

*Supporting Information for:*

**Photoelectrochemical Operation of a Surface-Bound, Nickel-Phosphine H<sub>2</sub>  
Evolution Catalyst on *p*-Si(111):  
A Molecular Semiconductor|Catalyst Construct**

Junhyeok Seo, Ryan T. Pekarek, and Michael J. Rose\*

*Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA*

**Experimental Procedures**

**A. Preparation of a Surface-bound Nickel Phosphine Catalyst**

**1) Preparation of Cl-Terminated Si(111) Wafer.** A single side polished *p*-type Si wafer was used for all experiments (Virginia Semiconductor Inc., VA, B-doped Czochralski (CZ) grown *p*-type Si wafer ( $381 \pm 25$   $\mu\text{m}$  thickness), 7–15  $\Omega\cdot\text{cm}$  resistivity). The silicon wafer was cleansed by sonication in acetone, ethanol, and distilled water sequentially for 10 min each. Solvents were removed by a stream of N<sub>2</sub> gas, and the wafer was oxidized in Piranha solution (1:3 volume ratio of aqueous hydrogen peroxide (30%, Fisher Scientific) and conc. sulfuric acid (96.6%, Fisher Scientific)) at 90 °C for 20 min. The sample was rinsed by de-ionized water, and dipped in a buffered HF (aq) solution (ammonium hydrogen difluoride solution, semiconductor grade, Transene Company, Inc.) for 1 min. After rinsing with de-ionized water, the sample was immersed in 40% NH<sub>4</sub>F (aq) solution (semiconductor grade, Transene Company, Inc.) for 20 min. The aqueous NH<sub>4</sub>F solution was bubbled with N<sub>2</sub> gas for 30 min prior to use and during the immersion of the sample. The sample was rinsed with de-ionized water, dried with N<sub>2</sub> stream, and immediately moved inside the N<sub>2</sub>-purged flush box. The sample was heated in a PCl<sub>5</sub>-saturated chlorobenzene with a few grains of benzoyl peroxide (reagent grade, 97%, Sigma Aldrich) at 90 °C for 1 h. The resulted Si(111)-Cl surface was rinsed with chlorobenzene and THF thoroughly (2

mL  $\times$  10 each).

**2) Attachment of Triflatophenyl to Si(111) Surface, and Passivation by Methylation.** The *4-bromophenyl trifluoromethanesulfonate*<sup>1</sup> (0.1 g, 0.33 mmol) was reacted with 0.18 mL of *n*-BuLi (0.29 mmol, 1.6 M in THF Sigma Aldrich) in 18 mL THF at  $-70$  °C for 1 h. The prepared *p*-Si(111)-Cl substrate was incubated with the lithiate in THF from  $-70$  °C  $\rightarrow$  RT for 1 h. Subsequently, the remaining Si(111)-Cl sites were passivated by methylation in 1 M CH<sub>3</sub>MgCl solution of THF (diluted from 3.0 M CH<sub>3</sub>MgCl in THF, Sigma Aldrich) at 60 °C for 30 min. The wafer was rinsed and sonicated in THF. All the coupling procedures were performed under N<sub>2</sub> atmosphere.

**3) Coupling of the PNP Ligand to Phenyl Linker on Si(111).** The triflatophenyl/methyl attached Si(111) surface was exposed to a solution of [Pd(PPh<sub>3</sub>)<sub>4</sub>] (6 mg in 20 mL toluene, Strem) for 2 h at room temperature. The Pd-attached sample was rinsed with toluene and THF thoroughly. A PNP ligand, *4-bromo-N,N-bis((diphenylphosphanyl)methyl)aniline*<sup>2</sup> (0.2 g, 0.36 mmol), was reacted with 0.2 mL (0.32 mmol) of *n*-BuLi (1.6 M in THF) at  $-70$  °C in 18 mL THF for 1 h. The 0.36 mL ZnCl<sub>2</sub> solution (0.36 mmol, 1M in Et<sub>2</sub>O, Sigma Aldrich) was reacted with the lithiate in THF, and the reaction solution was allowed to warm to room temperature for 0.5 h. The prepared Pd-attached sample was immersed in the reaction solution, and the solution was refluxed at 80 °C for 4 h. The sample was rinsed with THF and MeCN thoroughly (2 mL  $\times$  10 each).

**4) Preparation of *p*-Si[(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PNP-Ni(MeCN)<sub>2</sub>]/(ClO<sub>4</sub>)<sub>2</sub> (= Si-PNP<sup>1</sup>-Ni).** A small portion (30 mg, 0.08 mmol) of [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (Sigma Aldrich) was stirred in 14 mL of MeCN in the presence of Na<sub>2</sub>SO<sub>4</sub> for 4 h. The blue solution was cotton-filtered, where the PNP-ligand attached sample was immersed for 1 h. The sample was rinsed with MeCN and toluene thoroughly (2 mL  $\times$  10) as resulting Si-PNP<sup>1</sup>-Ni sample. For additional ligand attachment to prepare *p*-

Si|(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PNP-Ni-PNP(C<sub>6</sub>H<sub>4</sub>)Br/(ClO<sub>4</sub>)<sub>2</sub> (= Si-PNP<sup>2</sup>-Ni), the Si-PNP<sup>1</sup>-Ni sample was immersed in *4-bromo-N,N-bis((diphenylphosphanyl)methyl)aniline* solution (10 mg in 6 mL toluene) for 1 h at room temperature. The sample was rinsed with toluene and THF thoroughly (2 mL × 10 each).

## B. Sample Characterization

**1) X-ray Photoelectron Spectroscopy (XPS).** XP spectra were obtained as using an X-ray photoelectron spectrometer (Kratos Axis Ultra) with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 1486.5$  eV). Photoelectron take-off angle was 45° with respect to the X-ray beam, and analysis chamber pressure was retained around  $2 \times 10^{-9}$  Torr during the measurement. Obtained spectra were analyzed by the Casa XPS software (version 2.3.15, Casa Software Ltd.). The binding energy of each spectrum was calibrated by a Si 2*p* peak (99.15 eV).

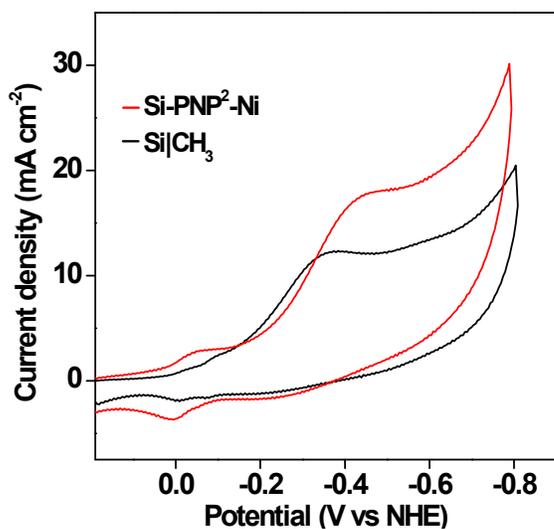
**2) Surface Recombination Velocity (SRV).** Surface recombination velocity was measured using a contactless microwave conductivity apparatus with 20 ns laser pulses at 905 nm from OSRAM laser diode and ETX-10A-93 driver (Growth Equipment, Inc.). The generated electron-hole pairs were diffused through the surface of Si wafer, and recombined through localized electronic states within the Si band gap. The carrier lifetimes were measured and the average of over 130 traces was obtained. The average plot was fitted to the single exponential decay, and the  $\tau$  (observed charge carrier lifetime) was converted to the surface recombination velocity ( $S$ ) by an equation:

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{2S}{d} \quad (1)$$

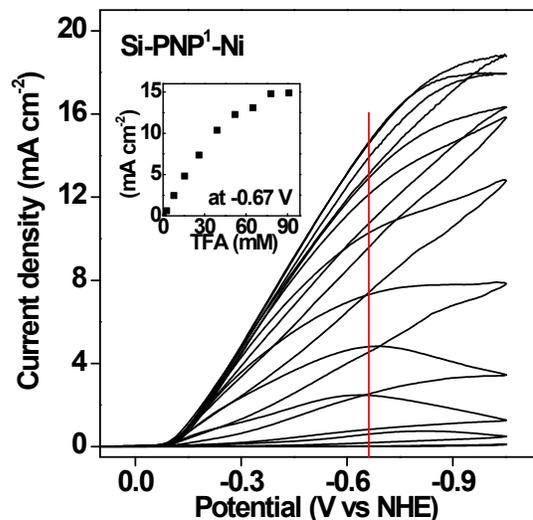
where  $\tau_B$  is a bulk lifetime,  $d$  is a wafer thickness.

**C. Photoelectrochemical (PEC) Measurements.** The PEC measurements were performed using CHI 660D (CH Instruments, Inc., USA) potentiostat. A three-electrode set-up was composed of a Si wafer working electrode, a Pt-wire (99.95%, Strem Chemicals, USA) counter electrode, and a

Ag-wire quasi-reference electrode (CHI112, CH Instruments, Inc., USA). To assemble the PEC cell, copper tape (Electron Microscopy Sciences, USA) was attached on a stainless steel base, where the Si wafer was placed after scratching the unpolished side with a diamond scribe. The ohmic contact was made with Ga/In eutectic (99.99%, Alfa Aesar). An O-ring was placed on the Si wafer, and the Teflon cell was placed on the top. The light active area was 0.07 cm<sup>2</sup>. A broadband LED bulb (Osram Sylvania Inc., Ultra LED 50 W) was used as a light source, and the light intensity was measured as ~33 mW cm<sup>-2</sup> under our experimental conditions. All PEC measurements were performed under N<sub>2</sub> atmosphere and room temperature. Ferrocene was used as an internal reference, and the obtained potentials were converted versus NHE ( $E_{1/2}$  of Fc<sup>0/+</sup> = 0.626 V vs NHE).



**Fig. S1.** PEC-CV scans of Si-PNP<sup>2</sup>-Ni (red line) and *p*-Si(111)|CH<sub>3</sub> (black line) samples. *Experiment conditions:* N<sub>2</sub> atmosphere inside glove box, 0.2 M LiClO<sub>4</sub> (MeCN), broadband LED 33 mW cm<sup>-2</sup>, 200 mV s<sup>-1</sup> scan rate.

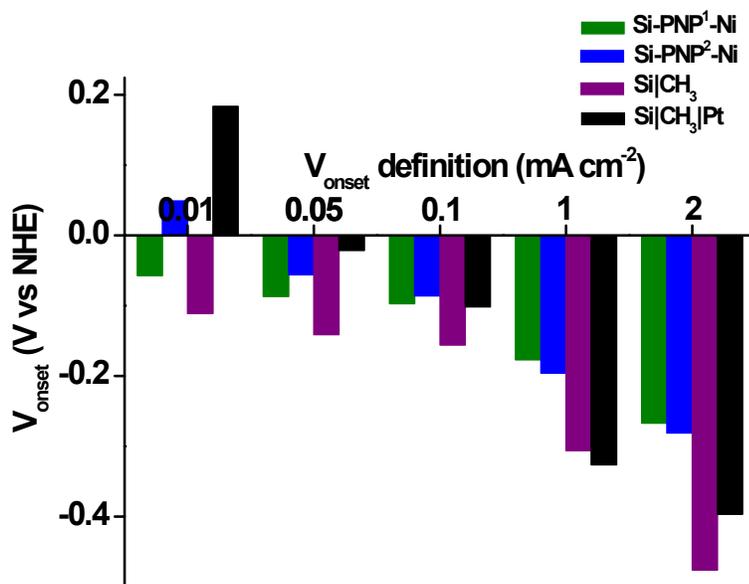


**Fig. S2.** PEC-CV scans of Si-PNP<sup>1</sup>-Ni sample. *Experiment conditions:* N<sub>2</sub> atmosphere inside glove box, 0.2 M LiClO<sub>4</sub> (MeCN), broadband LED 33 mW cm<sup>-2</sup>, 100 mV s<sup>-1</sup> scan rate.

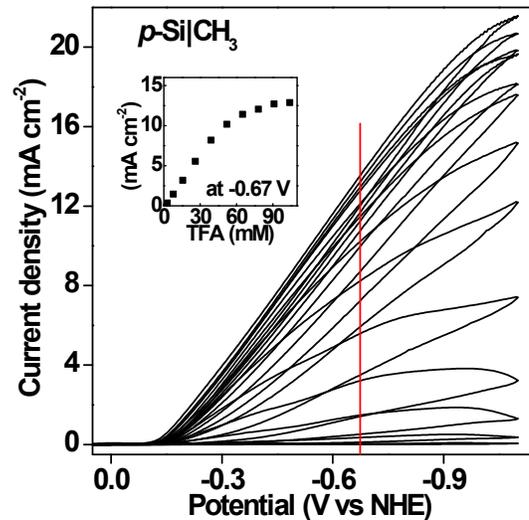
**Controlled Potential Coulometry.** For the experiment, the Si-PNP<sup>2</sup>-Ni was prepared according to the procedures described above, and all the preparation was done inside glove box. The back side of the wafer was scratched with a diamond tip scribe. Next, a tightly spiraled tip of copper wire was contacted to the wafer with GaIn eutectic, and the wafer/copper wire was sealed with epoxy (Devcon, 5 min Epoxy Gel). The wafer/electrode was introduced to the sealed PEC cell (~200 mL volume size) containing 0.2 M LiClO<sub>4</sub> solution (in 80 mL MeCN) while using a Pt counter electrode and a Ag wire as a reference electrode. After injection of 0.4 mL TFA (65 mM), the solution was stirred for a few minutes. The electrolysis was carried out at -1 V vs Ag QRE for 1h, and the 50 mL of headspace gas was collected by air-tight syringe. The gas sample was analyzed by GC-MS, and the product gas was confirmed to be hydrogen gas. Gas sample was analyzed by Shimadzu 2014 Gas Chromatography equipped with a TCD detector, and the product gas was confirmed as dihydrogen.

The onset potential ( $V_{\text{onset}}$ ) of the catalytic proton reduction was compared between *p*-Si|CH<sub>3</sub>, *p*-

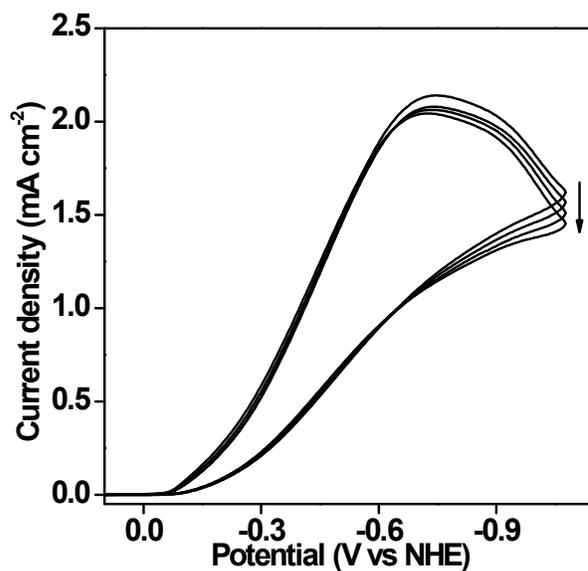
Si|CH<sub>3</sub>|Pt, Si-PNP<sup>1</sup>-Ni, and Si-PNP<sup>2</sup>-Ni, where the  $V_{\text{onset}}$  changes according to its definition current ( $V_{\text{onset}}$  was selected as the potential necessary to achieve a threshold of catalytic current: 0.01, 0.05, 0.1, 1 or 2 mA cm<sup>-2</sup>). Overall, the Si-PNP<sup>1</sup>-Ni and Si-PNP<sup>2</sup>-Ni samples show the similar  $V_{\text{onset}}$  except at 0.01 mA cm<sup>-2</sup>, and the *p*-Si|CH<sub>3</sub>|Pt shows more positive  $V_{\text{onset}}$  than the *p*-Si|CH<sub>3</sub> sample except at the 1 mA cm<sup>-2</sup> threshold. In the main manuscript, we defined the  $V_{\text{onset}}$  as a potential for the current of 0.05 mA cm<sup>-2</sup>, where the Si-PNP<sup>1</sup>-Ni and Si-PNP<sup>2</sup>-Ni samples show the similar  $V_{\text{onset}}$  and *p*-Si|CH<sub>3</sub>|Pt shows more positive  $V_{\text{onset}}$  than the *p*-Si|CH<sub>3</sub> sample.



**Fig. S3.** Effect of the variation of  $V_{\text{onset}}$  according to the chosen definition ( $J_{V_{\text{onset}}} = 0.01 \rightarrow 2$  mA cm<sup>-2</sup>). The main manuscript utilizes  $J_{V_{\text{onset}}} = 0.05$  mA cm<sup>-2</sup> as a standard benchmark for performance.



**Fig. S4.** PEC-CV scans of  $p\text{-Si}(111)|\text{CH}_3$  sample. *Experiment conditions:*  $\text{N}_2$  atmosphere, 0.2 M  $\text{LiClO}_4$  (MeCN), broadband LED  $33 \text{ mW cm}^{-2}$ ,  $100 \text{ mV s}^{-1}$  scan rate.



**Fig. S5.** Consecutive PEC-CV scans of Si-PNP<sup>2</sup>-Ni sample under 10 mM TFA concentration. *Experiment conditions:*  $\text{N}_2$  atmosphere (glovebox), 0.2 M  $\text{LiClO}_4$  (MeCN), broadband LED  $33 \text{ mW cm}^{-2}$ ,  $100 \text{ mV s}^{-1}$  scan rate.

(1) The *4-bromophenyl trifluoromethanesulfonate* was synthesized in this way: The 4-bromophenol (1.00 g, 5.78 mmol) was prepared in THF at 0 °C, where NaH (0.220 g, 9.48 mmol) was added. Into the reaction solution was added *N*-phenyl-bis(trifluoromethanesulfonimide) (2.27 g, 6.36 mmol), and the solution was stirred at 0 °C for 30 min, and additionally for 1 h at room temperature. The solution was refluxed overnight, and cooled to room temperature. After quenching with water, the organic product was extracted with dichloromethane, and it was purified by column chromatography. Spectral data of the resulted product was identical with the literature: Frantz, D. E.; Weaver, D. G.; Carey, J. P.; Kress, M. H.; Dolling, U. H. *Organic Letters* **2002**, *4*, 4717.

(2) The *4-bromo-N,N-bis((diphenylphosphanyl)methyl)aniline* was synthesized following the literature procedure: Durran, S. E.; Elsegood, M. R. J.; Hawkins, N.; Smith, M. B.; Talib, S. *Tetrahedron Letters* **2003**, *44*, 5255. In this work, the <sup>31</sup>P NMR spectral data was reported. Here, we report additional <sup>1</sup>H NMR spectral and elemental analysis data to confirm the identity and purity of the ligand. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.88 (d, 4H, *J*<sub>HP</sub> = 4.8 Hz), 6.62 (d, 2H), 7.21 (d, 2H), 7.32 (m, 20H) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -27.9 ppm. Anal. Calcd for C<sub>32</sub>H<sub>28</sub>BrNP<sub>2</sub>: C, 67.62; H, 4.97; N, 2.46. Found: C, 66.78; H, 4.89; N, 2.40.