

Supplementary Information

Exfoliation of triazole-based $C_3N_{4,8}$, C_3N_6 , and C_3N_7 nanosheets for efficient photocatalytic ammonia production

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Experimental

Exfoliation of $C_3N_{4.8}$, C_3N_6 , and C_3N_7 : Bulk $C_3N_{4.8}$, C_3N_6 , and C_3N_7 were synthesized by calcination of 5-amino-1H-tetrazole of 3.00 g at elevated temperature for 4 h under Ar gas flowing. The calcination temperatures were 400, 300, and 250 °C for synthesizing $C_3N_{4.8}$, C_3N_6 , and C_3N_7 , respectively. Each sample of 0.3 g was sonicated in isopropyl alcohol (>99.5%) of 100 mL at 180 W for 3 h in a bath sonicator (Sungdong ultrasound, SD-D300H). The resulting solution was centrifuged at 3,000 rpm for 3 min to remove unexfoliated carbon nitrides. Supernatant solution was obtained as a colloidal solution of exfoliated carbon nitrides. To solidify exfoliated carbon nitrides nanosheets, the colloidal solution was centrifuged at 14,000 rpm for 30 min, followed by drying at room temperature and vacuum conditions. Bulk g- C_3N_4 was synthesized by calcination of dicyandiamide of 3.00 g at 600 °C for 4 h under Ar gas flowing. Its exfoliation was achieved through same procedures to obtain g- C_3N_4 nanosheets as a reference material.

Characterization: The crystal structures of bulk and exfoliated samples were examined using a powder X-ray diffractometer (XRD; Rigaku, D/MAX-2200/VPC) with Cu K_α ($\lambda = 1.5418 \text{ \AA}$) radiation produced at 40 kV and 30 mA. Solid-state nuclear magnetic resonance (NMR) experiments were performed on a Bruker Avance III 400 spectrometer equipped with 4 mm double resonance magic angle spinning (MAS) probe (WS004 at KBSI Metropolitan Seoul Center). ^{13}C MAS NMR spectra were acquired at a ^{13}C operating frequency of 100.65 MHz with high-power proton decoupling, spinning frequency of 10 kHz and recycle delay of 10 s. ^{13}C MAS NMR spectrum of empty rotor was also collected using the same conditions with the samples for background subtraction. The crystal morphology of exfoliated samples was inspected by a high-resolution transmission electron microscope (HR-TEM; Jeol, JEM-2100F) at 200 kV. The thickness of the exfoliated samples was confirmed with an atomic force microscopy (AFM; Bruker, Dimension Edge AFM) in a tapping mode. X-ray photoelectron

spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed through the NEXSA (Thermo Fisher Scientific), equipped with an Al K_{α} X-rays (1486.7eV) radiation source at GIST Advanced Institute of Instrumental Analysis (GAIA). The near-edge X-ray absorption fine structure (NEXAFS) measurements of exfoliated samples were conducted at the 10A2 HRPES II beamline of Pohang Accelerator Laboratory (Pohang, Republic of Korea). The drop-cast films of exfoliated carbon nitride nanosheets were used for the NEXAFS and XPS analyses. The bandgaps of bulk and exfoliated samples were confirmed in diffuse reflectance mode by UV–Vis spectrophotometer (Shimadzu, UV-3600i Plus). The Zeta potential of the exfoliated samples was confirmed by a Zeta potential analyzer (Otsuka Electronics, ELS-2000ZS). Photoluminescence (PL) spectra of the exfoliated samples were measured under excitation wavelength of 320 nm by a PL spectrometer (Jasco, FP-8500). The XRD, TEM, AFM, UV–Vis spectrophotometer, Zeta potential analyzer and PL spectrometer were available at the National Research Facilities and Equipment Center (NanoBio·Energy Materials Center) at Ewha Womans University.

Photocatalysis for NRR: The photocatalytic performances of carbon nitrides toward N_2 reduction reaction (NRR) were evaluated in a quartz reactor under atmospheric pressure and room temperature. 30 mg of photocatalyst was suspended in 100 mL of distilled water/methanol (9/1 vol%) and the mixture was continuously stirred to achieve uniform dispersion. The reactor was sealed and purged with purified N_2 -feed gas at a flowrate of 50 mL min^{-1} for 30 min in dark to establish adsorption–desorption balance and saturate the solution. Then, irradiation was performed using a 300 W Xe lamp with a $\lambda > 420$ nm cut-off filter, and N_2 was bubbled with a rate of 50 mL min^{-1} through the solution. 1 mL of suspension was withdrawn at every 30 min intervals and passed through a 0.2 μm PTFE syringe filter to

remove solid catalysts. The concentration of ammonia was analyzed using the Nessler's reagent spectrophotometry method.¹

Fig. S1 X-ray diffraction (XRD) patterns of bulk $g\text{-C}_3\text{N}_4$, $\text{C}_3\text{N}_{4.8}$, C_3N_6 , and C_3N_7 in 2θ ranges of (left) $5^\circ\text{--}60^\circ$ and (right) $25^\circ\text{--}30^\circ$.

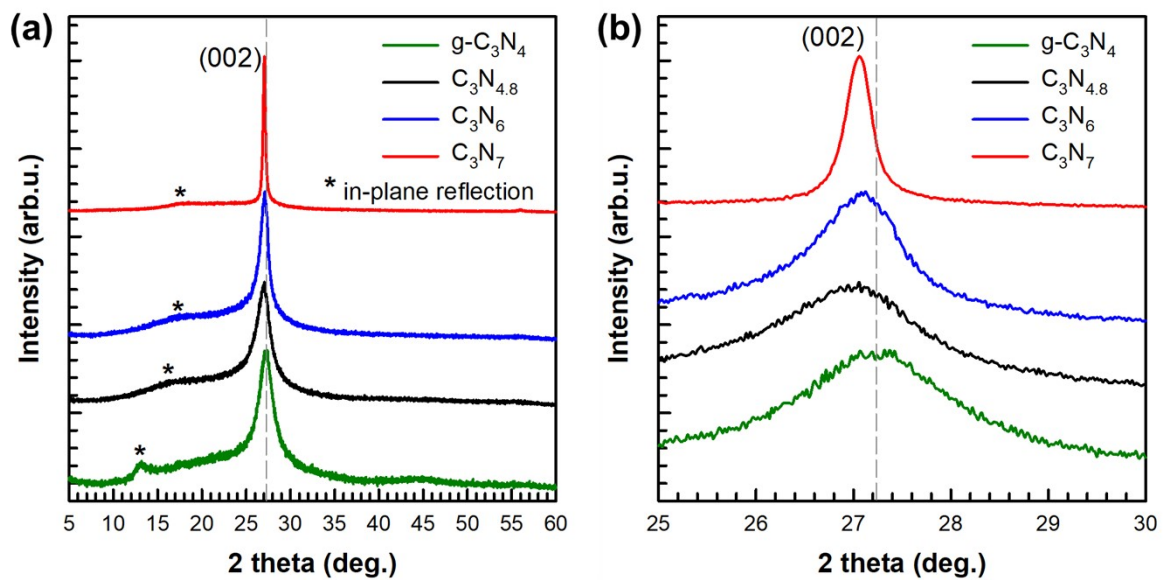


Table S1 Zeta potential of exfoliated g-C₃N₄, C₃N_{4.8}, C₃N₆, and C₃N₇ nanosheets.

	g-C₃N₄	C₃N₅	C₃N₆	C₃N₇
Zeta potential	-48.7 mV	-60.6 mV	-53.6 mV	-55.1 mV

Fig. S2 N₂ adsorption isotherms of (left) bulk and (right) exfoliated g-C₃N₄, C₃N_{4.8}, C₃N₆, and C₃N₇ nanosheets measured at 77 K

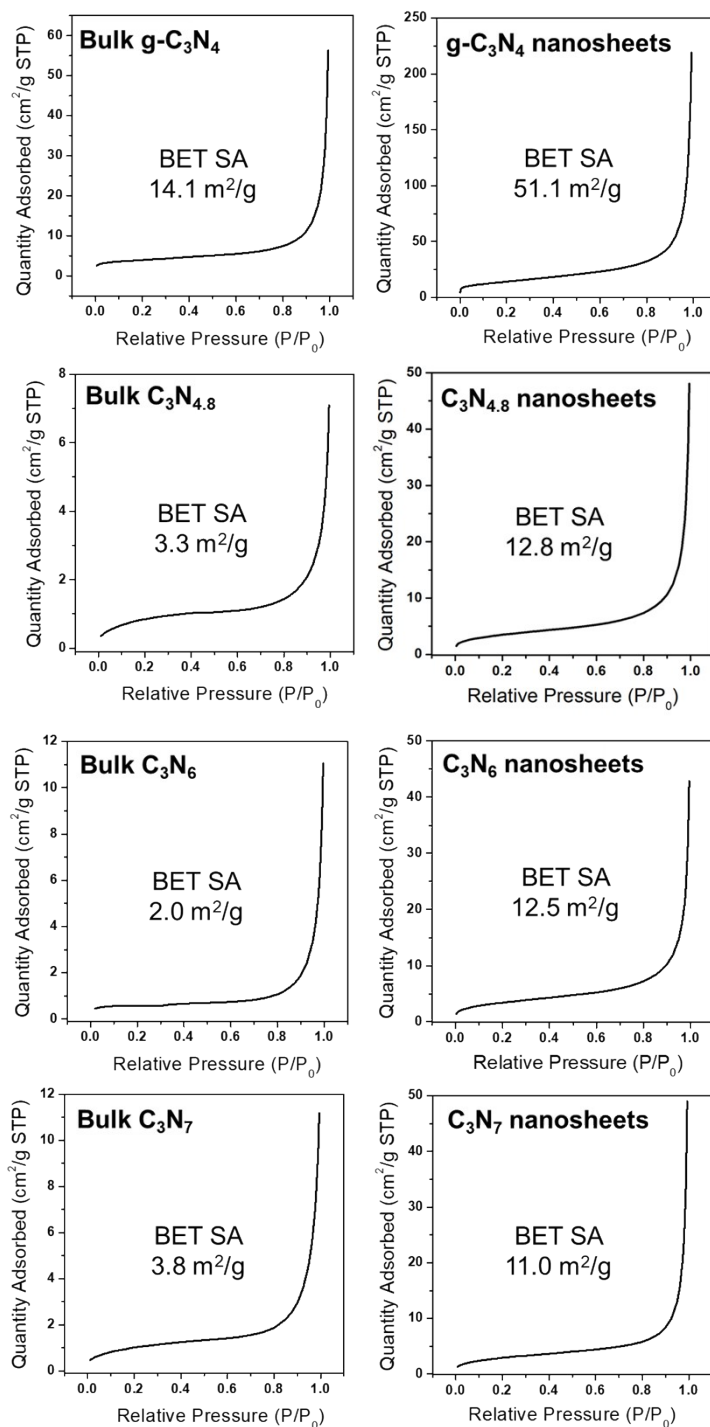


Fig. S3 High resolution C 1s X-ray photoelectron spectroscopy (XPS) data of exfoliated (a) g- C_3N_4 , (b) $C_3N_{4.8}$, (c) C_3N_6 , and (d) C_3N_7 nanosheets.

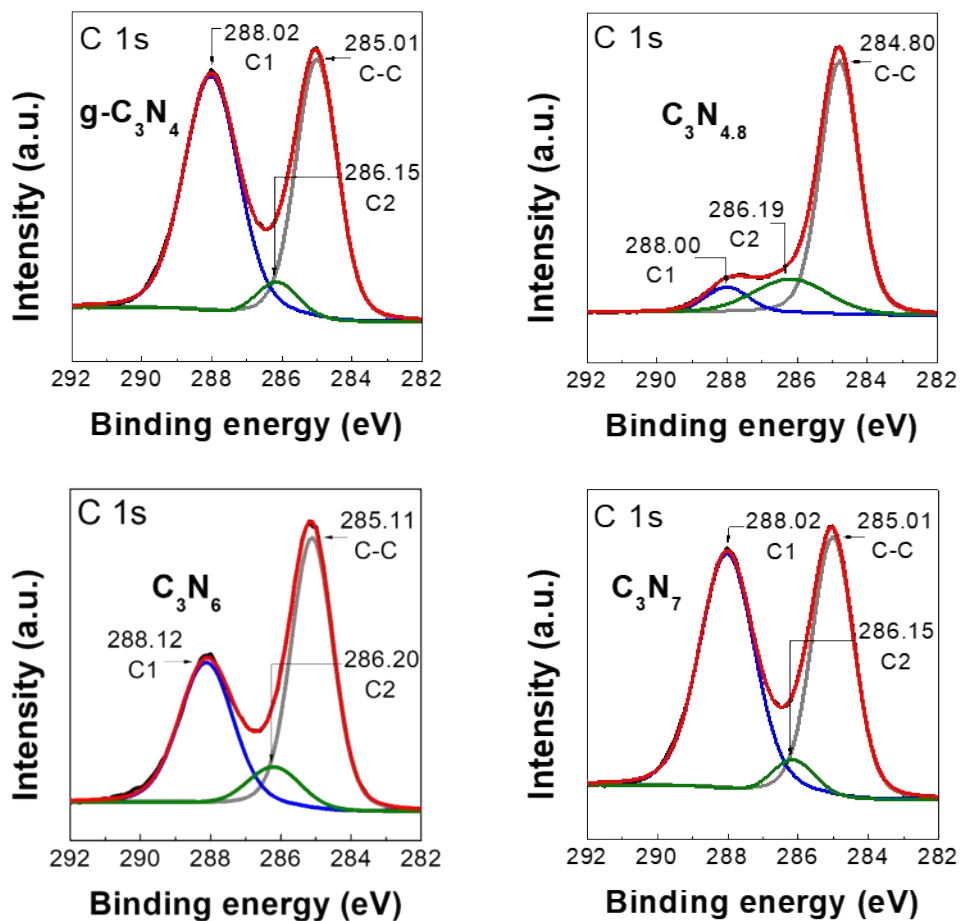


Fig. S4 High resolution N 1s XPS data of bulk (a) $g\text{-C}_3\text{N}_4$, (b) $\text{C}_3\text{N}_{4.8}$, (c) C_3N_6 , and (d) C_3N_7 nanosheets.

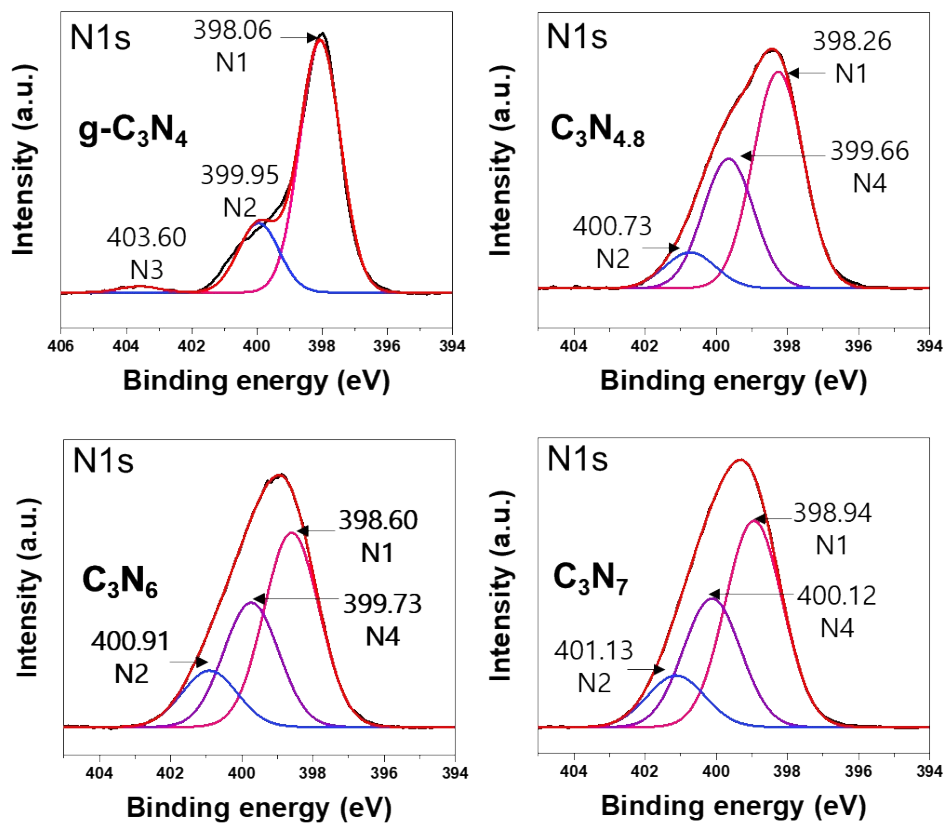


Fig. S5 TEM images of 30 days-aged $g\text{-C}_3\text{N}_4$, $\text{C}_3\text{N}_{4.8}$, C_3N_6 , and C_3N_7 nanosheets.

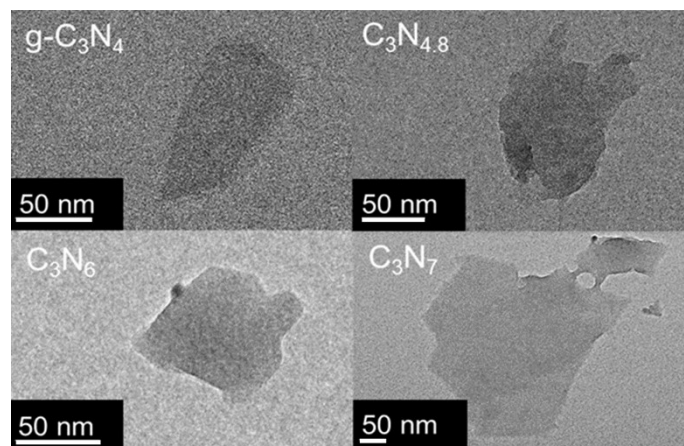
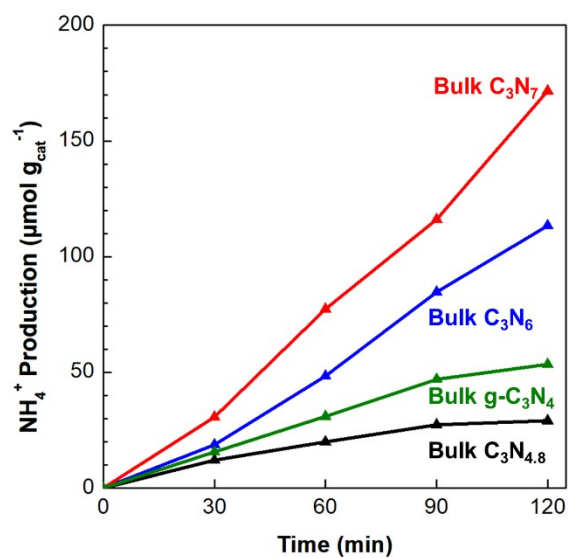


Fig. S6 Amounts of ammonia generated on bulk $g\text{-C}_3\text{N}_4$, $\text{C}_3\text{N}_{4.8}$, C_3N_6 and C_3N_7 under N_2 atmosphere.



Bulk $g\text{-C}_3\text{N}_4$, $\text{C}_3\text{N}_{4.8}$, C_3N_6 and C_3N_7 generates ammonia with rates of 27.7, 14.7, 58.5, and 85.7 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$, respectively.

Fig. S7 Comparison of amounts of ammonia generated on exfoliated C_3N_7 nanosheets under N_2 and Ar atmospheres

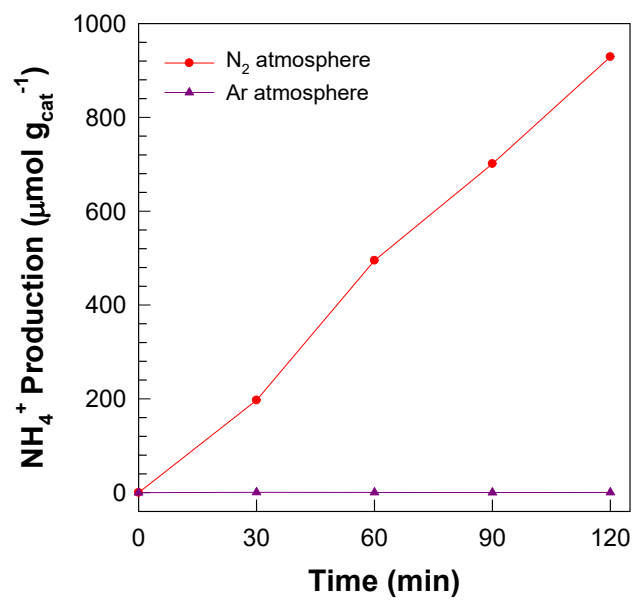
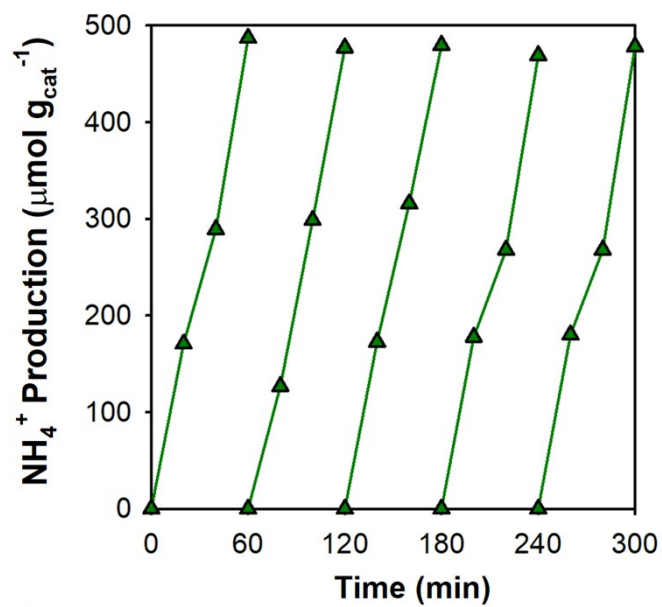


Fig. S8. Amounts of ammonia generated on exfoliated C_3N_7 nanosheets under N_2 atmosphere for consecutive 5 cycles.



Reference

1. X. He, H. Liu, J. Qin, Z. Niu, J. Mu, B. Liu, *Dalton Trans.* 2023, **52**, 10869.