

Supporting Information

Synergistic effect of biomass-derived carbon decoration and nitrogen defects on seaweed-like tubular g-C₃N₄ for enhanced photocatalytic H₂ evolution

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1. Experimental Section

1.1 Preparation of photocatalysts

1.1.1 Synthesis of Bulk $g\text{-C}_3\text{N}_4$ (BCN)

BCN was synthesized by thermal polymerizing of urea. In detail, 2 g urea was placed in a quartz boat and in N_2 flow (30 ml min^{-1}) at $550 \text{ }^\circ\text{C}$ for 4 h.

1.1.2 Synthesis of nitrogen deficient $g\text{-C}_3\text{N}_4$ (D-CN)

The D-CN was synthesized according to the previously reported literature with some modifications.¹ In a typical synthesis, 7.5 g urea and 5 mg KOH were dissolved in 15 ml H_2O , and the precursor was obtained by freeze-drying the above mixed solution. As follows, the obtained precursor was placed in a quartz boat, and the thermal polymerization process was performed in N_2 flow (30 ml min^{-1}) at $550 \text{ }^\circ\text{C}$ for 4 h. The obtained sample was filtered and washed with plenty of H_2O , dried in an oven at $65 \text{ }^\circ\text{C}$.

1.1.3 Synthesis of biomass-derived carbon decorated $g\text{-C}_3\text{N}_4$ (C-CN)

In a typical synthesis, 7.5 g urea and 3 mg sodium alginate were dissolved in 15 ml H_2O , and the precursor was obtained by freeze-drying the above mixed solution. The subsequent processing was consistent with that of D-CN, and the obtained sample was named C-CN.

1.1.4 Synthesis of biomass -derived carbon decorated nitrogen deficient $g\text{-C}_3\text{N}_4$ (C/D-CN)

In a typical synthesis, 7.5 g urea, 3 mg sodium alginate and 5 mg KOH were dissolved in 15 ml H_2O and the precursor was obtained by freeze-drying the above mixed solution. The subsequent processing was consistent with that of D-CN, and the obtained sample was named C/D-CN. In order to obtain the best performance catalyst, the dosage of sodium alginate (1, 3, 5, 10 mg) and KOH (3, 5, 7, 10 mg) were optimized.

1.1.5 Synthesis of sodium alginate-derived carbon material (sa-C)

In a typical synthesis, 2 g sodium alginate was dissolved in 100 ml H_2O by magnetic stirring. The resulting solution was freeze-dried for 48 h. As follows, the obtained white powder was placed in a quartz boat, and the thermal polymerization process was performed in N_2 flow (30 ml min^{-1}) at $550 \text{ }^\circ\text{C}$ for 4 h. The black sa-C was filtered and washed with a large amount H_2O , dried in an oven at $65 \text{ }^\circ\text{C}$.

1.2 Photocatalysts Characterization

The morphologies of the samples were examined by scanning electron microscopy (SEM, JEOL JSM-5600LV SEM) and transmission electron microscopy (TEM) images (JEM-2000EX TEM). X-ray diffraction (XRD) conducted on a D/Max 2400 diffractometer equipped with a $\text{Cu K}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$) were used to collect the

crystallographic information. The thermal polymerization behavior of the precursors was recorded with a thermogravimetric analyzer (TGA/SDTA851e), and the testing process was performed in N₂ flow (30 ml min⁻¹) with 10 °C min⁻¹ heating rate. The content and distribution of N and C elemental were determined with an elemental analyzer (Vario EL) and element mapping analysis (JEOL JSM-5600LV SEM), respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker EQUINOX55 infrared spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were obtained using an ESCALAB 250 XPS system (Al K α X-ray). All the binding energies were referenced to the C 1s peak at 284.8 eV. Nitrogen adsorption and desorption isotherms were measured on a Beishide apparatus of model 3H-2000PS1 system, and the specific surface areas were calculated via the BET method, and the pore size distributions were calculated via the BJH model (adsorption branch of the isotherm). The UV-Vis diffuse reflectance spectra (DRS) were recorded on a UV-Vis spectrometer (JASCO V-550). The room temperature photoluminescence (PL) spectra were investigated using a fluorescence spectrometer (Hitachi F-7000) and the excitation wavelength is 376 nm.

1.3 Photoelectrochemical Measurements

In a conventional three-electrode cell, the transient photocurrent response and electrochemical impedance spectra of samples were investigated on a CHI660e electrochemical workstation. The working electrode is the indium tin oxide (ITO) glass with coating samples, a Pt electrode as counter-electrode and an AgCl/Ag electrode as the reference. The 0.5 M Na₂SO₄ aqueous solution as electrolyte.

The measurement process of Mott-Schottky plots was consistent with above photoelectrochemical investigations 0.2 M Na₂SO₄ aqueous solution as electrolyte (pH = 7.1, 25 °C). AgCl/Ag electrode system can be converted to reversible hydrogen electrode (RHE) system by the following formula S1: ²

$$V_{\text{RHE}} = V_{\text{AgCl/Ag}} + V_{\text{AgCl/Ag VS NHE}}^0 + 0.059 \text{ pH} \quad (\text{S1})$$

Where $V_{\text{AgCl/Ag VS NHE}}^0$ is 0.1976 V at 25 °C.

1.4 Photocatalytic H₂ Evolution

The photocatalytic H₂ production reactions were performed in under 420 nm visible light irradiation. 10 mg photocatalyst, appropriate amount H₂PtCl₆ (the amount of Pt is 3 % of the photocatalyst) and 10 mL triethanolamine (TEOA) were dispersed in 90 ml distilled water. The air in the reaction system was removed completely by repeatedly air removal and N₂ injection. The experiment process was performed at 15 °C by re-circulating cooling water. The H₂ was detected using a gas chromatography device (GC9790 II, FuLi Instruments,

Zhejiang) equipped with a thermal conductive detector (TCD). Under different wavelength of lights (400, 420, 450 and 520 nm), the H₂ evolution apparent quantum yield (AQY) were obtained.

2. Supplementary Figures

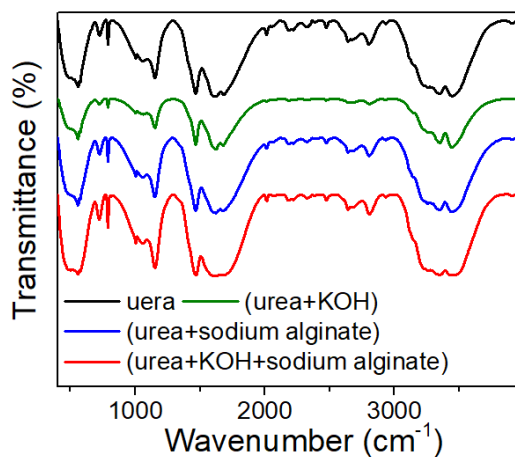


Figure S1. FT-IR spectra of the precursors

As shown in Fig. S1, the infrared spectrum lines of (urea + KOH), (urea + sodium alginate) and (urea + sodium alginate + KOH) precursors are the same as that of urea, which indicates that before thermal polymerization, each component of precursors was physical mixing without chemical complexation.

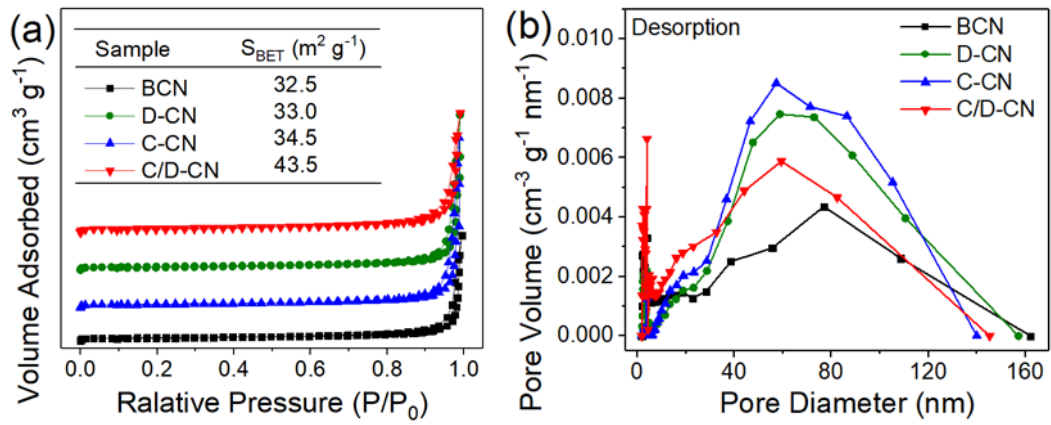


Figure S2. (a) N_2 adsorption-desorption isotherms and (b) BJH pore size distribution of BCN, D-CN, C-CN and C/D-CN.

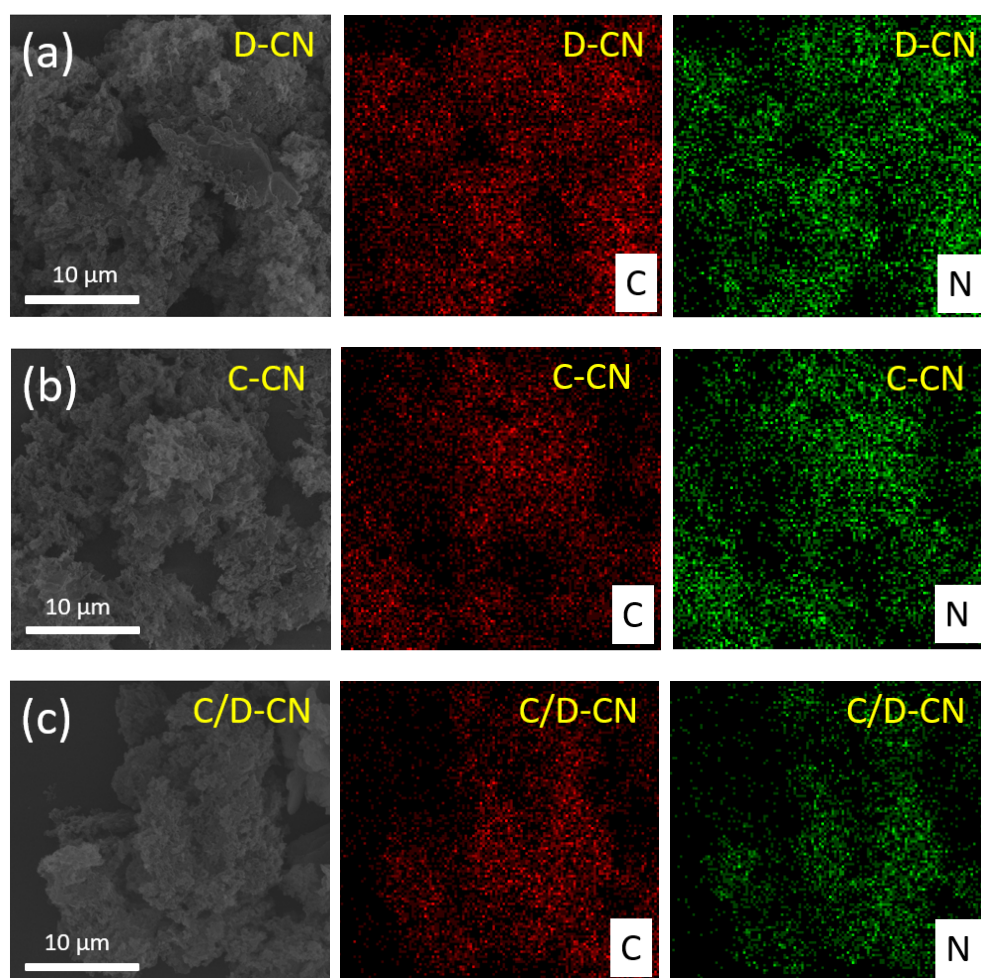


Figure S3. SEM images and corresponding EDS mappings of C element and N element of (a) D-CN, (b) C-CN, and (c) C/D-CN.

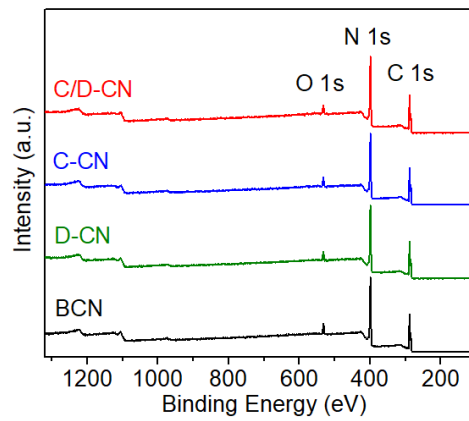


Figure S4. XPS full spectra of BCN, D-CN, C-CN and C/D-CN.

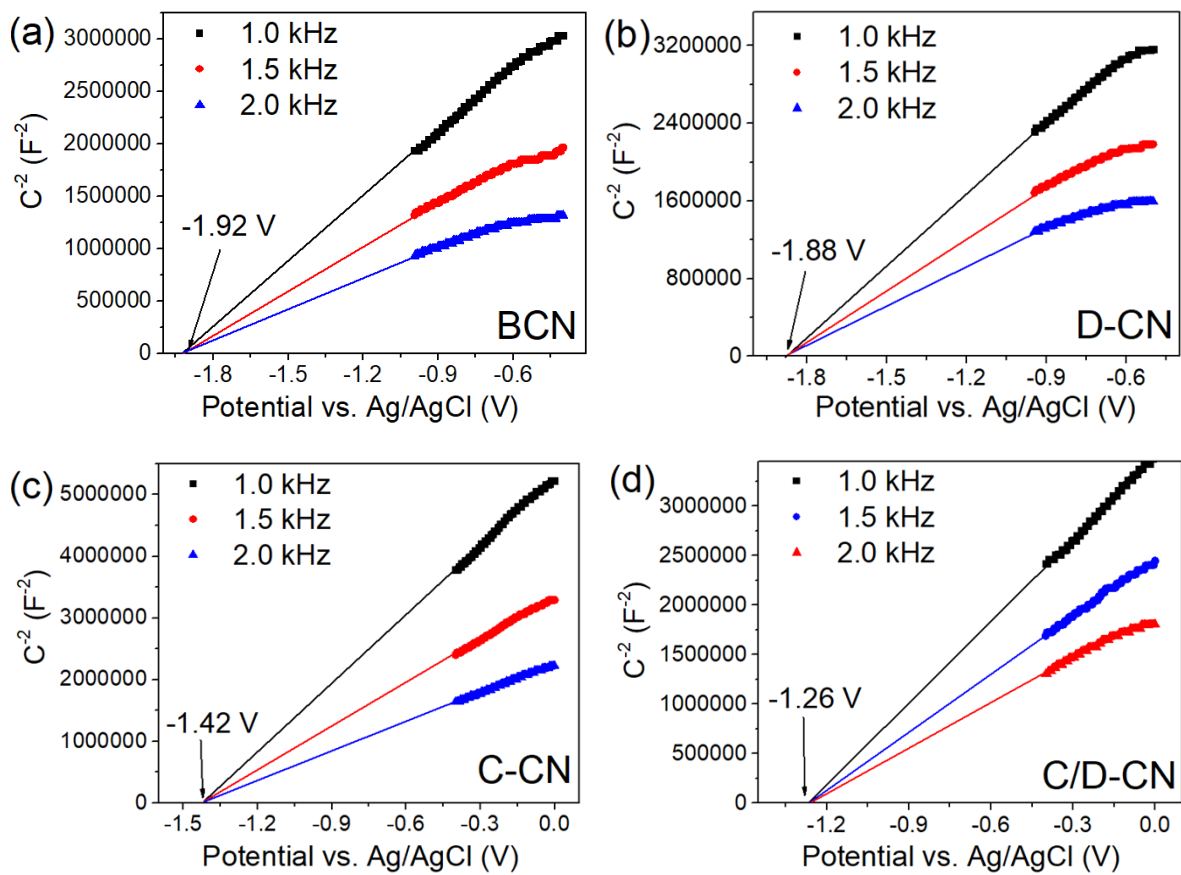


Figure S5. Mott-Schottky plots of (a) BCN, (b) D-CN, (c) C-CN, and (d) C/D-CN.

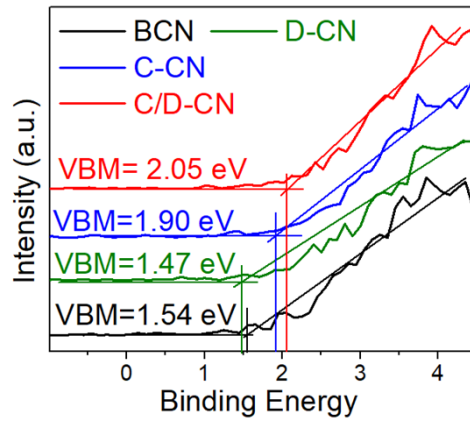


Figure S6. VB XPS spectra of BCN, D-CN, C-CN and C/D-CN.

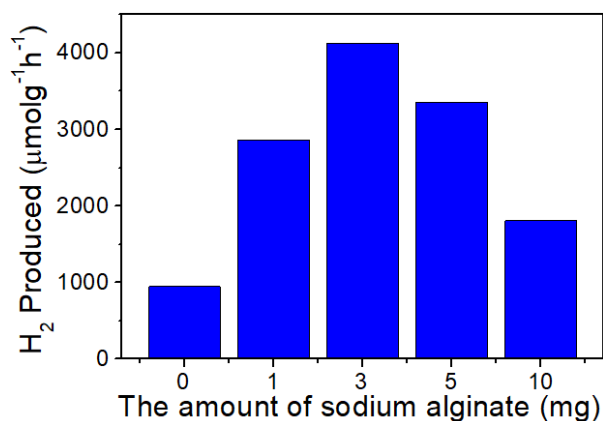


Figure S7. Photocatalytic H₂ generation histogram of a series of C/D-CN prepared with various amount of sodium alginate (W_{sa}).

The optimization process of the introduction amount of sodium alginate (W_{sa}):

A series of catalysts were obtained by thermal polymerization of various freeze-dried precursors mixture of 7.5 g urea, 5 mg KOH and x mg ($x = 0, 1, 3, 5, 10$) sodium alginate to investigate the influence of W_{sa} on photocatalytic H₂ generation activity, and the results as shown in Fig. S7. Compared with no sodium alginate introduction ($x = 0$), the introduction of sodium alginate ($x = 1, 3, 5, 10$) can significantly improve the photocatalytic activity of the samples. When the W_{sa} is 3 mg, C/D-CN shows the highest H₂ generation activity.

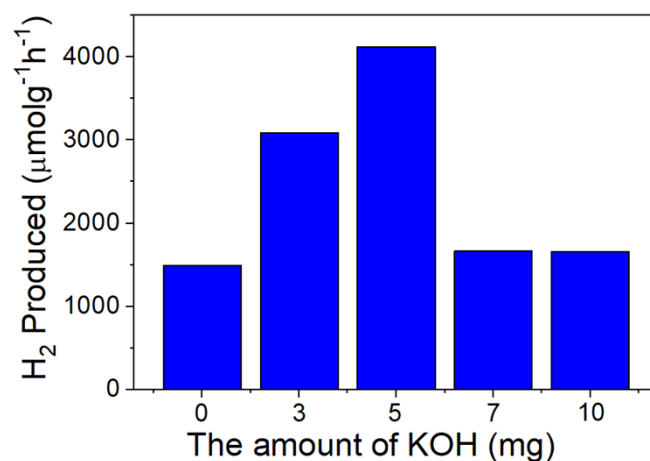


Figure S8. Photocatalytic H₂ generation histogram of a series of C/D-CN prepared with various amount of KOH (W_A).

The optimization process of the introduction amount of KOH (W_A):

A series of catalysts were obtained by thermal polymerization of various freeze-dried precursors mixture of 7.5 g urea, 3 mg sodium alginate and y mg ($y = 0, 3, 5, 7, 10$) KOH to investigate the influence of W_A on photocatalytic H₂ generation activity, and the results as shown in Fig. S12. Compared with no KOH introduction ($y= 0$), the introduction of KOH ($y = 3, 5, 7, 10$) can significantly improve the photocatalytic activity of the samples. When the W_A is 5 mg, C/D-CN shows the highest H₂ generation activity.

3. References

- 1 H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. N. Waterhouse, L.-Z. Wu, C.-H. Tung, T. Zhang, *Adv. Mater.*, 2017, **29**, 1605148.
- 2 F. F. Abdi and R. Krol, *J. Phys. Chem. C*, 2012, **116**, 9398-9404.