Supporting Information

Enhancing Light and Dark Photocatalytic Hydrogen Production via Graphene Conductive Network in Carbon Nitride Composites

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Method for determining electron storage capacity by methyl viologen

An anaerobic mixture of 4-MBA (24 mg) and the ^{NCN}CN catalyst (5 mg) in the custom reaction vessel was purged with N_2 for 30 min to remove oxygen. The reaction was then conducted under light irradiation for a specified duration. Subsequently, methyl viologen dichloride (2 mmol) was added to each mixture. Immediately after addition, the reactor was sealed and wrapped in aluminum foil to prevent light exposure. For analysis, an aliquot (volume V_1) was extracted from each reactor and prepared for the measurements by the UV-visible absorption spectroscopy.[1]

The number of electrons trapped in the material (μmol) is calculated according to the following formula:

$$\mathrm{N} = \frac{A \times V_1}{\varepsilon \times L \times V_2} \times V \times 1000$$

A- The absorbance of $MV^{\cdot+}$ solution at 600 nm;

V_1- Volume of solution removed from the total reaction system (mL);

V_2- The volume of the reaction mixture containing $MV^{\cdot+}$ for analysis (mL);

ε - Extinction coefficient of $MV^{\cdot+}$ ($M^{-1}cm^{-1}$); L-Optical path of Quartz cuvette (cm);

V - Total volume of reaction solution (mL)。

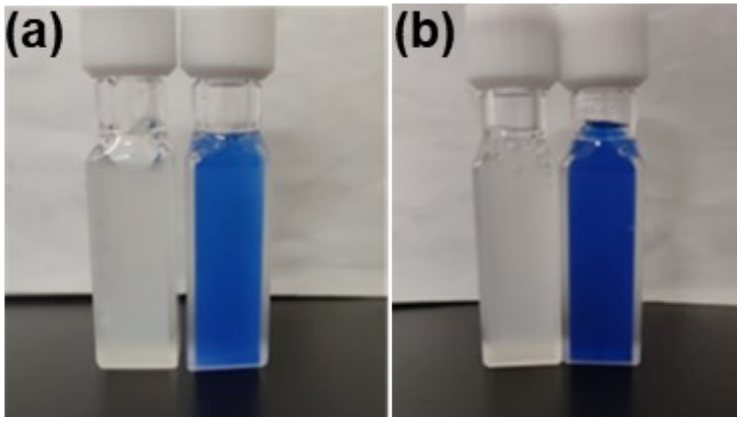

Fig S1. (a) The left picture shows the color change before and after the reaction of pure ^{NCN}CN. (b) The figure on the right shows the changes before and after the reaction of 0.5 wt.%G-^{NCN}CN.

Electrochemical test method

The catalyst ink was prepared by ultrasonically dispersing 5 mg of the material in 1 mL of deionized water for 10 min, followed by the addition of 10 μL of Nafion solution and an additional 30 min of sonication. Subsequently, 300 μL of the resulting ink was drop-cast onto

ITO glass substrates (pre-cleaned with acetone and ethanol) and dried at 50 °C for 5 h. The dried electrode was then mounted in the electrochemical workstation for testing.

Table S1. Relative Content of Different Elements in the Catalyst.

Sample	C content on the surface (%)	N content on the surface (%)	O content on the surface (%)	K content on the surface (%)
CN	43.86	53.66	2.48	0
^{NCN}CN	54.11	36.08	4.93	4.88
0.5wt% G-^{NCN}CN	50.91	39.68	6.04	3.37

The AQE is analyzed at different wavelength (450 nm, λ ± 10 nm) in the 300 W Xenon lamp. The other experimental condition is similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity is obtained with an optical power meter . For example, if 450 nm is used, the average light intensity is 107.98mW. The number of incident photons (N) is 8.8×10^{20} calculated by equation (1). The amount of H_2 molecules generated in 1 h are 3.13 μmol. The AQE is then calculated in equation

0.5wt% G-^{NCN}CN λ=450 nm

$$N = \frac{E\lambda}{hc} = \frac{107.98 \times 10^{-3} \times 1 \times 3600 \times 450 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 8.8 \times 10^{20} \quad (1)$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\% \quad (2)$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 3.13 \times 10^{-6}}{8.8 \times 10^{20}} \times 100\% = 0.43\%$$

^{NCN}CN λ=450 nm

$$N = \frac{E\lambda}{hc} = \frac{107.98 \times 10^{-3} \times 1 \times 3600 \times 450 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 8.8 \times 10^{20} \quad (1)$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\% \quad (2)$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 1.51 \times 10^{-6}}{8.8 \times 10^{20}} \times 100\% = 0.21\%$$

Table S2. The calculated AQE at different sample.

Sample	H_2 Evolved	Light Intensity	AQE
0.5wt% G-^{NCN}CN	3.13 μmol	107.98 mW	0.43%
^{NCN}CN	1.51 μmol	107.98 mW	0.21%

Table S3. Specific surface area and pore size distribution of different samples

Sample	BET Surface Area (m^2/g)	pore volume (cm^3/g)	average pore width (nm)
^{NCN}CN	52.53	0.082	4.63
0.5wt% G-^{NCN}CN	61.88	0.096	4.78

Table S4. Comparison of Hydrogen Production Performance Among Different Carbon Nitride/Graphene Composites.

Photocatalyst	Reaction condition	Rate	Ref.
N-Doped GO/g-C_3N_4	λ ≧ 420 nm, TEOA,3% Pt	139.6 μmol•h^{-1}•g^{-1}	2
Graphene/g-C_3N_4	25% methanol, 350W Xe arc lamp	451 μmol•h^{-1}•g^{-1}	3
B-Doped graphene/g-C_3N_4	10 vol% TEOA and 2.5 wt% $H_2PtCl_6 \cdot 6H_2O$, λ≦420nm	741.4 μmol•h^{-1}•g^{-1}	4
GCN-RGO-MoS_2	(λ > 420 nm) using TEOA	317 μmol•h^{-1}•g^{-1}	5
GCN-RGO $CoMoS_2$	TEOA and H_2O, 300W Xe lamp λ >400nm	684 μmol•h^{-1}•g^{-1}	6
$ZnIn_2S_4$/graphene/g-C_3N_4	Solar light in presence of 0.3 M Na_2S and Na_2SO_4	477 μmol•h^{-1}•g^{-1}	7
g-C_3N_4/graphene/CdS	350 W Xe lamp, lactic acid	1980.2 μmol•h^{-1}•g^{-1}	8
N-Doped GQDs/g-C_3N_4	λ > 420 nm, TEOA	139.6 μmol•h^{-1}•g^{-1}	9
G-^{NCN}CN	λ≧400nm，TEOA，1wt% Pt	3156 μmol•h^{-1}•g^{-1}	

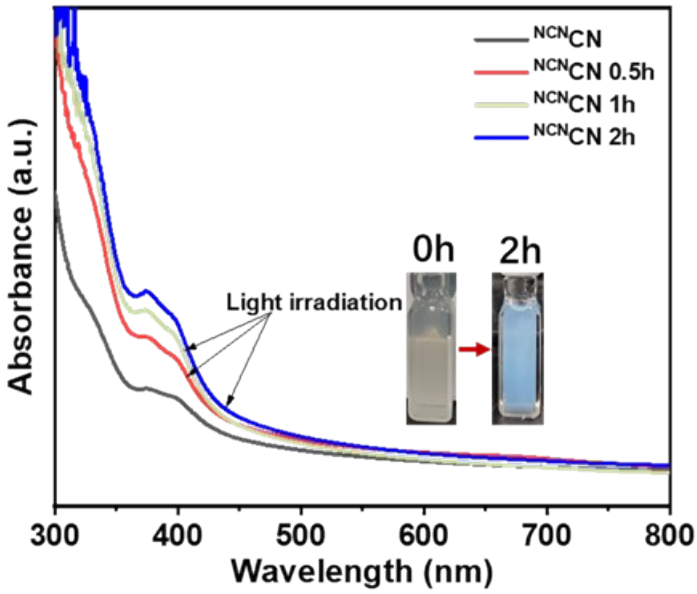

Fig. S2 Time-dependent UV-Vis absorption spectra of the ^{NCN}CN sample.

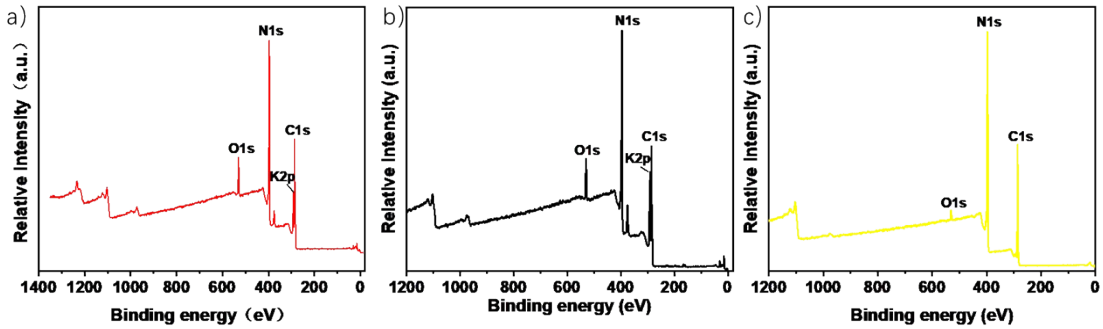

Fig S3. a) XPS spectrum of the G-^{NCN}CN sample; b) XPS spectrum of the ^{NCN}CN sample; c) XPS spectrum of the CN sample.

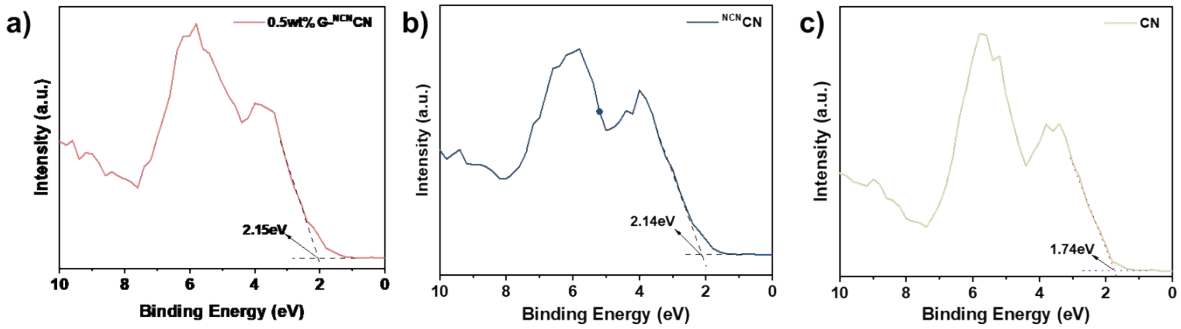

Fig. S4. The valence band spectrum of (a) G-NCNCN and (b) ^{NCN}CN 、(CN).

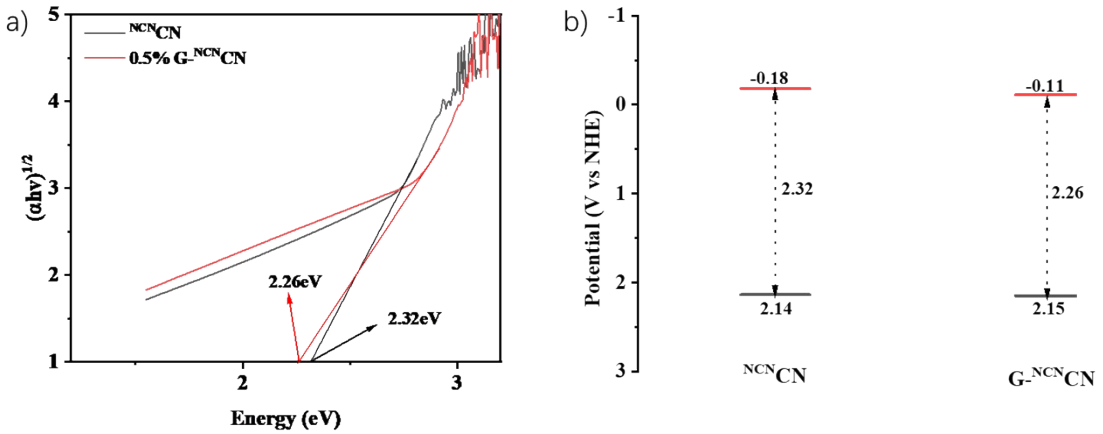

Figure S5. a) Tauc plots and b) band diagrams for ^{NCN}CN and G-^{NCN}CN

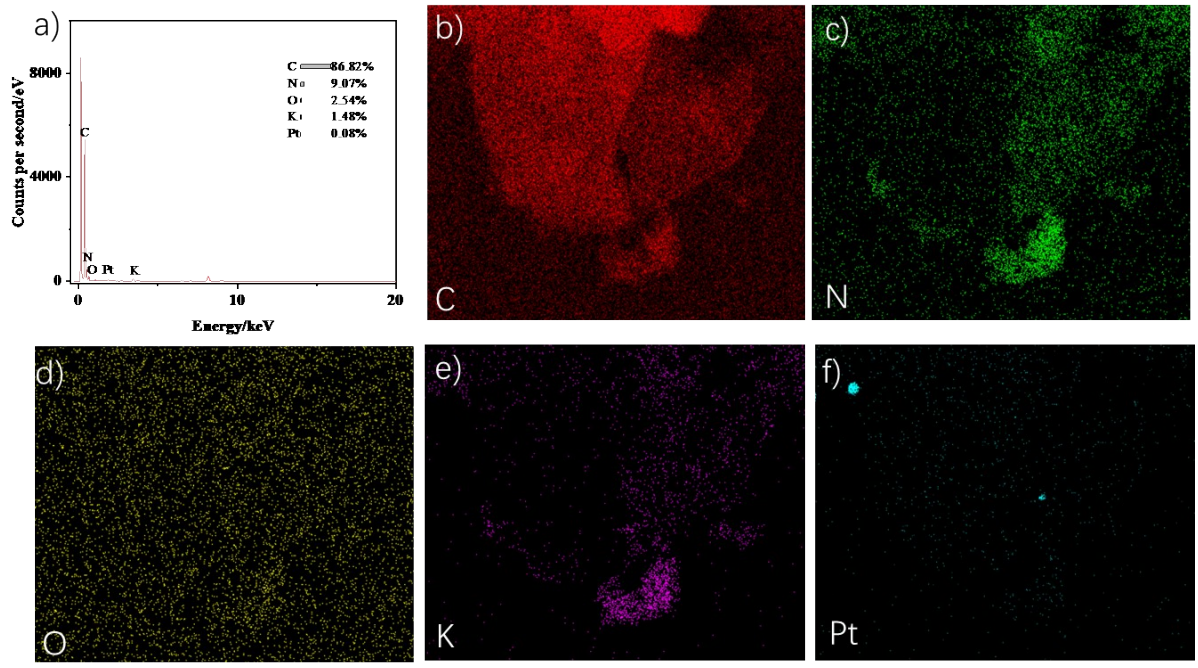

Fig S6. a) EDS spectrum of the G-^{NCN}CN sample and corresponding elements: b) C, c) N, d) O, e) K, f) Pt.

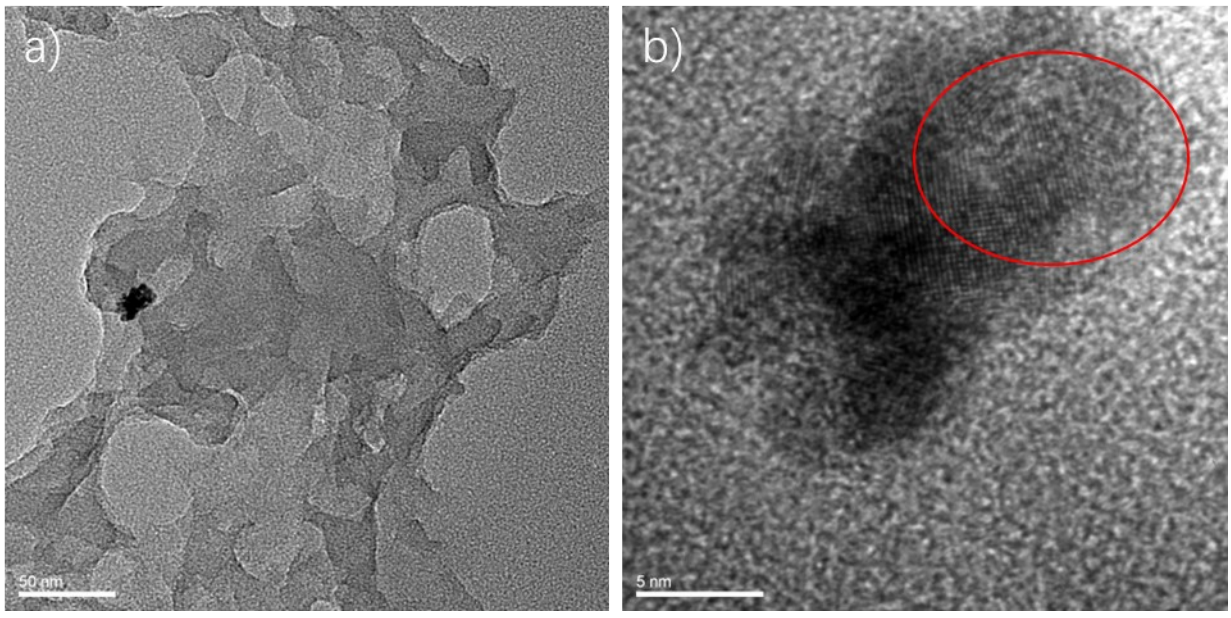

Fig S7.a) HRTEM image of Pt deposited on G-^{NCN}CN after reaction; b) Lattice fringe pattern of Pt particles

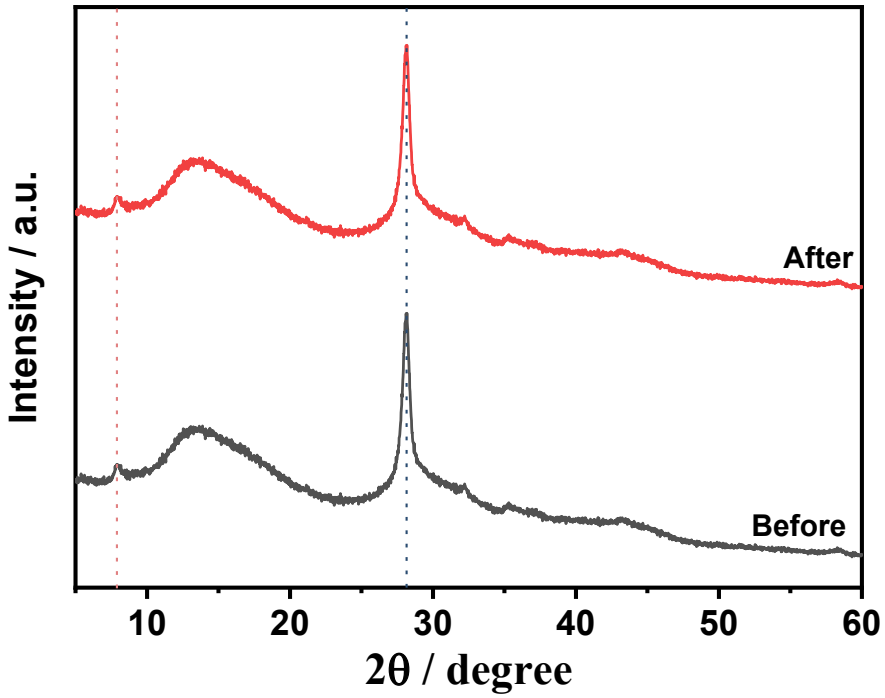

Fig S8. XRD patterns of G-^{NCN}CN samples before and after reaction

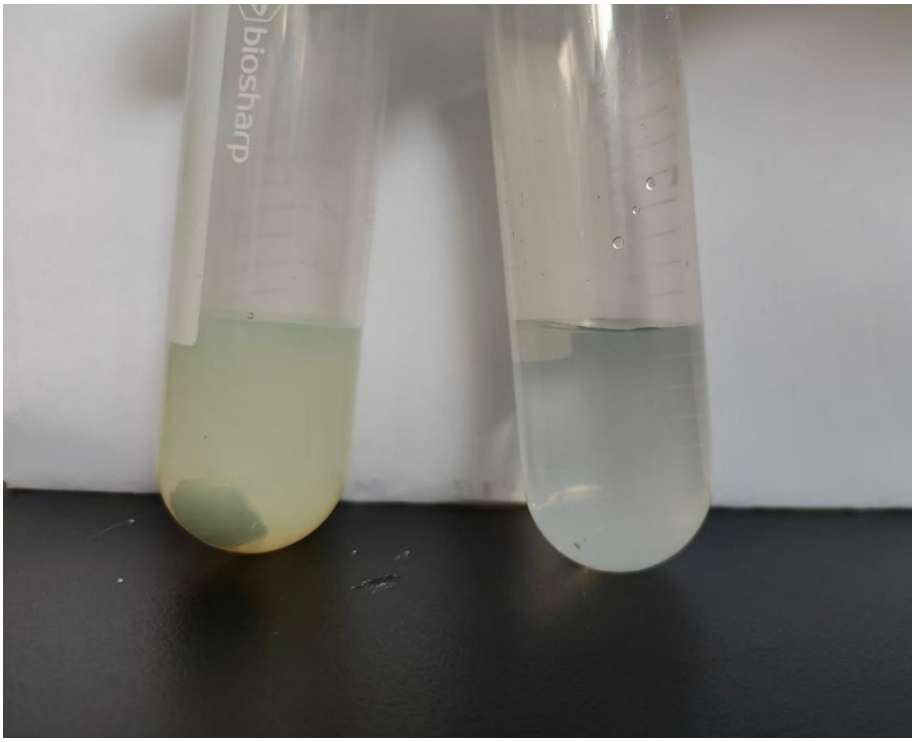

Fig S9. Photograph of G-^{NCN}CN solution sample after centrifugation at 10,000 rpm for 5 minutes.

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