Supporting Information

Durable Photoelectrochemical CO_2 Reduction with Water Oxidation using a Visible-Light Driven Molecular Photocathode

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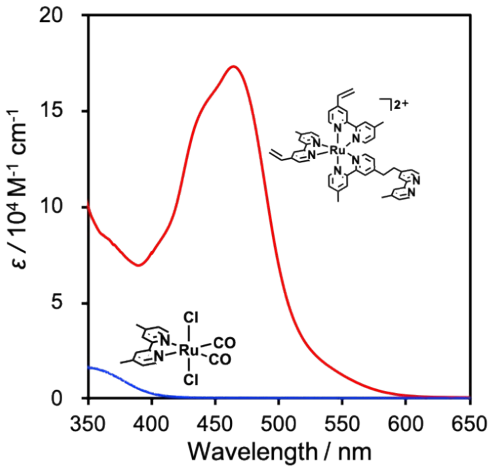


Figure S1. Absorption spectra of **VRu-N^N** (red line) and *cis*-(CO)-*trans*-(Cl)-Ru(dmb)$(CO)_2Cl_2$ (blue line) in MeCN solutions.

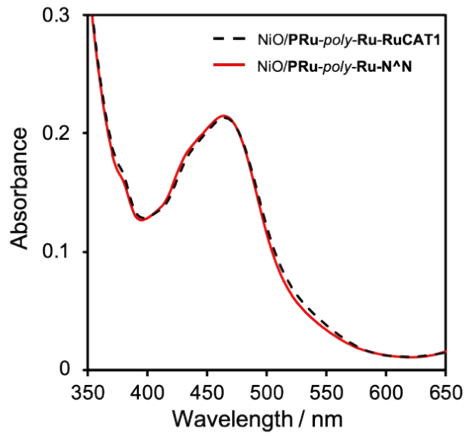


Figure S2. UV-vis absorption spectra of NiO/**PRu**-*poly*-**Ru-N^N** (red line), and NiO/**PRu**-*poly*-**Ru-RuCAT1** (black dashed line). FTO electrode was employed as the background.

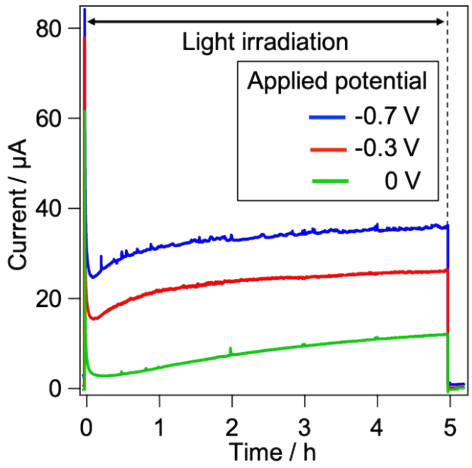


Figure S3. Time courses of photocurrent using NiO/**PRu**-*poly*-**Ru**-**RuCAT1** (electrode area: 2.5 cm^{-2}) at E = −0.7 (blue line), −0.3 (red line), and 0 (green line) V vs. Ag/AgCl under light irradiation (460 nm < λ_{ex} < 650 nm, 27 mW cm^{-2}) in a CO_2-purged $NaHCO_3$ (50 mM) aqueous solution (pH = 6.6).

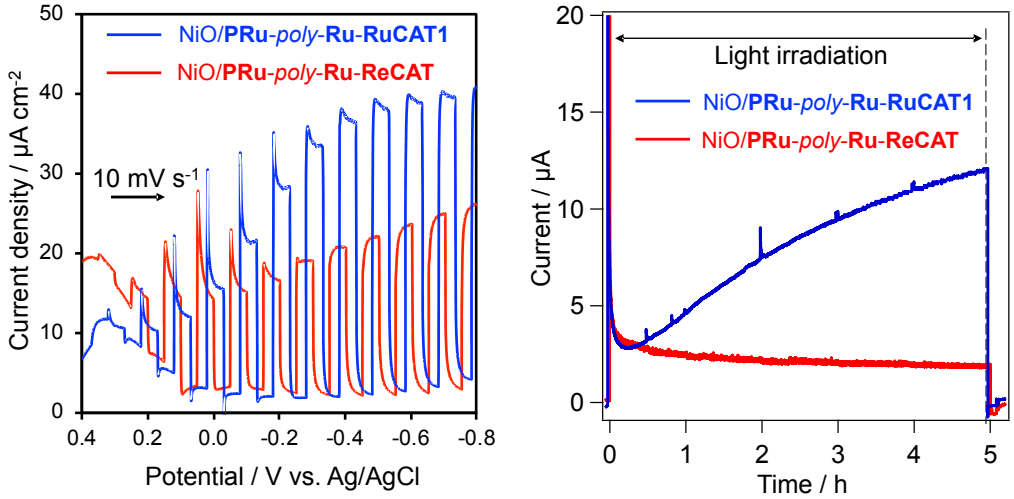


Figure S4. Current-potential curves and time courses of photocurrent at E = 0 V vs. Ag/AgCl using NiO/**PRu**-*poly*-**Ru**-**RuCAT1** and the polymer photocathode with Re catalyst (NiO/**PRu**-*poly*-**Ru**-**Re**)[1] under light irradiation (460 nm < λ_{ex} < 650 nm, 27 mW cm^{-2}) in a CO_2-purged $NaHCO_3$ (50 mM) aqueous solution (pH = 6.6).

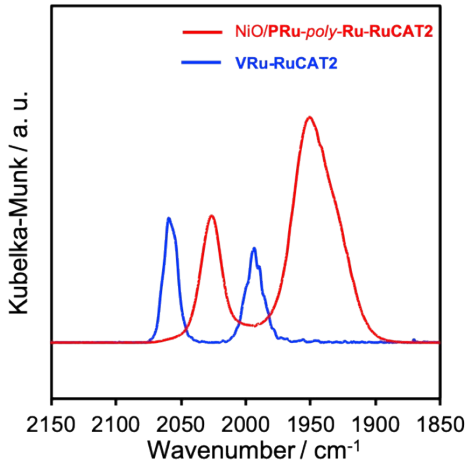


Figure S5. FT-IR spectra of NiO/**PRu**-*poly*-**Ru**-**RuCAT2** (red line) and **VRu**-**RuCAT** on NiO electrode (blue line). A diffuse reflection unit was used for the measurements and a bare NiO electrode was employed as the background.

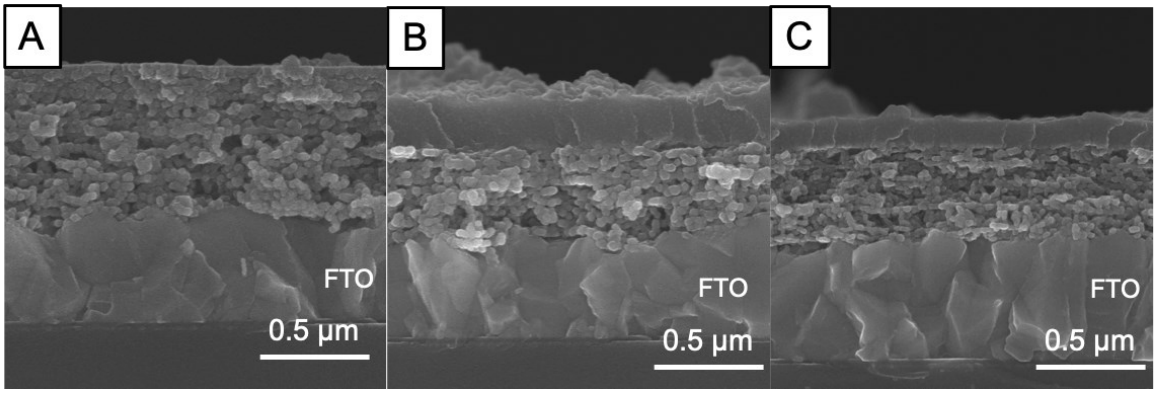
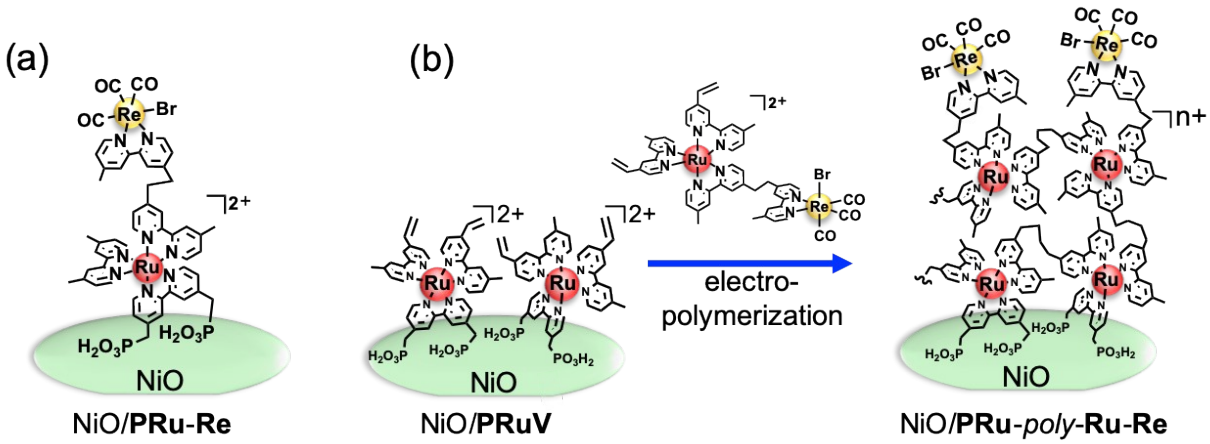


Figure S6. Cross-sectional scanning electron microscopy (SEM) images of A) NiO/**PRu**-*poly*-**Ru**-**RuCAT1**, B) NiO/**PRu**-*poly*-**Ru**-**RuCAT2** and C) NiO/**PRu**-*poly*-**Ru**-**Re**.

Table S1. Value of n_{cat}, n_{total}, and $n_{\mathbf{PRuV}}$.

Entry	$n_{\mathbf{PRuV}}$ / nmol	n_{total} / nmol	n_{cat} / nmol
1	11.6	82	35.2
2	12.9	78	32.6
3	12.3	87	37.4
4	13.3	94	40.8



Scheme S1. Preparation scheme for (a) NiO/**PRu**-**ReCAT** and (b) NiO/**PRu**-*poly*-**Ru**-**Re**.

Reference

1. R. Kamata, H. Kumagai, Y. Yamazaki, G. Sahara and O. Ishitani, *ACS Appl. Mater. Interfaces*, 2019, **11**, 5632-5641.