Supporting Information

Hybrid Photocathode Consisting of CuGaO$_2$ p-Type Semiconductor and a Ru(II)–Re(I) Supramolecular Photocatalyst: Non-Biased Visible-Light-Driven CO$_2$ Reduction with Water Oxidation

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1. Experimental

Electrochemical impedance spectroscopy of the bare CuGaO$_2$ 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 NaHCO$_3$ (pH 6.6) saturated with CO$_2$ was used as the electrolyte. The Mott–Schottky plot was measured at a frequency of 50 Hz and was calculated using Eq. S1:

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 q N_A} (E - E_{FB} - k_B T/q),
\]

where $C$ is the capacitance at the solid–liquid interface, $\varepsilon$ is the relative permittivity, $\varepsilon_0$ 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. CH$_3$CN purged with N$_2$ and containing 0.1 M Et$_4$NBF$_4$ 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:

\[
n = \frac{S}{F v},
\]

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 $v$ is the sweep rate (V s$^{-1}$).
2. Supporting Figures and Tables

Figure S1. XRD pattern of CuGaO₂ 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 CuGaO₂ powder, which was similar to that reported in previous research into CuGaO₂ powder.³,⁴

Figure S3. Top-view (A) and cross-sectional (B) SEM images of the CuGaO₂/FTO electrode.
Figure S4. Current–potential curves of a pristine CuGaO$_2$ under intermittent irradiation of visible light ($\lambda_{\text{ex}} > 460$ nm).

Figure S5. Mott–Schottky plot for the CuGaO$_2$ electrode in a 50 mM aqueous solution of NaHCO$_3$ (pH 6.6) saturated with CO$_2$. 
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 ($\lambda_{ex} > 460$ 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Estimated amount of RuRe/nmol</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Adsorbed (from absorbance)</td>
</tr>
<tr>
<td>1 (as prepared)</td>
<td>7.9</td>
</tr>
<tr>
<td>2 (after reaction)</td>
<td>7.7</td>
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</tbody>
</table>
Figure S8. XPS spectra of the RuRe/CuGaO$_2$ photocathode before and after the photoelectrochemical reaction. The spectra of bare CuGaO$_2$ 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 CuGaO$_2$. 
Figure S9. Time courses of photocurrent (a) and amount of evolved O₂ in the liquid phase (b) using the CoOₓ/TaON photoanode, which was irradiated at λ<sub>ex</sub> > 400 nm at a potential of +0.2 V vs. Ag/AgCl under a CO₂ 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/CuGaO$_2$ photocathode or the CoO$_x$/TaON photoanode in the photoelectrochemical cell, or both electrodes together, under short-circuit conditions.

3. References


