Ammonia-inducedRobustPhotocatalyticHydrogenEvolution of Graphitic Carbon Nitride

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Experimental section:

Preparation of the g-C₃N₄:

All chemicals were analytical-grade and used without further purification. The g-C₃N₄ was prepared by thermal treatment of urea precursor. In a typical synthesis, 10g urea was put in a Muffle Furnace and heated to 550°C for 3 hours (heating rates: 5k/min). To introduce carbon vacancies, the obtained g-C₃N₄ was heated at 450°C or 500°C in NH₃ atmosphere with a flow of 100 ml/min (heating rates: 5k/min). The carbon vacancies samples heated at 450°C for 4h, 500°C for 3h and 500°C for 4h, were denoted as g-C₃N₄ -450-4, g-C₃N₄ -500-3 and g-C₃N₄ -500-4, respectively.

We also used melamine as precursor to prepare $g-C_3N_4$. 10 g melamine was put in a Muffle Furnace and heated to 550°C for 3 hours (heating rates: 5k/min). And then, the yellow agglomerates were collected and ground into powder, denoted as $g-C_3N_4$ -M. To introduce carbon vacancies, $g-C_3N_4$ -M was heated at 500°C for 4h in a NH₃ atmosphere with a flow of 100 ml/min (heating rates: 5k/min), denoted as $g-C_3N_4$ -M-500-4.

Measurement of photocatalytic performance of the g-C₃N₄

The H₂ production reactions were performed using a flowing system (Ar gas with a flow rate at 1.2L/h) with an inner-irradiation-type Pyrex reactor and a 300W xenon lamp ($\lambda > 400$ nm, NaNO₂ aqueous solution (1 M) was used to filter out the UV light) under ambient temperature and pressure. The 50 mg sample was added into 210 ml

triethanolamine aqueous solution (30 ml triethanolamine, 180 ml water). Prior to photocatalytic reaction, an appropriate amount of H_2PtCl_6 was dissolved in the reactant solution and pre-loaded on the g-C₃N₄ (3 wt% Pt) under visible light for 1.5 h.

Then, the $Pt/g-C_3N_4$ reaction system was degassed by Ar purging for 30 min before the reaction. During the irradiation process, 1mL of gas was collected from the flowing system and then was injected into GC to analyze H₂ amount by gas chromatography (Beifen-Ruili: SP-2100, MS-5Å column, TCD, Ar carrier).

Characterization:

Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2010 microscope with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were investigated on a JSM-7001F microscope. Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet Magna-IR 550-II spectrometer using KBr pallets. UV-Visible absorption spectroscopy was analyzed using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer at room temperature. Photoluminescence (PL) was measured on a Hitachi F-7000 FL spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 XPS spectrometer. To eliminate the effect of sample surface charging the shift of the XPS peak of carbon (C1s whose binding energy is 284.8 eV) was used. X-ray powder diffraction pattern analysis was conducted on a D8 Advance Bruker X-ray diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) operating at 40 kV. The specific surface areas were measured by Brunauer-Enmet-Teller (BET) method employing N_2 adsorption at 77K using a Tristar-3000 apparatus. Elemental analysis was carried out on an elemental Analyzer (vario EL CUBE). The positron lifetime experiments were carried out with a fast-slow coincidence ORTEC system with a time resolution of 210 ps full width at half maximum. The sample powder was pressed into

a disk (diameter: 10 mm, thickness: 1.0 mm). A 13 μCi source of ²²Na was sandwiched between two identical samples. Measured spectra were analyzed by the computer programme LT9.0. The time-resolved fluorescence decay spectra were obtained on a Steady State and Time Resolved Fluorescence Spectrometers (FLSP920). Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was carried out on an iCAP 6300 ICP Spectrometer (Thermo). Atomic force microscopy (AFM) image was measured on a NanoScope IV instrument.



Fig S1 HRTEM images of $g-C_3N_4$ -500-3 (a) and $g-C_3N_4$ -500-4 (b)



Fig S2 SEM images of $g-C_3N_4$ (a) and $g-C_3N_4$ -500-4 (b)



Fig S3 AFM images of g- C_3N_4 (a) and g- C_3N_4 -500-4 (b)



Fig S4 N_2 adsorption–desorption isotherms of g-C_3N_4 (a), g-C_3N_4-450-4 (b), g-C_3N_4-500-3 (c) and g-C_3N_4-500-4 (d)



Fig S5 Pore size distribution of g-C₃N₄ (a), g-C₃N₄-450-4 (b), g-C₃N₄-500-3(c) and g-C₃N₄-500-4 (d)

Sample	C/mol%	N/mol%	O/mol%	C/N
g-C ₃ N ₄	44.3	54.8	0.9	0.808
$g-C_3N_4-450-4$	43.7	55.6	0.7	0.785
g-C ₃ N ₄ -500-3	43.0	56.4	0.6	0.762
g-C ₃ N ₄ -500-4	42.9	56.6	0.5	0.757

Table S1 Surface atomic ratio of all samples by XPS spectral analysis



Fig S6 C1s spectra of g-C₃N₄ (a), g-C₃N₄-450-4 (b), g-C₃N₄-500-3(c) and g-C₃N₄- 500-4 (d)

Table S2 Relative ratios of N-C=N and C=C of all samples by C 1s spectral analysis

sample	N-C=N		C=(C
	area	%	area	%
g-C ₃ N ₄	35428.2	87.6	4994.3	12.4
$g-C_3N_4-450-4$	33767.4	93.1	2531.8	6.9
$g-C_3N_4-500-3$	40036.5	93.8	2640.9	6.2
g-C ₃ N ₄ -500-4	40658.0	94.4	2392.1	5.6



Fig S7 N1s spectra of g-C₃N₄ (a), g-C₃N₄-450-4 (b), g-C₃N₄-500-3(c) and g-C₃N₄-500-4 (d)

Table S3 Relative ratios of C-N=C, N(C)₃ and C-NH of all samples by N 1s spectral analysis

sample	C-N=C		N(C) ₃		C-NH	
	area	%	area	%	area	%
$g-C_3N_4$	58889.5	75.1	5862.4	7.5	13701.6	17.4
$g-C_3N_4-450-4$	65570.8	72.0	5489.3	6.1	20000.2	21.9
$g-C_3N_4-500-3$	64024.3	71.8	4881.0	5.6	20190.2	22.6
g-C ₃ N ₄ -500-4	69167.9	71.6	5300.7	5.6	22008.4	22.8

Table S4 Elemental composition of all samples by elemental analysis

Sample	C / mol%	N/ mol%	H/ mol%	O/mol% (calculated)	C/N
$g-C_3N_4$	31.4	46.9	21.1	0.6	0.669
g-C ₃ N ₄ -450-4	32.2	47.9	19.4	0.5	0.672
g-C ₃ N ₄ -500-3	32.2	47.4	19.9	0.5	0.679
$g-C_3N_4-500-4$	32.1	47.5	20.1	0.3	0.675



Fig S8 Positron annihilation spectra of $g-C_3N_4$ and $g-C_3N_4$ -500-4



Fig S9 VB spectra of $g-C_3N_4$ and $g-C_3N_4$ -500-4



Fig S10 Photocatalytic H_2 evolution rates of all samples



Fig S11 Relationship between surface area and hydrogen evolution rate of g-C₃N₄



Fig S12 TEM, HRTEM images and Pt size distribution of $g-C_3N_4$ (a1, a2, a3), $g-C_3N_4$ -450-4 (b1, b2, b3), $g-C_3N_4$ -500-3(c1, c2, c3) and $g-C_3N_4$ -500-4 (d1, d2, d3)



Fig S13 TEM images of g-C $_3N_4$ -M (a) and g-C $_3N_4$ -M-500-4 (b)



Fig S14 N_2 adsorption–desorption isotherms of g-C₃N₄-M (a) and g-C₃N₄-M-500-4 (b)



Fig S15 Pore size distribution of $g-C_3N_4-M$ (a) and $g-C_3N_4-M-500-4(b)$



Fig S16 Photocatalytic H_2 evolution activity of g-C₃N₄-M and g-C₃N₄-M-500-4