

**H<sub>2</sub> Photogeneration using a Phosphonate-Anchored Ni-PNP Catalyst on a  
Band-Edge Modified *p*-Si(111)|AZO Construct**

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## Experimental

### A. Surface Functionalization Procedures of Si(111) Semiconductor

**1) Preparation of Cl-Terminated Si(111) Wafer.** A single side polished *p*-type Si wafer (Virginia Semiconductor Inc., VA, B-doped Czochralski (CZ) grown *p*-type Si wafer ( $450 \pm 25$   $\mu\text{m}$  thickness),  $1.4\text{--}9$   $\Omega\cdot\text{cm}$  resistivity) was used. A silicon wafer was sonicated in acetone, ethanol, and distilled water sequentially for 10 min prior to the following etching procedure. After blowing  $\text{N}_2$  gas onto the surface, the sample was immersed in Piranha solution (1:3 v/v of  $\text{H}_2\text{O}_2$  (aq) (30%, Fisher Scientific): $\text{H}_2\text{SO}_4$  (96.6%, Fisher Scientific)) at  $90^\circ\text{C}$  for 20 min. After rinsing with de-ionized water, the sample was dipped in a buffered HF solution (HF (aq), semiconductor grade, Transene Company, Inc.) for 1 min. The sample was rinsed with de-ionized water and subsequently dipped in a  $\text{N}_2$ -bubbled  $\text{NH}_4\text{F}$  solution (40% in water, semiconductor grade, Transene Company, Inc.) for 20 min. The sample was rinsed with de-ionized water and dried with  $\text{N}_2$  stream. For chlorination, the sample was moved inside a  $\text{N}_2$ -purged flush box and immersed in a  $\text{PCl}_5$ -saturated chlorobenzene with a few grains of benzoyl peroxide (Sigma Aldrich) at  $90^\circ\text{C}$  for 1 h. Lastly, the resulted chlorinated sample was rinsed with chlorobenzene and THF thoroughly ( $1\text{ mL} \times 10$  each).

**2) Attachment of Methyl and 3,5-Dimethoxyphenyl Groups on Si(111) Surface.** *i)*  $\text{Si-CH}_3$ :

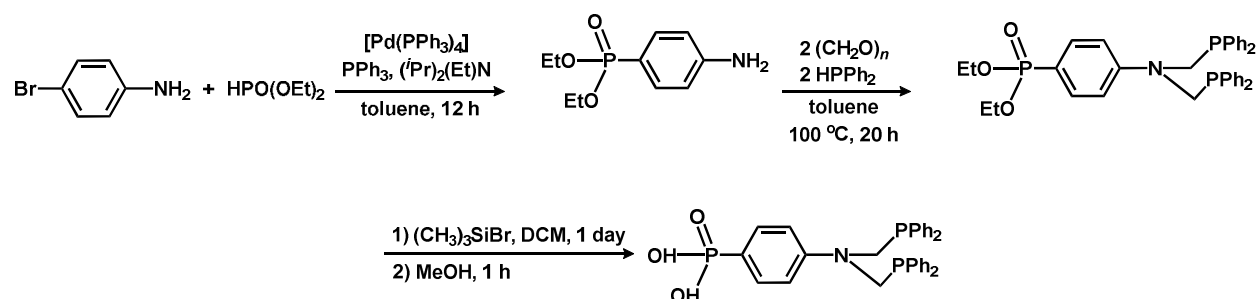
The prepared Cl-terminated Si(111) wafer was immersed in 1 M  $\text{CH}_3\text{MgCl}$  solution (diluted from 3.0 M  $\text{CH}_3\text{MgCl}$  in THF, Sigma Aldrich) at  $60^\circ\text{C}$  inside the  $\text{N}_2$ -purged flush box. After 30 min, the wafer was rinsed with THF thoroughly inside the flush box and then further cleansed by sonication in THF/MeOH for 10 min. The resulting  $\text{Si-CH}_3$  sample was finally rinsed with MeOH/THF and dried by  $\text{N}_2$  stream. *ii)*  $\text{Si-diMeOPh}$ : 0.08 g (0.36 mmol) of 1-bromo-3,5-

dimethoxybenzene (97 %, Acros) was prepared in 14 mL THF at  $-60\text{ }^{\circ}\text{C}$ , where 0.2 mL nBuLi (1.6 M in diethyl ether, 0.32 mmol) was dropwise added. After stirring the solution for 40 min, the Cl-terminated Si(111) wafer was immersed in the solution, and the solution was warmed naturally to room temperature for 1 h. The remaining Si(111)–Cl sites were methylated by immersing in the 1 M  $\text{CH}_3\text{MgCl}$  solution (THF) at  $60\text{ }^{\circ}\text{C}$  for 30 min inside the  $\text{N}_2$ -purged flush box.

**3) Atomic Layer Deposition (ALD) of Al-doped ZnO,  $\text{TiO}_2$  and Pt.** Savannah S100 apparatus (Cambridge Nanotechnology Inc., USA) was utilized for all atomic layer deposition (ALD) layers. Aluminum-doped Zinc oxide layer was deposited on methyl- or dimethoxyphenyl-functionalized Si(111) wafer using trimethylaluminum (TMA, Sigma Aldrich, unheated) and diethyl zinc (DEZ, Sigma Aldrich, unheated) as the Al and Zn precursors, respectively. The chromatography-grade  $\text{H}_2\text{O}$  was used for counter precursor and the reaction chamber was heated at  $150\text{ }^{\circ}\text{C}$ . Each pulse length of the Al, Zn and  $\text{H}_2\text{O}$  was 0.015 s, and the purging time of  $\text{N}_2$  gas between pulses was 20 s. To make consistent film thickness, the unit ALD cycle consisted of  $x$  cycles of ZnO and 1 cycle of  $\text{Al}_2\text{O}_3$  was repeated  $y$  times  $[(x:1)\times y = (\mathbf{16:1})\times\mathbf{5}, (\mathbf{20:1})\times\mathbf{4}, (\mathbf{27:1})\times\mathbf{3}, (\mathbf{41:1})\times\mathbf{2}, \text{ and pure ZnO } 83 \text{ cycles}]$ . From the growth rate supported by instrument supplier,  $1.66\text{ \AA}$  and  $1.01\text{ \AA}$  for ZnO and  $\text{Al}_2\text{O}_3$ , respectively, the estimated film thickness was  $138 \pm 0.2\text{ \AA}$ . The deposition of *a*- $\text{TiO}_2$  and Pt were result of reaction of tetrakis(dimethylamido)titanium (TDMAT, Sigma Aldrich,  $75\text{ }^{\circ}\text{C}$ ) with chromatography-grade  $\text{H}_2\text{O}$  and trimethyl(methylcyclopentadienyl)-platinum ( $[(\text{MeCp})\text{Pt}(\text{Me})_3]$ , Strem,  $70\text{ }^{\circ}\text{C}$ ) with high-purity  $\text{O}_2$  (99.999%), respectively. For the capping *a*- $\text{TiO}_2$  layer, the temperature of the substrate was maintained at  $150\text{ }^{\circ}\text{C}$ , and each pulse length of the Ti precursor and  $\text{H}_2\text{O}$  was 0.1 s

and 0.015 s, respectively, with 20 s of N<sub>2</sub> gas purging between each pulse (50 cycles). For the Pt nanoparticles, the temperature of substrate was maintained at 240 °C, and each pulse length of the Pt precursor and O<sub>2</sub> was 1.0 s and 0.015 s, respectively, with 5 s of N<sub>2</sub> gas purging between each pulse (20 cycles).

#### 4) Synthesis of Molecular Compounds



**Diethyl(4-aminophenyl)phosphonate (1).** A mixture of 4-bromoaniline (1 g, 5.8 mmol) and diethylphosphite (1.13 mL, 8.76 mmol) was prepared in 40 mL of toluene. Into the reaction mixture were added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.15 g, 2.5%), PPh<sub>3</sub> (1.53 g, 5.83 mmol), and diisopropylethylamine (5.0 mL, 25 mmol). After stirring overnight, the solution was treated with saturated NH<sub>4</sub>Cl (aq), and the organic compounds were extracted with dichloromethane. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the product was purified by column chromatography (hexanes/EA gradient of 1:10 to 1:3 ratio) as resulting in 0.11 g (~3% isolated yield). There was no attempt to improve yield, as minimal material was required for surface studies. <sup>1</sup>H NMR (d<sup>6</sup>-DMSO): δ 1.19 (t 6H), 3.90 (q 4H), 5.81 (s 2H), 6.61 (d 2H), 7.32 (d 2H) ppm. <sup>31</sup>P NMR (d<sup>6</sup>-DMSO): δ 21.2 ppm.

**Diethyl(4-(bis((diphenylphosphanyl)methyl)amino)phenyl)phosphonate (2).** Into 20 mL of toluene solution of **1** (0.11 g, 0.48 mmol) was added HPPH<sub>2</sub> (0.18 g, 0.96 mmol) and

paraformaldehyde (0.029 g) under N<sub>2</sub> atmosphere. The solution was then heated at 100 °C for 20 h under N<sub>2</sub> atmosphere, and all volatiles were removed under vacuum as heating at 60 °C to give 0.27 g product (90% yield), also isolated and stored under N<sub>2</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.31 (t 6H), 3.89 (d 4H), 4.08 (q 4H), 6.71 (d 2H), 7.33 (m 22H) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -27.5, 21.4 ppm.

**(4-(Bis((diphenylphosphanyl)methyl)amino)phenyl)phosphonic Acid (3).** The above compound **2** (0.270 g, 0.43 mmol) was dissolved in 5 mL dichloromethane under N<sub>2</sub> atmosphere, where bromotrimethylsilane (0.270 g, 1.76 mmol) was added. After stirring the reaction mixture for 1 day, the volatiles were removed by vacuum. The residue was dissolved in MeOH, and the solution was stirred for 1 h. After removing the solvent by vacuum, the residue was washed with DCM as resulting in 0.10 g product (41%). <sup>1</sup>H NMR (d<sup>6</sup>-DMSO): δ 3.90 (d 4H), 7.16 (d 2H), 7.23 (d 2H), 7.32 (m 8H), 7.39 (m 12H). <sup>31</sup>P NMR (d<sup>6</sup>-DMSO): δ -27.4 (PPh<sub>2</sub>), 14.7 (PO<sub>3</sub>) ppm. HR-MS(CI-MS): calcd. for [C<sub>32</sub>H<sub>30</sub>NO<sub>4</sub>P<sub>3</sub>]<sup>+</sup> 585.13480; found: 585.13680.

### 5) Preparation of *p*-Si|R|Metal Oxide|O<sub>3</sub>P(C<sub>6</sub>H<sub>4</sub>)PNP–Ni–PNP(C<sub>6</sub>H<sub>4</sub>)Br/(ClO<sub>4</sub>)<sub>2</sub>

*Attachment of the PNP Ligand to Metal Oxide on Si(111) Surface:* The metal oxide (AZO/TiO<sub>2</sub>) modified Si substrate was brought into an Ar glovebox, and immersed in a 9 mM solution of **3** in DMF for 24 h. The sample was then thoroughly rinsed with DMF and acetonitrile (10 × 1 mL each) and kept rigorously under argon atmosphere for storage and subsequent experiments.

*Metalation:* All of these operations were carried out in an argon atmosphere glovebox. A small portion of [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (30 mg, 0.08 mmol, 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 resulting blue solution was filtered and used directly for

the reaction. The O<sub>3</sub>P-Ar-PNP functionalized substrate was immersed in the Ni solution for 1 h. For samples prepared with the ‘capping’ PNP ligand: After rinsing with MeCN and toluene, the sample was immersed in a toluene solution containing the PNP(C<sub>6</sub>H<sub>4</sub>)Br ligand (*4-bromo-N,N-bis((diphenylphosphanyl)methyl)aniline*) (10 mg in 6 mL of toluene) for 1 h. The sample was then rinsed thoroughly with toluene and THF (10 × 1 mL each).

## **B. Physical Measurements and Photoelectrochemical (PEC) Characterization**

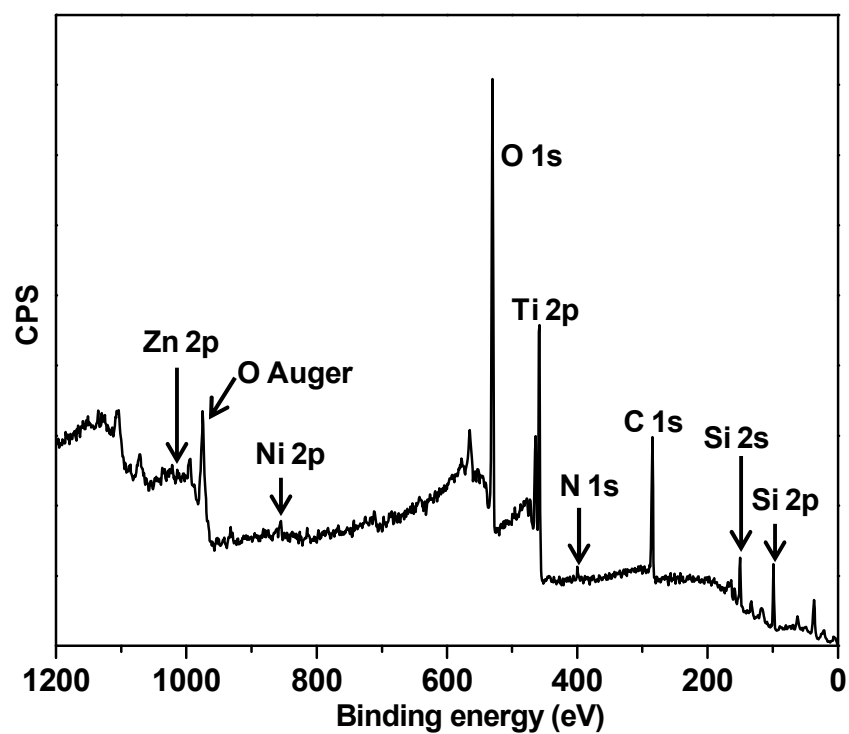
X-ray Photoelectron Spectra (XPS) were obtained by using a Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 1486.5$  eV). Photoelectron take-off angle was 45° with respect to the X-ray beam, and the analysis chamber pressure was maintained  $\sim 2 \times 10^{-9}$  Torr during the measurement. The obtained spectra were analyzed by the Casa XPS software (version 2.3.15, Casa Software Ltd.). The sheet resistance of Al-doped ZnO layers as a function of Al<sub>2</sub>O<sub>3</sub>:ZnO ALD ratio was obtained using a Lucas Labs SP4 four-point probe head combined with a Keithley 2400 source meter. The Park Scientific CP Research AFM (force constant of 0) was used for comparison of surface roughness of the methyl- and dimethoxyphenyl-functionalized *p*-Si|*R*|metal oxide surfaces. Vapor transfer of dodecylamine was performed for 10 minutes before analysis in a small glass chamber, and WSxM was used to analyze the images.<sup>1</sup>

PEC measurements were performed using an Interface 1000 (Gamry Instruments, USA) potentiostat. A three-electrode setup was composed of a Si wafer working electrode, a Pt-wire (99.95%, Strem Chemicals, USA) counter electrode, and an Ag-wire quasi-reference electrode (CHI-112, 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 back side with a diamond scribe. The ohmic contact was made with Ga/In eutectic (99.99%, Alfa Aesar). An O-ring (size 0.07 cm<sup>2</sup>) was placed on the Si wafer, and the Teflon cell was placed on the top. 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> at the sample site. All PEC measurements were performed under argon atmosphere and room temperature. Ferrocene was used as an internal reference, and the obtained potentials were converted versus NHE ( $E_{1/2}$  of  $\text{Fc}^{0/+} = 0.64$  V vs. NHE). The dataset for the Mott-Schottky plots was obtained under analogous conditions with a 10 kHz modulation frequency in 0.2 M  $\text{LiClO}_4/\text{MeCN}$  solution. The electrochemical impedance spectroscopy (EIS) measurements were carried out at various potentials between 0 V to -0.8 V vs. Ag under illumination with 10 mV AC amplitude over a frequency range of 10<sup>5</sup>-0.1 Hz. For the extraction of charge transfer resistance ( $R_{\text{ct}}$ ) from the EIS results, the Randles equivalent circuit was applied with Zview software (version 2.8d, Scribner Associate Inc.).

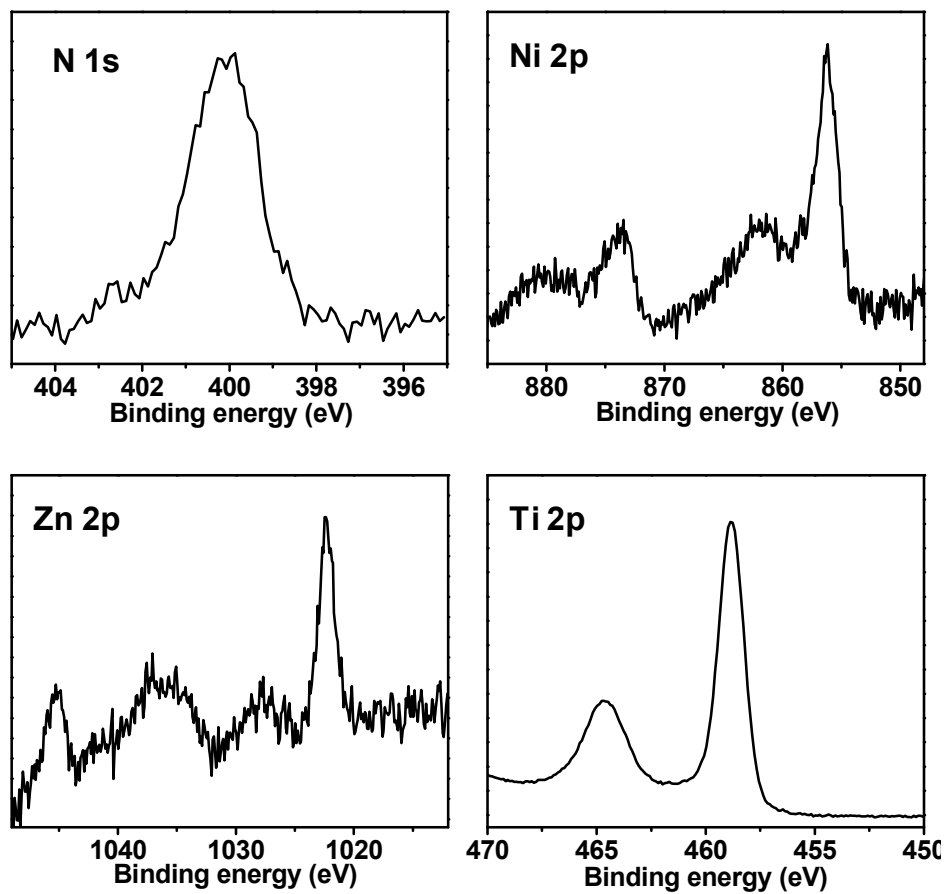
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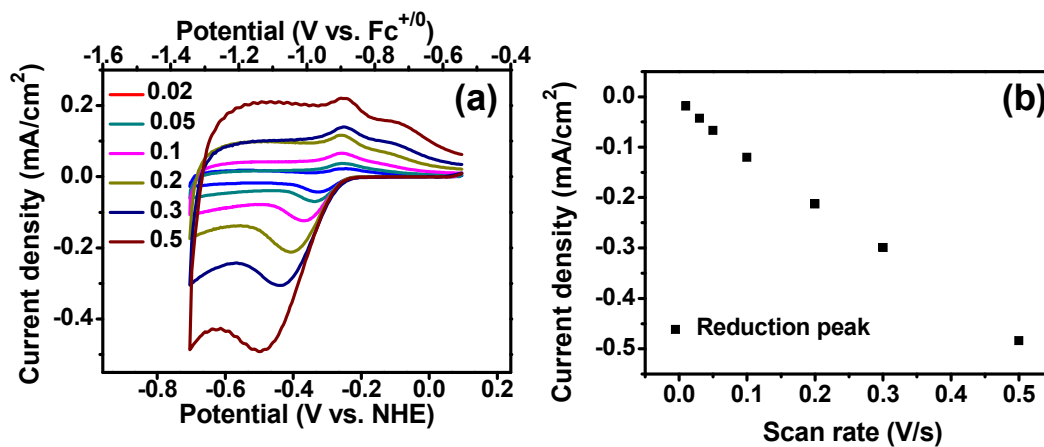


**Figure S1.** Survey X-ray photoelectron spectra for  $\text{Si|CH}_3\text{|AZO|TiO}_2\text{|O}_3\text{P(C}_6\text{H}_4\text{)PNP-Ni-PNP(C}_6\text{H}_4\text{)Br/(ClO}_4\text{)}_2\text{|}$ .

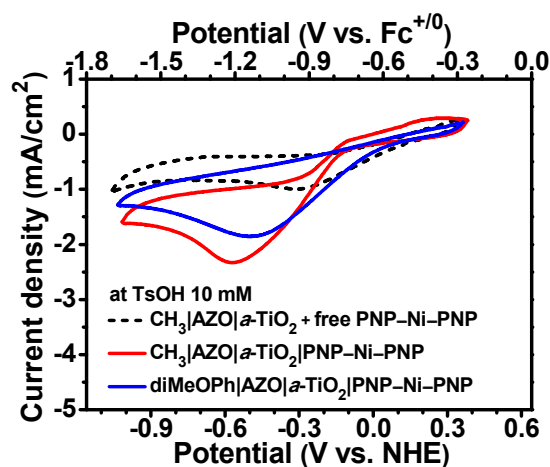




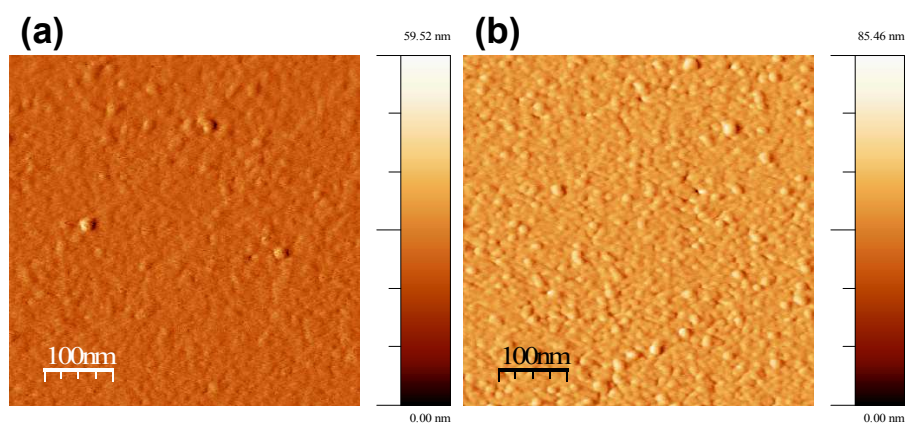
**Figure S2.** High-resolution region X-ray photoelectron spectra for selected elements for  $\text{Si|CH}_3\text{|AZO|TiO}_2\text{|O}_3\text{P(C}_6\text{H}_4\text{)PNP-Ni-PNP(C}_6\text{H}_4\text{)Br/(ClO}_4\text{)}_2\text{.}$



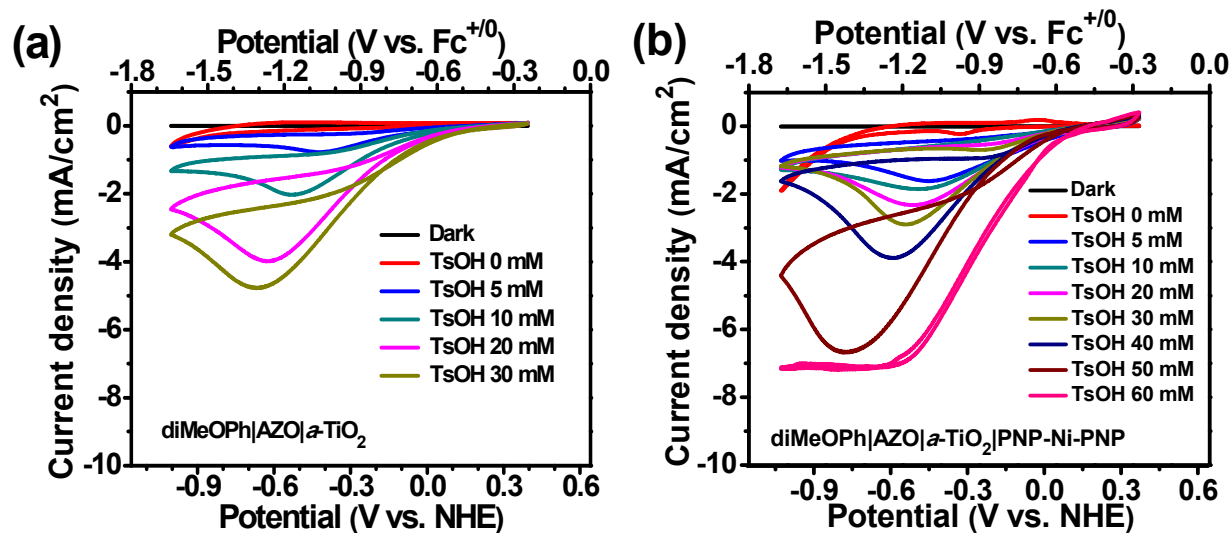
**Figure S3.** (a) Cyclic voltammograms for  $p\text{-Si}(111)\text{-CH}_3|\text{AZO}|\alpha\text{-TiO}_2|\text{PNP-Ni-PNP}$  as a function of scan rate (0.02 to 0.5  $\text{V s}^{-1}$ ) and its scan-rate dependence of (b) reduction current; *Experimental conditions:* 0.2 M  $\text{LiClO}_4$  electrolyte in MeCN, 33  $\text{mW cm}^{-2}$  broadband LED, argon atmosphere (glove box).



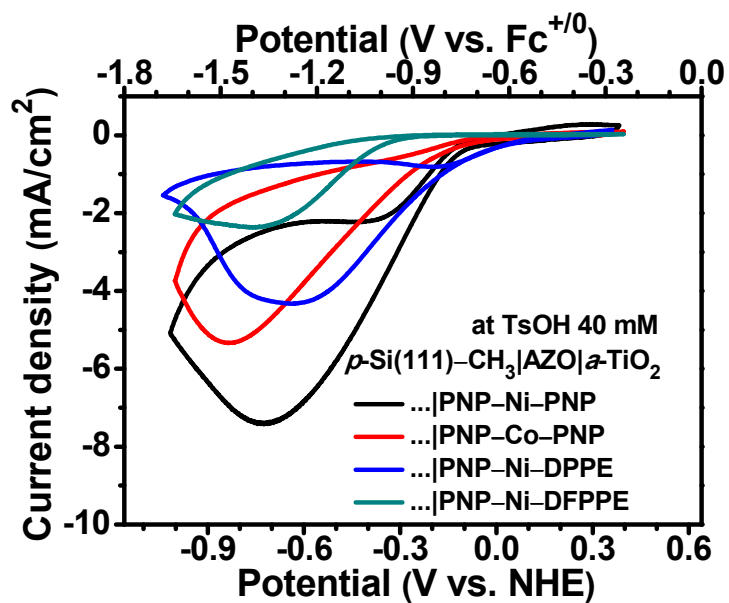
**Figure S4.** Catalytic CVs for comparison of  $p$ -Si(111)-CH<sub>3</sub>|AZO| $\alpha$ -TiO<sub>2</sub> + free Ni(PNP(C<sub>6</sub>H<sub>4</sub>)Br)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (dashed dark) solution,  $p$ -Si(111)-CH<sub>3</sub>|AZO| $\alpha$ -TiO<sub>2</sub>|PNP-Ni-PNP (red) and  $p$ -Si(111)-diMeOPh|AZO| $\alpha$ -TiO<sub>2</sub>|PNP-Ni-PNP (blue) at 10 mM TsOH. *Experimental conditions:* 0.2 M LiClO<sub>4</sub> electrolyte in MeCN, 33 mW cm<sup>-2</sup> broadband LED, 100 mV s<sup>-1</sup> scan rate, argon atmosphere (glove box).



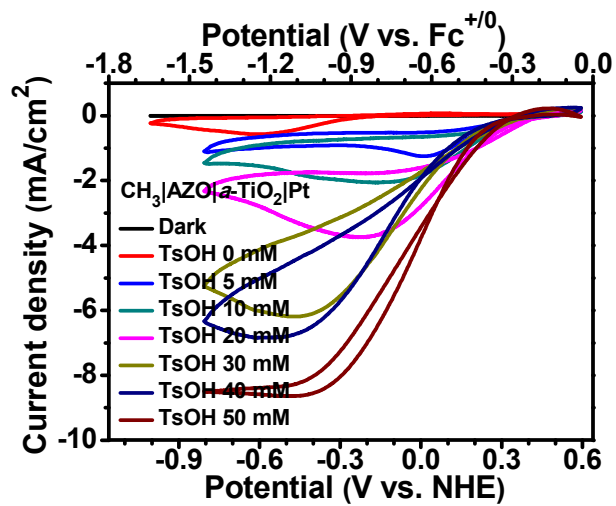
**Figure S5.** Atomic force microscopy images of (a)  $p$ -Si(111)-diMeOPh|AZO|TiO<sub>2</sub> and (b)  $p$ -Si(111)-CH<sub>3</sub>|AZO|TiO<sub>2</sub>.



**Figure S6.** Catalytic CVs for (a)  $p\text{-Si}(111)\text{-diMeOPh|AZO}|\alpha\text{-TiO}_2$ , (b)  $p\text{-Si}(111)\text{-diMeOPh|AZO}|\alpha\text{-TiO}_2\text{|PNP-Ni-PNP}$  as a function of [TsOH]; *Experimental conditions:* 0.2 M  $\text{LiClO}_4$  electrolyte in MeCN,  $33 \text{ mW cm}^{-2}$  broadband LED,  $100 \text{ mV s}^{-1}$  scan rate, argon atmosphere (glove box).



**Figure S7.** Catalytic CVs as a function of metal/ligand couples at 40 mM TsOH; *Experimental conditions:* 0.2 M LiClO<sub>4</sub> electrolyte in MeCN, 33 mW cm<sup>-2</sup> broadband LED, 100 mV s<sup>-1</sup> scan rate, argon atmosphere (glove box).



**Figure S8.** Catalytic CVs for  $p\text{-Si}(111)\text{-CH}_3|\text{AZO}|\alpha\text{-TiO}_2|\text{Pt}$  as a function of  $[\text{TsOH}]$ ; *Experimental conditions:* 0.2 M  $\text{LiClO}_4$  electrolyte in MeCN,  $33 \text{ mW cm}^{-2}$  broadband LED,  $100 \text{ mV s}^{-1}$  scan rate, argon atmosphere (glove box).