Electronic Supplementary Information

Porous carbon nitride rods as an efficient photoanode for water splitting and benzylamine oxidation

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Detailed synthetic procedures

Materials: Melamine (99%) was purchased from Sigma-Aldrich. Ethylene glycol (EG, ≥99.5%) and potassium persulfate ($K_2S_2O_8$, ≥99%) were bought from Merck. Dichloromethane (CH_2Cl_2, 99.5% amylene-stabilized), ethyl acetate (≥99%), (ethanol (≥99.9%) and acetone (99.5%) were purchased from Bio-Lab Ltd, Israel. Hydrochloric acid (HCl, AR, 35% wt.) was purchased from Carlo Erba. Potassium hydroxide pellets (KOH, AR, 85% wt.) sodium hydroxide (NaOH, 99%) and sodium sulfate anhydrous (Na_2SO_4, AR, 99%) were purchased from Loba Chemie, India. Triethanolamine (TEOA, ≥99.0%) was purchased from Glentham, UK. FTO-coated glass (12–14 Ω sq^{-1}) was bought from Xop Glass company, Spain. Deuterium oxide (D_2O, 99.9 at% D) was purchased from Sigma-Aldrich. Benzylamine ($BnNH_2$, >99%) was purchased from TCI. In addition, deionized (DI) water with 18.2 MΩ cm resistivity was obtained from a Millipore Direct-Q3 water purification system. All chemicals were used as received from the respective commercial vendors without further purification.

Characterization: The structural analysis of all synthesized films was performed using powder X-ray diffraction patterns (XRD) recorded by a PANalytical's Empyrean diffractometer, equipped with a position-sensitive detector X'Celerator. Data was recorded with a scanning time of ~15 min for 2θ ranging from 5° to 60° using Cu Kα radiation (λ = 1.54178 Å, 40 kV, 30 mA). Fourier-transform infrared spectroscopy (FTIR) was carried out to study the synthesized materials' functional groups on a Thermo Scientific Nicolet iS5 FTIR spectrometer (equipped with a Si attenuated total reflectance (ATR) accessory). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCALAB 250 (Al Kα, 1486.6 eV). The valence band (VB) maximum energy was estimated using ultraviolet photoelectron spectroscopy (UPS) measurements in a Thermo Scientific ESCALAB Xi+ with a HeI excitation source. UV–vis absorption spectroscopy (Cary 100 spectrophotometer, equipped with a diffuse reflectance accessory (DRA)) and steady-state photoluminescence (PL) spectroscopy

(Horiba Scientific FluroMax 4 spectrofluorometer) were used to study the optical properties of the materials. Time-resolved fluorescence measurements were carried out on a time-correlated single-photon counting (TCSPC) setup with a Horiba Fluorolog modular spectrofluorometer. The PL lifetimes (τ_{av}) were calculated from the time-resolved PL spectra decay curves fitted using a tri-exponential function. The morphology of the supramolecular precursor and the final photoelectrodes were characterized by scanning electron microscopy (SEM) using an FEI Verios ultrahigh-resolution SEM (equipped with a FEG source and a TLD detector), operated at U_0 = 3.5 kV and I = 25 pA; to avoid charging effects, some samples were sputtered with ≤ 5 nm Au-Pd alloy using a Quorum Q150T ES system). In addition, elemental analysis data for carbon, hydrogen, and nitrogen (C, H, and N) was obtained using a Thermo Scientific Flash Smart elemental analyzer OEA 2000.

PEC and electrochemical measurements: All the photoelectrochemical measurements were carried out using a standard three-electrode system on a single-channel PalmSens4 potentiostat (PalmSens, Netherlands). A Pt foil (1.0 cm^2) and Ag/AgCl (saturated KCl) were used as the counter- and reference-electrodes, respectively. 0.10 M KOH aqueous solution, (pH ~13.1) or 0.1 M KOH aqueous solution containing 10% v/v triethanolamine were used as the electrolyte for the photocurrent experiments. Additionally, 0.50 M Na_2SO_4 and 0.50 M H_2SO_4 aqueous solutions were also used for photocurrent measurements in neutral and acidic environments, respectively. The measured potentials ($V_{Ag/AgCl}$) were converted to the reversible hydrogen electrode (RHE) scale using the following equation (room temperature; Ag/AgCl in saturated KCl reference electrode):

$$V_{RHE} = V_{Ag/AgCl} + 0.0591 \times pH + 0.197 \text{ V}$$

Photocurrent density of the CN films was measured at a bias potential of V_{RHE} = 1.23 V (*i.e.*, 1.23 V versus (*vs.*) RHE) under 1 sun illumination (power density of ~100 mW cm^{-2}) supplied by a Newport LCS-100 solar simulator (100 W Xe lamp and an integrated AM 1.5 filter,

calibrated using a Newport 919P power meter). Linear sweep voltammetry (LSV) measurements were performed in the dark and under 1 sun illumination in the range of 0–1.8 V *vs.* RHE. Electrochemical impedance spectroscopy (EIS) measurements and Mott-Schotky were performed using an Autolab potentiostat (Metrohm, PGSTAT302N). Mott–Schottky plots of CN films were measured in 0.5 M Na_2SO_4 at a frequency of 1.0 kHz.

Oxygen (O_2) generation for $CN_{M-HCl(HT)}$ film in 0.1 M KOH solution was detected using an optical fiber-basedc oxygen meter (Firesting GmbH, Germany) under chronoamperometric condition (1.23 V *vs.* RHE, 1 sun illumination) in a three electrode cell. The cell was tightly sealed with a rubber septum and parafilm to avoid gas leakage. The electrolyte solution was purged with Ar for 30 min before the experiments. The O_2 measurement was performed for a duration of 1 hour. The presented data was acquired after background subtraction. The Faradaic efficiency (FE) was calculated using equations S1–S2:

$$n = \frac{I \times t}{z \times F} \hspace{4cm} \text{(Eq. S1)}$$

Where n is the O_2 amount (measured in mol), I stand for current (A), z is the number of transferred electrons (for O_2 evolution, $z = 4$), t is the time (s), and F is the Faraday constant (96,485C mol^{-1}).

The theoretical amount of O_2 was calculated from Equation S2:

$$FE(\%) = \frac{\text{Experimental } \mu\text{mol of } O_2}{\text{Theoretical } \mu\text{mol of } O_2} \times 100\% \hspace{2cm} \text{(Eq. S2)}$$

For incident photon-to-current conversion efficiency (IPCE) measurements, a Zahner CIMPS-QE/IPCE photoelectrochemical workstation coupled with a TLS03 tunable light source controlled by a PP211 potentiostat (Zahner-Elektrik, Germany) in a dedicated three-electrode photoelectrochemical cell (PEEC-2) using an Ag/AgCl (sat. KCl) reference electrode and Pt coil as the counter electrode was used. The IPCE calculations were performed using equation S3:

$$\text{IPCE}(\%) = \frac{J\left(\text{mA cm}^{-2}\right) \cdot 1240}{\lambda(\text{nm}) \cdot I_{\text{incident}}(\text{mW cm}^{-2})} \times 100\% \qquad \text{(Eq. S3)}$$

Where J is the photocurrent density, I is the (calibrated to illumination spot of 8 mm in diameter) incident illumination power, λ is the illumination wavelength, and 1240 is the units conversion factor. The calculation was performed by the coupled ThalesXT software.

Preparation of supramolecular assemblies: In a typical synthesis, melamine (3.00 g) was dissolved in 60.0 mL DI H_2O followed by the addition of HCl (0, 4.2, 8.4, or 12.6 mmol of HCl which corresponds to 0, 0.3, 0.6, or 0.9 mL of 35 wt. % HCl) and stirred at 600 rpm for 1 h. The resulting mixture was transferred into an 80 mL PTFE-lined autoclave and heated at 140 °C for 4 h. The supramolecular assemblies are denoted with the volume of used HCl and (HT) to mark the hydrothermal treatment (M(HT), M-HCl$_{4.2}$(HT), M-HCl$_{8.4}$(HT), and M-HCl$_{12.6}$(HT)). All samples were collected by centrifugation and kept inside an oven at 60 °C overnight. Note that if concentration is not noted in the shorthand notation M-HCl(HT) it refers to M-HCl$_{8.4}$(HT).

Synthesis of CN$_M$ films (serving as a reference or 'control' photoactive layer): In a typical synthesis, a CN$_M$ film was prepared by grinding melamine powder (1.00 g) in 0.6 mL ethylene glycol until obtaining a slurry. The obtained slurry was doctor-bladed onto a substrate (FTO-coated glass) with a predefined thickness achieved by setting L layers of scotach tape (in all samples L =2 unless stated otherwise for a thickness experiment where L was set also to 1 or 3). The obtained homogeneous slurry coating was subsequently dried on a hot plate (surface setpoint temperature, T_{SP} = 90 °C) for 30 min, and finally placed inside a glass test tube (d = 13 mm) with 0.5 g of melamine powder at the bottom of the test-tube. The test tube was closed with an aluminum foil and calcined in a tube furnace at T_{SP} = 530 °C for 4 h (heating profile from room temperature to T_{SP} at 5 °C min^{-1} heating rate) under a constant N$_2$ flow.

Note that all the FTO substrates were cleaned before use by a successive sonication in an aqueous detergent solution (1% w/v Alconox), then DI water, acetone, and ethanol, and finally dried before performing the doctor-blade procedure.

Synthesis of CN$_{M(HT)}$ and CN$_{M-HCl(HT)}$ films: CN$_{M(HT)}$ and CN$_{M-HCl(HT)}$ films were prepared by grinding 1.00 g of supramolecular assemblies (M$_{(HT)}$ and M$_{HCl(HT)}$, respectively) in 0.6 mL ethylene glycol until a homogeneous paste was obtained. The rest of the procedure (doctor-blading and calcination) is identical to the CN$_M$ film protocol. Unless stated otherwise, CN$_{M-HCl(HT)}$ refers to the films prepared from the supramolecular aggregate treated with 8.4 mmol HCl (*i.e.*, M-HCl(HT) is a short notation for M-HCl$_{8.4}$(HT)).

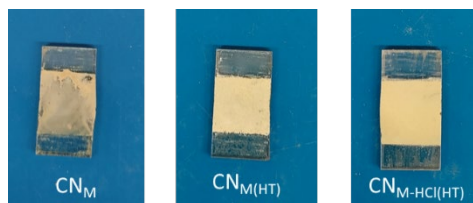**Electronic Supplementray Information Figures and Tables**

CN$_M$　　CN$_{M(HT)}$　　CN$_{M-HCl(HT)}$

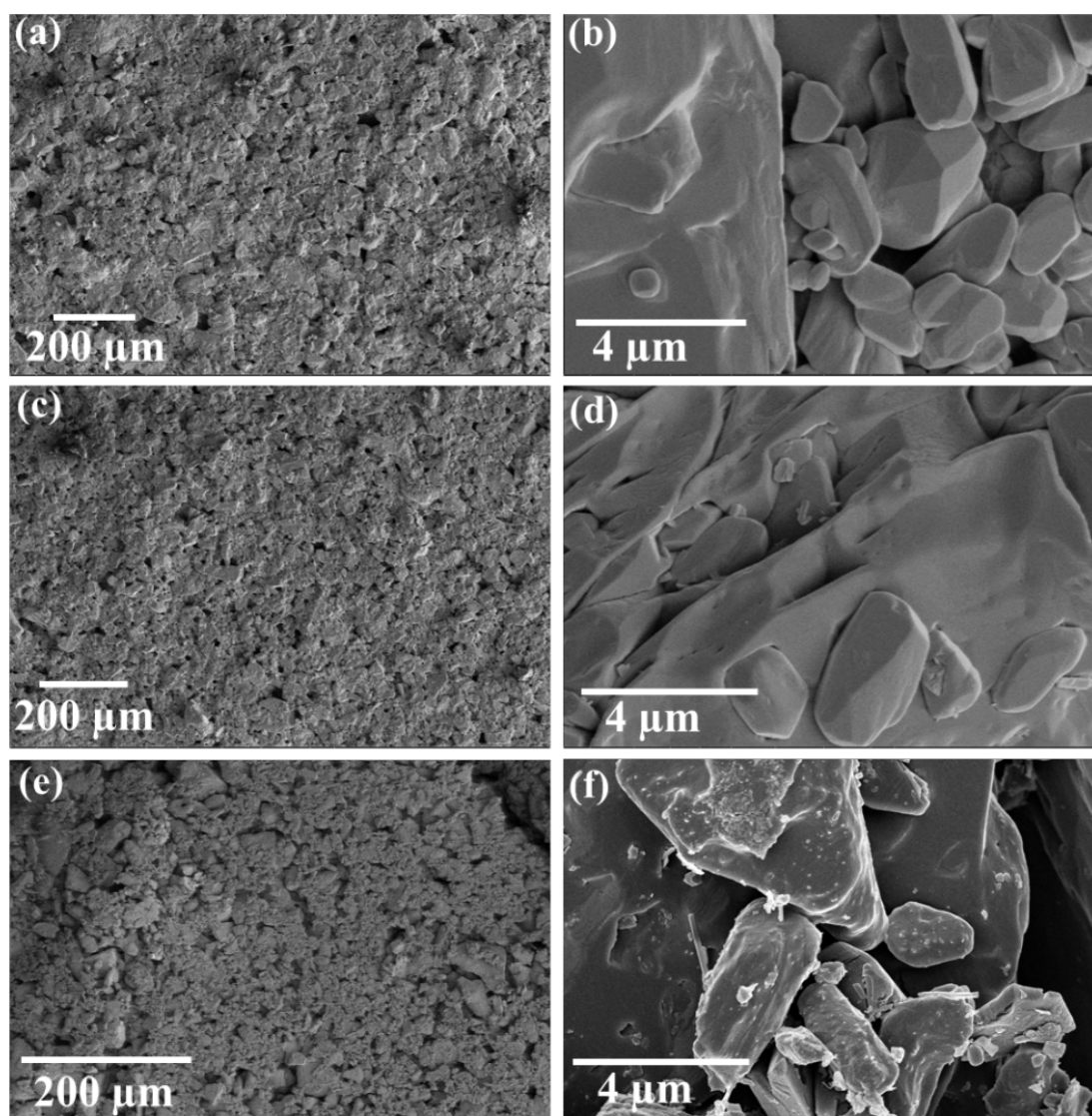**Fig. S1** Images of the CN films.

Fig. S2 Top-view SEM images of the supramolecular assemblies (the CN precursors) at two magnifications. (a,b) M, (c,d) M(HT), and (e,f) M-HCl(HT).
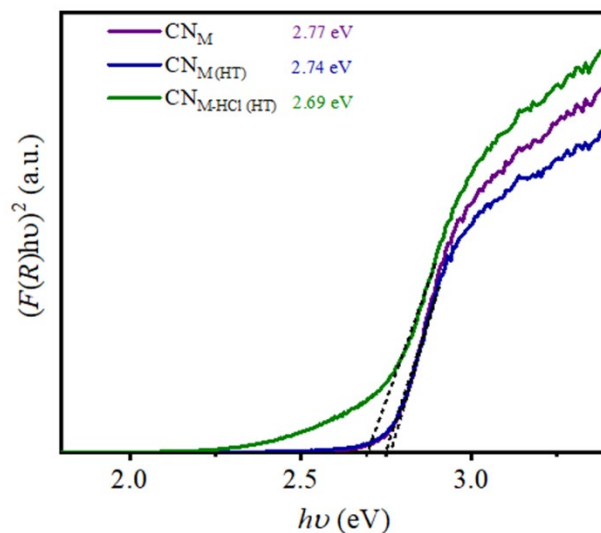
Fig. S3 Tauc plot analyses of CN$_M$, CN$_{M(HT)}$ and CN$_{M-HCl(HT)}$ films using a direct band gap assumption. As a measure of the absorbance coefficient, the Kubelka-Munk function, $F(R)$, is used.
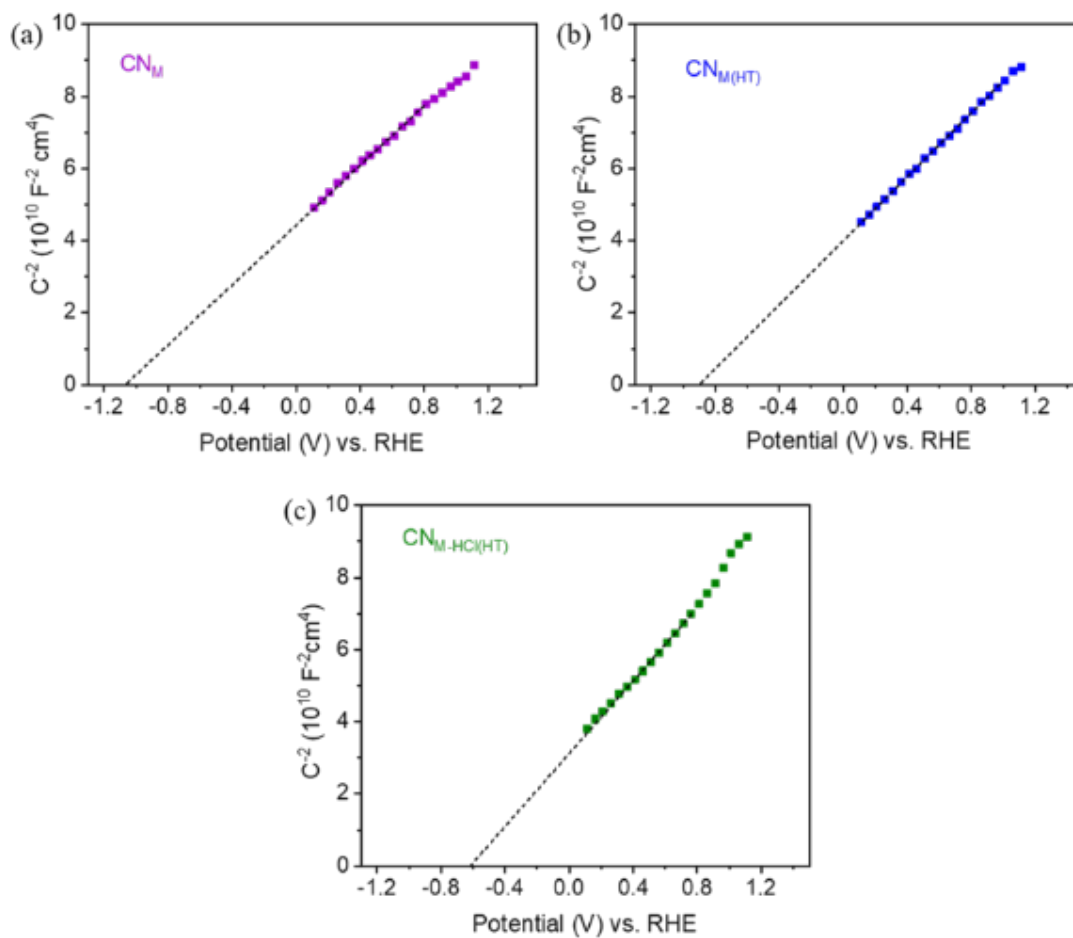

Fig. S4 Mott–Schottky plots of CN$_M$, CN$_{M(HT)}$, and CN$_{M-HCl(HT)}$ electrodes in 0.5 M Na$_2$SO$_4$ aqueous electrolyte (pH ~7) confirming n-type characteristic of the CN films.
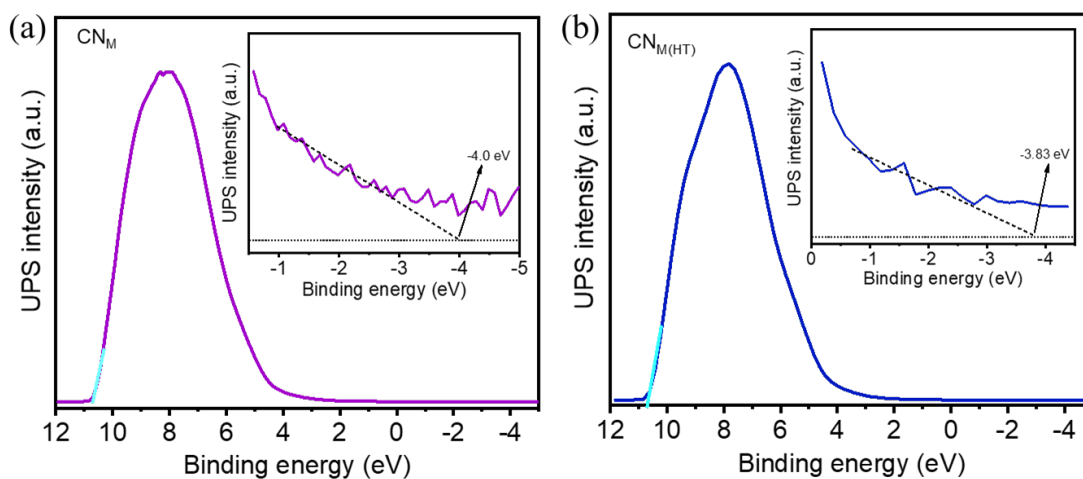
Fig. S5 Valence band UPS of CN$_M$ and CN$_{M(HT)}$ films.
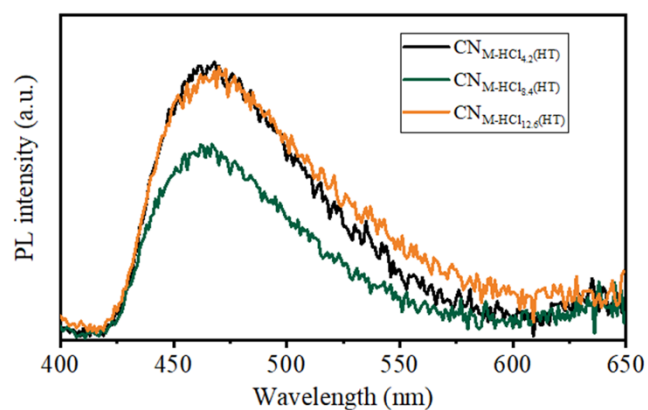
Fig. S6 Photoluminescence (PL) emission spectra (excitation wavelength: 380 nm) of CN films with different amount of HCl added during the supramolecular assembly formation.
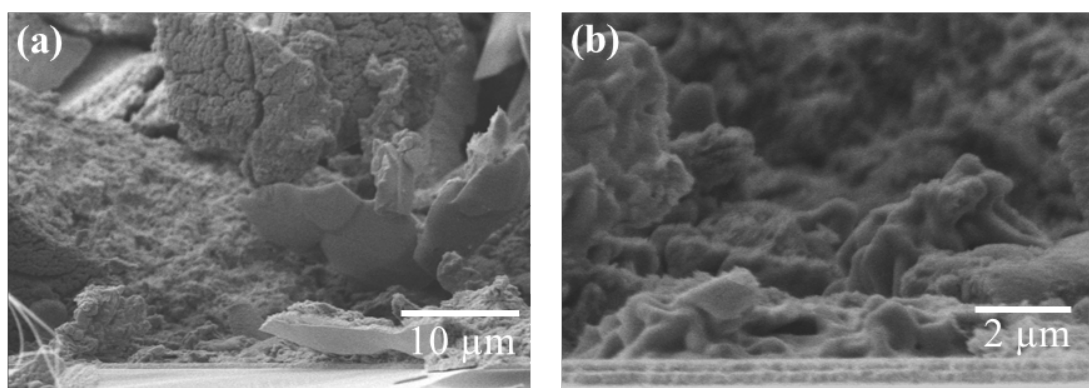
Fig. S7 Cross-sectional images of a CN$_{M-HCl(HT)}$ film, exhibiting its intimate contact with the FTO layer.

0 h   12 h   24 h   CN film after 24 h
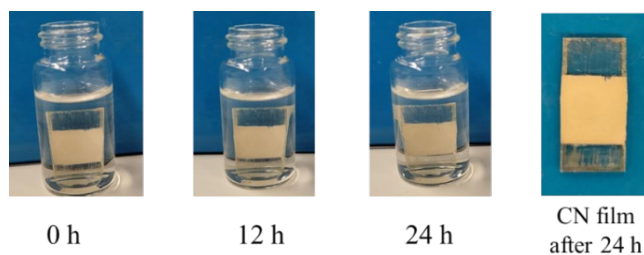
Fig. S8 Images of the porous 1D CN electrode in water for 24 h (water immersion experiment).
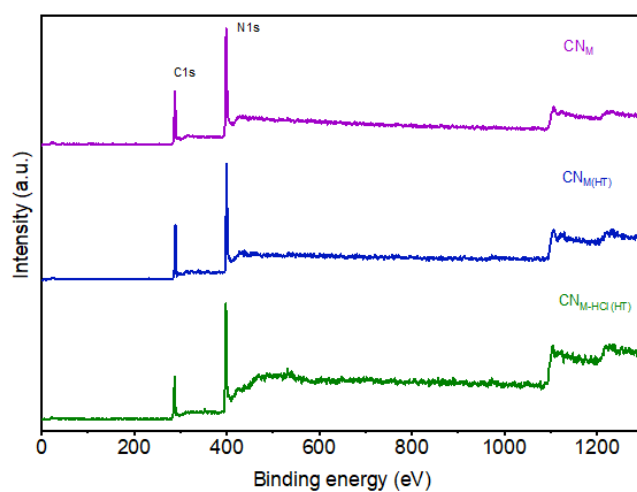
Fig. S9 XPS survey spectra of CN_M, $CN_{M(HT)}$, and $CN_{M-HCl(HT)}$ films.

Table S1. Elemental (C, H, N) analysis data of CN_M, $CN_{M(HT)}$, and $CN_{M-HCl(HT)}$ samples. Percentage of O in the table was obtained by subtracting all other elements amount from 100%.

Sample	C	N	H	O	C/N
CN_M	45.20%	47.88%	1.18%	5.74%	0.942
$CN_{M(HT)}$	43.25%	50.16%	1.47%	5.13%	0.865
$CN_{M-HCl(HT)}$	41.89%	53.01%	2.03%	3.07%	0.80
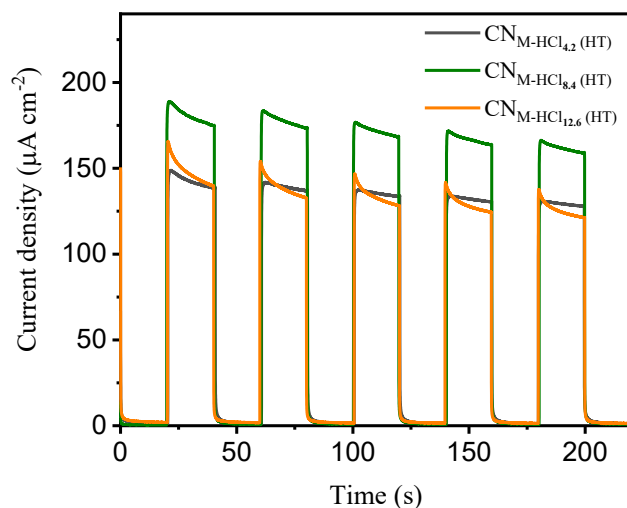
Fig. S10 Chronoamperometry plots using $CN_{M-HCl(HT)}$ photoanodes prepared by adding different amounts of HCl during the supramolecular assembly formation.
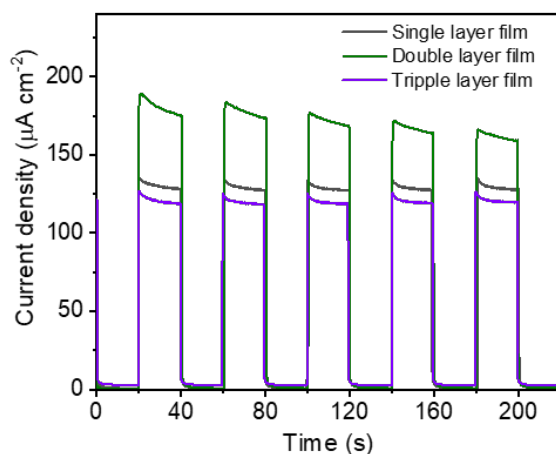

Fig. S11 Chronoamperometry plots using $CN_{M-HCl(HT)}$ photoanodes prepared by varying the number of scotch tape layers (L = 1, 2, or 3) used as the barrier during the doctor blading procedure at 1.23 V *vs.* RHE upon on/off 1 sun illumination in 0.1 M KOH.
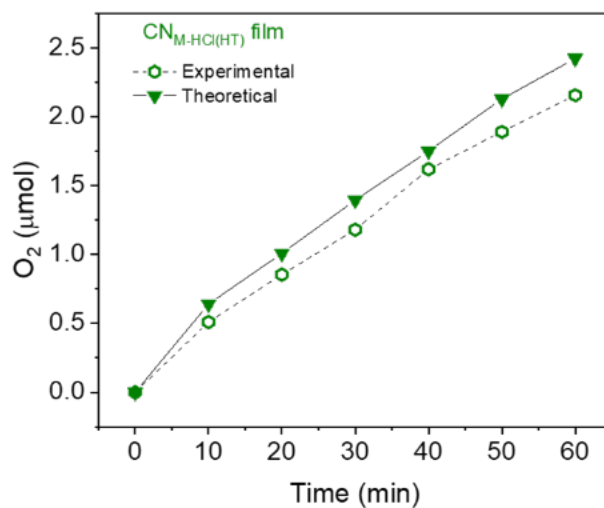
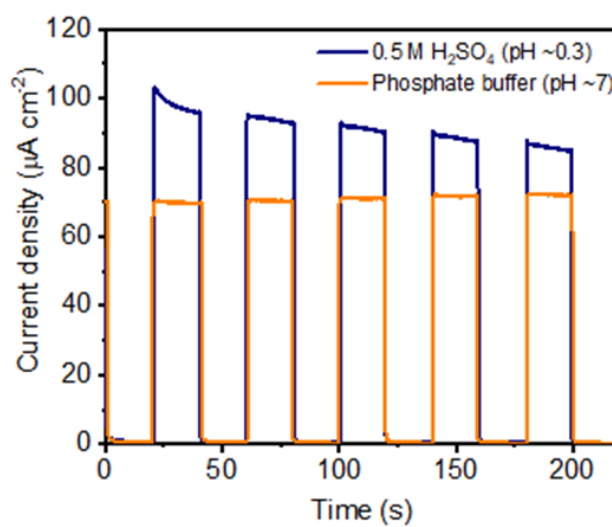**Fig. S12** Measured O_2 production for $CN_{M\text{-}HCl(HT)}$ film in 0.1 M KOH.

Fig. S13 Chronoamperometry plot using $CN_{M\text{-}HCl(HT)}$ photoanodes in neutral and acidic electrolytes.
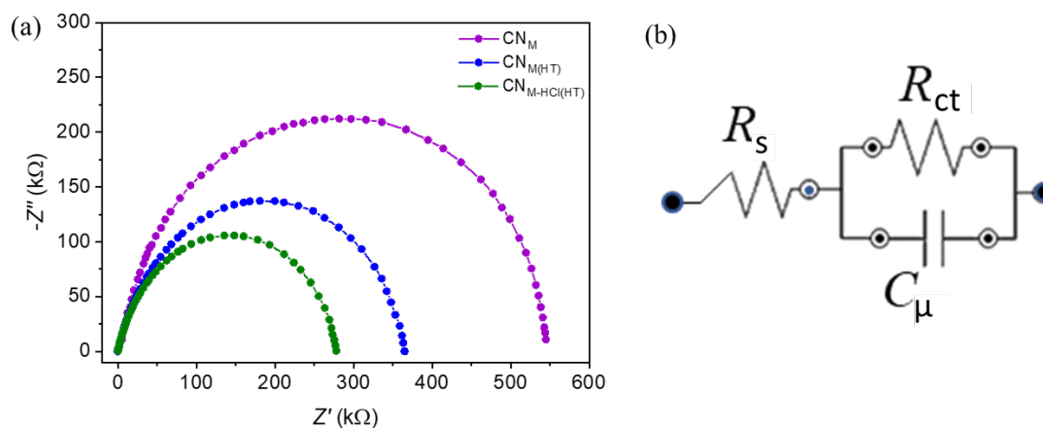
Fig. S14 EIS analysis of CN$_M$, CN$_{M(HT)}$, and CN$_{M-HCl(HT)}$ films. (a) Nyquist plots showing the experimental data points and the fitted semicircles. Measurements were carried out in 0.5 M Na$_2$SO$_4$ aqueous electrolyte (pH ~7), (b) The equivalent circuit that was used for fitting. The following R_{ct} values were obtained from fitting: R_{ct} of CN$_M$ = 545 kΩ, R_{ct} of CN$_{M(HT)}$ = 365 kΩ, R_{ct} of CN$_{M-HCl(HT)}$ 278 = kΩ.

In the equivalent circuit, R_s stands for series resistance, R_{ct} for charge transfer resistance, and C_μ for double-layer capacitance.
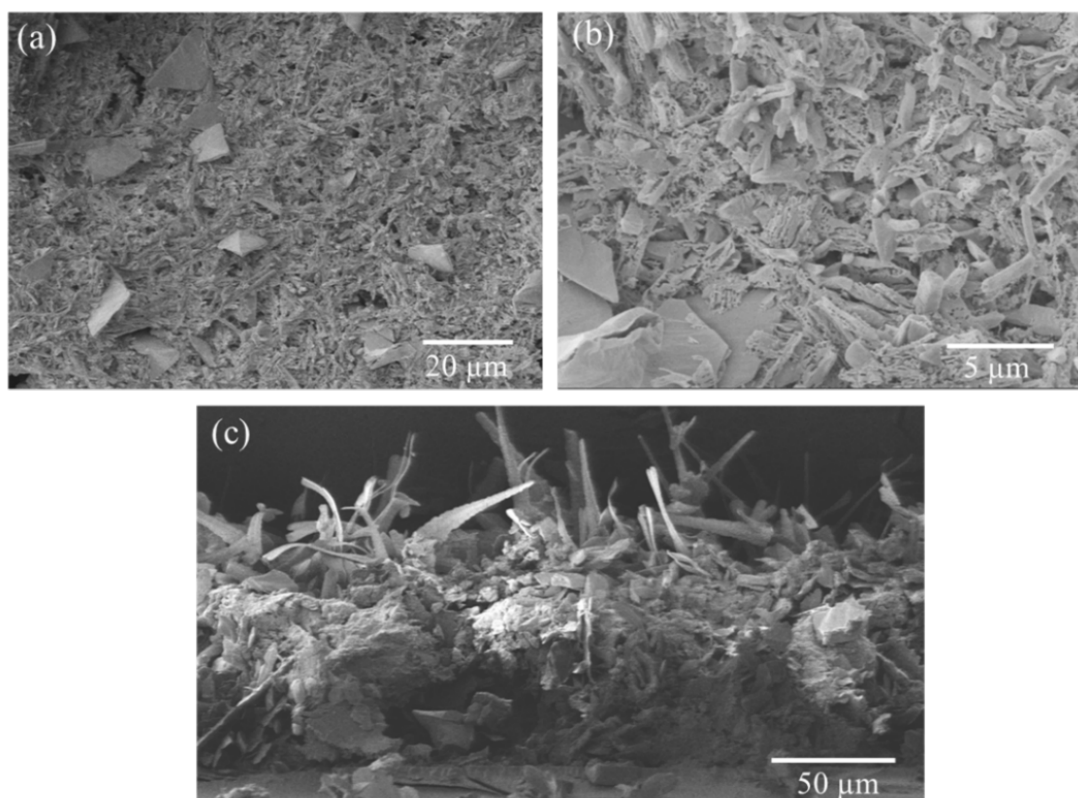

Fig. S15 SEM images of CN$_{M-HCl(HT)}$ photoanodes after the stability test. (a, b) Top-view and (c) cross-section.
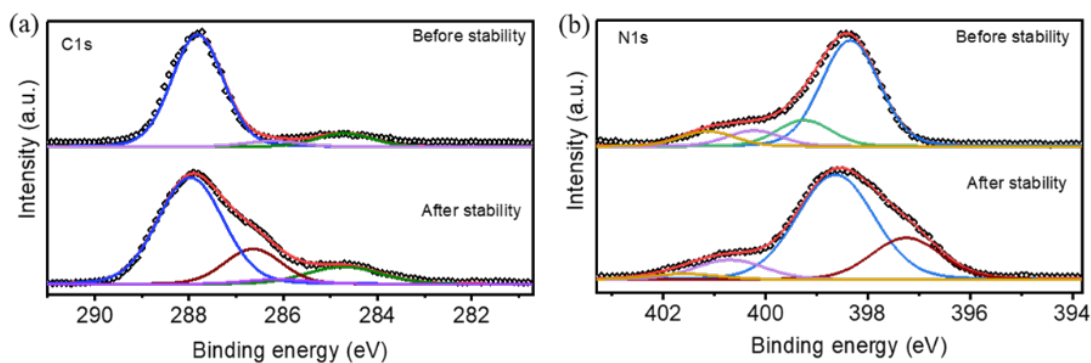
Fig. S16 XPS fitting to a CN$_{M-HCl(HT)}$ photoanode after 10 h of stability test. (a) C 1s and (b) N 1s.

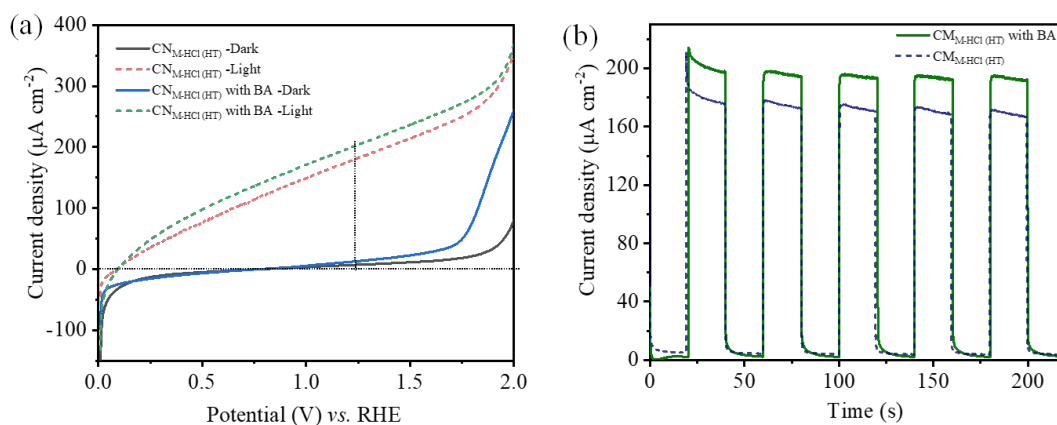**Fig. S17** (a) Linear sweep voltammetry of CN$_{M-HCl(HT)}$ with and without illumination under two different conditions: (i) with benzylamine (BA) and O$_2$ saturated electrolyte solution, and (ii) without BA, and without oxygen, *i.e.*, Ar saturation. Each condition is measured in the dark (complete lines) and under 1 sun illumination (dashed line), (b) Chronoamperometry plot of CN$_{M-HCl(HT)}$ under O$_2$ saturation conditions with and without BA in 1 M NaOH electrolyte under 1 sun illumination.