

## Supporting Information

### **Molten-salt-induced structural heterogeneity of carbon nitride for efficient photocatalytic H<sub>2</sub>O<sub>2</sub> production**

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## **1. Experimental section**

### **1.1. Synthesis of CN-0**

The traditional bulk carbon nitride CN-0 was prepared by the thermal polycondensation of melamine: 5.0 g melamine was placed into a covered crucible, and then heated at 550 °C for 4 h in a muffled furnace. After cooled to room temperature, the product was ground in a mortar and collected.

### **1.2. Synthesis of CN- $x$ ( $x = 1, 2, 5, 10$ )**

CN- $x$  ( $x = 1, 2, 5, 10$ ) was prepared through a molten-salt assisted polycondensation, using different amount of KCl/LiCl salts: 2.0 g melamine and  $2x$  g KCl/LiCl (45/55 wt %, m.p. = 352 °C) were thoroughly ground (The precursor/molten salt mass ratio is 1 :  $x$ ,  $x = 1, 2, 5, 10$ , respectively). The resulting mixture was transferred into a porcelain crucible and heated in a muffle furnace at 550 °C for 4 h. The heating rate was 2.5 °C·min<sup>-1</sup>. After cooling to room temperature, the obtained product was washed with hot water several times, collected by filtration and dried at 60 °C. Note when  $x = 10$ , the prepared CN-10 is PTI. Traditional bulk carbon nitride (BCN) was synthesized without KCl/LiCl, so it is denoted as CN-0 in this paper.

### **1.3. Synthesis of PTI/BCN- $y$ ( $y = 1, 2, 3$ )**

The van der Waals heterojunctions of heptazine and triazine based carbon nitrides PTI/BCN- $y$  ( $y = 1, 2, 3$ ) was prepared via an in situ growth of BCN on the surface of PTI: 1.0 g prepared PTI (also denoted as CN-10 in this paper) was thoroughly ground with  $y$  g ( $y = 1, 2, 3$ , respectively) melamine. The resulting mixture was transferred into a porcelain crucible and heated in a muffle furnace at 550 °C for 4 h. The heating rate was 2.5 °C·min<sup>-1</sup>. After cooling to room temperature, the obtained product was collected.

### **1.4. Characterization**

Scanning electron microscopy (SEM) images were collected on a Hitachi S-3400N microscopy. Transmission electron microscopy (TEM) characterization was performed on a JEM-2100 instrument at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained from a X-Pert Powder X-ray diffractometer (PANalytical). Fourier transform infrared (FT-IR) spectra were measured on a Thermo

Nicolet iS10 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Fisher ESCALAB Xi+ spectrometer with monochromic Al K $\alpha$  X-ray. UV-vis diffuse reflection spectra (DRS) were recorded on a Shimadzu UV-2600 Spectrophotometer. Steady-state photoluminescence (PL) spectra were measured on a FluoroMax+ spectrophotometer (HORIBA) using an excitation wavelength of 380 nm. Electron spin resonance (ESR) spectra were recorded on a Bruker MicroESR spectrometer.

### 1.5. Photocatalytic H<sub>2</sub>O<sub>2</sub> production

The photocatalytic reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> was performed in a top-irradiation reaction vessel. Typically, 50 mg prepared photocatalyst was dispersed in the mixture of 90 mL deionized water and 10 mL ethanol. The suspension solutions were stirred for 30 min in the dark with continually O<sub>2</sub> bubbling to reach the absorption-desorption equilibrium. Then the solutions were exposed to visible light provided by a 300 W Xe lamp with a 420 nm cut-off filter ( $P = 61.17 \text{ mW}\cdot\text{cm}^{-2}$ , measured by a Newport Oriel 91150V reference cell). A continuous magnetic stirrer and cooling water were applied during the experiment. During the irradiation, ~2 mL solution was sampled every 15 min and filtrated with a 0.45  $\mu\text{m}$  filter to remove the photocatalyst.

The amount of H<sub>2</sub>O<sub>2</sub> was analyzed by colorimetric method using horseradish peroxidase (HRP)/3,3',5,5'-tetramethylbenzidine (TMB) system. HRP is used to catalyze TMB in the presence of H<sub>2</sub>O<sub>2</sub> to produce chromogenic reaction. Typically, 2 mL Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> (0.1 M, pH 7.4) buffer, 10  $\mu\text{L}$  TMB (0.1 M), and 10  $\mu\text{L}$  HRP (0.1 M) were added to 100  $\mu\text{L}$  filtration from reaction solution. After 10 min, the solution was blue. Then 200  $\mu\text{L}$  H<sub>2</sub>SO<sub>4</sub> (3 M) was added to stop the reaction, giving rise to a yellow product that corresponds to the oxidation of TMB. The amount of oxidation product formed was quantified spectrophotometrically at 450 nm (The solution was diluted before UV-vis absorption measurement if necessary), from which the amount of H<sub>2</sub>O<sub>2</sub> produced during each reaction was estimated. Fig. S1 shows the linear fitting spectra for the H<sub>2</sub>O<sub>2</sub> standard solution.

The apparent quantum efficiency (AQE) for H<sub>2</sub>O<sub>2</sub> production was measured by replacing the cut-off filter with corresponding band-pass filter. The AQE is calculated

from the following equation:

$$\text{AQE} = \frac{2 \times \text{number of evolved H}_2\text{O}_2 \text{ molecules}}{\text{the number of incident photos}} \times 100\%$$

Further, the number of evolved H<sub>2</sub>O<sub>2</sub> molecules can be expressed as:

$$\text{the number of evolved H}_2\text{O}_2 \text{ molecules} = n(\text{H}_2\text{O}_2) \cdot N_A$$

And the number of incident photons can be expressed as:

$$\text{the number of incident photons} = \frac{E \times \lambda}{h \times c} = \frac{P \times S \times t \times \lambda}{h \times c}$$

Where  $n(\text{H}_2\text{O}_2)$  refers to the H<sub>2</sub>O<sub>2</sub> production (mol),  $N_A$  is the Avogadro constant ( $6.022 \times 10^{23} \text{ mol}^{-1}$ );  $E$  refers to the total energy of the incident photon (J),  $\lambda$  is the wavelength of incident light (m),  $h$  is the Planck constant ( $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ ),  $c$  is the light speed ( $3 \times 10^8 \text{ m}\cdot\text{s}^{-1}$ ),  $P$  refers to the average spectral irradiance ( $\text{W}\cdot\text{cm}^{-2}$ ),  $S$  is the irradiation area ( $27.34 \text{ cm}^2$  in this paper), and  $t$  is the irradiation time ( $3600 \text{ s}$  in this paper). By integrating above formulas, the AQE is obtained as follows:

$$\text{AQE} = \frac{2 \times n(\text{H}_2\text{O}_2) \cdot N_A \times h \times c}{P \times S \times t \times \lambda} \times 100\%$$

The measured values of  $n(\text{H}_2\text{O}_2)$  and  $P$  are listed in Table S1:

**Table S1.** The measured data and corresponding AQE

| $\lambda / 10^{-9} \text{ (m)}$ | $n(\text{H}_2\text{O}_2) / 10^{-6} \text{ (mol)}$ | $P / 10^{-3} \text{ (W}\cdot\text{cm}^{-2})^a$ | AQE (%) |
|---------------------------------|---|--|---------|
| 380                             | 90.1  | 0.9600   | 60.1    |
| 420                             | 71.9  | 0.8525   | 48.8    |
| 450                             | 75.1  | 2.900  | 14.0    |
| 475                             | 3.79  | 4.025  | 0.48    |
| 500                             | 2.01  | 2.150  | 0.45    |

<sup>a</sup> The average intensity of irradiation was measured by a Newport Oriel 91150V reference cell.

For example, the AQE at 420 nm is calculated as follows:

$$\text{AQE} = \frac{2 \times n(\text{H}_2\text{O}_2) \cdot N_A \times h \times c}{P \times S \times t \times \lambda} \times 100\%$$

$$= \frac{2 \times 71.9 \times 10^{-6} \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^8}{0.8525 \times 10^{-3} \times 27.34 \times 3600 \times 420 \times 10^{-9}} \times 100\%$$

$$= 48.8\%$$

## 1.6. Electrochemical and photoelectrochemical measurements

Electrochemical impedance spectra (EIS) and photocurrent were both performed by CHI-660E workstation (CH Instruments) in a standard three-electrode system using the prepared samples as the working electrodes, Ag/AgCl electrode as a reference electrode, and a Pt wire as the counter electrode. The electrolyte was 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The working electrodes were prepared as follows: ~5 mg sample was dispersed in 0.02 wt% Nafion solution to afford a suspension. The suspension was sonicated for 1 h and then spread on to a 1.0 cm × 1.0 cm exposed ITO glass, dried in the air. The photocurrent was measured under -0.2 V bias voltage and the light source was a 300 W Xe-lamp with a cut-off filter ( $\lambda > 420$  nm). For the EIS measurements, the applied potential was -0.3 V and the frequency range was from 0.05 Hz to 100 kHz with 5 mV amplitude.

Rotating disk electrode (RDE) measurements was conducted on a CHI-760E workstation (CH Instruments) coupled with a rotating disk electrode system. The three-electrode cell system was consisting of a Ag/AgCl electrode as the reference electrode and a Pt wire as the counter electrode. The working electrode was prepared as follows: 5 mg photocatalysts was dispersed in 0.5 mL ethanol containing 0.02 % Nafion by ultrasonication. The slurry (6  $\mu$ L) was put onto a disk electrode and dried at room temperature. The linear sweep voltammogram (LSV) were obtained in an O<sub>2</sub>-saturated 0.1 M KOH with a scan rate 2 mV s<sup>-1</sup>. The average transfer electron number (*n*) in the O<sub>2</sub> reduction was obtained by the slopes of Koutecky-Levich plots with the following equation:

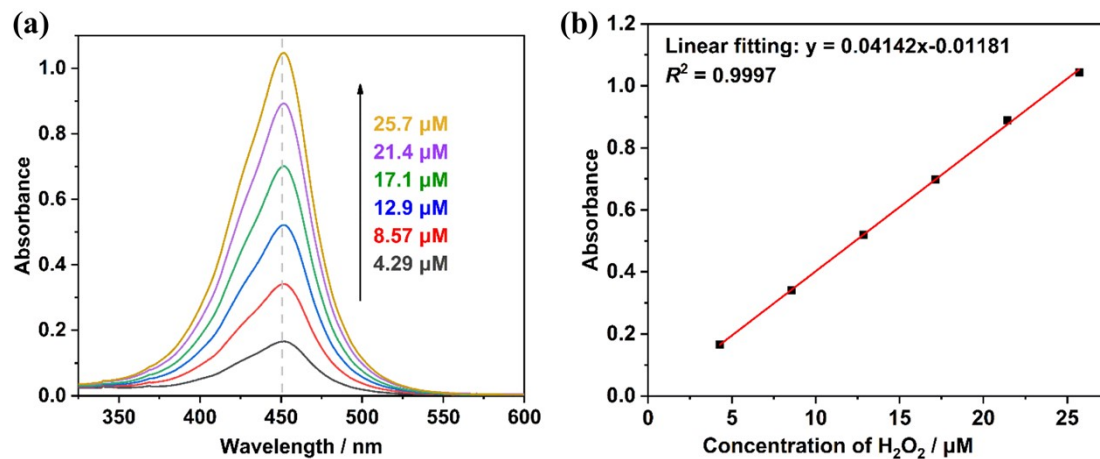
$$J^{-1} = J_k^{-1} + B^{-1}\omega^{-1/2}$$

$$B = 0.2nF\nu^{1/6}C_0D_0^{2/3}$$

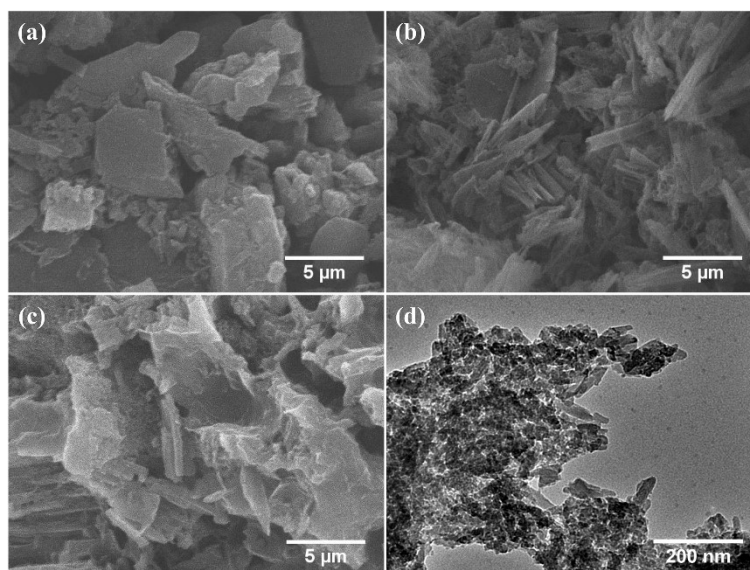
where *J*, *J<sub>k</sub>* and  $\omega$  are the tested current density, kinetic current density and rotating speed (rpm), respectively. *F* and  $\nu$  are the Faraday constant (96485 C mol<sup>-1</sup>) and kinetic

viscosity of water ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ),  $C_0$  and  $D_0$  are the bulk concentration of  $\text{O}_2$  in water ( $1.2 \times 10^{-3} \text{ mol L}^{-1}$ ) and the diffusion coefficient of  $\text{O}_2$  ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

## 2. Figures and Tables



**Fig. S1** (a) The standard spectra of the HRP/TMB solution with different concentration of  $\text{H}_2\text{O}_2$ . (b) The corresponding linear fitting: UV-vis absorption intensity at 450 nm vs. concentration of  $\text{H}_2\text{O}_2$ .



**Fig. S2** SEM and TEM images of (a) CN-0, (b) CN-10, and (c, d) CN-2.

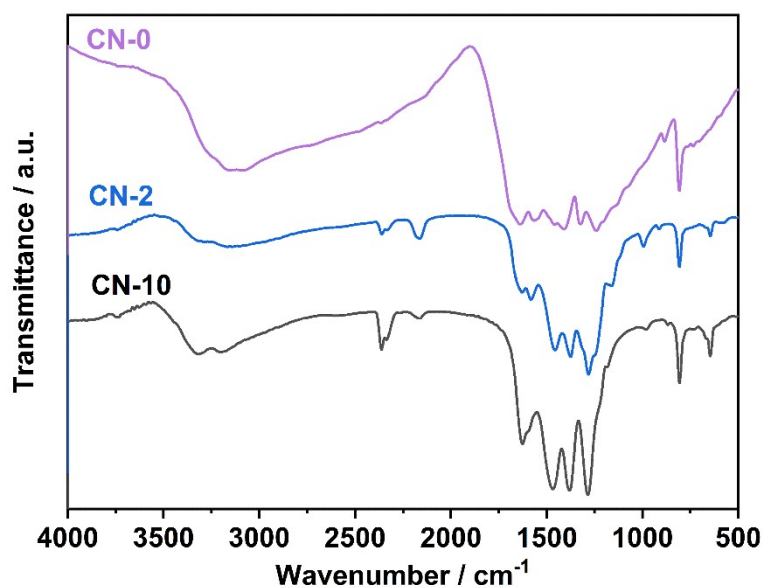


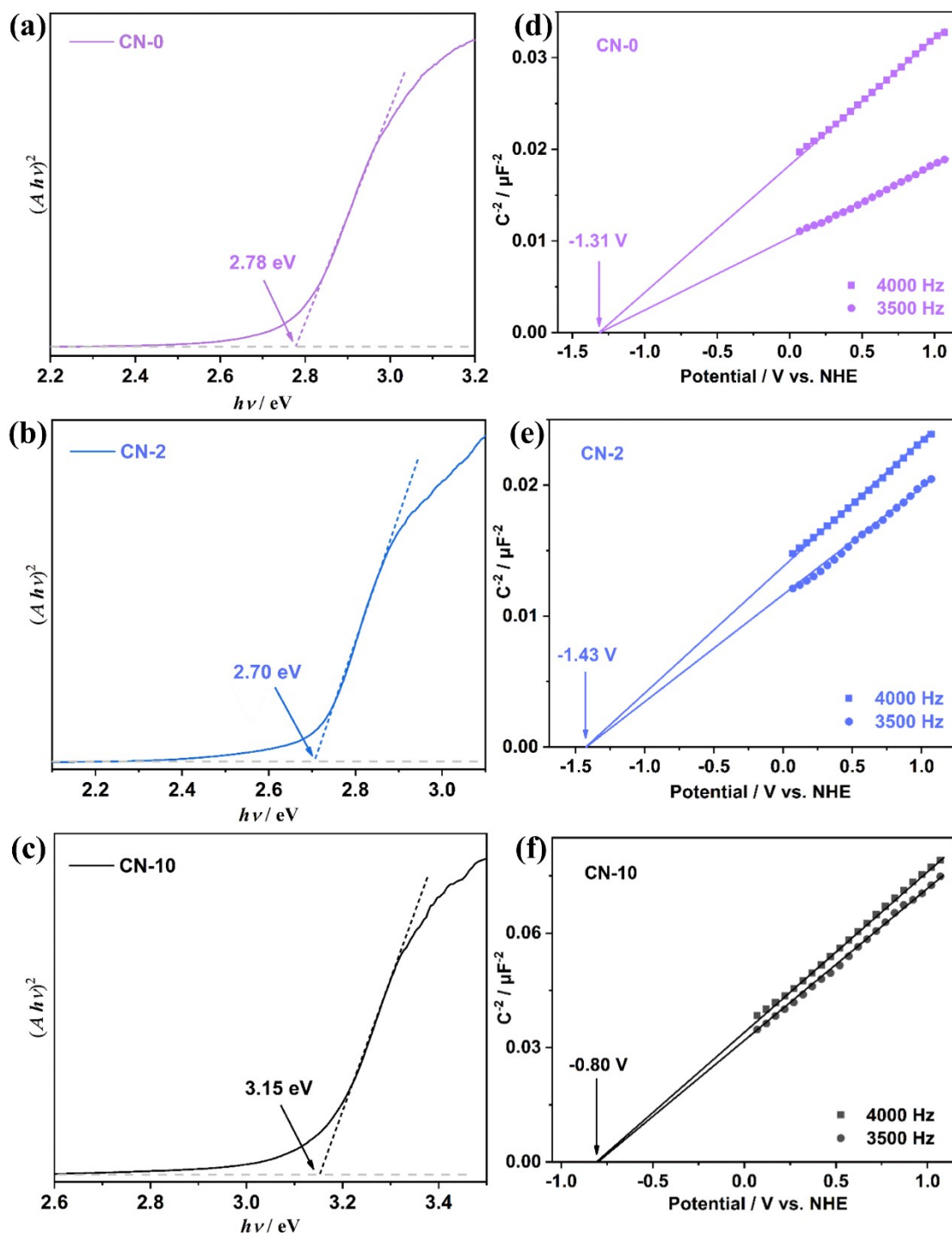
Fig. S3 FT-IR spectra of CN-0, CN-2, and CN-10.

**Table S2** Relative ratios of different N species in CN-0, CN-2, and CN-10, as determined by XPS high-resolution N1s spectra.

| Sample | C–N=C<br>[mol %] | –NH <sub>x</sub><br>[mol %] | N–(C) <sub>3</sub><br>[mol %] | N–(C) <sub>3</sub> /C–N=C<br><b>molar ratio</b> |
|--------|------------------|-----------------------------|-------------------------------|---|
| CN-0   | 67.5             | 21.6                        | 10.9                          | <b>0.162</b>                                    |
| CN-2   | 81.2             | 12.6                        | 6.19                          | <b>0.0762</b>                                   |
| CN-10  | 67.5             | 32.5                        | 0                             | <b>0</b>  |

In the heptazine-based carbon nitride, the heptazine/triazine molar ratio is 1 : 0, and the N–(C)<sub>3</sub>/C–N=C molar ratio is 1 : 6. In the triazine-based carbon nitride, the heptazine/triazine molar ratio is 0 : 1, and the N–(C)<sub>3</sub>/C–N=C molar ratio is 0 : 3. For the heptazine/triazine-based carbon nitride, we suppose that the heptazine/triazine molar ratio is 1 : x, then the N–(C)<sub>3</sub>/C–N=C molar ratio is 1 : (6+3x).

For CN-2, as determined by the XPS high-resolution N1s spectrum, 1 : (6+3x) = 0.0762. Therefore, x = 2.4. That is, the heptazine/triazine molar ratio is 1 : 2.4 in CN-2.



**Fig. S4** (a-c) Tauc plots and (d-f) Mott-Schottky curves of CN-0, CN-2, and CN-10.



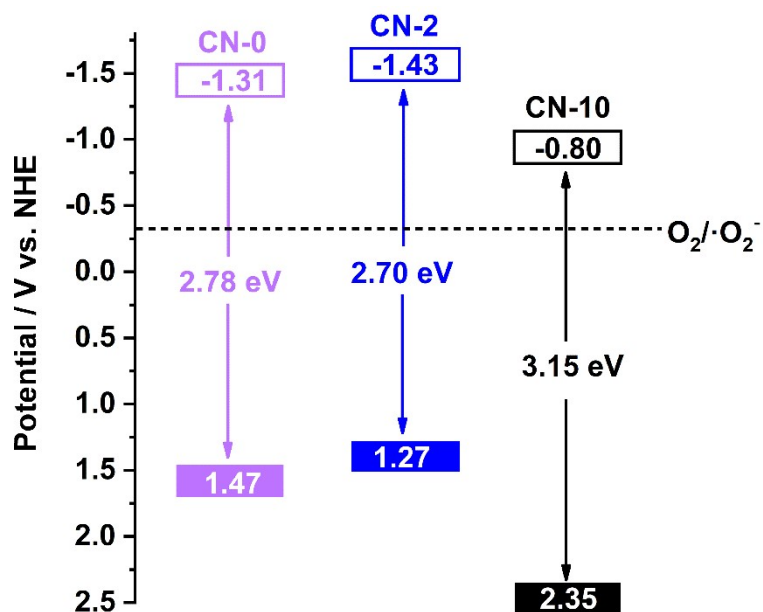


Fig. S5 band structure alignments of CN-0, CN-2, and CN-10.

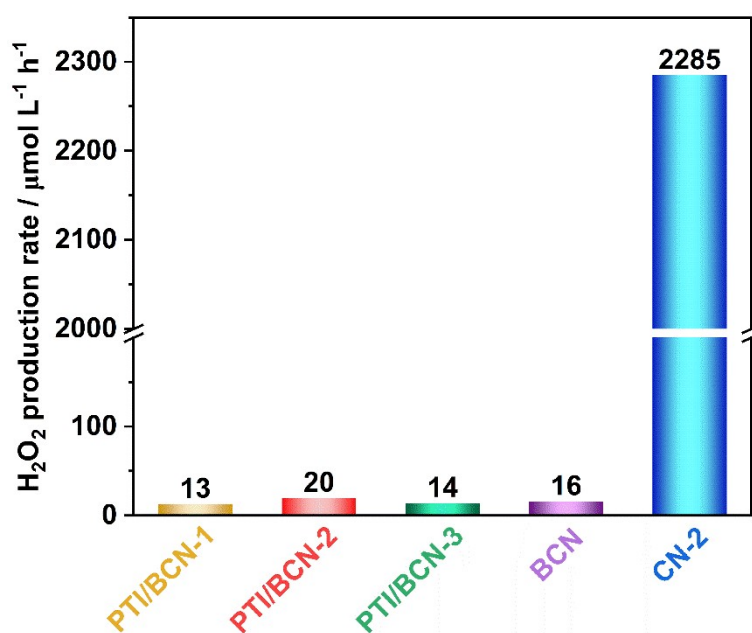


Fig. S6 Comparison of H<sub>2</sub>O<sub>2</sub> production rates of van der Waals heterostructured carbon nitrides (PTI/BCN-*y*, *y* = 1, 2, 3), pristine BCN, and molecular heterostructured CN-2. The synthetic procedures and XRD patterns of PTI/BCN-*y* are provided in the experimental section and in Fig. S4, respectively.

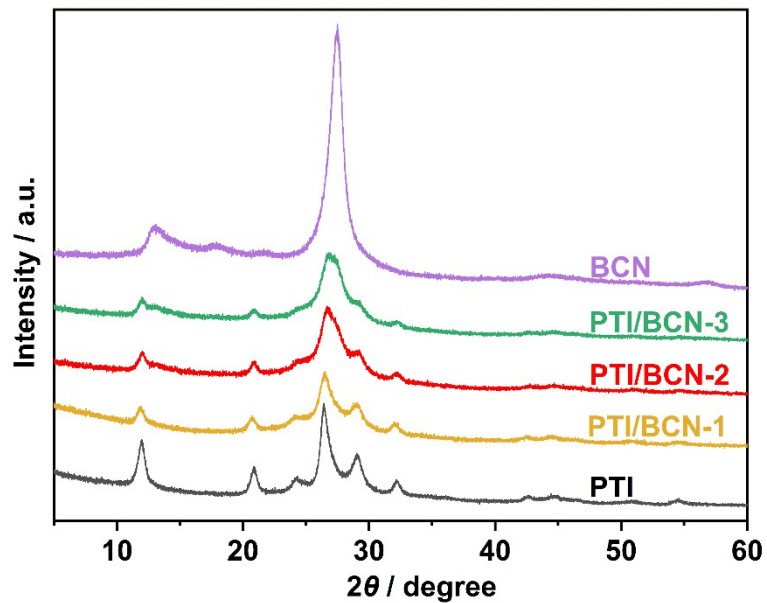


Fig. S7 XRD patterns of PTI/BCN- $y$  ( $y = 1, 2, 3$ ), BCN, and PTI.

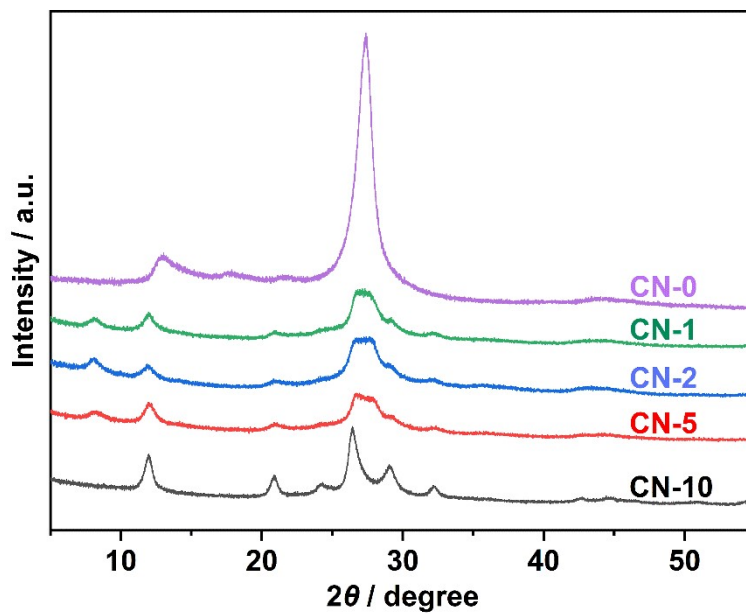


Fig. S8 XRD patterns of CN- $x$  ( $x = 0, 1, 2, 5, 10$ ).

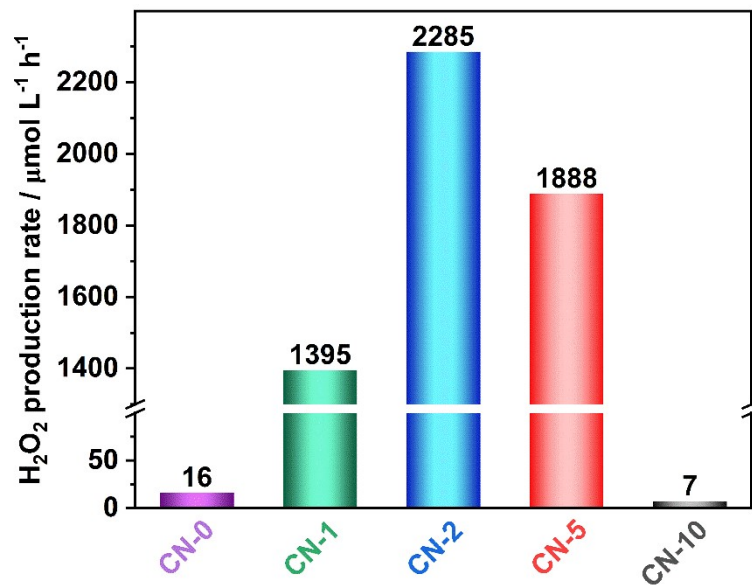


Fig. S9 photocatalytic H<sub>2</sub>O<sub>2</sub> production rates of CN-x (x = 0, 1, 2, 5, 10).

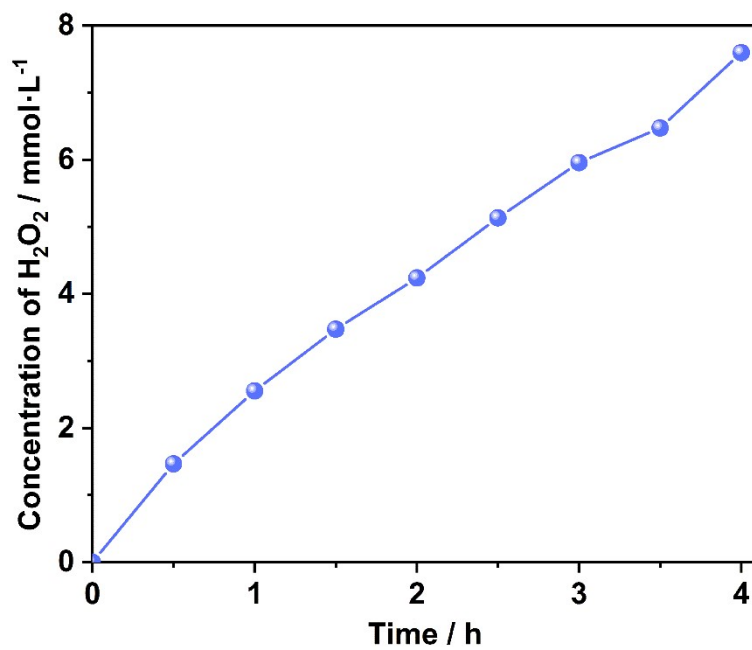
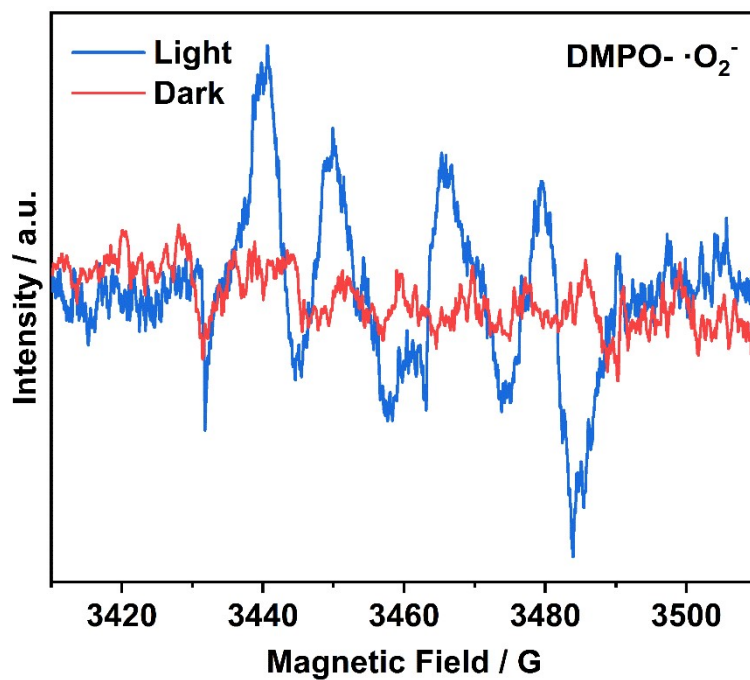


Fig. S10 photocatalytic stability test of CN-2 for H<sub>2</sub>O<sub>2</sub> production.

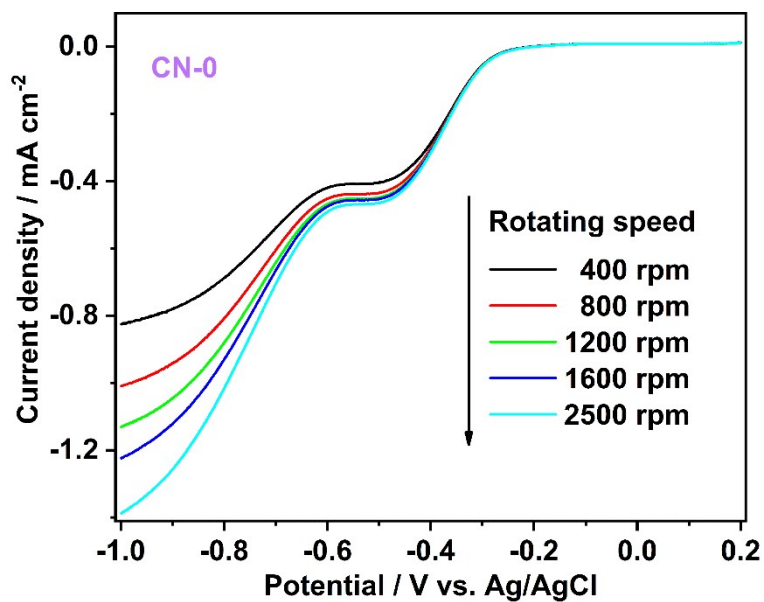
**Table S3** Comparison of AQE for H<sub>2</sub>O<sub>2</sub> production at 420 nm between this work and previous studies.

| Photocatalyst           | Dosage<br>(mg mL <sup>-1</sup> ) | Sacrificial agent  | AQE                | Ref.             |
|-------------------------|----------------------------------|--------------------|--------------------|------------------|
| <b>CN-2</b>             | <b>0.5</b>                       | <b>10% ethanol</b> | <b>48.8%</b>       | <b>This work</b> |
| CN-NH <sub>4</sub> -NaK | 0.5                              | 10% isopropanol    | 28.4%              | S1               |
| Na-PCN                  | 1                                | 10% ethanol        | 22.3%              | S2               |
| fl-CN-530               | 0.5                              | 10% ethanol        | 9.0%               | S3               |
| HTCN                    | 0.2                              | 1% isopropanol     | 21.5%              | S4               |
| akut-CN                 | 0.5                              | 10% ethanol        | 17.2%              | S5               |
| CNR                     | 0.4                              | 10% isopropanol    | 14.58%             | S6               |
| PHI-0.5                 | 0.2                              | 5% ethanol         | 17.8%              | S7               |
| O/K-PCN1.6              | 1                                | 5% ethanol         | 8.53% <sup>a</sup> | S8               |
| KCMCN                   | 0.4                              | 0.5% isopropanol   | 7.5%               | S9               |
| m-CNNP                  | 1                                | 10% isopropanol    | 0.55%              | S10              |
| ACNN                    | 0.5                              | 10% isopropanol    | 30.7% <sup>b</sup> | S11              |

<sup>a</sup> measured at 400 nm. <sup>b</sup> measured at 429 nm.



**Fig. S11** ESR spectra of DMPO-•O<sub>2</sub><sup>-</sup> for CN-2 suspensions under visible light irradiation for 3 min and under dark, respectively.



**Fig. S12** LSV curves of CN-0.

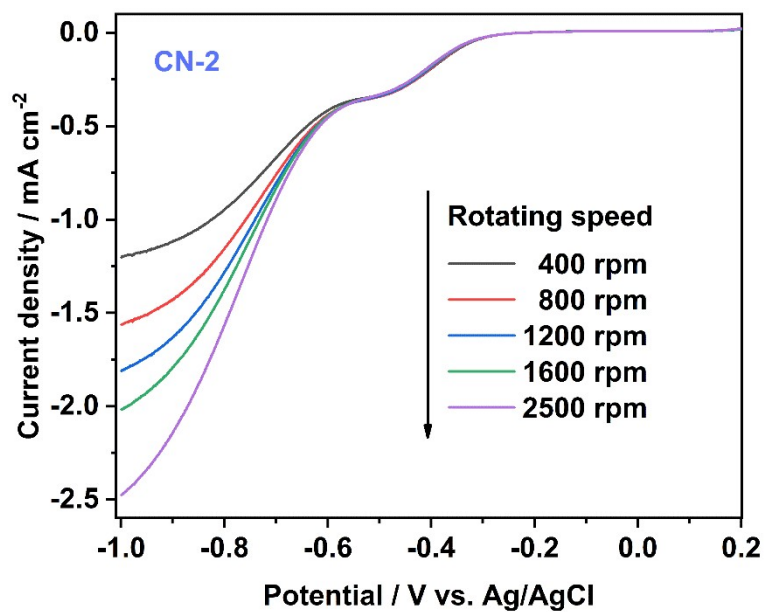


Fig. S13 LSV curves of CN-2.

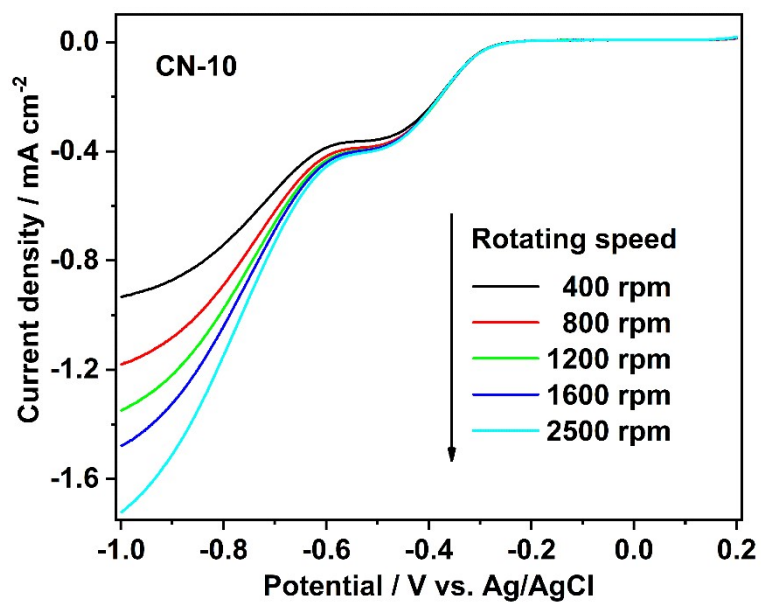


Fig. S14 LSV curves of CN-10.

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