Supporting information

Tuning redox potentials of CO_2 catalysts for carbon photofixation by Si nanowires

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1. Experiment Section

Ni catalysts were prepared by the addition of $Ni(BF_4)_2 \bullet 6H_2O$ and the appropriate ligand in a 1:3 ratio in ethanol for 1 hour. The resultant precipitate was washed with ether and dried overnight under reduced pressure.

Electroless etched SiNWs were prepared following a reported method. A p-type Si (100) substrate (Wafternet, 10^{15} cm^3, B-doped; 10–20 Ω•cm) was cleaned with acetone, methanol, and isopropanol sequentially and then oxidized in H_2O_2/H_2SO_4 1:3 at 90 °C for 10 minutes to remove heavy metals and organic species. The cleaned substrate was immersed into an $HF/AgNO_3$ solution (4.6 M HF and 0.02 M $AgNO_3$) for 30 minutes at 50°C to produce SiNWs. Electrode fabrication was done after Al post-treatment to form ohmic contact.

Photoelectrochemical experiments were performed on a CHI 609D Potentiostat. A three-electrode configuration was used, in which Pt or SiNW electrodes were used as the working electrode, a piece of high-purity Al foil (99.9995%, Alfa Aesar, USA) served as the counter electrode, and an SCE was used as the reference electrode. The electrolyte solution was composed of 5 mM Ni catalyst and 0.1 M tetrabutyl ammonium bromide (TBAB) (≥ 99.0%, Sigma-Aldrich, USA) in 20 mL acetonitrile. CO_2 (Airgas, USA; flow rate: 120 SCCM) was continuously bubbled through the solution. A 150 W Xenon lamp (model 71228, Newport, USA) equipped with an AM 1.5G filter and illumination intensity calibrated to be 100 mW cm^{-2} was used as the light source. The scan rates of cyclic voltammetry curves were 50 mV s^{-1}. The resultant product was analyzed by NMR and mass spectrometry.

2. CV on Pt with substrates in electrolyte

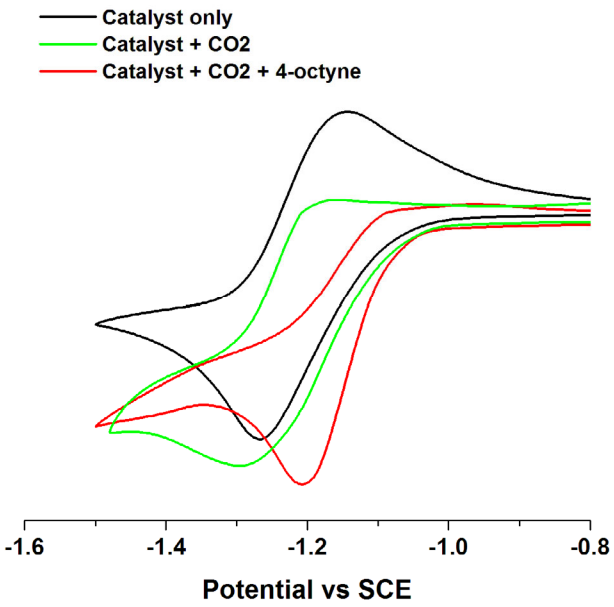

Figure S1. The solutions contain 5 mM Ni catalyst *1* and 0.1 M tetrabutylammonium bromide in acetonitrile. 0.05 M 4-octyne or CO_2 gas bubbling was introduced as indicated in caption.

3. Turn over of the catalyst on Si NWs

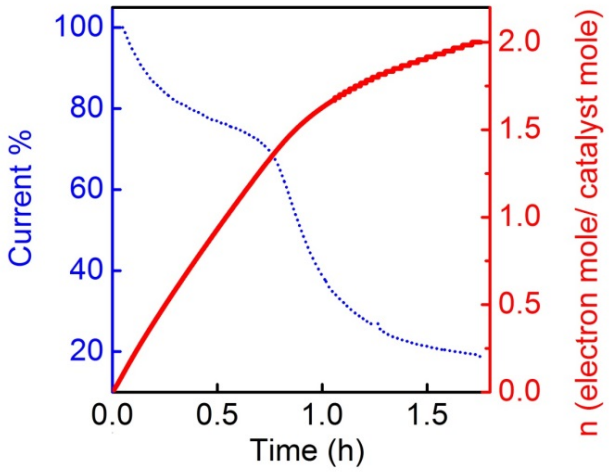

Figure S2 Current changed on Si NWs with catalyst 1 and CO2 bubbling. No 4-octyne was added into the solution.

4. Reduction potentials of the catalysts summary

Table S1. Reduction potentials of the catalysts on Pt and potential shifts on SiNWs.

Catalyst	V_{RP} on Pt/ V	V_{RP} on Pt with starting materials/ V	V_{RP} on SiNWs with starting materials/ V	V_{ph} on SiNWs
1	-1.25	-1.18	-0.73	450 mV
2	-1.26	-1.26	-0.83	430 mV
3	-1.09	-1.11	-0.71	400 mV
4	-0.51	-0.76	-0.33	430 mV
5	-1.37	-1.36	-0.95	410 mV
6	-1.35	-1.33	-0.90	430 mV