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Copolymerization of urea and murexide for efficient photocatalytic hydrogen evolution and tetracycline degradation

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Characterization

The X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The measurements were scanned over a range of 5° to 50° (2θ) with a step size 20° . Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEM-2100F microscope at an acceleration voltage of 200 kV. The scanning electron microscope (SEM) images were performed on a JEOL JSM 4800F SEM. EDS was used to measure the species and contents of component elements of the samples. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet iS10 FTIR spectrometer. Elemental analysis (C, N) was achieved by a Vario EL cube microanalyzer. The optical absorption spectra of the samples were recorded in a UV-2600 UV-Vis spectrophotometer (Shimadzu). The UV-Vis diffuse reflectance spectra (DRS) employed BaSO₄ as a reference by UV-2600 spectrophotometer. The TC concentrations were also detected by UV-2600 UV-vis spectrophotometer at 360 nm wavelength. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALABMKII spectrometer with an Al-K α achromatic X-ray source. The Brunauer-Emmett-Teller (BET) specific surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K with a Micromeritics Autosorb IQ instrument. Photoluminescence (PL) spectra and transient PL lifetime were tested on a spectrometer (Horiba Jobin Yvon Fluorolog-3) with a QY2 accessory and a time-correlated single-photon counting lifetime spectroscopy system. The electron paramagnetic resonance (EPR) measurements were carried out on a JEOL JES-FA200 spectrometer.

Electrochemical measurements

Electrochemical analysis was carried out using a CHI6082E electrochemical workstation in a conventional three electrode cell using a Pt plate and an Ag/AgCl electrode as counter electrode and reference electrode, respectively. Working electrodes were obtained as the following method: 30 mg of different catalysts was dispersed in solvent of 2 ml ethanol, and sonicated for 30 min to obtain a uniformly dispersed solution. Transferring photocatalyst suspensions onto a $1 \times 2 \text{ cm}^2$ FTO conductive glass by a spin-coating method. Finally, the working electrode was air-dried at room temperature. The electrolyte was a 0.2 M Na₂SO₄ solution. For photocurrent measurement (*i-t* curves), a 300 W (CEL-HXF300, AULIGHT) Xe lamp was utilized as the light source. For electrochemical impedance spectroscopy (EIS) experiment, frequency ranges from 0.01 Hz to 10 kHz at -0.2V, the others unchanged.

Photocatalytic hydrogen evolution test

The photocatalytic reactions were carried out in a quartz reaction vessel connected to a closed gas circulation and evacuation system (CEL-SPH2N, CEAULIGHT). 10 mg of the photocatalyst powder was dispersed in 120 mL of aqueous solution containing triethanolamine (10 vol%) as the sacrificial electron donor. 3 wt.% Pt co-catalyst was photo-deposited by dissolving H₂PtCl₆ in the above 120 mL reaction solution. The temperature of the reactant solution was kept at 283K by a flow of cooling antifreezing solution during the reaction. The suspension was thoroughly degassed and irradiated with a 300W Xe lamp (CEL-HXF300, AULTT) by attaching a 420nm cut-off filter at the light source. The evolved gases were analyzed by gas chromatography (GC-7900, CEAULIGHT) every 30 min equipped with a thermal conductive detector, using argon as the carrier gas. For the stability test, the reaction system was evacuated every 3 h and recycled for 5 runs. (15 h recycling experiment with intermittent evacuation every 3 h.

Apparent quantum efficiency (AQE) measurement

The apparent quantum yield (AQE) for H₂ evolution was obtained by using the 400, 420, 450, 500, 550, and 600 nm band-pass filter. The AQE was estimated as follows:

$$\text{AQE (\%)} = \text{number of evolved H}_2 \text{ molecules} \times 2 \times 100 / \text{number of incident photons}$$

Photocatalytic degradation of TC test

The photocatalytic degradation of tetracycline under visible light was used as a model to evaluate the photocatalytic performance of the samples. Visible light irradiation was achieved by a xenon lamp with a 420 nm cut-off filter. The device was connected to a circulating water-cooling system with a constant temperature of 25 °C. First, 20 ml of 20 ppm tetracycline solution and 20 mg of catalysts were placed in a beaker for ultrasonication and the reaction was in dark for 30 min under magnetic stirring to achieve adsorption-desorption equilibrium. Then the solution was illuminated for 2 h, 1 ml of suspension was taken every 20 min, centrifuged, and the supernatant was subjected to make a spectral test with an ultraviolet-visible spectrophotometer. Under the same conditions, the free radical trapping experiment was conducted by adding appropriate amounts of TEMPO, TEOA and IPA. TC and intermediates were monitored by LC-MS, which were obtained on an HP 6890GC-5973MSD mass spectrometer. A positive ionization electrospray ionization (ESI) source was used for spectrometer analysis in the m/z 100-500 range.

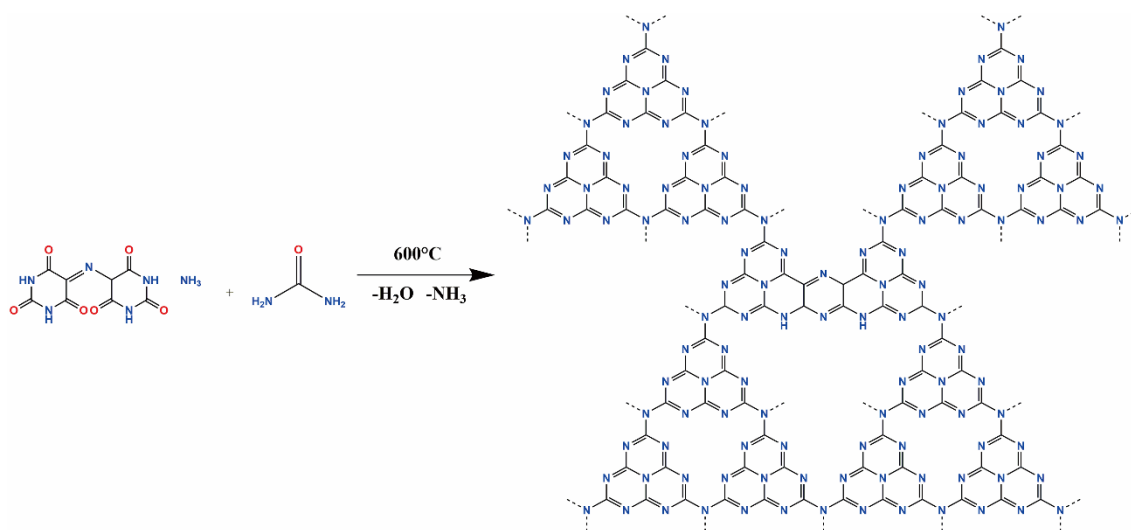


Fig. S1 Schematic illustration of the formation process of M₂₅CN.

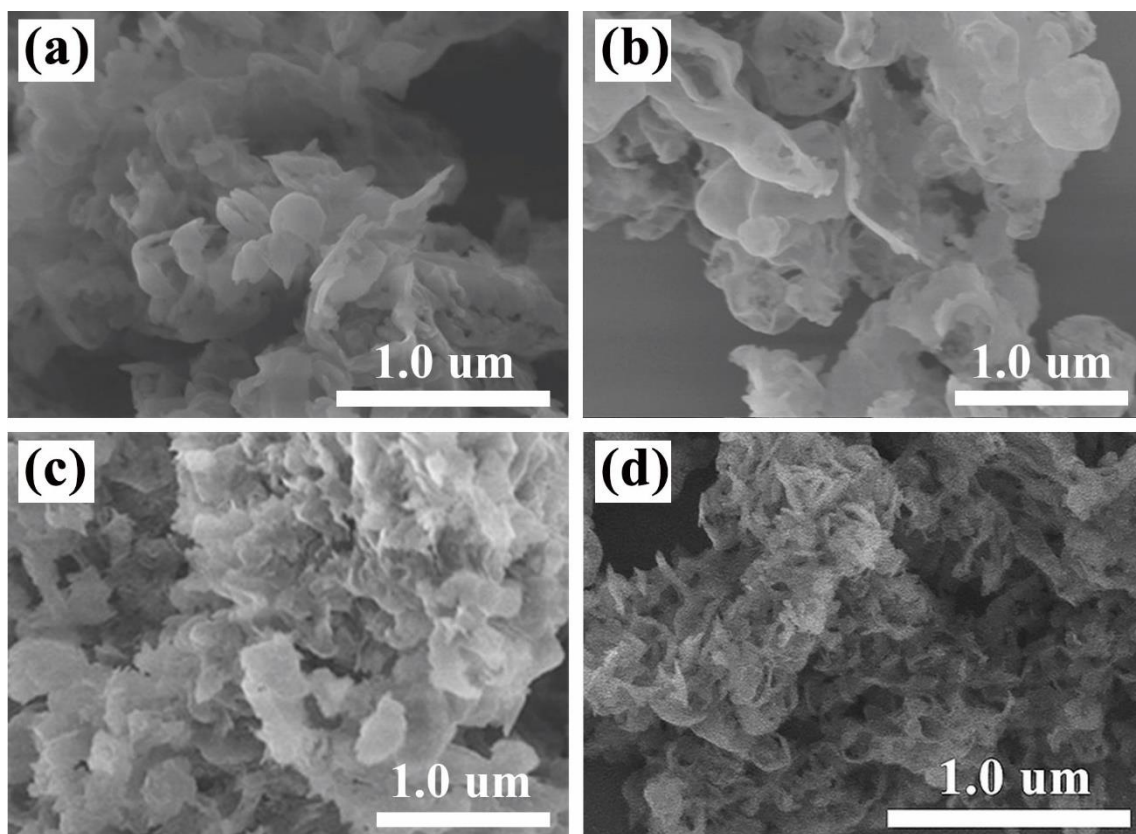


Fig. S2 SEM images of (a) M₅CN (b) M₁₅CN (c) M₅₀CN (d) M₁₀₀CN.

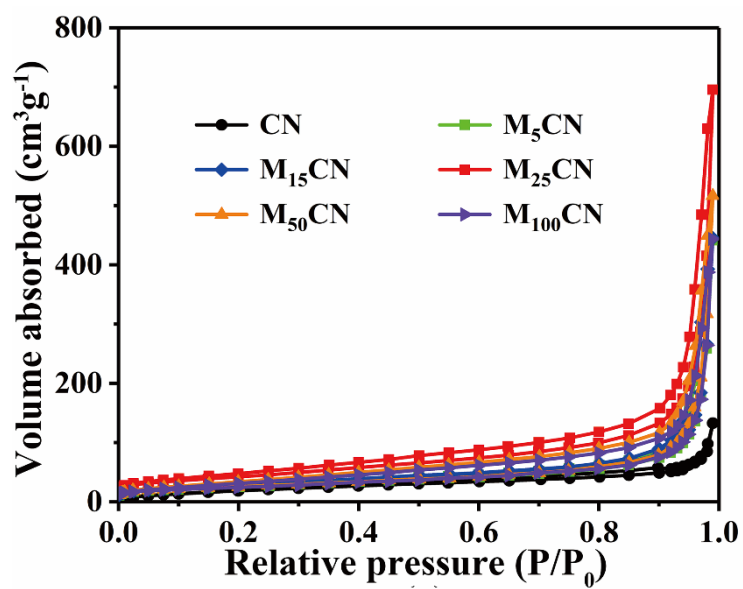


Fig. S3 Nitrogen adsorption-desorption isotherms of CN and M_xCN.

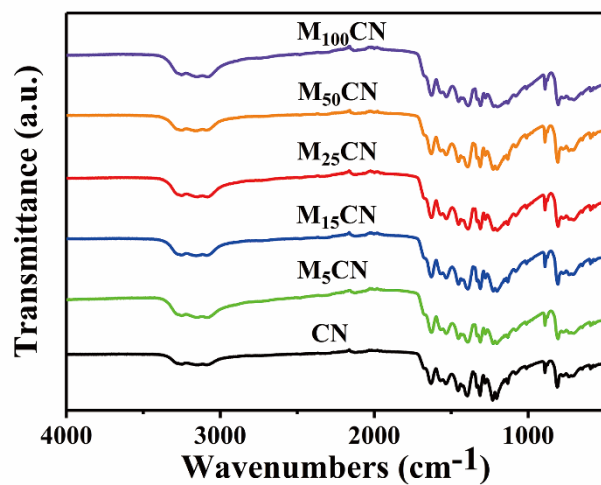


Fig. S4 FTIR spectra of CN and M_xCN.

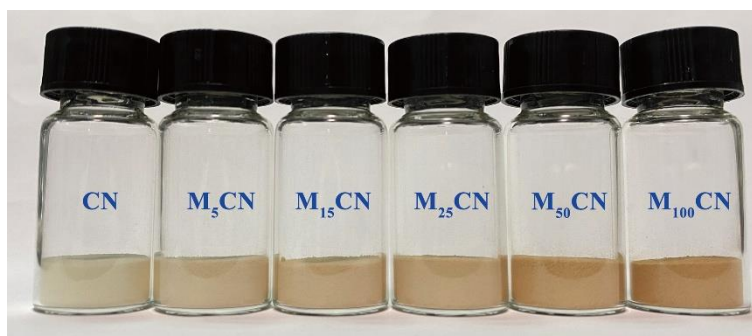


Fig. S5 The color of CN and M_xCN.

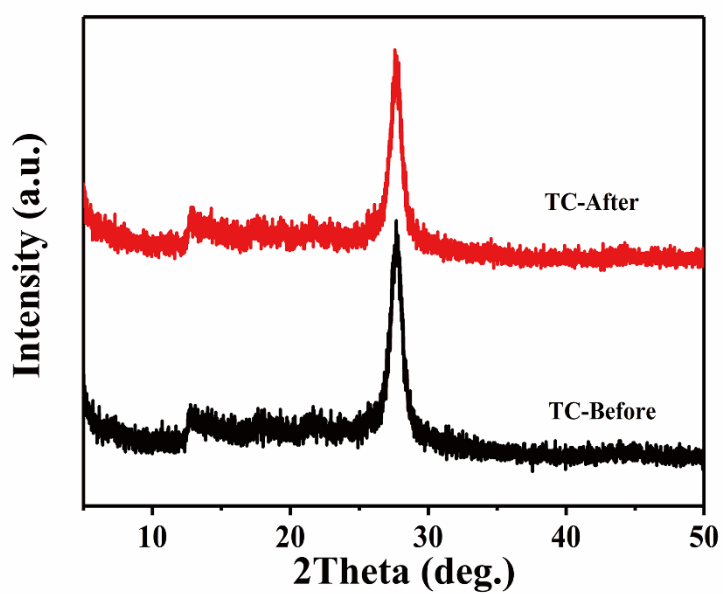


Fig. S6 XRD patterns of M₂₅CN before and after photodegradation of TC.

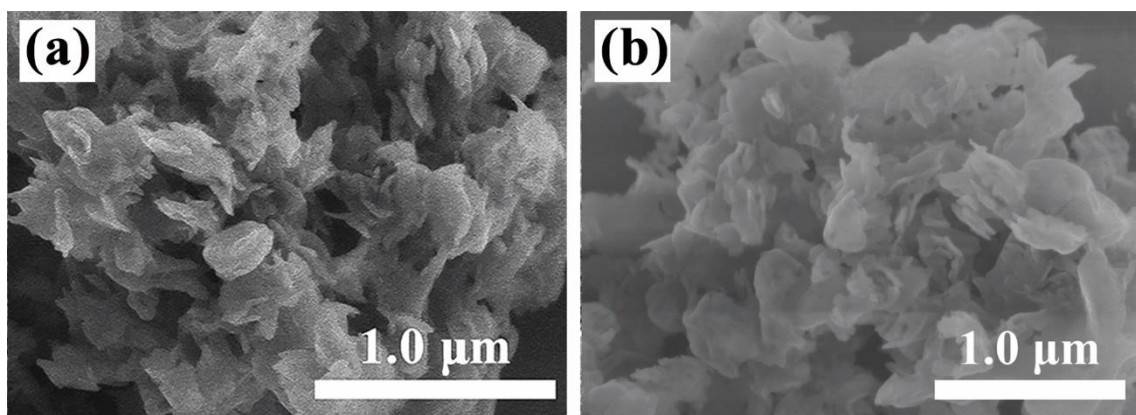


Fig. S7 SEM images of M₂₅CN before (a) and after (b) photodegradation of TC.

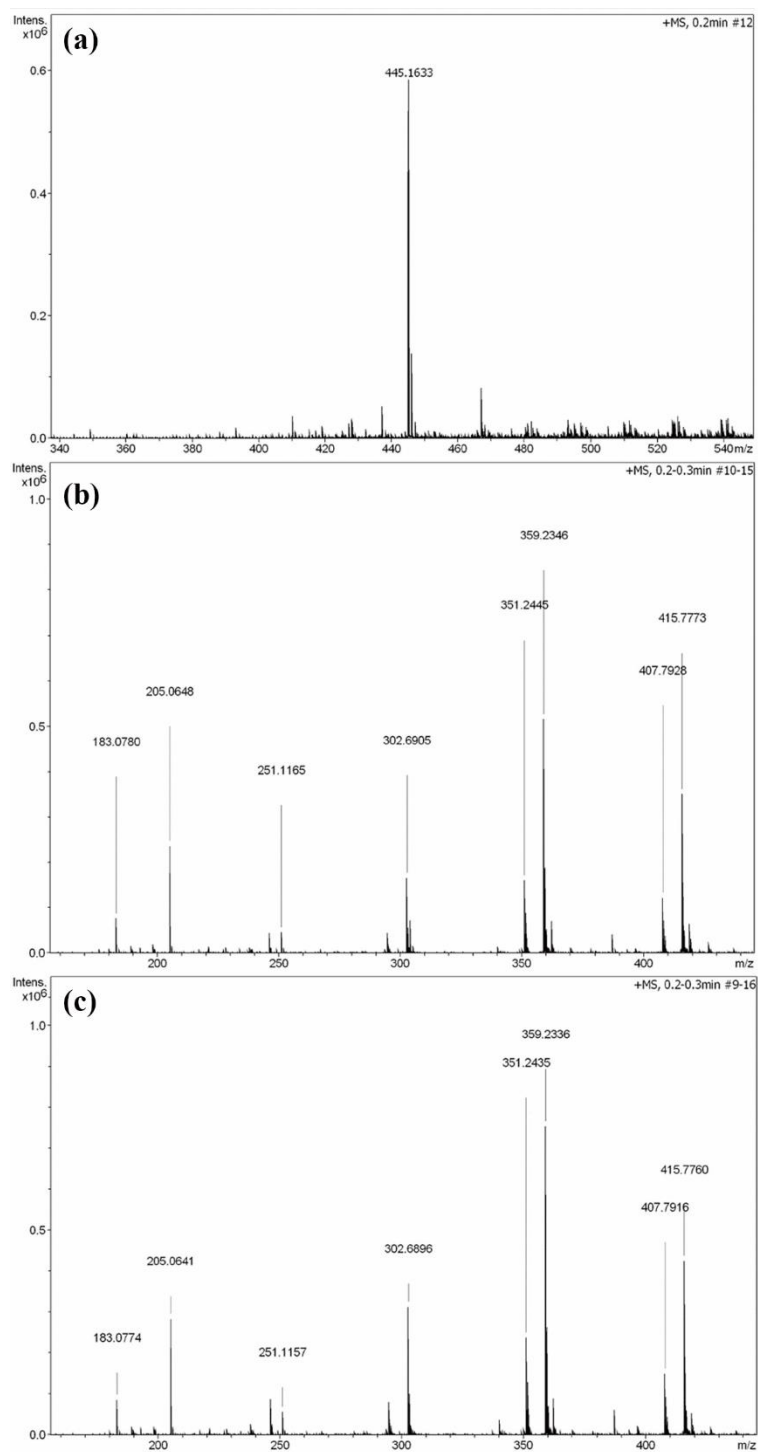


Fig. S8 LC-MS full scan spectra of the main intermediates in TC degradation for (a) 0, (b) 60 and (c) 120 min by M₂₅CN.

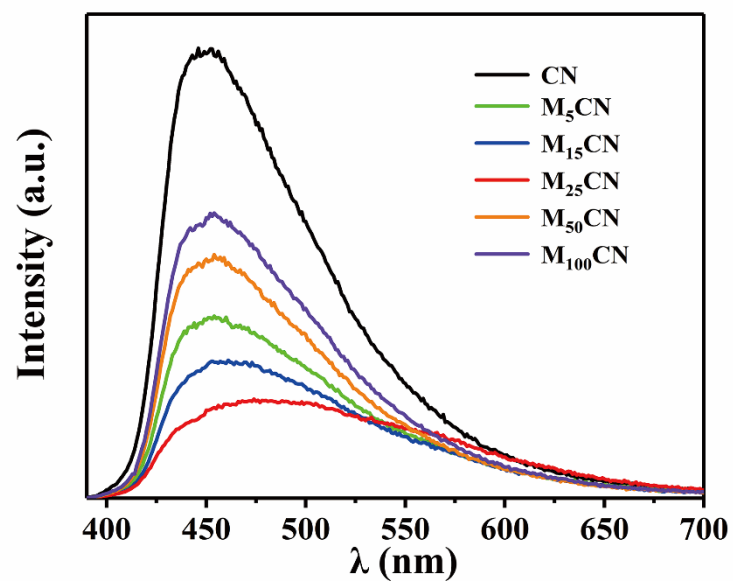


Fig. S9 PL emission spectra of CN and M_x CN ($\lambda_{ex} = 370$ nm).

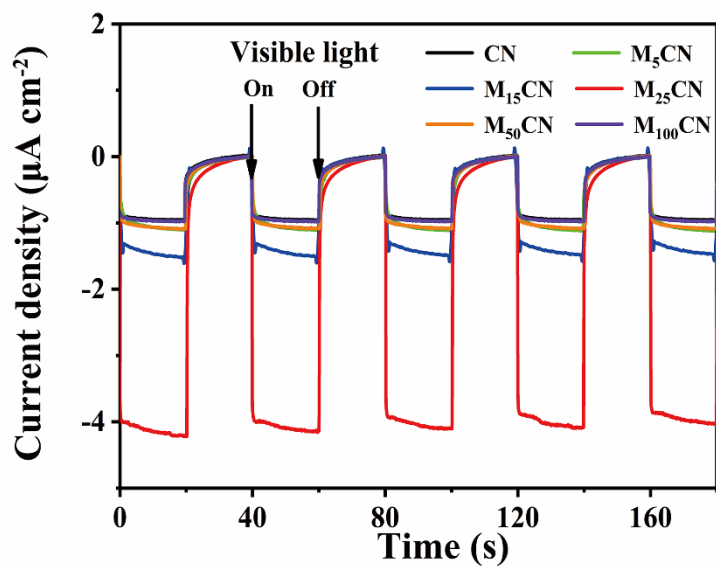


Fig. S10 (a) Photocurrent responses of CN and M_x CN with visible light irradiating ($\lambda \geq 420$ nm).

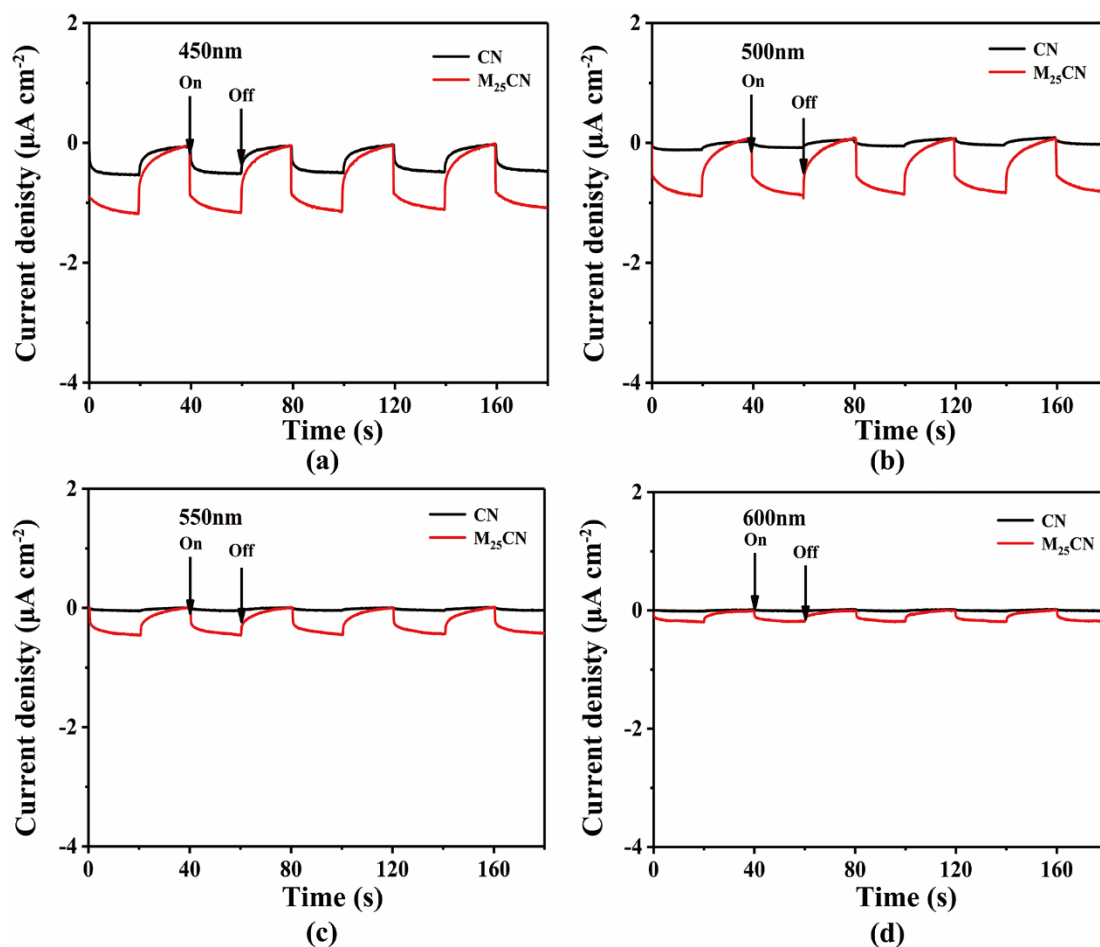


Fig. S11 Transient photocurrents of CN and $M_{25}\text{CN}$ at different wavelength bands ($\lambda = 450, 500, 550, 600 \text{ nm}$).

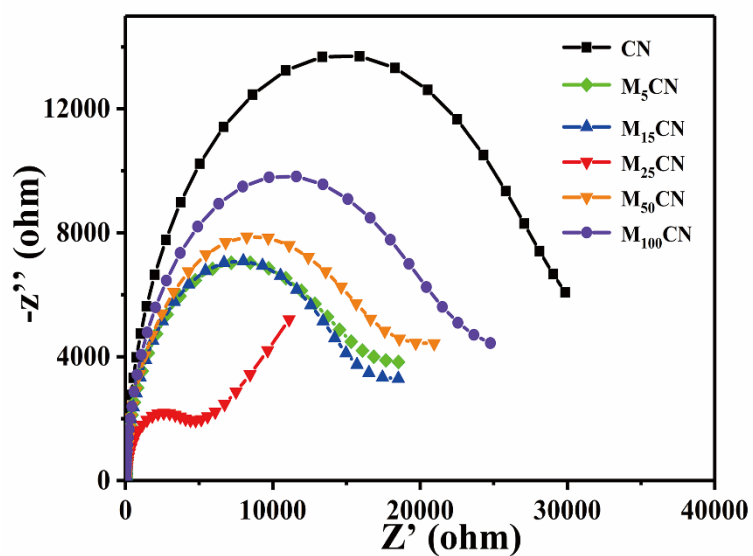


Fig. S12 Electrochemical impedance spectroscopy plots of CN and $M_x\text{CN}$ in the dark.

Table S1 The BET surface areas of CN and M_xCN.

Sample	CN	M ₅ CN	M ₁₅ CN	M ₂₅ CN	M ₅₀ CN	M ₁₀₀ CN
Surface area(m ² g ⁻¹)	77.22	90.80	99.06	154.47	91.86	87.16

Table S2 The elemental analysis data of CN and M₂₅CN.

Sample	C/wt.%	N/wt.%	C/N
CN	35.81	64.91	0.64
M ₂₅ CN	37.68	62.55	0.70

Table S3 Comparison of g-C₃N₄-based small molecule copolymers in photocatalytic hydrogen production (HER).

Samples	Amounts (mg)	HER (μmol h ⁻¹ g ⁻¹)	Wavelength (nm)	ref
MCN	10	6120	λ > 420	This work
CNAL	100	2260	420 < λ < 780	R1
CNQ	100	4360	420 < λ < 780	R2
Pt/CNU-M	50	8000	λ > 420	R3
CNB	100	294	λ > 420	R4
CN-ABN	100	1470	λ > 420	R5
Pt/CNU-ATCN	50	14500	λ > 420	R6
CNA	100	1310	λ > 420	R7
V-CN	10	13600	λ > 420	R8

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Table S4 The fitted parameters of fluorescence lifetime for CN and M₂₅CN. ($y=A_1 \cdot \exp(-x/\tau_1) + A_2 \cdot \exp(-x/\tau_2) + B$)

Sample	τ_1 /ns (rel.%)	τ_2 /ns (rel.%)	A ₁	A ₂	τ /ns
CN	3.63(0.58)	19.44(0.42)	617.28	83.67	10.27
M ₂₅ CN	2.26(0.61)	10.11(0.39)	944.38	133.82	5.32