Electronic Supplementary Information

Chemical Reaction of Graphitic Carbon Nitride Film with Glass Surface and Its Impact on Photocatalytic Activity

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§1. Identification of products

1.1 Bulk g-CN

In a typical condensation of melamine, a precursor used in this study, is converted into a polymeric form of melem. A vibrational absorption at 810 cm⁻¹ in FTIR (left-hand panel in Fig. 1b) originated from the out-of-plane mode of triazine and/or heptazine rings.¹ In the ¹³C solid-state CP MAS NMR spectrum of powdery g-CN, C1 (157.4 ppm) and C2 (163.7, 165.6 ppm) in the heptazine ring were identified (Fig. 1c).¹ The corresponding ¹⁵N solid-state CP MAS NMR spectrum contained peaks for the nitrogen atoms in the C=N-C bonds (N4, 201.0 and 190.7 ppm) and N(C)₃ (N3, 155.2 ppm) in the heptazine ring² (Fig. 1d). Vibrational absorptions between 1200 and 1350 cm⁻¹ in the IR spectrum, attributed to C-NH-C stretching, and the chemical shift originated from the bridging -NH- (N2, 135.3 ppm) in the ¹⁵N solid-state NMR spectrum suggested the formation of polymer of heptazine units. In addition, the vibrational absorptions of N-H stretching at 3000–3300 cm⁻¹ indicated unreacted amine (N1, 115.5 ppm), suggesting that the full condensation of melamine to two-dimensional g-C₃N₄ was not achieved under the present synthesis conditions. These results demonstrate that the majority of bulk g-CN is melon.

1.2 g-CN films

The ATR-FTIR spectrum of g-CN/Q contains typical vibrational absorptions of g-CN (Fig. 1b), consisting of the out-of-plane mode of heptazine rings (810 cm⁻¹), the stretching mode of the C-NH-C bond (1200–1350 cm⁻¹), and the N-H stretching absorption (3000–3300 cm⁻¹). Because these features agree well with those of bulk melon (Fig. 1b), g-CN/Q is identified as melon. The melon-derived absorptions are also observed for g-CN/G. The ¹³C solid-state cross-polarization (CP) magic angle spinning (MAS) NMR spectrum for g-CN/G also indicates heptazine ring formation. Chemical shifts at 157.4 and 164.7 ppm correspond to carbon atoms in a heptazine ring (C1) and those bound to NH and NH₂ (C2), respectively (Fig. 1c).¹⁻³ Dynamic nuclear polarization (DNP)-enhanced ¹⁵N solid-state CP MAS NMR also confirms the presence of NH₂ (N1, 115.5 ppm), NH (N2, 135.3 ppm), NC₃ (N3, 155.2 ppm), and C=N-C (N4, 195.2 ppm) in the heptazine units (Fig. 1d).¹⁻³ The assignment of chemical shifts at 115.5 and 135.3 ppm is supported by the amplified intensities when the spectrum is acquired at shorter contact time (2 ms), where the magnetic resonance originating from nitrogens adjacent to hydrogen is enhanced. These signals are weaker than the spectrum for melon acquired with the same contact time (10 ms). This implies consumption of amino groups by reactions with the glass. The XPS results support the NMR data. Based on the assignment of the XPS spectra in a previous study,⁴ the C=N-C bond is identified by dominant photoemissions at 288.1 (Fig. 2c) and 398.4 eV (Fig. 2d), and peripheral nitrogen N-(C)3 is confirmed by a photoemission at 400.8 eV (Fig. 2d). A separate peak at 398.9 eV originates from NH and NH₂ bonds (Fig. 2d). The results suggest that g-CN/G consists of heptazine polymers.

§2. GI-XRD profile



Fig. S1. GI-XRD profiles of g-CN films prepared on quartz (g-CN/Q) and a glass slide (g-CN/G).

§3. Additional characterization of g-CN/G



Fig. S2. ATR-FTIR spectra of g-CN films on various substrates. (a) IR spectra of the g-CN films on commercial glass slides purchased from different suppliers. (b) IR spectra of the g-CN films formed on alkali-free glass (AFG) and a glass substrate coated with a transparent electrode (TE). Arrows indicate symmetric and asymmetric absorptions of the metal-NC₂ bond. IR spectra of bulk melon and alkali-free glass are also shown for comparison.

Sample	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	K ₂ O	SO ₃	Fe ₂ O ₃	Note
Glass #1	70.0	11.0	7.0	_	0.7	4.5	_	_	BaO: 1.5 ZnO: 4.2
Glass #2	72.6	13.0	8.8	4.3	0.6	0.3	0.2	0.1	
Glass #3	—	—	_	_	_	_	_	_	_
Glass #4	70–73	—	7–12	1.0-4.5	1.0–2.0	—	—	0.08-0.14	$Na_2O + K_2O:$ 13–15

 Table S1. Chemical compositions of glass slides used in this study (in %).

-: not available.

Table S2. Chemical compositions of glass #1, a heated glass slide (glass #1), alkali-free glass, and g-CN

 films determined by XPS.

Sample	С	Ν	О	Na	K	Si	Са
Glass #1	2.92	_	66.50	1.28	0.67	27.49	1.14
Pre-heated glass #1 500 °C 20 h	6.18	_	60.27	10.82	1.80	20.93	_
Alkali-free glass	3.81	—	70.17	1.18	0.02	23.98	0.84
g-CN/AFG	45.84	52.74	1.24	0.07	0.10	0.00	0.02
g-CN/G	39.90	47.44	3.82	5.40	3.43	—	0.00
Boiled-water treated g- CN/G (g-CN/G-bw)	46.35	37.50	6.72	0.64	2.21	_	_
g-CN/AFG-HCl	47.90	49.70	2.04	0.13	0.00	0.23	0.00
g-CN/G-HCl	49.76	40.76	9.46	0.02	0.00	—	_
g-CN/hG	43.23	47.27	3.07	3.16	3.27	_	0.00
g-CN/hG-HCl	47.18	50.29	2.50	0.03	0.00	_	_

-: not determined.



Fig. S3. ¹H MAS NMR spectra of g-CN/G peeled from glass (a) and bulk melon (b). Top and bottom spectra were acquired for as-synthesized and vacuum-dried samples (120 °C for 2 days), respectively. The broad signal in the bottom spectrum of (a) at 9 ppm is presumably attributed to the bridging NH that interacts with residual adsorbed water.² The bottom spectrum in (b) was fitted with five Gaussian functions. The assignment given by Li *et al.*⁵ is shown in (b). The signal at 1.5 ppm was also detected by previous studies.^{2,5,6} Seyfarth *et al.* assigned this chemical shift as probe impurities,⁶ but it is not for this study. Thus, origins of the signal are elusive at present. (c) and (d) show ¹H–¹H DQ-SQ spectra of vacuum-dried g-CN/G and bulk melon, respectively. In (c), on the diagonal, the self-correlation peaks of the signals at 1.5 and 4.5 ppm appear. The broad signal of the bridging N-H at 9 ppm is correlated, which indicates that the protons in this range are close to each other. In (d), again, the self-correlation peaks of the signals at 1.5 and 4.5 ppm appear, but the latter is less intense. The correlation peak for the signal at 10 ppm is also visible.

§4. Effect of boiled water treatment on concentrations of alkali metals



Fig. S4. ATR-FTIR spectra of g-CN/G and boiled water-treated g-CN/G (denoted as g-CN/G-bw). Spectra for g-CN/Q and bulk melon are also shown for comparison. The inset in the right-hand panel magnifies absorption bands attributed to cyanamide stretching.



Fig. S5. XPS spectra of g-CN/G and g-CN/G-bw in the C 1s (a), N 1s (b), Na 1s (c), K 2s (d), and O 1s (e) regions.

Soaking g-CN/G in boiled water for 30 min, a treatment necessary for peeling off the film from the substrate, affects the IR spectrum. First, the absorptions at 994 and 1153 cm⁻¹ disappear (left-hand panel in Fig. S3), indicating that most of the alkali metals bound to NC₂ groups are washed away from g-CN/G. Indeed, the treatment attenuates the Na 1s and K 2s signals (Fig. S4c and d, respectively). The total alkali metal concentration decreases by 68%. The removal of Na⁺ is further verified by the disappearance of the Na KLL signal (Fig. S4e). The absorbance of the cyanamide absorption at 2151 cm⁻¹ decreases (inset in the right-hand panel of Fig. S3), indicating that the functional group bound to the alkali metals gives this wavenumber. Comparable IR and XPS measurements suggest that most of the remaining alkali metals are bound to cyanamide groups. The heptazine backbone of the polymer is not affected by the boiled water treatment because heptazine-related vibrational absorptions and photoemissions are observed.

§5. Presence of adsorbed water on a glass slide



Fig. S6. Sum frequency generation (SFG) spectrum of a glass slide (glass #1). Polarization combination for the measurement is ssp (SFG = s, visible = s, IR = p).

§6. Characterizations of g-CN/hG and g-CN/hG-HCl



Fig. S7. (a) ATR-FTIR spectra of g-CN/hG and g-CN/hG-HCl. (b) and (c) show XPS spectra of g-CN/hG and g-CN/hG-HCl in the Na 1s and K 2p regions, respectively.

§7. Photocatalytic degradation of methyl orange solutions



Fig. S8. (a) Analyses of degradation rates based on a first-order model, $\ln (C_0/C_t) = kt$, where k denotes rate constant, C_0 and C_t represent the initial equilibrium methyl-orange concentration and the residual concentration in the solution after reaction time t, respectively. The dashed lines show the fitting results with the model. The fitting analysis of g-CN/hG-HCl was done using the data between 0 and 3 h, because the tendency starts to deviate from the linear fitting after 4 h. (b) Blank data of g-CN/AFG and g-CN/hG-HCl.



Fig. S9. (a) Evolution of the degradation efficiencies of g-CN/hG prepared on glass slides purchased from different suppliers. UV-vis spectra of methyl orange solutions at each reaction time are shown in Fig. S11. (b) Evolution of the degradation efficiencies of g-CN/hG (glass #1), g-CN/hG treated with citric acid instead of HCl (denoted as g-CN/hG-CA), and g-CN film prepared on a piece of a broken glass followed by citric acid treatment (g-CN/glass cup-CA). UV-vis spectra of methyl orange solutions at each reaction time are shown in Fig. S12. (c) Evolution of the degradation efficiencies of g-CN/hG-HCl with different film thicknesses. UV-vis spectra of methyl orange solutions at each reaction time are shown in Fig. S12.



Fig. S10. (a) GI-XRD profile of TiO₂ film sputtered on alkali-free glass (AFG). All the diffractions observed are assigned to anatase.⁷ (b) UV-vis absorption spectra of methyl orange solutions during photodegradation experiments using TiO₂/AFG. (c) Evolution of the degradation efficiencies of TiO₂/AFG and g-CN/hG-HCl. For g-CN/hG-HCl, 0.99% isopropanol (IPA) is added as a hole scavenger.



Fig. S11. UV-vis absorption spectra of methyl orange solutions during photodegradation experiments using g-CN/hG-HCl prepared on (a) glass #2, (b) glass #3, and (c) glass #4.



Fig. S12. UV-vis absorption spectra of methyl orange solutions during photodegradation experiments using g-CN/films. (a) g-CN/AFG, (b) g-CN/AFG-HCl, (c) g-CN/hG, (d) g-CN/glass cup treated with citric acid, (e) g-CN/hG-HCl with film thickness of 393 nm, (f) g-CN/hG-HCl with film thickness of 151 nm, and (g) g-CN/hG-HCl with the addition of 0.99% isopropanol (IPA), and (h) g-CN/hG-CA.

§8. Determination of ionization energy of g-CN/G-HCl



Fig. S13. PYS spectrum of g-CN/G-HCl. The film was prepared on a conductive Au substrate. The Au background was subtracted.

Supplementary References

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