₃N₄ and Cv-g-C₃N₄ can be derived as 2.73 and 2.68 eV respectively (Figure 4c), indicating that carbon vacancy could narrow the band gap of g-C₃N₄. Thus, the excitation of valence band electrons in Cv-g-C₃N₄ will be much easier than that in g-C₃N₄. In order to determine the position of the conduction band and the valence band of g-C₃N₄ and Cv-g-C₃N₄, Mott–Schottky measurements were performed. As shown in Figure S4 (In supporting information), both of the two samples displayed n-type semiconductor characteristic. The flat-band potentials of both g-C₃N₄ and Cv-g-C₃N₄ is estimated to be about -1.29 eV versus SCE. For n-type semiconductor, the conduction band position is very close to their flat-band potential. Therefore, the conduction band potentials of both g-C₃N₄ and Cv-g-C₃N₄ is -1.29 eV versus SCE, which more negative than the redox potential of O₂/H₂O₂ (0.695 V). The VB potentials are calculated to be 1.44 and 1.39 eV for g-C₃N₄ and Cv-g-C₃N₄ by using the formula $E_g = E_v - E_c$ (E_g : band gap, E_v : VB potential, E_c : CB potential). This up shift of VB potential may be caused by the valence band broadening which could be attributed to the carbon vacancy.

To further understand the change of the band structure induced by carbon vacancies, the band structures and the electron densities of g-C₃N₄ and Cv-g-C₃N₄ were simulated via the plane-wave-pseudopotential approach based on the density functional theory. From Figures 4d and 4g, it can be seen that the carbon vacancies could narrow the band gap of g-C₃N₄ to enhance its visible light absorption. This parallels the results of UV-vis absorption spectra. Meanwhile, the energy level density of valence band of Cv-g-C₃N₄ is much higher than that of g-C₃N₄, revealing that

carbon vacancies make Cv-g-C₃N₄ instead of g-C₃N₄ possess more excitable electrons. This is understandable after considering that carbon vacancies reduced the symmetry of g-C₃N₄ and produced the effect of electron delocalization. The symmetry reduction and electron delocalization are shown in the electron density maps (Figures 4e and 4f).

Photoluminescence (PL) spectra were used to explore the recombination and separation of photogenerated electrons and holes in the g-C₃N₄ and Cv-g-C₃N₄ samples (Figure 5a). The emission peak appearing at about 455 nm is attributed to the direct electron-hole recombination of band transition. Compare with pure g-C₃N₄, Cv-g-C₃N₄ possess a much weaker emission peak, implying that the separation efficiency of photogenerated carriers is improved by carbon vacancies. The reason of increased separation efficiency can be explained by electrical conductivity. Electrochemical impedance spectroscopy (EIS) was employed to study the electrical conductivity of the resulting samples. Figure S5 (In supporting information) reveals that the Nyquist plots diameter of Cv-g-C₃N₄ is much smaller than that of g-C₃N₄, confirming that the carbon vacancies could increase the electrical conductivity. Carbon vacancies originate from the breaking of the covalent bonds between carbon and nitrogen atoms, accompany by many unsaturated N atoms. These unsaturated N atoms could act as the paramagnetic centers and attract photoelectrons from the conduction band of Cv-g-C₃N₄ (Figure 5b). Therefore, carbon vacancies could significantly inhibit the recombination of photogenerated carriers, thus increasing the yield of photoelectrons.

Based on the experimental observations in conjunction with theoretical calculation, the fact that Cv-g-C₃N₄ could produce more photoelectrons can be attributed to the following. First, carbon vacancies made Cv-g-C₃N₄ to hold more excitable electrons; second, carbon vacancies could narrow the band gap of g-C₃N₄ to enhance its visible light absorption; and third, carbon vacancies could significantly inhibit the recombination of photogenerated carriers.

Besides the amount of photogenerated electrons, the H₂O₂ production performance may also depend on the adsorption capacity and adsorption strength of molecular oxygen onto the surface of g-C₃N₄ because the photocatalytic process is surface related. In general, adsorption capacity is proportional to the surface area of a sample. The surface areas of g-C₃N₄ and Cv-g-C₃N₄ were analyzed through nitrogen adsorption-desorption isotherms. Figure 6a shows that the Brunauer–Emmett–Teller specific surface areas of g-C₃N₄ and Cv-g-C₃N₄ are 8.8 and 9.4 m²/g, respectively, indicating that the adsorption amount of molecular oxygen on Cv-g-C₃N₄ is approximate to that on g-C₃N₄.

For adsorption strength, it is strongly dependent on the interaction between surface sites and adsorbates, thereby classified into different adsorption types including physisorption and chemisorption. Temperature-programmed desorption (TPD) investigations were carried out to study the adsorption type and adsorption strength of molecular oxygen on the surface of two samples. As shown in Figure 6b (Detailed experiments can be found in supporting information), there are two types of O₂ adsorbed species present on Cv-g-C₃N₄ compared to only one on g-C₃N₄. The peak at

about 120 °C relates to physical adsorption. This peak from Cv-g-C₃N₄ is much weaker than that from g-C₃N₄. Moreover, the peak at 270 °C, corresponding to the strong chemisorption species of O₂, could be observed for Cv-g-C₃N₄ but not for g-C₃N₄. These observations suggest that, although the amount of molecular oxygen adsorbed on g-C₃N₄ and Cv-g-C₃N₄ is comparable, the adsorption strength of molecular oxygen on Cv-g-C₃N₄ is stronger than that on g-C₃N₄. According to previous reports, the oxygen atom of O₂ has a single electron, making the gas behave as a Lewis acid. Meanwhile, the N atom of amino group around carbon vacancy acts as a Lewis base. These behaviors indicate that O₂ can interact with the N atom of amino group via Lewis acid–base interactions. Therefore, the chemisorption of O₂ over Cv-g-C₃N₄ involves the O atom of O₂ bonding with the N atom of amino group around the carbon vacancy. The stronger the adsorption is, the easier the electrons transfer [34].

In order to explore the correlation between adsorption and electron transfer directly, photocurrent decay measurements were conducted. Under Ar atmosphere, the photocurrent generated on both g-C₃N₄ and Cv-g-C₃N₄ electrode is stabilized with irradiation time during the entire irradiation period (Figure 7a). However, the photocurrent of both g-C₃N₄ and Cv-g-C₃N₄ gradually decay under O₂ atmosphere (Figure 7b). Moreover, the photocurrent decay of g-C₃N₄ is much slower than that of Cv-g-C₃N₄. Since photocurrent decay mainly occurs due to the competition between O₂ and ITO glass for trapped electrons [34], it is concluded that carbon vacancies help the photogenerated electrons to transfer from g-C₃N₄ to the adsorbed O₂.

Chemical adsorption sites are often regarded as reaction centers capable of activating adsorbate [33, 34]. Activation generally refers to the process whereby adsorbate is excited for a subsequent reaction. Therefore, it will be easier to reduce molecular oxygen on Cv-g-C₃N₄ than on g-C₃N₄. To test this hypothesis, linear sweep voltammetry (LSV) was carried out to investigate the reduction of oxygen. Figure 7c shows the ORR catalytic performance for g-C₃N₄ and Cv-g-C₃N₄ under the LSV test. Compare with the LSV curve of g-C₃N₄, cathodic current is enhanced greatly on Cv-g-C₃N₄. This observation proves that carbon vacancies make the molecular oxygen reduction on Cv-g-C₃N₄ easier than that on g-C₃N₄ (Figure 7d).

Hydrogen peroxide might be generated through either a sequential two-step single-electron indirect reduction ($O_2 \rightarrow \cdot O_2^- \rightarrow H_2O_2$) or an one-step two-electron direct reduction ($O_2 \rightarrow H_2O_2$) route (Figure 8a). To clarify the mechanisms of photocatalytic H₂O₂ production on g-C₃N₄ and Cv-g-C₃N₄, DMPO spin-trapping ESR technique was employed to measure the $\cdot O_2^-$ in photocatalysis (Figure 8b). Four characteristic peaks of DMPO- $\cdot O_2^-$ are clearly observed in methanolic suspensions of g-C₃N₄, while no peak could be found in methanolic suspension of Cv-g-C₃N₄. The significant difference in DMPO- $\cdot O_2^-$ signals strongly implies that carbon vacancies change the transfer pathway of photoelectrons. Although Cv-g-C₃N₄ could not produce $\cdot O_2^-$, it could generate H₂O₂ directly under the visible light irradiation. Based on these observations, we speculate that H₂O₂ in g-C₃N₄ suspension is achieved through a two-step single-electron indirect reduction pathway ($e^- \rightarrow \cdot O_2^- \rightarrow H_2O_2$); while in Cv-g-C₃N₄ suspension, it is achieved through one-step two-electron direct

reduction pathway ($e^- \rightarrow H_2O_2$). To confirm this speculation, active species trapping experiments were further carried out. As shown in Figures 9a and 9b, the addition of p-benzoquinone (PBQ, 1 mM, $\cdot O_2^-$ scavenger) does not change the H_2O_2 generation on Cv-g- C_3N_4 while it could actually depress the H_2O_2 generation on g- C_3N_4 . This unambiguously proves that carbon vacancies change the H_2O_2 generation pathway over g- C_3N_4 under visible light from a two-step single-electron indirect reduction to an one-step two-electron direct reduction.

The one-step two-electron pathway of H_2O_2 production was further confirmed by the rotating disc electrode (RDE) experiment. For pristine g- C_3N_4 , the typical two-step pathway at around -0.5 V and -1.2 V is observed, indicating a successive single-electron reduction (Figure S6, in the supporting information). Interestingly, when g- C_3N_4 is replaced by Cv-g- C_3N_4 , the first reduction plateau vanished. The LSV curves show a single-step plateau, indicating an one-step two-electron direct reduction pathway.

Zhang and his coworkers have investigated the effects of various nitrogen species in ORR process [35]. They observed that electron transfer number depends on the amino nitrogen components in metal-free catalysts. In our system, carbon vacancies are surrounded by many N-dangling bands (unsaturated N atoms). Dangling bonds of N atoms are compensated by adsorbed hydrogen and form many amino groups. The formation of amino group on Cv-g- C_3N_4 is confirmed by FTIR measurements (Figure 10a). Therefore, the one-step two-electron reduction pathway could be attributed to amino groups around carbon vacancies. To clarify this point, it is necessary to remove

amino groups from Cv-g-C₃N₄ and then compare the H₂O₂ production performance before and after deamination. In this work, a simple and common chemical deamination approach was designed to remove the amino groups from Cv-g-C₃N₄ (Detailed experiments can be found in supporting information). As seen from Figure 10b that, after deamination, the absorption band of amino group is significantly decreased. This result suggests that amino groups are effectively removed in deamination approach. Furthermore, H₂O₂ and ·O₂⁻ measurements were carried out to evaluate the contribution of amino group to H₂O₂ production. As shown in Figure 11a, the deamination could greatly inhibit the generation of H₂O₂ in Cv-g-C₃N₄, while the ratio of maximum concentration of hydrogen peroxide after the deamination is only about 19.9% of that before the deamination. Moreover, it is very interesting to notice that deamidated Cv-g-C₃N₄ in methanol dispersion gives stronger ESR signals of DMPO-·O₂⁻ (Figure 11b). However, these generated superoxide radicals could not be produced before deamination, confirming that one-step two-electron direct reduction pathway is attributed to amino groups around carbon vacancies.

The stability of the Cv-g-C₃N₄ during the photocatalytic H₂O₂ production was evaluated by recycling test (Figure S7, in the supporting Information). No significant change in the photocatalytic activity occurs after four cycles, indicating that Cv-g-C₃N₄ is stable during the photocatalytic H₂O₂ production.

4. Conclusions

In summary, we have demonstrated that carbon vacancies could be introduced on the

surface of g-C₃N₄ by simple calcinations with argon gas. The carbon vacancies modified g-C₃N₄ could efficiently reduce atmospheric O₂ to H₂O₂ under visible light, without using any precious metal cocatalysts or organic scavengers. The presence of carbon vacancies could reduce the symmetry of g-C₃N₄ and narrow down its band gap, thus extending the visible light absorption and increasing the excitable electrons. Moreover, carbon vacancies could activate O₂ and change the H₂O₂ generation pathway from a two-step single-electron indirect reduction to a one-step two-electron direct reduction. This study not only provides a new strategy to improve the photocatalytic H₂O₂ production, but also underlines the significance of the correlation between the surface defect structure and the activity of semiconductor photocatalysts.

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Figure Captions

Scheme 1. (a) Schematic of g-C₃N₄; (b) carbon vacancy and amino group in g-C₃N₄.

Figure 1. (a) XRD patterns of g-C₃N₄ and Cv-g-C₃N₄; (b) C/N molar ratio in the g-C₃N₄ and Cv-g-C₃N₄.

Figure 2. (a) high-resolution XPS spectra of C 1s of g-C₃N₄ and Cv-g-C₃N₄; (b) high-resolution XPS spectra of N 1s of g-C₃N₄ and Cv-g-C₃N₄; (c) ESR spectra of g-C₃N₄ and Cv-g-C₃N₄; (d) possible formation mechanism of carbon vacancy.

Figure 3. (a) The concentration of generated H₂O₂ in different g-C₃N₄ systems; (b) The concentration of generated H₂O₂ in different Cv-g-C₃N₄ systems; (c) H₂O₂ production is accomplished by photocatalysis; (d) the concentration of H₂O₂ generated in g-C₃N₄ and Cv-g-C₃N₄ systems.

Figure 4. (a) The photocurrent generated on g-C₃N₄ and Cv-g-C₃N₄; (b) UV-vis diffuse reflectance spectra of g-C₃N₄ and Cv-g-C₃N₄; (c) plots of $(ah\nu)^2$ vs the energy of absorbed light of g-C₃N₄ and Cv-g-C₃N₄; (d) calculated band structure of g-C₃N₄; (e) calculated electron density of g-C₃N₄; (f) calculated electron density of Cv-g-C₃N₄; (g) calculated band structure of g-C₃N₄.

Figure 5. (a) photoluminescence (PL) spectra of g-C₃N₄ and Cv-g-C₃N₄; (b) carbon vacancy could significantly inhibit the recombination of photogenerated carriers.

Figure 6. (a) N₂ adsorption-desorption isotherms of g-C₃N₄ and Cv-g-C₃N₄; (b) TPD spectra of g-C₃N₄ and Cv-g-C₃N₄.

Figure 7. (a) Photocurrent decay measurements were conducted under Ar atmosphere; (b) Photocurrent decay measurements were conducted under O₂ atmosphere; (c) linear

sweep voltammetry (LSV) curves of g-C₃N₄ and Cv-g-C₃N₄; (d) carbon vacancy makes the molecular oxygen reduction on Cv-g-C₃N₄ easier than that on g-C₃N₄.

Figure 8. (a) The possible generation routes of H₂O₂; (b) 5,5-dimethyl-pyrroline N-oxide (DMPO) spin trapping ESR technique to measure ·O₂⁻ generated during the generation of H₂O₂.

Figure 9. (a) The influence of p-benzoquinone (PBQ, 1 mM, ·O₂⁻ scavenger) for the H₂O₂ generation on g-C₃N₄; (b) the influence of p-benzoquinone (PBQ, 1 mM, ·O₂⁻ scavenger) for the H₂O₂ generation on Cv-g-C₃N₄.

Figure 10. (a) FT-IR spectra of g-C₃N₄ and Cv-g-C₃N₄ samples; (b) FT-IR spectra of Cv-g-C₃N₄ before and after the deamination.

Figure 11. (a) The influence of deamination for the H₂O₂ generation on Cv-g-C₃N₄; (b) the influence of deamination for the ·O₂⁻ generation; (c) amino group changed the H₂O₂ generation pathway from single-electron reduction to two-electron reduction.

Figure Captions

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Figure 9. (a) The influence of p-benzoquinone (PBQ, 1 mM, $\cdot\text{O}_2^-$ scavenger) for the H_2O_2 generation on $\text{g-C}_3\text{N}_4$; (b) the influence of p-benzoquinone (PBQ, 1 mM, $\cdot\text{O}_2^-$ scavenger) for the H_2O_2 generation on $\text{Cv-g-C}_3\text{N}_4$.

Figure 10. (a) FT-IR spectra of $\text{g-C}_3\text{N}_4$ and $\text{Cv-g-C}_3\text{N}_4$ samples; (b) FT-IR spectra of $\text{Cv-g-C}_3\text{N}_4$ before and after the deamination.

Figure 11. (a) The influence of deamination for the H_2O_2 generation on $\text{Cv-g-C}_3\text{N}_4$; (b) the influence of deamination for the $\cdot\text{O}_2^-$ generation; (c) amino group changed the H_2O_2 generation pathway from single-electron reduction to two-electron reduction.

TOC Brief: We demonstrated that photocatalytic H_2O_2 production on $\text{g-C}_3\text{N}_4$ could be improved by as much as 14 times in the absence of organic scavenger through a carbon vacancy-based strategy. The presence of carbon vacancies changed the H_2O_2 generation pathway from a two-step single-electron indirect reduction to an one-step two-electron direct reduction.

TOC Art Figure