

Supporting information

Synthesizing crystalline g-C₃N₄ for enhanced photocatalytic hydrogen evolution under visible light

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Experimental Section

Synthesis of g-C₃N₄ (UCN) photocatalyst

UCN sample was prepared from urea precursor: 20 g urea were put into an alumina crucible and then the crucible was transferred into muffle furnace. Afterwards, the crucible was heated to 550°C by controlling the heating rate of 5 °C/min and maintained at this temperature for 3 hours. After natural cooling, light yellow powder was obtained. The obtained powder was placed in an open crucible and then again put in the muffle furnace. Subsequently, the crucible was continuously heated up to 600°C at 5°C / min and maintained for 2 hours. Finally, after cooling down, UCN sample was obtained.

Synthesis of hexagonal prism g-C₃N₄ (HPCN) photocatalyst

Firstly, 30 mg UCN was dissolved into 35 ml of deionized water and then fully stirred for 30 min. The evenly mixed suspension was transferred to the reaction kettle. The hydrothermal reaction was performed at 180 °C for 6 h in an oven. After cooling down, the product was carefully collected and adequately washed with deionized water and ethanol. Eventually, the white powder was obtained after dried by vacuum at 60°C for 24 h. The sample was labelled as HPCN.

Characterizations.

The crystalline phase of the samples was determined using the powder x-ray diffractometer (Rigaku D/Max-2000 diffractometer). The field-emission scanning electron images (FSEM) of the samples were collected by field emission scanning electron microscope (JSM-7500, Japan). The transmission electron microscope images (TEM) of the samples were obtained via the Field-emission transmission electron microscopy (JEM-2100F). A UV-visible diffuse reflection spectrometer (UV-3700, Japan) was used to analyze light absorption of all the samples. The Fourier transform infrared (FTIR, IRAffinity-1, Shimadzu) spectroscopy and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoScientific) were

collected to research the chemical transformation of the samples. The transient / steady-state fluorescence spectrometer (FLS1000, Edinburgh) was conducted to test the steady-state fluorescence spectrum (PL) and time-resolved fluorescence spectrum (TRPL), respectively. The electronic paramagnetic resonance spectra (EPR) were tested at room temperature (EMXnano, Bruker).

Photocatalytic hydrogen evaluation

A 300W LED lamp ($380\text{nm} < \lambda < 780\text{nm}$) was conducted as the visible light source in the photocatalytic test. 10 mg samples were dispersed in a reactor containing 18 ml of water under ultrasound dispersion. After that, 2 ml triethanolamine was added to the above suspension, and then adding 1% Pt as the cocatalyst. Afterwards, high purity air was pumped into the reactor for 30 min to removal the air, and then was placed under visible light. Finally, the amount of H_2 was detected by the gas chromatograph (GC-14C, Shimadzu, Japan).

Electrochemical performance test

Photoelectrochemical characterizations were conducted on a CHI 760E electrochemical workstation with a three-electrode experimental system. 0.5 M Na_2SO_4 solution acted as electrolyte. The prepared photocatalyst was mixed with adequate ethanol and nafion solution to form uniform emulsion. Afterwards, the emulsion was deposited quickly on the FTO to form working electrodes. The 300 W xenon lamp serves as the light source to test the Electrochemical impedance spectrum (EIS) and transient photocurrent response curves.

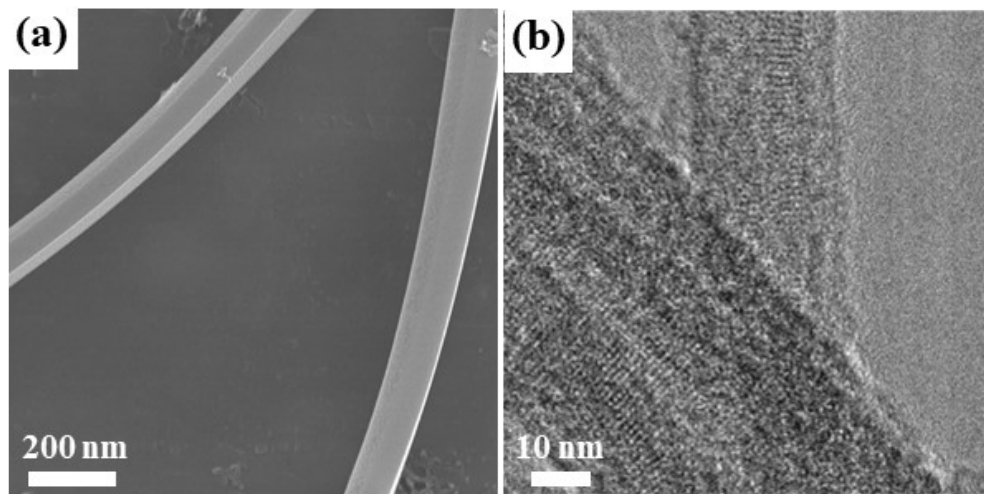


Figure S1. (a) SEM and (b) HRTEM images of HPCN

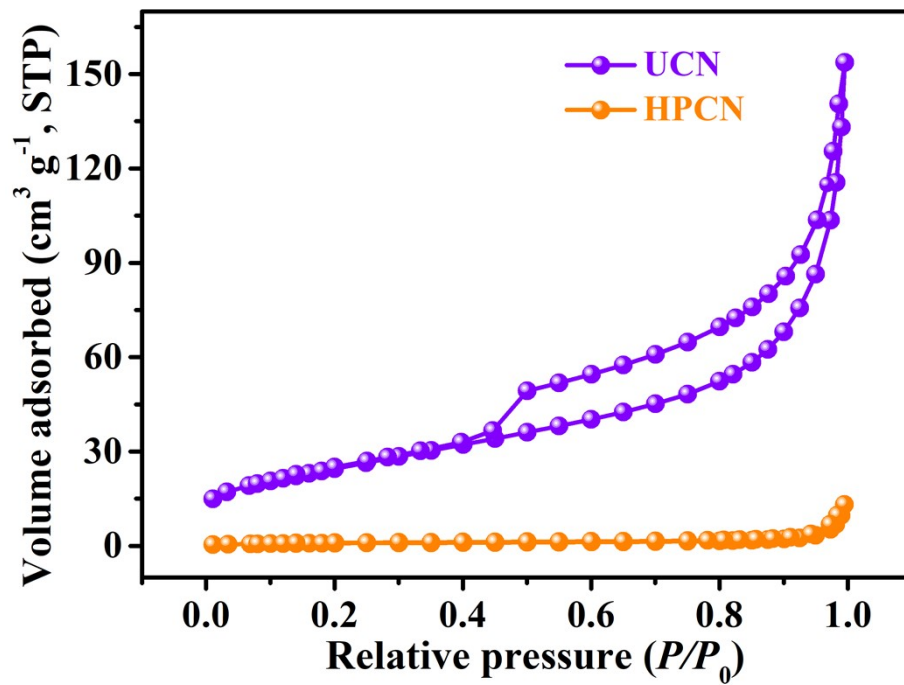


Figure S2. N_2 adsorption–desorption isotherms of UCN and HPCN

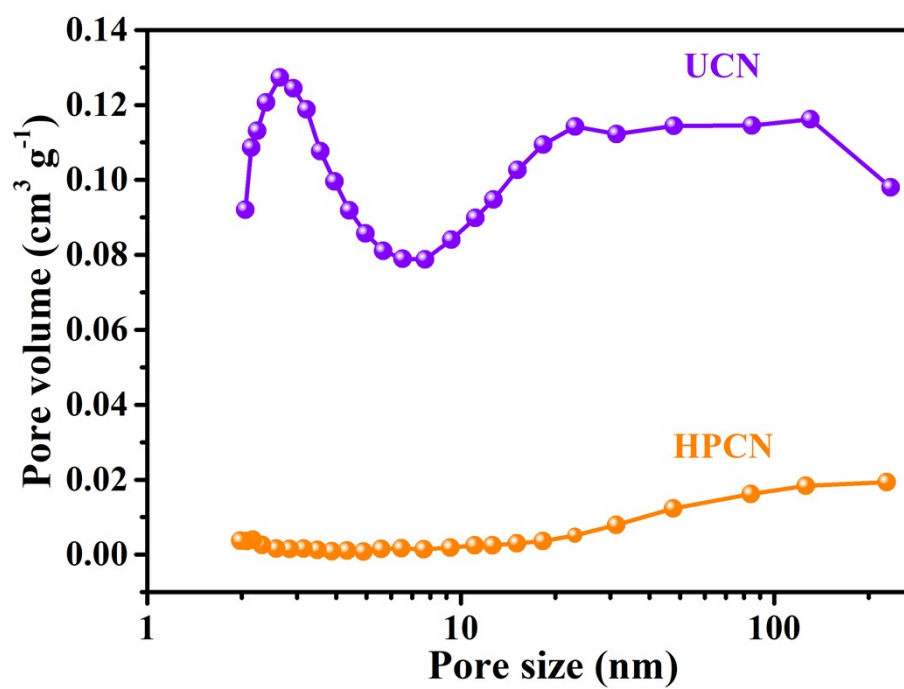


Figure S3. The pore size distribution (PSD) of UCN and HPCN

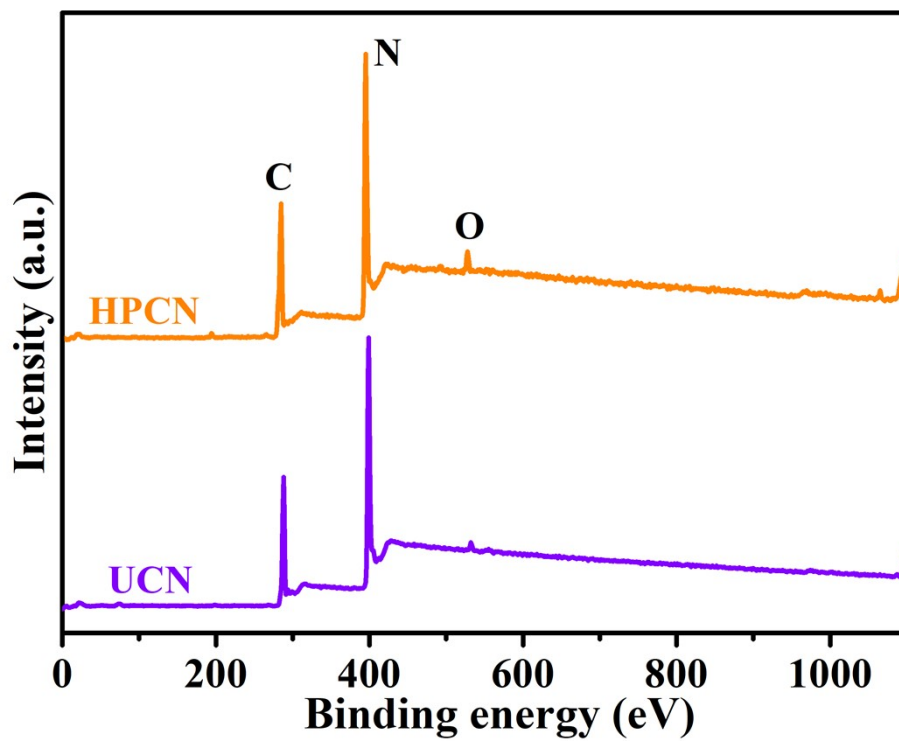


Figure S4. The survey XPS spectra of UCN and HPCN

Table S1: The summarized parameters obtained from N₂ adsorption-desorption isotherms.

Sample	V_{pore}	D_{pore}	S_{BET}
UCN	0.16	7.2	98
HPCN	0.008	32.4	11

V_{pore} represents total pore volume (cm³/g), D_{pore} represents average pore width (nm),

S_{BET} is the specific surface area (m²/g)

Table S2: The fitted parameters obtained from decay curves of samples.

Sample	τ_1 (ns) (Rel. %)	τ_2 (ns) (Rel. %)	τ_a
UCN	1.46(75.45)	18.91(24.54)	15.5
HPCN	1.51 (56.32)	7.23 (43.68)	6.0

τ_a represents the average lifetime (ns) of photogenerated carriers ; τ_1 , and τ_2 represent the lifetime (ns) in the radiative and non-radiative energy transfer process, respectively; A_1 and A_2 are the pre-exponential factors of decay curves.

Their TRPL spectra can be fitted by the following double exponential decay equation¹:

$$I_{(t)} = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

The average lifetime (τ_a) can be calculated according to the following equation²:

$$\tau_a = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$

Reference

1. P. Xia, M. Antonietti, B. Zhu, T. Heil, J. Yu and S. Cao, *Adv. Funct. Mater.*, 2019, **29**, 1900093.
2. W.-T. Hsu, Y.-L. Chen, C.-H. Chen, P.-S. Liu, T.-H. Hou, L.-J. Li and W.-H. Chang, *Nature communications*, 2015, **6**, 8963.