

Supplementary information

Quenching induced hierarchical 3D porous graphitic carbon nitride with enhanced photocatalytic CO₂ reduction activity

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Experimental sections

Preparation of samples

ACN was prepared by thermal polymerization of urea. In detail, 12 g of urea was put into a crucible with a lid and calcine at the temperature of 550 °C for 3 hours with a heating rate of 5 °C min⁻¹ and then underwent air cooling in a furnace. In contrast, HCN was prepared by adopting the same heating condition but cooled by rapidly

immersing the sample into iced water after taking out from the high-temperature furnace at 550 °C. Finally, the sample of HCN was obtained by centrifuging and drying at 80 °C for 12 h.

Characterization of samples.

The X-ray diffraction (XRD) patterns of the samples were obtained on an X-ray diffractometer (6100, Shimadzu, Japan). Transmission electron microscope (TEM) was performed to examine the morphology of the samples by Titan G2 60–300 microscopes operated at 300 kV. UV–vis diffuse reflectance spectra was attained by UV–visible spectrophotometer (UV–2550, Shimadzu, Japan), using BaSO₄ as the reference sample. Fourier transform infrared spectra (FTIR) were measured on an IR Affinity-1 FTIR spectrometer (Shimadzu, Japan). Field emission scanning electron microscope (FESEM) was employed to obtain the surface images of the samples by electron microscope (JSM-7500, JEOL, Japan) with an accelerating voltage of 10 kV. The surface morphology and thickness of HCN were measured by atomic force microscopy (SPM-9700 HT, Shimadzu, Japan). XPS measurements were conducted with a VG ESCALAB 210 electron spectrometer under Mg K_α irradiation. The C 1s peak (284.8 eV) was chosen to calibrate the binding energy. The nitrogen adsorption-desorption isotherm was obtained on a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA) to determine the Brunner–Emmett–Teller (BET) specific

surface area of the prepared samples through a multipoint BET method using the adsorption data at the relative pressure (P/P_0) range of 0.05–0.3. Prior to the test, the samples were degassed at 150 °C for 6h. Pore size distribution of the prepared samples was calculated through the Barret-Joyner-Halender (BJH) method. Pore volume and average pore size of the prepared samples were determined using the adsorbed nitrogen volume at the relative pressure of 0.994. CO₂ adsorption measurements of the prepared samples were carried out by Micromeritics ASAP 3020 equipment (USA) at room temperature and all prepared samples degassed at 150 °C for 6 h. Steady state photoluminescence (PL) spectra were obtained by F-7000 fluorescence spectrophotometer (Japan, Hitachi), where 365 nm was selected as an excitation wavelength. Time-resolved photoluminescence (PL) spectra were gathered by a FLS1000 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) with 375 nm as an excitation wavelength and 445 nm as an emission wavelength. Electrochemical tests were carried out on an electrochemical workstation (CHI66E) and the electrolyte was 0.5 M Na₂SO₄ solution.

Gas chromatography–mass spectrometry (GC–MS) was conducted to investigate the origin of the hydrocarbon compounds produced during photocatalytic CO₂ reduction. The above-mentioned CO₂ reduction test was also carried out during GC–MS characterization except that the CO₂ and H₂O vapor were generated by NaHCO₃ with different C-labelling. NaH¹²CO₃ and NaH¹³CO₃ were selectively used during

photocatalytic $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ reduction test, respectively. GC–MS (6980N network GC system–5975 inert mass selective detector, Agilent technologies, USA) was used to differentiate the mixed gas (250 μL) taken out from the reactor after 2 h of photocatalytic reaction.

Nicolet iS50 infrared Fourier transform spectrometer (TMO, USA) was used to record in–situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) of the prepared samples. Prior to the test, the prepared samples were degassed at 150 $^\circ\text{C}$ for 6 h and placed into the reaction chamber of DRIFTS. Then, the chamber was sealed and purged with the mixed CO_2 and H_2O vapor. The DRIFTS was carried out under dark condition (3 cycles, 20 min each) and 3 W 365 nm LED light irradiation (3 cycles, 20 min each).

Evaluation of photocatalytic CO_2 reduction activity

Photocatalytic CO_2 reduction activity of all the samples were evaluated in a 200 mL colorless glass reaction vessel at room temperature. Firstly, 100 mg of the prepared sample was added into the vessel and ultrasonically dispersed in ultrapure water. Then, the vessel was dried in an oven at 80 $^\circ\text{C}$ for 24 hours. Finally, a film consisted of as-prepared photocatalyst was prepared. Subsequently, 84 mg of NaHCO_3 was added into the vessel and then the vessel was flowing with N_2 for 30 mins to remove impurity gas. Afterwards, 1 mL of 2 M H_2SO_4 was added into the sealed container to

produce CO₂ and H₂O and then 300 W Xe arc lamp of simulating solar light was used as light source and placed vertically 10 cm above the vessel. After 1 hour of light irradiation, 1 mL of gas was extracted from the vessel and analyzed by gas chromatograph spectrometer (PGC-80, Changzhou Panna Instrument, China) equipped with flame ionized detector (FID) with N₂ as a carrier gas.

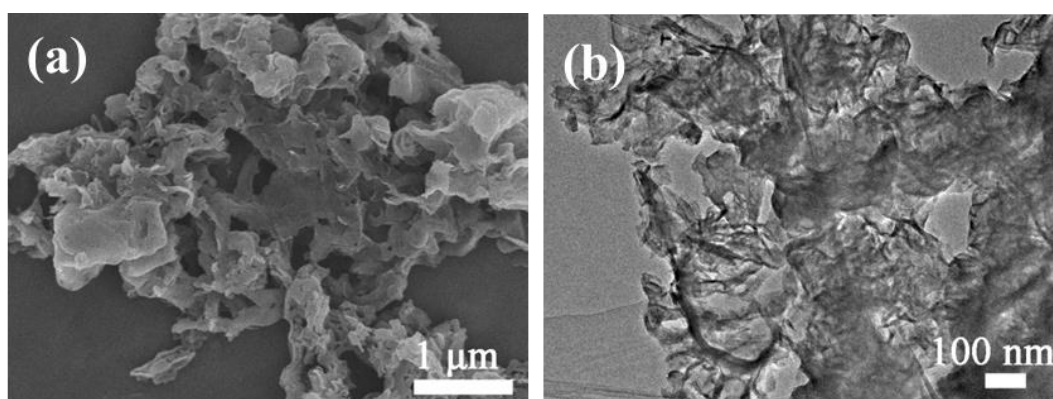


Fig. S1 (a,b) FESEM and TEM images of ACN.

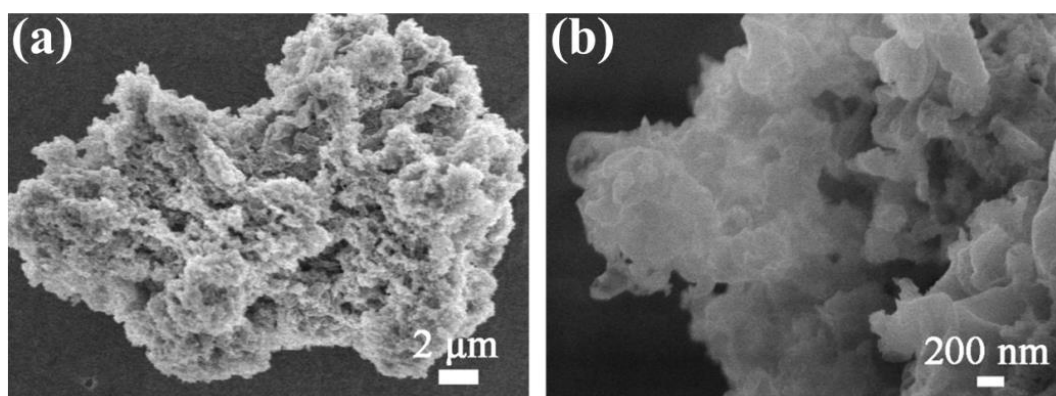


Fig. S2 (a,b) FESEM image at different magnifications of CN obtained by cooling in liquid nitrogen.

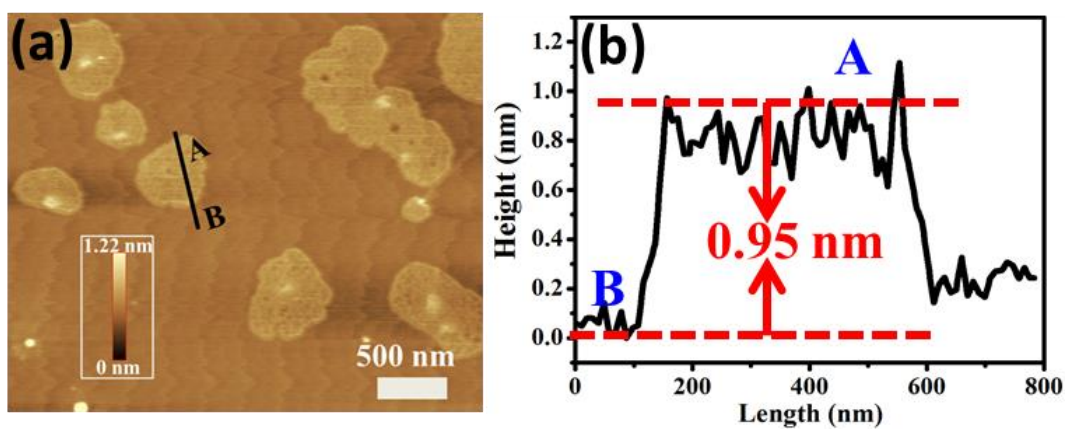


Fig. S3 (a) AFM image of nanosheets of HCN and (b) relevant height profile of nanosheet.

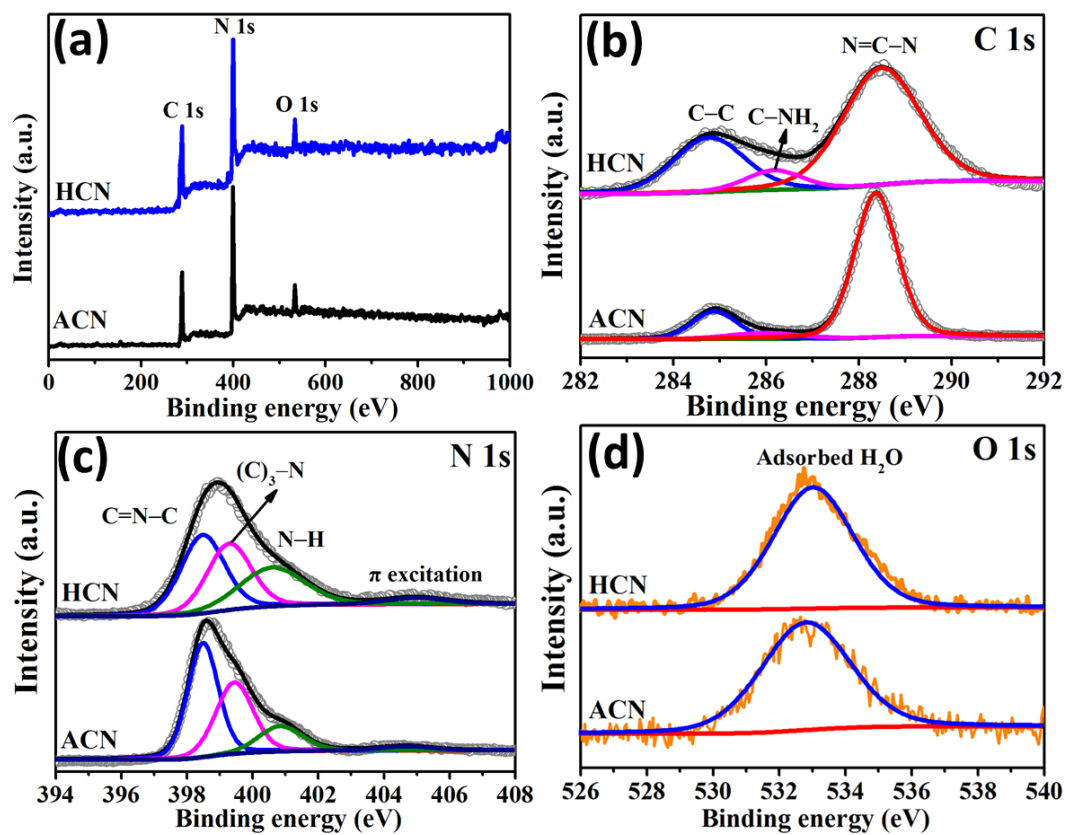


Fig. S4 (a) XPS survey spectra and (b, c, d) high-resolution O 1s, C 1s and N 1s XPS

spectra of ACN and HCN.

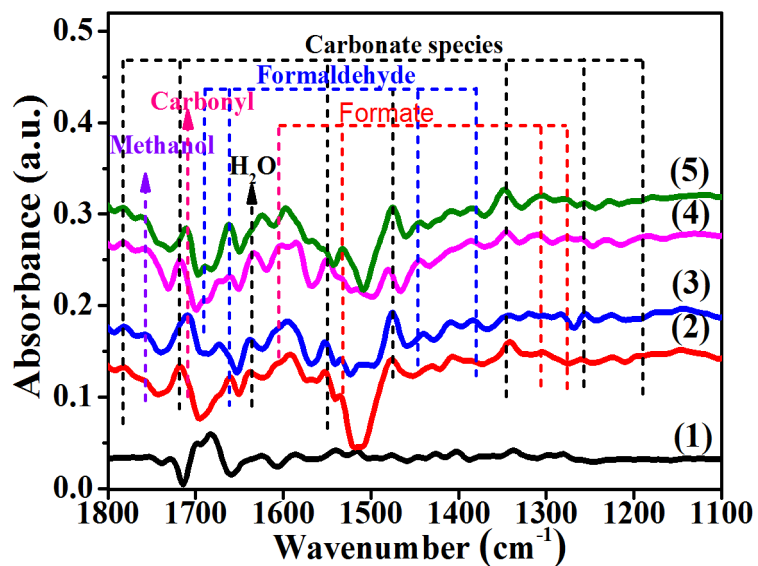


Fig. S5 In-situ DRIFTS spectra of photocatalytic CO₂ reduction over HCN under different conditions: (1) without light irradiation and CO₂ gas, (2) without light irradiation and with CO₂ gas flowing 60 mins, (3), (4) and (5) with CO₂ gas flowing and with light irradiation for 20, 40 and 60 mins, respectively.

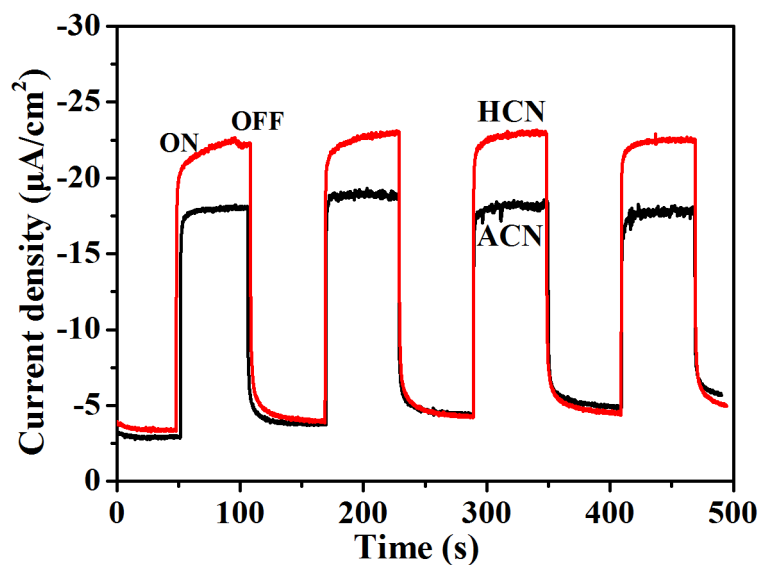


Fig. S6 Transient photocurrent current curves of ACN and HCN.

Table S1: The BET specific surface area, pore volume and average pore diameter of ACN and HCN.

| Samples | S_{BET} (cm^2/g) | V_{pore} (cm^3/g) | d_{pore} (nm) |
|---------|---|--|------------------------|
| ACN | 67 | 0.26 | 14.4 |
| HCN | 77 | 0.35 | 15.6 |

S_{BET} is the specific surface area (m^2/g), V_{pore} represents total pore volume (cm^3/g),

d_{pore} represents average pore width (nm).

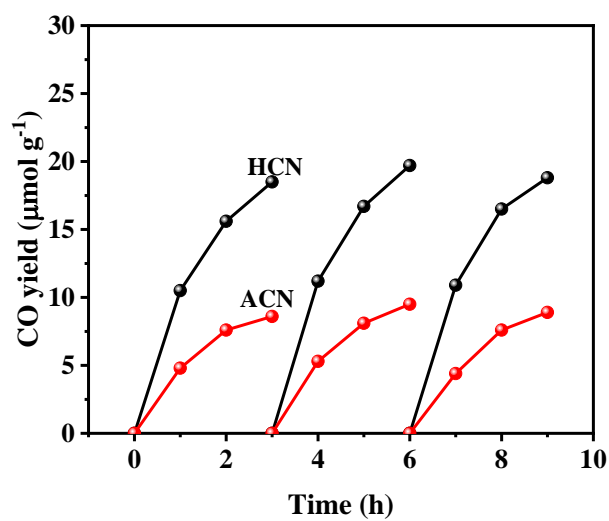


Fig. S7 9 h recycle photocatalytic CO_2 reduction performance of as-prepared samples

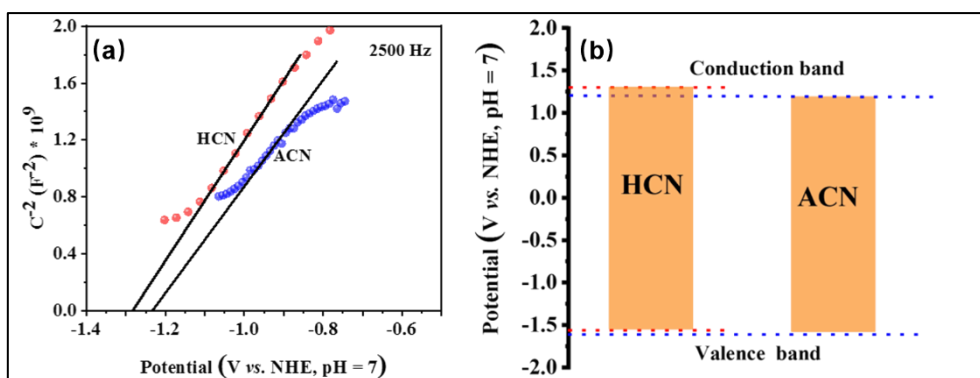


Fig. S8 Mott-Schottky plots (a), and band structure alignment (b) of HCN and ACN.