

Methylene Blue Incorporated Donor-Acceptor g-C₃N₄ Nanosheet Photocatalyst for H₂ Production

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亚甲基蓝嵌入的供体受体型g-C₃N₄纳米片光催化剂用于产H₂

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1 Materials

Dicyandiamide ($\geq 98.0\%$) and triethanolamine (TEOA, $\geq 99.0\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Methylene blue (MB, Ind) was obtained from Shanghai Macklin Biochemical Co., Ltd. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 38.0\%$, Pt basis) were received from Shanxi Kaida Chemical Engineering Co., Ltd. All chemical reagents were used without further purification.

2 Characterizations

Powder X-ray diffraction (XRD) patterns were recorded by a Japan Rigaku D/Max-RB X-ray diffractometer with Cu K_α radiation ($\lambda = 0.15418$ nm). Solid-state ^{13}C cross-polarization/magic-angle-spinning (CP/MAS) nuclear magnetic resonance (NMR) was carried out on a Bruker AVANCE NEO 400M spectrometer equipped with a 4 mm standard bore CP/MAS probe head whose X channel was tuned to 100.62 MHz for ^{13}C , using a magnetic field of 9.39T at 297 K. All ^{13}C CP/MAS chemical shifts were referenced to the resonances of adamantane ($\text{C}_{10}\text{H}_{16}$). Fourier transform infrared (FTIR) spectra were conducted on an IR Affinity-1 FTIR spectrometer (NICOLET iS50, Thermo Scientific, USA). The morphology images were taken on a field emission scanning electron microscope (FESEM) (JSM 7500F, JEOL, Japan) and a transmission electron microscope (TEM) (JEM-2100F, JEOL, Japan). X-ray photoelectron spectra (XPS) was tested on an electron spectrometer (ESCALAB 250 Xi, Thermo Scientific, USA) with Al K_α radiation ($h\nu = 1486.6$ eV), and all binding energies were referenced to the adventitious carbon C 1s peak at 284.8 eV. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were carried out on a UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan) with BaSO_4 as a reference. Photoluminescence (PL) spectroscopy was measured by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) with 368-nm excitation light. Time-resolved photoluminescence (TRPL) spectra were obtained by FLS1000 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) with an excitation wavelength of 375 nm. Brunauer-Emmett-Teller (BET) specific surface areas and Barrett-Joyner-Halenda (BJH) pore size distribution were acquired by N_2 adsorption-desorption on Micromeritics TriStar II 3020 (USA). The powder samples were degassed off-line at 120 °C for 12 h under a dynamic vacuum (10^{-5} bar, 1 bar = 10^5 Pa) before measurement. Electron paramagnetic resonance (EPR) test was performed on an EPR spectrometer (MEX-nano, Bruker, DEU).

3 Photocatalytic hydrogen production test

The photocatalytic activities of CN, CN-MB_x, TCN, and TCN-MB_x were evaluated by the photocatalytic hydrogen production rate. The experiments were carried out at ambient temperature and atmospheric pressure in a 100 mL three-neck flask. A 300 W Xe lamp with an AM 1.5 G filter was used as a light source. Typically, 20 mg of the TCN-MB₁₀ catalyst was dispersed in 80 mL of the aqueous solution containing 10% volume of triethanolamine (TEOA). 3.0% (w, mass fraction) Pt was loaded onto the surface of the photocatalyst with a photodeposition method by adding a certain amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The catalyst suspension was ultrasonically dispersed for 10 min before irradiation. Then 30 min nitrogen is passed through the reactor to remove air and dissolved oxygen. And the obtained gas was analyzed by gas chromatograph (GC-14C, Shimadzu, Japan, TCD).

The apparent quantum efficiency (AQE) was measured under the same reaction conditions, except that a 420 nm bandpass filter was used to replace the AM1.5 G filter. The AQE was calculated according to the following equation:

$$\text{AQE} [\%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 = \frac{\text{number of evolved hydrogen molecules} \times 2}{\text{number of incident photons}} \times 100$$

4 Photoelectrochemical measurements

The transient photocurrent response ($I-t$), electrochemical impedance spectra (EIS), and Mott-Schottky tests were investigated by an electrochemical workstation (CHI660C Instruments, China) with a standard three-electrode system in 0.5 mol·L⁻¹ Na_2SO_4 aqueous solution, where a saturated Ag/AgCl, a Pt plate and fluorine-doped tin oxide (FTO) glass coated with the sample worked as the reference, counter electrode, and working electrode respectively. Regarding the working electrode preparation, 10 mg of powder sample was first dispersed thoroughly in 20 μL 5% nafion solution (D-520, DuPont, USA) with 0.2 mL ethanol. Then, the mixture was evenly spun onto the conductive surface of FTO glass (1.0 cm $\times$ 1.0 cm) and dried at room temperature overnight. Moreover, an Xe lamp (400 < λ < 800 nm) was used as the light source during the $I-t$ curve of the samples. Besides, the 0.8 V and 1.6 V applied bias voltage was chosen for the $I-t$ curve and EIS studies, respectively, and the Mott-Schottky tests were obtained at different frequencies (1000, 2000 and 3000 Hz).

5 Computational methods

The density functional theory (DFT) was performed with the Vienna *Ab initio* Simulation Package (VASP) ¹. The projector augmented wave (PAW) methods were applied to the interactions of valence electrons with the atomic nucleus ². Specifically, C $2s^22p^2$, N $2s^22p^3$, and H $1s^1$ states were used as the valence configurations. The electron exchange correlation functional used the Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) ³. The k -point sampling of the Brillouin zone only used the

gamma point of the $1 \times 1 \times 1$ Monkhorst-Pack scheme⁴. The energy cutoff of the wave function in the plane-wave basis was selected as 450 eV. The DFT-D2 method was used to describe the van der Waals interaction for all the calculations⁵. The unit cell was set to $30 \text{ \AA} \times 30 \text{ \AA} \times 15 \text{ \AA}$ to avoid the interactions between neighboring substrates. Additionally, the calculations were terminated until the maximum force upon each atom and energy were less than $0.05 \text{ eV} \cdot \text{\AA}^{-1}$ and $1.0 \times 10^{-5} \text{ eV}$.

The adsorption free energy of a H atom adsorbed on the substrates was calculated by Eq. (1)⁶:

$$\Delta G_{H^*} = \Delta E_{Hads} + \Delta E_{ZPE} - T\Delta S \quad (1)$$

where ΔE_{ZPE} and ΔS are the changes of zero point energy and entropy, respectively, T is the absolute temperature, and $T\Delta S$ uses the experimental value under the room temperature. Here, $T\Delta S \approx 0.170 \text{ eV}$ (obtained from the National Institute of Standards and Technology (NIST) database). Meanwhile, ΔE_{Hads} represents the adsorption energy of a H atom on substrates and was calculated by Eq. (2):

$$\Delta E_{Hads} = E_{sub+H} - E_{sub} - \frac{1}{2} E_{H_2} \quad (2)$$

where E_{sub+H} , E_{sub} , and E_{H_2} are the total energies of a H atom on substrate, substrate without adsorption, and an isolated H_2 molecule, respectively.

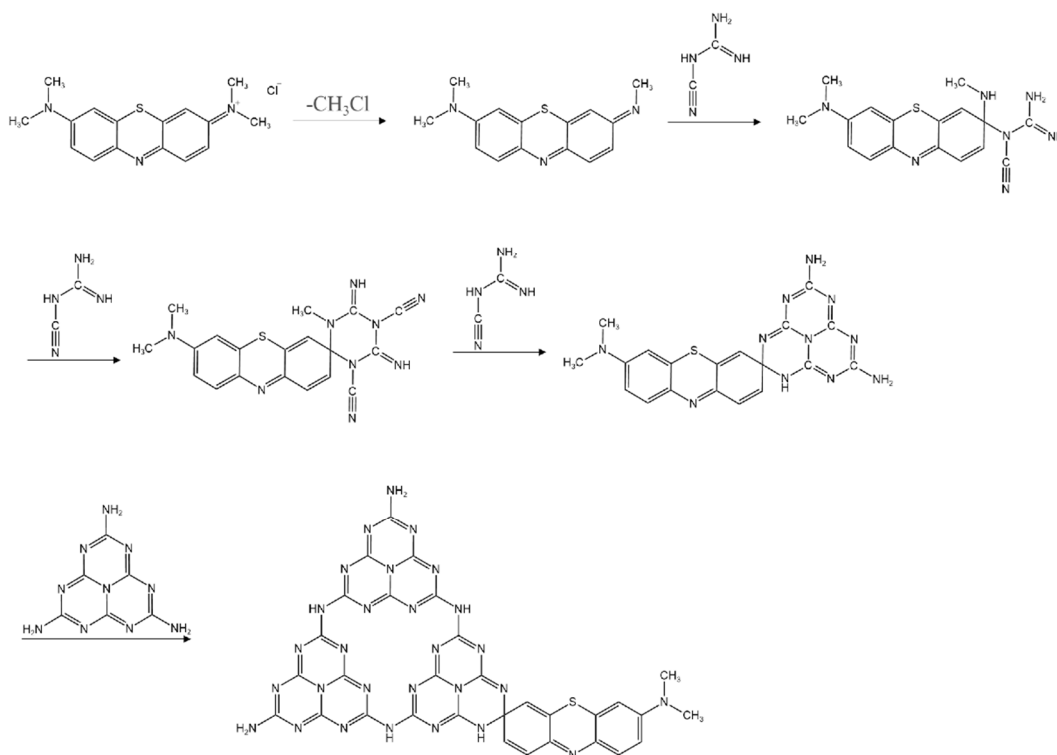


Fig. S1 Possible reaction path for incorporating MB indicator into g-C₃N₄ networks in thermal copolymerization process

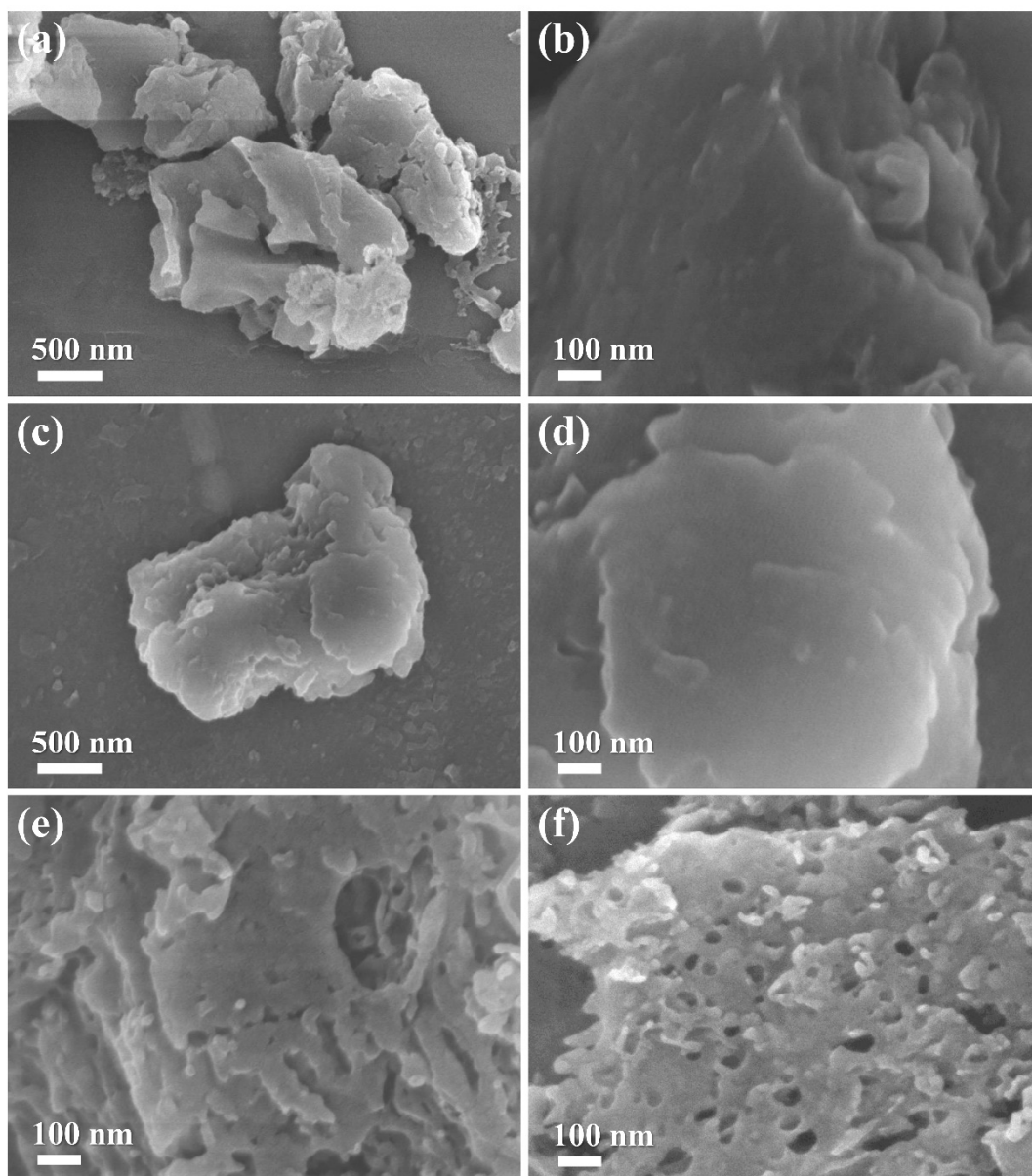


Fig. S2 FESEM images of (a, b) CN, (c, d) CN-MB₁₀, (e) TCN, and (f) TCN-MB₁₀.

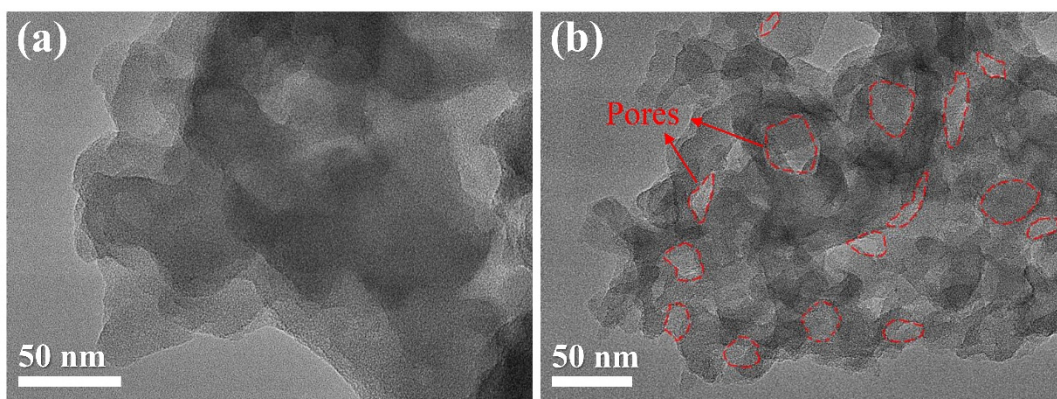


Fig. S3 TEM images of (a) CN-MB₁₀ and (b) TCN-MB₁₀.

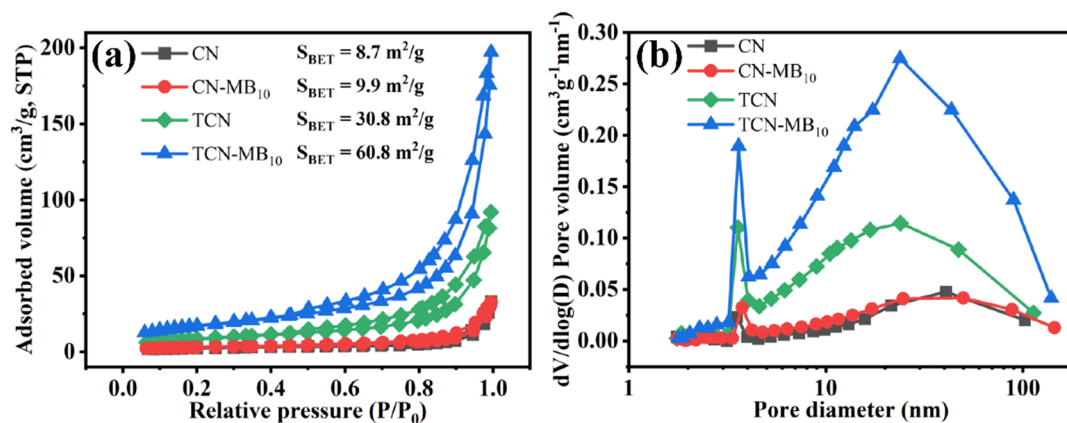


Fig. S4 (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore size distribution of CN, CN-MB₁₀, TCN, and TCN-MB₁₀.

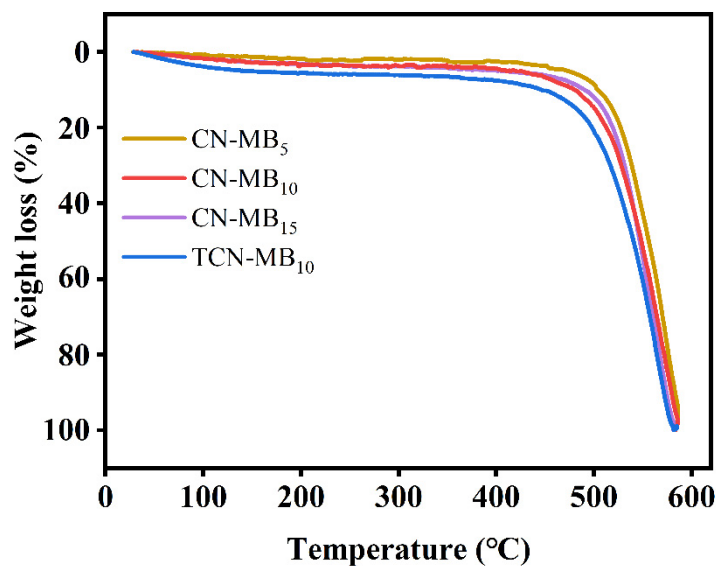


Fig. S5 TGA curves of CN-MB₅, CN-MB₁₀, CN-MB₁₅, and TCN-MB₁₀ under air atmosphere at a heating rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

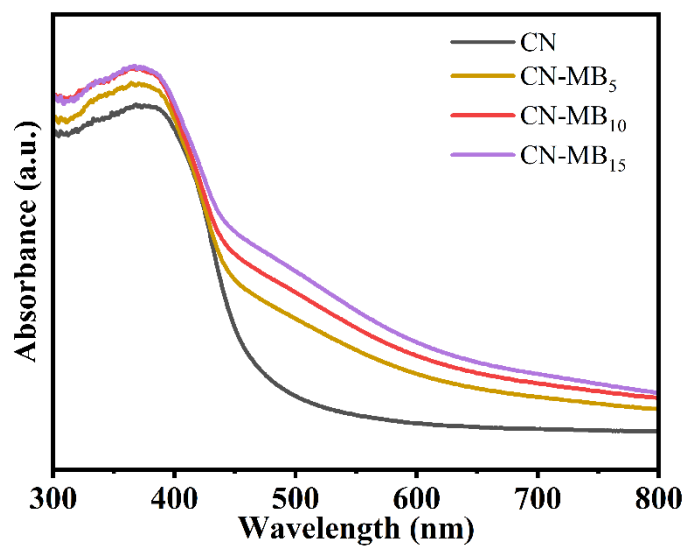


Fig. S6 UV-Vis DRS of CN, CN-MB₅, CN-MB₁₀ and CN-MB₁₅.

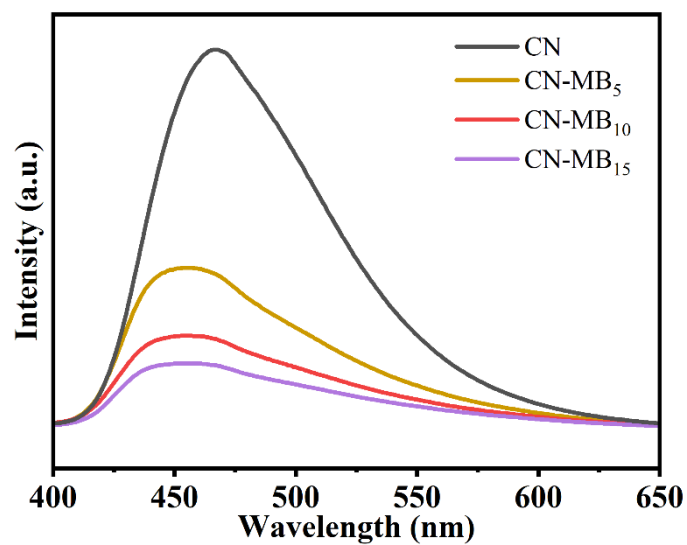


Fig. S7 PL spectra of CN, CN-MB₅, CN-MB₁₀ and CN-MB₁₅.

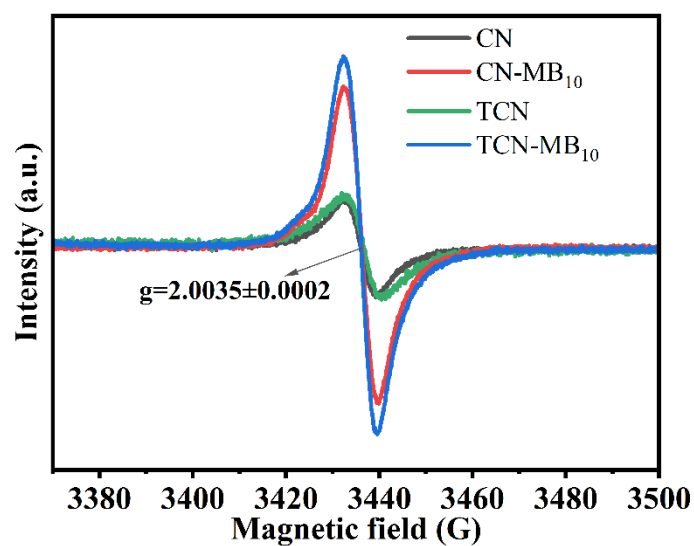


Fig. S8 EPR spectra of CN, CN-MB₁₀, TCN and TCN-MB₁₀.

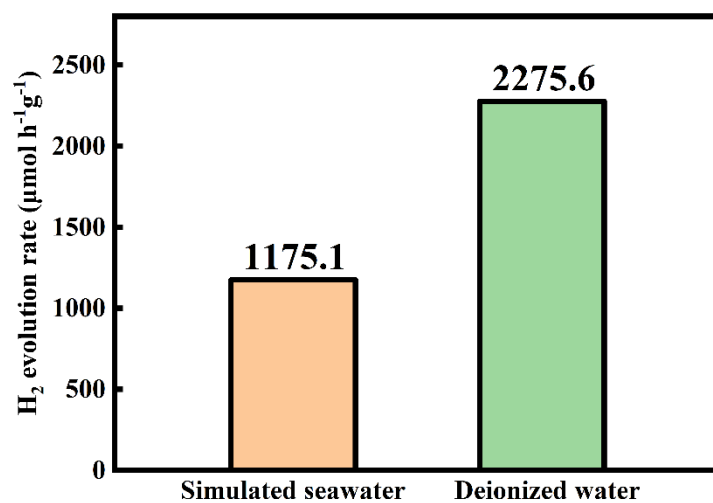


Fig. S9 Hydrogen evolution rates of TCN-MB₁₀ in simulated seawater and deionized water.

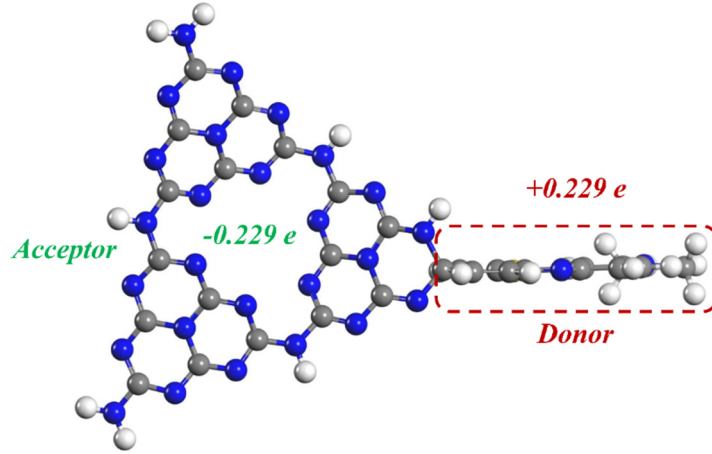


Fig. S10 Bader charge distribution on geometry optimized model of CN-MB₁₀ (top view), where the part circled by red dashline is MB segment and the grey, blue, and white spheres represent C, N, and H atoms, respectively.

Table S1 Structural parameters of CN, CN-MB₁₀, TCN, and TCN-MB₁₀.

Sample	N ₂ adsorption isotherm /hysteresis loop	$S_{\text{BET}}/(\text{m}^2\cdot\text{g}^{-1})$	Average pore volume /($\text{cm}^3\cdot\text{g}^{-1}$)	Average pore size/nm
CN	Type-IV/Type-H3	8.7	0.05	23.81
CN-MB ₁₀	Type-IV/Type-H3	9.9	0.05	20.66
TCN	Type-IV/Type-H3	30.8	0.14	18.49
TCN-MB ₁₀	Type-IV/Type-H3	60.8	0.31	20.06

Table S2 Surface elemental composition of CN, CN-MB₁₀, TCN, and TCN-MB₁₀ according to XPS survey spectra.

Sample	C/atomic %	N/atomic %	O/atomic %	S/atomic %	C/N
CN	43.35	53.41	3.24	0	0.81
CN-MB ₁₀	43.14	52.20	4.40	0.26	0.83
TCN	43.11	52.81	4.08	0	0.82
TCN-MB ₁₀	42.86	53.77	3.14	0.23	0.80

Table S3 The fitted fluorescence decay components and corresponding relative amplitude of CN, CN-MB₁₀, TCN, and TCN-MB₁₀.

Sample	Decay time (τ_i/ns) & Relative amplitude ($f_i/\%$)						τ_{ave}
	τ_1	f_1	τ_2	f_2	τ_3	f_3	
CN	0.94	29.55	4.24	49.12	23.30	21.33	7.33
CN-MB ₁₀	0.77	38.96	3.56	47.21	19.92	13.84	4.74
TCN	0.97	30.27	4.06	51.73	20.77	17.99	6.13
TCN-MB ₁₀	0.74	39.71	3.09	47.94	16.24	12.35	3.78

* The time-resolved fluorescence decay curve is fitted with a triple-exponential function (1) and the relavent average fluorescence lifetime is based on Eq. (2):

$$I(t) = A_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}} \quad (1)$$

$$\tau_{\text{ave}} = f_1 \tau_1 + f_2 \tau_2 + f_3 \tau_3 \quad (2)$$

Table S4 The relevant parameters for AQE calculation of CNDM₂₀₀.

Dosage	Cocatalyst	Reactant solution & Sacrificial reagent	Bandpass (λ)	Irradiation area (S)	Light irradiance (I)	Irradiation time (t)	Evolved H ₂ (n_{H_2})
20 mg	3 wt% Pt	Water (72 mL) & TEOA (8 mL)	420 nm	25.5 cm ²	3.0 mW·cm ⁻²	1 h	5.152 μmol

* The value of n_{H_2} was acquired from the first hour in cycle 2 during the stability test of CNDM₂₀₀.

$$\begin{aligned} \text{AQE} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 (\%) = \frac{\text{number of evolved hydrogen molecules} \times 2}{\text{number of incident photons}} \times 100 (\%) = \frac{2 \times N_A \times n_{\text{H}_2}}{I \times S \times t \times \frac{\lambda}{hc}} \times 100 (\%) \\ &= \frac{2 \times 6.02 \times 10^{23} [\text{mol}^{-1}] \times 5.152 \times 10^{-6} [\text{mol}]}{30 [\text{W} \cdot \text{m}^{-2}] \times 2.55 \times 10^{-3} [\text{m}^2] \times 3600 [\text{s}] \times \frac{420 \times 10^{-9} [\text{m}]}{6.63 \times 10^{-34} [\text{J} \cdot \text{s}] \times 3 \times 10^8 [\text{m} \cdot \text{s}^{-1}]}} \times 100 (\%) = 1.1\% \end{aligned}$$

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