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# ZIF-67/CoOOH cocatalyst modified g-C<sub>3</sub>N<sub>4</sub> for promoting photocatalytic deep oxidation of NO



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# ABSTRACT

The removal of nitrogen oxides (NO<sub>x</sub>) by semiconductor photocatalysis is an emerging technology in recent years. However, due to incomplete oxidation, the photocatalytic oxidation of NO<sub>x</sub> is usually accompanied by the generation of toxic intermediate by-products nitrogen dioxide (NO<sub>2</sub>), which causes secondary pollution and seriously limits its practical application. To tackle the issue, ZIF-67/CoOOH (ZIF-CH) cocatalyst was constructed via flexible strongly alkali oxidation treatment to modify g-C<sub>3</sub>N<sub>4</sub>, in which ZIF-67 was selected as a cobalt source of CoOOH. XRD, SEM, TEM and XPS demonstrated the ZIF-CH was successfully synthesized and anchored on CN. UV-vis, PL, EIS, transfer photocurrent response and DFT indicated that the introduction of ZIF-CH enlarged the response range to visible light, favored the separation and transfer of carriers and improved NO/NO2 adsorption ability. Consequently, the optimized ZIF-67/CoOOH/g-C3N4 (ZIF-CH/CN) exhibited a superior NO removal efficiency of 52.5% without any generation of toxic by-product NO<sub>2</sub>, and the cycling tests indicated the high stability of ZIF-CH/CN was obtained. In-suit DRIFTS and ESR were used to investigate the reaction pathway by comparing adsorption energy and detecting the reaction intermediates and products. More importantly, this result reveal that amount of hydroxyl radical (-OH) increased after introducing ZIF-CH cocatalyst, which promotes the deep oxidation of NO. These findings could supply a convenient and effective strategy for the design of a cocatalyst to enhance the photocatalytic oxidation performance of NO and inhibit the production of toxic by-product NO<sub>2</sub>.

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# 1. Introduction

The emission of nitrogen oxides  $(NO_X)$  in atmosphere has been increasing greatly due to the rapid development of industrialization and the huge consumption of fossil fuels [1]. The increased concentration of  $NO_X$  will cause acid rain, photochemical smog and ozone pollution, resulting in immeasurable damages to plants, soil and serious threats to human health [2–5]. Thus, various techniques and methods for  $NO_X$  removal have been explored, such as physical adsorption, selective catalyst reduction and wet scrubbing [2,3]. However, not only high energy is consumed, but also secondary pollution is usually caused through the above methods. Therefore, scientists were committed to develop sustainable and efficient methods for  $NO_X$  removal. Among these methods, semiconductor photocatalysis has attracted much more attention because of its green and sustainable utilization [6-10].

So far, many photocatalysts have been investigated for NO<sub>X</sub> removal, such as TiO<sub>2</sub>, BiOX (X=Cl, Br, I), SrTiO<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, et al. [11–15]. Among them,  $g-C_3N_4$  is attractive in photocatalytic NO<sub>X</sub> removal because of its appropriate visible light absorption capacity and simple preparation method [16–18]. However, there are still some problems need to be solved over g-C<sub>3</sub>N<sub>4</sub> for obtaining enhanced photocatalytic NO<sub>x</sub> removal efficiency. Firstly, active species such as superoxide radical  $(\cdot O_2^{-})$  and hydrogen peroxide  $(H_2O_2)$  could be easily generated under visible light on the surface of g-C<sub>3</sub>N<sub>4</sub>. But it's difficult to produce the stronger oxidizing species hydroxyl radical (·OH) [19], resulting in the massive production of nitrogen dioxide  $(NO_2)$ . As well known,  $NO_2$  is much more harmful to human than NO. Even ppb level of NO<sub>2</sub> can cause a variety of respiratory disorders (emphysema and bronchitis) and even syncope and shock [6,10,19,20]. In addition, the adsorption and deep oxidation capacity of g-C<sub>3</sub>N<sub>4</sub> to NO<sub>2</sub> is not desired, which leads to the high content of

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 $NO_2$  in the final products [21]. Considering the above problems, it is still a challenge to improve the photocatalytic  $NO_X$  removal performance of g-C<sub>3</sub>N<sub>4</sub>-based photocatalyst.

Up to now, many tactics have been applied to improve the photocatalytic oxidation capacity of g-C<sub>3</sub>N<sub>4</sub> by doping g-C<sub>3</sub>N<sub>4</sub> with metals (Au@CN) [22] or nonmetals (C<sub>v</sub>-gCN) [23], coupling with other semiconductors to form heterojunction (Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>,  $SnO_2/g-C_3N_4$  [20,24], and cocatalyst modification. It's worth noting that cocatalyst modification has attracted much attention because it can combine the advantages of both cocatalyst and photocatalyst. Usually, the photocatalytic performance of semiconductors could be improved by loading the noble metals co-catalyst such as Pt [25], Pd [26], Ag [27], et al. However, the practical applications of noble metals are limited because of the scarce reserves and high prices. To solve this problem, the noble-metal-free co-catalysts such as  $Ti_3C_2$ [17], Ni-based [28,29] co-catalysts and so on have been studied. Recently, Zhang, et al. [28] prepared the layered material  $g-C_3N_4/\alpha$ -Ni(OH)<sub>2</sub>. The g-C<sub>3</sub>N<sub>4</sub>/ $\alpha$ -Ni(OH)<sub>2</sub> exhibited outstanding NO removal rate and inhibited the generation of NO<sub>2</sub>. Therefore, transition metal hydroxides may well inhibit the production of NO<sub>2</sub>. As we all know, the CoOOH has been widely used in electrochemistry because of its rapid transmission of electrons, which may improve the efficiency of electron-hole separation. However, there is still a problem for CoOOH to overcome, which is that CoOOH could not provide enough active sites for photocatalytic reactions due to the small specific surface area [30]. Recently, metal-organic frameworks (MOFs) have attracted significant attention for photocatalysis because of their well-defined crystalline structure and high surface area [31,32]. Meanwhile, previous studies suggest that Zeolitic Imidazolate Framework-67(ZIF-67) has a uniform distribution of cobalt ions and controllable structure. Hence, ZIF-67 could be used as a precursor to increase the specific surface area of CoOOH [33].

In this study, ZIF-67 was selected as a cobalt source to construct a monolithic co-catalyst ZIF-67/CoOOH (ZIF-CH) via strong alkali oxidation treatment. Then ZIF-CH were anchored on the surface of g- $C_3N_4$  via facile magnetic stirring. It can be found that ZIF-CH could not only inhibit the recombination of photo-generated carriers, but also promotes the production of the stronger oxidizing species-OH. Benefiting from these, NO could be deeply oxidized and the formation of NO<sub>2</sub> could be inhibited over ZIF-CH/g-C<sub>3</sub>N<sub>4</sub> composites, demonstrating its great potential for air purification. This finding supplies an effective strategy for the better design of MOFs derived photocatalysts in the area of deep NO oxidation by photocatalysis.

#### 2. Experimentation

#### 2.1. Preparation

# 2.1.1. Synthesis of $g-C_3N_4$

 $g-C_3N_4$  was synthesized by the thermolysis of 15 g urea precursor [28]. Urea was positioned in an aluminum oxide crucible with a cover. Then the crucible was heated to 550 °C and held for 1 h. Finally, the light-yellow  $g-C_3N_4$  powder was obtained.

#### 2.1.2. Synthesis of ZIF-67

As reported earlier [34], 5.820 g of  $Co(NO_3)_2$  and 6.568 g of 2-Methylimidazole were melted in 500 mL methanol, and the obtained mixed solution was aged for 24 h. The violet product was collected by centrifugation and then dried at 60 °C.

#### 2.1.3. Synthesis of ZIF-67/CoOOH

200 mg of ZIF-67 was added in 40 mL deionized water, then 600 mg NaOH and 2 mL NaClO (Active content  $\geq$ 5.5%) were dispersed into the above solution and stirred. The dark-purple sample was washed and collected by centrifuged, then dried at 60 °C to obtain ZIF-67/CoOOH (ZIF-CH).

2.1.4. Synthesis of ZIF-CH/g-C<sub>3</sub> $N_4$ 

ZIF-CH/g-C<sub>3</sub>N<sub>4</sub> photocatalysts were prepared by magnetic stirring at room temperature. ZIF-CH and g-C<sub>3</sub>N<sub>4</sub> were dissolved in 40 mL ethanol at a certain mass ratio and then stirred for 3 h. The mass ratios of ZIF-CH to g-C<sub>3</sub>N<sub>4</sub> (CN) were kept in 10%, 20%, 30% and 40%, the obtain samples were respectively marked as ZIF-CH(10%)/ CN, ZIF-CH(20%)/CN, ZIF-CH(30%)/CN and ZIF-CH(40%)/CN.

#### 2.2. Characterization

Powder X-ray diffraction (XRD) was carried out to study the phase structure of the catalyst in PANalytical X'pert diffractometer using Cu K $\alpha$  radiation. The microstructure of the samples was studied by scanning electron microscope (SEM) and transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS Thermo Scientific Escalab 250Xi spectrometer) was used to study the chemical composition and state of the samples. UV–vis spectroscopy (Shimadzu 2600 spectrophotometer) utilizing barium sulfate (BaSO<sub>4</sub>) as the reflectance standard sample and photoluminescence (PL Hitachi F-7000 fluorescence spectrometer) using the light source of MVL-210 were recorded to test optical properties of samples. Electron spin resonance (ESR) spectroscopy was tested to research the main active species on a JES-FA200 spectrometer.

# 3. Results and discussion

#### 3.1. Crystal structure

To investigate the crystal structures and phase compositions of the CN, ZIF-CH, and different mass ratios of ZIF-CH/CN nanocomposites, XRD was tested as shown in Fig. 1. The two peaks at 13.1° and 27.4° were attributed to the (100) and (002) planes of CN [16]. As for ZIF-67, all the diffraction peaks was consisted with previous study [34,35]. Compared to ZIF-67, the three main characteristic peaks at 20.2°, 36.9°, 38.8° were corresponded to (003), (101), (012) of CoOOH (JCPDS 07-0169) in ZIF-CH [30], illustrating that ZIF-CH monolithic co-catalyst was successfully prepared. For ZIF-CH/CN nanocomposites, the diffraction peaks of both ZIF-CH and CN were clearly detected, which indicated that ZIF-CH/CN nanocomposites were successfully fabricated.



Fig. 1. XRD of g-C<sub>3</sub>N<sub>4</sub>, ZIF-CH, and different ratio of ZIF-CH/CN.



Fig. 2. The NO removal of different samples (a); NO<sub>2</sub> generation of different samples (b); The NO removal ratio (c) and NO<sub>2</sub> generation (d) of ZIF-CH(20%)/CN in recycle experiment.

#### 3.2. Photocatalytic NO oxidation performances

To study the effect of ZIF-CH on the photocatalytic activity. ZIF-CH/CN was applied for photocatalytic oxidation of NO. Meanwhile, the generation rate of toxic by-product NO<sub>2</sub> was recorded during the NO oxidation reaction. As depicted in Fig. 2(a) and (b), CN showed NO oxidation ratio of 34.4%, and the generation rate of NO<sub>2</sub> reached to 15.5% after visible light irradiation for 30 min. While ZIF-CH showed little activity for photocatalytic NO oxidation. Meanwhile, as shown in Fig. S1, the concentration of NO did not obviously decrease over CoOOH, which illustrates that ZIF-CH is mainly used as a cocatalyst. And the photocatalytic stability of ZIF-67(20%)/CN obviously increased compared with CH/CN (Fig. S2), indicating ZIF-67 could improve the stability of photocatalytic NO oxidation. Obviously, the photocatalytic performances of ZIF-CH/CN nanocomposites were better than pure CN and ZIF-CH. As shown in Fig. 2(a), the oxidation ratio of NO first increased and then decreased with the increased mass ratio of ZIF-CH. Among these sample, ZIF-CH(20%)/ CN exhibited the highest NO oxidation ratio of 52.5%. As shown in Fig. 2(a), the photocatalyst activity of ZIF-67(20%)/CN and ZIF-CH (20%)/CN were investigated in order to reveal the effect of ZIF-67 cocatalyst and ZIF-CH co-catalyst. Compared with ZIF-67(20%)/CN, the performance of ZIF-CH(20%)/CN was increased by 12.6%. Remarkably, no NO<sub>2</sub> was tested during the NO photocatalytic oxidation over ZIF-CH/CN in Fig. 2(b). Further cyclic illumination test was performed on ZIF-CH(20%)/CN, as show in Fig. 2(c) and (d). After four recycles, the NO oxidation ratio of ZIF-CH(20%)/CN could be kept at around 47% without any NO<sub>2</sub> generation, which prove the striking stability over ZIF-CH(20%)/CN in combination with the XRD of samples after reaction (Fig. S3). These results revealed that the introduction of CoOOH on the surface ZIF-67 co-catalyst not only effectively improved the NO oxidation capability of CN, but also completely inhibited the generation of NO<sub>2</sub>.

#### 3.3. Morphology and surface compositions

The microstructure of ZIF-67, ZIF-CH, ZIF-CH(20%)/CN were tested by SEM and TEM. As displayed in Fig. 3(a) and (d), ZIF-67 was well-dispersed dodecahedron structure with a size of roughly 500 nm and a fairly smooth surface. After strong alkali oxidation treatment, the original morphology of ZIF-67 was not changed drastically except new nanorods microstructure emerged as shown in Fig. 3(c). Specifically, the lattice spacing observed in Fig. 3(e) was 0.438 nm, corresponding to the (003) crystal plane of CoOOH [36]. It could be illustrated that CoOOH and ZIF-67 were successfully combined to form a ZIF-CH cocatalyst. From the observation of Fig. 3(c)and (f), it was clearly that the ZIF-CH was successfully anchored on CN, which may increase the active sites of ZIF-CH(20%)/CN. It is proving that ZIF-CH/CN nanocomposites were prepared, which was consistent with XRD results. In addition, the nitrogen adsorption isotherms and BJH (Barrett-Joyner-Halenda) pore diameter distribution were measured to obtain the specific surface area (SSA) of the different sample (Fig. S4). The SSA of ZIF-CH(20%)/CN (241.9 m<sup>2</sup>/ g) was 4.1 times than that of CN (58.4  $m^2/g)\!$  , which illustrated that the combination of ZIF-CH cocatalyst could obviously increase SSA



Fig. 3. SEM and TEM images of (a), (d) ZIF-67 and (b), (e) ZIF-CH and (c), (f) ZIF-CH (20%)/CN.

and provide more active sites for the photocatalytic oxidation reaction.

XPS spectra of ZIF-67, ZIF-CH and ZIF-CH(20%)/CN were measured to study the surface chemical compositions and chemical status in Fig. 4. For ZIF-67, there were two peaks located at 781.4 eV and 796.97 eV corresponding to Co  $2p_{3/2}$  and  $Co2p_{1/2}$ , as well as the other two peaks at 802.45 and 786.6 eV were relevant to their satellite peaks [37], respectively. Two emergent peaks appeared at



Fig. 4. XPS of ZIF-67, ZIF-CH and ZIF-CH(20%)/CN: (a) Co 2p; (b) C 1s; (c) N 1s; (d) O 1s.

779.9 eV and 795.1 eV, which was assign to Co<sup>3+</sup> of CoOOH in ZIF-CH [30]. The disappearance of the peak at 795.1 eV in ZIF-CH(20%)/CN might be due to the low anchoring amount of ZIF-CH. Moreover, the relative content of Co was determined by XPS and the results were shown in Table S1. The actual amount of Co in ZIF-CH sample is 6.7% and the content in ZIF-CH(20%)/CN was 1.2%. For C 1s spectra, two peaks at 285.8 eV and 284.8 eV were associated with C-N and C-C/ C=C in ZIF-CH, respectively [33]. The positions of C 1s of ZIF-CH were in line with that of ZIF-67, indicating that the CoOOH only grow on the framework of ZIF-67 without changing its skeleton. And for ZIF-CH(20%)/CN, the peak of 288.04 eV was attributed to carbon of sp<sup>2</sup> hybridization (C-N<sup>=</sup>C) in CN [16], while the other peaks did not change, indicating that ZIF-CH/CN was successfully combined. Moreover, for the XPS spectra of N 1s, the two peaks at 398.8 eV and 400.1 eV in ZIF-67 and ZIF-CH were attributed to N-C<sub>3</sub> and H-N-C<sub>2</sub> peaks. For the N 1s of ZIF-CH(20%)/CN, the peak at 398.0 eV was resulted in the sp<sup>2</sup> hybrid nitrogen (C-N<sup>=</sup>C) [25,38]. Compared with N-C<sub>3</sub> and H-N-C<sub>2</sub> bond peak of ZIF-CH and ZIF-67, the corresponding peak shifted to 399.4 eV and 400.4 eV respectively [39], which also showed that there was a strong interaction between ZIF-CH and CN. For O 1s spectra, the only one peak located at 531.3 eV could be corresponding to Co-OH in ZIF-67 [40]. After the in-situ growing of CoOOH, a new characteristic peak was observed at 529.3 eV, demonstrated the existence of Co-O in CoOOH and the successful preparation of ZIF-CH [41].

### 3.4. Optical and electrochemical properties

UV-Vis absorption spectrum was used to evaluate the light-absorption ability of the photocatalyst. The UV-vis absorption spectra of CN, ZIF-67, ZIF-CH and ZIF-CH(20%)/CN were shown in Fig. 5(a). A strong absorption peak at the 580 nm were observed in ZIF-CH and ZIF-67, demonstrated that alkali oxidation treatment had no affect on the light absorption properties of ZIF-67. Compared with  $g-C_3N_4$ , an weak absorption peak was also appeared at 580 nm in ZIF-CH (20%)/CN, which enhanced its visible light response. The photoluminescence (PL) spectrum is an effective method to investigate the separation of the electron-hole pairs. The PL spectra of g-C<sub>3</sub>N<sub>4</sub> and ZIF-67(20%)/CN ZIF-CH(20%)/CN were presented in Fig. 5(b). CN has higher electron-hole recombination due to its higher  $\pi$  bond conjugated interface [21], but the fluorescence intensities of the composites decreased obviously after doping ZIF-67. The ZIF-CH(20%)/CN possessed the weakest fluorescence intensities, proved that the CoOOH further increased interfacial charge transfer and inhibited electron-hole recombination. Meanwhile, transient photocurrent response (TPC) and electrochemical impedance spectra (EIS) also were applied to explore photogenerated carrier transfers performance. As shown in Fig. 5(c), it was apparent that CN has lowest photocurrent density (less than 0.03 uA/cm<sup>2</sup>), which was attributed to the quick recombination of photo-generated electron-hole pairs. But the photocurrent density significantly increased to 0.15 uA/cm<sup>2</sup>



Fig. 5. UV-vis absorption (a) PL of different samples (b), photocurrent transient responses (c) and (d) EIS spectra of the catalysts.



Fig. 6. Adsorption energy of NO and NO<sub>2</sub> over both CoOOH and g-C<sub>3</sub>N<sub>4</sub>.

after doping ZIF-67. ZIF-CH(20%)/CN shows the strongest photocurrent intensity (0.3 uA/cm<sup>2</sup>) that is twice as strong as ZIF-67(20%)/ CN, indicating the recombination of carriers was lagged. The efficient separation of electron-hole pairs was further confirmed with EIS shown in Fig. 6(d). Compared with pristine CN, the arc radius of the ZIF-67(20%)/CN, ZIF-CH(20%)/CN composites obviously were shortened, and ZIF-CH(20%)/CN possessed the smallest arc radius in the EIS plots both in light and dark conditions. The above result suggested that a rapidly interfacial charge transfer occurred and an effectively separation of photogenerated charge carrier after the comprise of ZIF-CH/CN, which was consistent with the above PL results. Undoubtedly, ZIF-CH was an effective co-catalyst which significantly inhibited the recombination of electrons and holes to produce more photo-generated carriers.

#### 3.5. The process of photocatalytic NO oxidation

In the general NO oxidation process, NO was firstly adsorbed on the surface of catalysts, and then oxidized to NO<sub>2</sub> and finally oxidized to nitrate by free radicals [25]. Therefore, adsorption of NO and NO<sub>2</sub> was the key step to ensure the final products were non-toxic nitrate. Here, DFT calculation was employed to investigate the adsorption of NO and NO<sub>2</sub> over CoOOH and g-C<sub>3</sub>N<sub>4</sub>. Based on the XRD and TEM characterization, the (003) surface was mainly exposed over CoOOH. Hence, the atomic structure of CoOOH (003) surface was built as shown in Fig. S5. Calculation results showed that both NO and NO<sub>2</sub> were more easily adsorbed on CoOOH than  $g-C_3N_4$ , because of the more negative adsorption energy over CoOOH (-2.02 and -3.18 eV) than that of  $\text{g-C}_3\text{N}_4$  (-1.46 and -1.64 eV) in Fig. 6. Importantly, the adsorption of NO<sub>2</sub> was one of the key steps to inhibit the generation of NO<sub>2</sub>. The adsorption energy of NO<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> is obviously lower than that of CoOOH, indicating that NO<sub>2</sub> is easier to desorption from g-C<sub>3</sub>N<sub>4</sub> surface and result in a toxic NO<sub>2</sub> byproduction. Conversely, the high adsorption energy of NO<sub>2</sub> on the CoOOH surface was beneficial for NO<sub>2</sub> further oxidation to nitrate.

To study the intermediates and products in the photocatalytic NO process, in situ DRIFTS was carried out (Fig. 7). As shown in Fig. 7(a), the absorb peak of NO ( $1089 \text{ cm}^{-1}$ ) were obtained meaning physical absorption rather than chemical absorption was realized [24]. The adsorption bands at  $1048 \text{ cm}^{-1}$  was ascribed to N<sub>2</sub>O<sub>2</sub>, which

illustrated that NO adsorbed on ZIF-CH(20%)/CN could combine together. According to previous research, the N<sub>2</sub>O<sub>2</sub> is easily oxidized to NO<sub>2</sub> in the air. But no characteristic peak of NO<sub>2</sub> was observed. Besides, the adsorption peak of N<sub>2</sub>O<sub>4</sub> was observed at 893 cm<sup>-1</sup>, which demonstrated that the NO<sub>2</sub> could rapidly transform into N<sub>2</sub>O<sub>4</sub>. Meantime, the adsorption bands of NO<sub>3</sub><sup>-</sup> appeared at 994 cm<sup>-1</sup>, which illustrate that a slowly NO removal process could be conducted under dark condition [24]. After reaching the adsorption equilibrium, visible light was exposed to measure the FTIR spectra of ZIF-CH(20%)/CN photocatalysts for NO removal dynamically (Fig. 7b). Noticeably, the adsorption peak of NO (1089 cm<sup>-1</sup>) declined and the adsorption peak of NO<sub>3</sub><sup>-</sup> (994 cm<sup>-1</sup>) increased with the increasing visible-light irradiation time [17]. Similarly, no adsorption peak of NO<sub>2</sub> was observed. These results indicate that ZIF-CH(20%)/CN photocatalyst can effectively inhibit the production of NO<sub>2</sub>.

In addition, ESR of ZIF-67, ZIF-CH and ZIF-CH(20%)/CN were measured to study the generation of hydroxyl radical (•OH) and superoxide radical (•O<sub>2</sub><sup>-</sup>) in Fig. 7. The ESR of ZIF-67, ZIF-CH and ZIF-CH(20%)/CN and CN showed no obvious signal peaks for •OH and  $\cdot O_2^-$  under dark condition (Fig. S6). As shown in Fig. 8(a) and (b), ZIF-CH(20%)/CN has the strongest signal peak of  $\cdot O_2^-$  and  $\cdot OH$  due to more electron holes were generated and separated effectively, which endowed ZIF-CH(20%)/CN strongest oxidation performance. Notablely, the signal peak intensity of •OH in ESR over ZIF-CH(20%)/CN was significantly higher than that of  $\bullet O_2^-$ , and  $\bullet OH$  could oxidize NO to  $NO_3^-$ , thus reducing the production of  $NO_2$  [19]. The ESR results might explain the •OH source of ZIF-CH and ZIF-67. As shown in Fig. 7(a) and (b), a strong  $\cdot O_2^-$  and a weak  $\cdot OH$  signal peaks were observed in ZIF-67 under light illumination. While for ZIF-CH, the weaker  $\cdot O_2$  signal and a stronger  $\cdot OH$  signal peak were found, which were attributed to the reaction of surface hydroxyl ions and photogenerated holes to produce •OH. Moreover, active species capture experiments indicated •OH is the mainly active specie (Fig. S7).

Based on the above calculation and analysis, a possible NO oxidization process could be expressed in Eqs. (1)–(6). Under visible light illumination, the electron-hole pairs were generated, and oxygen was activated photo-electrons by to form  $\cdot O_2^-$ . Meanwhile ,  $\cdot OH$  were generated by hydroxyl ions reacting with the photo-holes.

$$ZIF - OH/CN + hv \rightarrow e^- + h^+$$
(1)



Fig. 7. In situ IR spectra of NO adsorption (a) and visible light reaction processes (b) over ZIF-CH(20%)/CN photocatalysts.



**Fig. 8.** ESR profile for (a)  $\cdot O_2^-$  and (b)  $\cdot OH$  for ZIF-CH(20%)/CN,CN, ZIF-CH and ZIF-67.

(5)

 $O_2 + e^- \rightarrow \bullet O_2^- \tag{2}$ 

 $OH^- + h^+ \rightarrow \bullet OH$  (3)

 $NO + 2H_2O + 3h^+ \rightarrow NO_3^- + 4H^+$  (4)

 $NO + \bullet O_2^- \to NO_3^-$ 

$$NO_2 + \bullet OH \rightarrow HNO_3$$
 (6)

# 4. Conclusion

In summary, a ZIF-67/CoOOH cocatalyst was successfully constructed by simply alkali oxidation treatment. Then ZIF-CH were loaded on g-C<sub>3</sub>N<sub>4</sub> surface by magnetic stirring. The successful combination of ZIF-CH/CN not only enlarged its visible light response range, but also boosted the separation of electron-hole pairs. Most important of all, much more highly oxidizing-OH generated on ZIF-CH/CN could react directly with NO to remove rapidly and steadily NO and improve its deep oxidation capacity. As a result, the NO removal efficiency of g-C<sub>3</sub>N<sub>4</sub> was improved from 34.4% to 52.5% after the combination of ZIF-CH and CN. Meanwhile, the toxic by-product  $NO_2$  was almost completely inhibited. This work could supply a novel insight into the design of photocatalyst for air purification.

#### **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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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.160318.

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