Supporting Information

Decoupling Kinetics and Thermodynamics of Interfacial Catalysis at a Chemically Modified Black Silicon Semiconductor Photoelectrode

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Experimental Methods

General Procedures

Isopropanol (electronic grade, Fisher) and acetone (ACS grade, VWR) were used without further purification. Toluene (ACS grade, Acros) and CH₃CN (HPLC grade, Fisher) were purified by stirring over CaH₂ overnight and distilling under N₂. Silicon wafers (boron-doped Si(100), 1–5 Ω cm, 255–305 µm thick) were purchased from Topsil. Styrene and 4-trifluoromethylstyrene were dried by stirring over CaH₂ in an inert atmosphere for 3 hours and subsequently purified via vacuum transfer. 1-vinylpyrene¹ and [TBA][Co(bdt)₂]² were prepared using previously published procedures and dried under vacuum using P₂O₅ as a desiccant. All other reagents were purchased from commercial suppliers and used without further purification. *Sample Preparation*

Silicon wafers were cut into 1 cm x 10 cm strips with a diamond scribe. The strips were sonicated in acetone and isopropanol for 10 minutes each, drying under a stream of compressed air after each solvent. Kapton tape was applied to the backside of the strips. The strips were sonicated in deionized water for 10 minutes and blown dry. Strips were then etched by immersing in an aqueous 2 M HF solution for 60 seconds, rinsed with deionized water, and dried under a stream of N₂. Planer wafers were immediately brought into an Ar filled glovebox.

Black silicon wafers were prepared using a previously published metal-assisted chemical etch procedure.³⁻⁵ Clean and etched silicon strips were soaked in 1 mM AgNO₃/0.4 M HF for 30 seconds to deposit Ag nanoparticles on the surface. The strips were then immersed in a freshly prepared MACE solution (1.25 M HF/0.16 M H₂O₂) for 6 minutes while tapping on the bench top approximately once per second with the etched side of the strip facing up to release bubbles from the surface. Next, the strips were soaked in 35 % HNO₃ for 6 minutes, 55 M (CH₃)₄NOH for 2 seconds, and finally 2 M HF for 30 seconds. The strips were rinsed with deionized water and dried under a stream of N₂ between each step and brought into an Ar filled glovebox immediately after preparation.

Black silicon strips for surface functionalization were cut into approximately 1 cm x 1 cm wafers with a diamond scribe inside an Ar filled glovebox. Covalent functionalization with the various aromatic molecules was achieved by placing freshly etched planar silicon or freshly prepared black silicon wafers at the bottom of a scintillation vial with 1 mL of a 1 mM solution in toluene. The vials were then sealed and placed on a preheated hotplate at 105 °C for 2 h. The solution was removed from the vials and the wafers sonicated in toluene for 10 minutes. Pyrene-modified wafers were then dried and stored in an Ar-filled glovebox until further use. Catalyst attachment was achieved by soaking pyrene-modified wafers in 1 mM CH_3CN solutions of [TBA][Co(bdt)₂] for 16 h.

Electrodes for electrochemical analysis were prepared according to the following procedure: copper tape was applied to a glass microscope slide and a drop of Ag paint was applied to the copper tape. The backside of a b-Si sample was scratched and coated with Ga/In eutectic. The sample was pressed onto the copper tape over the drop of Ag paint. Kapton tape was used to cover exposed copper tape and epoxy (Loctite EA 615) was used to seal the electrode. Samples were cured at room temperature for 2 h before analysis. A picture of a finished sample is shown in Figure S19.

Physical Methods

FTIR spectra were recorded using a Nicolett 6700 spectrometer. Spectra were recorded in transmission mode and samples were illuminated at 75° off of the surface normal. All spectra were baseline corrected and smoothed using Spectragryph software.

X-Ray photoelectron spectroscopy (XPS) measurements were obtained on a Physical Electronics 5600 system using monochromatic Al K α radiation that has a spot size of 1 - 2 mm x 1 - 2 mm. The raw atomic concentration has a 5% error due to surface inhomogeneties, surface roughness, literature sensitivity values for peak integration, etc. For the work function and corelevel measurements, the XPS setup was calibrated with Au metal, which was cleaned via Ar-ion sputtering. The work function measurements require biasing the sample (we use -45 V) to direct the ~ 0 kinetic energy electrons into the detector. The work function measurements have a $\pm 50 \text{ meV}$ energy uncertainty that is due to our known energy uncertainty of our monochromataic Al source and detector.

Photoelectrochemical experiments were performed using a Biologic SP-300 potentiostat and EC-Lab software. Experiments were performed in 0.1 M H₂SO₄ (pH = 1.5) under 1 sun illumination (ABET Technologies Sun 3000 Solar Simulator) with a Ag/AgCl reference electrode and an iridium oxide counter electrode at a scan rate of 100 mV/s. The onset potential was recorded as the potential at which current reached -1 mA/cm^2 . Potentials were converted to RHE using the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059*\text{pH}.^6$

While typically a fill factor would be used to quantify the shape of the voltammograms, this is challenging as we operate negative of RHE and our power is therefore negative. Instead, we report a 'pseudo-fill factor (pFF)' using the equatin below:

$$pFF = \frac{\int JdV}{J_{max} \times dV}$$

where $\int JdV$ is the area between the curve at x-axis (estimated using the trapezoid rule, $\Delta V = 0.1$ mV), J_{max} is the max current, and dV is the potential range of the curve. Relative efficiencies (RE) were calculated using the following equation: RE = 100 x (pFF_x – pFF_{min})/pFF_{min}, where pFF_x is the pFF of a given electrode and pFF_{min} is the minimum pFF of the electrodes analyzed.

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. As previously described,^{3, 5} a lock-in amplifier (SR 830) introduced an AC frequency (100 kHz, 10 mV amplitude) to a potential applied by a potentiostat (PAR 283). 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 (Δ R). 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 was taken as the potential where the Δ R value deviated significantly (> 4 standard deviations) from the average value of the flat region of the curve for two consecutive points.

As described previously,⁵ pH-dependent IMHFR experiments were performed in various buffered solutions (Hydrion buffers purchased from Aldrich: phthalate, pH 3; phosphate, pH 6; and carbonate, pH 9) containing 50 mM methyl viologen (MV) as a pH-independent redox couple and 0.25 M K₂SO₄ as supporting electrolyte. Carbon cloth was used for counter and reference electrodes and the silicon sample was used as the working electrode. The potential was referenced to the MV^{2+/+} redox couple, measured using a platinum foil working electrode for the silicon

sample. In all experiments the solution was rapidly stirred to avoid accumulation of the dark MV reduction product.



Figure S1. Transmission mode FTIR spectra of b-Si|Aromatic samples. Samples were illuminated at 75° off of the surface normal. All spectra were baseline corrected and smoothed using Spectragryph software. The periodic noise is attributed to interference fringes; the non-reflective nature of b-Si only applies to visible and near-IR regions thus infrared reflection remains present here.⁷



Figure S2. IR spectrum of 1-vinylpyrene.

Table S1. sp² IR stretches for surface-bound and free aromatics

Sample		$v_{\rm C-H} ({\rm cm}^{-1})$	<i>v</i> _{C-H} (cm ⁻¹)	
	-	on b-Si surface	free molecule	
	Pyr	3046	3043ª	
	Nap	3062	3054 ⁸	
	Sty	3065, 3031	3060, 3028 ⁹	
	StyCF ₃	3047	309510	
а г .				

^aFigure S2

Table S2. Compositional analysis of b-Si, b-Si|Aromatic, and b-Si|Aromatic|[Co].

I		2	/ /			IL J -	
Sample	Si	С	0	Со	S	Ν	F
b-Si	70.8	16.7	10.4	0	0.5	0.5	1.0
b-Si Pyr	40.7	45.7	13.1	0	0.2	0	0.4
b-Si Nap	47.6	37.0	14.8	0	0.1	0	0.5
b-Si Sty	47.0	36.7	15.3	0	0.2	0.1	0.8
b-Si StyCF ₃	41.8	36.3	16.7	0	0.1	0.4	4.5
b-Si Pyr [Co]	30.4	43.4	24.6	0.1	0.4	0.8	0.4
b-Si Nap [Co]	33.7	35.2	28.3	0.1	0.7	1.4	0.5
b-Si Sty [Co]	35.4	42.7	19.3	0.1	0.9	0.9	0.8
b-Si StyCF ₃ [Co]	33.1	32.7	24.2	0.1	0.7	0.8	3.8

Sample	%Si vs SiO _x	S:Co	\$ (eV) ^a
b-Si	99.6	-	3.99
b-Si Pyr	93.8	-	4.04
b-Si Nap	94.2	-	4.03
b-Si Sty	92.9	-	3.93
b-Si StyCF ₃	89.8	-	4.19
b-Si Pyr [Co]	70.3	5:1	3.73

b-Si Nap [Co]	67.0	8:1	3.89
b-Si Sty [Co]	81.5	8:1	3.93
b-Si StyCF ₃ [Co]	72.1	7:1	3.92

a. Energy uncertainty is $\pm 0.05 \text{ eV}$



Figure S3. High-resolution XPS spectrum of the Co 2p region of b-Si|Nap and b-Si|Nap|[Co].



Figure S4. High-resolution XPS spectrum of the Co 2p region of b-Si|Sty and b-Si|Sty|[Co].



Figure S5. High-resolution XPS spectrum of the Co 2p region of b-Si|StyCF₃ and b-Si|StyCF₃|[Co].



Figure S6. High-resolution XPS spectrum of the Si 2p region of b-Si, b-Si|Pyr, and b-Si|Pyr|[Co].



Figure S7. High-resolution XPS spectrum of the Si 2p region of b-Si, b-Si|Nap, and b-Si|Nap|[Co].



Figure S8. High-resolution XPS spectrum of the Si 2p region of b-Si, b-Si|Sty, and b-Si|Sty|[Co].



Figure S9. High-resolution XPS spectrum of the Si 2p region of b-Si, b-Si $|StyCF_3|$, and b-Si $|StyCF_3|$ [Co].



Figure S10. The secondary electron cut-off region for XPS measurements of b-Si|Aromatic and b-Si|Aromatic|[Co].



Figure S11. Linear sweep voltammograms of b-Si and b-Si|Aromatic samples in 0.1 M H_2SO_4 under 100 mW/cm² white-light illumination. The inset shows the region near the onset potential of -1 mA/cm^2 .



Figure S12. $J_{b-Si|Aromatic|[Co]} - J_{b-Si|Aromatic}$ vs potential for all electrodes. $J_{b-Si|Aromatic|[Co]} - J_{b-Si|Aromatic}$ is obtained by subtracting the current densities from the linear sweep voltammograms of b-Si|Aromatic from those of b-Si|Aromatic|[Co].

Calculation S1. Required turnover frequency to sustain 20 mA/cm².

Using the following equation:

$$TOF = J \cdot F^{-1} \cdot \Phi^{-1} \cdot n^{-1}$$

Where J is the current density, F is Faraday's constant, Φ is the surface coverage (moles per unit area), and n is the number of electrons required for a single turnover

And assuming surface coverage is similar to our reported coverage of ferrocene on black silicon (1 nmol/cm²):⁵

TOF required to sustain 20 mA/cm² = 110 s^{-1} .



Figure S13. IMHFR plots for b-Si|Aromatic and b-Si|Aromatic|[Co]. The vertical lines represent the flatband potential which is taken as the potential where the ΔR value deviated significantly (> 4 standard deviations) from the average value of the flat region of the curve for two consecutive points.



Figure S14. IMHFR plots for b-Si and b-Si|[Co]. The vertical lines represent the flatband potential which is taken as the potential where the ΔR value deviated significantly (> 4 standard deviations) from the average value of the flat region of the curve for two consecutive points.



Figure S15. Current density vs potential corrected for Vonset for b-Si|[Co] and b-Si|Pyr|[Co]. Solid lines represent the average current across three samples and shaded areas denote the standard error.



Figure S16. Current density vs potential corrected for Vonset for b-Si|[Co] and b-Si|Sty|[Co]. Solid lines represent the average current across three samples and shaded areas denote the standard error.



Figure S17. Current density vs potential corrected for Vonset for b-Si|[Co] and b-Si|StyCF3|[Co]. Solid lines represent the average current across three samples and shaded areas denote the standard error.



Figure S18. V_{FB} as a function of pH for b-Si|Pyr and b-Si|Pyr|[Co].



Figure S19. Example of a modified b-Si electrode used for (photo)electrochemical experiments.

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