

SUPPORTING INFORMATION

A Carbon Nitride/Fe Quaterpyridine Catalytic System for Photo-stimulated CO₂-to-CO Conversion with Visible Light

Claudio Cometto,^a Ryo Kuriki,^{b,c} Lingjing Chen,^d Kazuhiko Maeda,^b Tai-Chu Lau,^e Osamu Ishitani^b and Marc Robert^a

^aUniversité Paris Diderot, Sorbonne Paris Cité, Laboratoire d'Electrochimie Moléculaire, UMR 7591 CNRS, 15 rue Jean-Antoine de Baïf, F-75205 Paris Cedex 13, France

^bDepartment of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-NE-1 Okayama, Meguro-ku, Tokyo 152-8550, Japan

^cJapan Society for the Promotion of Science, Kojimachi Business Center Building, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan

^dSchool of Environment and Civil Engineering, Dongguan University of Technology, Guangdong 523808, P. R. China

^eDepartment of Chemistry and Institute of Molecular Functional Materials, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

Materials. Acetonitrile (Acros, >99.9%, extra dry over molecular sieves) and the supporting electrolyte NBu_4PF_6 (Fluka, purriss) were used as received. Triethanolamine (Kanto Chemical Co. Inc.) was distilled under reduced pressure (<1 Torr). **Fe(qpy)** was synthesized according to the procedure reported in the literature.¹ The mpg- C_3N_4 was prepared according to the previously reported method;² cyanamide (Alfa Aesar, >98%) was dissolved in a 40% dispersion of colloidal SiO_2 particles (Aldrich, LUDOX HS-40), of which size was 12 nm. The ratio of SiO_2 to cyanamide was 1/1 (w/w). After the mixture was stirred at 333 K for one night, the temperature of the mixture increased with a rate of 2.3 K min^{-1} up to 823 K, and then this temperature was kept for 4 h. The obtained powders were dispersed into an aqueous NH_4HF_2 (Sinopharm Chemical Reagents Co. >98%) and stirred for overnight to remove the silica template. The powders were corrected by filtration, followed by washing with distilled water and ethanol. The powders were dried at 343 K overnight. The g- C_3N_4 was prepared according to the previously reported method;² cyanamide was heated with a heating rate of 2.3 K min^{-1} up to 823 K, and then this temperature was kept for 4 h.

Physicochemical characterization. UV-vis absorption spectra were recorded on a JASCO V-565 or V-670 spectrophotometer. X-ray diffraction was measured with a Rigaku MiniFlex 600. The Brunauer-Emmett-Teller (BET) surface areas of samples were measured by using a BELSORP-mini apparatus (BEL Japan) at liquid nitrogen temperature (77 K).

Photocatalytic reactions. The mpg- C_3N_4 (8 mg) was dispersed into an CH_3CN -TEOA (4:1 v/v) solution (4 mL) containing **Fe(qpy)** (20 μM). The solution was poured to the Pyrex-glass test tube with an inner volume of 8 mL. After bubbling with CO_2 (Taiyo Nippon Sanso Co., > 99.995%) for ca. 30 min, the solution was irradiated by a 400 W high-pressure Hg lamp (SEN) combined with an aqueous NaNO_2 solution ($\lambda_{\text{ex}} > 400 \text{ nm}$). The gaseous reaction products, i.e., H_2 and CO , were analyzed by gas chromatography with a TCD detector (GL science, GC323), an activated carbon column, and argon as the carrier gas after the solution was kept in the dark enough time to remove the products from the solution to the gas phase. HCOOH in the liquid phase was analyzed using a capillary electrophoresis system (Otsuka Electronics Co. CAPI-3300). Note that using methanol as a sacrificial donor instead of TEOA did not lead to any reduction product. Note also that due to the fact that the Fe complex has absorption in the visible region, higher concentration of the complex would induce higher inner-filter effect to the photocatalytic reaction. It would thus lead to lower excitation efficiency for the mpg- C_3N_4 photosensitizer, and lower quantum yield for CO formation. Thus, too high concentration of the Fe complex is not suitable.

Apparent Quantum Yield. Apparent quantum yield (AQY) for CO formation was measured using a 300 W xenon lamp (Asahi Spectra, MAX-303) fitted with a 400-nm (FWHM = 10 nm) band-pass filter. The AQY was calculated on the following equation:

$$\text{AQY}(\%) = (2 \times R/I) \times 100$$

where R and I represent the rates of CO production and incident photons, respectively. The incident photons (ca. 13 mW) were measured using a spectroradiometer (Eko Instruments, LS-100). The AQYs were measured by using the reaction solutions containing various amounts of **Fe(qpy)** (20–200 μM) and mpg-C₃N₄ (20 mg or 40 mg), and the highest value was reported in the main text.

Table S1. Apparent quantum yield (AQY) of CO production under various reaction conditions^a

Entry	mpg-C ₃ N ₄ / mg	[Fe(qpy)] / μM	CO / μmol	AQY / %
1	20	20	1.1	1.6
2	20	60	2.9	4.0
3	20	100	3.3	4.2
4	20	200	2.4	3.2
5	40	100	2.3	3.1

^aSolvent, 10 mL of CH₃CN–TEOA (4:1 v/v) solutions; reaction vessel, Pyrex-glass cell (26 mL); light source, a 300 W Xe lamp with a band pass filter of 400 nm; light intensity, ca. 13 mW; irradiation time, 1 hour.

Isotope tracer experiments. Isotope-labeling experiment for CO formation *via* CO₂ reduction was performed using 4 mg of mpg-C₃N₄. ¹³CO₂ (13C 99%; Aldrich Co.) was introduced into a 2-mL CH₃CN–TEOA (4:1 v/v) solution containing 20 μM of **Fe(qpy)** and 4 mg of mpg-C₃N₄ after degassed by three-times freeze-pump-thaw cycles, and the final pressure in the test tube was about 80 kPa. The reaction solution in the sealed test tube was irradiated for 4 hours by using the 400 W high-pressure Hg lamp (SEN) in combination with the NaNO₂ solution filter. The gas phase was analyzed by using a gas chromatography with a mass-spectrometer (Shimadzu, QP-2010-Ultra) equipped with a Molsieve5A capillary column.

Cyclic voltammetry. The working electrode was a 3 mm-diameter glassy carbon (Tokai) disk carefully polished using diamond paste of various sizes (from 15 to 1 μm), and ultrasonically rinsed in absolute ethanol and dried before use. The counter-electrode was a platinum wire and the reference electrode was an aqueous SCE electrode. All experiments were carried out under argon or carbon dioxide atmosphere at 298 K, the double-wall jacketed cell being thermostated by

circulation of water. Cyclic voltammograms were obtained by use of a Metrohm AUTOLAB instrument. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument.

Additional data

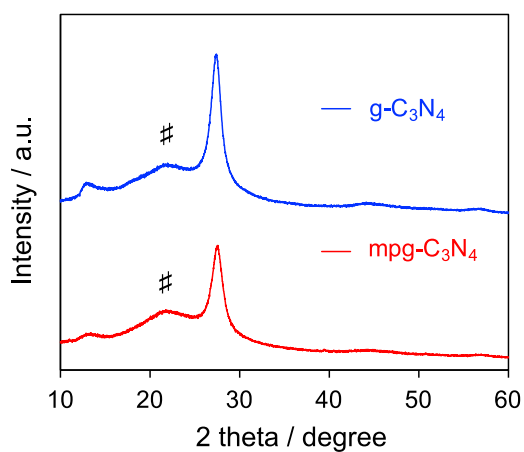


Figure. S1. XRD patterns of g-C₃N₄ and mpg-C₃N₄. # is attributed to glass of the used cell.

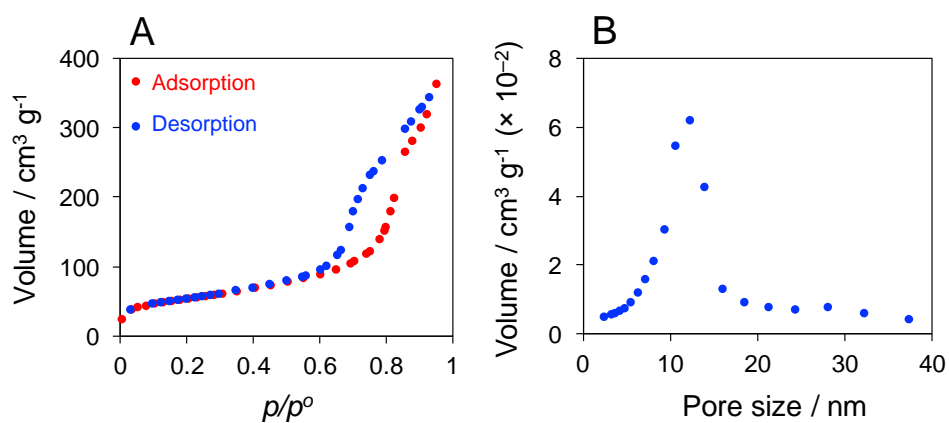


Figure. S2. (A) Nitrogen adsorption-desorption isotherms and (B) the corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution curve of mpg-C₃N₄.

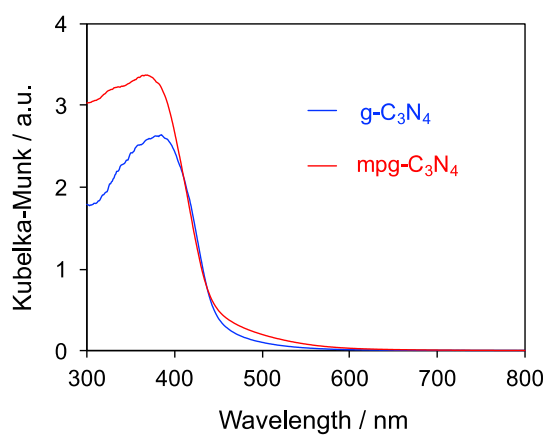


Figure. S3. UV-visible diffuse reflectance spectra of g-C₃N₄ and mpg-C₃N₄.

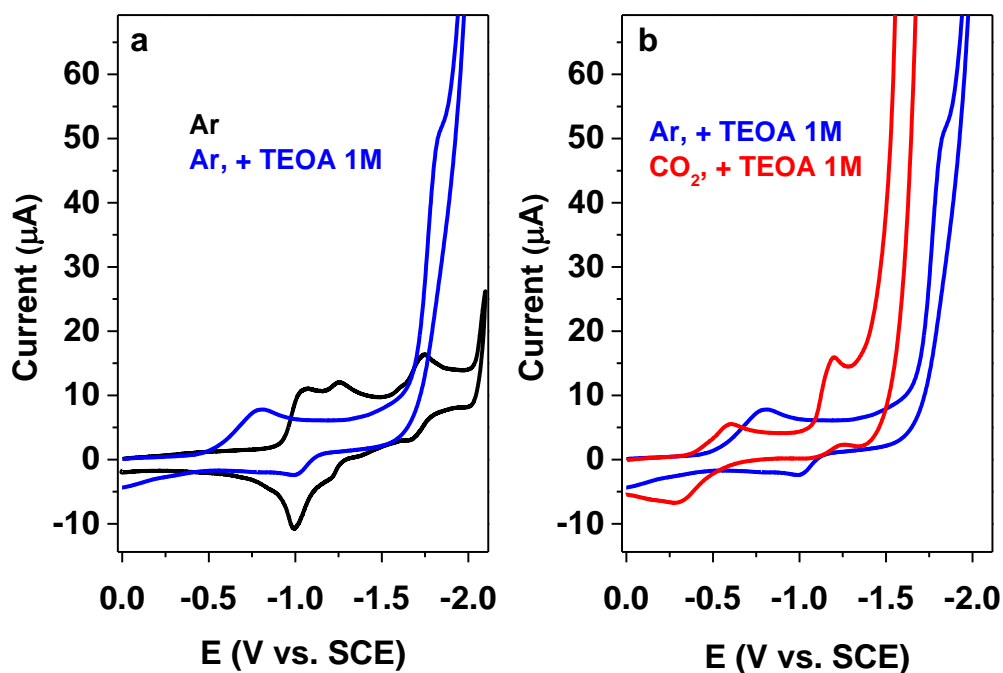


Figure. S4. CVs of **Fe(qpy)** (0.5 mM) in CH_3CN solution (0.1 M NBu_4PF_6) at $v = 0.1$ V/s and $T = 298$ K: **a**, in absence (black) and presence (blue) of TEOA 1 M, under Ar; **b**, under Ar (blue) and CO_2 (red), in presence of TEOA 1 M.

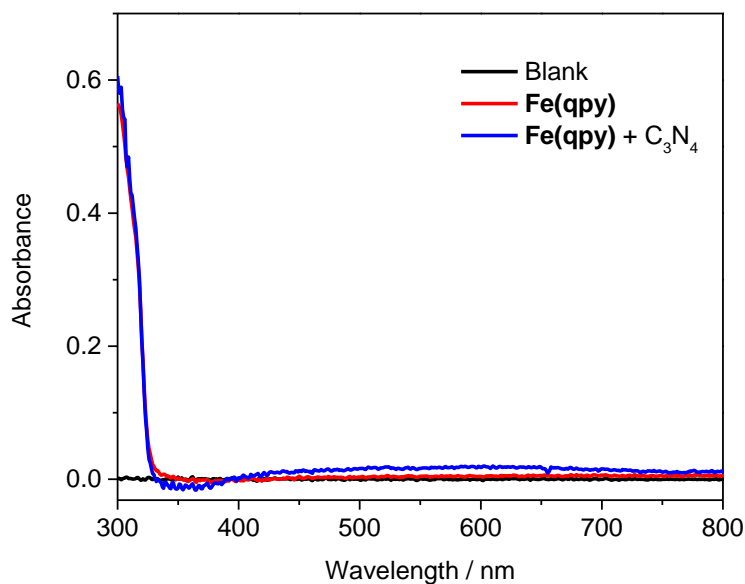


Figure. S5. UV-visible absorption spectra of the MeCN/TEOA (4:1, 4 ml) solutions containing **Fe(qpy)** (20 μM , red line).

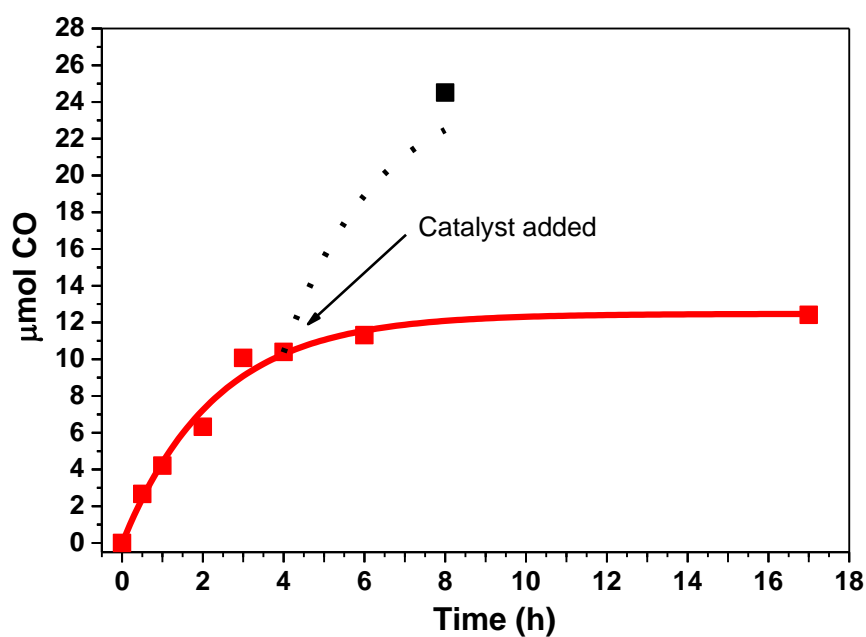


Figure. S6. Long-term activity of **Fe(qpy)/mpg-C₃N₄** (red solid line) and effect of adding more catalyst after 4 h (black dashed line).

References

- (1) Guo, Z.; Cheng, S.; Cometto, C.; Anxolabéhère-Mallart, E.; Ng, S. M.; Ko, C. C.; Liu, G.; Chen, L.; Robert, M.; Lau, T. C. *J. Am. Chem. Soc.* **2016**, *138*, 9413–9416.
- (2) Maeda, K.; Kuriki, R.; Zhang, M.; Wang, X.; Ishitani, O. *J. Mater. Chem. A* **2014**, *2*, 15146–15151.