Supporting Information

Enhanced Photocatalytic Hydrogen Evolution of Carbon Quantum Dot Modified 1D Protonated Nanorods of Graphitic Carbon Nitride

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Material Characterization

The crystal and chemical structures of samples were analyzed on an X-ray diffractometer (XRD, Bruker, D8 Advance) with a Cu target. The morphology and microstructure of samples were investigated on a field emission scanning electron microscopy (FESEM, LEO 1530) operated at 20 kV and transmission electron microscopy (TEM, FEI Tecnai G220) operated at 300 kV. The chemical state and intimate interaction of samples were studied through X-ray photoelectron spectroscopy (XPS) using an Sengyang SKL-12 electron spectrometer with VG CLAM 4 MCD electron energy analyzer under Al Ka radiation (1496.3 eV) at a current of 15 mA and 10 kV. The adventitious C1s line at 284.8 eV was used as reference for the binding energies. The diffuse reflectance spectra (DRS) were obtained by a UV-vis-NIR spectrometer (PerkinElmer, Lamda 750) equipped with an integrating sphere using BaSO4 as a reference. Photoluminescence (PL) spectra were obtained by fluorescence spectrophotometer (PTI QM-4) with the excitation wavelength of 365 nm. Fourier transform infrared (FT-IR) spectroscopy was recorded on Nicolet iS50 (Perkin, Elmer Paragon 1000 PC). The time-resolved fluorescence measurements were recorded on an Edinburgh FLS980 with an excitation wavelength of 365 nm. The obtained curves were fitted by using the following equation:

$$f(t) = B + A_1 \times exp(-t/\tau_1) + A_2 \times exp(-t/\tau_2) + A_3 \times exp(-t/\tau_3)$$

Where τ_1 , τ_2 and τ_3 present the decay time constants, A₁, A₂ and A₃ are fractional contributions for time-resolved decay lifetime of τ_1 , τ_2 and τ_3 .⁴⁹

The average emission lifetime was calculated via the following equation:

$$\tau_{ave} = [A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2]/[A_1\tau_1 + A_2\tau_2 + A_3\tau_3]$$

Zeta-potential measurement

The zeta potentials of BCN, HCN, HCNC-0.50, CQDs were measured at 293K using Malvern nano ZS. Typically, 5 mg samples were dispersed in 100 ml of water and ultrasonicated for 30 min. The zeta potential of samples was measured three times.

Photocatalytic Water Splitting

A 500 W xenon arc lamp (Zhong Jiao Jin Yuan, Model CEL-HXF300) coupled with a 420nm cut-off filter was used as the trigger light source. The distance between the reactor and light source was 15 cm. The incident light radiation intensity was measured by a UV-A dualchannel radiation meter UV intensity meter (Beijing Normal University, Model FZ-A), and the average light intensity (15 cm away from the lamp, 15 A) was ca. 44.5 mW/cm² with 420 nm filter.

The photocatalytic hydrogen (H₂) evolution experiments were performed in a quartz tube reactor (25 ml) sealed with a rubber septum, gas-closed system, at ambient temperature and pressure. Initially, the as-prepared photocatalyst powder (15 mg) was suspended in aqueous triethanolamine solution (TEOA, 10 mL, 10 vol%) under constant stirring. Then, 3 wt.% of Pt as co-catalyst was loaded by in situ photoreduction deposition method³⁸, under the light irradiating for 30 min, H₂PtCl₆ aqueous (0.025mg/ml) as Pt source. The suspension was

purged with nitrogen gas for 30 min to ensure anaerobic conditions and then it was placed at the position of 15 cm away from lamp and irradiated under visible light by using the 420 nm cut-off filter. After 1h irradiation, the released gas (400 µL) was collected by syringe from the headspace of the reactor and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure nitrogen as a carrier gas) equipped with a TDX-01(5 Å molecular sieve conductivity Eventually, column) and а thermal detector (TCD). the total content of photocatalytic H₂ evolution was calculated according to the standard curve. Continuous stirring was applied to the whole process to keep the photocatalyst particles in suspension state and get the uniform irradiation.

The apparent quantum efficiency (QE) was measured under the similar photocatalytic re action conditions. Four low-power LEDs with monochromatic light (3 W, 420 nm) (Shenzhe n LAMPLIC Science Co. Ltd., China), which were placed 1cm away from the vial from four different directions, were applied as light sources. The focused intensity and illuminated area s for each LED were ca. 80.0 mW/cm² and 0. 28 mm², respectively. QE was calculated via th e following equation:

 $QE = (2 \times number of H_2 molecules/number of incident photons) \times 100\%$.

The turnover number (TON) was calculated after 1 hours by using the following formula;

TON (turnover number) = moles of H_2 molecules evolved / moles of active sites (platinum on the photocatalyst).

Photoelectrochemical Measurement

Photoelectrochemical tests were performed on a three-electrode system using an electrochemical workstation (CHI660C Instruments, China) with Pt wire (counter electrode)

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and saturated calomel electrode (SCE, reference electrode). The working electrode was fluorine-doped tin oxide (FTO) glass coated with a sample film on the conductive surface. Typically, 10 mg of sample and 10 μ L of 5% Nafion solution (DuPont) were dispersed in 1 mL of ethanol, and the mixture was ground to a sticky paste and then applied on the conductive surface of FTO glass using doctor blade method. The obtained working electrode was heated at 70 °C for 2 h to evaporate the residual solvent and achieve an intimate contact between the sample film and FTO glass. The light source was an LED monochromatic point lamp (3 W, 420 nm). The light spot effective area on the working electrode was set as 28.26 mm2. 8 mL volume of 0.5 M Na2SO4 aqueous solution acted as the electrolyte. The opencircuit voltages were set as the initial bias voltages in the transient photocurrent responses tests. The electrochemical impedance spectroscopy (EIS) were recorded over a frequency range of 1-105 Hz with an amplitude of 5.0 mV. The linear sweep voltammogram (LSV) plots were also recorded by using the impedance-potential mode. The potential was scanned from 0.0 to -0.4 V (vs SCE, pH 7).



Figure S1. Synthesis of HCNC-x (x = 0.0, 0.25, 0.50, 0.75, 1.00) via top-down approach at

room temperature (color changed from yellow to white then to light brown).



Figure S2. FT-IR spectra of samples BCN, HCN, HCNC-0.50 and CQDs.



Figure S3. UV-vis absorption spectra of the samples, Inset: Kubelka Munk-Energy spectra of the samples



Figure S4. VB XPS (b) of BCN, HCNC-0.0 and HCNC-0.50.



Figure S5. The photocatalytic performance of no catalyst, HCNC-0.50 in the dark, BCN, BCNC-0.50, PBCNC-0.50 and PHCNC-0.50.



Figure S6. LVS curves of FTO, HCNC-0.0/FTO, and HCNC-0.50/FTO electrodes.