

SUPPORTING INFORMATION

**Photoelectrochemical Reduction of CO₂ to HCOOH on Silicon
Photocathodes with Reduced SnO₂ Porous Nanowire Catalysts**

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Si/Sn-pNW interface cross-section

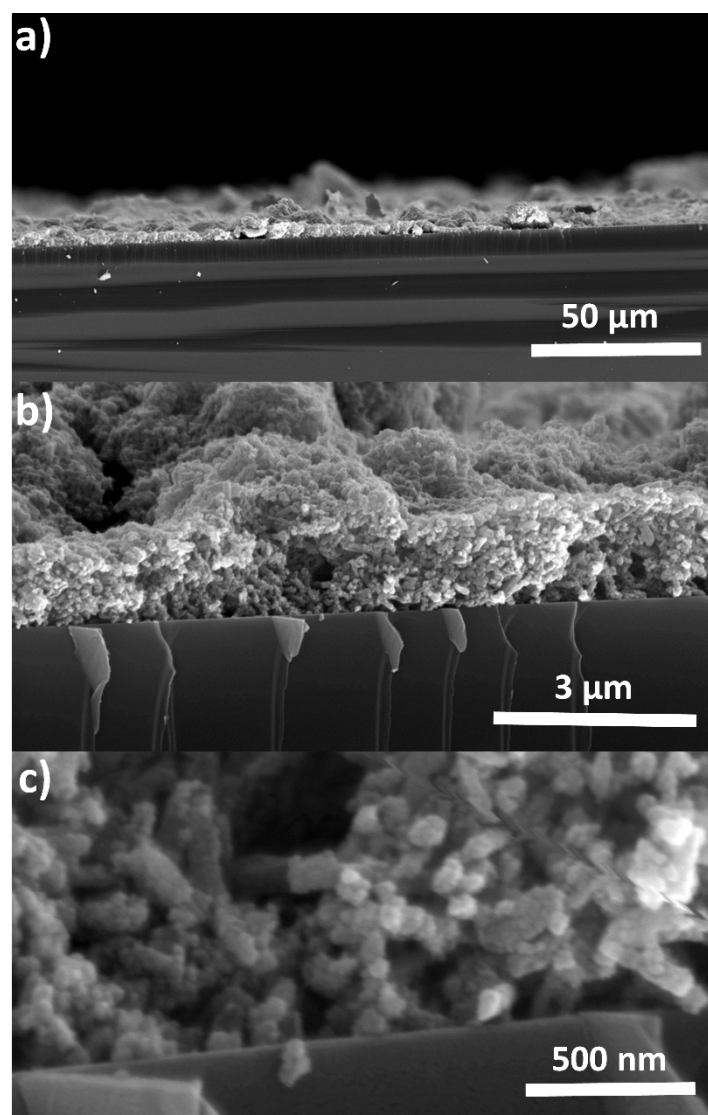


Fig. S1. SEM cross-sectional images of as-deposited Sn-pNWs on Si at low (a), mid (b), and high (c) magnification.

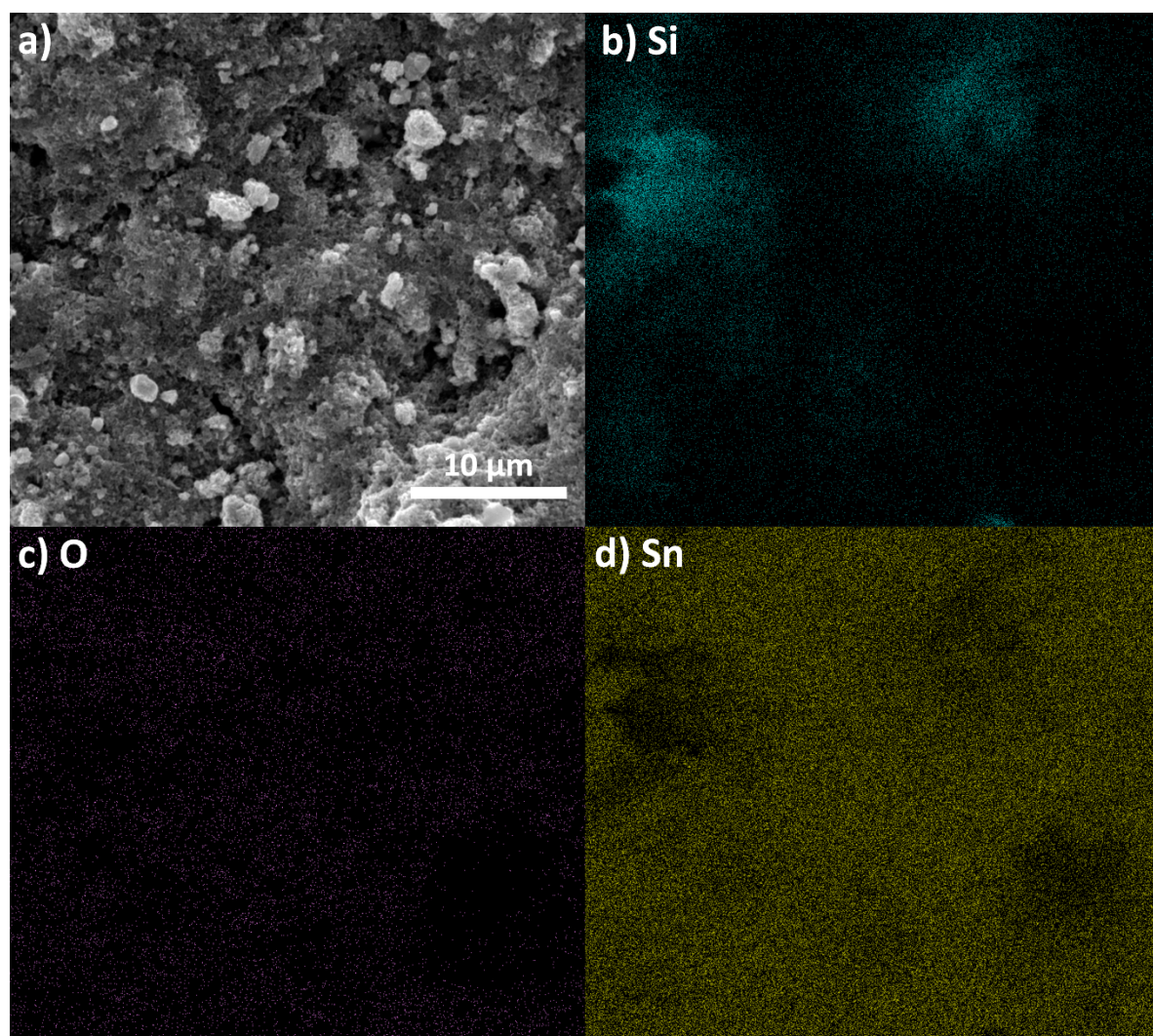
Si/Sn-pNW elemental mapping

Fig. S2. Top-down (a) SEM image and corresponding EDS map for (b) Si, (c) O, and (d) Sn for an n^+p -Si/Sn-pNWs electrode.

Cyclic voltammetry for FTO/Sn-pNWs

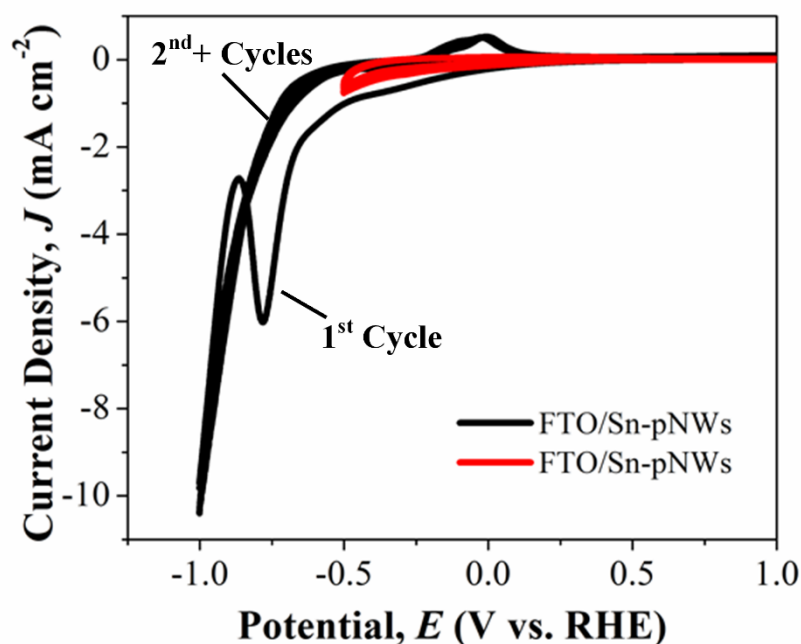


Fig. S3. Current density vs. potential (J - E) behavior for FTO/Sn-pNW electrodes in 0.1 M KHCO_3 bubbled with CO_2 in the absence of stirring. One electrode was measured to cathodic potentials up to -1.0 V vs. RHE (black), while a second electrode was only measured to -0.5 V vs. RHE.

When the Sn-pNWs on an FTO substrate were first measured as-deposited, significant reductive current was observed as the potential was scanned more cathodic. This reduction current began at ~ -0.1 V vs. RHE and spiked at -0.75 V vs. RHE. This reductive current is likely ascribable to the reduction of the oxide form of the Sn-pNW catalysts. Once the oxide is fully reduced electrochemically, this behavior was not observed on subsequent scans. However, an oxidative current peak at ~ 0 V vs. RHE, which was not observed on the first scan, showed up consistently in subsequent scans. A second electrode was measured in which the cathodic vertex potential was limited to -0.5 V vs. RHE (red curve above) and did not show this anodic redox peak over 4+ cycles. Thus, it was concluded that the oxidative peak represents the oxidation of products that were formed by the reductive current on the electrode when it was at potentials below -0.5 V vs. RHE. In this range, the FTO/Sn-pNWs form primarily HCOOH and H_2 (see main manuscript Fig. 3a). From the shape of the oxidation current peak, it appears to consist of two redox events. The hydrogen evolution redox potential is 0 V vs. RHE, but CO_2 reduction to HCOOH occurs at -0.25 V vs. RHE.¹ Thus, the oxidation current observable at < 0 V was attributed to the oxidation of formic acid, and above 0 V, the oxidation of hydrogen contributed as well.

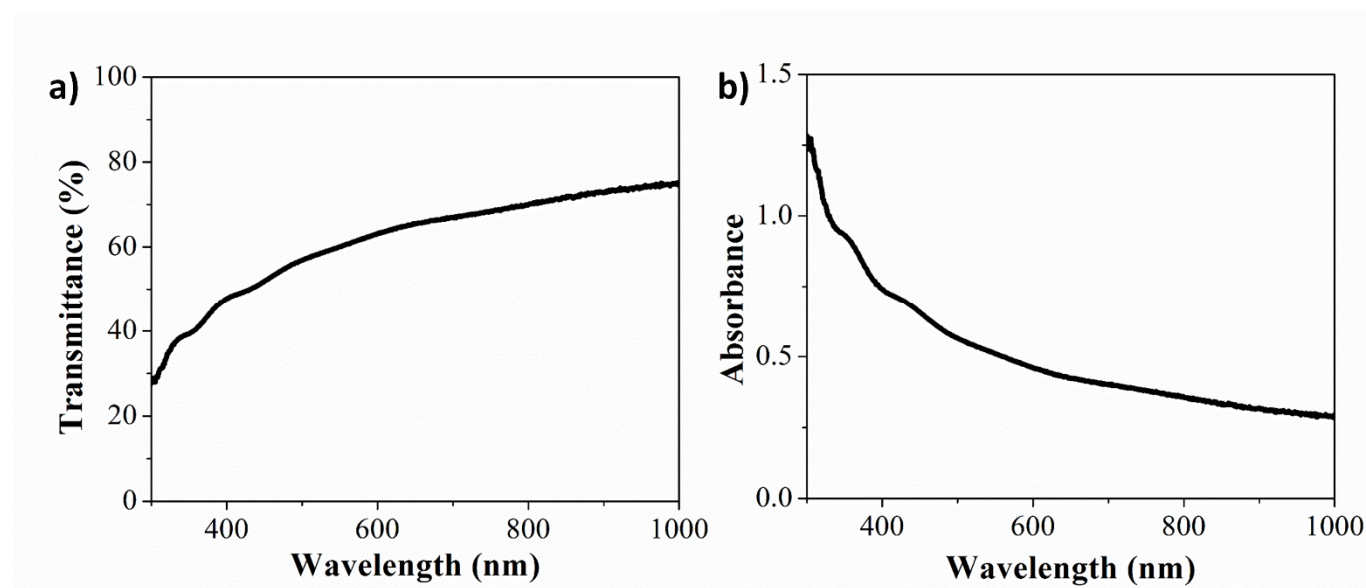
Transmittance and absorbance of the catalyst layer

Fig. S4. (a) Transmittance and (b) absorbance vs. wavelength for the Sn-pNWs catalyst layer measured on an FTO/glass substrate with UV/vis spectroscopy.

Photocurrent stability

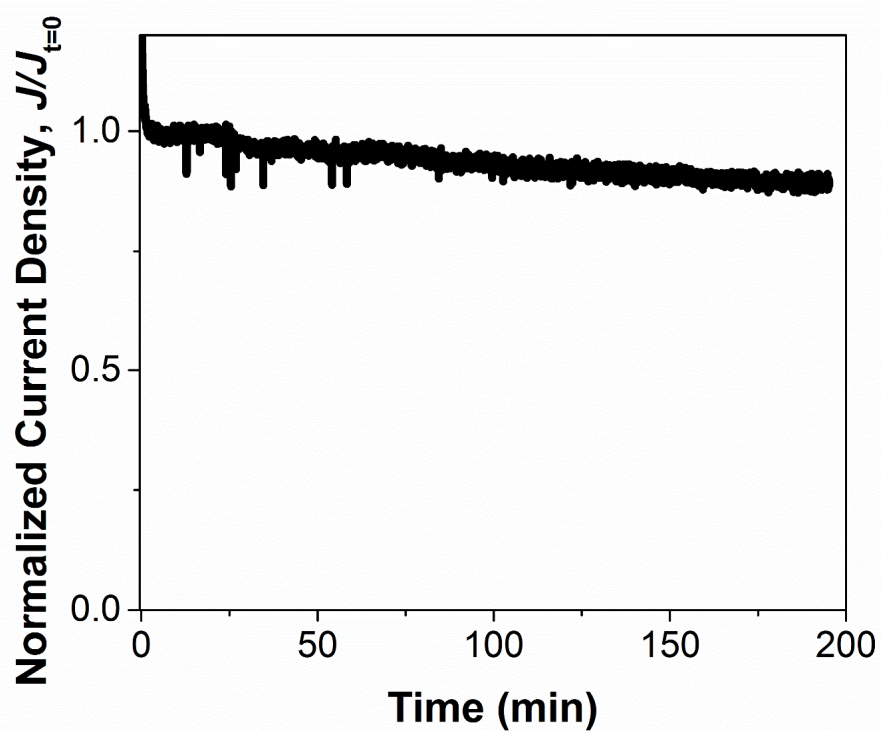


Fig. S5. Current density relative to the initial current density vs. time for n⁺p-Si/Sn-pNWs at -0.4 V vs. RHE under 1 Sun AM1.5 illumination in CO₂-saturated 0.1 M KHCO₃.

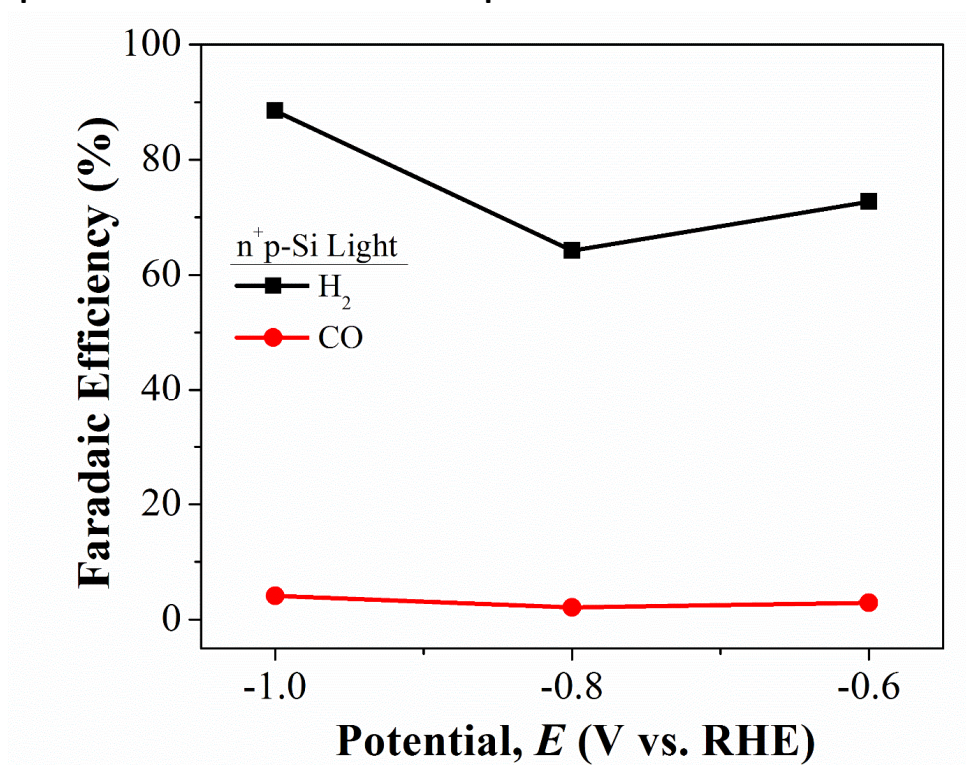
CO₂ reduction product distribution of a bare Si photoelectrode

Fig. S6. CO₂ reduction product distribution in CO₂-saturated 0.1 M KHCO₃. Faradaic efficiency vs. potential for bare n⁺p-Si under 1 Sun AM1.5 illumination.

References

1. B. Kumar, J. P. Brian, V. Atla, S. Kumari, K. A. Bertram, R. T. White and J. Spurgeon, *Catal. Today*, 2016, **270**, 19-30.