Supplementary Data

Insight into the surface properties modification enhanced C$_3$N$_4$ performance of photocatalytic nitrogen fixation

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Preparation of g-C$_3$N$_4$

Synthesis of bulk g-C$_3$N$_4$: g-C$_3$N$_4$ was prepared by melamine pyrolysis according to a previous method. Briefly, 3 g of melamine was calcined at 550 °C in a muffle furnace for 4 h using a heating rate of 2°C/min.

Preparation of x.g-C$_3$N$_4$

Synthesis of x.g-C$_3$N$_4$: 5 g of melamine and 0.15 g of succinic acid/adipic acid/decanedioic acid were added into 40 ml of absolute ethanol. The mixture was transferred into a ball mill tank, then fixed on a planetary ball mill (zirconia balls, 300 r/min for 24 hours). After the ball milling, the emulsion was transferred to a beaker and placed in an oven at 60°C to dry for 24 hours to obtain a melamine-succinic acid/adipic acid/sebacic acid supramolecular pre-assembled precursor. Grind the block precursor into a powder in a mortar, transfer it into a porcelain boat that is heated in a muffle furnace at 550 °C for 4 hours (5 °C/min), and then naturally cooled to room temperature after the end. Take out the product and grind it into a powder in a mortar. The collected product is the nitrogen-rich defect x.g-C$_3$N$_4$.

Characterization

The XRD patterns were obtained by an X-ray diffractometer (XRD, Purkinje XD-3, Cu Kα radiation, λ=0.15418 nm). The transmission electron microscopy (TEM) was performed on a Tecnai G2 F30 S-TWIN instrument with an acceleration voltage of 300 kV. Fourier transform infrared (FT-IR) spectroscopy was recorded on a Nicolet-iS10 spectrometer (32 scans). The composition and surface state of the samples were verified by X-ray photoelectron spectroscopy (XPS, PHI QUANTERA II, Al Kα X-ray radiation). The binding energy 284.8 eV was used as the carbon (C–C) correction value. UV–vis diffuse reflectance spectroscopy (DRS) spectra were recorded on a Shimadzu UV-2600 spectrophotometer. N$_2$-temperature programmed desorption (N$_2$-TPD) measurements were performed on a ChemiSorb 2040 instrument. Transient photocurrents and Mott–Schottky plots were measured on an electrochemical

workstation (CHI 760E, three-electrode system in 0.5 M Na_2SO_4 aqueous solution as an electrolyte). The working electrode was fabricated using a drop-casting method. 5 mg of the photocatalysts were dispersed in 1 mL ethanol containing 40 μL Nafion solution (5%) by sonication for 30 min. Then, the dispersive suspension was drop-cast onto a pretreated fluorine-doped tin oxide (FTO) glass substrate, and dried at 60 ℃ in air for 2 h to improve the adhesion.

Photocatalytic nitrogen fixation

The photocatalytic N_2 fixation was conducted in a 100 mL jacketed reactor with an external circulating water system. The water maintained 35℃ (or other specific) which is the reaction temperature. Briefly, 50 mg of the catalyst was dispersed in 50 mL methanol aqueous solution (20 vol%), and purity nitrogen gas was bubbled into the reaction solution with a flow rate of 30 mL min^{-1}. A 300 W Xe lamp (PLS-SXE300/300UV, working current 15A, output light wavelength 200-2500nm) was turned on as a light source after stirring for 30 min in the dark. At given irradiation time intervals, 2 mL of the reaction solution was taken out and liquid sample was separated by centrifugation at 4200 rpm for 10 min. The concentration of ammonia was determined by Nessler's reagent method (JB7478-87) with a UV–vis spectrophotometer (T6 New Century, Beijing). The ammonia concentration was calculated by ammonia nitrogen standard curve. To verify the NH_3 was produced from N_2, the N_2 was replaced by Ar to experiment in comparison. Before starting the reaction, Ar was introduced for 1h to drive off nitrogen in the water, and then an Ar atmosphere is maintained above the solution. Apart from this, other reaction conditions are the same as the above-mentioned photocatalytic nitrogen fixation reaction.
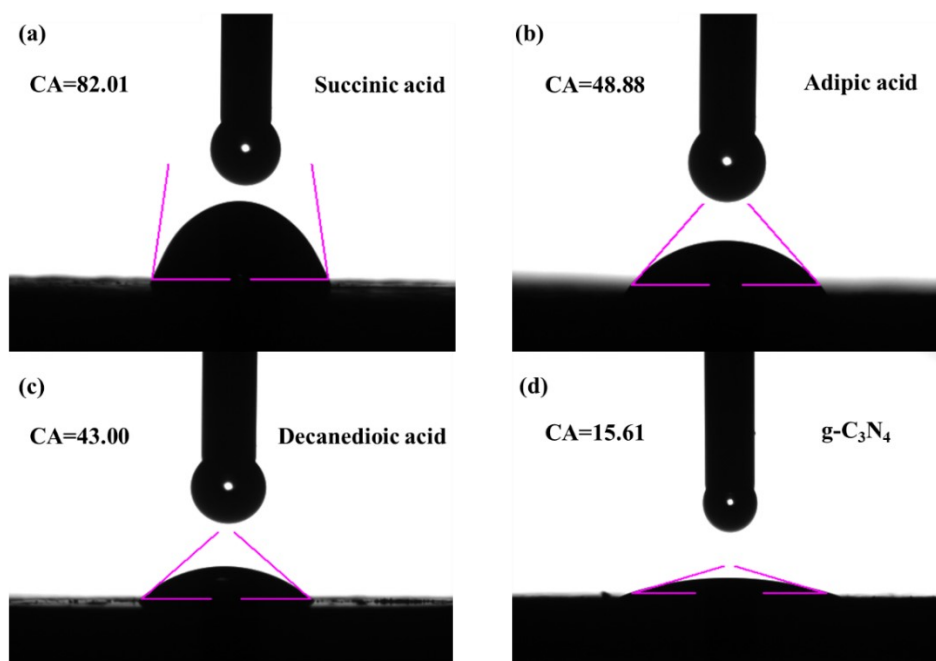
Supplementary Figures
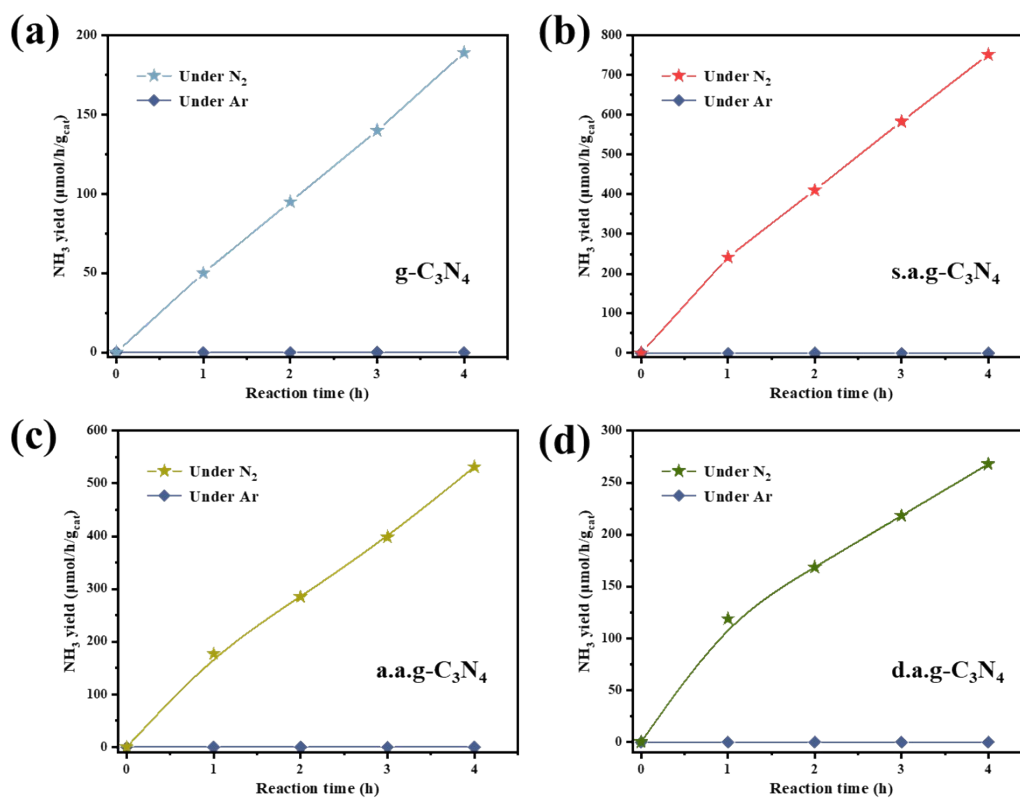

Fig. S1. Contract angle of the materials.

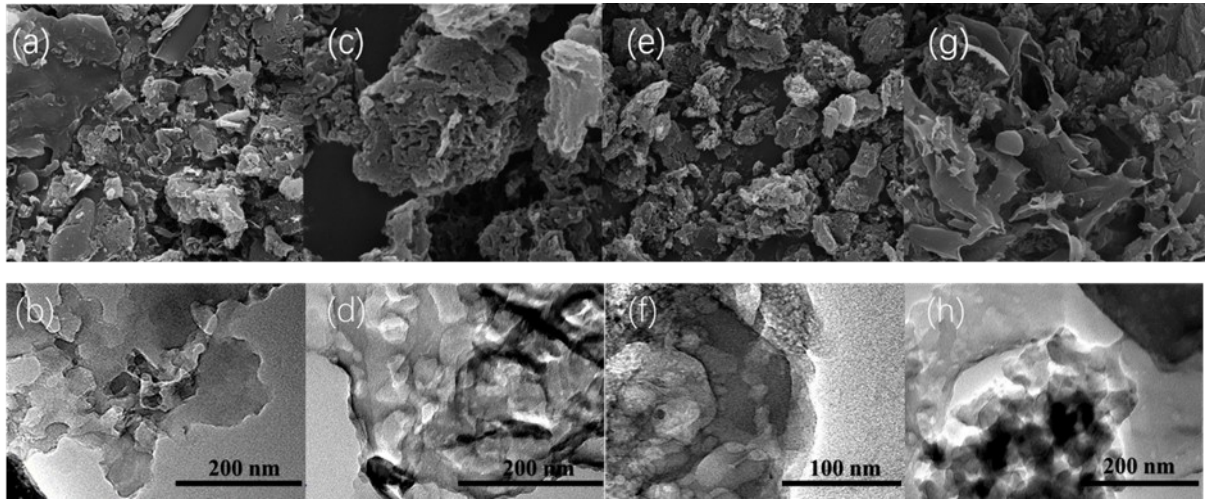**Fig. S2.** The NH$_3$ yields of g-C$_3$N$_4$ and x.g-C$_3$N$_4$ under N$_2$ and Ar in comparison.

Fig. S3. SEM **(a, c, e, g)** and TEM **(b, d, f, h)** image of g-C$_3$N$_4$, s.a.g-C$_3$N$_4$, a.a.g-C$_3$N$_4$ and d.a.g-C$_3$N$_4$.
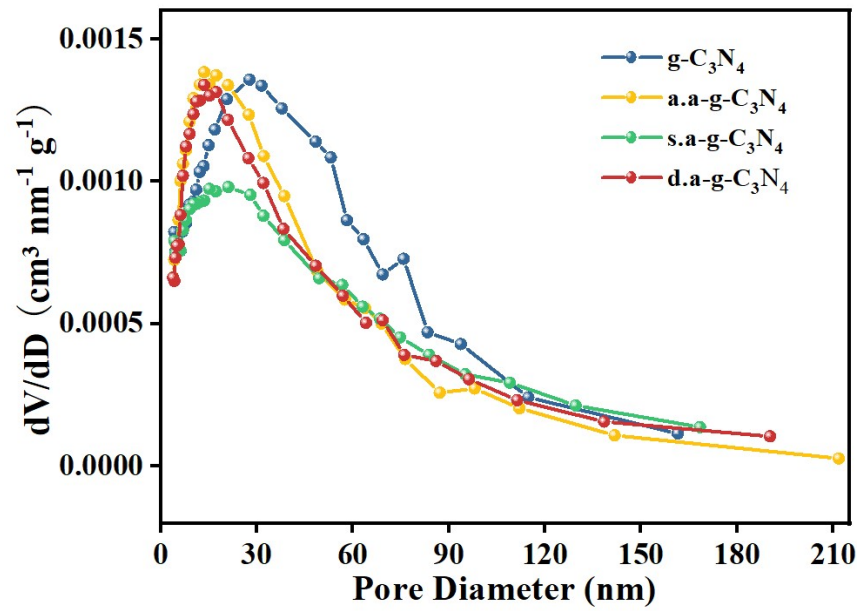
Fig. S4. pore size distribution of g-C$_3$N$_4$, s.a.g-C$_3$N$_4$, a.a.g-C$_3$N$_4$ and d.a.g-C$_3$N$_4$.
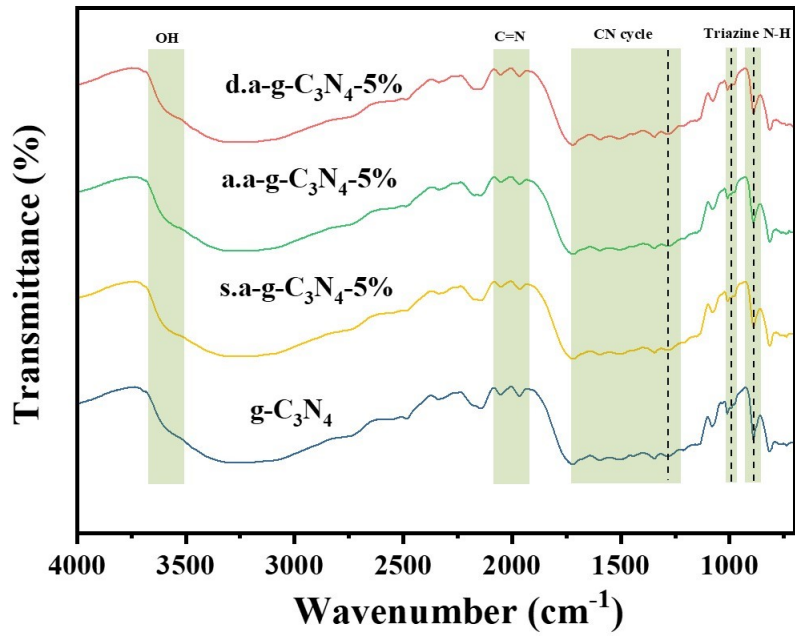
Fig. S5. FT-IR of g-C_3N_4, s.a.g-C_3N_4, a.a.g-C_3N_4 and d.a.g-C_3N_4.
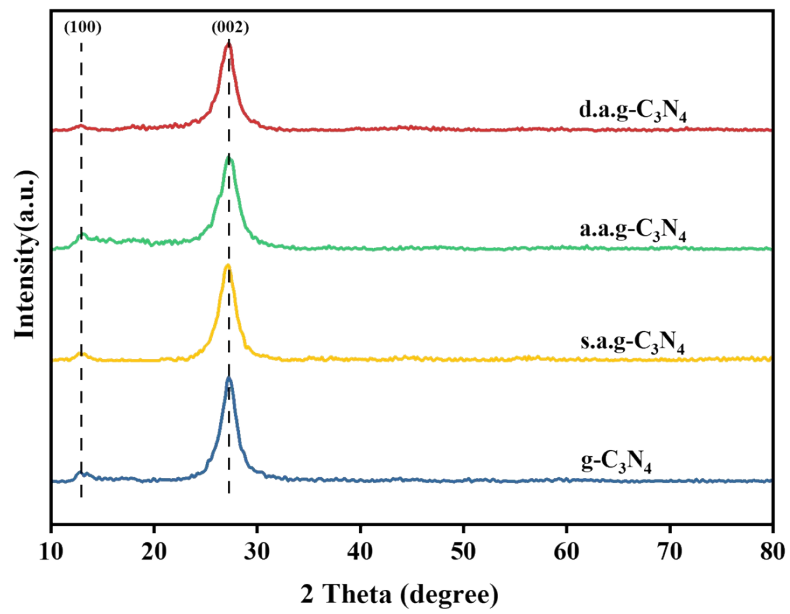
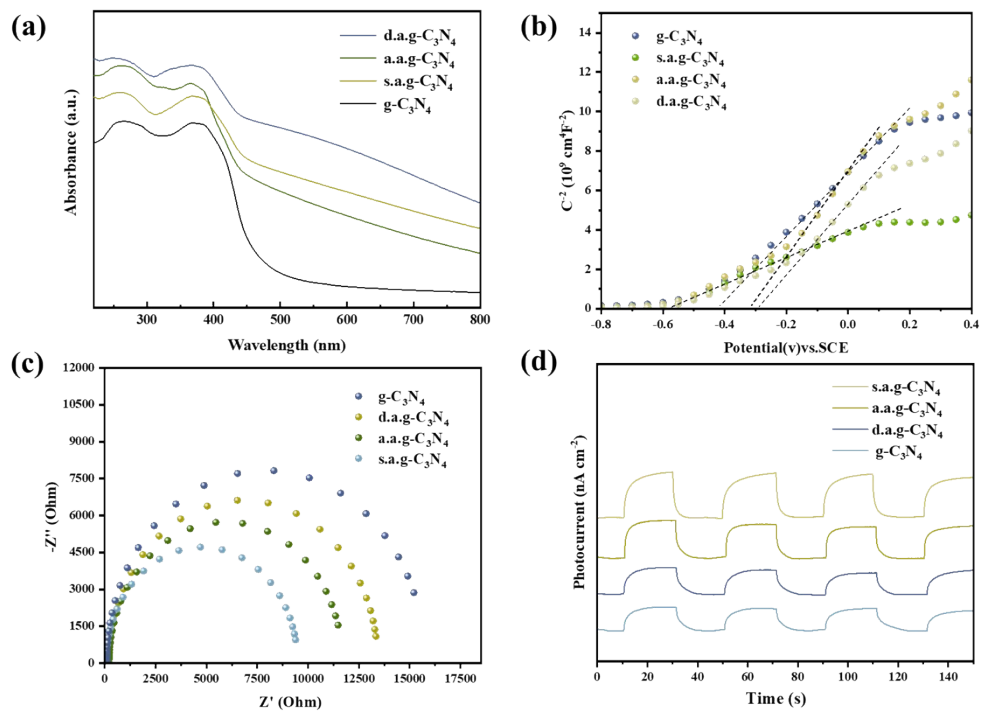**Fig. S6.** XRD of g-C_3N_4, s.a.g-C_3N_4, a.a.g-C_3N_4 and d.a.g-C_3N_4.

Fig. S7. (a) UV-vis DRS spectra, (b) Mott–Schottky plots, (c) electrochemical impedance spectra,

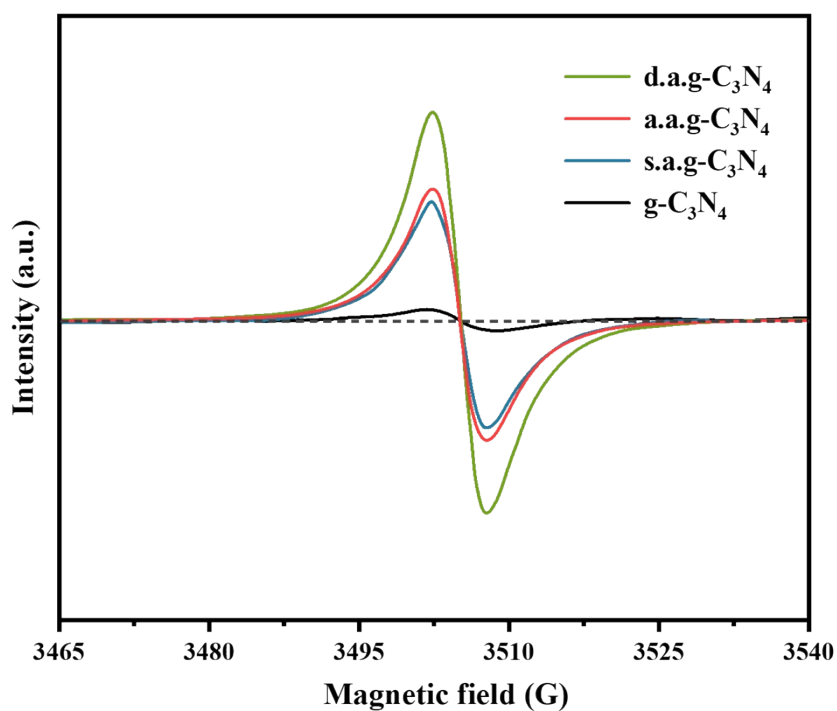(d) the transient photocurrent response of x.g-C_3N_4 and g-C_3N_4.

Fig. S8. EPR of g-C_3N_4, s.a.g-C_3N_4, a.a.g-C_3N_4 and d.a.g-C_3N_4.
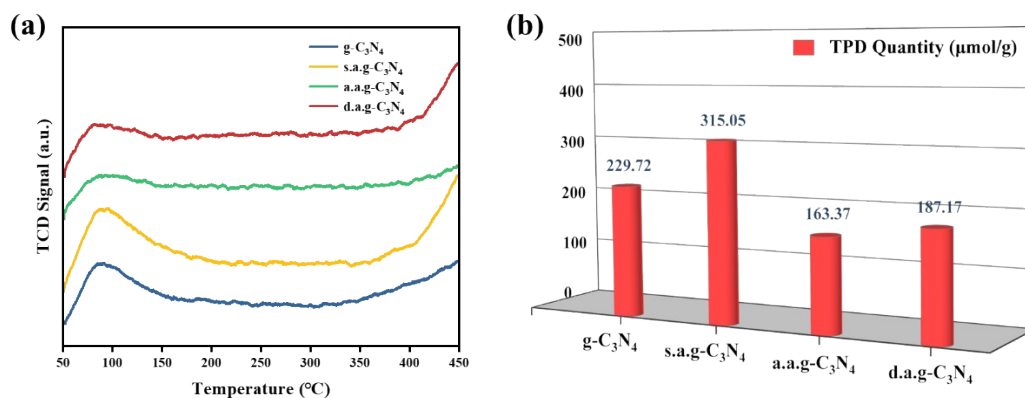
Fig. S9. TPD of g-C$_3$N$_4$, s.a.g-C$_3$N$_4$, a.a.g-C$_3$N$_4$ and d.a.g-C$_3$N$_4$ (The adsorption capacity was integrated between 50°C and 150°C).

NOTE: After completing the TPD test, we provide the analyzer with a series of known gas concentrations and it records a signal associated with each known concentration. The analyzer correlates the signal readings collected during the analysis with the amount of gas absorbed at any given point in the analysis, and then uses this information to calculate the concentration associated with the signal it recorded during the analysis. Finally, the peak area data generated by the test are converted to volume data.

Supplementary Table

Tab.S1. surface area and pore volume of the catalyst calculated by the BET mode.

	Surface area (m²/g)	Pore volume (cm³/g STP)
g-C$_3$N$_4$	19.8519	4.5609
s.a.g-C$_3$N$_4$	17.0793	3.9240
a.a.g-C$_3$N$_4$	18.5882	4.2706
d.a.g-C$_3$N$_4$	18.7658	4.3114