Electronic Supplementary Information

CO_2 Reduction with Re(I)-NHC Compounds: Driving Selective Catalysis with a Silicon Nanowire Photoelectrode

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Content

Experimental Procedures

General. All reagents were obtained from commercial suppliers and used as received unless otherwise noted. DRIFTS spectra were recorded on a ThermoNicolet 6700 spectrophotometer. Cyclic voltammograms were collected on a PAR model VersaSTAT 4 potentiostat using a single compartment cell. Conditions for electrochemical studies: supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, scan rate 100 mV/s, a glassy carbon working electrode (geometric surface area 0.0314 cm^2), a Pt counter electrode, a non-aqueous $Ag/AgNO_3$ reference electrode ($AgNO_3$ concentration 0.01 M), and ferrocene as an internal standard. The electrochemical cell was purged with Ar or CO_2 for 20 min before every scan. The morphology of SiNWs was analyzed with a JOEL JSM 6340F scanning electron microscope.

Photoelectrode Fabrication. SiNWs were prepared following a previously reported method.[S1] A p-Si (100) (10^{15} cm^{-3} B doped; ρ: 10~20Ω•cm) wafer was cleaned sequentially in acetone, methanol, isopropanol, and deionized (DI) water. The cleaned wafer was oxidized in H_2O_2/H_2SO_4 (1:3) at 90 °C for 15 min to remove heavy metals and organic species. After rinsing with DI water, the substrate was cut into pieces and then immersed into an $HF/AgNO_3$ solution (4.6 M HF and 0.02 M $AgNO_3$) for 30 min at 50 °C. Silver residue was removed from SiNWs' surface by soaking in 70% HNO_3 for 30 min. The SiNWs were then rinsed by DI water and dried by N_2 flow. A film of Al (300 nm) was sputtered onto the backside of the substrates (as-prepared SiNWs and clean p-Si (100) wafer) by radio frequency magnetron sputtering (AJA International, Orion 8, USA). Then the samples were annealed in Ar (flow rate: 5000 standard cubic centimeter per minute, SCCM) at 450 °C for 5 min. Afterwards, a Cu wire was stuck to Al film by Ag paste (MG Chemicals, 8331 Silver Conductive Epoxy Adhesive) and then protected with non-conductive epoxy (Loctite® 615 Hysol Epoxy Adhesive) to cover all the Al film.

Photocatalytic CO_2 Reduction. In photocatalysis, 1.0 μmol of a Re(I)-NHC complex and 4.0 μmol of $Ru(dmb)_3(PF_6)_2$ were dissolved in 4.0 mL of a dimethylformamide-triethanolamine (3:1 v/v) solution in a Pyrex test tube. Prior to photocatalytic testing, the reaction solution was bubbled with CO_2 (99.999%, Airgas) for 20 min. The reaction solution was then irradiated with a 300 W xenon lamp equipped with a water filter (light intensity 113 mW/cm^2). The head space above the reaction solution was sampled with a gas-tight syringe at different time intervals for product analysis using an Agilent 7820 GC equipped with a TCD detector and a 60/80 Carboxen-1000 packed column (Supelco).

Photoelectrochemical CO_2 reduction. In controlled potential experiments, cyclic voltammograms were collected prior to bulk electrolysis studies, which were carried out in a three-necked flask containing 10.0 ml of 1 mM catalyst in acetonitrile. Prior to photoelectrochemical measurements, the flask (total cell volume 22.7 ml) was bubbled with CO_2 (99.999%, Airgas) for 20 min. A SiNW photoelectrode (geometric surface area measured individually, varies around 0.05 cm^2) were used as the working electrode in photoelectrochemical CO_2 reduction. The reaction solution was then irradiated with a 300 W xenon lamp equipped with a water filter (light intensity 113 mW/cm^2). The head space (volume 12.7 ml) above the reaction solution was sampled with a gas-tight syringe for product analysis using the Agilent 7820 GC.

Ref. S1. R. Liu, C. Stephani, J. J. Han, K. L. Tan and D. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 4225.

Supplementary Table

Table S1. Performance of compounds **1** and **2** in photoelectrochemcial and photocatalytic CO_2 reduction.

Catalysts		**1**		**2**	
		CO	H_2	CO	H_2
FEs in Photoelectrolysis [a]	**Dry** [b]	57%	0%	53%	0%
	5% H_2O [c]	20%	54%	68%	9%
TONs in Photocatalysis [d]		18.1	10.5	20.4	10.5

[a] In calculating Faradaic Efficiencies (FEs), the amounts of CO produced due to photochemical decomposition, which were measured without any applied bias potential, were subtracted from the total amounts of CO generated in photoelectrolysis.

[b] FEs after photoelectrolysis for 4 h on SiNWs in acetonitrile; potentials were fixed at -1.65 V (**1**) and -1.48 V (**2**) vs Fc^+/Fc; total charges passed in 4 h were measured to be 3.3 Coulombs (**1**) and 1.5 Coulombs (**2**).

[c] FEs after photoelectrolysis for 4 h on SiNWs in an acetonitrile solution containing 5% H_2O (by volume); potentials were fixed at -1.74 V (**1**) and -1.51 V (**2**) vs Fc^+/Fc; total charges passed in 4 h were measured to be 18.0 Coulombs (**1**) and 4.2 Coulombs (**2**).

[d] Turnover numbers (TONs) after photocatalysis for 4 h in the presence of $Ru(dmb)_3^{2+}$. In the absence of the Re(I)-NHC catalysts, TONs were measured to be 0.6 and 3.0 for CO and H_2, respectively.

Supplementary Figures

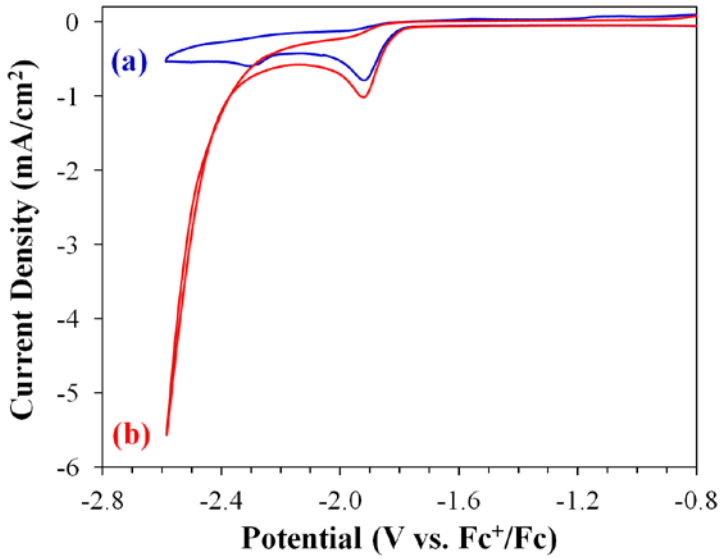

Figure S1. Cyclic voltammograms of **2** under (a) Ar and (b) CO_2 atmospheres on a glassy carbon electrode.

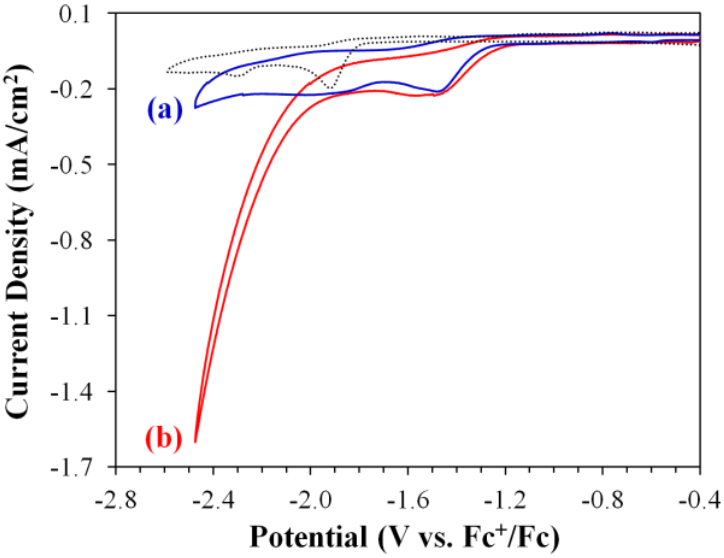

Figure S2. Cyclic voltammograms of 2 under (a) Ar and (b) CO_2 atmospheres on a SiNW photoelectrode under light irradiation. Cyclic voltammogram under Ar on a glassy carbon electrode is also plotted for comparison (dotted trace).

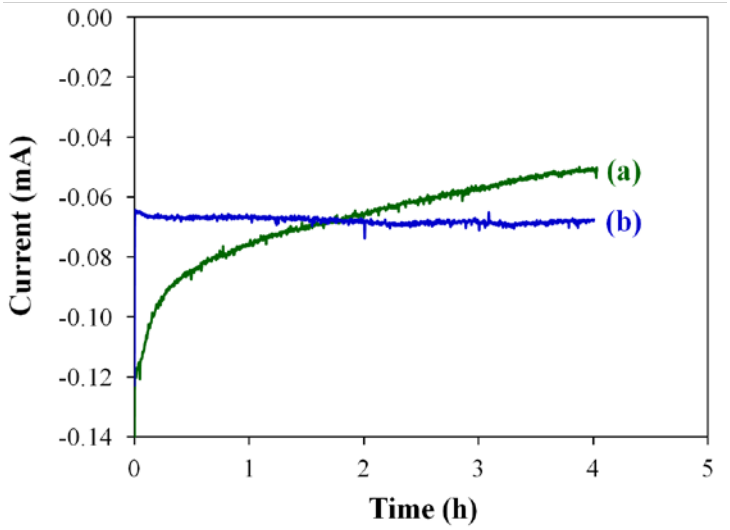

Figure S3. Photocurrent vs. time during photoelectrochemical CO_2 reduction using (a) **1** and (b) **2** on a SiNW photoelectrode in acetonitrile.

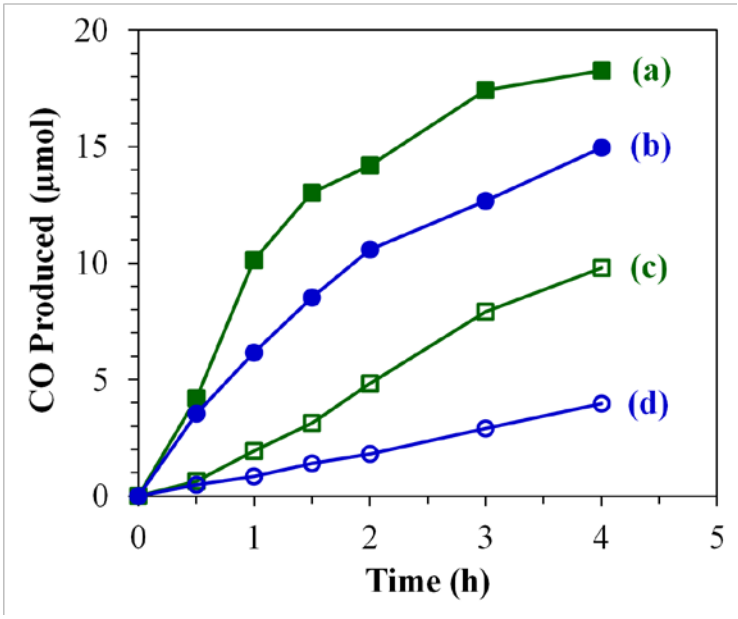

Figure S4. CO production during photoelectrochemical CO_2 reduction using 10 µmol of catalysts: (a) **1** and (b) **2** in an acetonitrile solution containing 5% H_2O (by volume); (c) **1** and (d) **2** in acetonitrile. The amounts of CO produced due to photochemical decomposition were subtracted from the total amounts of CO generated in photoelectrolysis.

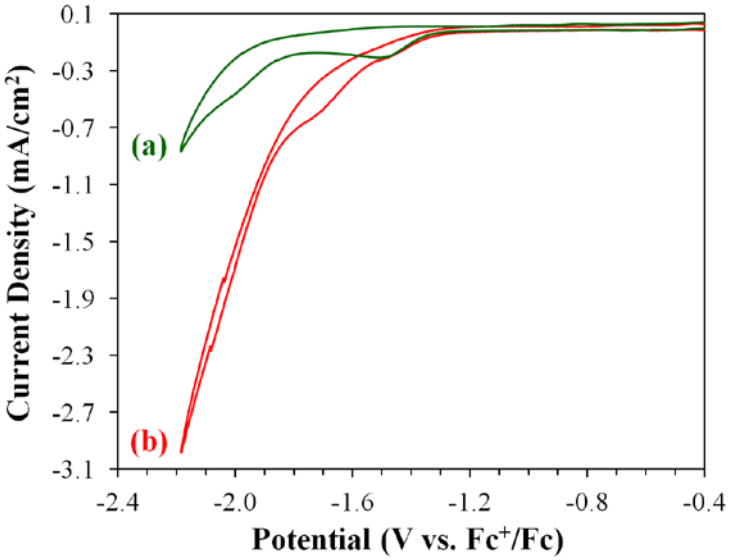

Figure S5. Cyclic voltammograms of **1** under (a) Ar and (b) CO_2 atmospheres on a SiNW photoelectrode in an acetonitrile solution containing 5% H_2O (by volume).

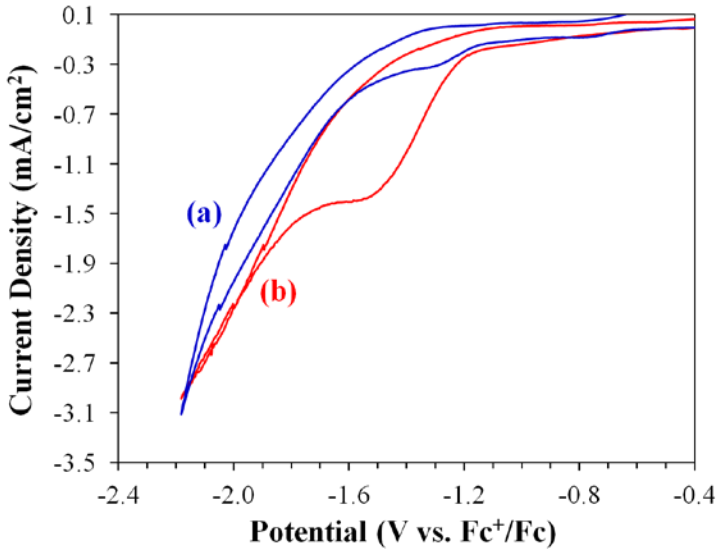

Figure S6. Cyclic voltammograms of **2** under (a) Ar and (b) CO_2 atmospheres on a SiNW photoelectrode in an acetonitrile solution containing 5% H_2O (by volume).

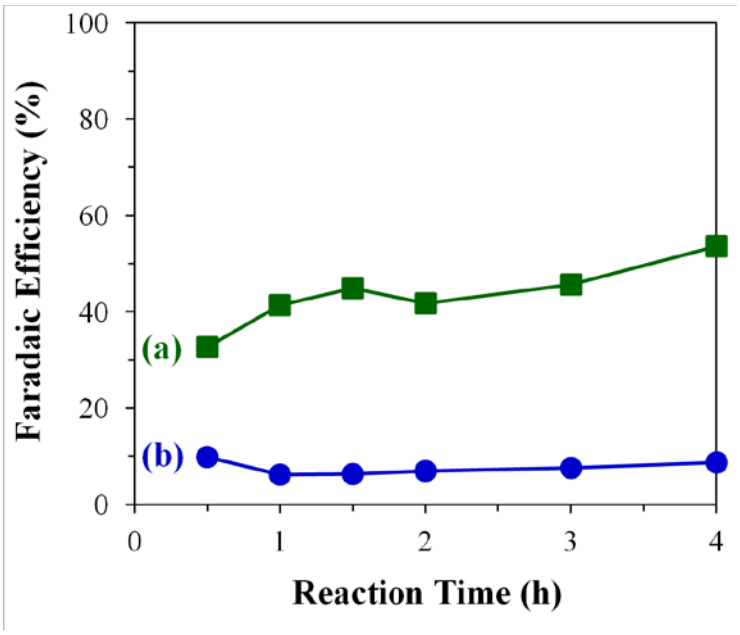

Figure S7. Faradaic efficiencies for H_2 production using (a) **1** and (b) **2** on SiNWs in an acetonitrile solution containing 5% H_2O (by volume).

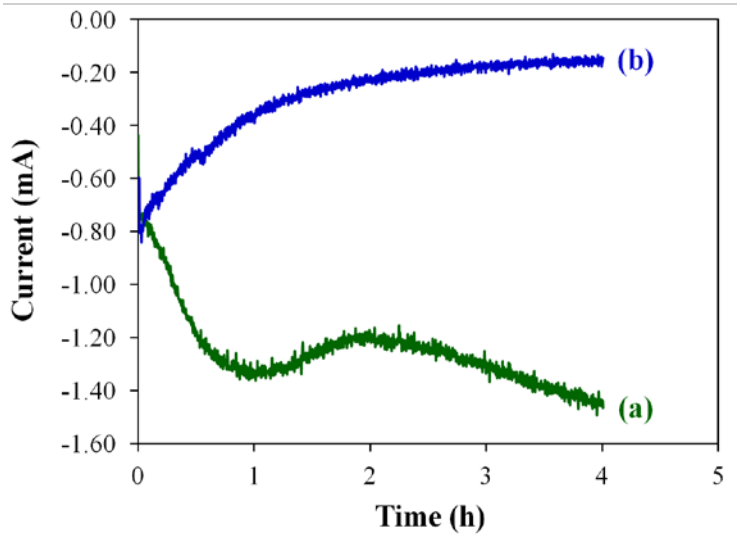

Figure S8. Photocurrent vs. time during photoelectrochemical CO_2 reduction using (a) **1** and (b) **2** on a SiNW photoelectrode in an acetonitrile solution containing 5% H_2O (by volume).