Supporting Information for:

Scalable and super-stable exfoliation of graphitic carbon nitride in biomassderived γ -valerolactone: Enhanced catalytic activity for alcoholysis and cycloaddition of epoxides with CO₂

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Experimental Section

Materials: 1,2-Epoxyhexane (96.0%) was obtained from Alfa Aesar. Glycidyl phenyl ether (>99.0%) and 1,2-butylene oxide (>99.0%) were provided by TCI (Shanghai) Development Co., Ltd. Styrene oxide (97.5%), γ -valerolactone (98%), anisole (99%), melamine (99%), and epichlorohydrin (99.0%), were purchased from J&K Scientific Ltd. Methanol, ethanol, ethyl acetate, 1-propanol, *n*-butanol, and ethyl ether were A. R. grade and were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. All chemicals were used as received. CO₂ was supplied by Beijing Analytical Instrument Factory with a purity of 99.99%.

Preparation of the bulk g-C₃N₄. The bulk *g*-C₃N₄ was synthesized according to a procedure reported in the literature with some modifications.^[S1] Briefly, melamine (6 g) was put into an alumina crucible with a cover, which was heated to 550 °C with a heat rate of 2 °C min⁻¹ in a muffle furnace and maintained at 550 °C for 4 h. All experiments were performed in a following nitrogen atmosphere.^[S2] The yellow product was collected and ground into powder for further use.

*Exfoliation of bulk g-C*₃ N_4 *to generate few-layer g-C*₃ N_4 *nanosheets.* The few-layer *g*-C₃ N_4 nanosheets were obtained by liquid exfoliating of the as-prepared bulk *g*-C₃ N_4 in γ -valerolactone. In detail, 150 mg of bulk *g*-C₃ N_4 powder was dispersed in 50 mL GVL and then ultrasonicated in a KQ-100DB ultrasonic bath (100 W) at 40 kHz frequency for 24 h using water cooling coil and

an ice-bath to control the bath temperature below 30 °C during sonication. The initial formed suspension was then centrifuged at about 4000 rmp for 30 min to remove the residual unexfoliated g-C₃N₄. Finally, the suspension of few-layer g-C₃N₄ nanosheets was used for further study. The solid few-layer g-C₃N₄ nanosheets was obtained by centrifuged at about 16000 rmp, washed by ethanol, and then was dried at 50 °C for 12 h under vacuum.

Characterization of the g-C₃N₄-based materials. The transmission electron microscopy (TEM) images were obtained using a TEM JeoL-1011 with an accelerating voltage of 120 kV. The sample was dispersed in ethanol with the aid of sonication and dropped on an amorphous carbon film, supported on a copper grid, for the TEM analysis. High resolution TEM (HRTEM) images were characterized using a TEM JEOL-2100F operated at 200 kV acceleration voltage. X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer (D/MAX-RC, Japan) operated at 40 kV and 200 mA with Cu Ka (λ =0.154 nm) radiation. FT-IR spectra were recorded on Bruker Tensor 27 IR spectrometer and the sample was prepared by the KBr pellet method. The XPS measurements were carried out on an ESCAL Lab 220i-XL spectrometer at a pressure of ~3×10⁻⁹ mbar (1 mbar=100 Pa) using Al K α as the excitation source (hv=1486.6 eV) and operated at 15 kV and 20 mA. AFM was taken on a Bruker Multimode 8 instrument under the AC mode (tapping mode).

Alcoholysis of various epoxides. In a typical experiment, epoxide (1 mmol), alcohol (4 g) and g-C₃N₄-based catalyst (0.1 g) were added into a stainless steel reactor of 20 ml equipped with a magnetic stirrer. After being sealed, the reaction mixture was stirred at 120 °C with a desired reaction time. After the reaction was finished, the products were analyzed using anisole as the internal standard by gas chromatography (GC, Agilent 6820) equipped with a flame-ionized detector (FID) and a HP-5MS capillary column (0.25 mm in diameter, 30 m in length), and identification of the products was done by GC-MS (Agilent 5977A).

*Reusability of few-layer g-C*₃ N_4 *nanosheets.* In the experiments to test the reusability of few-layer g-C₃ N_4 nanosheets, the catalyst was recovered by centrifugation, washed using ethanol and ethyl ether. After drying under vacuum at 80 °C for 12 h, the catalyst was reused for the next cycle. The

recovered few-layer g-C₃N₄ nanosheets were also characterized by TEM and HR-TEM.

*Cycloadditions of various epoxides with CO*₂. Epoxide (10 mmol) and *g*-C₃N₄-based catalyst (50 mg) were added in a stainless steel reactor of 20 ml equipped with a magnetic stirrer. After being sealed, the reactor was put into a constant-temperature air bath to reach the desired temperature. CO_2 was then purged into the reactor until the desired pressure (2.5 MPa) was reached, and the stirrer was started. After a desired time, the reactor was then cooled in an ice-water bath, and the excess CO_2 was released slowly passing through a cold trap with ethyl acetate as the absorbant. Then ethyl acetate in the cold trap and internal standard *n*-butanol were added into the reactor. After the catalyst was precipitated, the product was analyzed by GC (Agilent 7890) equipped with a flame-ionized detector (FID) and a HP-5MS capillary column (0.25 mm in diameter, 30 m in length), identification of the products was done by GC-MS (Agilent 5977A).



Fig. S1. Standard curve of absorbance per length of the cell (A/l, l = 1 cm) at different concentrations of g-C₃N₄ nanosheets for $\lambda = 313$ nm in GVL.

The concentrations (c) of g-C₃N₄ nanosheets were calculated by using the Lambert-Beer law (A/*l*= α c), in which A/l is the absorbance per length of the cell and α is the extinction coefficient. Figure S1 shows the standard curve of A/*l* at different concentrations of supernatants of g-C₃N₄ nanosheets at the wavelength $\lambda = 313$ nm, indicating a perfect linear relationship with the concentration (c). This behavior is consistent with the Lambert-Beer law, yielding an absorption coefficient of α = 4522 mL mg⁻¹ m⁻¹. Such consistence suggests the good dispersion of *g*-C₃N₄ nanosheets in GVL. Based on this result, the concentration of the obtained *g*-C₃N₄ nanosheets in GVL could be calculated.



Fig. S2. The images for two samples of the dispersion of few-layer g-C₃N₄ nanosheets in GVL, (a) fresh prepared; (b) stored for twelve months. From Fig. S2, we cannot see precipitation or aggregation generated in twelve months later.



Fig. S3. FT-IR spectra for the few-layer g-C₃N₄ nanosheets stored in GVL for a period of 12 months and the bulk g-C₃N₄.



Fig. S4. The color for the bulk g-C₃N₄ and g-C₃N₄ nanosheets.

The color of powder, as can be seen in Fig. S4, changed from yellow to white when the bulk g- C_3N_4 had been exfoliated into few-layer, indicating a change in light absorption.



Fig. S5. Large-scale exfoliation of *g*-C₃N₄.



Fig. S6. The TEM image of the bulk g-C₃N₄.



Fig. S7. XPS survey spectra (a), high-resolution C 1s XPS spectra (b), and high-resolution N 1s XPS spectra (c) for the bulk g-C₃N₄.



Fig. S8. (a) Raman spectra for bulk g-C₃N₄ and the exfoliated few-layer g-C₃N₄ nanosheets. (b) The corresponding enlarged Raman spectra.



Scheme S1. Alcoholysis of epoxides and cycloaddition of epoxides with CO_2 over *g*- C_3N_4 -based catalysts.



Fig. S9. Effect of reaction temperature on the alcoholysis of glycidyl phenyl ether over g-C₃N₄ nanosheets. Reaction conditions: glycidyl phenyl ether, 1 mmol; methanol, 4 g; catalyst, 0.1 g; reaction time, 5 h.

From Fig. S8, we could see that the reaction temperature significantly affected the activity of the alcoholysis of glycidyl phenyl ether. The yield of the product increased with the rising reaction temperature, and a maximum could be achieved at 120 °C under our reaction conditions. Therefore, we selected 120 °C as the reaction temperature to study other reaction parameters.



Fig. S10. Reusability of the few-layer g-C₃N₄ nanosheets for alcoholysis of glycidyl phenyl ether. Reaction conditions: glycidyl phenyl ether, 1 mmol; methanol, 4 g; catalyst, 0.1 g; reaction temperature, 120 °C; reaction time, 5 h.



Fig. S11. TEM (a) and HR-TEM (b) images for the recovered g-C₃N₄ nanosheets in the experiment of alcoholysis of glycidyl phenyl ether.

Table S1. Reusability of the few-layer g-C₃N₄ nanosheets for cycloaddition of glycidyl phenyl ether with CO₂.^a

| Cycle | Yield (%) ^b |
|-------|------------------------|
| 1 | 99.2 |
| 2 | 98.4 |
| 3 | 98.6 |
| 4 | 97.8 |

^aReaction conditions: epoxide, 10 mmol; few-layer g-C₃N₄ nanosheets, 50 mg; CO₂, 3 MPa; temperature, 120 °C; time, 4 h. ^bThe yields were determined using ¹H NMR method.^[S3]



Fig. S12. TEM (a) and HR-TEM (b) images for the recovered g-C₃N₄ nanosheets in the experiment of cycloaddition of glycidyl phenyl ether with CO₂.

References:

[S1]. X. She, H. Xu, Y. Xu, J. Yan, J. Xia, L. Xu, Y. Song, Y. Jiang, Q. Zhang and H. Li, *J. Mater. Chem. A*, 2014, 2, 2563.

[S2]. Y. J. Zhang, T. Mori, J. H. Ye and M. Antonietti, J. Am. Chem. Soc., 2010, 132, 6294.

[S3]. X. Jiang, F. Gou, F. Chen and H. Jing, *Green Chem.*, 2016, 18, 3567.