

Supporting Information

Bottom-Up Enhancement of g-C₃N₄ Photocatalytic H₂ Evolution Utilising Disordering Intermolecular Interactions of Precursor

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Section S1: Experimental Methods:

Photocatalytic test. The photocatalytic reaction was performed in a pyrex glass cell connected to a glass closed gas circulation system. The as-obtained products were loaded with 3 wt% Pt and calcinated at 180 °C for 30 min (ramp: 2 °C min⁻¹). H₂ evolution analysis was performed by dispersing 50 mg of catalyst power in an aqueous solution containing triethanolamine (100 mL, 10 vol. %) as the sacrificial electron donor. The reactant solution was evacuated several times to remove air completely before the reaction. A 300 W Xe lamp with a 420 nm cutoff filter was used as the light source. A flow of cooling water was used during the reaction to maintain the temperature of the reactant solution at 15 °C. The amount of evolved H₂ evolved was analyzed by gas chromatography (TECHCOMP, 7890 II).

Electrochemical Analysis. For electrochemical measurement, catalysts were transformed from powders into film electrodes. The working electrode was prepared on fluoride-tin oxide (FTO) glass plates. The FTO glass pieces with a size of 3 × 1.0 cm were sonicated in acetone and ethanol, and then rinsed with millipore water and dried

in an air stream. 10 mg of the powder was ground in a agate mortar with 50 μL nafion and 200 μL DMF solution to produce slurry. The obtained slurry was used for spreading onto FTO glass substrate, whose side part was previously protected using Scotch tape. After air drying, the electrode was fired at 200 $^{\circ}\text{C}$ for 30 min in air to improve adhesion. A copper wire was connected to the side part of the FTO glass. Electrochemical performances were performed in a conventional three electrode cell, using a Pt slice and an Ag/AgCl electrode as counter electrode and reference electrode, respectively. A 0.2 M Na_2SO_4 aqueous solution containing 10 vol. % triethanolamine was chosen as the supporting electrolyte and was purged with nitrogen to remove O_2 before any measurements. The EIS experiments were carried out on a CH Instruments Electrochemical Workstation under 1.0 V vs. Ag/AgCl.

Section S2: Crystal and chemical structures.

Table S1. The results of elemental analysis for the bulk CN and D-CN.

Samples	N%	C%	H%	Others%	C/N
CN	60.84	35.18	2.09	1.89	0.675
D-CN	59.15	34.25	2.05	4.55	0.676

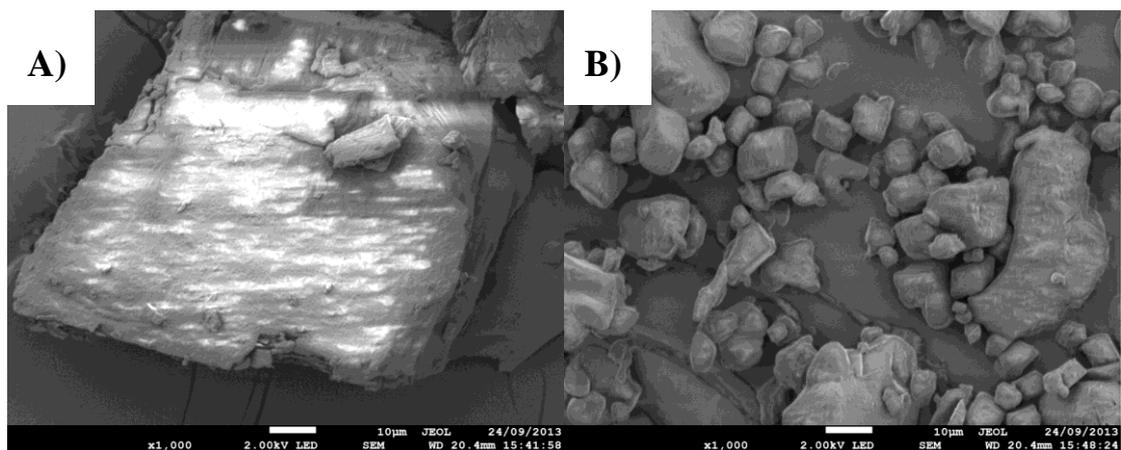


Figure S1. SEM images of A) DCDA and B) D-DCDA samples.

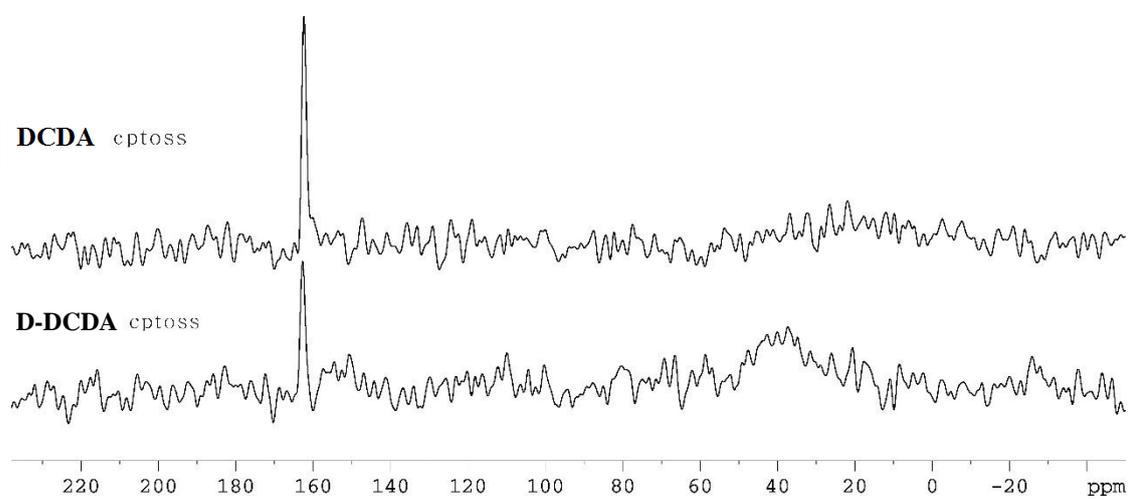


Figure S2. ¹³C MAS solid-state NMR spectrum for DCDA and D-DCDA.

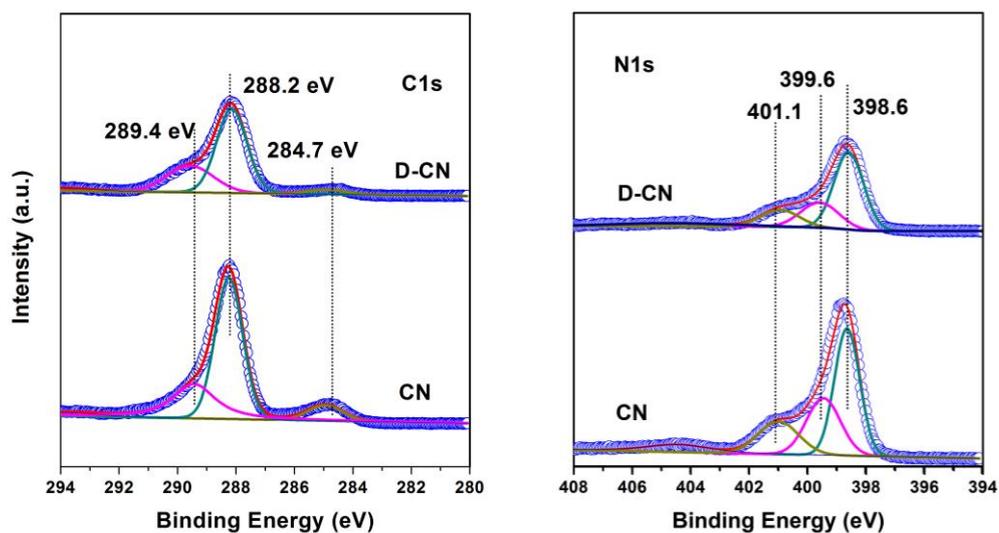


Figure S3. The corresponding high-resolution spectra of C 1s (A) and N 1s (B) that are obtained from the CN and D-CN.

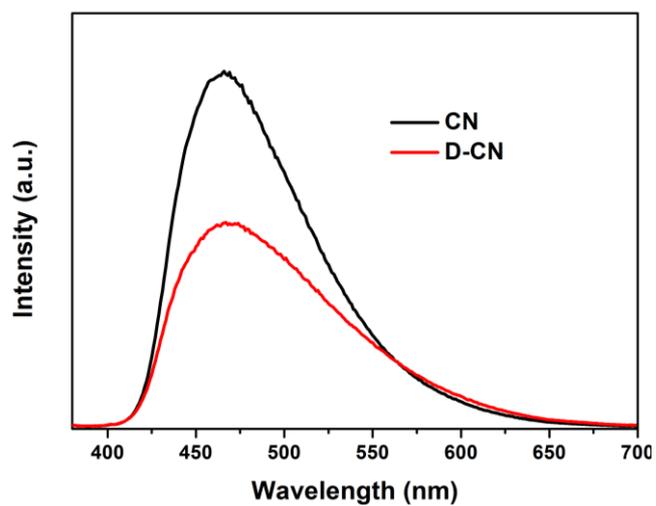


Figure S4. Fluorescence emission spectra of the CN and D-CN samples.