Alkaline Salt-Promoted Construction of Hydrophilic and Nitrogen Deficient Graphitic Carbon Nitride with Highly Improved Photocatalytic Efficiency

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Experimental Procedures

1. Materials

Urea, lithium bis(trimethylsilyl)amide, triethanolamine, ethanol, tetrahydrofuran, and chloroplatinic acid were purchased from commercial sources (Fisher Scientific and Sigma-Aldrich) and were used without further purification unless indicated otherwise.

2. Characterization

The powder X-ray diffraction (PXRD) data were recorded with a PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA (scanning step: 0.02° per step). The diffraction patterns were recorded in the range of 10–80°. $\lambda = 0.1540598$ nm. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm⁻¹ in the spectral range from 4000 to 500 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements: XPS experiments were performed with a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV. Samples were mounted on foil since the C1s binding energy was used to calibrate the binding energy shifts of the sample (C1s = 284.8 eV). The nitrogen adsorption isotherms were measured at 77 K under a Gemini 2360 surface area analyzer. The samples were outgassed at 150 °C for 16 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. SEM imaging was performed by using a Zeiss Auriga microscope with an electron beam operation of 5 keV, which is a dual beam FIB (Focused Ion Beam) with a field-emission electron column for high-resolution electron imaging and a Canion Ga+ column for precision ion beam milling. Transmission electron microscopy (TEM) was conducted on an aberration-corrected FEI Titan S 80-300. The UV–visible (UV–vis) absorption spectra were measured by a UV–vis spectrophotometer (HITACHI U-4100). Water contact angles of the samples were tested by an OSA60 (LAUDA Scientific). TRFDS spectra was tested by an CHI601E (CH Instruments Ins). Photoluminescence (PL) spectra was measured by Fluorescence Spectrometer (Thermo Scientific Lumina) in 350 nm of excitation wavelength and 370-680 nm of absorption wavelength: 370-680 nm. Electron paramagnetic resonance (EPR) was collected on an EPR spectrometer (Bruker ER 200D SRC) at room temperature.

3. Synthesis of g-C₃N₄ precursor

10 g of urea was placed in an alumina crucible and heated under air to $550 \,^{\circ}$ C for 2 h at ramping rate of 1 $^{\circ}$ C min⁻¹. The obtained carbon nitride (yellow color) was named as g-C₃N₄.

4. Fabrication of ND-g-C₃N₄ product

In a typical procedure, the as prepared g-C₃N₄ precursor (1 g) and Lithium bis(trimethylsilyl)amide (16 g) were mixed and placed in a nickel crucible, which was then heated in a tubular furnace under flowing N₂ (100 mL/min) to a target temperature of 250 °C with ramping rate of 5 °C/min, keeping for 24 h. The resultant powder was washed with deionized water, ethanol, tetrahydrofuran and dried under vacuum at 100 °C for 24 h. The afforded product was named as ND-g-C₃N₄.

The mass ratio of $g-C_3N_4$ precursor to LiHMDS, thermal treatment temperature, and the reaction time were changed accordingly for the investigation of different treatment parameters.

5. Photoelectrochemical characterization

The transient photocurrent responses, Motto-Schottky plots, and electrochemical impedance spectroscopy (EIS) measurements were carried out with a CorrTest electrochemical station in a quartz cell with a conventional three-electrode system. The samples loaded on fluorine-doped tin oxide (FTO) glass, Pt foil, and Ag/AgCl electrode served as the working electrode, counter electrode, and reference electrode, respectively. The electrolyte was 0.1 M of Na₂SO₄ aqueous solution. A solar simulator of 300 W Xe lamp was used as the excitation light source. Long-pass filters were utilized to cut off the light. The photoanode surface area illuminated was 1 cm², and the scanning rate was 5 mV/s.

6. Photocatalytic H₂ evolution and catalyst recycling

Photocatalyst with 2 wt.% Pt was photo-deposited in mixed H_2PtCl_6 solution under light irradiation for 3 h, the resulted samples was washed with water several times and dried in oven at 60 °C. Photocatalytic H_2 production experiment was carried out in a 250 mL standard reaction vessel under 15 °C and standard vacuum environment, which connected to a glass-closed gas circulation system (Perfect Light Labsolar-6A). The excitation light source is 300 W xenon lamp. 50 mg catalyst was added in the solution with 70 mL of DI water and 30 mLof triethanolamine. Prior to illumination, the reactor was vacuumed for 240 min. The amount of produced H_2 was determined with the gas chromatography (7890B, Agilent Technologies, TCD, Ar as carriers).

Supplementary Figures



Figure S1. XPS survey spectra of g-C₃N₄ and ND-g-C₃N₄.



Figure S2. EPR spectra of (A) $g-C_3N_4$ and (B) ND- $g-C_3N_4$.



Figure S3. TGA results of $g-C_3N_4$ and ND- $g-C_3N_4$ under N_2 atmosphere with a ramping rate of 10 °C min⁻¹.



Figure S4. N₂ adsorption isotherms (77 K) of g-C₃N₄ and ND-g-C₃N₄.



Figure S5. XRD patterns of the ND-g-C₃N₄ product obtained within different reaction time. Mass ratio of g-C₃N₄ precursor: LiHMDS was 1:16. Temperature was 250 °C.



Figure S6. XRD patterns of the ND-g-C₃N₄ product obtained at different temperatures. Mass ratio of g-C₃N₄ precursor:LiHMDS was 1:16. Reaction time was 24 h.



Figure S7. XRD patterns of the ND-g- C_3N_4 product obtained with different Mass ratio of g- C_3N_4 precursor:LiHMDS. Treatment temperature was 250 °C. Reaction

time was 24 h.



Figure S8. Motto-Schottky plots of $g-C_3N_4$ and $ND-g-C_3N_4$.



Figure S9. EIS spectra of g-C₃N₄ and ND-g-C₃N₄.



Figure S10. PL spectra of $g-C_3N_4$ and $ND-g-C_3N_4$.



Figure S11. Transient photocurrent responses of $g-C_3N_4$ and $ND-g-C_3N_4$ at different potentials.



Figure S12. Recyclability test of 2 wt% Pt loaded ND-g- C_3N_4 for photocatalytic H₂ evolution.

 Table S1. Properties of LiHMDS.

Chemical formula	C ₆ H ₁₈ LiNSi ₂
Molar mass	167.326 g/mol
Appearance	White solid
Density	0.86 g/cm ³ at 25 °C
Melting point	71 to 72 °C (160 to 162 F; 344 to 345 K)
Boiling point	80 to 84 °C (176 to 183 F; 353 to 357 K) (0.001 mm Hg)
Solubility	Most aprotic solvents: THF, hexane, toluene
Acidity (pK _a)	26