Supporting Information

Durable Photoelectrochemical CO₂ Reduction with Water Oxidation using a Visible-Light Driven Molecular Photocathode

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Figure S1. Absorption spectra of \textit{VRu-N^N} (red line) and \textit{cis-(CO)-trans-(Cl)-Ru(dmb)(CO)\textsubscript{2}Cl\textsubscript{2}} (blue line) in MeCN solutions.

Figure S2. UV-vis absorption spectra of NiO/PRu-poly-Ru-N^N (red line), and NiO/PRu-poly-Ru-RuCAT1 (black dashed line). FTO electrode was employed as the background.
Figure S3. Time courses of photocurrent using NiO/PRu-poly-Ru-RuCAT1 (electrode area: 2.5 cm$^{-2}$) at $E = -0.7$ (blue line), $-0.3$ (red line), and 0 (green line) V vs. Ag/AgCl under light irradiation ($460 \text{ nm} < \lambda_{\text{ex}} < 650 \text{ nm}$, 27 mW cm$^{-2}$) in a CO$_2$-purged NaHCO$_3$ (50 mM) aqueous solution (pH = 6.6).

Figure S4. Current-potential curves and time courses of photocurrent at $E = 0$ V vs. Ag/AgCl using NiO/PRu-poly-Ru-RuCAT1 and the polymer photocathode with Re catalyst (NiO/PRu-poly-Ru-Re)$^1$ under light irradiation ($460 \text{ nm} < \lambda_{\text{ex}} < 650 \text{ nm}$, 27 mW cm$^{-2}$) in a CO$_2$-purged NaHCO$_3$ (50 mM) aqueous solution (pH = 6.6).
**Figure S5.** FT-IR spectra of NiO/PRu-poly-Ru-RuCAT2 (red line) and VRu-RuCAT on NiO electrode (blue line). A diffuse reflection unit was used for the measurements and a bare NiO electrode was employed as the background.

**Figure S6.** Cross-sectional scanning electron microscopy (SEM) images of A) NiO/PRu-poly-Ru-RuCAT1, B) NiO/PRu-poly-Ru-RuCAT2 and C) NiO/PRu-poly-Ru-Re.
**Table S1.** Value of $n_{\text{cat}}$, $n_{\text{total}}$, and $n_{\text{PRuV}}$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$n_{\text{PRuV}}$ / nmol</th>
<th>$n_{\text{total}}$ / nmol</th>
<th>$n_{\text{cat}}$ / nmol</th>
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<td>4</td>
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**Scheme S1.** Preparation scheme for (a) NiO/PRu-ReCAT and (b) NiO/PRu-poly-Ru-Re.

**Reference**