Electronic Supplementary Information (ESI)

A polymeric-semiconductor–metal-complex hybrid photocatalyst for visible-light CO_2 reduction

Kazuhiko Maeda,[1,2] Keita Sekizawa,[1] and Osamu Ishitani[1]*

[1] *Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-NE-2 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.*

[2] *Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan.*

*To whom corresponding author should be addressed.

TEL: +81-3-5734-2239, FAX: +81-3-5734-2284, Email: maedak@chem.titech.ac.jp

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Experimental section

Synthesis of mpg-C_3N_4

According to the previous method[S1,S2] with some modifications, mesoporous graphitic carbon nitride (mpg-C_3N_4) was prepared by heating cyanamide (40 g) dissolved with a 40 wt% dispersion of 12 nm SiO_2 particles (Ludox HS40, Aldrich) in water, with stirring at 333 K overnight. The mass ratio of silica/cyanamide was 1/1. The resulting transparent mixtures were then heated at a rate of 2.3 K min^{-1} over 4 h to reach a temperature of 823 K and then kept at this temperature for another 4 h. The as-obtained powder was treated with a NH_4F solution (more than 1 molar ratio than SiO_2) for 24 h to remove the silica template. The treated powder was then centrifuged and washed three times with distilled water and twice with ethanol. Finally, the sample was dried at 373 K in air in an oven overnight.

Elemental analysis showed that the C/N molar ratio of the as-prepared sample was 0.71, smaller than the theoretical value (C/N = 0.75). This is due to the presence of hydrogen that results from structural defects and surface NH_2 groups.[S2]

Adsorption of the Ru complex on mpg-C_3N_4

Ru was adsorbed onto the surface of mpg-C_3N_4 at room temperature. The solid complex was dissolved in methanol, and mpg-C_3N_4 (50 mg) was dispersed in the methanol solution containing an appropriate amount **Ru** (25 mL) under continuous stirring in the dark to establish adsorption/desorption equilibrium. After 20–24 h, the solid was separated from the suspension by filtration, and the resulting supernatant was then analysed by using a UV-visible spectrometer (Jasco, V-570). The amount of **Ru** adsorbed was calculated from the difference in absorbance between the initial solution and the supernatant. The resulting solid sample was washed with methanol several times, and was dried under vacuum at room temperature overnight.

Photocatalytic reaction

Reactions were conducted at room temperature using a test tube of 11 mL capacity as a reaction vessel that contains 4 mL of solution (20 vol.% triethanolamine in acetonitrile unless otherwise stated) and 8 mg of photocatalyst powder. A 450 W high-pressure Hg lamp (Ushio) was employed as a light source, in combination with an aqueous $NaNO_2$ solution to allow for visible light irradiation ($\lambda > 400$ nm). Prior to irradiation, the suspension was purged with CO_2 (Taiyo Nippon Sanso Co., > 99.995%) for 20–30 min. The gaseous reaction products H_2 and CO were analysed using a gas chromatograph with a TCD detector (GL science, GC323), an active carbon column, and argon carrier gas. HCOOH in liquid phase was analysed using a capillary-electrophoresis system (Otsuka Electronics Co. CAPI–3300). Before analysis, the reacted solution was subject to filtration to remove the photocatalyst particle. After diluting the resulting solution with H_2O (1:1 v/v), analyses by capillary-electrophoresis were made.

Apparent quantum yields (AQYs) for HCOOH production were measured using a 300 W xenon lamp (Asahi Spectra, MAX-303) fitted with a band pass filter, and were estimated by the equation:

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

where R and I represent the rates of HCOOH production and incident photons, respectively. The total number of incident photons (30 mW) was measured using a spectroradiometer (Eko Instruments, LS-100).

Isotope-tracer experiments

$^{13}CO_2$ (^{13}C 99%) was purchased from Aldrich Co., and was introduced into photocatalyst suspensions after degassing them by freeze-pump-thaw cycling. It was confirmed by means of GC/MS (Shimadzu, QP–2010–Ultra) and ^{13}C–NMR that no contamination of ^{13}CO and $H^{13}COOH$ in the $^{13}CO_2$ gas could be identified. After the samples were irradiated, the gas phase was analysed by GC/MS with a Molsieve5A capillary column. The ^{1}H–NMR (no-deuterium method) and

^{13}C–NMR spectra of reactant solutions were also measured using JEOL ECX–500. Before measurements, solids were removed by filtration, and reactant solutions were treated with CO_2 to adjust the pH. The acquisition time was 1 s, with the integration number of 20000 and 256 for measuring ^{13}C–NMR and ^{1}H–NMR, respectively.

References

S1. X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu and M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680.

S2. F. Goettmann, A. Fischer, M. Antonietti and A. Thomas, *Angew. Chem. Int. Ed.* **2006**, *45*, 4467.

Table S1. Apparent quantum yields of HCOOH production by **Ru**/mpg-C_3N_4 photocatalyst at 400 nm under various reaction conditions[a]

Entry	Amount of photocatalyst / mg	Reaction time / h	Amount of HCOOH produced / nmol	Apparent quantum yield / %
1	10	1	1878	1.0
2	10	2	3310	0.9
3	10	5	7139	0.8
4	20	1	2008	1.1
5	30	1	2640	1.5

[a] Reaction conditions: photocatalyst, **Ru** (39.2 μmol g^{-1})-loaded mpg-C_3N_4; solution, a mixture of acetonitrile and triethanolamine (4:1 v/v) 10 mL; reaction vessel, Pyrex top-irradiation type cell with septums (26 mL capacity); light source, 300 W xenon lamp with a band pass filter of 400 nm; light intensity, 30 mW.

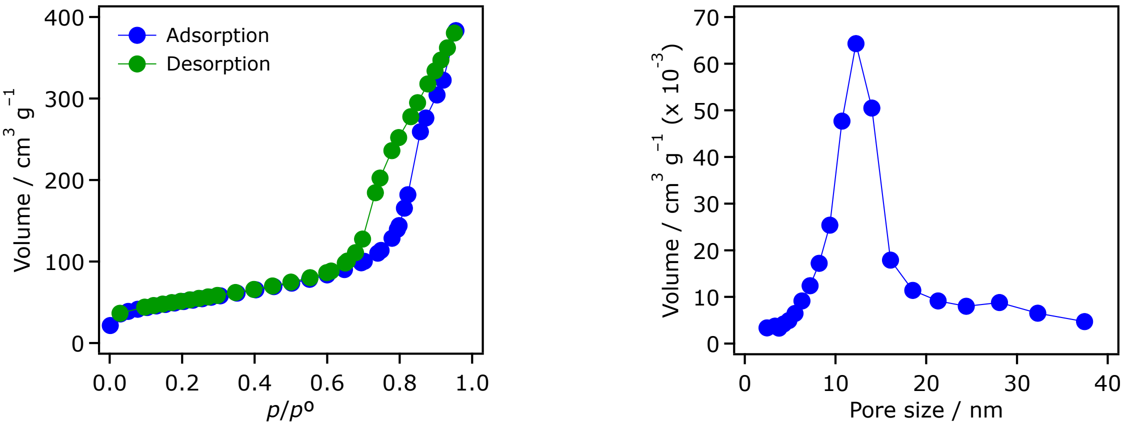

Fig. S1. Nitrogen adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution curve of mpg-C_3N_4. The pore-size distribution was determined from the desorption branch of the isotherms.

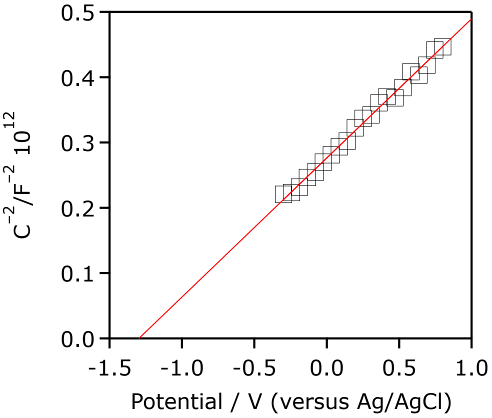

Fig. S2. Mott-Schottky plot of mpg-C_3N_4 recorded at 1.5 kHz.

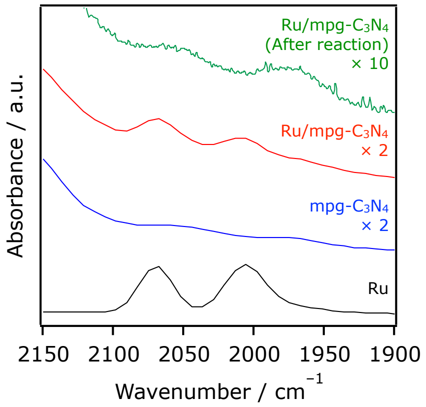

Fig. S3. FT-IR spectra of **Ru**, mpg-C_3N_4, and **Ru**(39.2 μmol g^{-1})/mpg-C_3N_4 (before and after photocatalytic reaction; Table S1, entry 3) in KBr pellets. The reacted sample was collected by filtration, followed by washing with methanol and drying in air at room temperature overnight.

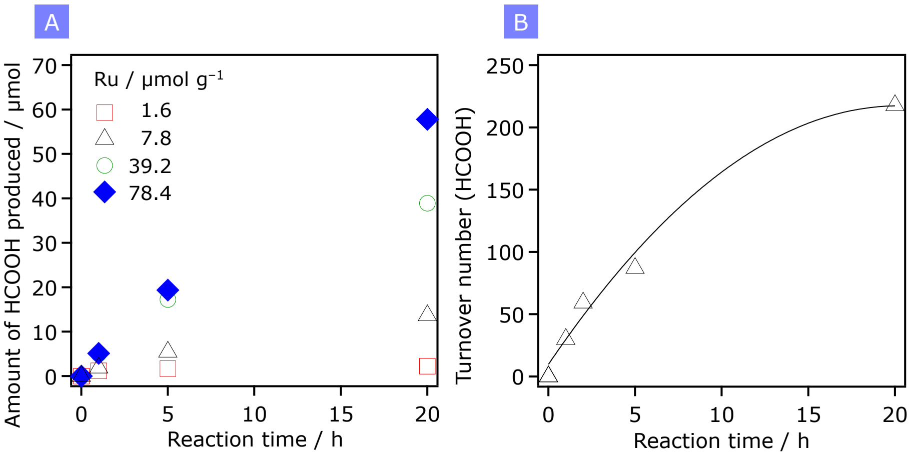

Fig. S4. (A) Time courses of HCOOH production under visible light ($\lambda > 420$ nm) by **Ru**/mpg-C_3N_4 with different amount of **Ru** added. (B) The corresponding data for the turnover number of **Ru**(7.8 μmol g^{-1})/mpg-C_3N_4. Reaction conditions: photocatalyst, **Ru**(7.8 μmol g^{-1})-loaded mpg-C_3N_4 8.0 mg; solution, a mixture of acetonitrile and triethanolamine (4:1 v/v) 4 mL; reaction vessel, Pyrex test tube with a septum (11 mL capacity); light source, 450 W xenon lamp with a $NaNO_2$ solution filter.

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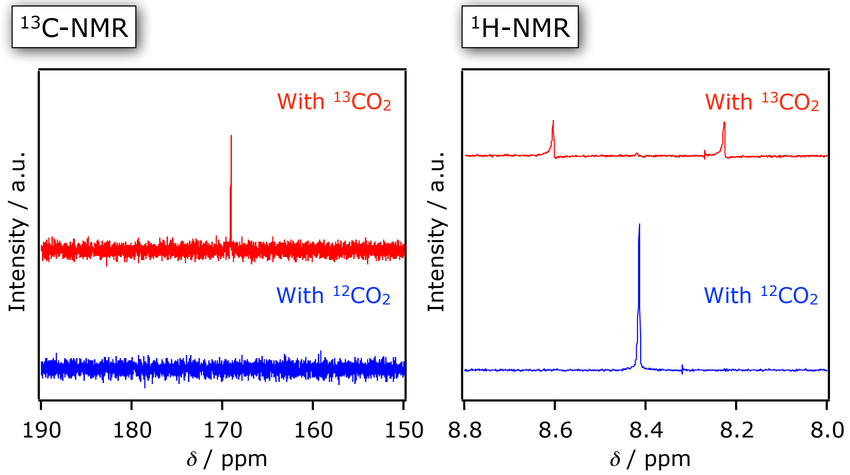

Fig. S5. ^{13}C–NMR and ^{1}H–NMR spectra of a reacted solution (acetonitrile/triethanolamine, 4:1 v/v, 2 mL) containing 4.0 mg of **Ru**(39.2 μmol g^{-1})-loaded mpg-C_3N_4, which was measured after filtration. The photocatalyst suspension was subject to visible-light irradiation from a 450 W high-pressure mercury lamp with a $NaNO_2$ solution filter for 5 h under $^{13}CO_2$ (610 Torr) and saturated CO_2.

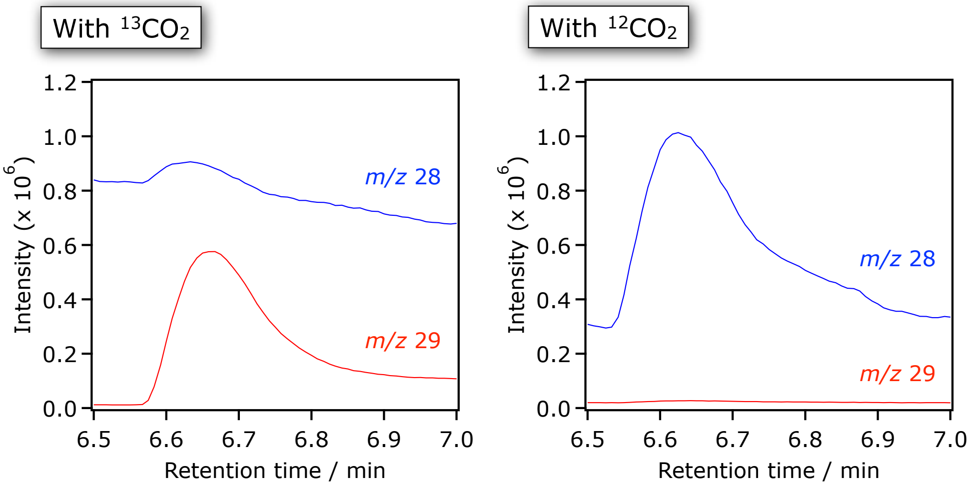

Fig. S6. Gas chromatograms of the gas phase products using mass spectrometry as a detector (*m/z* 28 and 29). A mixture of acetonitrile and triethanolamine (4:1 v/v) solution (2 mL) containing 4.0 mg of **Ru**(39.2 μmol g^{-1})-loaded mpg-C_3N_4 was subject to visible-light irradiation from a 450 W high-pressure mercury lamp with a $NaNO_2$ solution filter for 5 h under $^{13}CO_2$ (610 Torr) and saturated CO_2. The molar ratio of ^{12}CO (*m/z* 28) to ^{13}CO (*m/z* 29) in the left panel was 13:87 based on the area ratio with corrected ^{12}CO and ^{13}CO sensitivities.