Supplementary Material

Green and alcohol-free H_2O_2 generation paired with simultaneous contaminant treatment enabled by sulfur/cyano-modified $g-C_3N_4$ with efficient oxygen activation and proton adsorption

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Summary of the supporting information: 27 pages, 5 Tables, and 18 Figures

Chemical materials

Commercial reagents were utilized as received without additional purification. Melamine, thiourea, ethanol (EtOH, 99.99%), *n*-propanol (99.9%), *i*-propanol (HPLC), methanol (99.9%), *t*-butanol (99.9%), phemethylol (99.9%) were purchased from the National Pharmaceutical Company (China). 1,4-Benzoquinone (BQ, 98%), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 99%), 2,2,6,6-tetramethyl-1-piperidi-nyloxy (TEMPO, 98%), 2,2,6,6-tetramethylpi (TEMP, 98%) were supplied by Sigma-Aldrich Company. Methylene blue (MB, 99%), Rhodamine B (RhB, 99%), Methyl orange (MO, 99%) were purchased from Macklin Biochemical Company. Potassium hydroxide (KOH), hydrogen chloride (HCl) potassium chloride (KCl), potassium iodide (KI), sodium sulphate (Na_2SO_4), potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium hexacyanoferrate ($K_4Fe(CN)_6 \cdot 3H_2O$), barium sulfate ($BaSO_4$), silver nitrate ($AgNO_3$) were obtained from Sinopharm Chemical Reagent Company. Deionized water was prepared by the Hitech laboratory water purification system (R = 18.25 kohm).

The preparation of photocatalysts

Synthesis of CN: The mixture of melamine and thiourea in different proportions was placed in a crucible in a muffle furnace. Briefly, 9 g thiourea and 1 g melamine were mixed together in a lidded crucible, and was calcined at 550 °C for 4 h with a heating rate of 10 °C min^{-1}, the final product was named as CN.

Synthesis of MCN: 10 g melamine was added to the flask, along with the addition of 30 mL KOH solution (26.67 g L^{-1}) for dissolving, and the solution was transferred to a clean surface dish and was dried an oven at 120 °C. In this case, the dried powder was calcined at 550 °C for 4 h in a muffle furnace, the final product was named as MCN.

Synthesis of TCN: 10 g thiourea was added to the flask, along with the addition of 30 mL KOH solution (26.67 g L^{-1}), and the solution was transferred to a clean surface dish and was dried an oven at 120 °C. The dried powder was calcined at 550 °C for 4 h in a muffle furnace, the final product was named as TCN.

Synthesis of MTCN: Melamine and thiourea (10 g) were added to the flask at a certain mass ratio (1/9, 3/7, 5/5, 7/3, 9/1), with the addition of 30 mL KOH solution (26.67 g L^{-1}) for dissolving, and the solution was transferred to a clean surface dish and was dried an oven at 120 °C. In this case, the dried powder was calcined at 550 °C for 4 h in a muffle furnace.

The photocatalytic reduction of O_2 into H_2O_2

In a typical reaction, 25 mg photocatalyst was dispersed in a mixed solution containing 45 mL H_2O and 5 mL sacrificial agent (e.g. ethanol, *n*-propanol, *i*-propanol, methanol, *t*-butanol, phemethylol) in a quartz tube, with dark adsorption for 20 min to ensure the adsorption-desorption equilibrium. The pH was adjusted to specific values varying from 3 to 11 using 0.1 M NaOH and HCl. Following that, the reaction solution was irradiated with a 300 W xenon lamp equipped with AM 1.5 or cut 420 filter as the simulated light source. Samples are taken at regular intervals and was treated with a 0.22 μm filter for the measurement of H_2O_2 generation.

Free radical capture experiments were conducted to explore the existing radicals in the reaction. Add the radical capture agents (*p*-BQ, TEMP, TEMPO, DDQ) to capture superoxide radicals ($\cdot O_2^-$), singlet oxygen ($^1O_2$), hydroxyl radicals ($\cdot OH$) and electrons (e^-). In a typical reaction, 25 mg photocatalyst and 0.3 mmol free radical capture agents were added into a mixed solution containing 45 mL H_2O and 5 mL sacrificial agent (e.g. ethanol, *n*-propanol, *i*-propanol, methanol, *t*-butanol, phemethylol) in a quartz tube, with dark adsorption for 20 min to ensure the adsorption-desorption equilibrium. Following that, the reaction solution was irradiated with a 300 W xenon lamp equipped with AM 1.5 filter as the simulated light source. Samples are taken at regular intervals and was treated with a 0.22 μm filter for the measurement of H_2O_2 generation.

H_2O_2 quantification methods

Iodine dosimetry was employed to study the H_2O_2 generation in this system, based on a standard curve detected using Ultraviolet-visible (UV-vis) spectroscopy. In a typical procedure, 500 μL filtrate, 50 μL of $(NH_4)_6MoO_{24} \cdot 4H_2O$ (0.01 M), and 2000 μL of KI solution (0.1 M) were mixed together, and the absorbance of the sample at 350 nm was determined with UV-vis spectroscopy after standing for 30 s.

Photocatalytic H_2O_2 generation and pollutants degradation

In a typical reaction, 25 mg photocatalyst was dispersed in a solution (with the concentration of RhB of 100 mg L^{-1}) in a quartz tube, with dark adsorption for 20 min to ensure the adsorption-desorption equilibrium. The pH was adjusted to specific values varying from 3 to 11 using 0.1 M NaOH and HCl.

Following that, the reaction solution was irradiated with a 300 W xenon lamp equipped with AM 1.5 as the simulated light source. Samples are taken at regular intervals and was treated with a 0.22 μm filter for the measurement of H_2O_2 generation.

Free radical capture experiments were conducted to explore the existing radicals in the reaction. Add the radical capture agents (*p*-BQ, TEMP, TEMPO, DDQ) to capture superoxide radicals ($\cdot O_2^-$), singlet oxygen ($^1O_2$), hydroxyl radicals ($\cdot OH$) and electrons (e^-). In a typical reaction, 25 mg photocatalyst and 0.3 mol free radical capture agents were dispersed in 50 mL solution (with the concentration of RhB: 100 mg L^{-1}) in a quartz tube, with dark adsorption for 20 min to ensure the adsorption-desorption equilibrium. Following that, the reaction solution was irradiated with a 300 W xenon lamp equipped with AM 1.5 filter as the simulated light source. Samples were taken at regular intervals and was treated with a 0.22 μm filter for the measurement of H_2O_2 generation.

Characterizations

The crystalline structures of samples were determined by X-ray diffration (XRD, RigakuD/MAX 2550) patterns with Cu Kα radiation source. The Fourier transform infrared (FTIR, Nicolet Magna 550) and the X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA) were applied to detect the characteristic groups and the change of chemical bonds of samples. The solid-state ^{13}C NMR spectra of the sample was tested by German Bruker 500M standard cavity CP MAS probe-BL4. The microstructure of samples was characterized by transmission electron microscope (TEM, JEM-1400), high-resolution transmission electron microscope (HRTEM, JEM-2100) and scanning electron microscope (SEM, S-4800) image. The thickness of the samples was investigated by a nano-scale atomic force microscope (AFM, E-Sweep, Seiko, Japan). The room temperature electron paramagnetic resonance (EPR) spectroscopy was performed on JES X320 spectrometer. The ultraviolet–visible (UV-vis) spectra were carried out through a spectrophotometer (UV-5100B) furnished with an integrating sphere assembly. And the light absorption ability of samples was got from a Scan ultraviolet visible (UV-vis) spectrophotometer (UV-2400), with BaSO$_4$ as the reflectance sample. The photoluminance spectra of the samples were tested at room temperature excited by an incident light of 350 nm by using a spectrofluorophotometer (Shimadzu, RF-5301). Steady and time-resolved fluorescence emission spectra were recorded at room temperature with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). Electrochemical and photoelectrochemical analyses were performed by an electrochemical workstation (CHI660E) in a three-electrode setup. The Pt plate electrode was used as a counter electrode, Ag/AgCl electrode was applied as the reference electrode, and Indium Tin Oxide (ITO) covered with different materials was donoted as the working electrode. Transient photocurrent and Mott-Schottky curve measurements were performed with 0.5 M Na$_2$SO$_4$ as an electrolyte, electrochemical impedance spectroscopy (EIS) measurements were performed with 25 mM K$_3$[Fe(CN)$_6$], 25 mM K$_4$[Fe(CN)$_6$] and 0.1 M KCl mixed aqueous solution as the electrolyte, linear sweep voltammetry (LSV) measurements were performed with 1 mM K$_3$[Fe(CN)$_6$] and 1 M KCl mixed aqueous solution as the electrolyte.

Measurements and calculations of AQY

The apparent quantum yield (AQY) of photocatalytic H_2O_2 generation was measured under the similar photocatalytic reaction condition except for the light source. The light source was 300 W Xenon lamp equipped with monochromatic mass filter at 365, 420, 475, and 520 nm, respectively, with an irradiation time of 1 h.

The AQY was calculated using the equation (1) and (2)

$$AQY = \frac{2 \times H_2O_2 \, formed \, (mol)}{the \, number \, of \, incident \, photons \, (mol)} \times 100\% \tag{1}$$

$$The \, number \, of \, incident \, photons \, (mol) = \frac{E\lambda}{h\upsilon} \times 100\% \tag{2}$$

where E, λ, h and ʋ represent the energy absorbed by Xenon lamp (Light intensity = 13.12 mW cm^{-2}, the irradiated area = 1.69 cm^2, and the irradiation time = 3600 s), the wavelength of the light (365 nm, 420 nm, 475 nm, 520 nm), Planck constant (6.626×10^{-34} J s) and speed of light (3×10^8 m s^{-1})

Theoretical calculations

In this work, vienna ab-initio Simulation Package (VASP) was applied for density functional theory (DFT) calculations. The description of core-valance electron interaction adopted Projected Augmented Wave (PAW) method.[1, 2] Generalized-gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional form was introduced to handle the electron exchange and correlation effects.[3, 4] Monkhorst-Pack grid of 2×2×1 was employed for calculation. Energy cutoff of 400 eV for plane-wave basis was set to ensure the computational precision. Meanwhile, vacuum layer with 20 Å were applied in all slab models to avoid the vertical interactions between C_3N_4 monolayer. The atomic positions were fully relaxed until each atom's remaining force was less than 0.05 eV/Å. For the adsorption over substrate, long-range van der Waals interactionwas simulated with the DFT-D3 method.[5] The proton-coupled electron transferring was calculated via the computational hydrogen electrode (CHE) mode. The steps for O_2 hydrogenation to produce H_2O_2 were illustrated according to eqs. (3)-(6):

$$* + O_2 \rightarrow *O_2 \tag{3}$$

$$O_2 + H^+ + e^- \rightarrow *OOH \tag{4}$$

$$*OOH + H^+ + e^- \rightarrow *H_2O_2 \tag{5}$$

$$*H_2O_2 \rightarrow * + H_2O_2 \tag{6}$$

During which, gibbs free energies (G) were defined by eq. (7):

$$G = E_{DFT} + E_{ZPE} - TS \tag{7}$$

where EDFT, EZPE and TS are the electronic energy, zero-point energy and entropy, respectively. All gibbs free energies for comparation were given at 298.15 K.
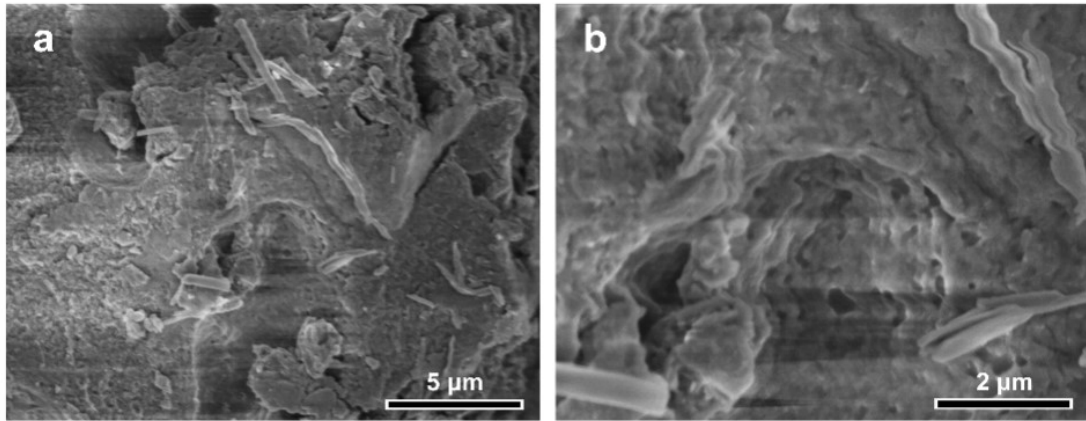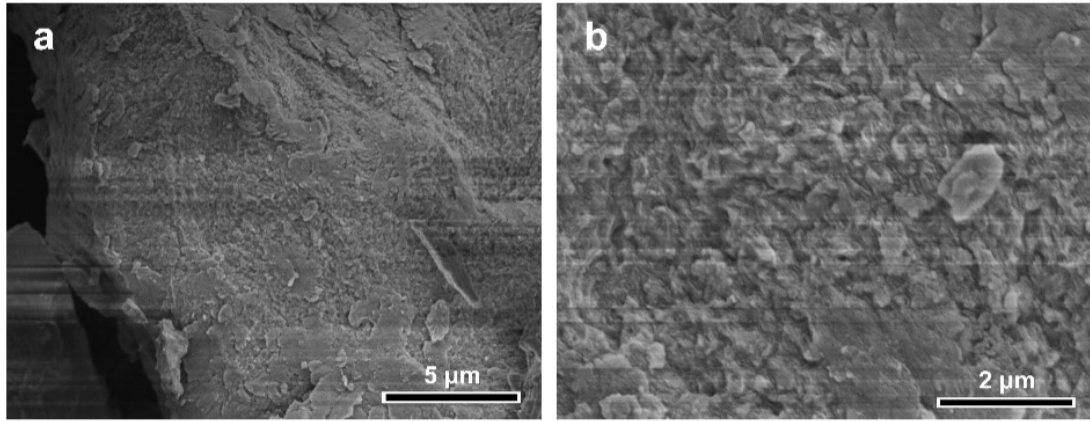
Figure S1. SEM images of CN.
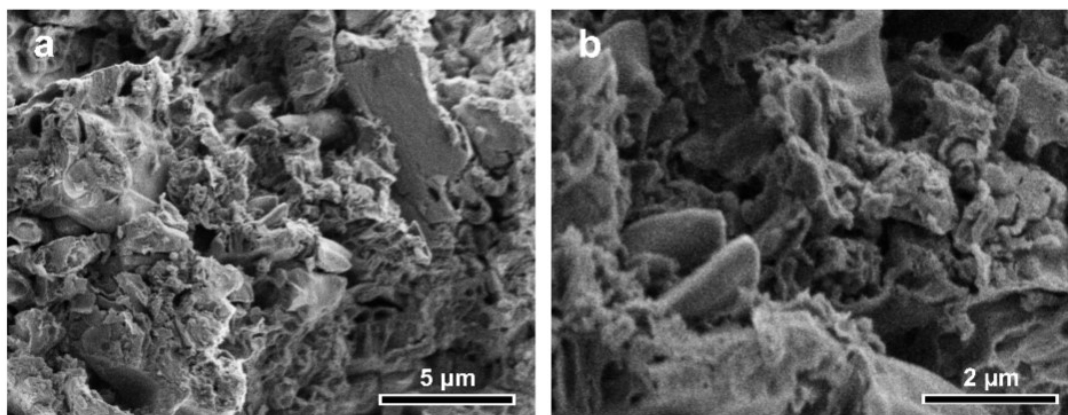
Figure S2. SEM images of MCN.
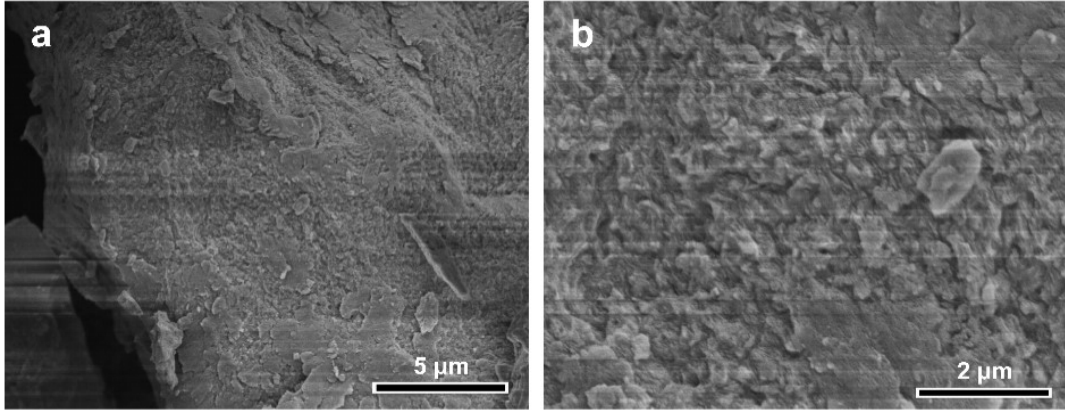
Figure S3. SEM images of TCN.
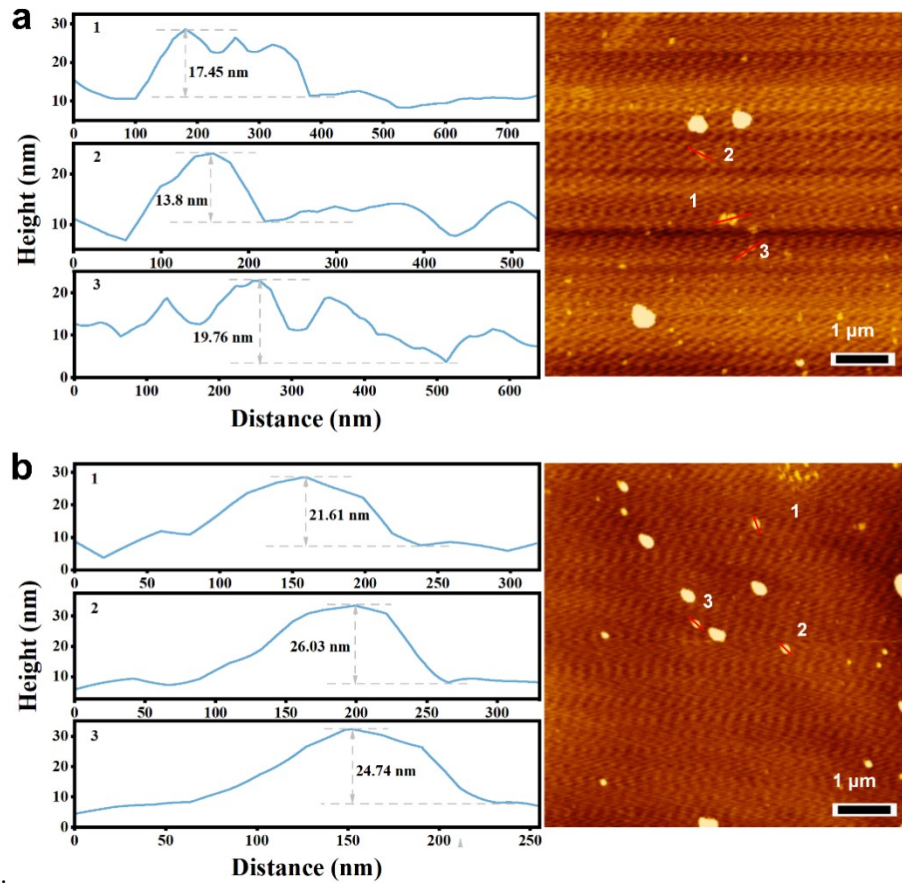
Figure S4. SEM images of MTCN.
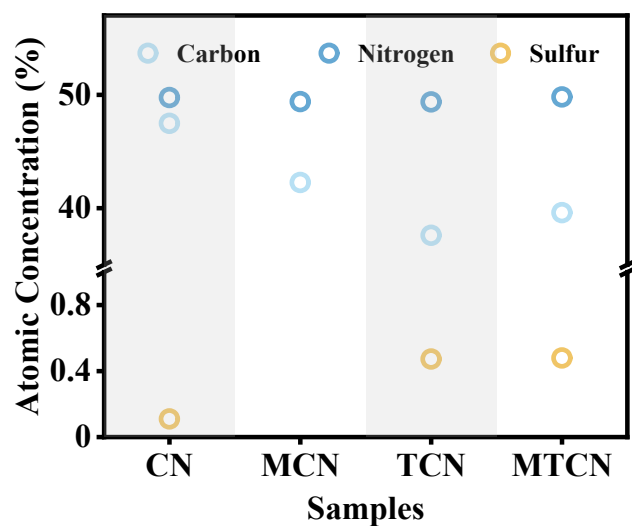
Figure S5. AFM images of (a) CN and (b) MTCN.

Figure S6. The proportion of elements in samples determined by XPS.
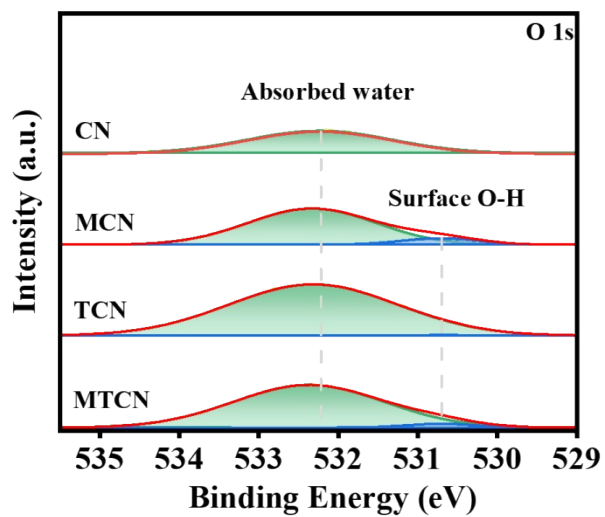
Figure S7. O 1s XPS spectra.

The O 1s spectrum exhibits two peaks at around 530.80 and 532.46 eV, corresponding to absorbed water and surface adsorbed O-H,[6, 7] which may contribute to the residue of water and alkali during sample treatment.
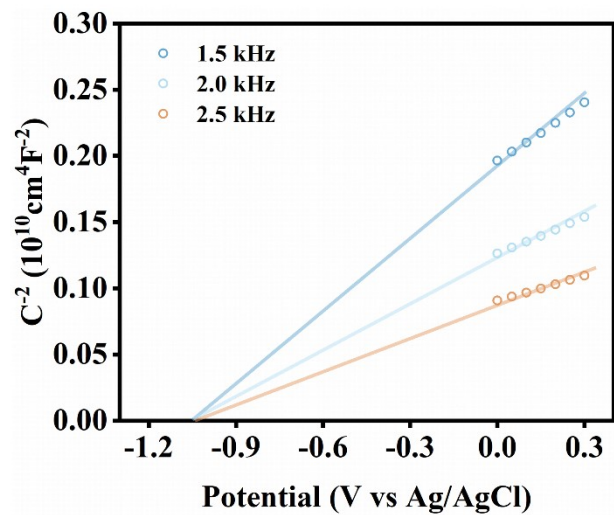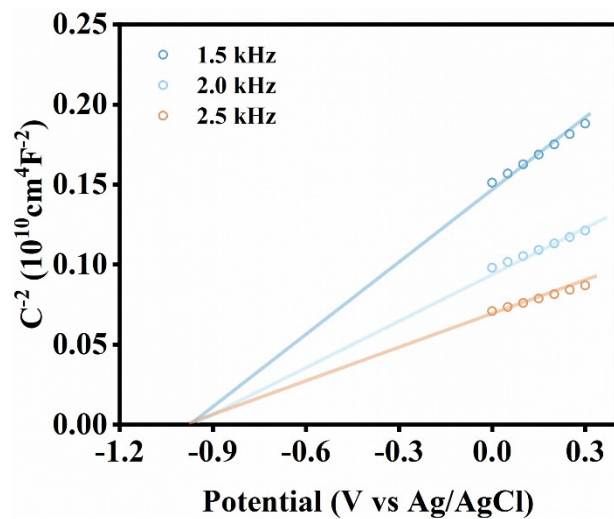
Figure S8. Mott-Schottky plots of CN.
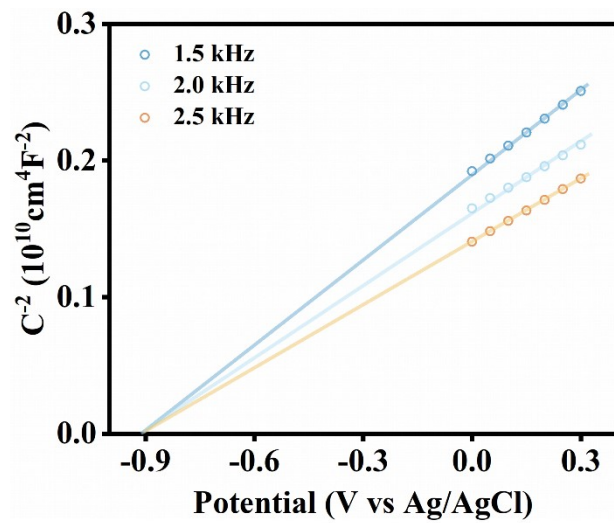
Figure S9. Mott-Schottky plots of MCN.
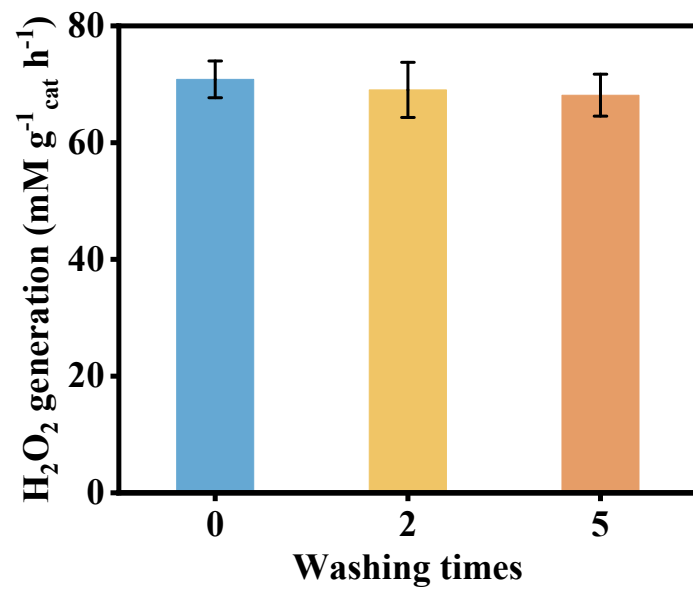
Figure S10. Mott-Schottky plots of TCN.

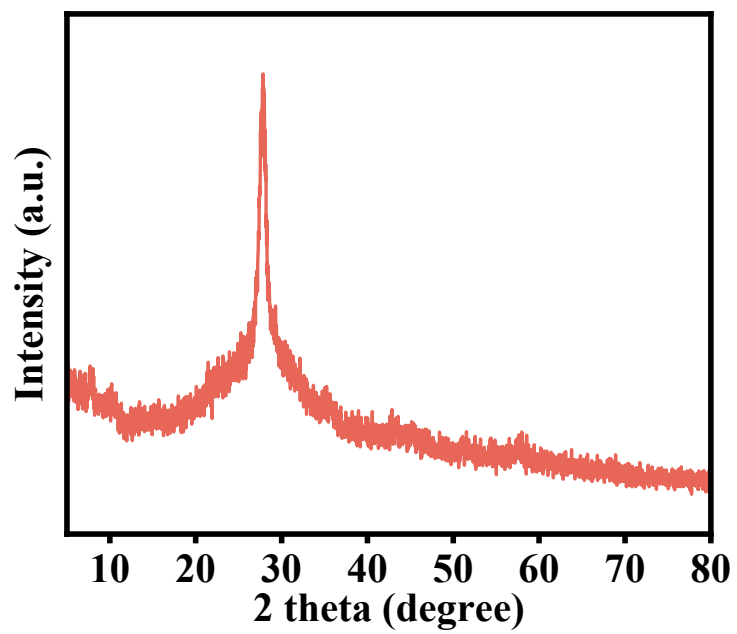**Figure S11.** Comparison of H_2O_2 generation of MTCN with varying washing times.

Figure S12. XRD pattern of MTCN after 10 cycles.

Figure S13. TEM image of MTCN after 10 cycles.
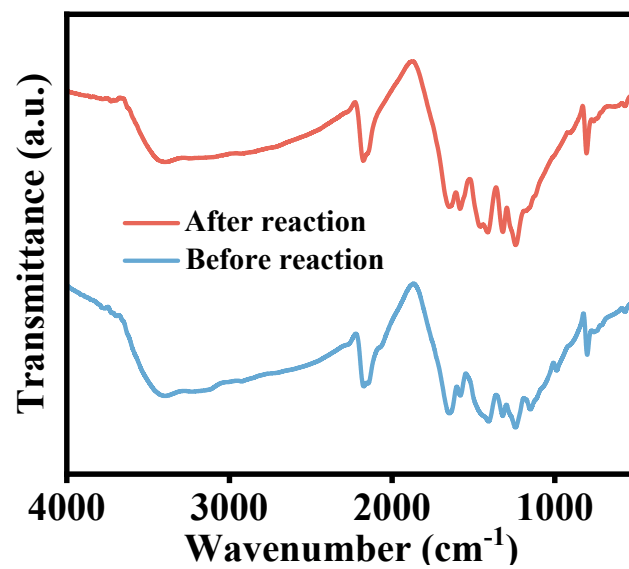
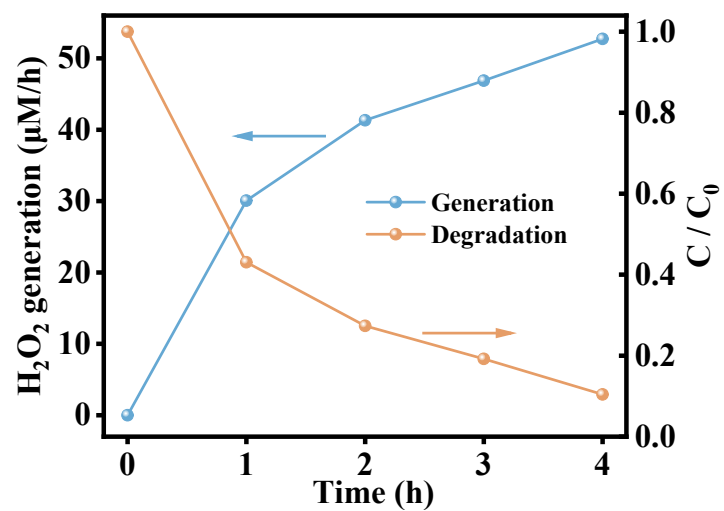**Figure S14.** FTIR spectra of MTCN after 10 cycles.

Figure S15. The scale-up reaction of in-situ H_2O_2 generation and organic pollutants over MTCN.
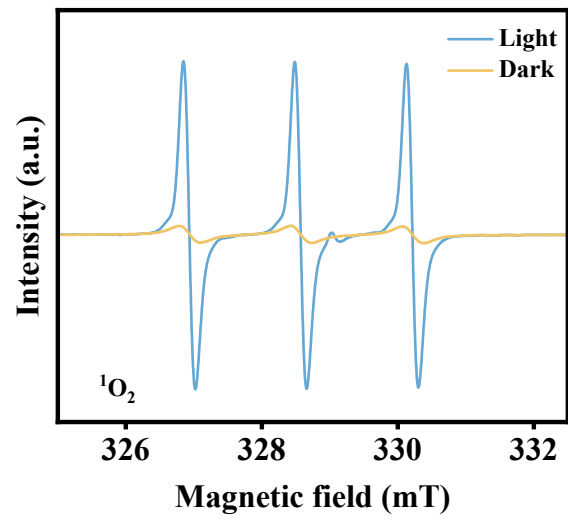
Figure S16. EPR spectra of $^1O_2$ of H_2O_2 generation of MTCN.
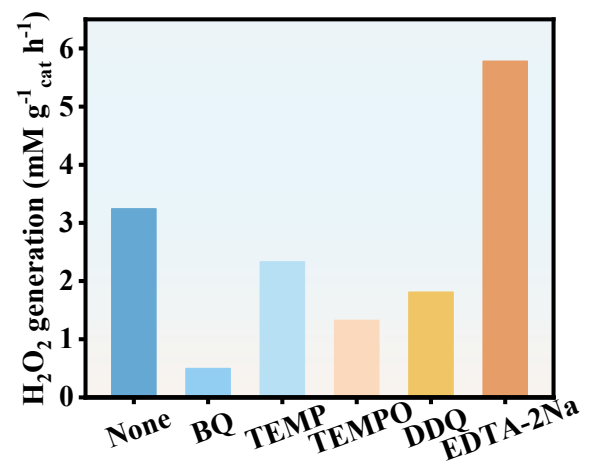
Figure S17. H_2O_2 generation performance of free radical trapping experiment of simultaneous reaction without the addition of alcohol.
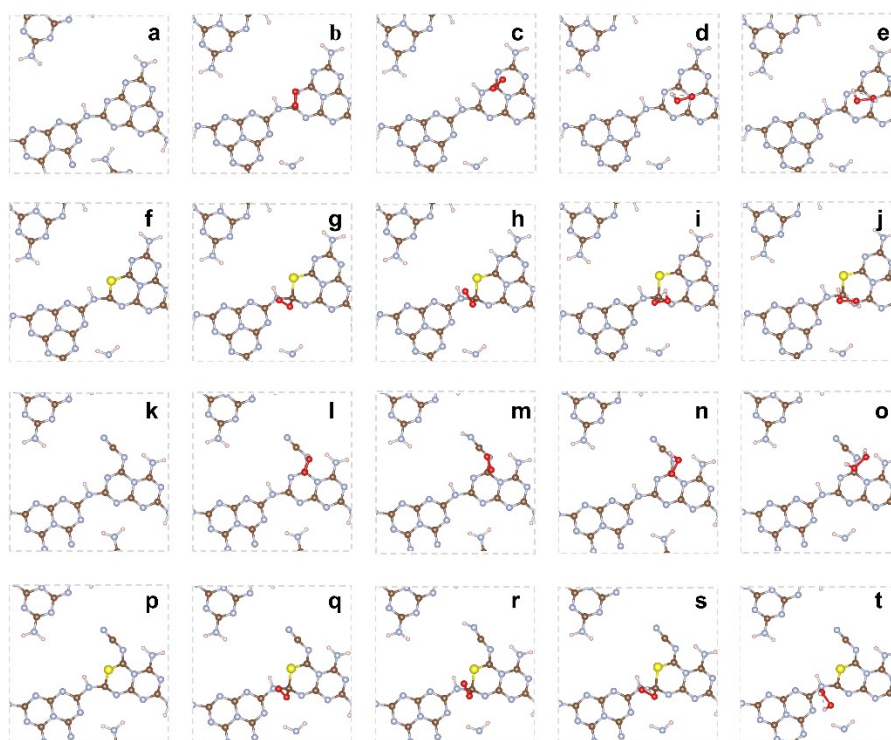
Figure S18. The activation process of defect modified C_3N_4, (a-e) CN, (f-j) S-C_3N_4, (k-o) CN-C_3N_4 and (p-t) MTCN: a, f, k and p are the models of CN, S-C_3N_4, CN-C_3N_4 and MTCN, respectively; a-e, f-j, k-o and p-t represent the O_2 activation and ORR H_2O_2 generation reaction process on each model.

Table S1. BET specific surface areas (m^2 g^{-1}) of CN, MCN, TCN and MTCN.

Samples	CN	MCN	TCN	MTCN
BET surface area (m^2/g)	10.0189	1.9074	0.1555	0.4434
Average Pore diameter (nm)	29.9984	50.4241	76.2079	30.8653
Total pore volume (cm^3/g)	0.02248	0.01617	0.00184	0.00243
Micropore volume (cm^3/g)	0.001117	0.000689	0.000181	0

Table S2. The wavelength-dependent AQY for photocatalytic H_2O_2 generation by MTCN. Conditions: 10% EtOH, pH=7, 0.5 g L^{-1} catalyst.

Wavelength (nm)	365	420	475	520
H_2O_2 generation (μmol)	46.436	44.282	0.903	0.727
Light intensity (mW cm^{-2})	13.12	14.3	11.2	14.8
Irradiation area (cm^2)	42.99	42.99	42.99	42.99
Irradiation time (h)	1	1	1	1
AQY (%)	64.46	49.01	1.12	0.62

Table S3. Photocatalytic H_2O_2 generation rate and experimental conditions of some other reported g-C_3N_4-based samples.

Catalysts	Sacrificial reagent	Light Source	H_2O_2 yield (mM g^{-1} h^{-1})	Reference
MTCN	**ethanol (10%)**	**300 W Xe lamp (>420 nm)**	**10.778**	**This work**
g-C_3N_4	ethanol (90%)	2 kW Xe lamp (>420 nm)	0.492	[8]
g-C_3N_4/PDI$_{51}$	isopropanol (90%)	2 kW Xe lamp (>420 nm)	0.699	[9]
KTTCN	isopropanol (0.5%)	300 W Xe lamp (>420 nm)	0.72	[10]
N_v-C_3N_4	methanol (5%)	300 W Xe lamp (>420 nm)	1.01	[11]
AKCN	ethanol (10%)	300 W Xe lamp (>420 nm)	2.666	[12]
AKMT	ethanol (10%)	300 W Xe lamp (>420 nm)	3.4	[13]
CNS-500	isopropanol (10%)	300 W Xe lamp (>420 nm)	4.978	[14]
TP-PCN	isopropanol (10%)	300 W Xe lamp (>420 nm)	6.53	[15]

Table S4. TRPL data of CN and MTCN.

Samples	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_A (ns) [a]
CN	0.64616	5201.62893	0.64611	483.33354	0.646155749
MTCN	0.64539	4917.0088	0.64537	702.58572	0.6453875

[a] The calculation formula of the average TRPL lifetime is: $\tau_A = \dfrac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$, where τ_i is the time coefficient and A_i is the corresponding amplitude of each component.

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