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The photocatalytic $^{\bullet}$OH production activity of g-C_3N_4 improved by the introduction of NO

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ABSTRACT

The efficiency of photocatalytic pollutant removal largely depends on the ability of the photocatalytic system to produce hydroxyl radicals ($^{\bullet}$OH). However, the capability of photocatalyst to produce $^{\bullet}$OH is not strong at present. Advancing the capacity of photocatalytic system to produce $^{\bullet}$OH has always been a tough problem and challenge in the field of environmental science. In this research, it was found that introducing nitric oxide (NO) into the graphitic carbon nitride (g-C_3N_4) photocatalytic system could memorably enhance the ability of producing $^{\bullet}$OH group. This study provides a new idea for improving the capacity of photocatalytic $^{\bullet}$OH production.

Active oxygen species (AOS) are effective green oxygenants for environmental-pollution control. AOS have many types, including superoxide radical ($^{\bullet}O_2^-$), hydrogen peroxide (H_2O_2), and hydroxyl radical ($^{\bullet}$OH) [1–8]. To remove environmental pollution, many methods such as electrochemistry, Fenton reaction, and photocatalysis have been developed to produce $^{\bullet}$OH. Electrochemistry method requires substantial electric energy, and Fenton reaction requires extra H_2O_2 [9–11]. Moreover, these two methods may harm the environment. For example, electrochemistry method may release metal ions and harmful gas, and Fenton reaction may produce iron sludge [12,13]. Photocatalytic technology has sufficient energy source (sunlight) and is environmentally friendly [14]. Meanwhile, photocatalytic technology could produce $^{\bullet}$OH under mild conditions. Thus, photocatalytic $^{\bullet}$OH production has the potential for practical applications [15]. However, the $^{\bullet}$OH production efficiencies of photocatalysts remain at a low level because the recombination rate of photogenerated electron and hole is relatively high. Many methods have been developed to solve this problem. For example, the photocatalyst can be modified by various modification methods (*e.g.*, doping, heterojunction formation, and noble-metal deposition) to suppress the recombination of photogenerated electron and hole, or a sacrificial agent may be added to improve the redox half-reaction [12,16–18]. However, photocatalyst modification is a complicated process [19–21], and adding a sacrificial agent may cause environmental pollution. For example, Xiao's team attempted to improve the photocatalyst with ozone (O_3) as a sacrificial agent [5,7,8,15]. O_3 is known to be harmful to human health and the environment because of the lung damage it inflicts. Thus, developing a new method of improving the photocatalytic production of $^{\bullet}$OH is very important.

Nitrogen oxide (NO_x), a major pollutant in the atmosphere, originates from the combustion of fossil fuel in boilers and motor vehicles (exhaust gas) [22]. The N atom of NO has an unpaired electron, so NO possesses strong reducing property (Fig. S1 in Supporting information) [23,24]. Therefore, we believe that NO can be used as a sacrificial agent for photogenerated hole, meaning that photocatalytic AOS production can be improved by NO bubbling. Meanwhile, NO can be oxidized to NO_2 by using a photogenerated hole, and then the generated NO_2 is absorbed by water (became NO_3^-) [25]. In this case, the NO in the exhaust gas can be used and further removed. To verify the above analysis, the visible-light photocatalyst g-C_3N_4 was used to produce $^{\bullet}$OH through NO bubbling. We found that the introduction of NO could improve the photocatalytic $^{\bullet}$OH generation activity of g-C_3N_4. In this process, the structure and activity of g-C_3N_4 are very stable [22,26]. The improvement mechanism was studied systematically. The details can be found as below.

We detected the generation of active oxygen species (AOS) with or without NO gas (500 ppb, diluted by air stream) bubbling.

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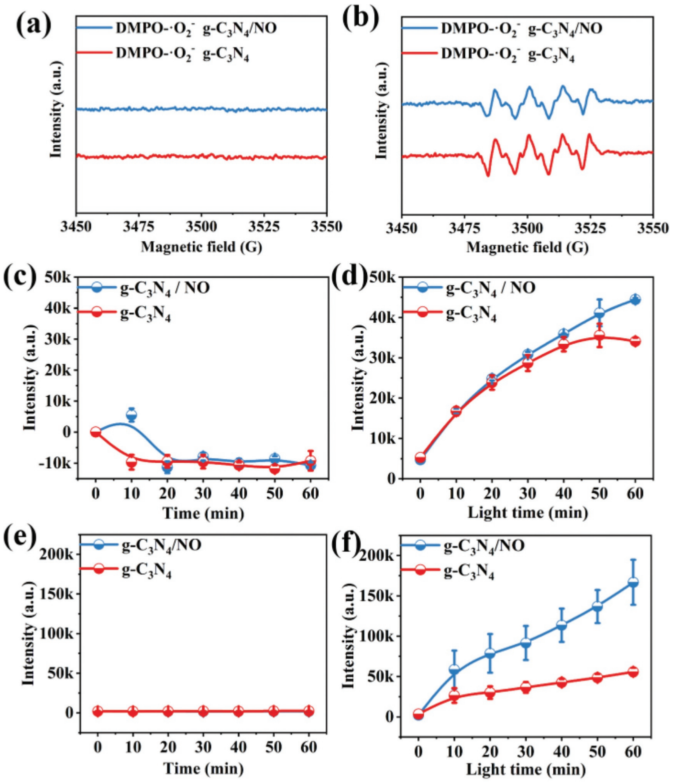

Fig. 1. (a) DMPO EPR spin-trapping for ${}^{\bullet}O_2^-$ radicals in dark and (b) under visible light illumination ($\lambda > 420$ nm). (c) Fluorescence test of H_2O_2 production in dark and (d) under light irradiation. (e) Fluorescence test of ${}^{\bullet}OH$ production in dark and (f) under light.

Figs. 1a and b show the EPR signal of ${}^{\bullet}O_2^-$. No clear ${}^{\bullet}O_2^-$ signal was observed in darkness. After the light was turned on, ${}^{\bullet}O_2^-$ can be produced in g-C_3N_4 suspension and g-C_3N_4/NO suspension. However, the bubbling of NO did not significantly affect the intensity of generated ${}^{\bullet}O_2^-$. Figs. 1c and d display the generated H_2O_2 under dark and light-irradiation conditions. H_2O_2 can be produced only under light irradiation in the presence of g-C_3N_4 sample. Similarly, with ${}^{\bullet}O_2^-$, NO bubbling did not significantly affect the intensity of generated H_2O_2. As for ${}^{\bullet}OH$, the effect of NO bubbling was highly significant. Fig. 1e shows that ${}^{\bullet}OH$ was undetected in darkness. After the light was turned on, ${}^{\bullet}OH$ can be produced in g-C_3N_4 suspension and g-C_3N_4/NO suspension (Fig. 1f). Surprisingly, the concentration of generated ${}^{\bullet}OH$ in the g-C_3N_4/NO system was nearly twice as high as that in the g-C_3N_4 suspension. Therefore, NO bubbling helped g-C_3N_4 produce more ${}^{\bullet}OH$ under light irradiation (see Supporting information for details).

To understand the mechanism of NO in inducing g-C_3N_4 to produce more ${}^{\bullet}OH$ under light irradiation, we analyzed the converted products of NO during photocatalysis. In the photocatalytic reaction of NO in the gas-solid phase (Eq. 1 and Fig. 2a), most reaction products were NO_2 [3]. However, the NO_2 signal disappeared when the hole scavenger was added, suggesting that NO can be oxidized to NO_2 by hole. This can be further proved by the hole capture experiment (Fig. S3a in Supporting information). Interestingly, NO_2 cannot be detected when the photocatalytic reaction proceeded in the liquid-solid phase (Fig. 2b). This result suggested that the generated NO_2 decomposed (Eq. 2) or absorbed (Eq. 3) in water. If NO_2 decomposes, the generated oxygen free radicals (${}^{\bullet}O$) would react with water to produce ${}^{\bullet}OH$ [27]. To verify this mechanism, NO_x was bubbled in water (without the presence of photocatalysts) under light irradiation ($\lambda = 420$ nm). The results are displayed in Fig. 2c. ${}^{\bullet}OH$ can be detected in the NO_2-bubbled water but not in the NO-bubbled one. These results confirmed Eqs. 2 and 4. Accordingly, NO_2 photolysis can contribute to the increase in ${}^{\bullet}OH$ yield. Fig. 2d shows that NO_2 photolysis (70 ppb) could produce only 3.33% of the ${}^{\bullet}OH$ increment. Thus, other reasons for the ${}^{\bullet}OH$ increment besides NO_2 photolysis must exist. The photolysis-mechanism diagram of NO_2 is shown in Fig. 2e. Extra NO_2 would be absorbed by water and became NO_3^-. Besides, the conversion rate of NO to NO_3^- is 47%. (Fig. S4 in Supporting information).

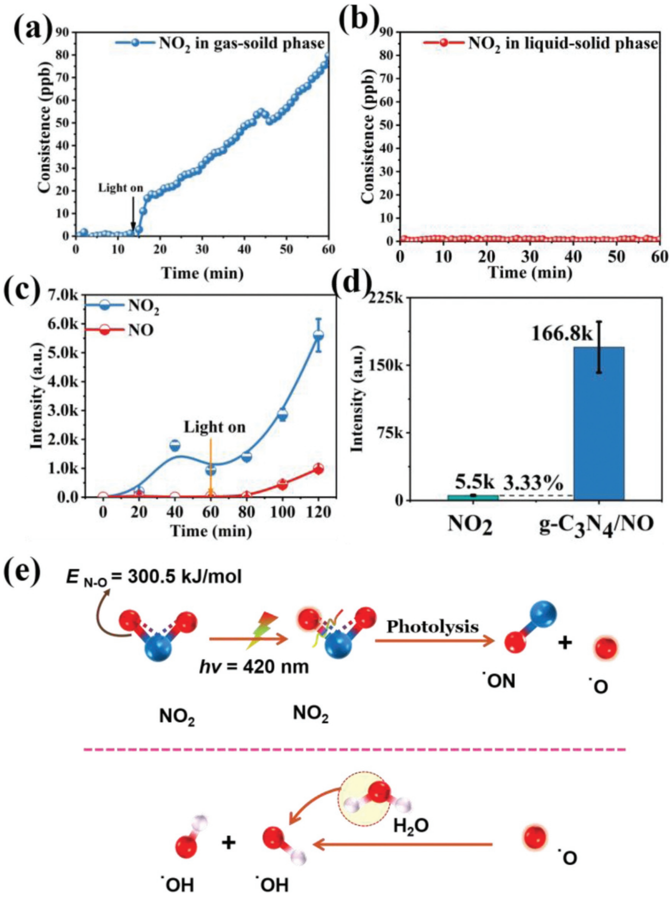

Fig. 2. (a) NO_2 concentration in the gas-solid phase reaction and (b) NO_2 concentration in the liquid-solid phase reaction. (c) The amount of hydroxyl radicals produced over time. (d) Histogram comparison of the ${}^{\bullet}OH$ yield of NO_2 to the total ${}^{\bullet}OH$ yield. (e) Schematic diagram of NO_2 photolysis to produce hydroxyl.

$$NO + O_2 + h\nu \rightarrow NO_2 \tag{1}$$

$$NO_2 + h\nu \rightarrow NO + {}^{\bullet}O \tag{2}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \tag{3}$$

$$O + H_2O \rightarrow 2{}^{\bullet}OH \tag{4}$$

Since NO could consume hole and inhibit the recombination of photogenerated carriers. Interestingly, NO bubbling obviously improved the photocurrent signal of g-C_3N_4 under the same condition. And the further confirmation could be found in Fig. S3b (Supporting information). This phenomenon ensured that NO could inhibit the recombination of photogenerated carriers. Consequently, the valence band of g-C_3N_4 can provide more excitation electrons for the higher fluorescent signal (Fig. S3c in Supporting information). For a visual expression, the reaction-mechanism diagram is shown in Fig. S3d (Supporting information). The more

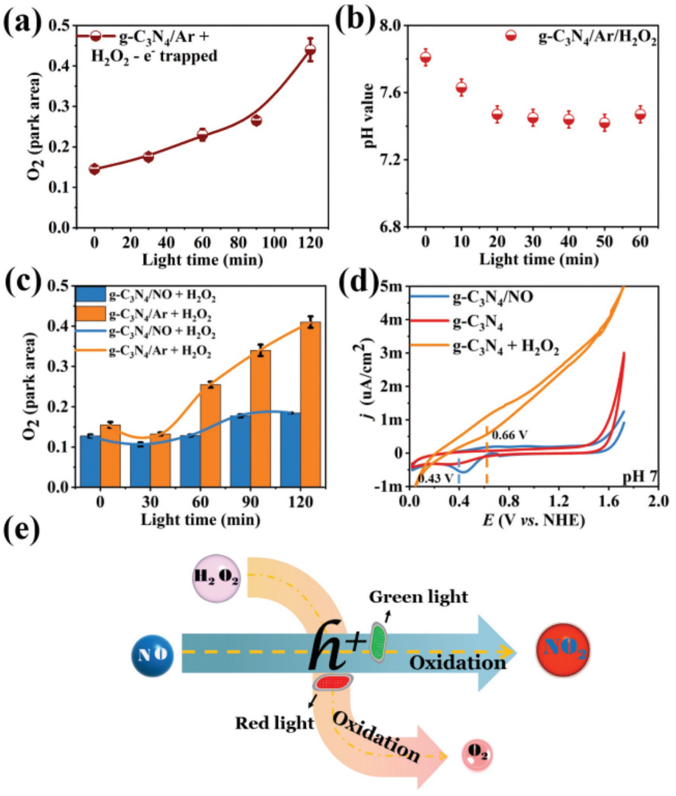

Fig. 3. (a) O_2 production under argon atmosphere plus hydrogen peroxide $AgNO_3$ as capture electron condition. (b) Change of pH value of hydrogen peroxide added in argon atmosphere. (c) O_2 production of CN and H_2O_2 under NO atmosphere (blue) and argon atmosphere (orange). (d) Cyclic voltammetry curves of the g-C_3N_4 in NO ambience and pure g-C_3N_4 and g-C_3N_4 with H_2O_2. (e) Schematic diagram of the H_2O_2 decomposition with the presence of NO.

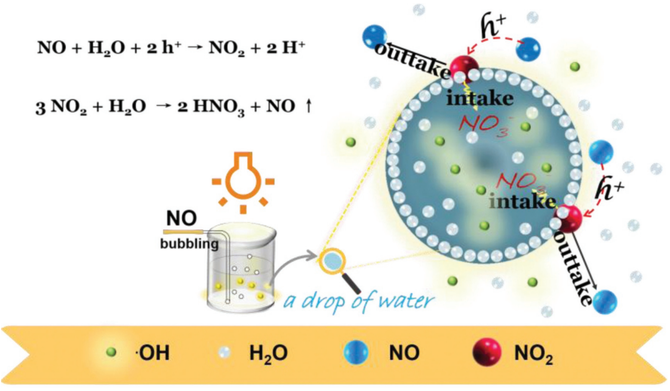

Fig. 4. Conversion process of NO_x in the photocatalytic reaction: Schematic diagram of the dissolution of NO_x in reaction system.

consumption of photogenerated hole could be created, the more adsorbed O_2 molecules could be reduced.

Based on the redox potential of H_2O_2/O_2 (0.659 V) [28] and the valence-band potential of g-C_3N_4 (1.4 eV) [29], H_2O_2 may be oxidized to O_2 by the photogenerated holes (Eq. 5). This speculation can be proven by H_2O_2 catalytic-decomposition experiment. (Figs. 3a and b and S2.3 in Supporting information). To investigate the effect of NO on H_2O_2 catalytic decomposition, NO was introduced in the above experiments. Fig. 3c shows that the amount of produced O_2 significantly decreased after NO introduction, indicating that NO can inhibit the oxidation reaction of H_2O_2 caused by photogenerated holes consumed. Meanwhile, the redox potential of NO/NO_2 (0.428 V) was smaller than that of H_2O_2/O_2 (0.659 V), which can be proven by the cyclic voltammetry curve in Fig. 3d. In this case, H_2O_2 can be protected by NO from the oxidation of photogenerated holes, just like the drawing in Fig. 3e. Therefore, more H_2O_2 can be used to produce $^{\bullet}OH$ (Eq. 6).

$$H_2O_2 + 2h_{vb}{}^{+} \rightarrow O_2 + 2H^{+} \quad (5)$$

$$H_2O_2 + e^{-} \rightarrow {}^{\bullet}OH + OH^{-} \quad (6)$$

After $^{\bullet}OH$ generation, it diffused in water. However, NO is insoluble in water, so NO cannot consume the $^{\bullet}OH$ generated in our system. When NO was oxidized to NO_2 by photogenerated holes, NO_2 was adsorbed by water and became $NO_3{}^{-}$ and NO. However, $NO_3{}^{-}$ cannot be further oxidized, so it cannot consume the generated $^{\bullet}OH$. In this case, NO_2 did not consume the generated $^{\bullet}OH$ in our system. Based on the above experimental results and discussion, although NO was used as the hole sacrificial agent, and it did not consume $^{\bullet}OH$. For this reason, our system could accumulate more $^{\bullet}OH$ for the degradation of organic pollutants [30] (Fig. S5 and S2.4 in Supporting information). Herein, Fig. 4 can be well matched with this theme.

Stability is an important evaluation indicator for the application value of one technology or sample [31]. Accordingly, cycling experiments were conducted to investigate the stabilities of this technology and g-C_3N_4 sample [32,33]. Fig. S6a (Supporting information) shows that the $^{\bullet}OH$ yield did not decrease after five cycles of use. Meanwhile, the degradation rate of tetracycline performed using our technology was very stable throughout the five cycles of repeat experiments (Fig. S6b in Supporting information). These results suggested that our technology was stable and recyclable. The stability can be further confirmed by the XRD, FT-IR, UV-DRS, and SEM characterizations. A detailed analysis can be found in Figs. S6c, S6d, S7 and S8 (Supporting information).

In conclusion, the introducing NO could significantly enhance the photocatalytic $^{\bullet}OH$ production ability of g-C_3N_4. After a series of mechanism studies, we found that there were four reasons for this improvement: (1) The $^{\bullet}O$ produced by the NO_2 photolysis can react with H_2O to form $^{\bullet}OH$; (2) NO can be used as a hole-capture agent, which makes g-C_3N_4 generate more photo-generated electrons to reduce O_2; (3) H_2O_2 can be protected by NO from being oxidized by holes; (4) $^{\bullet}OH$ cannot be consumed by NO or NO_2. Since NO could enhance the $^{\bullet}OH$ production, NO was introduced in the photocatalytic tetracycline removal process. It was found that NO could enhance the mineralization rate of tetracycline from 59% to 86%. Moreover, the presence of NO in the photocatalytic process does not affect the stability of g-C_3N_4.

Declaration of competing interest

The authors report no declaration of competing interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2021.12.071.

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