

Supporting Information

Alkyl group-decorated g-C₃N₄ toward enhanced gas-phase CO₂ photoreduction

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Experimental section

Chemicals

Melamine (MA), isopropanol (IPA), and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. Cyanuric acid (CA) was obtained from Shanghai Titan Scientific Co., Ltd. 1-decene was obtained from Sigma-Aldrich. All the chemicals were used as received without further purification. Deionized water (DIW) was used in all experiments.

Fabrication of photocatalysts

Fabrication of g-C₃N₄: Specifically, MA (2 g) and CA (2 g) were dispersed into DIW (80 mL), and stirred overnight to obtain the white suspension. Then, the white solids were obtained by centrifugation and freeze-drying. Under N₂ atmosphere, the white solids were calcinated at 550 °C for 4 h with a ramp rate of 2.3 °C min⁻¹. Finally, the light-yellow g-C₃N₄ was obtained, which was denoted as CN.

Regulating hydrophilicity of g-C₃N₄: Typically, 1-decene (3 mL) and IPA (4 mL) were mixed in a three-necked flask, followed by the addition of the as-synthesized CN sample (0.1 g) to obtain the mixture. Subsequently, N₂ was bubbled into the mixture for 30 min to remove O₂ in the flask. After irradiating the mixture with a 300 W Xe lamp (CEL-HXF300), the solids were separated, and washed 3 times with IPA and once with acetone. Lastly, the solids were dried overnight under vacuum, and the obtained samples were denoted as DCNT (T is referred to irradiation time; T = 30, 60, 90, and 120 min).

Characterizations

To study the crystal structures of photocatalysts, X-ray diffractometer (XRD, D8 ADVANCE, Bruker) with Cu K α irradiation source was conducted. Fourier transform infrared spectra (FTIR, Nicolet iS 50, Thermo Scientific) and X-ray photoelectron spectra (XPS, Escalab 250xi, Thermo Scientific) were used to analyze the chemical structures of the photocatalysts. Water contact angle (Theta Lite, Biolin Scientific, Finland) tests were carried out to characterize the hydrophilicity of samples. The morphology of photocatalysts was directly observed via field emission scanning electron microscopy (FESEM, JSM 7500F, Japan) and transmission electron microscopy (TEM, Titan G2 60-300, FEI). Atomic force microscopy (AFM, SPM-9700, Shimadzu) was implemented to measure the thickness of samples. The Brunner–Emmet–Teller specific surface area (S_{BET}), pore distribution, and CO₂ uptake of samples were measured using gas adsorption apparatus (ASAP3020, Micromeritics). To evaluate the light absorption of samples, UV–vis diffuse reflectance spectra (DRS) were tested by UV–vis spectrophotometer (UV-2600, Shimadzu). Electron paramagnetic resonance (EPR, MEX-nano, Bruker) spectra were obtained to analyze the electron density of photocatalysts. Time-resolved photoluminescence (TRPL, FLS-1000, Edinburgh) spectra and steady-state photoluminescence (PL, F-7000, Hitachi) were recorded to analyze the separation of photogenerated charge carriers.

Photoelectrochemical tests

Transient photocurrent, electrochemical impedance spectra (EIS), and Mott–Schottky (M–S) curves were recorded via electrochemical workstation (CHI660, CH Instruments, Shanghai) using a standard three-electrode system. The Pt electrode, Ag/AgCl electrode, and the prepared samples were taken as the counter electrode, reference electrode, and working electrodes, respectively. Na₂SO₄ solution (0.5 M, pH = 6.7) was used as the electrolyte. During the tests of photocurrent and EIS, the working electrodes were fabricated by coating the photocatalyst slurry onto the indium tin oxide (ITO) conductive glasses. In the process of M–S curves measurements, the working electrodes were obtained by dripping a drop of the photocatalyst slurry on a glassy carbon electrode. The relevant conversion formulas are as follows.

$$E_{\text{Ag/AgCl}} = E_{\text{RHE}} - 0.059\text{pH} - 0.197 \quad \text{S1}$$

$$E_{\text{NHE}} = E_{\text{RHE}} - 0.059\text{pH} \quad \text{S2}$$

Photocatalytic CO₂ reduction tests

Photocatalytic performance of samples was evaluated via CO₂ photoreduction. Before reaction, all the samples were degassed at 150 °C for 6 h to remove the adsorbed purities on the surface of samples. Typically, photocatalysts (50 mg) and DIW (10 mL) were added into a home-made reactor with two necks, which was sonicated for 5 min to obtain the uniform suspension. Then, the suspension was dried out at 80 °C to obtain a photocatalyst film deposited on the bottom of the reactor. Subsequently, high-purity CO₂ gas through DIW was blown into the reactor for 30 min to exclude the air in the reactive system, which was then sealed. Here, moist CO₂ gas (dry CO₂ + H₂O vapor) was used as the reactant. Lastly, the photocatalyst film was illuminated via a 300 W Xe lamp (CEL-HXF300) to initiate the photocatalytic reaction. Every 1 h, the produced gas (1 mL) was withdrawn, and injected into a gas chromatography (GC-2014C, Shimadzu) for the detection of products. During the cycling tests, the recycled photocatalyst was not washed, and directly used for the next cycling tests. Other reaction conditions keep consistent with that of the first photocatalytic test.

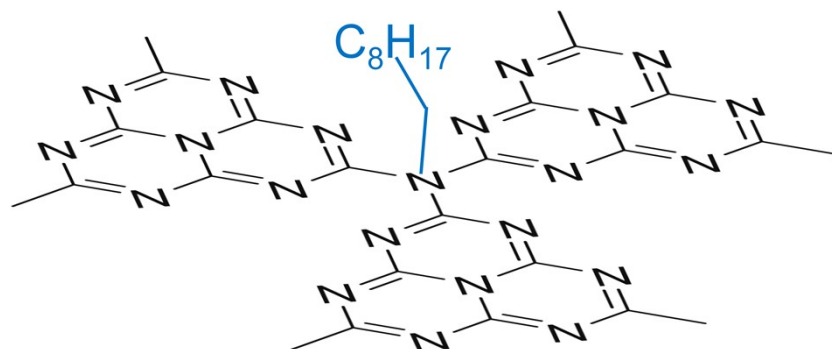


Fig. S1 Chemical structure of g-C₃N₄ after grafting alkyl groups. The tri-coordinated nitrogen atoms (N-C₃) in g-C₃N₄ can transform into the nitrogen atoms carrying positive charges (H-N⁺-C₃) by radical reactions under the irradiation. Subsequently, additional reaction occurs between H-N⁺-C₃ and olefinic bond in 1-decene, resulting in the successful grafting of alkyl groups onto g-C₃N₄.

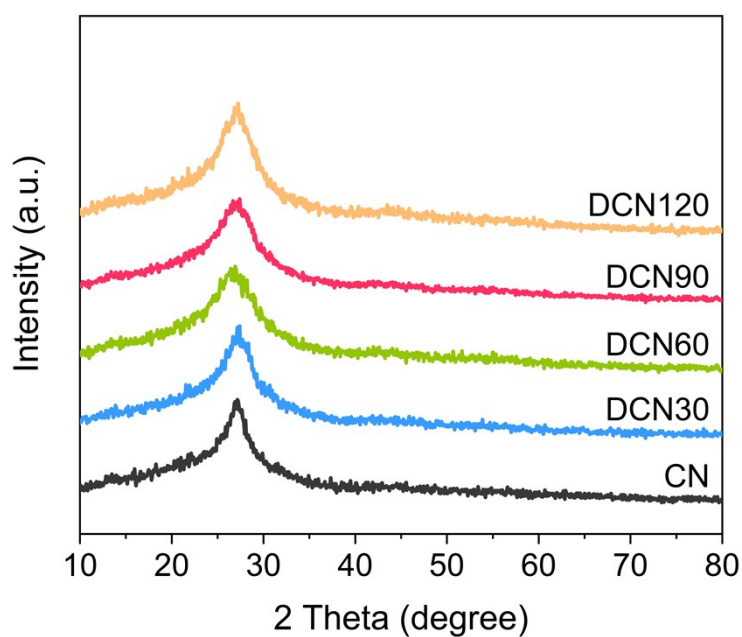


Fig. S2 XRD patterns of various samples.

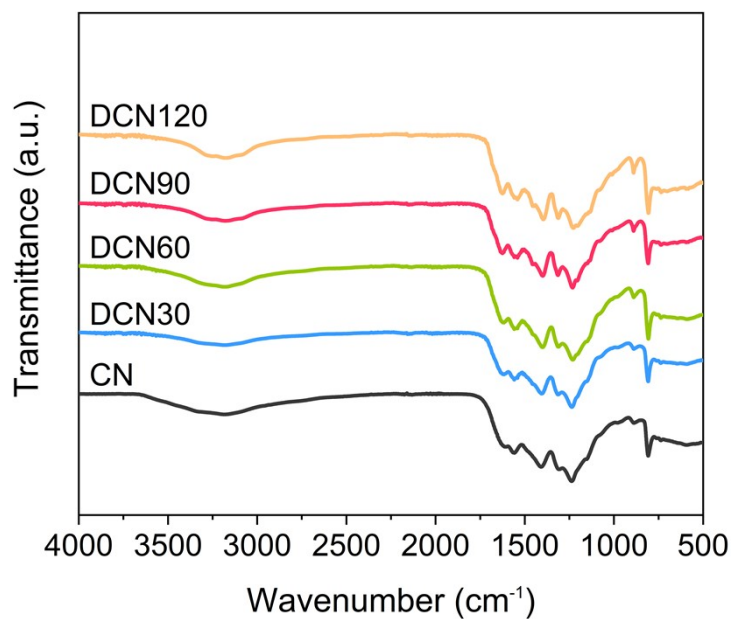


Fig. S3 FTIR spectra of various samples.

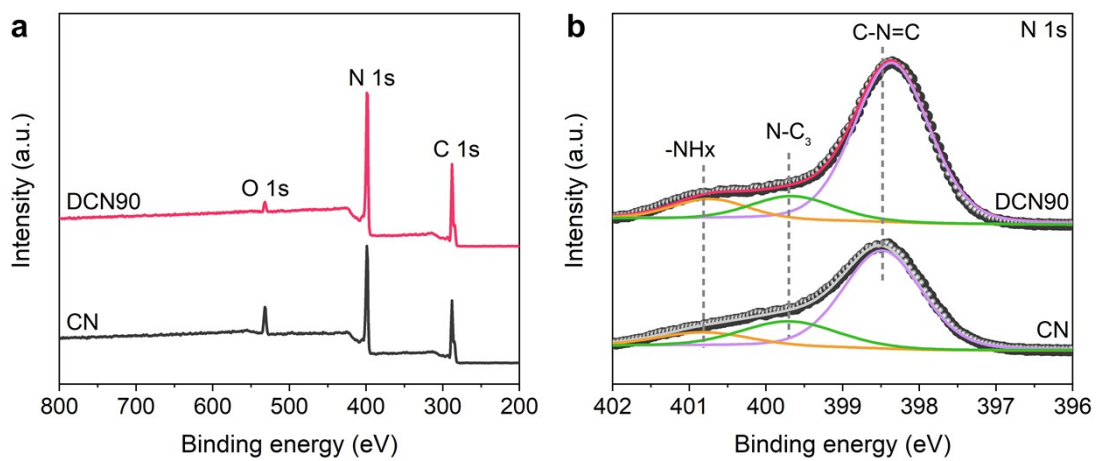


Fig. S4 (a) XPS survey spectra and (b) high-resolution XPS N 1s spectra of CN and DCN90.

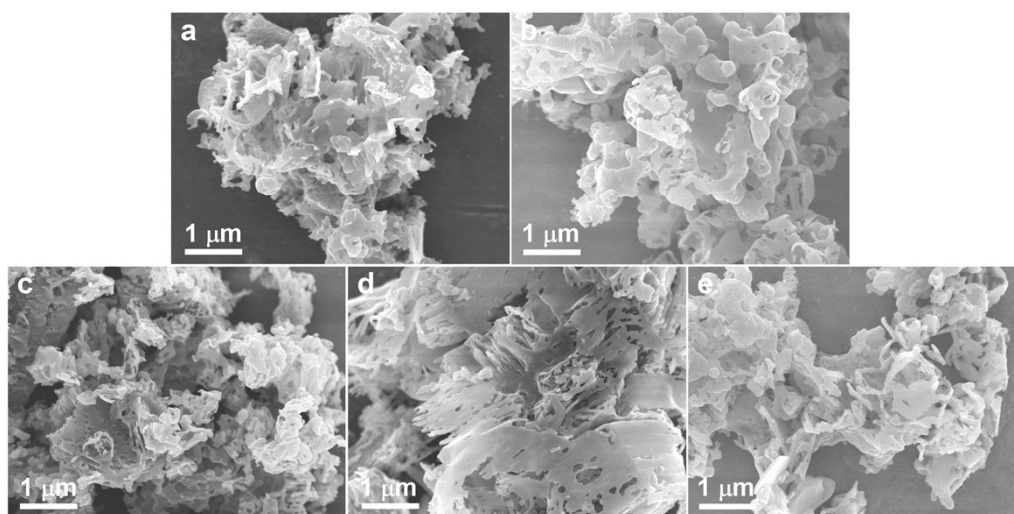


Fig. S5 FESEM images of (a) CN, (b) DCN30, (c) DCN60, (d) DCN90, and (e) DCN120.

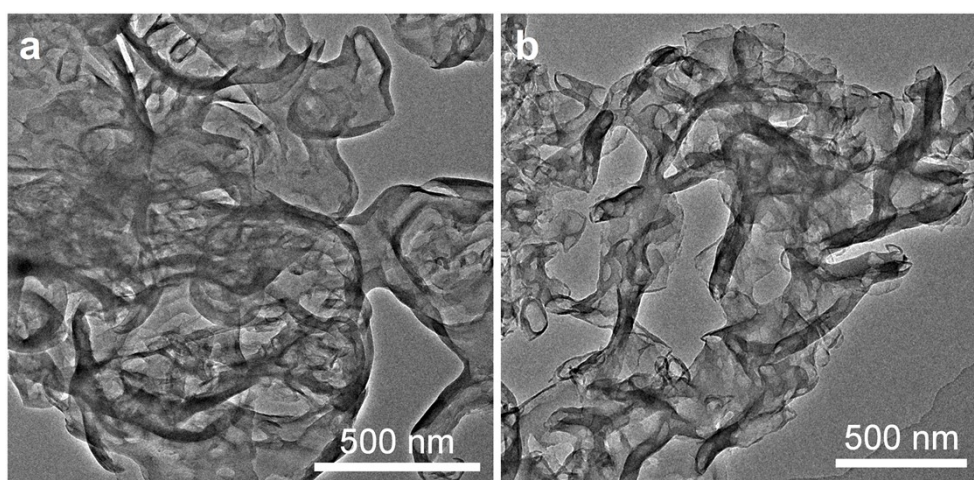


Fig. S6 TEM images of (a) CN and (b) DCN90. The TEM images show that CN and DCN90 display obvious nanosheet-like morphology, further confirming that the morphology of g-C₃N₄ is still retained after grafting alkyl groups.

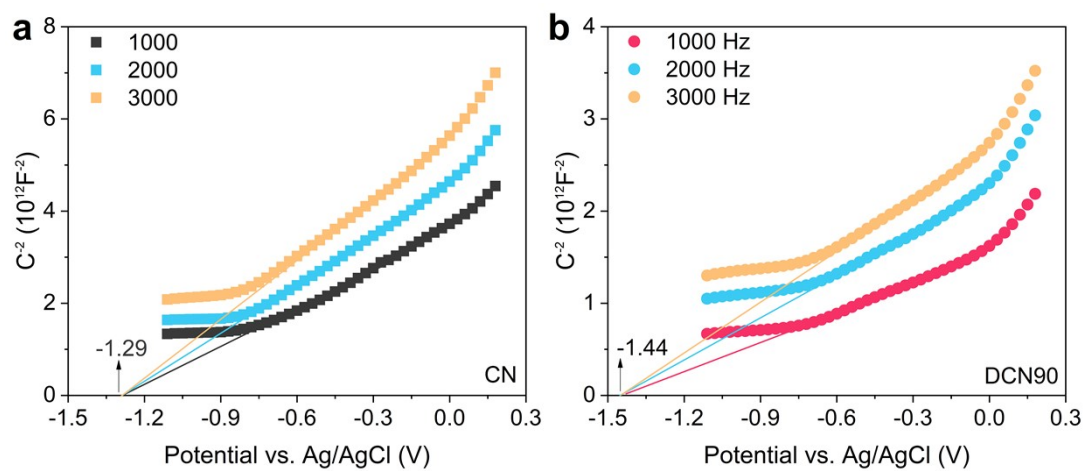


Fig. S7 M–S curves of (a) CN and (b) DCN90 tested in Na_2SO_4 solution (0.5 M, pH = 6.7) under different frequency.

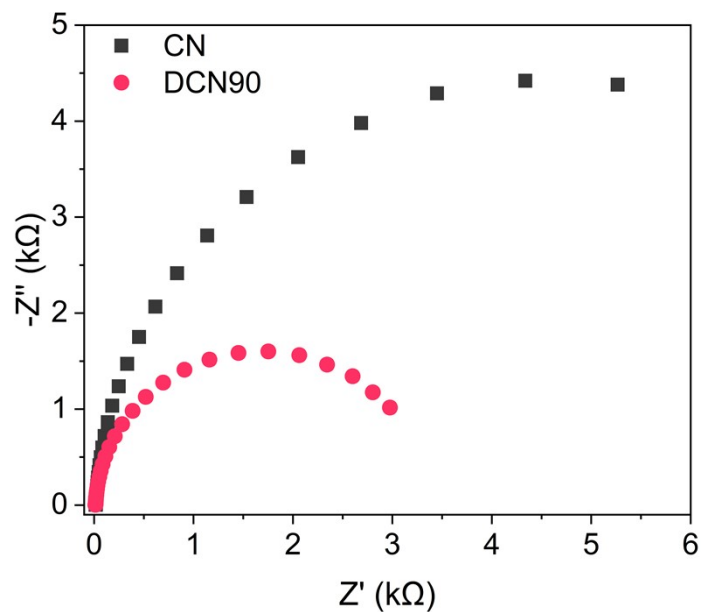


Fig. S8 EIS plots of CN and DCN90.

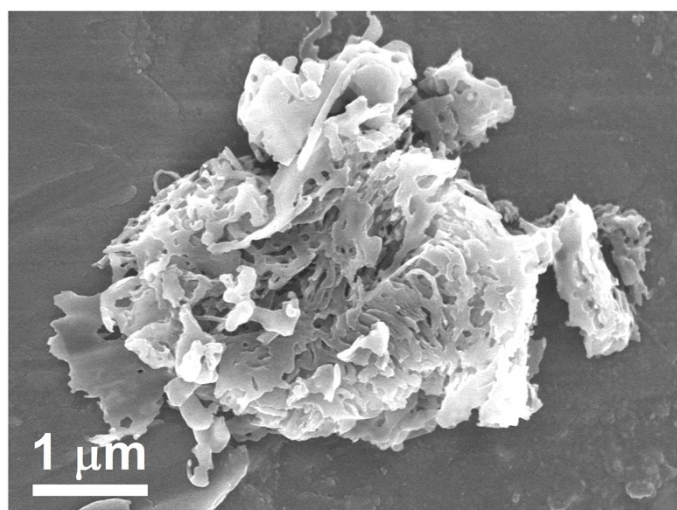


Fig. S9 FESEM image of DCN90 after three photocatalytic cycle tests.

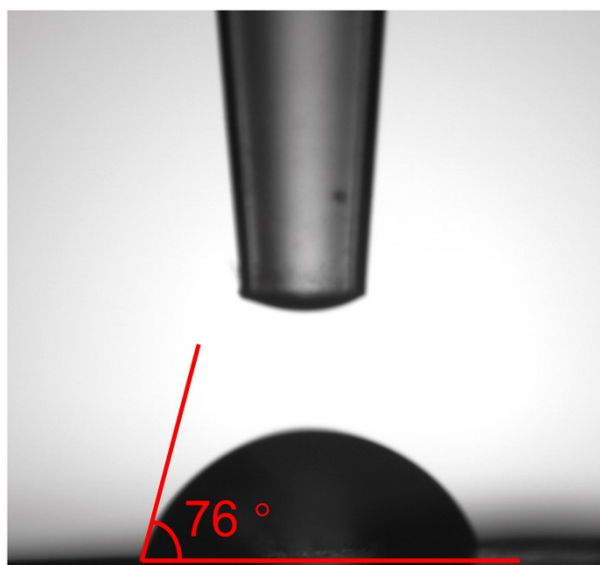


Fig. S10 Water contact angle of DCN90 after three photocatalytic cycling tests. Compared with fresh DCN90, the recycled DCN90 shows no obvious change of the water contact angle, confirming the good stability of DCN90.

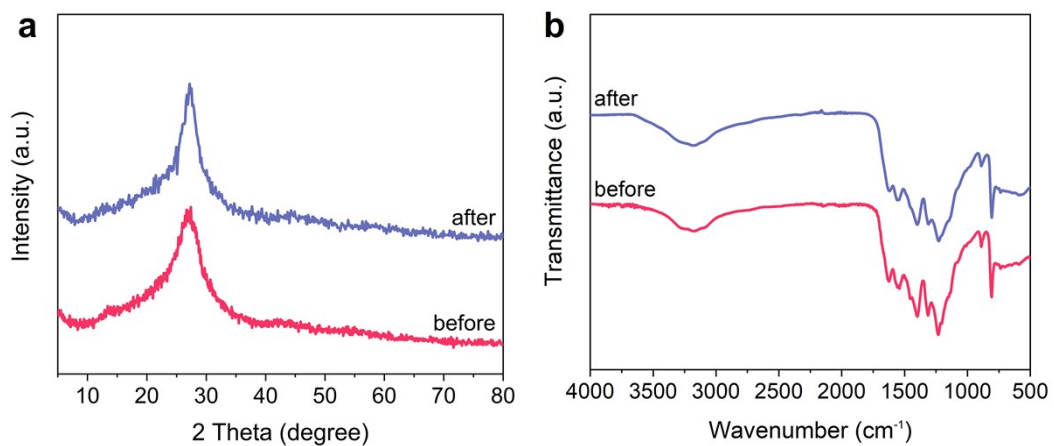


Fig. S11 (a) XRD patterns and (b) FTIR spectra of DCN90 before and after three photocatalytic cycling tests. No obvious change of XRD patterns and FTIR spectra after reactions indicates that the chemical structure of DCN90 is retained, confirming that DCN90 possesses an excellent stability.