Electronic Supplementary Information

Construction of π-conjugated crystalline carbon dots with carbon nitride nanofragments for efficient photocatalytic H$_2$ evolution

Fang He,[*a] Hubo Yuan,[#a] Yan Hu,[#a] Jiawei Huang,[b] Zhenxing Wang,[a] Shaoqin Peng,[a] Yuexiang Li[*a]

aSchool of Chemistry and Chemical Engineering, Nanchang University, Nanchang, 330031, P.R. China

bSchool of Physics and Materials Science, Nanchang University, Nanchang, 330031, P.R. China

AUTHOR INFORMATION

Corresponding Author

*E-mail: hefang1009@163.com (F. He); liyx@ncu.edu.cn (Y. Li)

Experimental Section

Materials. Potassium chloride (KCl), lithium chloride (LiCl), melamine (MA, $C_3H_6N_6$), tannic acid (TA), were obtained from Aladdin (China). Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and triethanolamine (TEOA) were acquired from Chemical Reagent Co. of Sinopharm. The chemicals practiced in the experiments were not further purified.

Synthesis. The final CCDs-CNx were synthesized by secondary heating, and other samples were synthesized by less process or ingredient. Firstly, 2 g melamine (MA) was stirred in tannic acid (TA) aqueous solution with 12 h, then removed water through centrifugation, and then dried for 12h at 80 °C to gain TA/MA precursor. The TA/MA powders were heated to 550 °C with 10 °C min^{-1} heating rate, and held for 2 h. The obtained samples were denoted as CDs-CN. CN was synthesized by single melamine without TA at the same process as contradistinction. The CCDs-CNx heterojunctions were synthesized as following: 400 mg obtained CDs-CNx sample were evenly mixed with 2 g mixed salt of (55-45) wt% KCl-LiCl together. The above mixture was heated to 500 °C with the heating rate of 10°C min^{-1}, and kept for 2 h. Waiting until it cools to room temperature, the final material was cleaned by excessive deionized water, and then dried at 80 °C overnight. The products were symbolled as CCDs-CNx, where x refers to 5,10, 20 (weight percentage of TA). CCDs-CN0 was synthesized by the same steps using CN in the secondary heating for a comparison.

Characterization. The XRD result of the acquired samples was measured via a XD-2/3 diffractometer using Cu Kα radiation. FT-IR spectra were detected on a Cary630 (Agilent, America). The XPS spectra were implemented utilized a Thermo Fisher Scientific ESCALAB250Xi apparatus with an X-ray source of Al Kα, using C1s line at 248.8 eV to calibrate the binding energy. The morphology of the catalyst was obtained by SEM (Regulus 8100, Hitachi) and TEM (JEM-F200). And JEM-F200 with an EELS (Gatan Model 1077 Continuum S). ESR spectra were gained on a Bruker EMXplus ESR spectrometer. The BET test was measured by the JW-BK132F. And the catalyst light absorption was conducted on a Hitachi U-3310 UV–vis diffuse reflectance spectrometer using $BaSO_4$ as the reference. PL spectra was acquired by a Perkin-Elmer LS-55 luminescence spectrometer with the excitation wavelength of 370 nm. Time-resolved fluorescence decay spectra were performed on a FLS1000 steady state (Edinburgh, Britain). Organic element analysis was recorded on a vario EL III. The solid-state ^{13}C MAS NMR spectra were examined by a 400WB spectrometer (Bruker Avance Neo).

Electrochemical Measurements. Mott-Schottky curves and Electrochemical impedance spectroscopy (EIS) were recorded from a Netherlands IVIUM electrochemical equipment. Three-electrode system were composed of platinum electrode, glassy carbon electrode as work electrode, and Ag/AgCl electrode. The phosphate buffer solution (PBS) solution was as the electrolyte. The working electrode using glassy carbon electrode was made by the following steps: 1 mg of catalyst was evenly dispersed 1 mL water solution containing 10 μL Nafion, then

diluting the suspension tenfold with water and homogenizing by ultrasound. Finally, taking 10 μL of the above slurry drop onto the surface of glassy carbon electrode, and then dried naturally. The frequency range of EIS is 10^5 to 10^0 Hz. The test frequency of Mott-Schottky curves was constantly 1000 Hz.

Transient photocurrent was implemented on CHI660E (Shanghai Chenhua Limited, China) in alternating light and dark environments, which is the same standard three-electrode system that FTO conductive glass replaces glassy carbon electrode as working electrode. Using a 300 W Xe arc lamp ($\lambda > 400$ nm) as the test light source, and 0.1 mol L^{-1} Na_2SO_4 aqueous solution as an electrolyte. Utilizing the following methos to make the working electrode: At first, cleaning the 1.0×3.0 cm FTO glasses sequentially by acetone, alcohol, and water via ultrasonication for 20 min. Afterwards, 5 mg powder of prepared samples was evenly dispersed in 1 mL water by 4 h ultrasound. And then, 10 μL slurry was spread onto 1.0×1.0 cm FTO conducting glassy and occupied at central position, and dried naturally.

Photocatalytic H_2 evolution Measurements. Photocatalytic experiment was conducted in a 200 mL closed flat Pyrex flask. The dosage of the sample was 50 mg, and it was dispersed in 100 mL aqueous solution contained 10 mL triethanolamine (TEOA) with 3 wt% Pt loading. The resultant mixture was sonicated for 10 min. The closed system was input continuously with N_2 for 30 min, then irradiated by a Xe lamp (300 W, $\lambda \geq 400$ nm), and kept magnetic stirring. The amount of H_2 production was determined on a GC1690 gas chromatograph (KeXiao Chemical Equipment Co. Ltd.).

The apparent quantum efficiency (AQE) of the CCDs-CN10 was consistent with the photocatalytic hydrogen production reaction conditions. First, 50 mg of catalyst was treated with loading platinum by Xe lamp with same element. The flask was removed oxygen with N_2 blowing 30 min before radiation every time. The light source was measure by the monochromatic LED lamp (several monochromatic LED lamps were used). The effective area of the irradiation was about 0.80 cm^2.

The AQE can be calculated by the following equation:

$$AQE[\%] = \frac{2 \times number\ of\ evolved\ H_2\ molecules}{number\ of\ incident\ photons}$$
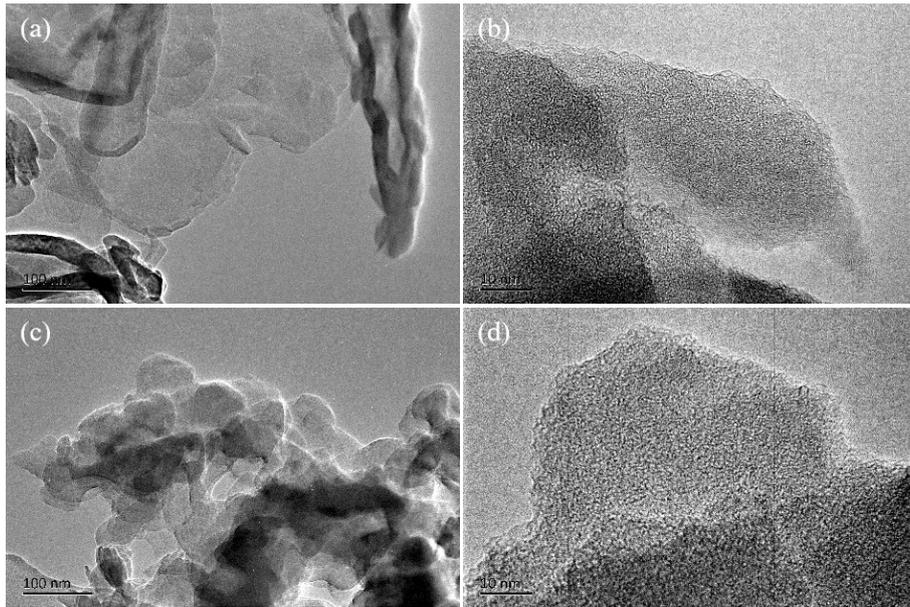
Fig. S1 TEM (a, c) and HRTEM images (b, d) of CDs-CN.
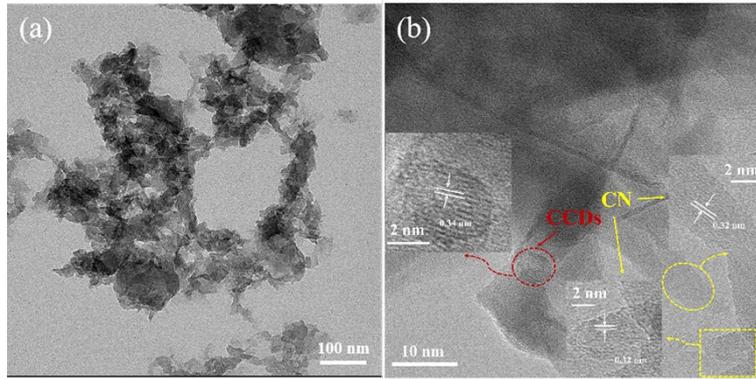
Fig. S2 The TEM (a) and HRTEM image (b) of CCDs-CN5.
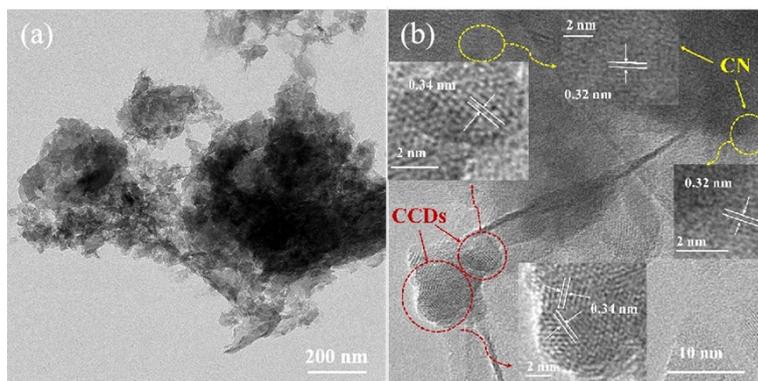
Fig. S3 The TEM (a) and HRTEM image (b) of CCDs-CN20.
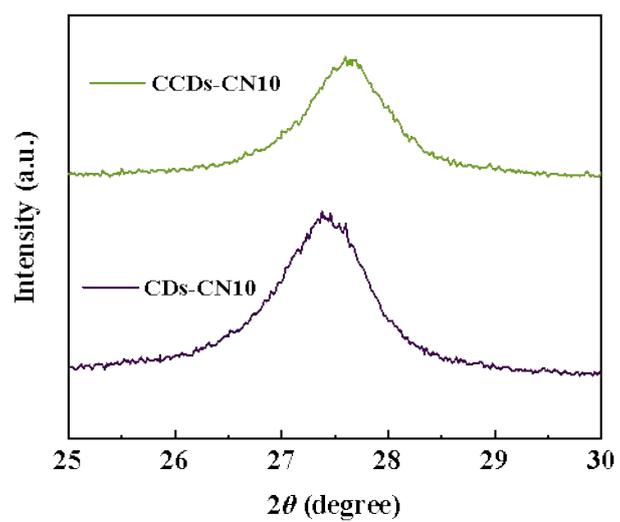
Fig. S4 The amplified XRD patterns of CDs-CN10 before and after molten salt treatment.
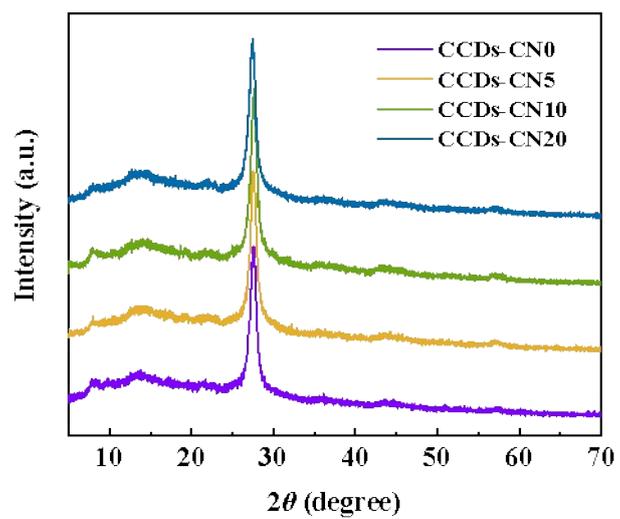
Fig. S5 XRD patterns of CCDs-CNx with different content of CCDs.
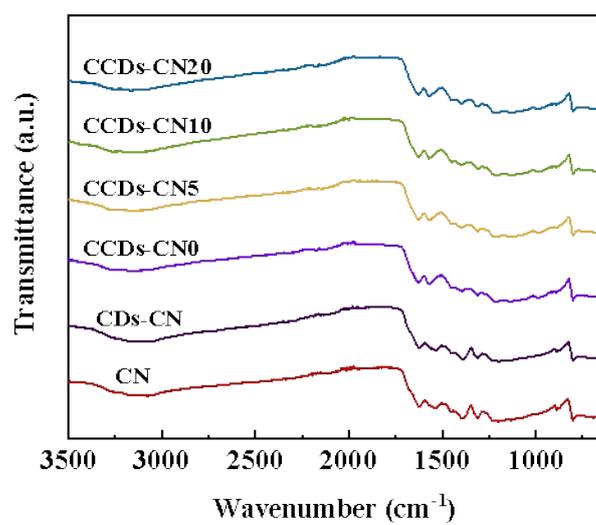
Fig. S6 FT-IR spectra for pristine CN, CDs-CN, and CCDs-CNx composites with different content of CCDs.
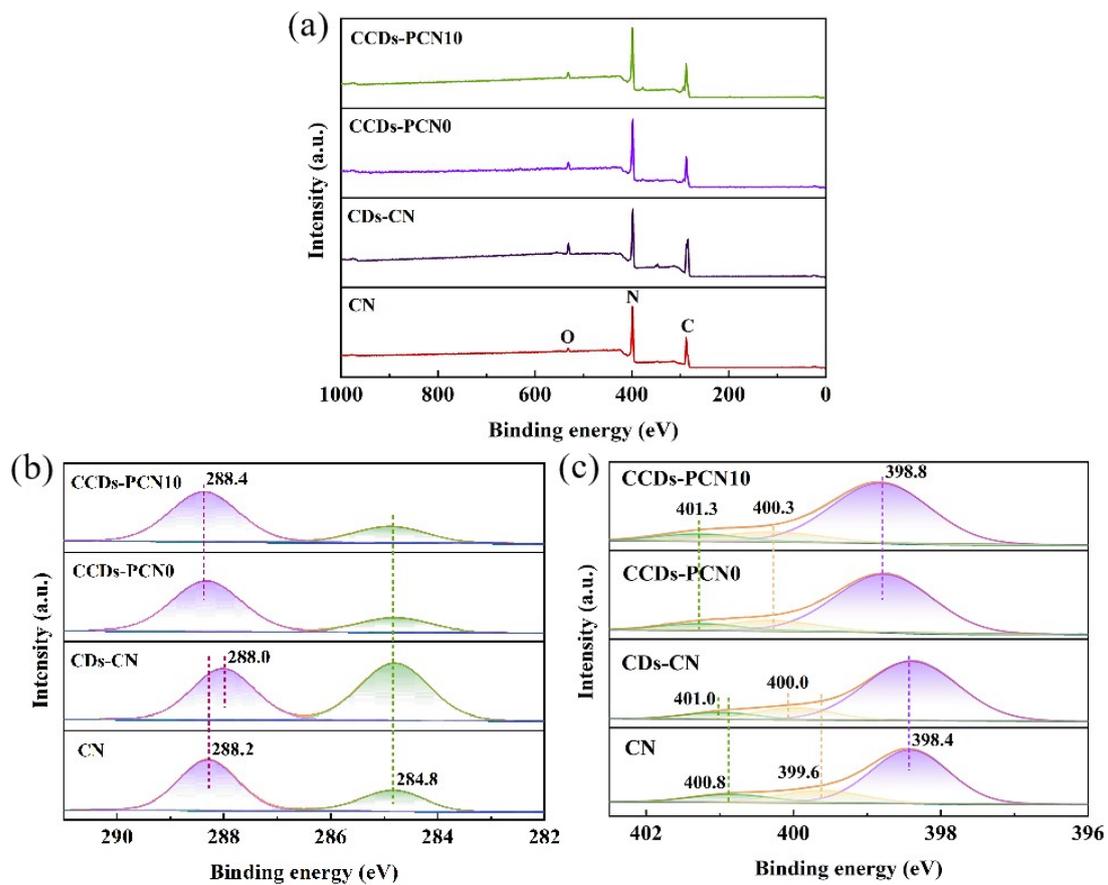
Fig. S7 XPS survey spectra (a), C 1s (b) and N 1s (c) XPS spectra for CN, CDs-CN, CCDs-CN0, and CCDs-CN10.
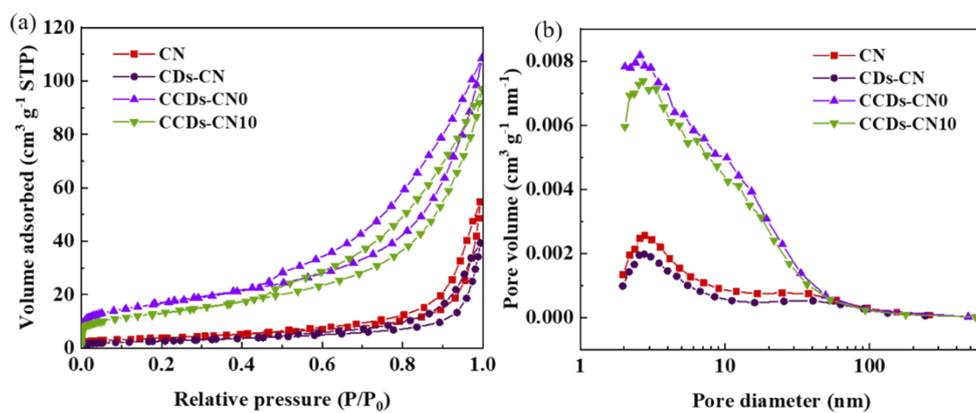
Fig. S8 The N_2 adsorption-desorption isotherms (a) with the corresponding pore

diameter distribution curves (b) of CN, CDCN, CCCN0 and CCCN10 composite.
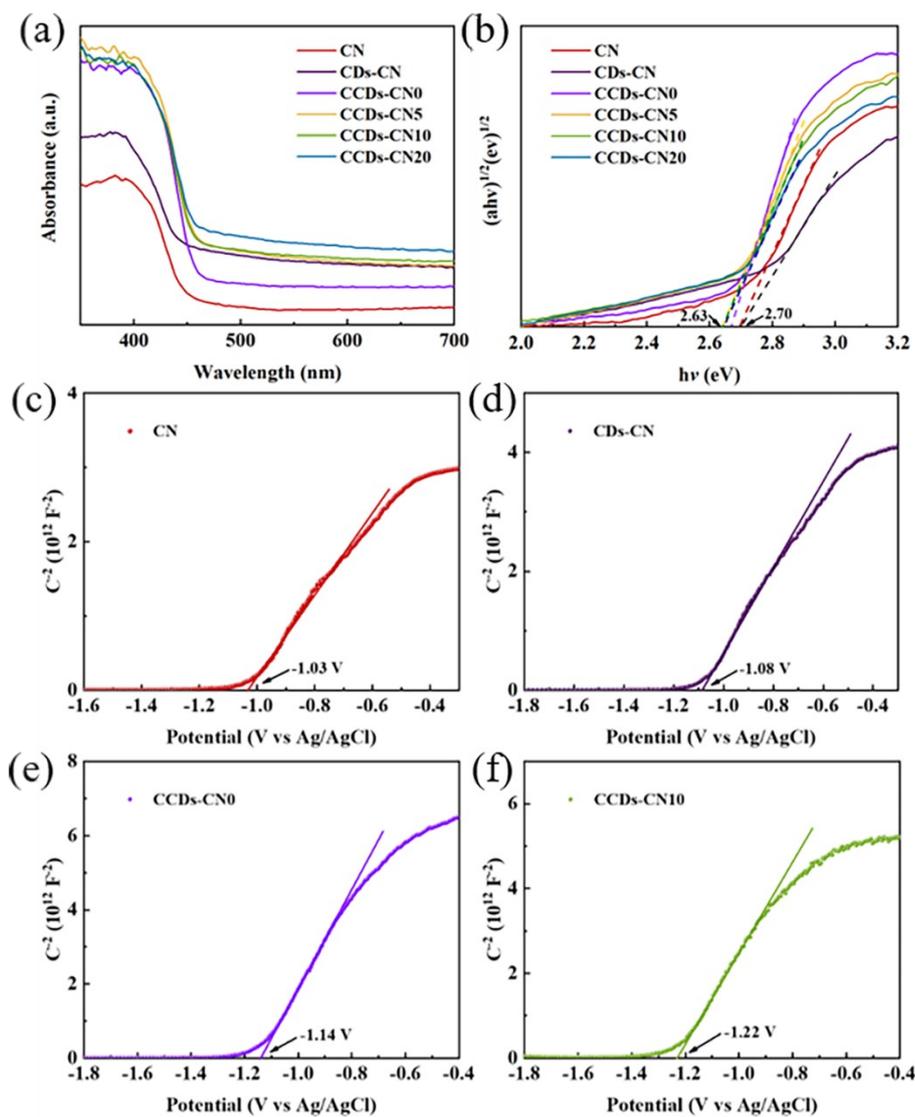
Fig. S9 The UV-vis absorption spectra (a) with the corresponding band gaps (b) for pristine CN, CDs-CN, CCDs-CN0, and CCDs-CNx composites with different content of CCDs. Mott-Schottky plots for pristine CN (c), CDs-CN (d), CCDs-CN0 (e), and CCDs-CN10 composite (f).
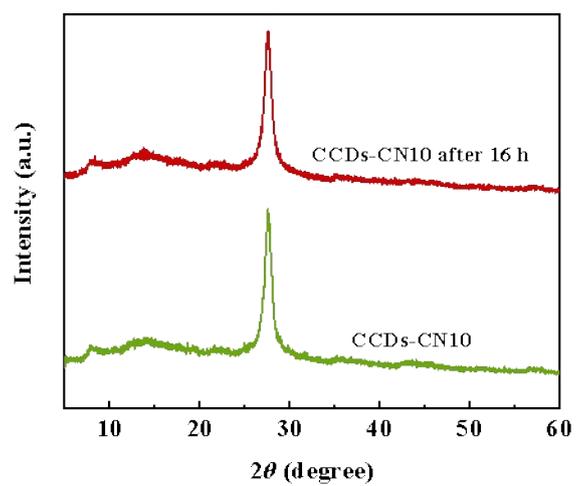
Fig. S10 XRD patterns of the CCDs-CN10 before and after the photocatalytic H$_2$ evolution reaction.

Table S1 The comparison of CCDs-CN10 with some recent reported CN-based photocatalysts for H$_2$ evolution.

Photocatalyst Composition	Reaction Solution Sacrificial Agent (Content)	Cocatalysts	Illumination Condition	HER Rate (μmol h^{-1} g^{-1})	Reference
3-MC/C$_3$N$_4$	100 mL TEOA (10 vol%)	Pt (4.0 wt%)	300 W Xe Lamp (λ＞420 nm)	2040	[1]
C, P co-doped CN	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞400 nm)	4485.7	[2]
MS-550	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞420 nm)	661	[3]
1 wt% C-PDA-CN-ms	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞400 nm)	3860	[4]
2D-CN/NGQDs	200 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞400 nm)	3000	[5]
GCN-HC	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞420 nm)	339.4	[6]
0.1HCCN	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	350 W Xe Lamp (λ＞420 nm)	683.5	[7]
HCCN-1.2	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞420 nm)	3550.2	[8]
CCDS-CN10	100 mL TEOA (10 vol%)	Pt (3.0 wt%)	300 W Xe Lamp (λ＞400 nm)	5912	This work

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