- 1 Supplementary Information

3 Constructing built-in electric field by grafting strong 4 electronegative small molecules for photocatalytic H₂ production

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1 Experimental section

2 Catalyst synthesis

The chemicals urea (99%) and chloroplatinic acid (H₂PtCl₆·6H₂O) were procured from the Shanghai Mai Lin Biochemical Co. 2-amino-4,6-difluoropyrimidine (AD-F), 2-amino-4,6-dichloropyrimidine (AD-Cl) and 2-amino-4,6-dibrompyrimidine (AD-Br) were obtained from the Shanghai Bide Pharmaceutical Technology Co. Triethanolamine (TEOA) was purchased from the Shanghai Aladdin Biochemical Technology Co. All chemicals were utilized in their original state, without any additional processing.

In order to synthesize bulk polymeric carbon nitride (g-C₃N₄), 8 g of urea was ground 10 into powder and placed into a crucible with a lid. The crucible was then transferred to 11 a muffle furnace and heated to 550 °C at a heating rate of 2 °C/min under a static air 12 atmosphere. The furnace was subsequently maintained at this temperature for a period 13 of 4 h. Once the yellowish, lumpy sample had cooled to room temperature, it was 14 ground, collected, and labeled as CN. The conditions for the synthesis of FCN were 15 identical to those previously described for the preparation of bulk CN, with the 16 exception that a specific quantity of AD-F was incorporated into the raw material in 17 conjunction with urea during grinding. The specific procedure was as follows: 8 g of 18 urea and a specified quantity of AD-F (20 mg, 40 mg, 60 mg, 80 mg, and 120 mg) were 19 ground thoroughly in an agate mortar and subsequently placed in a crucible with a lid. 20 Subsequently, the crucible was transferred to a muffle furnace and heated to 550 °C at 21 a rate of 2 °C/min, held for four hours, and then allowed to cool to room temperature. 22

1	The resulting samples were collected after grinding and designated FCN-1, FCN-2,
2	FCN-3, FCN-4, and FCN-5, respectively. The synthesis of ClCN and BrCN was
3	conducted in a manner analogous to that employed for FCN. However, the quantity of
4	urea was fixed at 8 g, maintaining the same molar ratio (AD-F/urea = AD-Cl/urea =
5	AD-Br/urea). Additionally, AD-Cl or AD-Br was utilized in place of AD-F, with the
6	resulting samples designated as ClCN-1, ClCN-2, ClCN-3, ClCN-4, ClCN-5, BrCN-1,
7	BrCN-2, BrCN-3, BrCN-4, and BrCN-5. For greater clarity, the optimal samples, FCN-
8	2, ClCN-2, and BrCN-2, were simplified as FCN, ClCN, and BrCN, respectively.
9	Taking FCN as an example, the specific synthesis process can be found in Scheme 1.



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11 Scheme 1 Illustration of the preparation process of FCN through the co-polymerization method.

12 Characterization

13 The phase structure of catalysts was recorded by X-ray powder diffraction (XRD)

1 powder diffraction instrument with monochromatized Cu Ka radiation (λ = 1.5406 nm) at room temperature. The functional groups of catalysts were characterized by Fourier 2 transform infrared spectroscopy (FTIR). The elemental surface composition and 3 chemical state of catalysts were investigated via X-ray photoelectron spectra (XPS). 4 The morphology and microstructure of catalysts were observed using scanning electron 5 microscopy (SEM), transmission electron microscopy (TEM), and high-resolution 6 transmission electron microscopy (HRTEM). The organic element analyzer measured 7 the specific content of C and N in the samples. A Cary 5000 (America Varian) 8 spectrophotometer was applied to record UV-vis diffuse reflectance spectra (DRS) of 9 catalysts. The recombination rate of photogenerated electrons and holes was determined 10 by measuring the photoluminescence (PL) spectrum of catalysts using a Hitachi F-4600 11 fluorescence spectrophotometer. The excitation wavelength is 290 nm, the scanning 12 range is 300-800 nm, and the scanning speed is 1200 nm/min. In-situ KPFM 13 measurement was conducted in an AFM testing system equipped with SKPM modules 14 and Xenon lamps to obtain the surface potential of the catalyst. 15

16 Photoelectrochemical measurements

Photoelectrochemical measurements were implemented by an electrochemical workstation (CHI 660E) equipped with three electrodes to obtain photocurrent response, electrochemical impedance spectra (EIS), and Mott-Schottky plots. Ag/AgCl electrode and platinum wire worked as reference electrodes and counter electrodes, respectively. An ITO electrode with an 8 cm² area covered by catalysts was utilized for the working electrode. To prepare the working electrode, 8 mg of the sample was suspended in 800 µL of ethyl cellulose solution with a concentration of 1mg/mL and
 ultrasonically mixed evenly. Then the mixture was evenly dispersed on the surface of
 ITO conductive glass, and dried in an oven at 100 °C. 0.1 mol/L Na₂SO₄ solution was
 used as the electrolyte. The tests were conducted under visible light with a cutoff filter
 of 420 nm.

6 Photocatalytic hydrogen evolution

The photocatalytic performance of the prepared samples was evaluated by H₂O 7 splitting for H₂ production under visible light irradiation ($\lambda > 420$ nm). Typically, 20 8 mg of the catalyst powder was dispersed in 50 mL aqueous solution containing 5 mL 9 triethanolamine (TEOA) as the sacrificial agent. The sealed reaction vessel was 10 evacuated and purged by N₂ for about 20 min to completely remove air before 11 irradiation. By using a condenser, the temperature of the circulating condensate H₂O in 12 the reactor was always maintained at 5 °C. To detect the amount of H_2 , 0.5 mL gas 13 component was extracted from the vessel and then injected into a gas chromatograph 14 (GC-2014C, Shimadzu, nitrogen carrier gas) equipped with a TCD detector. 15

16 Theoretical calculations

17 All the density functional theory (DFT) calculations were performed by 18 GAUSSIAN16. Geometry optimizations and frequency calculations were launched in 19 B3LYP/6-31G* level, and no imaginary frequencies appeared after optimizations. The 20 HOMO/LUMO and Electrostatic potential (ESP) analyses were acquired using 21 Multiwfn and VMD software.



4 Fig. S1 (a) FTIR spectra, (b)the survey XPS spectra, and (c) XPS N 1s spectrum of CN, FCN, ClCN,
5 and BrCN.

The FTIR (Fig. S1a) was conducted to analyze the surface state of samples, and results 6 showed that copolymerization with small molecules did not change the characteristic 7 peaks of CN. All the samples exhibit three characteristic sets of peaks. The peak at 812 8 cm⁻¹ originates from the breathing vibration mode of the heptazine ring, the peak in the 9 range of 1200-1700 cm⁻¹ is consistent with the typical aromatic C-N heterocyclic 10 stretching mode, and the peak between 2800-3700 cm⁻¹ belongs to the stretching 11 vibration mode of -NH residual uncondensed amino groups or the O-H stretching of 12 adsorbed H₂O molecules. 13

The survey XPS spectra (Fig. S1b) reveal the presence of C, N, and O elements in CN, FCN, ClCN, and BrCN. The high-resolution N 1s XPS spectrum (Fig. S1c) reveals three principal peaks at 398.8, 400.5, and 401.4 eV, corresponding to C-N=C, N-(C)₃, and C-N-H, respectively. These peak positions uniformly migrate towards low binding energy, which may be ascribed to the increase in electron density caused by electron migration nearby. The observed changes in binding energy further suggest alterations

- 1 in the nitrogen environment, confirming the successful incorporation of AD-F, AD-Cl,
 - ¹μm CN ¹μm FCN ¹μm CICN ¹μm BrCN
- 2 and AD-Br molecules.

3





2 Fig. S3 Mott-Schottky plots of (a) CN, (b)FCN, (c)ClCN, and (d) BrCN, (e) schematic diagram of

3 the energy band of CN, FCN, ClCN, and BrCN.

4



2 Fig. S4 (a) H₂ production of FCN, ClCN, and BrCN with different amounts of AD-F, AD-Cl, and

3 AD-Br added under visible light ($\lambda > 420$ nm) irradiation (b) Comparative experiments of FCN.





6 Fig. S5 (a) XRD and (b-c) SEM plots of FCN before and after hydrogen production.





³ of (a) CN, (b) FCN, (c) ClCN, and (d) BrCN.