

Supporting information for:

Carbon Dioxide Droplets Stabilized by g-C₃N₄

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Experimental Procedures

Materials. Triethanolamine (TEOA) was provided by Acros Organics, USA. CO₂ was supplied by Beijing Analytical Instrument Factory with purity of >99.99%. Dimethyl formamide (DMF), potassium chloride (KCl) and dimethylsulfoxide (DMSO) were purchased from Beijing Chemical Works. Urea and formic acid were supplied by Sinopharm Chemical Reagent Co., Ltd.

g-C₃N₄ preparation. g-C₃N₄ was prepared by thermal treatment of urea according to literature.¹ In a typical process, 5.0 g of urea was put in a porcelain boat with a cover. It was calcined in a muffle furnace and heated to 600 °C for 2 h in air with a heating rate of 2.5 °C min⁻¹. After cooled down to 300 °C with a rate of 10 °C min⁻¹, the final product was collected after naturally cooled down to the room temperature.

Characterization. X-ray diffraction (XRD) was performed using a Rigaku D/max-2500 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 200 mA. The morphology of catalyst was characterized by SEM (HITACHI S-4800) and HRTEM (JEM-2100F). Electrical conductivity meter was produced by Shanghai Precision Scientific Instrument Co., Ltd. (Model DDS-307). The porosity properties were obtained from N₂ adsorption-desorption isotherms using a NOVA 2200e system. The optical absorption was characterized by ultraviolet visible diffuse reflectance spectrum (UV-vis DRS, UV-2600, SHIMADZU).

Emulsion preparation. The sample cell is composed of a cubic stainless steel cell with two pairs of rounded quartz windows, which are 3.0 cm in diameter and 0.7 cm in thickness. The net volume of the cell is 6.0 mL, without the volume of magnetic stirring. In a typical experiment, the desired amount of aqueous dispersion of g-C₃N₄ was added into the sample cell. CO₂ was subsequently charged. As the desired pressure was reached under thermal equilibrium (25.0 °C) with the aid of a water bath, the emulsion was formed under vigorous stirring. The phase behavior of the CO₂/H₂O/g-C₃N₄ mixture was observed and photographed.

High-pressure conductivity measurement. The apparatus consists mainly of a cylindrical stainless steel vessel with a Teflon inner cell, a pair of electrode welded in the vessel, and an electrical conductivity meter connected outside (with a precision of $\pm 0.5\%$). The electrodes are made of Pt foil. The conductivity meter was calibrated with KCl standard aqueous solutions (0.01 M) before measurement. The net volume of the sample cell is 24.0 mL without the volume of magnetic stirring and electrodes. In a typical experiment, the desired amount of aqueous dispersion of g-C₃N₄ was added into the vessel, CO₂ was charged subsequently under vigorous stirring. The conductivities were recorded at desired pressure. The conductivities were self-calibrated into the standard value at 25.0 °C.

Photocatalytic reaction. The photocatalytic reaction was carried out in a self-designed cylindrical autoclaves. There is a circular quartz window (1.2 cm in diameter and 0.6 cm in thickness) on the top of the autoclave. The net volume of the sample cell is 4.0 mL. The Xe lamp (300 W) was provided by Zhongjiaojinyuan Co., Ltd. In a typical experiment for the photocatalytic reaction in the g-C₃N₄-stabilized CO₂/water emulsion at different pressure, 6 mg of g-C₃N₄ was pre-dispersed in TEOA/water solution (1mL/2mL), where TEOA acted as sacrificial electron donor during the photocatalytic reduction process of CO₂. Subsequently, CO₂ was charged under vigorous stirring. As the desired pressure was reached under thermal equilibrium (25.0 °C) with the aid of a water bath, artificial sunlight was supplied by a 300 W Xe lamp to start the photoreaction. After reaction for 2 h, CO₂ was removed by depressurization. The left mixture was centrifuged into solid and liquid phase. The product in the liquid phase was identified by ¹H NMR spectroscopy (BrukerAvance III 400 HD). The product yield was calculated from the integration of ¹H NMR peaks using dimethylsulfoxide as the internal standard.

Results and Discussion

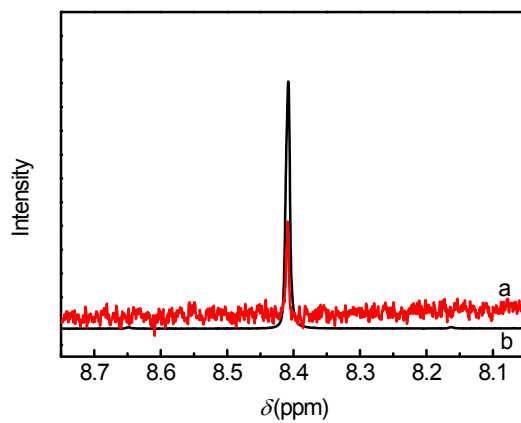


Figure S1. ¹H NMR spectrum of the liquid phase for the photocatalytic reaction in CO₂-in-water emulsion stabilized by g-C₃N₄ at 8.02 MPa. ¹H NMR spectrum for original solution (a) and the same sample with added formic acid (b).

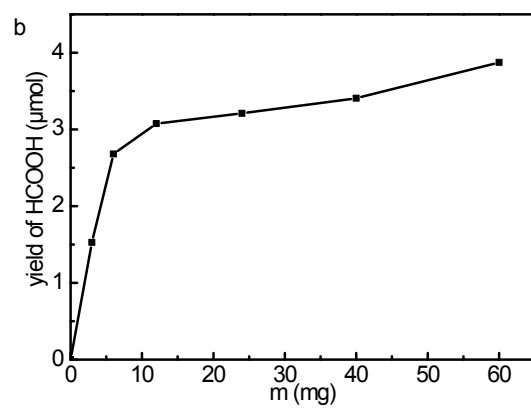
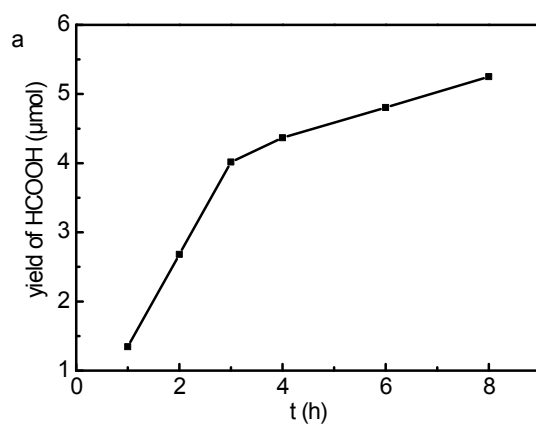


Figure S2. Yields of formic acid produced by the photocatalytic reaction in CO_2 -in-water emulsions with different reaction time (a) and different mass of $\text{g-C}_3\text{N}_4$ (b). The pressure was fixed at 8.02 MPa.

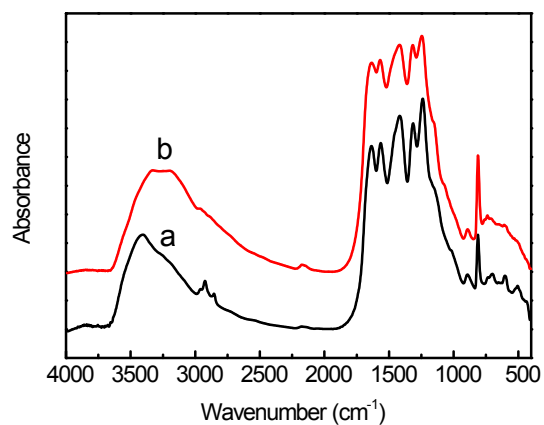


Figure S3. Infrared spectra of the pristine $g\text{-C}_3\text{N}_4$ (a), and that after used for the photocatalysis (b). The broad band between 3500-3000 cm^{-1} can be attributed to the strong N-H and N-H₂ stretches, which indicates the uncondensed amino functional groups. Peaks at 1636 cm^{-1} , 1564 cm^{-1} , and 1418 cm^{-1} are attributed to the stretching vibrations of heptazine-derived repeating units. Peaks at 1314 cm^{-1} and 1240 cm^{-1} are derived from the typical out-of-plane bending vibrations of heptazine rings. The absorption band at 893 cm^{-1} is attributed to the deformation mode of N-H, which results from the incomplete condensation of amino groups. The peak at 812 cm^{-1} is the characteristic breathing mode of heptazine.²

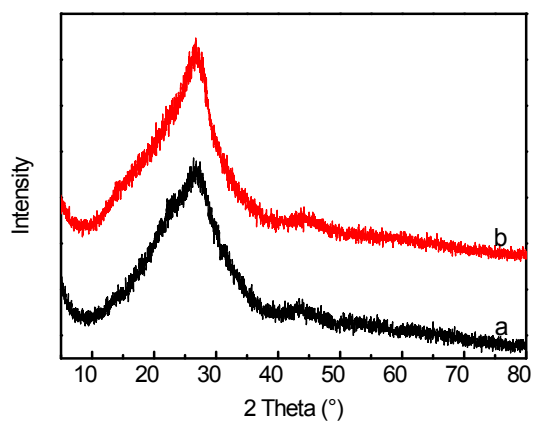


Figure S4. XRD patterns of the pristine g-C₃N₄ (a) and that after used for the photocatalysis (b).

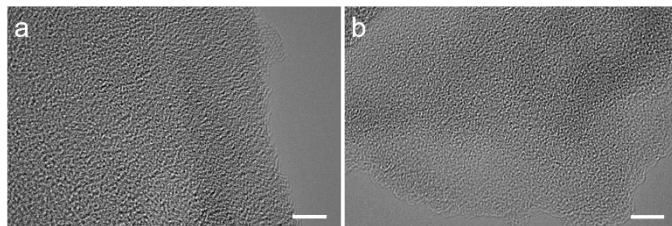


Figure S5. HRTEM images of the pristine g-C₃N₄ (a) and that after used for photocatalysis (b). Scale bars: 5 nm. No obvious difference was observed, indicating the structure stability of g-C₃N₄.

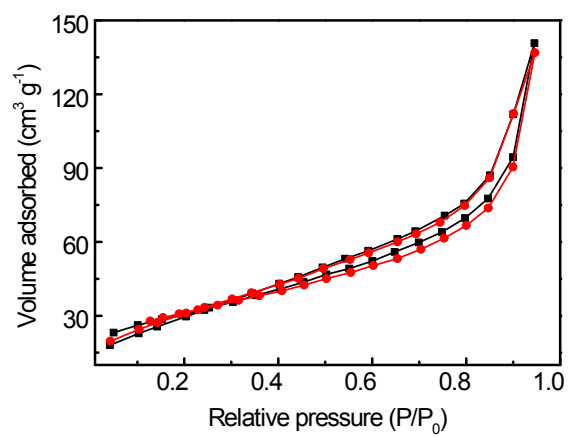
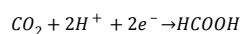


Figure S6. N₂ adsorption-desorption isotherms of the pristine g-C₃N₄ (black) and that after used for the photocatalysis (red). The BET surface areas of the g-C₃N₄ were determined to be 57.0 m² g⁻¹ and 54.6 m² g⁻¹, respectively.



Equation S1. Chemical reaction for the photocatalytic CO₂ reduction to formic acid.

Table S1. Production of formic acid and the corresponding reaction conditions catalysed by Ru-complex/g-C₃N₄ hybrid systems in literature.

Entry	Photocatalyst	Amount of formic acid formed (μmol)	TOF/μmol·g ⁻¹ ·h ⁻¹
1	RuP/C ₃ N ₄	5.8	290
2	RuP/Ag/C ₃ N ₄	19.2	960
3	RuRu'/C ₃ N ₄	0.6	30
4	RuRu'/Ag/C ₃ N ₄	42.3	2115
5	Ag/C ₃ N ₄	1.2	60
6	RuRu'/Cu/C ₃ N ₄	0.3	15
7	Cu/C ₃ N ₄	0	
8	RuRu'/Au/C ₃ N ₄	1.7	85
9	Au/C ₃ N ₄	0.5	25
10	RuP/C ₃ N ₄	8.8	1100
11	RuP/C ₃ N ₄	68	425
12	RuP/C ₃ N ₄	1.854	46.35

Reaction conditions: entry 1-9, photocatalyst, 4.0 mg (Ru complex loading, 3.4 μmol g⁻¹; metal loading, 5.0 wt %); solution, 4.0 mL of 4:1 (v/v) N,N-dimethylacetamide (DMA)/TEOA; reaction time, 5 h; λ > 400 nm.³ Entry 10, photocatalyst, 8.0 mg RuP (7.8 μmol g⁻¹)/C₃N₄; solution, 4.0 mL of 4:1 (v/v) DMA/TEOA; reaction time, 1 h, λ > 400 nm.⁴ Entry 11, photocatalyst, 8.0 mg RuP (7.8 μmol g⁻¹)/C₃N₄; solution, 4.0 mL of 4:1 (v/v) DMA/TEOA, reaction time, 20 h, λ > 400 nm.⁵ Entry 12, photocatalyst, 8.0 mg RuP (3.9 mmol g⁻¹)/C₃N₄; solution, 4.0 mL of 4:1 (v/v) acetonitrile/TEOA; reaction time, 5 h, λ > 400 nm.⁶ RuRu' is a Ru(II) binuclear complex, RuP is a mononuclear Ru(II) complex Ru{4,4'-(PO₃H₂)₂-2,2'-bipyridine}(CO)₂Cl₂. TOF values were calculated with respect to the amount of photocatalyst.

References

- 1 G Zhang, Z-A Lan, L Lin, S Lin and X Wang, *Chem. Sci.*, 2016, **7**, 3062.
- 2 (a) B. Zhu, P. Xia, W. Ho and J. Yu, *Appl. Surf. Sci.*, 2015, **344**, 188; (b) D. O. Adekoya, M. Tahir and N. A. S. Amin, *J. CO₂ Util.*, 2017, **18**, 261.
- 3 R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani and K. Maeda, *J. Am. Chem. Soc.*, 2016, **138**, 5159.
- 4 R. Kuriki, K. Sekizawa, O. Ishitani and K. Maeda, *Angew. Chem. Int. Ed.*, 2015, **54**, 2406.
- 5 K. Maeda, R. Kuriki, M. Zhang, X. Wang and O. Ishitania, *J. Mater. Chem. A*, 2014, **2**, 15146.
- 6 R. Kuriki, O. Ishitani and K. Maeda, *ACS Appl. Mater. Interfaces*, 2016, **8**, 6011.