

Supporting Information

Hybrid Photocathode Consisting of CuGaO₂ p-Type Semiconductor and a Ru(II)–Re(I) Supramolecular Photocatalyst: Non-Biased Visible-Light-Driven CO₂ Reduction with Water Oxidation

Hiromu Kumagai,^a Go Sahara,^a Kazuhiko Maeda,^a Masanobu Higashi,^b Ryu Abe,^b and Osamu Ishitani*,^a

^aDepartment of Chemistry, School of Science, Tokyo Institute of Technology, O-okayama 2-12-1-NE-1, Meguro-ku, Tokyo 152-8550, Japan.

^bDepartment of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

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1. Experimental

Electrochemical impedance spectroscopy of the bare CuGaO₂ electrode was carried out using a three-electrode setup with a potentiostat (BAS, ALS660E), a Pt wire counter electrode, and a Ag/AgCl (in a saturated aqueous solution of KCl) reference electrode. A 50 mM aqueous solution of NaHCO₃ (pH 6.6) saturated with CO₂ was used as the electrolyte. The Mott–Schottky plot was measured at a frequency of 50 Hz and was calculated using Eq. S1:

$$1/C^2 = (2/\varepsilon \varepsilon_0 q N_A)(E - E_{\text{FB}} - k_{\text{B}}T/q), \quad (\text{S1})$$

where C is the capacitance at the solid–liquid interface, ε is the relative permittivity, ε_0 is the permittivity of vacuum, N_A is the density of acceptors, E is the applied electrode potential, E_{FB} is the flat band potential, k_{B} is the Boltzmann constant, T is the absolute temperature, and q is the elementary charge.

Estimations of electrochemically active Ru species in the photoelectrodes were conducted by cyclic voltammetry, as in the reported procedure.¹ A three-electrode setup was utilized with a potentiostat (BAS, ALS660E), a Pt wire counter electrode, and a Ag/AgCl (in a saturated aqueous solution of KCl) reference electrode. CH₃CN purged with N₂ and containing 0.1 M Et₄NBF₄ was used as the electrolyte. The scan rate was set at 5 mV s⁻¹, and the amount of electrochemically active Ru species (n/mol) was calculated using Eq. S2 from the third cycle for each sample:

$$n = S/F \nu, \quad (\text{S2})$$

where S is the area of the oxidation peak of Ru^{II}/Ru^{III} (A V), F is the Faraday constant (96485 C mol⁻¹), and ν is the sweep rate (V s⁻¹).

2. Supporting Figures and Tables

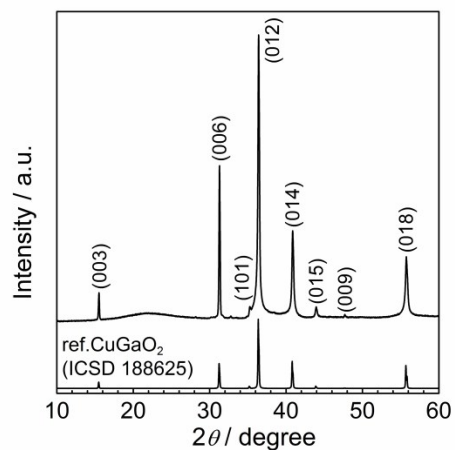


Figure S1. XRD pattern of CuGaO_2 powder. Information on the crystal plane attribution of the diffraction peaks was obtained from the literature.² The broad peak around 22° was derived from the glass holder.

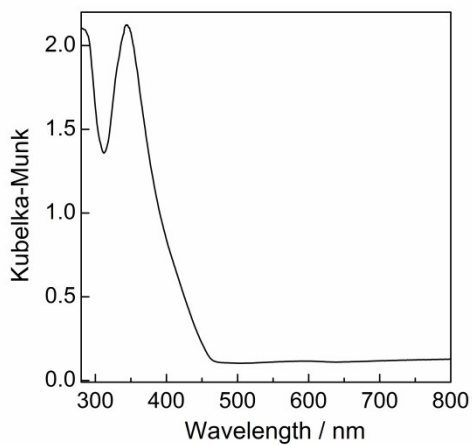


Figure S2. UV-vis diffuse reflectance spectrum of synthesized CuGaO_2 powder, which was similar to that reported in previous research into CuGaO_2 powder.^{3,4}

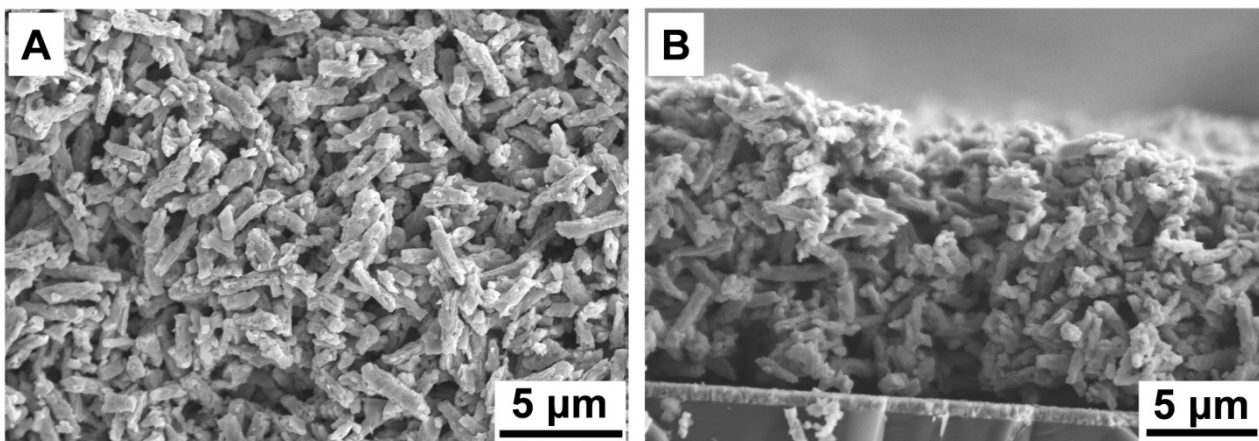


Figure S3. Top-view (A) and cross-sectional (B) SEM images of the $\text{CuGaO}_2/\text{FTO}$ electrode.

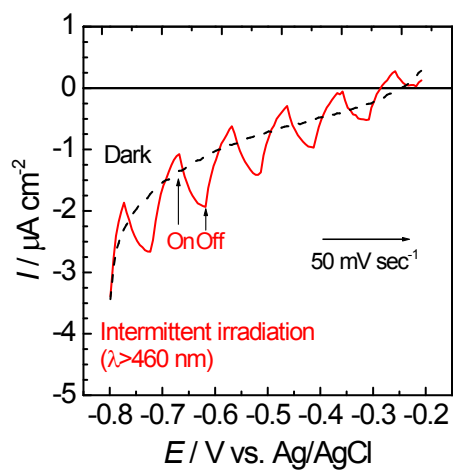


Figure S4. Current–potential curves of a pristine CuGaO₂ under intermittent irradiation of visible light ($\lambda_{\text{ex}} > 460$ nm).

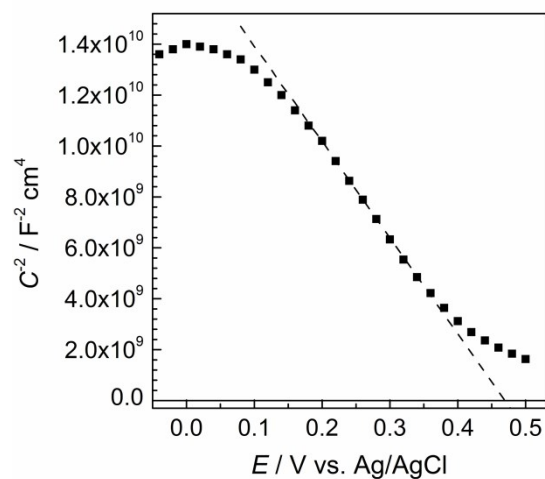


Figure S5. Mott–Schottky plot for the CuGaO₂ electrode in a 50 mM aqueous solution of NaHCO₃ (pH 6.6) saturated with CO₂.

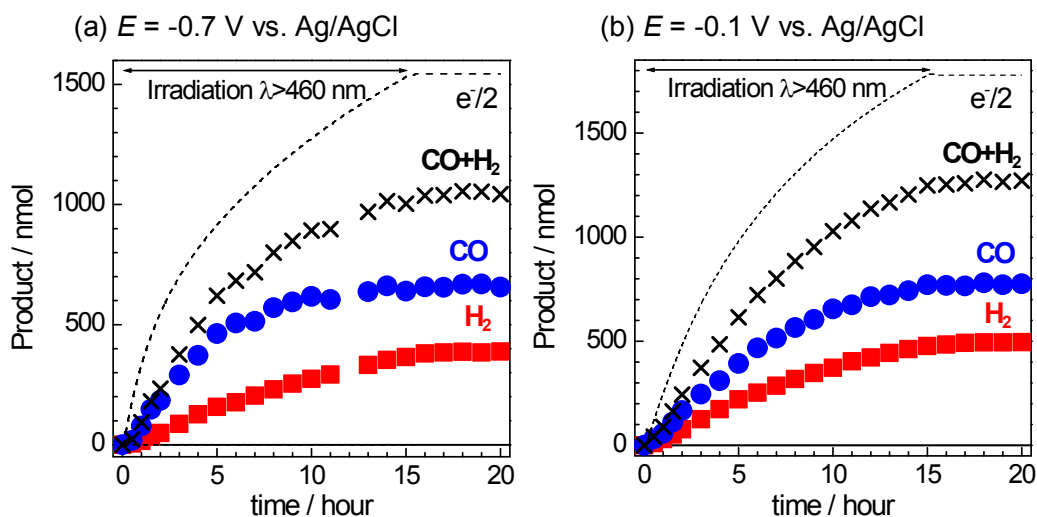


Figure S6. Time courses of the chemical products (CO and H₂) and a half amount of electrons passing through the **RuRe**/CuGaO₂ photocathode under continuous visible-light irradiation ($\lambda_{\text{ex}} > 460$ nm) at (a) -0.7 V and (b) -0.1 V vs. Ag/AgCl. A 50 mM aqueous solution of NaHCO₃ (pH 6.6) saturated with CO₂ was used as the electrolyte.

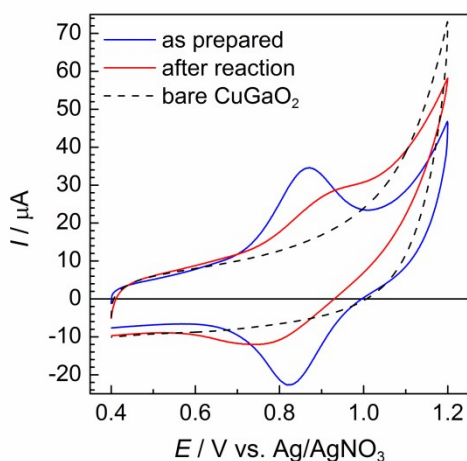


Figure S7. Cyclic voltammograms of the **RuRe**/CuGaO₂ photocathode in CH₃CN purged with N₂ and containing 0.1 M Et₄NBF₄ as the electrolyte recorded at a scan rate of 5 mV s⁻¹. The third cycle is shown for each sample. The specimen denoted “after reaction” was irradiated for 15 h at a potential of -0.3 V vs. Ag/AgCl.

Table S1. Estimated amount of **RuRe** on the RuRe/CuGaO₂ electrode.

Entry	Estimated amount of RuRe /nmol	
	Adsorbed (from absorbance)	Electrochemically active (from cyclic voltammetry)
1 (as prepared)	7.9	5.3
2 (after reaction)	7.7	0.9

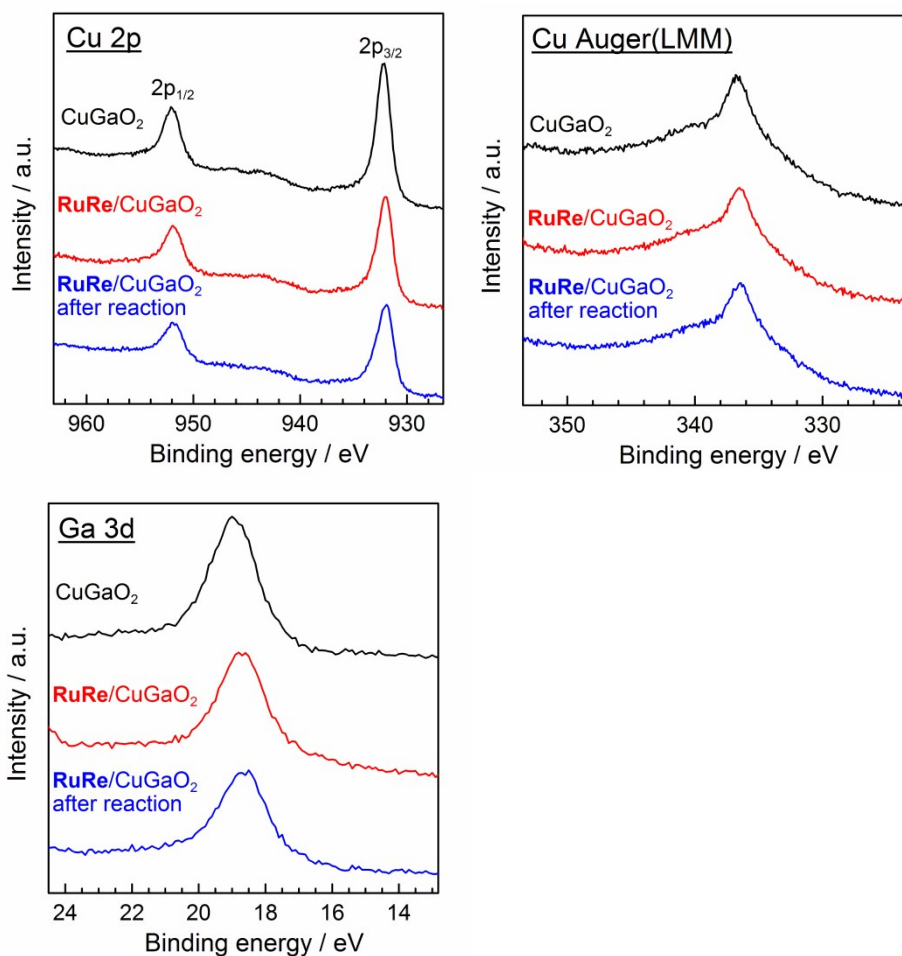


Figure S8. XPS spectra of the **RuRe**/CuGaO₂ photocathode before and after the photoelectrochemical reaction. The spectra of bare CuGaO₂ are also shown. The binding energies were corrected by the C 1s peak (284.6 eV) for each sample. The specimen denoted “after reaction” was irradiated for 15 h at a potential of -0.3 V vs. Ag/AgCl. Note that peaks of Ru and Re could not be identified for each sample, possibly due to the low loading density of **RuRe** on CuGaO₂.

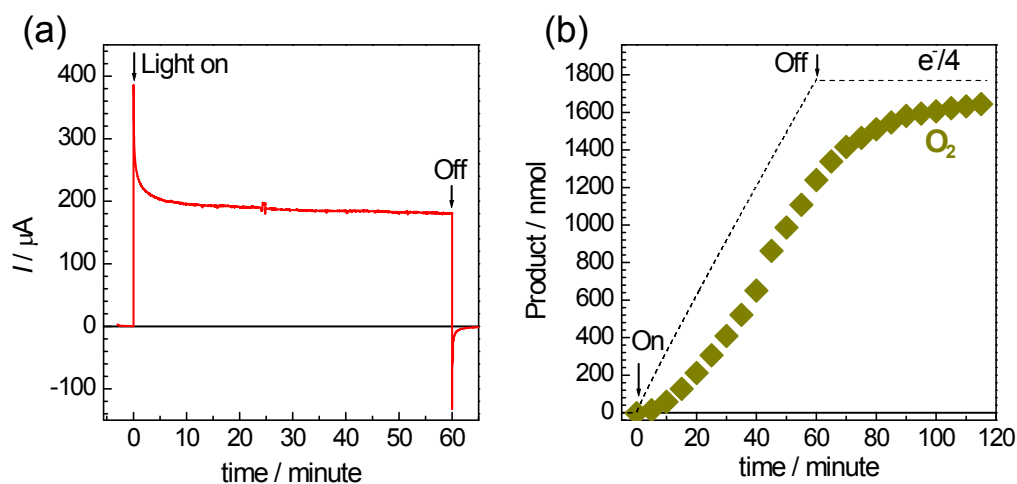


Figure S9. Time courses of photocurrent (a) and amount of evolved O_2 in the liquid phase (b) using the $CoO_x/TaON$ photoanode, which was irradiated at $\lambda_{ex} > 400$ nm at a potential of +0.2 V vs. Ag/AgCl under a CO_2 atmosphere.

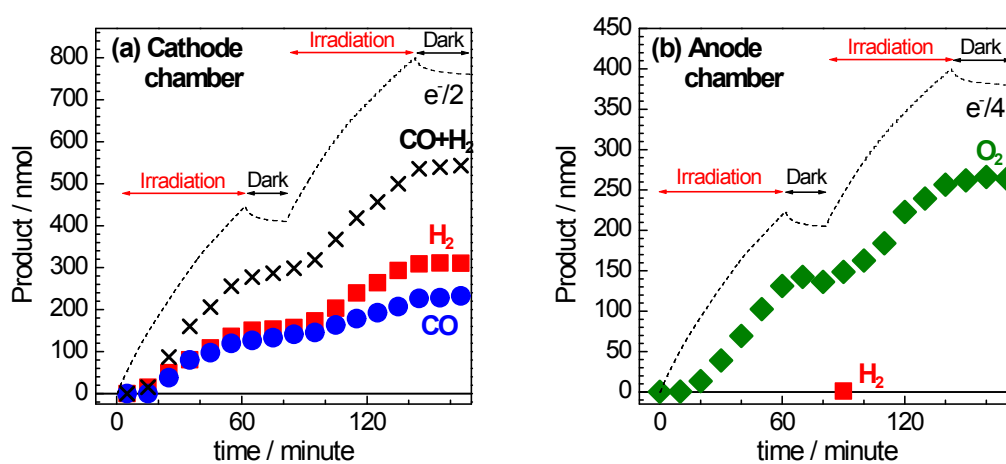


Figure S10. Time courses of the chemical products in the cathode chamber (a) and anode chamber (b) during Z-scheme photoelectrolysis.

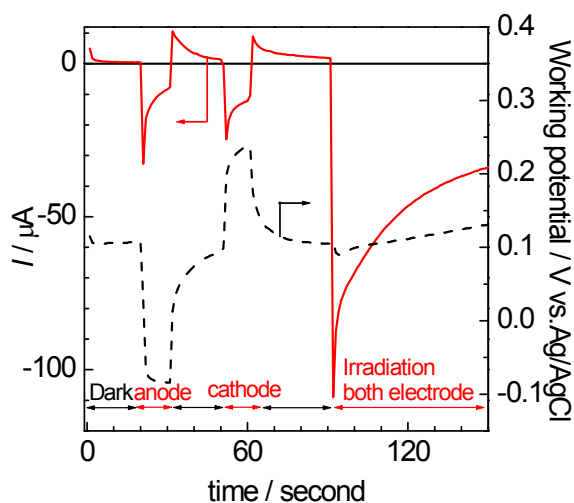


Figure S11. Photocurrent and working potential of the electrodes during visible-light irradiation of either the **RuRe**/CuGaO₂ photocathode or the CoO_x/TaON photoanode in the photoelectrochemical cell, or both electrodes together, under short-circuit conditions.

3. References

- (1) Sahara, G.; Kumagai, H.; Maeda, K.; Kaeffer, N.; Artero, V.; Higashi, M.; Abe, R.; Ishitani, O. *J. Am. Chem. Soc.* **2016**, *138*, 14152–14158.
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- (3) Lekse, J. W.; Underwood, M. K.; Lewis, J. P.; Matranga, C. *J. Phys. Chem. C* **2012**, *116*, 1865–1872.
- (4) Lee, M.; Kim, D.; Yoon, Y. T.; Kim, Y. Il. *Bull. Korean Chem. Soc.* **2014**, *35*, 3261–3266.