Unveiling real active site for photocatalytic H₂O₂ evolution: A combined experimental and DFT-TDDFT study

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Article

Keywords: photocatalytic H₂O₂ evolution, DFT calculation, TDDFT calculation, experiment, multiple modification sites, real active site

Posted Date: October 6th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-84216/v1>

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Abstract

Photocatalyst with multiple modification sites (MSs) exhibited better performance than single site in photocatalytic H_2O_2 evolution, while the corresponding reaction mechanism is more complicated. However, neither experiment nor density functional theory (DFT) based on ground state wavefunction cannot precisely confirm the role of each site in photocatalyst with multiple MSs. Here, we propose a universal method that flexibly combines experiments, DFT and time-dependent DFT (TDDFT) calculations to reveal the photocatalytic mechanism and active site of nitrogen deficiency g- C_3N_4 (NDCN) containing two MSs (bicoordinated nitrogen vacancy and cyano group). Characterization techniques and control experiments prove that generation of H_2O_2 on NDCN is a two-step single electron transfer process, and NDCN exhibits enhanced charge separation efficiency and higher selectivity for two-electron oxygen reduction. DFT-TDDFT calculations further indicate that nitrogen vacancy is the real catalytic site for activating O_2 , which promotes O_2 adsorption and continuously formation of $\cdot\text{O}_2^-$, thus inhibiting electron-hole recombination.

Introduction

Hydrogen peroxide (H_2O_2), an liquid resource, is useful for water purification, antibacterial, pulp bleaching and fuel cells^{1,2}. The most commonly used anthraquinone method for preparing H_2O_2 has the shortcomings of high cost and emission of toxic by-products³. In contrast, photocatalytic technology provides a new opportunity for H_2O_2 preparation in a low-cost and environmentally friendly way. Photocatalytic H_2O_2 production through the O_2 two-electron reduction process ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$) has attracted wide attention^{4,5}. With the continuous efforts of researchers, a large number of photocatalysts for H_2O_2 evolution have been developed⁶⁻¹⁸. Among them, photocatalysts with multiple modification sites (MSs) exhibited more superior performance as compared to their catalytically inaccessible counterparts of single sites materials¹⁴⁻¹⁷. Nevertheless, it is worth noting that the same kind of MS exhibited diametrically opposite effects when the other MSs are different in the same primitive material^{15-17,19}. For instance, Shiraishi et al. reported that amino group reduced the selectivity of H_2O_2 in mesoporous graphitic carbon nitride (CN)¹⁹. But in the CN modulated by carbon vacancies, the amino group was the active site that significantly enhanced the H_2O_2 production¹⁷. Besides, Zhu et al. reported that the cyano group acted as an electron acceptor to promote the photocatalytic H_2O_2 evolution under the synergistic effect of nitrogen vacancy¹⁶. However, Xie et al. proposed that in the defect CN containing three kinds of MSs, the cyano group has no effect on the formation of H_2O_2 ¹⁵. Different preparation methods led to different coordination environments at the same kind of MS. In addition, there are also some differences between analysis methods used in the reports mentioned above, which also be an pivotal reason for the opposite effect of the same MS. Therefore, the research method of investigating the role of MS should be emphasized.

To reveal the true reaction mechanism of photocatalytic H_2O_2 evolution promoted by photocatalysts with multiple MSs, experimental scholars have made many efforts. In order to determine the role of each site in a material with three MSs (CKCN-0.03), Xie et al. first prepared a material, CN (V1), containing only two MSs in CKCN-0.03. Then CN(V1 + V2) was prepared by introducing the third MS into CN(V1), which also has three MSs in CKCN-0.03 with the same content. By comparing the properties of CKCN-0.03, CN (V1) and CN(V1 + V2) experimentally, the specific role of each site was confirmed, respectively¹⁵. Similarly, Dong and his co-workers also used the controlled variable method to study the role of each MS experimentally¹⁷. Regrettably, this method has inherent limitations: (1) More materials need to be prepared and characterized to ensure the same MS content in the materials used for comparison, which greatly increases the cost and research time. (2) Compared with the simultaneous introduction of multiple MSs into the material, stepwise modification must change original preparation method, which could not guarantee that other important factors affecting the catalytic effect are completely unchanged. For example, for the CKCN-0.03 and CN(V1 + V2) mentioned above, although they both have the same number and content of MSs, the photocatalytic H_2O_2 production rate of CKCN-0.03 is 1.5 times higher than that of CN(V1 + V2). (3) Zhang et al. recently prepared a photocatalyst containing five MSs, achieving a millimolar level of H_2O_2 production per hour¹⁴. For such materials with more MSs, it is difficult to analyze the effect of each MS through experimental controlled variable methods.

In simulation, each MS can be constructed flexibly without affecting other factors. Then the role of each MS can be uncovered by analyzing the calculation results of density functional theory (DFT), such as band structure^{20,21}, charge density^{21,22} and electrostatic potential²³, etc. This makes up for the lack of experiments to some extent. Yu et al. analyzed the roles of the two types of defects by comparing the calculated bandgaps²¹. Zhao et al. verified the effect of each MS on the separation of light-excited carriers through the charge density distribution of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)²². However, electronic excitation process is a transition from the ground state to excited state, rather than an occupied orbital to a non-occupied orbital^{24,25}. Excited state is formed by linear combinations of different orbital transitions²⁴. In order to more accurately explore the complex light reaction process, time-dependent DFT (TDDFT) calculations need to be performed. Unfortunately, only a few reports focusing on experimental research have used TDDFT calculations^{5,19,26}. The huge potential of multiple MSs in the photocatalytic H_2O_2 evolution, as well as the current challenges in revealing the in-depth photocatalytic mechanism, provide us with a strong motivation to explore a universal method to uncover the specific reaction mechanism, role of each MS, and essential reason for O_2 activation.

In this work, we use the nitrogen deficiency CN (NDCN) containing two MSs as a model photocatalyst, and combine the experimental method with DFT-TDDFT calculation to reveal the mechanism behind the enhanced photocatalytic activity. The structural information of photocatalyst, separation efficiency of light-excited charge, as well as the active specie and reaction pathway are studied in detail experimentally. Based on the characterization results, accurate models are constructed and use for

simulation. The DFT-TDDFT calculations verify the real active site and its specific catalytic role, and reveal the essential reason for the effectively charge separation of and generation of active specie.

Results

Discussion of experimental characterization. NDCN was successfully prepared by adding NaOH to the precursor of CN (see Methods for details). The chemical structure of CN and NDCN were first characterized by X-ray diffraction (XRD) patterns. The XRD pattern of CN (Fig. 1a, top line) showed two distinct diffraction peaks at 13.0° and 27.4° , which can be assigned to the in-plane packed heptazine units (100) and interfacial stacking (002) of graphitic CN, respectively²⁷. It can be observed that the two characteristic peaks of NDCN were weakened and broadened, implying the loss of ordered structures within the framework to some extent. The Fourier transform infrared spectroscopy (FTIR) spectrum for CN (Fig. 1b) showed that the peak at 810 cm^{-1} can be assigned to the out-of-plane bending mode of heptazine rings, and the peaks in the range of $900\text{--}1800\text{ cm}^{-1}$ refers to $\text{N-C}=\text{N}$ heterorings in CN framework. Multiple broad peaks located in the region of $3000\text{--}3500\text{ cm}^{-1}$ can be attributed to N-H stretching vibrations. After adding NaOH, the peak at 2156 cm^{-1} typical for the cyano groups ($\text{-C}\equiv\text{N}$) was emerged²⁸. Meanwhile, the intensity of the N-H stretching peaks was significantly reduced. The results indicate that the addition of NaOH leads to the decrease of N-H groups and introduction of cyano groups.

Organic elemental analysis (OEA) was used to confirm the changes in bulk elemental composition of the samples. The N/C atomic ratio of NDCN was slightly reduced in compartion to that of CN (Supplementary Fig. 2). Next, the changes of surface element composition were further studied by XPS. Compared with that of bulk, the addition of NaOH made the surface N/C atomic ratio decreased more significantly (Supplementary Fig. 2). It is worth noting that the introduction of cyano groups and reduction of N-H groups does not cause the reduction of N elements. Therefore, this indicates that the treatment of NaOH resulted to the generation of surface N defects. Meanwhile, the O/C atomic ratio in NDCN increased (Supplementary Fig. 1a), which may be attributed to the increase of oxygen-containing species adsorbed on the surface²⁹. On the other hand, valence band (VB) XPS spectra (Supplementary Fig. 1b) showed that the treatment of NaOH did not affect energy level position of VB. In addition, the morphology of NDCN had not changed significantly compared to that of CN (Supplementary Fig. 3).

Narrow scan C1s and N1s XPS spectra further proved the introductions of cyano group and N defects. For the C1s XPS spectra (Fig. 1c), it contained three peaks of 287.89, 286.23, and 284.5 eV, representing $\text{N-C}=\text{N}$, C-NH_x ($x = 1, 2$) and adventitious hydrocarbons, respectively. The corresponding peak of C-NH_x of NDCN was higher than that of CN, which proves the generation of $\text{C}\equiv\text{N}$, because the cyano group has similar binding energy of C1s³⁰. For the N1s XPS spectra (Fig. 1d), the intensity of bicoordinated nitrogen ($\text{N}_{2\text{C}}$) in NDCN was reduced in comparison to that of CN. Combined with the decrease of N/C in XPS (Supplementary Fig. 2), it can be inferred that the generation of nitrogen defect was caused by the absence of N atoms in $\text{N}_{2\text{C}}$. The intensity of tricoordinated ($\text{N}_{3\text{C}}$) increased and the peak shifted to lower

binding energy. This can be attributed to the introduction of $C \equiv N$ groups, because their binding energy lies between the binding energy of N_{3C} and N_{2C} ³⁰. Based on the above characterization, we can conclude that after NaOH treatment, N_{2C} vacancies (NVs) were formed. Meanwhile, with the decrease of N-H groups, cyano groups were generated.

The optical properties of the samples were further characterized by DRS. Compared with CN, the absorption edge of NDCN has a significant red shift (Supplementary Fig. 4a) and the band gap is reduced from 2.64 to 2.04 eV (Supplementary Fig. 4b). Combining the above results of the VB XPS, the narrowing of the band gap is due to the decrease of conduction band (CB) position, while the VB position remains unchanged.

Evaluation of photocatalytic performance. The photocatalytic performances of CN and NDCN were evaluated. Under the irradiation of visible light, the 60 min production of H_2O_2 for NDCN was 476 μM (Supplementary Fig. 5a), which is 9.7 times higher than that of CN (47 μM) and better than many reported yields in recent years (Supplementary Table 1). In addition, after 5 cycle experiments, the photocatalytic performance did not decrease significantly (Supplementary Fig. 6). Comparing the XRD patterns of samples before and after 5 cycles, there was no obvious difference (Supplementary Fig. 7), indicating that NDCN has excellent stability in the photocatalytic H_2O_2 production. Therefore, it is meaningful to investigate the reaction mechanism of photocatalytic H_2O_2 production for NDCN.

The effects of defects on separation efficiency of photoexcited charge carriers were investigated. Photoluminescence (PL) spectroscopy measurements were performed to examine the charge separation ability³¹ of samples. As shown in Supplementary Fig. 5b, a intense PL signal was observed on CN, due to the serious recombinations of carriers. In contrast, the PL intensity of NDCN was weaker, indicating a signally suppressed electron-hole recombination. Supplementary Fig. 5c showed the transient photocurrent response curve of the samples, which is directly related to their charge separation ability. Compared with CN, NDCN exhibited a larger photocurrent density, indicating that nitrogen defects can greatly accelerate the separation of photoexcited carriers³². The electrical conductivity and interfacial charge transfer capability of the samples were evaluated by electrochemical impedance spectroscopy (EIS). As shown in Supplementary Fig. 5d, the EIS slop of NDCN decreased significantly in compartion to that of CN, implying that NDCN has better electrical conductivity, which is conducive to effective charge separation and transfer in the photocatalytic process.

Experimental research on reaction mechanism. To understand the reaction mechanism of photocatalytic reaction, a series of control experiments and measurements were conducted. Figure 2a showed the ESR spectra of $DMPO \cdot O_2^-$ adduct for the CN and NDCN samples. It can be seen that the $DMPO \cdot O_2^-$ adduct signal of NDCN was much stronger than that of CN, suggesting that NDCN can promote the generation of $\cdot O_2^-$ more effectively. The results of control experiment further illustrated the importance of $\cdot O_2^-$ in the photocatalytic reaction. After adding $\cdot O_2^-$ scavenger, p-benzoquinone (PBQ), the yield of H_2O_2 was 0 (orange curve in Fig. 2b). It is worth mentioning that the iodometry for determining H_2O_2 production do

not be affected by PBQ³³. Hence, it can be concluded that the consumption of $\cdot\text{O}_2^-$ can completely inhibit generation of H_2O_2 , indicating that the generation of H_2O_2 is a two-step single electron transfer process ($\text{O}_2 \rightarrow \cdot\text{O}_2^- \rightarrow \text{H}_2\text{O}_2$)^{17,33}. In the dark, the H_2O_2 production was also 0 (blue curve in Fig. 2b), implying that light irradiation is a necessary condition for the catalytic reaction. In the absence of isopropanol (IPA), the yield of H_2O_2 was significantly reduced (yellow curve in Fig. 2b), because IPA is the main provider of H source for H_2O_2 evolution. In the photocatalytic reaction, the holes oxidize IPA to generate two H^+ ($\text{CH}_3\text{CHOHCH}_3 + 2\text{h}^+ \rightarrow \text{CH}_3\text{COCH}_3 + 2\text{H}^+$), which can further combine with the reduced O_2 to generate H_2O_2 . Without IPA, holes can only react with water to produce H^+ , resulting in an excessively high energy barrier. Interestingly, when the reaction conditions changed from oxygen to air, the yield of H_2O_2 was only slightly reduced, implying that NDCN could still adsorb and reduce O_2 well even in air, which will be further discussed below. Since the formation of H_2O_2 involves two-electron O_2 reduction process, the average number of electrons (n) involved in the oxygen reduction is a vital indicator for the selectivity of reaction products. Figure 2c and Supplementary Fig. 8 showed the linear sweep voltammetry (LSV) curves of NDCN and CN on a rotating disk electrode at different rotate speeds, respectively. n is the slope of Koutecky-Levich plots based on the LSV curve⁹. As shown in Fig. 2d, the measured n value for CN was only 1.5, while that of NDCN reached 1.95, close to 2, indicating that NDCN is highly selective for the two-electron reduction of O_2 .

Through the above characterization and experiments, we have a basic understanding of the role of N defects in photocatalytic reaction and the path of O_2 reduction. However, there are still some problems to be solved: (1) NDCN contains two MSs, $\text{N}_{2\text{C}}$ vacancy (NV) and cyano group. Which site is causing the enhanced photocatalytic performance? (2) Is there a synergy between the two MSs? (3) What is the essential reason for O_2 activation? To solve the problems, DFT and TDDFT calculations were performed.

Confirmation of the optimal model. First, the most stable and reasonable geometry was constructed and verified. Eleven possible models (M_1 - M_{11} in Supplementary Fig. 9) were considered, and the most stable geometric structure of NDCN was selected by comparing their Gibbs free energy. As shown in Supplementary Fig. 10, model with the lowest Gibbs free energy is M_3 whose cyano group and NV are located at the edge of the two melon frameworks, respectively. The calculated FTIR spectrum for M_3 was similar to the experimentally measured spectrum (Fig. 3a), which again proved the rationality of M_3 . Meanwhile, the structure of M_3 was also consistent with what Zhang et al. reported²¹. Thus, we will directly label the M_3 as NDCN for discussion below. In order to clearly describe each site of NDCN, the NDCN model was divided into three regions: NV, cyano, and primitive melon. The key atoms were numbered to clearly identify each site (Fig. 3b).

Confirmation of $\cdot\text{O}_2^-$ and active site. In order to initially confirm the possible O_2 activation sites, the calculated ultraviolet visible (UV-vis) spectrum and electron-hole distribution of each excited state were analyzed. The oscillator strength (f) in the UV-vis spectrum represents the transition probability of

electrons from ground state to each excited state. The f of 0.01 is generally the critical point of transition²⁴. Specifically, if the f is lower than 0.01, the corresponding transition is generally considered to be forbidden, otherwise the transition can occur with a probability determined by f . For NDCN, the f of $D_0 \rightarrow D_1$, $D_0 \rightarrow D_2$, and $D_0 \rightarrow D_4$ excitations were all greater than 0.01 (Fig. 4a), indicating that photo-generated e^- can indeed be excited to the green regions of Fig. 4c1, 4c2 and 4c4, respectively, that is, these excitations are bright. The f of the $D_0 \rightarrow D_3$ excitations was almost zero (Fig. 4a), implying that the excitation is dark. On the basis, the electron-hole distribution of each excited state was visualized. As shown in Fig. 4c, for the $D_0 \rightarrow D_1$, electrons were mainly concentrated at 1,4 site near the NV (NV 1,4 site). In the $D_0 \rightarrow D_2$, electrons were clustered at 1,4 sites near the cyano group (cyano 1,4 site) and primitive melon (primitive 1,4 site). For the $D_0 \rightarrow D_4$, the electrons were distributed on the NV site. Since the $D_0 \rightarrow D_3$ excitation was dark, photo-generated electrons could not be directly excited to corresponding electron distribution area. Based on the above results, it is found that the activation sites of O_2 may be NV 1,4 and NV sites, as well as cyano 1,4 and primitive 1,4 sites.

To further confirm the real active site, O_2 were adsorbed on the 4 possible sites mentioned above, respectively. When O_2 was adsorbed on the NV 1,4 site of NDCN [$O_2@NDCN$ (NV 1,4 site)], electrons might be excited to O_2 in the excitations of $D_0 \rightarrow D_1$ and $D_0 \rightarrow D_2$, while holes might remain the NV region (Supplementary Fig. 11a). The IFCT method implemented in Multiwfn³⁴ can further calculate the specific number of electrons transferred from NDCN to O_2 in each excitation. As shown in Supplementary Table 2, for $O_2@NDCN$ (NV 1,4 site), there might be 0.96 and 0.95 electrons transferred from NDCN to O_2 in the $D_0 \rightarrow D_1$ and $D_0 \rightarrow D_2$ excitations, respectively. Similarly, the probability of electron excitation needs to be evaluated by f . The f of $D_0 \rightarrow D_1$ and $D_0 \rightarrow D_2$ excitations for $O_2@NDCN$ (NV 1,4 site) were 0.0017 and 0.0136, respectively [$O_2@NDCN$ (NV 1,4 site) in Supplementary Table 2], suggesting that it is feasible to transfer 0.96 e^- from the NV 1,4 site to O_2 through the $D_0 \rightarrow D_2$ excitation, indicating that electrons can be directly excited from NDCN to O_2 through the $D_0 \rightarrow D_2$ excitation while $D_0 \rightarrow D_1$ was forbidden. Therefore, combining the electron-hole distribution, IFCT and UV-vis spectrum results, it can be concluded that O_2 adsorbed on NV 1,4 site could be directly excited by light to generate $\cdot O_2^-$, which is consistent with the results of ESR, RDE and control experiments (Fig. 2). Using the same method, the adsorption of O_2 on cyano 1,4 [$O_2@NDCN$ (cyano 1,4 site)] and primitive 1,4 sites [$O_2@NDCN$ (primitive 1,4 site)], as well as NV sites [$O_2@NDCN$ (NV site)] were also analyzed. Although the electron-hole distribution and IFCT results showed that in the $D_0 \rightarrow D_1$ and $D_0 \rightarrow D_2$ excitations, the electronic transitions of $O_2@NDCN$ (cyano 1,4 site) and $O_2@NDCN$ (primitive 1,4 site) were all from the NDCN to O_2 (Supplementary Fig. 11b, 11c and Supplementary Table 2), but the corresponding oscillator strengths were too low (Supplementary Fig. 12b, 12c and Supplementary Table 2). Only 0.2 e^- could be transferred from primitive 1,4 site to O_2 through $D_0 \rightarrow D_3$ excitation, but this was not enough to activate O_2 . Photogenerated e^- cannot be directly excited to dark excited state, but can only be promoted to bright excited state with higher energy, and then may relax to low energy dark state. However, in this indirect process, the possibility of carrier

recombination or structural relaxation is greatly increased, which is not conducive to O_2 reduction. Hence, the cyano 1,4 and primitive 1,4 sites had no major contribution to the generation of $\cdot O_2^-$. When O_2 was adsorbed on the NV site of NDCN [$O_2@NDCN$ (NV site)], it might get electrons through the $D_0 \rightarrow D_1$ and $D_0 \rightarrow D_2$ excitations (Fig. 4d). Although the f of $D_0 \rightarrow D_1$ excitation was negligible, through the $D_0 \rightarrow D_2$ excitation with f of 0.0428 (Fig. 4b), NDCN could transfer $0.85 e^-$ to O_2 (Supplementary Table 2). A higher f indicates that the NV site has a greater probability of generating $\cdot O_2^-$ compared to that of the NV 1,4 site. The results of vertical absorption of O_2 on the surface of NDCN were summarized in Supplementary Table 2. The highlighted part indicates that the excitation is bright, which allows photogenerated electrons to transfer from NDCN to O_2 . Obviously, only NV and NV 1,4 site can effectively activate O_2 , promoting the generation of $\cdot O_2^-$, while cyano 1,4 and primitive 1,4 site cannot.

Confirmation of endoperoxide. In electronic excitation, the transition of electrons occurs first, leading to a change in the electronic structure, which inevitably cause the evolution of geometry. In this section, the kinetic process of reaction system was investigated. Adding excess electrons to the photoreaction system for simulating light conditions is a common method^{35,36}. First, two excess electrons were added to the $O_2@NDCN$ (NV site) and $O_2@NDCN$ (NV 1,4 site) models, respectively. After the structure was fully relaxed, O_2 in the $O_2@NDCN$ (NV site) and $O_2@NDCN$ (NV 1,4 site) models finally both stabilized on the NV site (inset of Fig. 4e and Supplementary Fig. 13a), and the bond length of O-O increased from 1.199 and 1.194 Å to 1.383 and 1.382 Å, respectively. Moreover, the density of states (DOS) of two models were almost the same. Meanwhile, the two β -LUMO orbitals that were originally degenerate in the isolated O_2 (Supplementary Fig. 13b) were split, one of which became β -HOMO-1 and the other β -LUMO + 1 (Fig. 4e and Supplementary Fig. 13a), suggesting that O_2 got an electron^{37,38}. This indicate that after the O_2 adsorbed on the NV or NV 1,4 site becomes $\cdot O_2^-$ by vertical absorption, the further relaxation of structure lead to an increase of the O-O bond length, which generate more stable $\cdot O_2^-$. The e^- stabilized in the $\cdot O_2^-$ are effectively separated from the h^+ left on the NV surface, effectively avoiding the recombination of photogenerated carriers, which explain the experimental result that NDCN exhibited a more effective charge separation ability (Supplementary Fig. 5b-d). When the excess electrons in the two models increased to 3, the O-O bond length in the $O_2@NDCN$ (NV site) and $O_2@NDCN$ (NV 1,4 site) models further increases to 1.600 and 1.591 Å, respectively. Meanwhile, the two β -LUMO orbitals that were originally degenerate in the isolated O_2 all became occupied orbitals (Supplementary Fig. 14), indicating that O_2 obtained two electrons, which became endoperoxide on the NDCN surface^{38,39}.

For CN, the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ excitations were confirmed to be bright by f (Supplementary Fig. 16a). The photogenerated electrons were mainly distributed in the 1,4 site of melon (Supplementary Fig. 15a₃, a₄), indicating that this position may be the O_2 activation site in CN, which is consistent with the previous report^{4,19}. However, compared to the 2.08 eV excitation energy of the first bright state of NDCN (596 nm for $D_0 \rightarrow D_1$ in Fig. 4a), that of CN was as high as 3.7 eV (330 nm for $S_0 \rightarrow S_3$ in Supplementary Fig. 16a), indicating that nitrogen defects can significantly expand the light response range of CN, in agreement

with UV-vis DRS experimental results (Supplementary Fig. 4). When O_2 was adsorbed on the 1,4 site of CN, the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations (Supplementary Fig. 15b) that might allow O_2 to obtain photogenerated e^- were all dark states (Supplementary Fig. 12d). The photogenerated electrons could only be promoted to the $S_0 \rightarrow S_{25}$ excitation with an energy as high as 3.8 eV (Supplementary Fig. 12d), and then relaxed inefficiently to the dark state that can activate O_2 (Supplementary Fig. 15b and Supplementary Table 2). In contrast, on the NV or NV 1,4 site of NDCN, the excitation energy for converting O_2 to $\cdot O_2^-$ was only 1.61 eV. It is worth mentioning that the calculated excitation energies were only used for qualitative comparison due to the influence of multiple factors, such as theoretical methods⁴⁰, spin orbit coupling⁴¹ and overlap between absorption peaks of different transitions⁴², etc.

Investigation on the role of NV and cyano. The above discussion proved that after introducing cyano and NV, the NV and NV 1,4 site were both the real active sites for photocatalytic H_2O_2 production. Although the cyano cannot efficiently activate O_2 , whether the high catalytic activity of NDCN is due to the synergy between cyano group and NV need to be verified. For this purpose, we constructed nitrogen deficient CN containing only NV (NDCN-NV) and cyano group (NDCN-cy), respectively. The results indicated that the excited energy in the same excitation (Fig. 4f), UV-vis spectrum (Fig. 4a vs. Supplementary Fig. 16b) and electron-hole distribution (Fig. 4c vs. Supplementary Fig. 17a) of NDCN and NDCN-NV were almost identical, while those of CN and NDCN-cy were very similar (Fig. 4f, Supplementary Fig. 16a vs. Supplementary Fig. 16c, and Supplementary Fig. 15a vs. Supplementary Fig. 18a). Subsequently, based on the electron-hole distribution of bright excited state, O_2 was adsorbed to the corresponding sites of NDCN-NV (Supplementary Fig. 17b-d) and NDCN-cy (Supplementary Fig. 18b, c), respectively. By observing the number of transferred electrons and f for each excitation (Supplementary Table 3), it can be confirmed that the NV and NV 1,4 sites of NDCN-NV can also promote the generation of $\cdot O_2^-$, which are the same as the two sites of NDCN. However, NDCN-cy cannot effectively transfer photogenerated electrons to O_2 (Supplementary Table 4). It can be concluded that the introduction of NV is the only reason to promote high-efficiency production of H_2O_2 , while cyano group do not make any contribution to this.

The essential reason for O_2 activation. In order to reveal the essential reason for O_2 activation, the electronic structures of each substance before and after adsorption were analyzed. To facilitate discussion of the role of each region and molecular orbitals (MO), NDCN was divided into three regions: cyano modified melon (melon-cy), NV modified melon (melon-NV) and primitive melon (melon-pri), as shown in Fig. 5. The key molecular orbitals (MO_1 - MO_{10} in Fig. 5) were marked in DOS (Fig. 5a-c). It can be seen from Supplementary Table 1 that no matter where O_2 was adsorbed on NDCN, the transition orbital pairs corresponding to the excited state all belonged to β spin. Thus, the focus of analysis was on the β spin orbits. For NDCN, β -HOMO (MO_5 in Fig. 5) was concentrated on melon-NV, while β -LUMO (MO_4 in Fig. 5) was distributed on melon-cy and melon-pri, indicating that NV and cyano have impacts on the original optical response range of CN, which is consistent with previous report²¹. It is worth distinguishing

that photogenerated e^- could be excited to the cyano 1,4 site of NDCN (Fig. 4a, 4c₂), but they could not further effectively activate O_2 due to the negligible f mentioned above.

Before interacting with NDCN, the β -LUMO of O_2 is degenerate (MO_9 and MO_{10} in Fig. 5). The formations of $\cdot O_2^-$ and endoperoxide are the results of β -LUMO being occupied by one and two electrons, respectively. When O_2 was adsorbed on the NV site of NDCN, MO_9 and MO_{10} of O_2 interacted with MO_5 of NDCN to generate MO_8 (Fig. 5d). Note that MO_8 was an occupied orbital. The contribution of non-occupied MO_9 and MO_{10} to MO_8 indicated that the NV site was chemically adsorbed with O_2 in the ground state, making O_2 obtain a small amount of e^- . Moreover, the adsorption energy of O_2 at NV site was -0.12023 eV, which is the lowest value among the four sites of NDCN (Supplementary Fig. 19a), indicating that the NV site could effectively adsorb O_2 , and thus is beneficial for subsequent O_2 reduction process. The spin density map (Supplementary Fig. 19b) showed that there was unpaired β e^- on melon-NV, so that the NV site could be acted as an electron donor to effectively adsorb O_2 in the ground state. On the other hand, the key point of activating O_2 was the electron excitation from MO_8 to MO_7 (see “Hb $\rightarrow$ Lb 97.4%” in Supplementary Table 2). The formation of MO_7 was also due to the interaction of MO_5 , MO_9 and MO_{10} . The lower energy MO_5 contributed 6.24% to the MO_7 (Fig. 5d), effectively reducing the excitation energy for activating O_2 . O_2 @NDCN (NV 1,4 site) was basically the same as O_2 @NDCN (NV site). Since oxygen was located on the NV 1,4 site instead of the NV site, the corresponding adsorption energy increased slightly, but the value was still negative (Supplementary Fig. 19a). Moreover, the contribution of MO_5 to MO_7 was also slightly reduced (Fig. 5e), leading to a slight increase in the excitation energy of O_2 activation, but the NV 1,4 site could still effectively transfer photogenerated e^- to O_2 . Combining the results of the control experiment in air (green curve in Fig. 2b), it can be concluded that when the saturated O_2 environment was replaced with air, the reason why NDCN could still maintain high catalytic activity was the strong adsorption capacity of NV for O_2 . On the other hand, cyano 1,4 and primitive 1,4 sites showed complete inertness for O_2 adsorption due to the positive adsorption energy (Supplementary Fig. 19a). It is worth mentioning that in the simulation of structural optimization, even if O_2 was placed on top of the cyano group as the initial structure, O_2 eventually stabilized at the cyano 1,4 site, indicating that cyano cannot adsorb O_2 . This was due to its own quite stable $C \equiv N$. Moreover, since O_2 was not on melon-NV, MO_9 and MO_{10} could not interact with MO_5 , but could only interact with higher energy orbitals corresponding to cyano 1,4 (Supplementary Fig. 20a) or primitive 1,4 site (Supplementary Fig. 20b), making the corresponding excitation energy higher.

For materials containing more modification sites, there are more possible geometries and O_2 activation sites, resulting in an increase in the workload and complexity of simulation. But it should be emphasized that even so, the amount of work required is still far less than the currently widely used first-principles molecular dynamics⁴³ and transition state calculations⁴⁴. The more complex simulations resulting from more MSs can be completed accurately and quickly through high-throughput calculations⁴⁵ and machine learning⁴⁶. Therefore, the proposed method is universal and extensible.

We proposed a universal method combining experiments and DFT-TDDFT calculations to investigate the in-depth reaction mechanism of NDCN containing two MSs for photocatalytic H_2O_2 evolution. PL technology and electrochemical measurements proved that the introduction of defects could effectively enhance charge separation. The results of ESR, RDE and control experiments indicated that $\cdot\text{O}_2^-$ was the key active specie and photocatalytic reaction was a two-step single electron transfer process. After constructing accurate models based on characterization results, DFT-TDDFT calculations proved that NV could efficiently convert O_2 to $\cdot\text{O}_2^-$, while cyano group could not directly activate O_2 and had no synergy with NV. Meanwhile, the introduction of NV promoted O_2 adsorption and reduced the excitation energy for activating O_2 , significantly facilitating H_2O_2 evolution. This work provides a reference for the joint connection of experiments and DFT-TDDFT calculations and has general guiding significance for photocatalytic research involving O_2 activation.

Methods

Synthesis of CN samples. Pristine g- C_3N_4 (CN) was prepared as following process. Typically, 15 g melamine was calcined at 550°C in a muffle furnace for 4 h with a rate of $10^\circ\text{C min}^{-1}$.

Synthesis of nitrogen deficient CN samples. 15 g melamine was dissolved with stirring into aqueous NaOH solutions containing 30 mL H_2O and 1.5 g NaOH. Then the water in the solution was evaporated to dryness. The resulting solid mixtures were then calcined at 550°C in a muffle furnace for 4 h with a rate of $10^\circ\text{C min}^{-1}$. The obtained samples were washed with water and alcohol for several times. The final products were denoted as nitrogen deficient CN (NDCN).

Characterization. The phase structures of the samples were analyzed by XRD measurement on a Bruker D8 Advance instrument with Cu K α radiation ($\lambda = 0.15418\text{ nm}$). The morphologies were collected on a FEI Quanta 250 scanning electron microscopy (SEM). The surface chemical compositions were studied by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher). The diffuse reflectance absorption spectra (DRS) of the samples were measured by a Varian Cary 300 spectrophotometer with BaSO_4 reference from 200 to 800 nm. The photoluminescence (PL) spectroscopy was monitored by a PerkinElmer LS-55 fluorescence spectrophotometer with an excitation wavelength of 350 nm at room temperature. FTIR was measured on an IR Prestige-21 spectrometer using samples embedded in potassium bromide (KBr) pellets. The electron spin resonance (ESR) signals of $\cdot\text{O}_2^-$ was monitored by using 5,5-dimethyl-L-pyrroline N-oxide (DMPO) as spin-trapped reagent on a JEOL JES-FA200 spectrometer under visible light irradiation ($\lambda > 420\text{ nm}$).

Photoelectrochemical measurements. The photoelectrochemical responses of the samples were measured by a CHI 660D workstation with a standard threeelectrode model. A Pt and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. fluorine-doped tin oxide (FTO) electrodes covered in samples were used as the working electrode. 0.2 M Na_2SO_4 solution was used as supporting electrolyte.⁴⁷

Rotating disk electrode (RDE) measurements. The measurements were performed on a Model 636A electrochemical system by Princeton Parstat3000A-DX workstation using an Ag/AgCl electrode and a Pt wire electrode as the reference and counter electrode, respectively.⁴⁸ The linear sweep voltammogram (LSV) were obtained in an O₂-saturated 0.1 M phosphate buffer solution (pH = 7). The average number of electrons (n) involved in the overall O₂ reduction was determined by the slopes of the Koutecky-Levich plots with the following equation:

$$j^{-1} = j_k^{-1} + B^{-1} \omega^{-1/2} \quad (1)$$

$$B = 0.2nF\nu^{-1/6}CD^{2/3} \quad (2)$$

where j , j_k and ω are the current density, kinetic current density and rotating speed (rpm), respectively, F and ν are the Faraday constant (96485 C mol⁻¹) and kinetic viscosity of water (0.01 cm² s⁻¹), C and D are the bulk concentration of O₂ in water (1.26×10⁻³ mol cm⁻³) and diffusion coefficient of O₂ (2.7×10⁻⁵ cm² s⁻¹), respectively.

Photocatalytic H₂O₂ production. 100 mg of catalyst was uniformly dispersed into 100 mL of water or mixed solution containing 10 mL of IPA and 90 mL of water with ultrasonication for 10 min. Then the suspension solutions were stirred for 30 min in the dark to reach the absorption-desorption equilibrium. The light source was provided by a 300 W xenon lamp (PLS-SXE300/300UV, Perfect Light, China) with 420 nm cutoff filter. At certain time intervals, 3 mL suspension was sampled and centrifuged to remove the photocatalysts. The amount of H₂O₂ was measured by iodometry⁴⁹.

Computational details. Geometry optimizations, frequency calculations and excited state simulations were carried out via PBE0-D3 exchange-correlation functional^{50,51} with the 6-311G(d,p)⁵² basis set, as implemented in Gaussian 16 C.01 code.⁵³ The atoms at the boundary (except for defect sites) were fixed to simulate the periodic structure of the catalyst. In order to be consistent with the experimental solution environment, self-consistent reaction field (SCRF) with the SMD model⁵⁴ were used and water was chosen as the solvent. All analyses were finished via the Multiwfn 3.7(dev) code.³⁴ Most structure and isosurface maps were visualized by VMD.⁵⁵ Single-point energies were computed via PWPB95-D3(BJ) double-hybrid functionals in conjunction with the def2-TZVPP⁵⁶ basis set, as implemented in ORCA 4.2.1 code.⁵⁷ The RIJCOSX technique⁵⁸ was used to increase the speed of calculation.

At room temperature, the Gibbs free energy for each photocatalyst model is calculated by the following equation

$$G = E + \text{ZPE} + H(T) - H(0) - T^*S \quad (3)$$

where E is electron energy calculated by ORCA. ZPE, H and S are zero point energy, enthalpy and entropy computed by Gaussian, respectively. T is the room temperature (298.15 K). In order to further improve the accuracy of Gibbs free energy, correction factors 0.9812, 0.9856 and 0.9915 are used to correct ZPE, $H(T)-H(0)$ and S , respectively.⁵⁹

The adsorption energy of O_2 is defined as

$$E_{\text{ads}}(O_2) = E(*O_2) - E(*) - E(O_2) \quad (4)$$

where $E(*O_2)$ is the the total energy of photocatalyst surface with O_2 adsorbed, $E(*)$ and $E(O_2)$ are the energy of pristine photocatalyst surface and O_2 , respectively.

Data availability. The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information. Further information is also available from the corresponding authors upon reasonable request.

Declarations

Competing interests:

The authors declare no competing interests.

Author contributions

C.-Z.F. and L.T. conceived and directed the research. J.L. and M.Y. performed the calculations and analyzed the simulated data. J.L., Y.-N.L., S.-J.Y, M.L.L., M.-E.W., C.-Y.F., X.-L.O.Y., and J.-J.W. performed the experiments and analyzed the experimental data. J.L., C.-Z.F., L.T., C.-Y.F., L.-L.W and L.X., co-wrote the paper. All authors discussed the results and commented on the manuscript.

Acknowledgments

This research was financially supported by the project of National Natural Science Foundation of China (NSFC): 51679084, 52070075; Natural Science Foundation of Hunan Province: 2020JJ4187; the National Innovative Talent Promotion Program of China (2017RA2088); the Funds for Innovative Province Construction of Hunan Province of China (2019RS3012).

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Figures

Figure 1

Characterizations of photocatalysts. a XRD patterns and b FTIR spectra of CN and NDCN. c C1s and d N1s XPS spectra of CN and NDCN.

Figure 2

Experimental research on reaction mechanism. a ESR spectra of $DMPO \cdot O_2^-$ under visible-light illumination ($\lambda > 420$ nm). b Comparison of the photocatalytic production of H_2O_2 under different conditions for NDCN. c NDCN measured on an RDE at different rotating speeds. d Koutecky-Levich plots of the data obtained at the constant electrode potential (-1.0 V vs. Ag/AgCl) for NDCN and CN.

Figure 3

Confirmation of the optimal model. a Calculated and experimental FTIR spectra of NDCN. b Structure models of NDCN. The white, brown and blue spheres represent H, C and N atoms, respectively.

Figure 4

TDDFT simulation. Simulated UV-Vis spectrum for a NDCN and b O_2 -adsorbed NDCN on NV site for different excited states, respectively. Discrete black spikes represent calculated oscillator strengths (f) of excitations. The continuous curves correspond to molar absorption coefficient (MSC) broadened by calculated excitation energies and f. The electron-hole distribution of c NDCN and d O_2 -adsorbed NDCN on NV site for different excited states, respectively. Green and blue isosurfaces represent electron and

hole distributions, respectively. The isosurface value is 0.003 e/Å³. e Projected density of states (PDOS) of O₂-adsorbed NDCN on NV site under the illumination simulated by two excess electrons. f Excitation energy of different excited states for NDCN, NDCN-NV, NDCN-cy and CN.

Figure 5

Electronic structure analysis. PDOS of a NDCN, b O₂-adsorbed NDCN on NV site and c O₂ molecule. MO1-MO11 represent the molecular orbitals marked in a-c. The orbital interaction of O₂ and NDCN at d NV site and e NV 1,4 site by charge decomposition analysis (CDA), respectively. The percentage represents the contributions of the original orbits to the new orbits after the interaction.

Supplementary Files

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