Supporting Information for:

Energetic Effects of Hybrid Organic/Inorganic Interfacial Architecture on Nanoporous Black Silicon Photoelectrode

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Experimental

Sample Preparation

Materials and Chemicals. Silicon wafers (boron-doped Si(100), 1–5 Ω cm, 255–305 μ m thick) were purchased from Topsil. Electronic grade acetone (J.T. Baker) and isopropanol (Fischer) were used as received. Acetonitrile (MeCN, HPLC grade, Fisher) and tetrahydrofuran (THF, Fisher, HPLC Grade) were stirred over calcium hydride overnight and distilled at their respective boiling points under N₂ atmosphere. Dimethylformamide (DMF, Aldrich, Reagent Grade) was dried over calcium hydride overnight and vacuum distilled (~50 mTorr, 50 °C). Lithium perchlorate (Aldrich, 99.99% trace metals basis) was dried by heating to 160 °C under vacuum (~50 mTorr) for 48 h. 1,4-Butanediol (Aldrich, 99% ReagentPlus) was placed under reduced pressure for 24 h and vacuum distilled (~50 mTorr, 150 °C, activated 4Å sieves). Ferrocenecarboxylic acid (Alfa Aesar, 98%), 1,1'-Azobis(cyclohexanecarbonitrile) (Aldrich, ≥98%), N,N'-dicyclohexylcarbamide (Aldrich, ≥99%), dimethylaminopyridine (Aldrich, ≥99%), p-toluenesulfonic acid monohydrate (Aldrich, ReagentPlus ≥98%) were dried via repeated (5) vacuum (5 min, ~0.05 mTorr, room temp.)/nitrogen cycles. Hydrofluoric acid (Sigma, 48% Reagent Grade), silver nitrate (Aldrich, Reagent Grade ≥99%), hydrogen peroxide (Fisher, 30% Reagent Grade), nitric acid (J.T. Baker, 70% Electronic Grade), tetramethylammonium hydroxide 30-hydrate (Sigma, ≥98.0%), chloroplatinic acid hydrate (Aldrich, 99.9%), sulfuric acid (J.T. Baker, 96% Reagent Grade), potassium sulfate (Acros, ≥99.0%), methyl viologen dichloride hydrate (Aldrich, 98%), titanium(IV) chloride (Aldrich, 99%), platinum(II) acetylacetonate (Strem, 98%), and galliumindium eutectic (Alfa Aesar, 99.99% metals basis) were used as received. Various Hydrion buffers (Aldrich) were prepared: pH 3 (phthalate), pH 6 (phosphate), pH 9 (carbonate), pH 12 (phosphate). The pH of final buffer solutions was measured with a Thermo Scientific Orion 2-star benchtop pH meter.

Planar and Nanoporous Black Silicon Preparation. Silicon wafers cut to ~1 cm × ~10 cm strips with a diamond scribe. The strip was then sonicated in acetone and isopropanol for 10 min each, blowing dry after each via an N₂ stream. One side of the strip was then masked with Kapton tape, sonicated in deionized water and blown dry. Wafers were etched for 60 s in 2 M HF, rinsed with deionized water, and dried via N_2 stream. Afterward, planar samples were brought into an Arfilled glovebox with <1 ppm O₂ and H₂O. Wafers to be nanotextured were then subjected to a metal assisted chemical etch (MACE) based on an existing procedure¹ where the strip was soaked in a series of solutions, rinsing with deionized water and drying via N_2 after each step. First, silver nanoparticles were deposited onto samples by soaking the strip in a solution of 1 mM AgNO₃ and 0.4 M HF for 30 s. Then, the strip was etched in a freshly prepared MACE solution (used within 6 hours of preparation: 1.25 M HF, 0.16 M H_2O_2) for 6 min in a sealed centrifuge tube. To prevent interference in the etching by bubbles on the surface, the tube was agitated regularly (approximately once per second) throughout the etch and held at a ~45° angle (with the desired surface facing up) to minimize bubble adhesion to the surface. The agitation rate is important as too slow or rapid agitation results in a visibly heterogenous surface. The silver particles were then removed by soaking the strip in 7.9 M HNO₃ (35%) for 6 min. A brief 2 s etch in 55 mM (Me₄N)OH was performed to decrease the surface area and roughness of the nanostructures. Wafers were then either a) etched in 2 M HF for 30 s and brought into the glovebox, b-Si; or b) exposed to a second MACE to bury Pt particles into the silicon, B-Pt/b-Si. To deposit the Pt on the surface, the strip was soaked in a solution of 1 mM H₂PCl₆ and 0.4 HF for 60 s. Next, a brief metal-assisted etch was performed as described previously but for 90 s. Finally, the wafer was soaked for 30 s in a 2 M HF solution and brought into the glovebox. All wafers were thoroughly rinsed with deionized water and blown dry with a nitrogen gas stream before bringing them into the glovebox. In the box, each strip was cut into several ~1 cm × ~1 cm wafers.

Monolayer Formation. Etched silicon samples were functionalized by exposing the H-terminated wafer to the molecule to be bound to the surface in a sealed vial. The wafer was submerged in the neat 1,4-butanediol. A small amount (< 10 mg) of a radical initiator, 1,1'-Azobis(cyclohexanecarbonitrile), was also added to each reaction. Once sealed, the vials were heated to 150 °C for 2 h. The wafer was then rinsed, sonicated, and rinsed again with dry THF. Attempts to bind 1,5–hexadiene (thermal, radical, or light–activated) resulted in polymerization. Reactions using 1,4-butanediol via the light–activated method (254 nm, UVP Pen-Ray lamp model 11SC-1) were also unsuccessful.

As shown in Scheme S1, ferrocenecarboxylic acid was bound to the surface via Steglish esterification.² In the glovebox, a solution of ferrocenecarboxylic acid (0.2 M), N,N'-dicyclohexylcarbamide (0.2 M), 4-dimethylaminopyridine (0.1 M), and *p*-toluenesulfinic acid (0.1 M) was freshly prepared in dry DMF and added to vials containing the wafers to be treated. The vials were sealed and heated to 50 °C overnight. Afterward the wafers were rinsed and sonicated (10 min) in dry DMF, then rinsed with dry MeCN. All reactions were performed in an argon-filled glovebox with O₂ and H₂O levels <1 ppm.





*TiO*₂ and Pt Deposition. Atomic layer deposition (ALD) was used to grow titania and Pt on the surface. Titania ALD was performed using a Beneq TFS 200 ALD system equipped with an air-free transfer arm connected to a glovebox. Samples were transferred to the ALD chamber without exposure to air. To deposit the titania, the wafers were heated to 200 °C and the precursors, TiCl₄ and water were kept in stainless-steel bubblers at room temperature (20 °C). For both precursors a 150 ms dose was used followed by a 3 s purge. For samples where platinum was deposited on the titania, the wafers were transferred to a viscous flow reactor built in-house similar to that by Elam *et. al* and heated to 240 °C.³ The precursor, platinum(II) acetylacetoneate, was heated to 50 °C, and O₂ (99.999% purity) was used as the oxidant. The Pt dose length was 10 s with a 15 s purge and O₂ was dosed for 5 s and purged for 60 s. For simplicity, we label the TiO₂ thickness

on the black silicon substrates using the 0.05 nm/cycle growth rate expected for planar oxidized Si(100).^{4,5}

Sample Characterization

Electrochemistry. Cyclic voltammetry in nonaqueous solvent (0.2 M LiClO₄ in MeCN) was used to calculate the number of ferrocene molecules bound to the surface. To perform the measurement, the back of the sample was scratched and GaIn eutectic was applied. The wafer was placed on a strip of copper tape fixed to a stainless-steel base. Finally, a custom-build Teflon piece with a cup for solution and hole in the bottom to expose the wafer was placed over the assembly and held in place with stainless steel screws. A detailed schematic has been described previously.⁶ A Kalrez O-ring (internal area of 0.11 cm²) was used to keep solution from leaking and standardize coverage between measurements. As shown in Figure S1, unbound ferrocenecarboxylic acid redox potential is ~270 mV positive of ferrocene and is therefore ~5.26 eV negative of the vacuum energy.⁷ As the silicon valence band is 5.17 eV negative of vacuum, after equilibration with the bound redox couple the silicon will be in accumulation (see Figure S2). As the photovoltage in this regime is zero, sample illumination is unnecessary and there is no difference between light and dark behavior. This behavior has been observed previously for vinylferrocene bound to p-type Si(100).⁸ Voltammograms were collected with a Ag pseudoreference electrode, Pt counter electrode, and the silicon sample via the copper tape as the working electrode. Coverage was determined from the slope when peak current (J_{o}) is plotted against scan rate $(v)^7$:

$$J_p = \frac{n^2 F^2}{4RT} \nu A \Gamma \tag{1}$$

where *n*, *F*, *R*, and *T* are the number of electrons per reaction, Faraday's number, the ideal gas constant, and the temperature (298 K), respectively; *A* is the area of the electrode and Γ is the coverage of the surface-bound species.



Fig. S1 Cyclic voltammogram of 10 mM each of unbound ferrocene (Fc) and ferrocenecarboxylic acid (FcCOOH) in acetonitrile with 0.2 M LiClO₄ as a supporting electrolyte. As shown, the FcCOOH redox potential is 272 mV positive of Fc.



Fig. S2 Band diagram before (left) and after (right) the silicon and surface-bound redox couple equilibrate.

Proton Reduction Characterization. To prepare samples for aqueous electrochemistry, the back side was scratched, and Galn eutectic was spread on the back (as above). A drop of silver paint was used to maintain electrical contact between the wafer and the copper. Kapton tape was then affixed to cover exposed copper tape and the area around the was sealed with epoxy (Loctite 9460). After curing for 48 h, aqueous voltammograms were obtained in 0.5 M H₂SO₄ (pH 0.3) under 1 sun illumination (300 W tungsten light source), scanning negative to positive at 100 mV/s. A Ag/AgCl reference (3M NaCl) and Pt foil counter electrode were used to complete the circuit. To convert the values referenced to Ag/AgCl to RHE, 0.210 V was added to the potential referenced to Ag/AgCl.⁹ The onset potential (V_{onset}) was taken as the potential where the current was -1 mA/cm^2 . Potentiostatic experiments were conducted with a Hg/HgSO₄/H₂SO₄ reference electrode.

Flatband Potential Characterization. As we described previously,¹⁰ the flatband potential was determined by measuring the difference in the dark and illuminated sample resistivity (R) via intensity-modulated high frequency resistivity (IMHFR) spectroscopy. Briefly, a lock-in amplifier (SR 830) introduced an AC frequency (100 kHz, 10 mV amplitude) to a potential applied by a potentiostat (PAR 173). A Labview program was used to set the potential and read the R values from the lock-in amplifier. The sample was subjected to light/dark cycles using a Uniblitz chopper set to 5 Hz and a broadband light source (41720-series Cole Parmer, 150 W tungsten halogen lamp). The LabView program bins light and dark R values, then calculates the difference between them (ΔR). The measurement was made using the same electrochemical cell described above for acidic *J*–*V* data collection (unless otherwise stated). The potential was stepped at 2 mV intervals throughout the potential range. The flatband potential (V_{fb}) was taken as the potential where the flat region of the curve for two consecutive points.

To evaluate the pH dependence of the flatband potential, the IMHFR experiment was performed in various buffered solutions. Similar to previously reported experiments,¹¹ carbon cloth reference and counter electrodes were used and the silicon sample was the working electrode. The buffered solutions contained 50 mM methyl viologen as a pH-independent redox couple and 0.25 M K₂SO₄ as supporting electrolyte. The potential was referenced to the MV^{2+/+} redox couple, measured substituting a platinum foil working electrode for the silicon sample.

TEM Imaging. TEM lamella was prepared by a standard focused ion beam (FIB) lift-out technique and followed by Ga ion milling to reduce the final thickness to less than 100 nm. TEM observations were performed on an FEI Tecnai F20 TEM equipped with a Gatan Enfinium EELS spectrometer and GIF Quantum K2 system at an acceleration voltage of 200 kV. An energy shift of 400 eV and a dispersion of 0.25 eV/channel were employed to obtain a strong signal-to-noise ratio of Ti-L and O-K edges. EEL spectra in the STEM mode was recorded with a CCD camera. The acquisition time for each spectrum was 200 ms.

Blocking and Uncovering Pt NPs with TiO₂ on 'buried Pt' Samples

We found that the thickest TiO₂ layer studied (15 nm) was sufficient to prevent a direct electrolyte | Pt nanoparticle junction as evidenced by a V_{onset} of -0.4 V vs. RHE (Figure S3a). Unexpectedly, repeated scanning shifts the *J*–*V* curves to more positive potentials. After just five scans, V_{onset} shifts by 0.5 V to >0.1 V vs. RHE. This V_{onset} shift to more positive potentials with the number of *J*–*V* scans also holds for a 10 nm thick TiO₂ ALD oxide, but to a lesser degree (Figure S3b). In contrast, the 5 nm TiO₂ thickness sample exhibits an initial V_{onset} positive of RHE that decreases slightly (by 0.01 V) over 5 scans. We attribute these effects to electrochemical etching of TiO₂ as the TiO₂ Pourbaix diagram shows that oxide dissolution is favorable in acidic media at negative potentials. Notably, this behavior is not observed for the 'surface Pt' samples (see Figure S4) and therefore is a property of the 'buried Pt' architecture. As proton reduction is unfavorable when the Pt catalyst is buried beneath the TiO₂, we hypothesize that the photoexcited electrons perform the next most favorable reaction – TiO₂ reduction. Alternatively, the TiO₂ degradation may also occur in the Pt/TiO₂/diol/*b*-Si case but is unobservable electrochemically.



Fig S3 (a) Repeated voltammograms for TiO₂/diol/B-Pt/*b*-Si after depositing 15 nm of TiO₂. (b) Proton reduction onset potential (V_{onset} , the potential where current = -1 mA/cm^2) as function of repeated electrochemical scans.



Fig. S4. Representative repeated voltammograms of Pt/15 nm TiO₂/diol/*b*-Si.

Potentiostatic Operation of B-Pt/b-Si Architecture



Fig. S5. Potentiostatic experiment with a fresh 6.25 nm/diol/B-Pt/*b*-Si in a three-electrode configuration (Hg/HgSO₄/0.5 M H₂SO₄ reference electrode; IrO₂ counter electrode) 0.5 M H₂SO₄. The potential was held at 0 V vs RHE and the inset shows voltammograms before and after the potentiostatic experiment.

Comparison of 'Surface Pt' and 'Buried Pt' Thickness-dependent V_{fb}



Figure S6. Comparison of thickness-dependent V_{fb} characterization on Pt/x nm TiO₂/diol/b-Si (green squares, Figure 4a inset) and x nm TiO₂/diol/B-Pt/b-Si (blue squares, Figure 5b).

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