Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Preparation of bulk g-C_3N_4 and g-C_3N_4 nanosheets. Bulk g-C_3N_4 powder was synthesized according to a modified procedure described in a previous paper [1, 2]. In detail, dicyandiamide (Aldrich, 99%) was heated at 550 °C for 4 h in static air with a ramp rate of 2.3 °C/min and then cooled to room temperature. The resultant yellow agglomerates were milled into powder in a mortar. The nanosheets were prepared according to our previous work [3]. Bulk g-C_3N_4 in an open ceramic container was heated at 500 °C for 2 h with a ramp rate of 5 °C/min. A light yellow powder of g-C_3N_4 nanosheets was obtained.

Characterization. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer using Cu irradiation. Their structure was determined by scanning electron microscopy (SEM) performed on Nova NanoSEM 430. Chemical compositions and valence band spectra of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, with a monochromatic Al K_α X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

Photoreduction of CO_2. The photoreduction experiments of CO_2 were conducted in a home-made Teflon-lined stainless reaction chamber with a quartz window at the top for light irradiation. The volume of the chamber was 50 cm^3. 20 mg of the sample was laid at the bottom of the reaction chamber. 0.1 ml H_2O was added in the system. Prior to filling the gaseous CO_2, the chamber was evacuated by a mechanical pump. Then, CO_2 bubbled from water was added to the chamber to reach a pressure of 0.06 MPa. The total amount of products generated in the chamber after light irradiation was determined by analyzing a 1 mL gas from the chamber with a gas chromatograph (Agilent Technologies). The hydrocarbon product was carried by argon gas, separated by chromatographic column (Agilent 19095P-Q04) at 100°C and detected by a FID detector at 250 °C. The hydrogen product was carried by argon gas, separated by chromatographic column (Agilent 19095P-MS0) at 100°C and detected by a TCD detector at 180°C. The CO product was carried by hydrogen gas, separated by chromatographic column (MNK PQ and MNK 5A) at 100°C and detected by a TCD detector at 250 °C. The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV). The wavelength of incident light in the visible light photocatalytic reactions was satisfied by using a 400 nm long-pass glass filter. The light density is around 200 mW/cm^2.

References

[1] F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angew. Chem. Int. Ed.*, 2006, **45**, 4467.

[2] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, 2009, **8**, 76.

[3] P. Niu, L. L. Zhang, G. Liu, H. M. Cheng, *Adv. Func. Mater.*, 2012, **22**, 4763.

[4] S. N. Habisreutinger, L. S. Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.*, 2013, **52**, 7372.

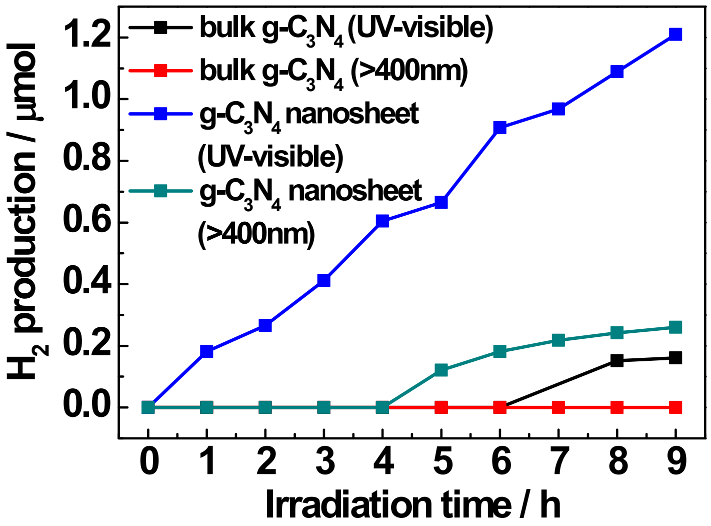

Fig. S1 Light irradiation-time dependent H_2 evolution during the photoreduction of CO_2 with bulk g-C_3N_4 and g-C_3N_4 nanosheets.

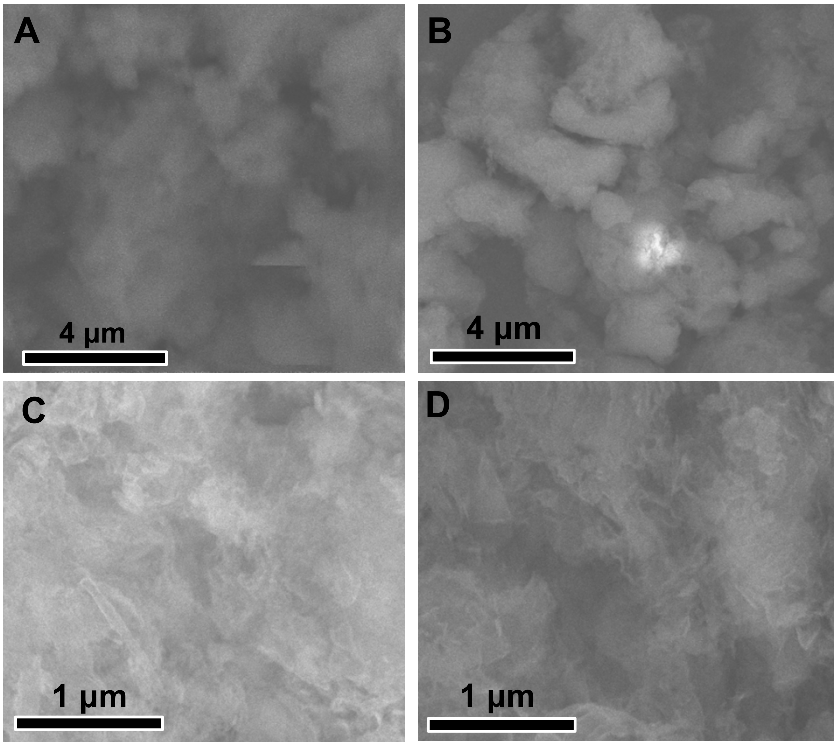

Fig. S2 SEM images of (A, B) bulk g-C_3N_4 and (C, D) g-C_3N_4 nanosheets before and after photoreduction of CO_2 under UV-visible light.

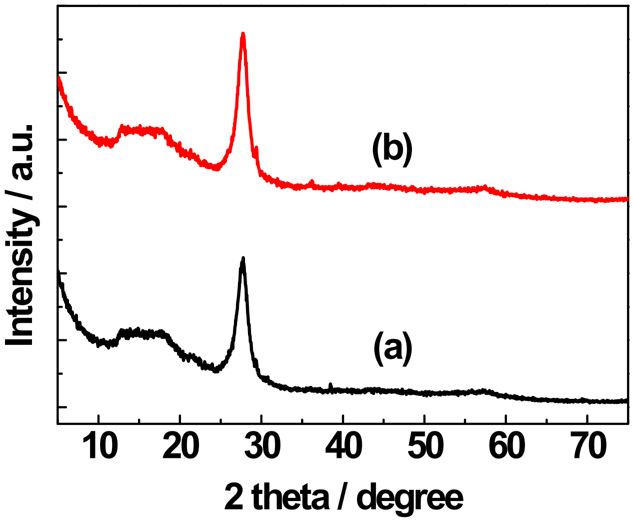

Fig. S3 XRD patterns of g-C_3N_4 nanosheets (a) before and (b) after photoreduction of CO_2 under UV-visible light.

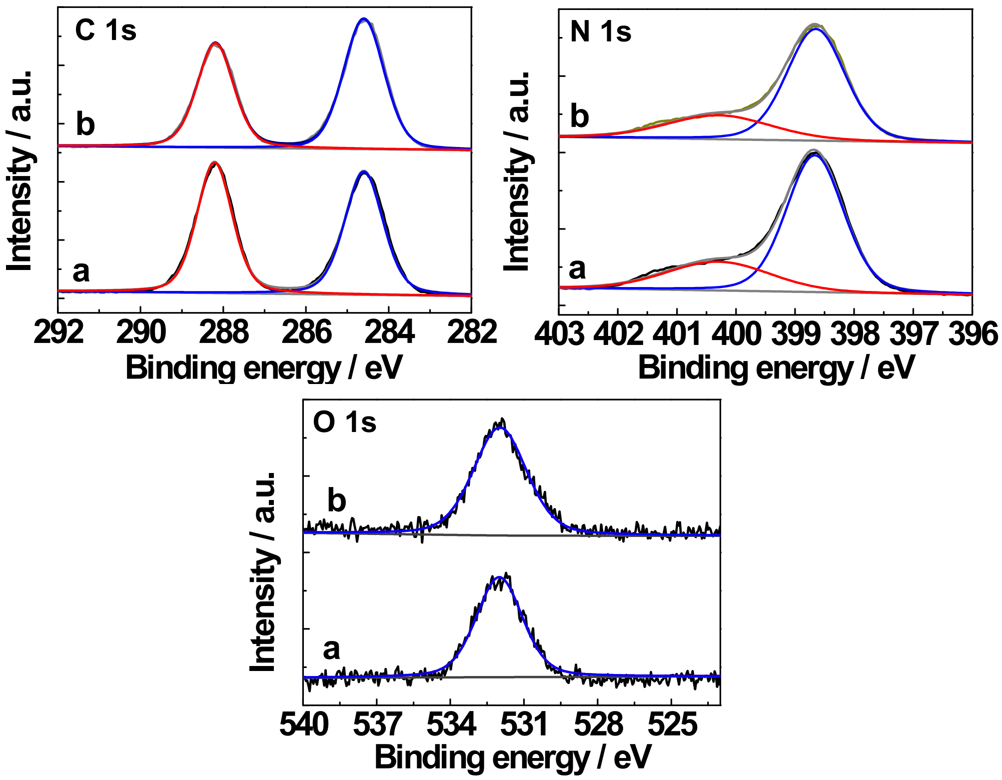

Fig. S4 High resolution XPS spectra of C 1s, N 1s, O 1s of g-C_3N_4 nanosheets (a) before and (b) after CO_2 photoreduction.

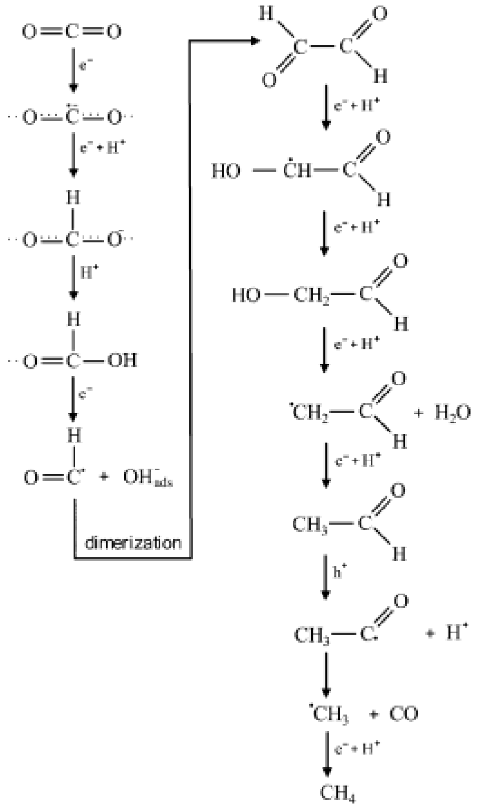

Fig. S5 The proposed glyoxal pathway of CO_2 reduction [4].

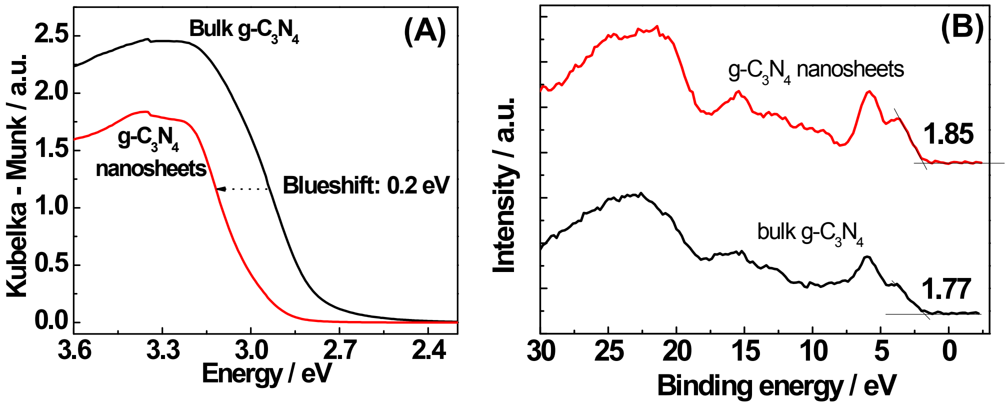

Fig. S6 (A) The UV-visible absorption spectra and (B) XPS valence band spectra of bulk g-C_3N_4 and g-C_3N_4 nanosheets.