Green and alcohol-free H$_2$O$_2$ generation paired with simultaneous contaminant treatment enabled by sulfur/cyano-modified g-C$_3$N$_4$ with efficient oxygen activation and proton adsorption†

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Photocatalytic H$_2$O$_2$ generation is compelling for sustainable solar-to-chemical conversion, but it is an emerging challenge to realize efficient conversion without the consumption of any alcohols. Also, the in-depth mechanism for the structure-induced activity enhancement is still unclear but remains pivotal for practical application. Herein, cyano groups and S atoms were collectively introduced into carbon nitride (MTCN), and the vital roles and detailed mechanism were investigated. Specifically, MTCN exhibited a laudable H$_2$O$_2$ generation of 68.12 mM g$_{cat}^{-1}$ h$^{-1}$, together with an apparent quantum yield of 49.01% at 420 nm. Intriguingly, it was observed that the existence of some contaminants can promote H$_2$O$_2$ generation and, in turn, accelerate degradation. Additionally, it is revealed that the S atoms and cyano group could facilitate oxygen adsorption and H$^+$ adsorption, respectively. This study shows a promising strategy to construct modified g-C$_3$N$_4$ and exhibits a clear mechanism for H$_2$O$_2$ generation paired with simultaneous contaminant treatment.

1. Introduction

As a high-value and environmentally friendly chemical for social development and industrial application, hydrogen peroxide (H$_2$O$_2$) has been widely utilized in medical disinfection, chemical smelting, environmental treatment, materials bleaching, etc. However, the current anthraquinone (AQ) method for the industrial production of H$_2$O$_2$ in large scale still faces some disadvantages, like the consumption of energy and unavoidable environmental pollution caused by toxic by-products. The photocatalytic reduction of oxygen for H$_2$O$_2$ generation seems to be an energy-saving and sustainable strategy when considering synchronous solar-to-chemical conversion and environmental protection. Nevertheless, the trade-off between high yields and unavoidable costs over excessive usage of alcohols as sacrificial agents and low reaction activity in pure water still makes this process not green enough. Hence, it is urgently necessary to investigate efficient and environmentally friendly approaches for H$_2$O$_2$ generation and further cascade reactions.

Among diverse semiconductors, noble-metal-free graphitic carbon nitride (g-C$_3$N$_4$) has the characteristics of environmental friendliness, easy modification, and mild synthesis conditions, making it attract widespread attention for various applications, including water splitting, carbon dioxide reduction, nitrogen fixation, H$_2$O$_2$ generation, organic synthesis, and contaminant treatment, owing to its inherent advantages like suitable bandgap, easily modulated structure, certain stability, and visible light response. Nevertheless, the photocatalytic performance of carbon nitride is still limited, attributed to its poor photo-generated charge separation and strong charge recombination, insufficient surface active sites for redox reactions, and restricted light absorption during the whole photosynthesis process. In this scenario, diverse modifications have been employed to adjust the light absorption and charge separation of g-C$_3$N$_4$, such as morphology construction, co-catalyst loading, heterojunction formation, defect engineering, and element doping.

Defect engineering and element doping are common and effective strategies for the structural modification and performance enhancement of photocatalysts. The introduction of surface defects like vacancies or functional groups can modulate the electronic structure of g-C$_3$N$_4$ and suppress charge
recombination, thus accelerating H$_2$O$_2$ production. For instance, Zheng’s group attempted to fabricate carbon nitride with the co-existence of N vacancies and cyano group and further demonstrated the roles of dual defect sites over g-C$_3$N$_4$ for H$_2$O$_2$ production. The result clearly showed that the introduction of dual defect active sites might lead to the formation of an electron-rich structure and a more localized charge density distribution, thus enhancing light absorption, accelerating charge separation, and improving the selectivity for H$_2$O$_2$ production. In addition to defect engineering, the effect of heteroatom doping has also been investigated to promote the selectivity and activity of the photocatalytic H$_2$O$_2$ system. For instance, Choi and co-workers demonstrated the synergistic association of sulphur and alkali dopants in the material which significantly promoted the charge transportation and polarization of electrons for the reaction. These studies motivated constant in-depth investigations on the role of each active site inside carbon nitride with specific properties in photocatalytic redox reactions. In this sense, discovering the underlying mechanisms and accurate roles of various functional species in carbon nitride for boosting H$_2$O$_2$ generation and further degradation is challenging but worth exploring.

Herein, a novel system based on the formation of graphitic carbon nitride with abundant cyano groups and S atoms (MTCN) was constructed through a low energy consumption and pollution-free one-pot strategy and its reactivity was further investigated for alcohol-free H$_2$O$_2$ generation paired with simultaneous contaminant treatment. The synthesized MTCN exhibited promoted H$_2$O$_2$ generation rates of 68.12 mM $g_{\text{cat}}^{-1}$ h$^{-1}$ and 7.49 mM $g_{\text{cat}}^{-1}$ h$^{-1}$ under simulated solar light irradiation and visible light irradiation, respectively, at pH = 7, attributed to the synergistic effect of the functional cyano group and S atom dopants. Additionally, with the existence of contaminants, outstanding H$_2$O$_2$ generation was observed, 7 times higher than that in pure water, without the addition of any alcohols. In this work, we systematically clarified the accurate structure and investigated the roles of diverse active sites through experiments and theoretical calculations. The co-existence of dual active sites contributed to the enhancement of light absorption, acceleration of charge transfer, and inhibition of charge recombination. Furthermore, the introduction of S atoms led to the increase of oxygen adsorption and activation, while the formation of cyano groups resulted in the strong adsorption of H protons, thus accelerating the generation and hydrogenation of *OOH intermediates and promoting the formation of H$_2$O$_2$.

2. Results and discussion

2.1. Structure analysis

Firstly, X-ray diffraction (XRD) patterns were obtained to explore the crystal and phase structures of the synthesized samples, which were synthesized by mixing melamine and thiourea in certain proportions or by adding a portion of them as raw materials. As shown in Fig. 1a, the two characteristic peaks at 13.4° and 27.3° correspond to the (100) and (002) planes of carbon nitride, representing the classical periodic graphite stacking of the in-plane repeat and the conjugated aromatic system of the 3-s-triazine ring motif, respectively. Thereafter, it can be observed that the (100) peak gradually disappeared and the (002) peak became weaker with the addition of KOH, implying a disrupted aromatic system and inhibited accumulation inside the samples, thus adjusting the nanostructure to modulate the electronic structure with promoted capacity for oxygen adsorption and proton activation. Besides, Fourier transform infrared (FTIR) spectra was utilized to analyze the characteristic peaks of samples accordingly. As exhibited in Fig. 1b, the characteristic respiration pattern of the triazine unit was observed at the position of 802 cm$^{-1}$, and the aromatic structure of the formation of C-N-C=N bonds was at 1300–1654 cm$^{-1}$. Interestingly, the emerging peak at 2177 cm$^{-1}$ was attributed to the formation of cyano groups, demonstrating enhanced an cyano group peak in MTCN as compared to CN, which might be attributed to the addition of KOH and is beneficial for the introduction of the cyano group into the structure of carbon nitride by the etching effect of KOH during the calcination process. It is worth mentioning that it is hard to observe the peak connected with S-related functional groups, which is ascribed to a lower percentage of sulfur doping or overlapping with C–N bond peaks. Additionally, fragmented structures with varying thickness can be observed in MTCN, implying that the addition of KOH can etch the material surface to some extent (Fig. 1c, d and Fig. S1†). Furthermore, the thicknesses of CN and MTCN were measured using an atomic force microscope (AFM), and it can be observed that the average thicknesses of CN and MTCN were 20.28 nm and 21.88 nm, respectively (Fig. S5†).

X-ray photoelectron spectroscopy (XPS) was carried out to investigate the chemical environment of elements in samples. As shown in the C 1s spectra (Fig. 1e), the peaks could be divided into three peaks at 284.6 eV, 286.3 eV, and 288.0 eV, ascribed to the C=C bond, the tertiary carbon C$_3$ bonds, and the sp$^3$-hybridized carbon in the aromatic rings (N–C=N), respectively. Intriguingly, the reduced proportion of N–C=N and the increased cyano group content in MTCN compared to CN further disclosed the fact that KOH addition might lead to the breaking and reconstitution of chemical bonds at the N–C=N site. The N 1s spectra in Fig. 1f could be divided into three peaks at 398.6, 400.2, and 401.3 eV, corresponding to bi-coordinated N (N$_2$C), tri-coordinated N (N$_3$C), and amino N (–C-NH$_2$). The significant shift of N–(C)$_3$ groups toward a lower binding energy from the N 1s XPS might be caused by the emerging cyano group, with binding energy between N$_2$C and N$_3$C. As displayed in Fig. 1g and Fig. S6, the S 2p spectra exhibit two peaks at around 164.0 and 168.43 eV, corresponding to the C=S bond and surface adsorbed sulfate, respectively. Furthermore, a shift to a lower binding energy could be observed for the C=S bond, confirming the C=S bond emerging with the S doping at the N position. In addition, a slightly increasing trend was observed for O 1s peaks that may be attributed to the higher O$_2$ adsorption capacity of the
In order to further confirm the existence of the cyano group, solid-state $^{13}$C NMR measurement was employed (Fig. 1h). The spectra showed two strong peaks at 138.97 and 131.87 ppm associated with the carbon atom in C$_{3N}$ and C$_{2N}$ in the triazine ring, respectively. The peak at 117.27 ppm was consistent with the chemical shift of the cyano group. The NMR result confirmed the appearance of the cyano group in the C$_3$N$_4$ structure. Furthermore, it can be observed that the introduction of cyano groups and S atoms could affect the electronic structure of g-C$_3$N$_4$, as shown in Fig. 1i. Intriguingly, the Lorentz lines of all samples have the same $g$ value ($g = 2.062$) owing to the sp$^2$-carbon atoms in the p-conjugated aromatic rings generating the same type of unpaired electrons and the corresponding intensity of the groups. This is mainly due to the strong electron-withdrawing characteristic of the cyano groups. Since a higher electron paramagnetic resonance (EPR) intensity is the evidence of a higher concentration of uncoordinated electrons, it can be inferred that the addition of KOH and the appropriate ratio of melamine to thiourea benefit the formation of more abundant reactive sites, which provides more advantages for the adsorption capacity of O$_2$ and the production of H$_2$O$_2$. The above results indicate that the co-modification of the dual defect sites optimizes the electronic structure of C$_3$N$_4$, and this electron-rich structure would be beneficial to providing more electrons to participate in photocatalysis. Meanwhile, the decreased surface area of MTCN as compared to CN, MCN, and TCN might be ascribed to the fact that the addition of KOH might destroy the original structure of the material (Fig. 1j and Table S1†). Additionally, the EDX spectrum and its corresponding element mapping are shown in Fig. 1k and l, giving the average distribution of the elements inside MTCN.

2.2. Band structure

The detailed band structures of the photocatalysts were investigated and calculated through a series of characterizations, and the results are displayed in Fig. 2. As shown in Fig. 2a, stronger light absorption was observed for MTCN compared with CN, MCN, and TCN, which is consistent with the color change of the four samples. The red-shifted light absorption edge of MTCN has been extended to 520 nm, but is nearly 471 nm for CN, and is attributed to the introduction of the cyano group and sulfur atoms to some extent. The band structure was calculated based on the UV-vis DRS via the Kubelka-Munk function (Fig. 2b), and a narrower bandgap was observed for MTCN (2.67 eV) compared to bulk CN (2.84 eV).

Additionally, the conduction band (CB) and valence band (VB) were further calculated through the VB XPS spectra and
Mott–Schottky plots. As exhibited in Fig. 2c, a VB of 1.83 eV was observed for CN, while a 1.77 eV position was detected for the other three samples. Moreover, the flat-band potentials \( (E_{FB}) \) of the above four samples were estimated from the Mott–Schottky plots (Fig. 2d and Fig. S8–S10†). All samples exhibited n-type characteristics, and the EFB of the Mott–Schottky plot test sample was approximately equal to its conduction band potential. Therefore, the CB potentials of the four samples were determined to be \(-1.01\), \(-0.98\), \(-0.91\) and \(-0.9\) eV \( \text{vs. Ag/AgCl, pH = 7} \), which were consistent with the UV-vis DRS and VB XPS data.

### 2.3. Photocatalytic H\(_2\)O\(_2\) generation

Photocatalytic H\(_2\)O\(_2\) generation was investigated in a neutral environment (pH = 7). As shown in Fig. 3a, an optimum H\(_2\)O\(_2\) generation of 1.703 mM h\(^{-1}\) (68.12 mM g\(_{\text{cat}}\) h\(^{-1}\)) could be achieved, nearly 10 times that of CN, with the ratio 1/9 of melamine and thiourea (named MTCN), attributed to the synergistic effect of the functional group and S atom doping. The performance of MTCN before and after washing several times was further evaluated to determine the light utilization efficiency of MTCN (Fig. 3e and Table S2†). It was clearly observed that the curve made by the AQY values of MTCN matches well with its absorption spectrum, with a remarkable AQY up to 64.46% at 365 nm and 49.01% at 420 nm. In addition, CN’s photocatalytic H\(_2\)O\(_2\) generation was explored without the addition of any sacrificial agent, in addition to its performance under simulated visible light irradiation (Fig. 3f). Intriguingly, H\(_2\)O\(_2\) generation of 16.46 \( \mu \text{M} \) was observed in pure water, and a production of 749.17 \( \mu \text{M} \) (7.49 mM g\(_{\text{cat}}\) h\(^{-1}\)) could be achieved under visible light irradiation in a mixed solution with ethanol, demonstrating the outstanding photocatalytic performance of MTCN. This performance is superior to those of the most recent reports in terms of pure water systems (Fig. 3g and Table S3†). As seen in Fig. 3h, the preservation of 71% of the initial activity after 10 reactions manifests the excellent stability of MTCN in photocatalytic O\(_2\) reduction to H\(_2\)O\(_2\), and the XRD pattern, TEM images and FTIR spectra of the sample after 10 cycles (Fig. S12–S14†) exhibit no obvious changes compared to those of the pristine catalyst.

### 2.4. H\(_2\)O\(_2\) generation paired with simultaneous contaminant treatment

Following this, the alcohol-free H\(_2\)O\(_2\) generation was further investigated with the addition of contaminants. As demonstrated, the reaction of photocatalytic H\(_2\)O\(_2\) generation and further wastewater treatment were carried out in a neutral environment (pH = 7). As exhibited in Fig. 4a, using RhB as a typical contaminant, the H\(_2\)O\(_2\) generation performance in 50 mg L\(^{-1}\) RhB solution reached 1.26 mM g\(_{\text{cat}}\) h\(^{-1}\), which was 7 times that of pure water. Furthermore, the performance of this reaction was also detected in air, demonstrating its future in practical application in industry. In order to investigate the ability of the as-synthesized photocatalyst when dealing with different concentrations of sewage, the reactions were carried out in RhB solutions with different concentrations. It can be observed in Fig. 4b and c that multiplying the concentration of contaminant did not lead to an increase in H\(_2\)O\(_2\) generation performance, which might be a result of the increasing utilization of H\(_2\)O\(_2\) for further degradation. Following this, we chose a contaminant concentration of 100 mg L\(^{-1}\) and further explored the in situ simultaneous photocatalytic H\(_2\)O\(_2\) generation and contaminant treatment activities of different contaminants (Fig. 4d and e), suggesting that MTCN is suitable for systems with different contaminants.

Additionally, given the importance of environmental conditions, the in situ photocatalytic H\(_2\)O\(_2\) generation with simultaneous contaminant treatments at different pH values was evaluated (Fig. 4f and g). Different from the activity regulation of H\(_2\)O\(_2\) generation, a promoted degradation performance could be observed in acidic environments, while superior H\(_2\)O\(_2\) generation can be observed at pH 7, attributed to the fact
that the rapid degradation of contaminants causes the \( \text{H}_2\text{O}_2 \) generation system to tend towards a pure water system. Additionally, the cycle test in Fig. 4h and i manifested the maintained stability of MTCN over 5 cycles, demonstrating the sustainable utilization of this photocatalyst for the further application of MTCN in environmental treatment. Moreover, the scaled-up reaction was carried out with 250 mg photocatalyst in a 500 mL reaction system in air atmosphere and the outstanding performance further implied the practical application value of MTCN (Fig. S15†).

2.5. Photo-generated charge carrier dynamics for photocatalysts and radical investigation during the photocatalytic process

The separation and recombination behaviours of the charge carriers were first investigated by photoluminescence and time-resolved photoluminescence spectra. The PL spectra were acquired at an excitation wavelength of 400 nm at room temperature (Fig. 5a). MTCN displayed a decreased PL intensity compared to the strong and broad emission peak of CN, implying promoted charge separation and suppressed recombination of photo-excited carriers. The time-resolved fluorescence decay spectra of samples were also studied (Fig. 5b and Table S4†), and the average lifetimes of CN and MTCN were 0.6462 ns and 0.6454 ns, respectively. The above results together demonstrated the remarkable ability of MTCN to suppress carrier recombination, which is related to the rapid capture of electrons by the dual defects. In addition to the PL and lifetime measurements, the charge transfer efficiency was determined using transient photocurrent response spectra, electrochemical chemical impedance spectra, and linear sweep voltammetry plots (Fig. 5c–e). These substantiated that MTCN has a lower mass transfer impedance, a better carrier transfer performance and a larger current density. This phenomenon can be attributed to the introduction of cyano groups and S doped sites, which successfully built an internal electric field to promote separation of photogenerated carriers.34,53

To unravel the reactive species responsible for the photocatalytic \( \text{H}_2\text{O}_2 \) production, \( p\)-BQ, TEMP, TEMPO and DDQ were
used as 'O$_2^-$, ^1O$_2$, 'OH, and e$^-$ scavengers, respectively (Fig. 5f). The generation activity dropped sharply when BQ and DDQ were used as scavengers, demonstrating that electrons and 'O$_2^-$ both play an essential part in H$_2$O$_2$ generation. Furthermore, a similar inhibition phenomenon was observed when TEMP was utilized as the scavenger, attributed to the fact that the catalysts could reduce ^1O$_2$ to 'O$_2^-$ through a two-electron reaction pathway ($^1$O$_2$ $\rightarrow$ 'O$_2^-$ $\rightarrow$ H$_2$O$_2$). Meanwhile, both 'O$_2^-$ and ^1O$_2$ could react with electrons to produce H$_2$O$_2$, thus realizing promoted H$_2$O$_2$ generation performance. In addition, EPR tests were conducted to further identify the free radicals acting in the H$_2$O$_2$ generation process. In Figures 5g and S16, the signals for superoxide 'O$_2^-$ and ^1O$_2$ were observed under light irradiation, indicating their roles as reactive species in the subsequent processes. This observation is consistent with the findings from the free radical trapping experiments. Additionally, to further explore H$_2$O$_2$ generation and RhB degradation, the corresponding free radical trapping experiment and EPR spectra are displayed. p-BQ, TEMP, TEMPO, DDQ and EDTA-2Na were used as 'O$_2^-$, ^1O$_2$, 'OH, e$^-$, h$^+$ scavengers, respectively (Fig. 5h and Fig. S17†). Interestingly, it can be concluded that h$^+$ played a vital role in contaminant degradation. Moreover, it can be observed that the degradation activity dropped sharply when TEMPO was used as the scavenger, demonstrating that 'OH plays a vital role in this process, as further confirmed by the EPR spectra in Fig. 5i.

2.6. Mechanism of photocatalytic oxygen activation and proton adsorption on theoretical calculation

To gain deep insight into the activation mechanism of each defect site (S atoms and cyano group) during the photocatalytic 2e$^-$ ORR process, we established C$_3$N$_4$ model compounds with different defect structures in the activation process (CN, S-C$_3$N$_4$ and CN-C$_3$N$_4$ are pristine C$_3$N$_4$, S atom doped C$_3$N$_4$ and cyano group modified C$_3$N$_4$, Fig. S18†) and performed density functional theory (DFT) calculations to study the elementary steps of photocatalytic 2e$^-$ ORR. Based on the construction of models over various samples, the charge differences between O$_2$ and C$_3$N$_4$ with different structures are displayed in Fig. 6a–c and confirm the O$_2$ adsorption over various samples. Compared with CN, the charge redistribution between oxygen
and S-C₃N₄ is more moderate, reflecting the stronger interaction when S atoms are introduced to replace N atoms and demonstrating the promoted O₂ adsorption of samples during the photocatalysis. Furthermore, when cyano groups were further introduced along with the S atoms, the strongest O₂ adsorption was observed for the model of MTCN.

The free energy diagram of the H₂O₂ generation reaction path of each model is shown in Fig. 6d. The free energies of O₂* of S-C₃N₄ (−0.1032 eV) and MTCN (−0.2718 eV) are much lower than those of CN (−0.005663 eV) and CN-C₃N₄ (−0.0496 eV), demonstrating that the doping of S atoms could effectively reduce the free energy of oxygen adsorption. Moreover, the simulation calculations showed that the most favorable H⁺ absorption sites on CN-C₃N₄ and MTCN were the cyano groups. The free energy of the absorption of H⁺ on CN-C₃N₄ (0.133037 eV) is lower than that of CN (0.279992 eV), and that of MTCN (−0.139817 eV) is lower than that of S-C₃N₄ (0.241436 eV), demonstrating that the appearance of the cyano group effectively activates hydrogen protons, which is consistent with the previous reports. In addition, it can be observed that OOH* and H₂O₂ were formed with the lowest free energy path using MTCN, further proving that the introduction of S atoms and cyano groups is advantageous for OOH* formation and further H₂O₂ generation.

Based on the series of experiments and theoretical calculations, the possible mechanism of MTCN in photocatalytic H₂O₂ generation or simultaneous H₂O₂ generation over organic contaminant treatment is revealed in Fig. 7. The electrons and holes boosted by the absorption of photons over MTCN could quickly be transferred to the active sites under the irradiation of solar light. Meanwhile, RhB and ethanol acted as sacrificial agents and were oxidized by the holes, thus generating many H protons. The efficient separation of the photogenerated electron–holes can oxidize H₂O to release O₂. Accordingly, the main ORR pathway of photocatalytic H₂O₂ generation was a two-step single electron oxygen reduction.
reaction. When RhB or some other contaminants were introduced as sacrificial agents, part of the generated H₂O₂ could be split into \( \cdot \text{OH} \) and engage in the degradation reaction, while the promoted charge transfer might accelerate the H₂O generation.

3. Conclusions

In summary, the cyano group and S atoms were introduced into C₃N₄ through a simple one-step method, and this study delved into how the dual defect sites modify the structure to boost the absorption of oxygen and promote the H proton activation that increased the reaction activity for photocatalytic H₂O₂ generation and contaminant treatment. The production of H₂O₂ by MTCN reached 68.12 mM g⁻¹ h⁻¹, outstanding compared to other reported photocatalysts. Furthermore, the reactivity of alcohol-free H₂O₂ generation in contaminant solutions reached 3.244 mM g⁻¹ h⁻¹, which was 7 times higher than that in pure water. Additionally, through a series of meticulous experimental characterizations and theoretical calculations, the key roles of the S atoms and cyano group in the photocatalytic reaction were clearly identified: facilitating O₂ and H⁺ adsorption, respectively. This work provides a new idea for the design and synthesis of environmentally functional materials in practical sustainable development.

Author contributions


Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Natural Science Foundation of Zhejiang Province (LQ23B030003), the National Natural Science Foundation of China (no. 22171064), and Hangzhou Normal University.

References


