Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Atomically dispersed s-Block metal Ca sites modified mesoporous g-C_3N_4 for boosting photocatalytic N_2 reduction

Guoliang Pan,‡[a] Wensheng Zhang,‡[b] Tianren Liu,[a] Qingmei Tan,[a] Binzhe Wei,[a] Kaihang Ye,[a] Yingxin Yang[a], Dongxue Han[a, c] Zhenbang Liu[d]* and Li Niu[a]*

[a] School of Chemistry and Chemical Engineering Guangzhou Key Laboratory of Sensing Materials & Devices, Center for Advanced Analyti-cal Science, Guangzhou University, Guangzhou 510006, P. R. China

[b] School of Civil Engineering c/o Center for Advanced Analytical Science, Guangzhou University, Guangzhou 510006, P. R. China

[c] Guangdong Provincial Key Laboratory of Psychoactive Substances Monitoring and Safety，Anti-Drug Tethnology Center of Guangdong Province, Guangzhou 510230, P. R. China

[d] School of Computer Science and Cyber Engineering, Guangzhou University, Guangzhou 510006, P. R. China

**E-mail: dxhan@gzhu.edu.cn, cczbliu@gzhu.edu.cn*

‡These authors contributed equally to this work.

1. Experimental sections

1.1 Photocatalytic N_2 fixation measurement

The photocatalytic N_2-fixation NH_3 synthetic assay was finished in the self-assembled photocatalysis reaction platform. The photocatalytic N_2 fixation is achieved on the three-phase interface, including N_2 in the gas, H_2O in the liquid, and the catalyzer in the solid phase. Synthesis NH_3 property assays were completed under room temperature and atmosphere pressure. A 300 W Xe lamp (full-spectrum, 400 $mW \cdot cm^{-2}$) was utilized as the illuminant and 10 cm away from the illuminant to the fluid level. Firstly, 20 mg photocatalyst were dispersed in 50 mL deionized water in a cell equipped with water circulation. Secondly, the dispersion solution was continuously stirred in the dark with N_2 bubbled for 30 min, then turn on the light and 4.0 mL of solution was taken out in every 1.0 h. The reaction was purified by removing the photocatalyst by using the 0.22 μm filter. The obtained solution was used for further analysis through indophenol blue method.

1.2 Electrochemical Tests

The electrochemical test was completed via a CHI760-1 electro-chemistry workstation (Shanghai Chenhua, China) with a three-electrode cell. The glass-carbon electrode loaded catalyzer was the work electrode, and the saturated Ag/AgCl electrode and platinum foil were the reference electrode and anti-electrode, separately. The transient photocurrent response curves were harvested during the illumination (on/off) every 40 s at an applied potential of 0 V (vs Ag/AgCl) in 0.1 M Na_2SO_4 solution from the back side of the work electrode. The Nyquist plots were measured on electrochemical workstation (CHI 760E, Chenhua Instrument, China). The working electrode is our sample coated on the FTO with a coating area of 1 cm^2, the counter electrode was platinum wire, and the reference electrode was Ag/AgCl (3M KCl). Na_2SO_4 solution (0.1 M, pH = 7) was used as electrolyte. The Mott–Schottky experiment was in progress in 0.1 M Na_2SO_4 solution with the potential window ranged from 0 to +1.0 eV, using 800, 1000, 2000Hz and an AC amplitude of 10 mV at each of the potentials.

1.3 $^{15}N_2$ isotope labeling experiments

Isotopic labeling experiments labeled $^{15}N_2$ gas was purchased from Sigma-Aldrich Chemical Company. It was used to confirm that the detected ammonia originates form N_2. A low-velocity gas flow system was adopted due to the limited supply and high expense of $^{15}N_2$. Firstly, 20 mg photocatalyst were dispersed in 50 mL deionized water in a cell equipped with water circulation. Secondly, the mixture was continuously stirred in the dark with high-purity N_2 bubbled at a flow rate of 100 mL·min^{-1} for 10 min, then turn on the light and 4.0 mL of reaction solution was taken out after 30 min illumination and further removing the photocatalyst by using the 0.22 μm filter. Estimation of obtained $^{15}NH_4^+$ was done indirectly using the indophenol method, owing to the low mass of $^{15}NH_4^+$ for LC-MS studies. The samples for LC-MS analysis were prepared as follows. 0.5 mL phenol nitroprusside solution (P6994, Sigma-Aldrich) and 0.5 mL of alkaline hypochlorite solution (A1727, Sigma-Aldrich) were then added to 2.0 mL of the resulting solution. The MS studies were carried on an Agilent 1260-6460 (LC-MS).

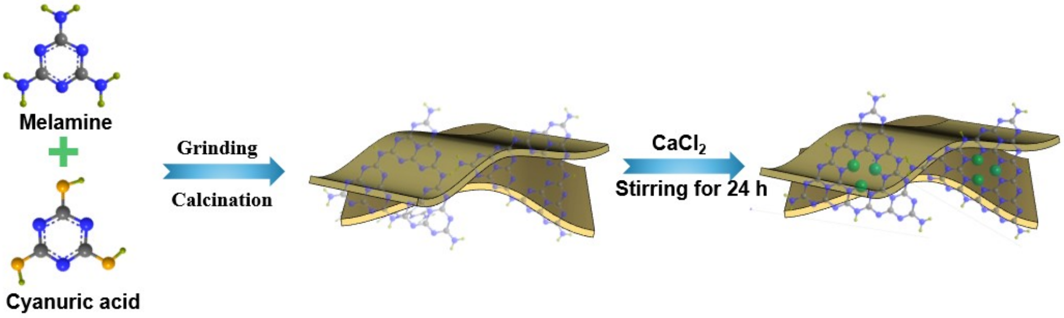
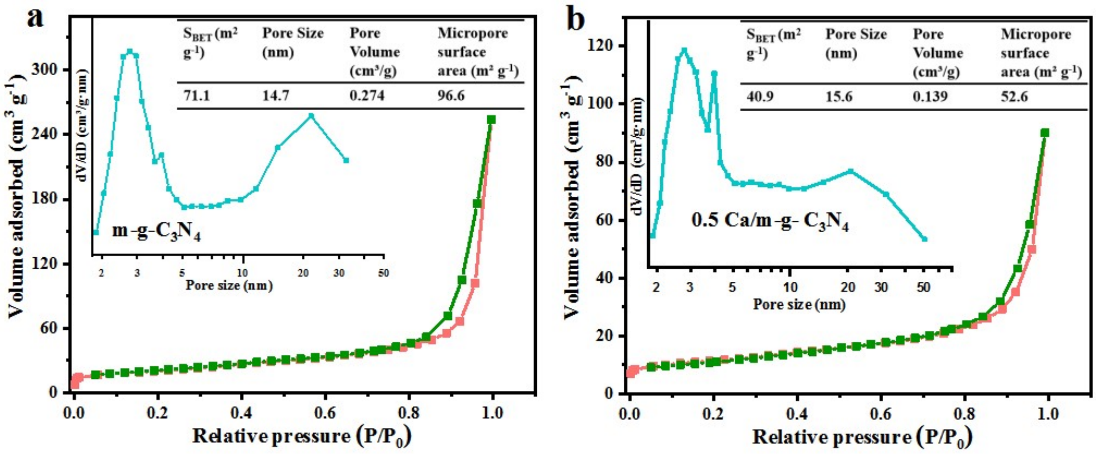


Fig. S1 Schematic illustration for the preparation of Ca/m-g-C_3N_4.



S_{BET} (m^2 g^{-1})	Pore Size (nm)	Pore Volume (cm^3/g)	Micropore surface area (m^2 g^{-1})
71.1	14.7	0.274	96.6

S_{BET} (m^2 g^{-1})	Pore Size (nm)	Pore Volume (cm^3/g)	Micropore surface area (m^2 g^{-1})
40.9	15.6	0.139	52.6

Fig. S2 N_2 adsorption-desorption isotherms curve and the corresponding pore size distribution curves (insert) of m-g-C_3N_4 (a) and 0.5 Ca/m-g-C_3N_4 (b).

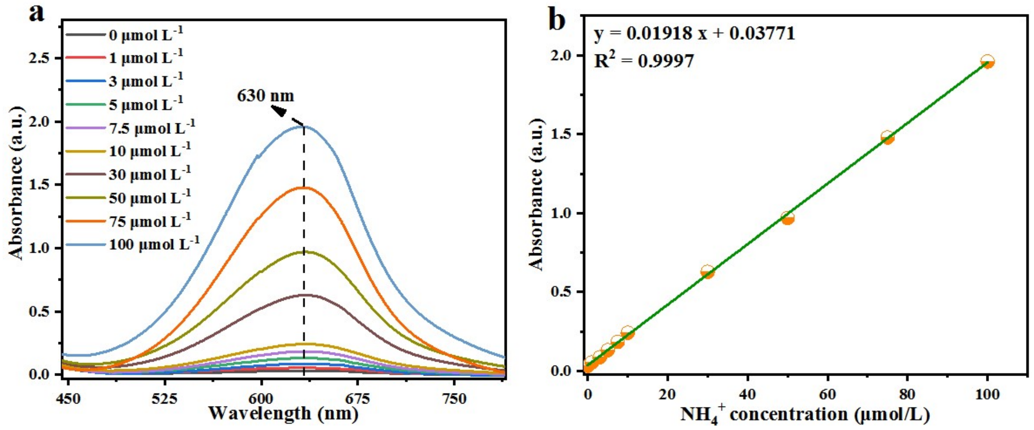


Fig. S3 Absolute calibration of the indophenol blue method using NH_4Cl solutions of known concentration as standards. (**a**) UV-vis curves of indophenol assays with NH_4^+ after incubated for 0.5 h at room temperature. (**b**) Calibration curve used for estimation of NH_3 by NH_4^+ concentration. The absorbance at 630 nm was measured by UV-vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH_4^+ concentration ($y = 0.01918$ x + 0.03771, $R^2 = 0.9997$) of calibration curves.

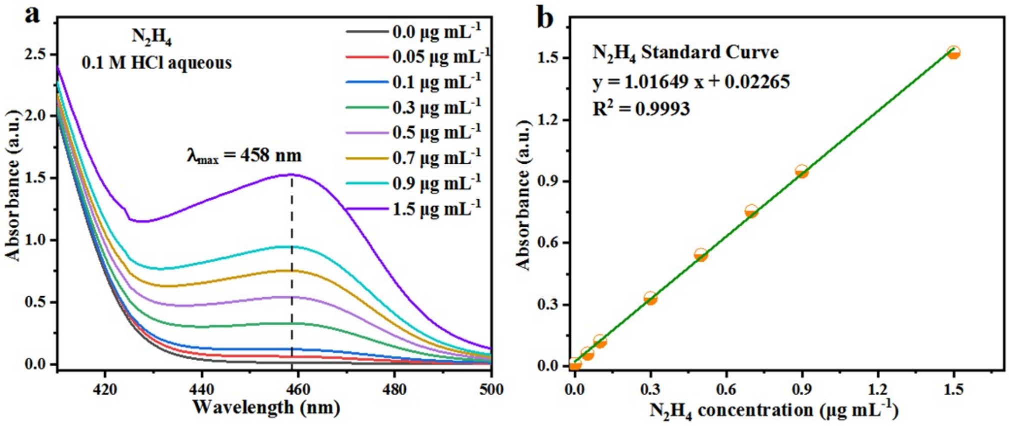


Fig. S4 (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 20 min at room temperature. (b) Calibration curve used for estimation of N_2H_4 concentration. The absorbance at 458 nm was measured by UV-vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N_2H_4 concentration (y = 1.01649 x + 0.02265, R^2 = 0.9993) of calibration curves.

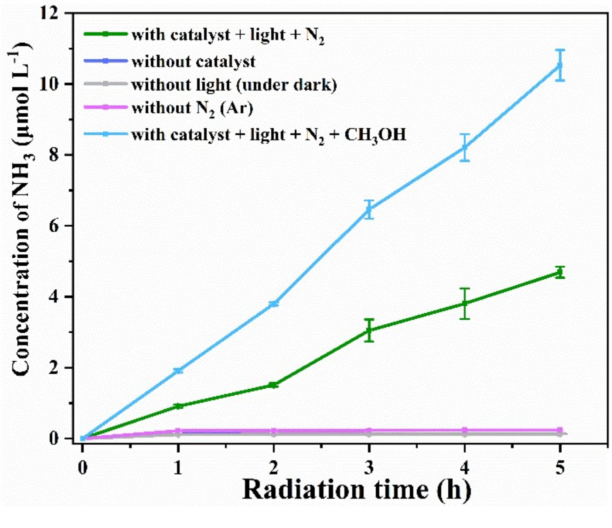


Fig. S5 NH_3 synthesis rates of 0.5 Ca/m-g-C_3N_4 measured by the indophenol method under different conditions.

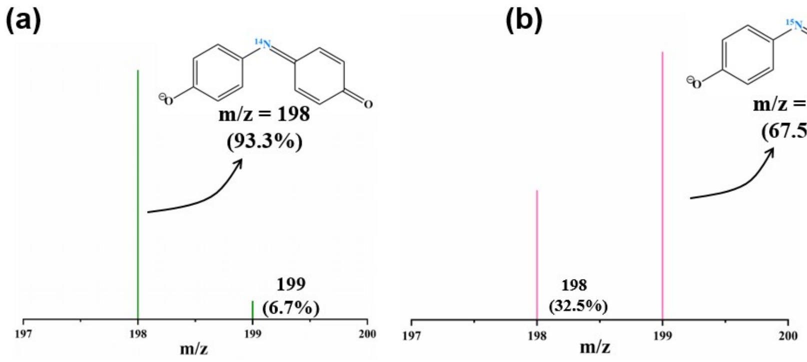


Fig. S6 Mass spectral illustrations of the indophenol from diverse atmospheric conditions. (a) The mass spectral illustrations of the indophenol prepared from $^{14}N_2$ atmospheric conditions. (b) The mass spectra of the indophenol prepared from $^{15}N_2$ atmospheric conditions.

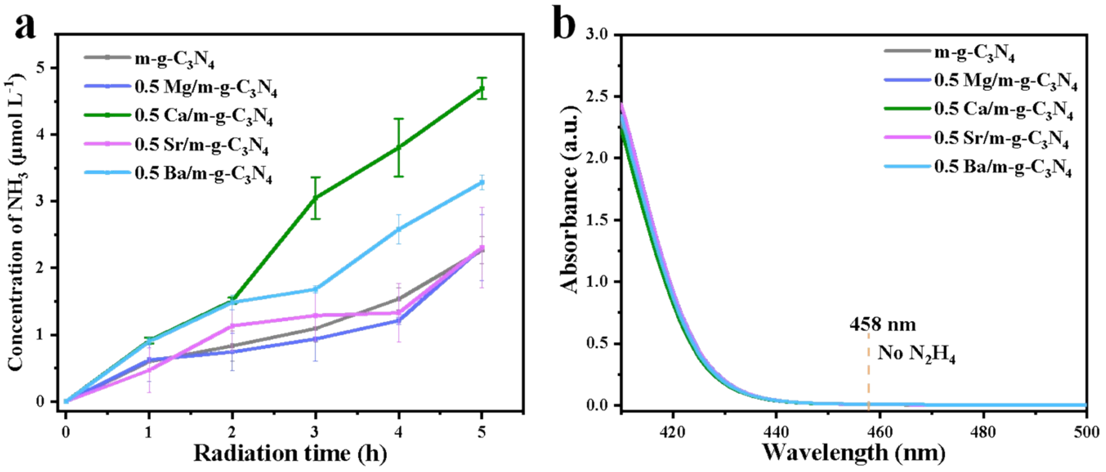


Fig. S7 (a) Quantitation measurement of the produced NH_3 by full spectra illumination with an indophenol indicator over different systems in N_2. (b) UV-vis absorption spectra of reaction solution by different catalysts. No N_2H_4 was detected at 458 nm.

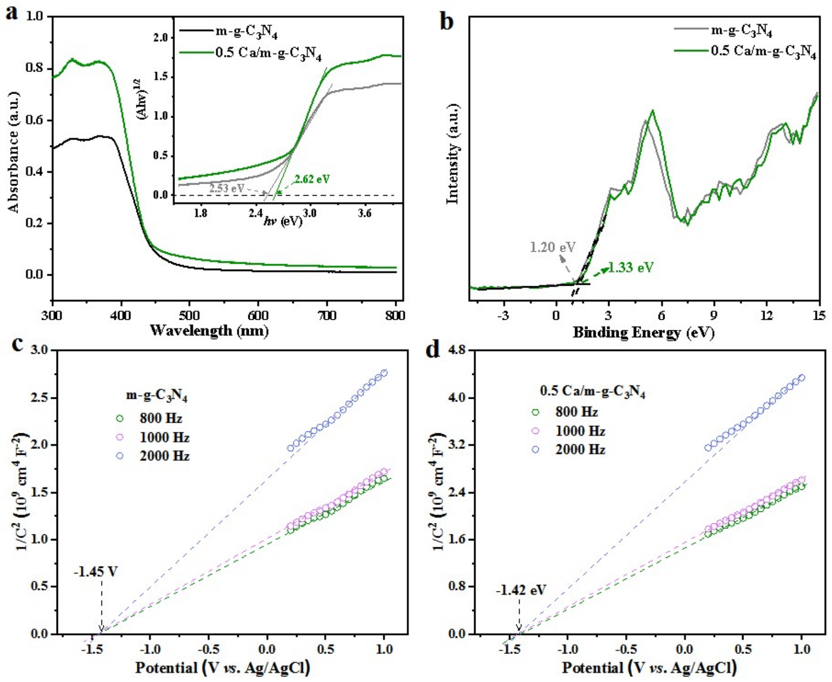


Fig. S8 (a) UV-vis diffuse reflectance spectra of m-g-C_3N_4 and 0.5 Ca/m-g-C_3N_4 samples (insert the corresponding Tauc plots diagram) and (b) XPS valence band spectra of m-g-C_3N_4 and 0.5 Ca/m-g-C_3N_4. The Mott-Schottky plots of m-g-C_3N_4 (c) and 0.5 Ca/m-g-C_3N_4 (d).

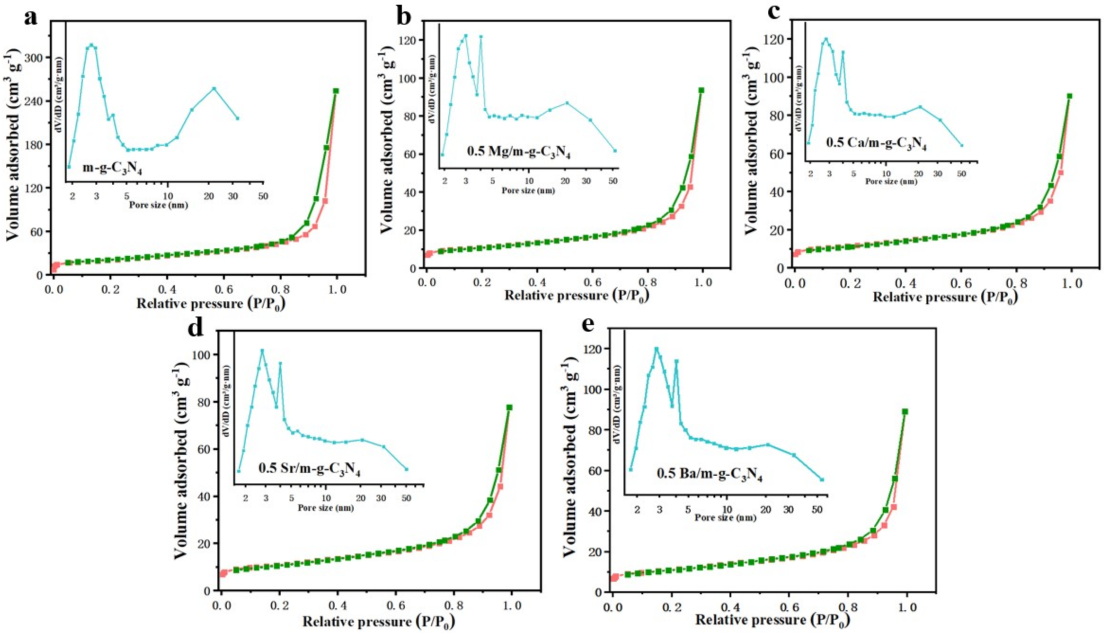


Fig. S9 N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (insert) of (a) m-g-C_3N_4, (b) 0.5 Mg/m-g-C_3N_4, (c) 0.5 Ca/m-g-

C_3N_4, (d) 0.5 Sr/m-g-C_3N_4, and (e) 0.5 Ba/m-g-C_3N_4. (New supplemented data)

Table S1 BET surface area, average pore size, pore volume and micropore surface area of the different samples. (New supplemented data)

Samples	S_{BET} (m^2 g^{-1})	Pore Size (nm)	Pore Volume (cm^3 g^{-1})	Micropore surface area (m^2 g^{-1})
m-g-C_3N_4	71.1	14.7	0.274	96.6
0.5 Mg/m-g-C_3N_4	39.1	17.5	0.144	49.6
0.5 Ca/m-g-C_3N_4	40.9	15.6	0.139	52.6
0.5 Sr/m-g-C_3N_4	38.6	14.0	0.120	49.90
0.5 Ba/m-g-C_3N_4	38.7	15.2	0.139	50.71

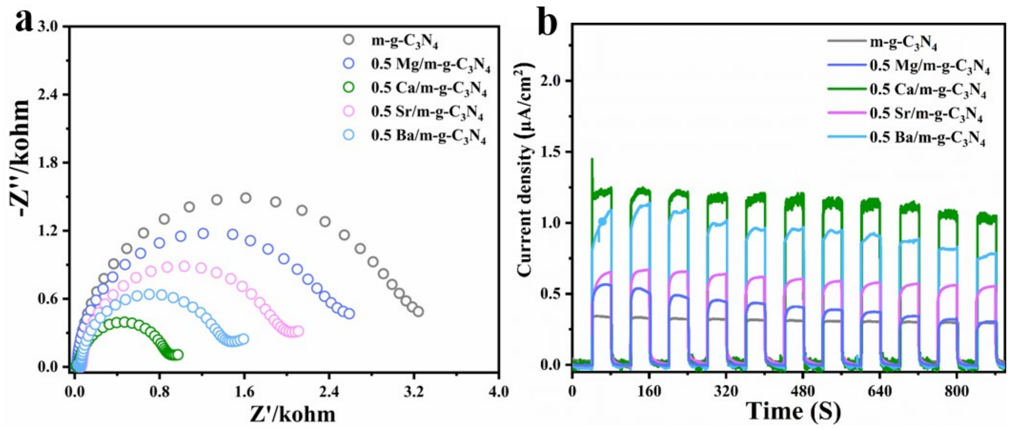


Fig. S10 (a) Electrochemical impedance spectroscopy response for m-g-C_3N_4, 0.5 Mg/mg-C_3N_4, 0.5 Ca/mg-C_3N_4, 0.5 Sr/mg-C_3N_4 and 0.5 Ba/mg-C_3N_4 samples in 0.1 M Na_2SO_4 aqueous solution. (b) The transient photocurrent spectra of the as-prepared samples. (New supplemented data)