Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2019

Support information:

A Donor-Chromophore-Catalyst Assembly for Solar CO_2 Reduction

Degao Wang,[1a] Ying Wang,[1a] Matthew D. Brady,[1] Matthew V. Sheridan,[1] Benjamin D. Sherman,[2] Byron H. Farnum,[1] Yanming Liu,[1] Seth L. Marquard,[1] Gerald J. Meyer,[1] Christopher J. Dares,[3] Thomas J. Meyer[1]*

1. Department of Chemistry, University of North Carolina Chapel Hill, Chapel Hill, North Carolina 27599, United States
2. Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, United States
3. Department of Chemistry and Biochemistry, Florida International University, 11200 SW Eighth Street, Miami, Florida 33199, United States

a: D.W and Y.W contributed equally to this work.

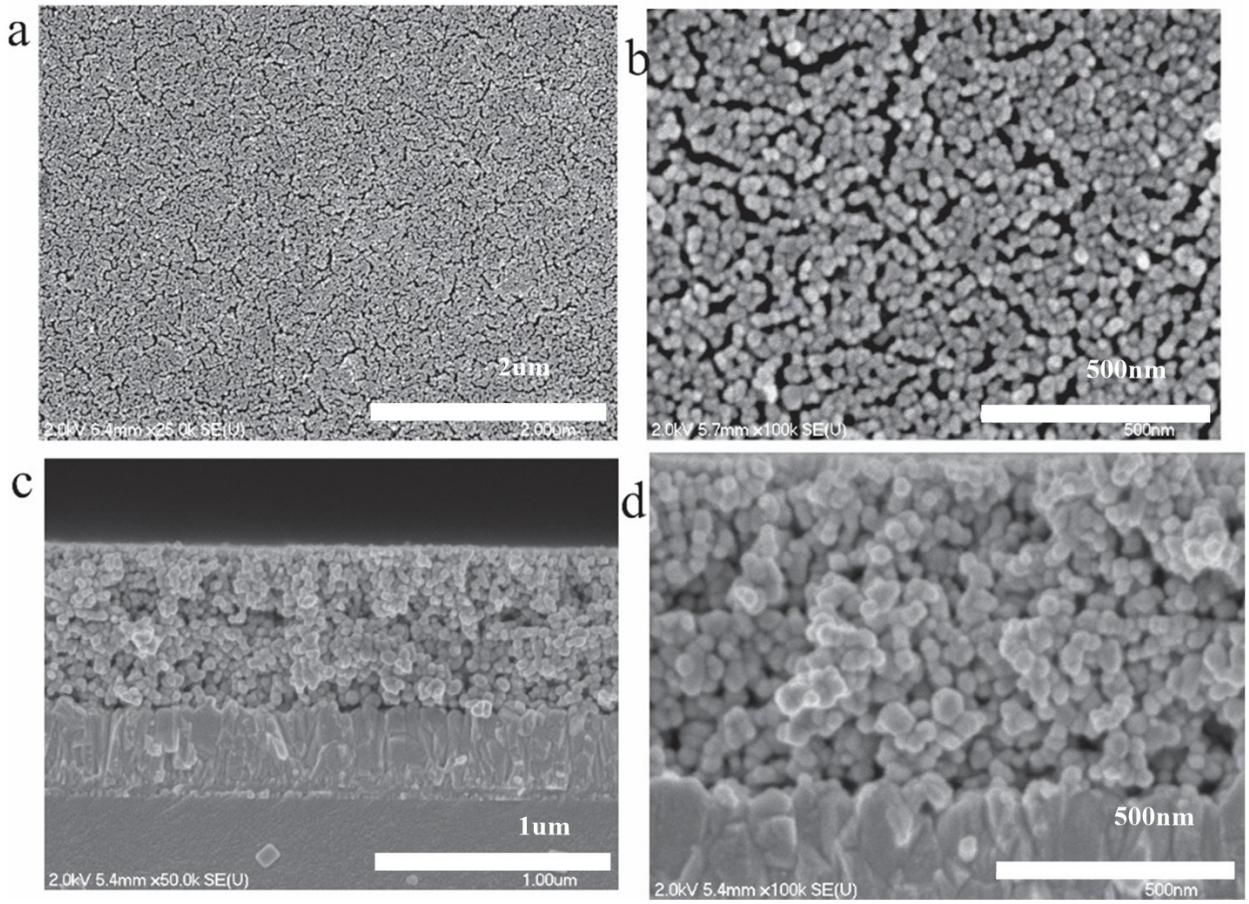


Figure S1. SEM pictures viewed from the top of the prepared NiO film (a and b). Cross-section images of the prepared NiO film (c and d).

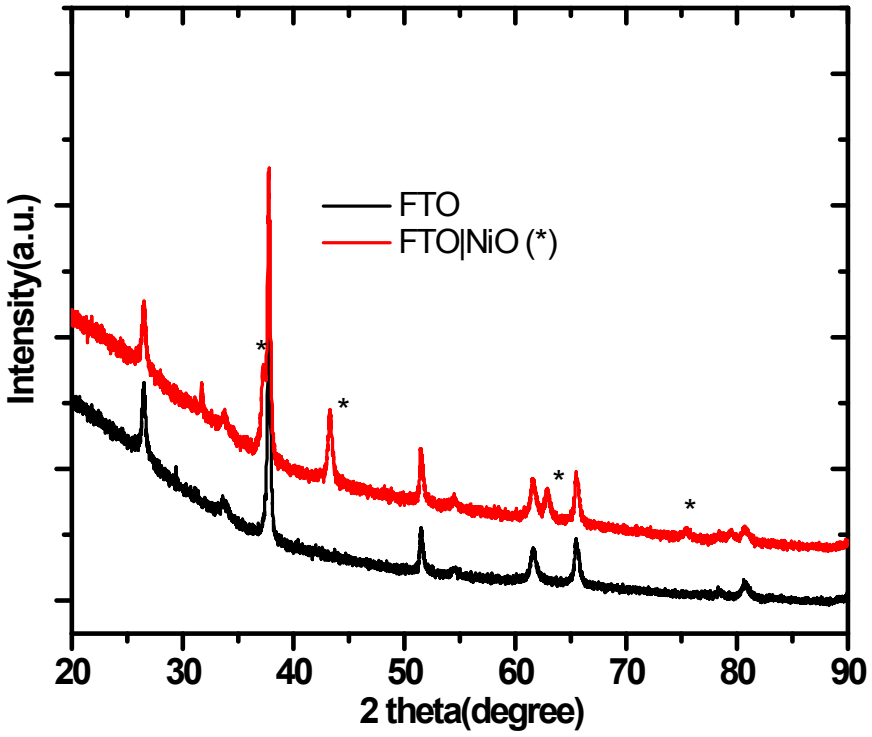


Figure S2: XRD pattern for the FTO substrate (black) and FTO-NiO film (red).

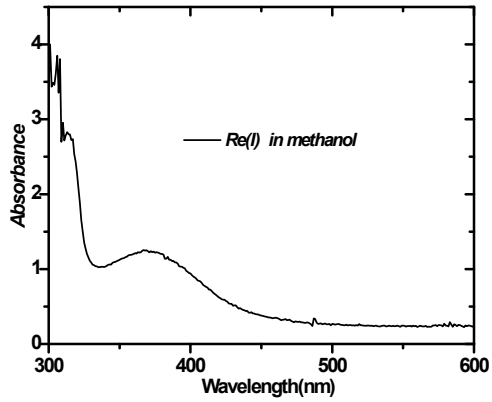
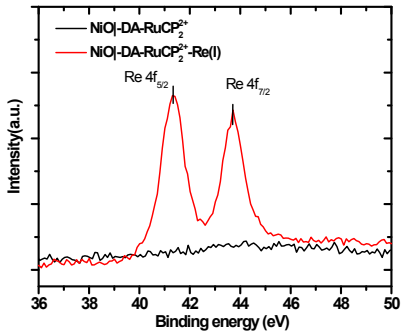


Figure S3. Absorbance spectrum of the CO_2 catalyst Re(I)((4,4'-$PO_3H_2CH_2)_2$-2,2'-bipyridine)$(CO)_3Cl$ methanol.



Peak	Type	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
Ru 3d	Comp	284.991	0.737	1114.8	4.273	101.069	0.48	2.30
C 1s	Comp	286.614	1.397	7319.8	0.278	12.011	48.55	27.60
Re 4f	Reg	41.640	1.019	1418.1	3.961	186.210	0.71	6.25
P 2p	Reg	132.540	1.699	996.2	0.486	30.974	3.95	5.79
N 1s	Reg	399.940	1.092	1530.2	0.477	14.007	5.71	3.78
O 1s	Reg	529.040	1.010	13260.2	0.780	15.999	28.97	21.94
Ni 2p	Reg	853.540	3.331	30880.9	4.044	58.702	11.64	32.34

Figure S4: XPS measurements and elemental analysis for the assembly NiO|-DA-$RuCP_2^{2+}$-Re(I).

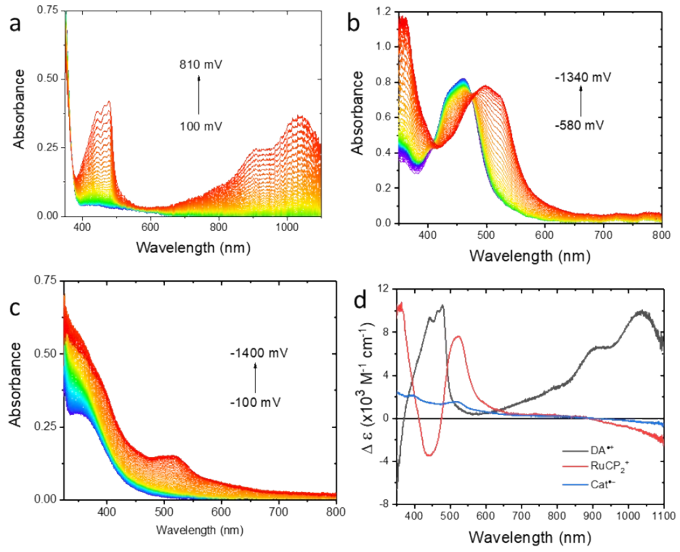


Figure S5: Spectroelectrochemical measurements of *nano*ITO|-DA (*E'* ($DA^{+\bullet/0}$) = 0.71 V vs. NHE) (a), *nano*ITO|-$RuCP_2^{2+}$ (*E'* ($RuCP_2^{2+/+}$) = −1.20 V vs. NHE) (b), and *nano*ITO|-Re(I) *(E'*

($Re(I)^{-\bullet/0}$) = −1.19 V vs. NHE) (c). The delta extinction coefficient spectra for $DA^{+\bullet}$ (blue), $RuCP_2^{2+}$ (red), and $Re(I)^{-\bullet}$ (green) in argon-sparged 0.1 M $LiClO_4$ acetonitrile are shown in (d). Based on the data, DA displayed a reversible one-electron oxidation and $RuCP_2^{2+}$ also displayed a reversible one-electron reduction with a characteristic red-shift of its low energy absorption band consistent with the one-electron reduction of Ru polypyridyl complexes. The *E'* ($Ru^{2+*/+}$) excited-state reduction potential for $RuCP_2^{2+}$ was estimated as *E'* ($Ru^{2+*/+}$) = *E'* ($RuCP_2^{2+/+}$) + ΔG_{ES}, where ΔG_{ES} is the Gibbs free energy stored in the excited state. A ΔG_{ES} = 2.10 eV value was estimated from a linear extrapolation of the higher energy side of the corrected PL spectrum of $RuCP_2^{2+}$ sensitized to ZrO_2, resulting in *E'* ($Ru^{2+*/+}$) = 0.90 V vs. NHE. The Re(I) catalyst exhibited a quasi-reversible one-electron reduction and a delta extinction coefficient spectrum with a magnitude approximately 4× smaller than the other complexes.

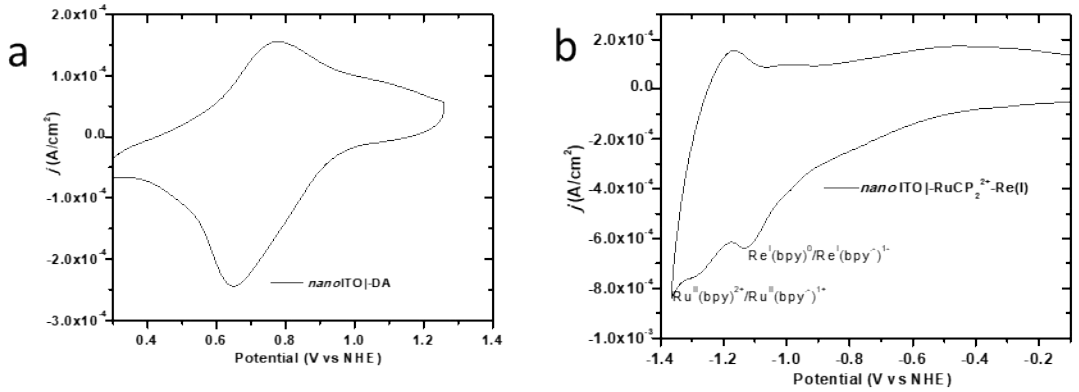


Figure S6: Cyclic voltammograms obtained for DA and $RuCP_2^{2+}$ -Re(I) surface-bound to nanoITO in 0.1 M $NaClO_4$ acetonitrile electrolyte. (A) shows the response of *nano*ITO|-DA and (B) shows that for *nano*ITO- $RuCP_2^{2+}$-Re(I). All CVs were collected at a scan rate of 50 mV/s.

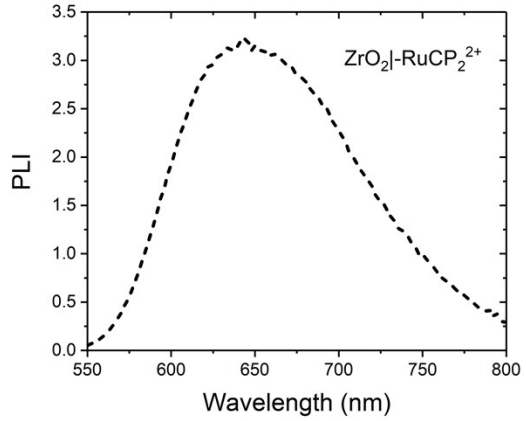


Figure S7: PL spectrum of $RuCP_2^{2+}$ bound to ZrO_2 for ΔG_{ES} calculation.

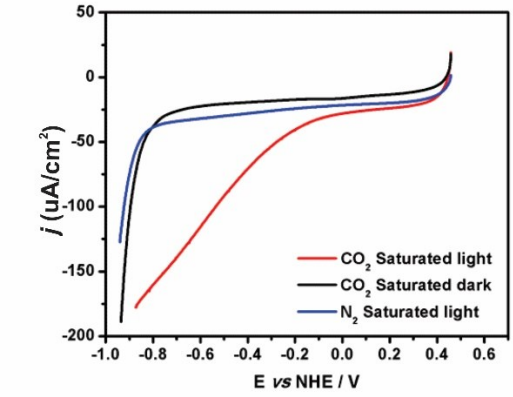


Figure S8: Linear scan voltammograms for the assembly NiO|-DA-$RuCP_2^{2+}$-Re(I) performed under N_2 and CO_2 saturated acetonitrile with 0.1 M $NaClO_4$. All LSVs were collected at a scan rate of 50 mV/s.

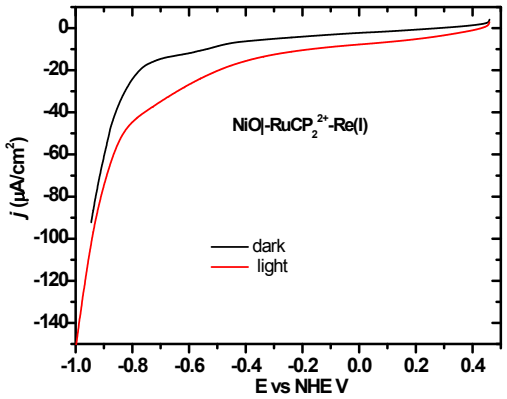


Figure S9: Linear scan voltammograms for the assembly NiO|-$RuCP_2^{2+}$-Re(I) performed under dark and light conditions in CO_2 saturated acetonitrile with 0.1 M $NaClO_4$. All CVs were collected at a scan rate of 50 mV/s.

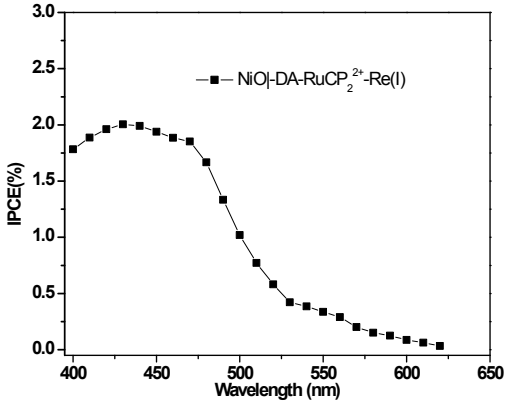


Figure S10. IPCE spectrum for NiO|-DA-$RuCP_2^{2+}$-Re(I) under an applied bias of -0.54 vs. NHE in CO_2 saturated acetonitrile with 0.1 M $NaClO_4$.