

Electronic Supplementary Information

Confined synthesis of condensed π -conjugation C-PAN/MS-CN nanotubes for efficient photocatalytic H₂ evolution

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Experimental Section

Materials. Melamine (MA, C₃H₆N₆), KCl and LiCl were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd., polyacrylonitrile (PAN, average Mw 150000) were purchased from Shanghai Macklin Biochemical Co., Ltd, triethanolamine (TEOA), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were not purified by further and were analytic grade.

Synthesis. The C-PAN/MS-CN were prepared as follows: 1 g of melamine with a certain content of PAN (0, 0.5 wt%, 1.0 wt%, 2.0 wt%) was respectively mixed with KCl (2.75 g) and LiCl (2.25 g) via grinding for 15 minutes. Then the mixture placed in an alumina crucible with a cover heating in N₂ flow at 500 °C for 4 h with a rate of 10 °C min⁻¹. The calcined samples were washed using the boiled water to get rid of the needless salts for several times and dried at 80 °C in oven for 12 h. The sample was marked as MS-CN, 0.5 wt% C-PAN/MS-CN, 1.0 wt% C-PAN/MS-CN and 2.0 wt% C-PAN/MS-CN respectively. As a control, carbonized PAN marked as C-PAN was obtained from sintering PAN at the same condition. pristine CN or 1.0 wt% C-PAN/CN was obtained by directly heating melamine or 1.0 wt% PAN with melamine in N₂ flow at 500 °C for 4 h with a rate of 10 °C min⁻¹ without KCl and LiCl.

Characterization. X-ray diffraction (XRD) was measured on a XD-2/3 polycrystalline X-ray diffractometer with nickel-filtered Cu K α radiation as the X-ray source. Fourier transform infrared (FT-IR) spectra were taken utilizing a IS 10

AKZ1800251. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB250Xi (ThermoFisher Scientific) equipped with an Al K α X-ray source using C1s peak at 284.6 eV as the internal reference. The scanning electron microscopy (SEM) images were performed on a JEOL JSM 6701 F. The transmission electron microscopy (TEM) of the prepared samples were observed on a JEM-2100 electron microscope (JEOL Ltd). N₂ adsorption-desorption isotherm were tested by specific area and porosity analyzer on the JW-BK132F. UV-vis diffuse reflectance spectroscopy was carried out on a Hitachi U-3310 spectrophotometer equipped with an integrating sphere accessory with BaSO₄ as a reference. The photoluminescence (PL) was conducted on a Perkin-Elmer, LS-55 luminescence spectrometer at room temperature using 370 nm as the excitation wavelength, and time-resolved fluorescence decay spectra were obtained on a FLS1000 steady state and lifetime fluorescence spectrometer (Edinburgh, Britain). Electron paramagnetic resonance (EPR) spectra were obtained using an EPR spectrometer (Bruker EMXplus) at room temperature.

Electrochemical and Photoelectrochemical Measurements. Electrochemical tests containing Electrochemical impedance spectroscopy (EIS) and Mott-Schottky plots were conducted in a standard three-electrode system on an Ivium electrochemical instrument. The working electrode was prepared as following: 5 mg catalyst was uniformly dispersed 990 μ L H₂O and 10 μ L Nafion by sonication for an hour, then taking out 100 μ L and dispersed 900 μ L H₂O by sonication for 2 hours. Finally, 10 μ L of dispersion was drop into the glassy carbon electrode and dried at the room

temperature. The Ag/AgCl and the platinum filament were respectively as a reference electrode and a counter electrode. The PBS solution was as the electrolyte. EIS was implemented on the alternating voltage of 10 mV at the frequency range of 10^5 to 10^{-2} Hz. Mott-Schottky curve was carried out the constant frequency of 1000 Hz (vs Ag/AgCl).

Photocurrent was measured by LK 98BII electrochemical workstation in a three-electrode system, using $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ aqueous solution as electrolyte. The reference and the counter electrode were the same with EIS. The working electrode was made of photocatalyst using a fluorine-doped tin oxide (FTO) conducting glass: Firstly, FTO conducting glasses ($1.0 \times 3.0 \text{ cm}$) were ultrasonic rinsed using alcohol and water for 20 min: 5 mg catalyst was decentralized in 250 μL of dimethyl formamide (DMF) by sonication for 4 hours. Then, 10 μL of uniform slurry was coated onto a $1.0 \times 1.0 \text{ cm}$ FTO conducting glassy and dried at room temperature.

Photocatalytic Measurements. The photocatalytic H_2 evolution reaction was performed on a gas-tight circulation system with a side window. 0.1 g of photocatalyst powder was suspended by sonication in 100 mL of 10 vol% triethanolamine (TEOA) aqueous solution with 3 wt% Pt loading. Prior to irradiation, the suspension was bubbled with N_2 for 25 min to remove O_2 . The suspension was irradiated using a 300 W Xe lamp with a cutoff filter ($\lambda > 400 \text{ nm}$) from Beijing Perfect light Technology Co., Ltd. (PLS-SXE300D) keeping magnetic stirring. The amount of H_2 was determined on an online GC1690 gas chromatograph (TCD) with N_2 gas as the carrier gas.

The apparent quantum efficiency (AQE) of 1 wt% C-PAN/MS-CN at 420 nm monochromatic incident light was estimated by the following equation:

$$AQE[\%] = \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}}$$

The reaction conditions including the reactor were the same as those for the above photocatalytic reaction except using 420 nm monochromatic LED lamps (UVEC-4, Shenzhen LAMPLIC Science Co Ltd, China) with effective lighting area of 0.70 cm². The intensity of incident light was measured to be 3.8 mW/cm².

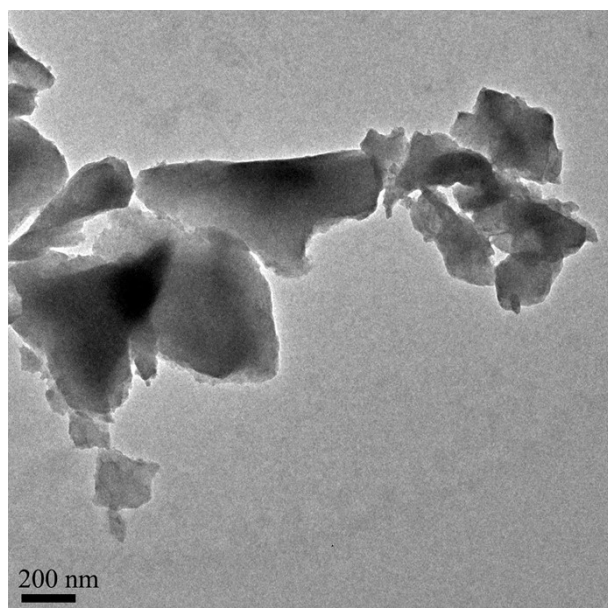


Fig. S1 TEM images of C-PAN synthesized by calcining PAN to 500 °C in N₂ flow for 4 h in the presence of KCl and LiCl.

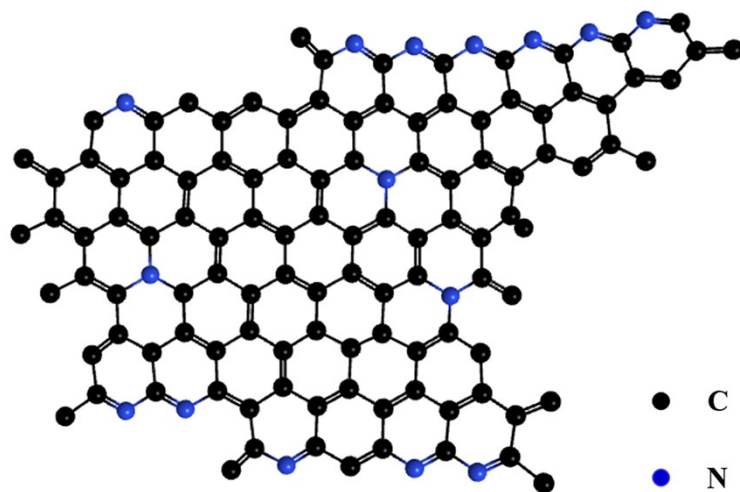


Fig. S2 The conjugate network structure C-PAN.

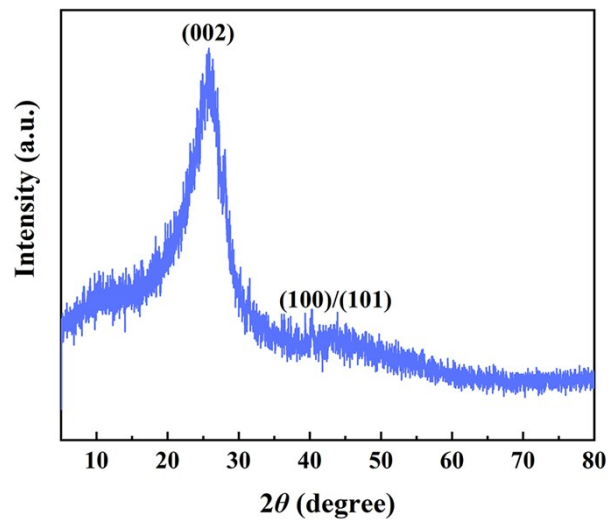


Fig. S3 XRD pattern of C-PAN obtained by heating PAN to 500 °C in N₂ flow for 4 h in the presence of KCl and LiCl.

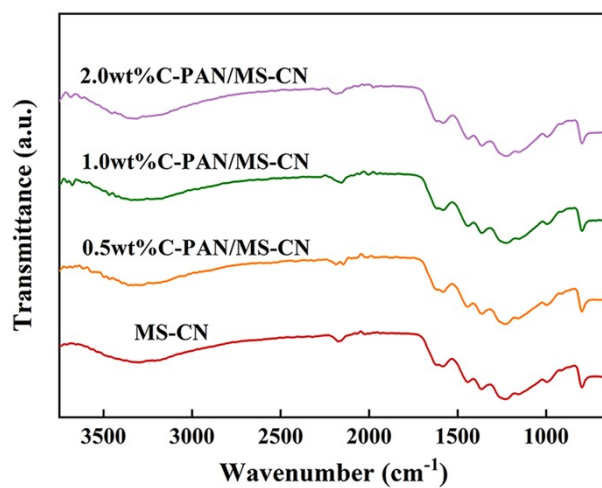


Fig. S4 FT-IR spectra of MS-CN and C-PAN/MS-CN with different C-PAN contents.

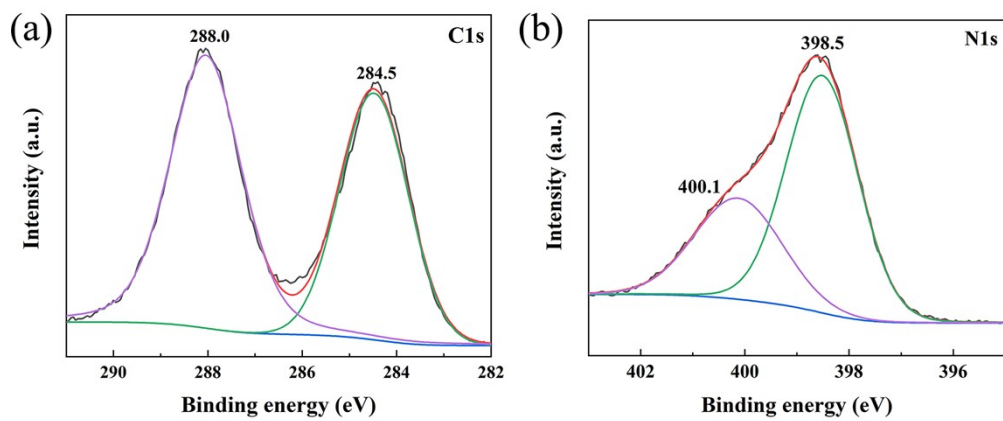


Fig. S5 (a) high-resolution XPS spectra of C1s, and (b) N1s for 1 wt% C-PAN/MS-CN nanotubes.

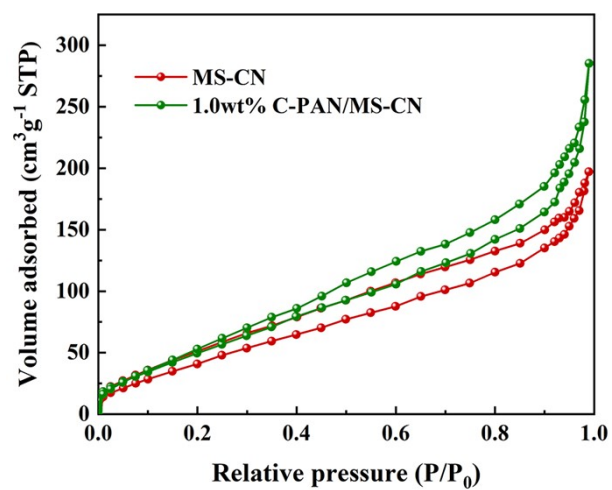


Fig. S6 N₂ adsorption-desorption isotherm of MS-CN and 1 wt% C-PAN/MS-CN.

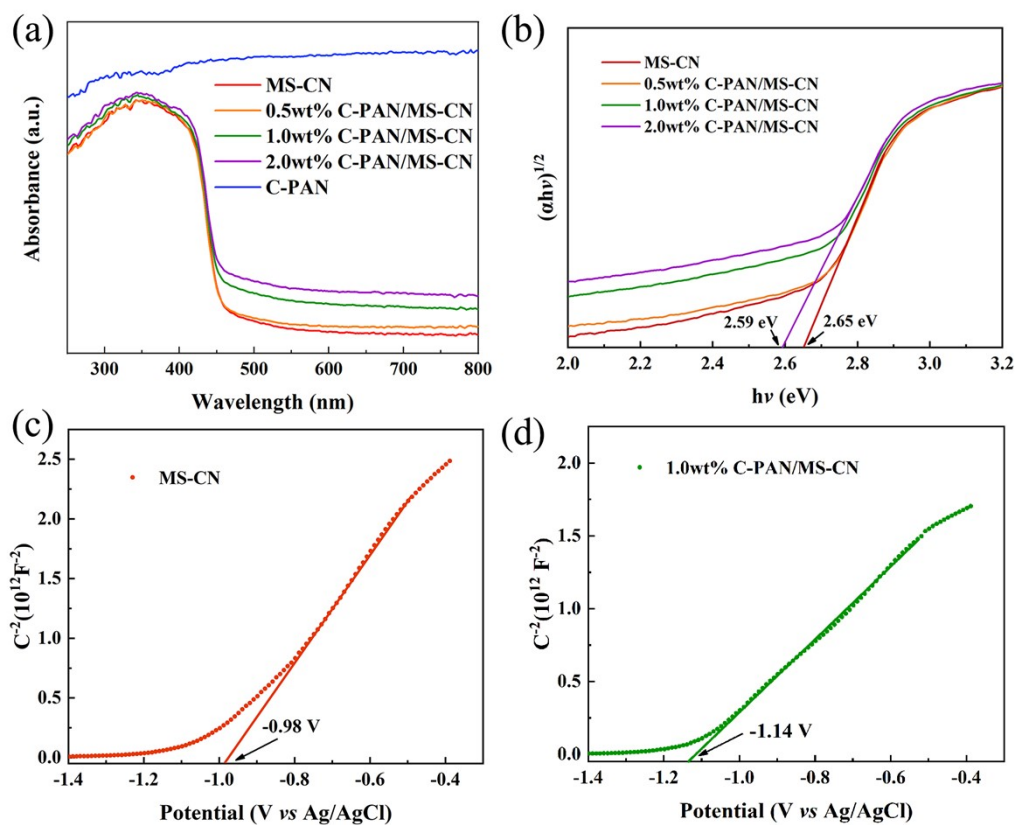


Fig. S7 (a) UV-vis light absorption spectra and (b) bandgap energies of MS-CN and C-PAN/MS-CN nanotubes with different C-PAN content. Mott-Schottky plot of MS-CN (c) and 1 wt% C-PAN/MS-CN nanotubes (d).

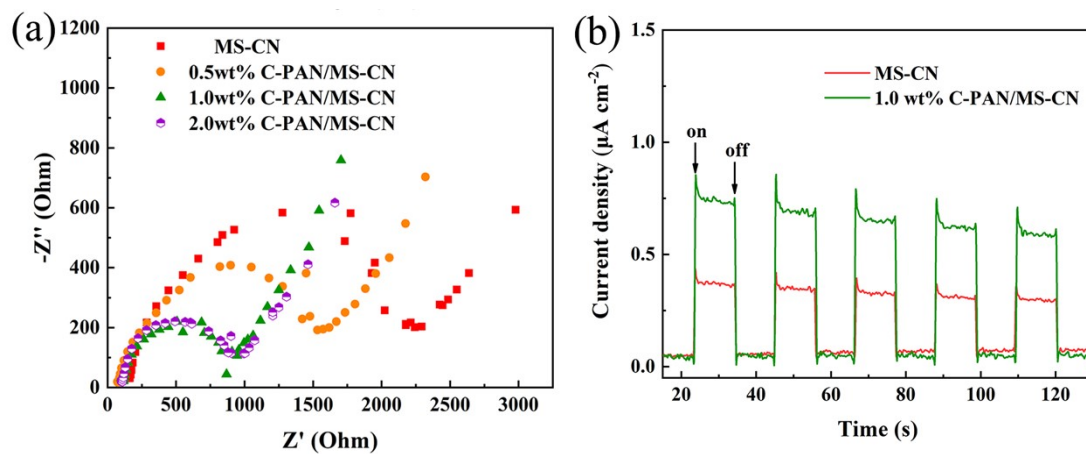


Fig. S8 (a) EIS Nyquist plots of MS-CN and C-PAN/MS-CN nanotubes with different C-PAN content. (b) Transient photocurrent curves of MS-CN and 1 wt% C-PAN/MS-CN nanotubes.

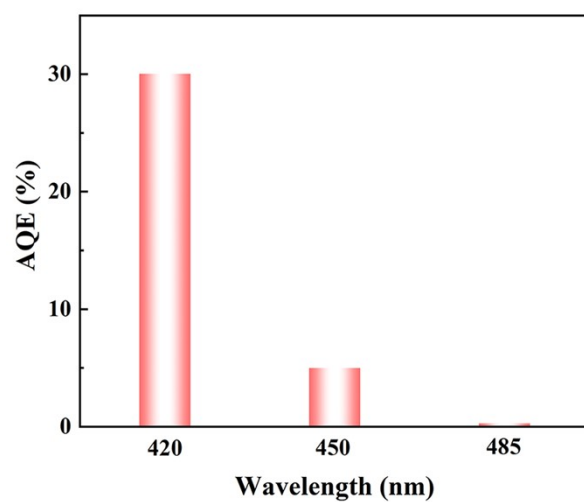


Fig. S9 Apparent quantum efficiency (AQE) of H₂ evolution for 1wt% C-PAN/MS-CN nanotubes at different monochromatic wavelengths.

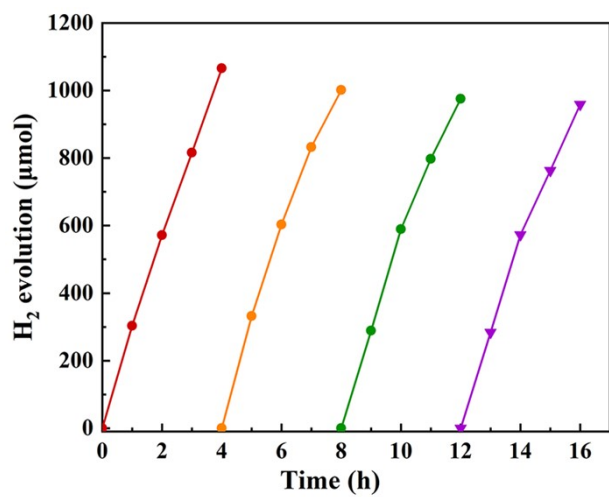


Fig. S10 Photocatalytic H₂ evolution as a function of reaction time for 1wt% C-PAN/MS-CN

nanotubes.

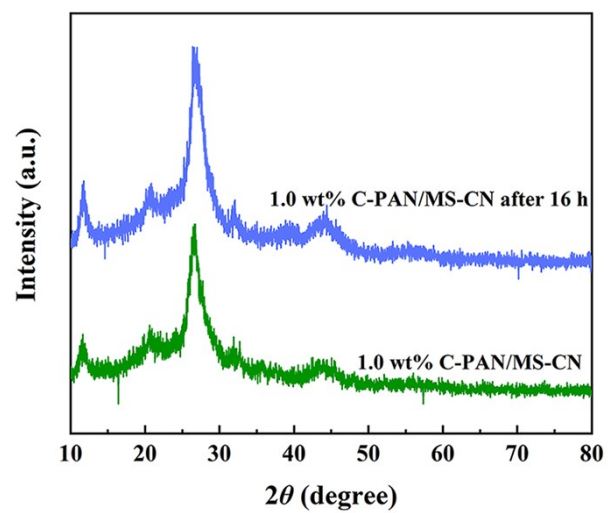


Fig. S11 XRD patterns of the 1 wt% C-PAN/MS-CN nanotubes before and after the irradiation reaction for 16 h.