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# Coupled Thermodynamic and Kinetic Changes in the Electrochemistry of Ferrocenyl Monolayers Induced by Light

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**ABSTRACT:** We report on the light-induced systematic changes to the thermodynamics and kinetics of ferrocene units attached to a n-type silicon(100) photoelectrode. Both the reaction rate, as well as the energetics of the charge transfer, are simultaneously affected by changes to the intensity of the incident light. Cyclic voltammetry shows that increases in intensity of illumination can drive the redox process toward less positive potentials, with a downhill shift in  $E_{in}$  of ca. 160 mV by increasing light intensity from 3 to 94 mW cm<sup>2</sup>. This thermodynamic shift is however paralleled by an increase in the kinetics of the charge transfer. This latter observation - light-induced kinetic effects at monolayers on silicon electrodes - is only made possible by the stability of the surface chemistry construct. Furthermore, electrochemical impedance measurements showed that the electrodes exhibit faster electron transfer kinetics under illumination than previously reported for ferrocene-terminated highly doped silicon (around one order of magnitude

faster). An explanation for the kinetics effects is proposed based on the consistent increase of photogenerated charge carriers inside silicon, and the enlarged potential difference between valence band of silicon and the surface attached ferrocene.

#### INTRODUCTION

In our previous work, the well-defined alkyne-terminated silicon(100) surfaces were reported using a one-step thermal hydrosilylation procedure, followed by the derivatization of the alkyne-terminated monolayers with redox active molecules using our previously reported 'click' chemistry approach.<sup>23, 24</sup> This surface chemistry has been shown to be effective in limiting the

oxidation of the underlying silicon for hundreds of redox cycles where the potential is swept anodically.<sup>26, 26</sup> Additionally, the concept of light activated electrochemistry has been well demonstrated on these surfaces in aqueous electrolyte, on which the light can be used to 'wire' specific regions of a monolithic modified silicon electrode, where illuminated, to allow the electrochemical '*reading*' and '*writing*' of information with microscale spatial resolution.<sup>\*</sup> It was further shown that with an anthraquinone derivatized p-type silicon both the thermodynamics and kinetics of electron transfer were a function of both the light intensity and pH. Specifically, the oxidation process can be selectively facilitated by increasing pH, while the cathodic process can be modulated independently by the illumination intensity.<sup>27</sup> As interesting as these results are, the complexity of the proton-coupled electron transfer process of the anthraquinone electrochemistry made it difficult to decipher the subtleties of the mechanism. Thus, a need exists for the evaluation of a simpler one electron redox species to clearly illustrate the relationship between the redox process and band energetics of silicon.

The purpose of this paper is to explore the potential applicability of light to regulate the redox process on n-type silicon(100). The one-step thermal hydrosilylation procedure used previously was utilized to afford the well-defined alkyne-terminated silicon(100) surfaces.<sup>20, 20</sup> Ferrocene moieties were covalently tethered to the silicon surface to explore the relationship between a simple redox process and light intensity, or indeed the band energetics, at the semiconductor/electrolyte interface. The strategy also allows for introducing a better acquaintance with the photo effects on well-passivated n-type silicon in aqueous, which would be valuable for its application including electro-catalysis and energy conversion.

## EXPERIMENTAL SECTION

**Chemical and Materials.** 1,8-Nonadiyne (Sigma-Aldrich, 98%) was redistilled under reduced pressure (65-70 °C, 25-30 Torr) with sodium borohydride (Sigma-Aldrich,  $\geq$ 99%), and stored in dry argon atmosphere prior to use. The redox species azidomethylferrocene were synthesized from commercially available ferrocenemethanol according to the previously reported procedure,<sup>a</sup> and the details are presented in Supporting Information. Milli-Q<sup>TM</sup> water with a resistivity of  $\geq$  18 MΩ cm was obtained from Millipore<sup>TM</sup> water purification system for chemical reactions and solutions preparation. The solvents for silicon wafer cleaning, chemical modification, and purification procedures were redistilled prior to use. Prime-grade silicon wafers (Alfa-Aesar, US), 100-oriented (<100>  $\pm$  0.9°), n-type (phosphorous) with resistivity of 8-12 Ω cm were referred as poorly doped n-type silicon. Prime-grade silicon wafers (Virginia Semiconductors Inc, US), 100-oriented (<100>  $\pm$  0.9°), p-type (boron), with resistivity of 0.007-0.009 Ω cm, were referred as highly doped silicon. All chemicals were used as received, unless otherwise specified.

**Preparation of Ferrocene-modified Silicon.** Firstly, the self-assembly of monolayers of 1,8– nonadiyne was performed on silicon following the previously reported procedure, as shown in Scheme 1.<sup>39</sup> In short, the silicon wafer was cleaned with hot Piranha solution (1:3 v/v of 30 % H<sub>2</sub>O<sub>2</sub> and 98% H<sub>2</sub>SO<sub>2</sub>), and etched in 2.5% hydrofluoric acid for 90s. Silicon was then transferred to a thoroughly degassed 1,8–nonadiyne (through more than 5 freeze-thaw cycles) in a customdesigned Schlenk flask. The reaction vessel was kept under argon atmosphere at 165 °C for 3 h. After reaction, the silicon wafer was cleaned thoroughly with dichloromethane. Subsequently, the azidomethylferrocene derivative was attached on the obtained alkyne-functionalised silicon through the Cu(I)-catalyzed alkyne-azide cycloaddition reaction.<sup>20,39</sup> Briefly, the silicon sample was placed in isopropanol/water (2: 1 ratio) solution containing 45 mM of azidomethylferrocene, 0.36 mM of copper (II) bromide, and 36 mM sodium ascorbate. The coupling reaction was carried out at room temperature for 45 min without excluding air from the reaction environment. The prepared silicon samples were rinsed consecutively with copious amounts of water, ethanol, and dichloromethane, blown dry under argon, and stored under argon prior to use.

**X-ray Photoelectron Spectroscopy.** An ESCALAB 220iXL spectrometer equipped with Al Kα (1486.69 eV) X-ray source was utilized for XPS measurements. All binding energies are corrected by applying a rigid shift to bring the C 1s signal to 284.6 eV. The Thermo Avantage software was used for the analysis of XPS data.

**Electrochemical measurements.** All electrochemical experiments were performed in a PTFE three-electrode cell with the modified silicon as the working electrode and a platinum mesh as the counter electrode, all the potential values are referred to AglAgCll1M KCl electrode. The cyclic voltammetry were performed on ferrocene-terminated silicon electrode in the dark or under illumination with different light intensities. The apparent rate constant for electron transfer ( $k_{a}$ ) was calculated from the equivalent circuit<sup>16</sup> of electrochemical impedance spectroscopy.<sup>21</sup> The half wave potential ( $E_{aa}$ ) was set as the DC bias potential and AC amplitude was set to 10 mV. Experiments were performed in 1 M HClO<sub>4</sub>, and the solution was degassed prior to experiments by bubbling argon for 20 min. Flat band potential values were calculated from the extrapolation to  $C_{ac}^{2}=0$  of Mott-Schottky plots ( $C_{ac}^{2}$ vs. *E*).

An ACE® Light Source (SCHOTT AG, Mainz, Germany) was employed as the light source for the topside (electrolyte-side) illumination during electrochemical experiments. The light intensities were determined using a 1918–R optical power meter (Newport, Inc. Bozeman, USA).

#### RESULTS

**XPS Characteristics of Silicon Surfaces.** The XPS analysis was performed on the silicon surfaces after each step of the modification strategy shown in Scheme 1. The chemical passivation of the

silicon(100) has been extensively characterized,<sup>32, 26, 27</sup> and the representative spectra of alkynepassivated silicon are shown in Figure S1 (Supporting Information). Signals for Si, C, and O are observed in XPS survey scan. In high-resolution Si 2p spectra, the two split peaks for Si  $2p_{32}$  and Si  $2p_{32}$  are found at 99.5 and 100.1 eV, respectively. The absence of silicon oxidation states is evidenced by the lack of emissions in the 102-104 eV region. Three main functions centred at 283.6, 285, and 286.5 eV are exhibited in the C 1s region, showing direct evidence for the C–Si, C–C, and C–O–H bonds.<sup>32,33</sup> Debate continues with regards to the origin of the peak at ca. 286 eV as to whether it is adventitious C–O<sup>34</sup> or comes from –C=C– groups.<sup>35</sup>



**Scheme 1.** Surface modification strategies: (a) silicon(100) wafers immersing in 2.5 % HF for 90 s to remove the silicon oxidation layer; (b) the obtained hydride-terminated surface was reacted with neat 1,8-nonadiyne *via* hydrosilylation process; (c) Copper catalysed azido-alkyne cycloaddition 'click' addition of ferrocene on acetylene terminated silicon(100) surfaces.

The covalent attachment of ferrocene moieties to the silicon surface was determined by XPS spectrum, as shown in Figure 1 and Figure S2. The results show the signals for Fe and N after the 'click' reaction compared with the alkyne-terminated silicon (Figure S2). The three bands due to C–Si (283.4 eV), C–C (285.0 eV), and C–O–H (286.4 eV) are presented on C 1s spectra as

discussed previously. In agreement with expectation, the high-resolution Fe 2p spectra shows two distinct peaks for Fe  $2p_{v_2}$  and Fe  $2p_{v_2}$  at 708.2 and 721.1 eV, respectively, thereby indicating a predominating state for Fe (II)-derived ferrocene moieties.<sup>36,37</sup> The absence of ferricenium species on XPS spectra suggests there is no oxidation of ferrocene under the reaction conditions.<sup>38</sup> The N 1s signal shows the typical two peaks with binding energies at 401.7 and 400.3 eV in approximately 1:2 ratio, which are attributed to the triazole N–N=N and C–N–N, respectively, indicating a positive outcome for the 'click' reaction.<sup>36,37</sup> There is an incredibly minor increase in silicon oxide in 102-104 eV after performing electrochemistry in aqueous solution, indicating the high quality of monolayer and its ability to obviate appreciable oxidation during electrochemistry (Figure 1).



**Figure 1.** High-resolution XPS spectrum of Si 2p, C 1s, N 1s, and Fe 2p regions for ferroceneterminated poorly doped n-type silicon surface.

Cyclic Voltammetry Behavior of Ferrocene Moieties at Poorly Doped n-type Silicon. The knowledge of band energetics of silicon electrodes assists in understanding the electrochemical

behaviour of the redox-active species on silicon.<sup>26,27</sup> Knowing the position of the silicon energy bands is contingent on knowing the flat band potential  $(E_{\mu})$ . Hence, the  $E_{\mu}$  of the ferrocenefunctionalized n-type silicon electrode was firstly measured using Mott-Schottky plots.<sup>40,41</sup> As shown in Figure S3, the reciprocal square of capacitance was plotted versus potential, and a straight line was obtained in the depletion region, with the potential intercept giving the value of  $E_{p} + kT/q$ according to the Mott-Schottky equation. The room temperature value of kT/q is 25 mV, hence the measured  $E_{p}$  for poorly doped n-type silicon in this case is -450 mV vs. AglAgCll1M KCl. Considering the band gap is 1.1 eV for intrinsic silicon, the valence band potential will thus be around 650 mV vs. Ag|AgCl|1M KCl if it is assumed that the  $E_{h}$  is very close to the conduction band potential for an n-type semiconductor.<sup>42</sup> Considering the  $E_{1/2}$  of ferrocene moieties at highly doped silicon (metallic behaviour) is around 360 mV vs. AglAgCll1M KCl as previously determined,<sup>38</sup> the ferrocene-functionalized poorly doped n-type silicon will be in depletion after contacting with electrolyte due to the energy difference between silicon and the redox species. The silicon being in depletion is a prerequisite for light activated electrochemistry. Specifically, owing to the limited minority charge carriers (holes for n-type silicon), the oxidation process of ferrocene will be blocked in the dark. However, upon illumination large amount of photogenerated holes will be driven to the interface due to the disparate electrochemical potentials between the bulk silicon and its interface, the oxidation reaction can be activated and then the whole redox process of ferrocene will proceed at poorly doped silicon electrode.

The cyclic voltammograms for ferrocene-derivatized silicon in the dark or under illumination are given in Figure 2. The CVs show a tiny cathodic peak but without discernable anodic current in the dark, while under illumination symmetrical anodic and cathodic peaks were observed. This

observation is consistent with previously reported photoelectrochemistry on semiconductor electrodes,<sup>43,44</sup> and the concept of light activated electrochemistry.<sup>26,27</sup>

Figure 2a also shows the impact of light intensity on the cyclic voltammetry of ferroceneterminated poorly doped n-type silicon. With light intensity increasing from 2.8 mW cm<sup>2</sup> to 94.2 mW cm<sup>2</sup>, both the anodic and cathodic peaks move to more negative potentials, thereby leading to  $E_{s2}$  changing from -68 mV to -216 mV vs. AglAgCll1M KCl. The negative shift in  $E_{s2}$  is attributed to the magnitude of the band bending<sup>a</sup> (energy bands of silicon) becoming smaller at higher light intensity, and thus the quasi-Fermi level of electrode will be more cathodic. In Figure 2b, it can be seen that light intensity has a measurable impact on the  $E_{s2}$  of silicon/ferrocene system, and the  $E_{s2}$  value obtained in the applied light intensity range was found ~580 mV more negative compared with the  $E_{s2}$  at ferrocene-terminated highly doped p-type silicon (with resistivity of 0.007-0.009  $\Omega$  cm).<sup>29</sup>



**Figure 2.** (a) Cyclic voltammograms for ferrocene-terminated poorly doped n-type silicon in 1.0 M HClO<sub>4</sub> solution under different light intensity; (b) plot of  $E_{1/2}$  versus light intensity, the dashed line is plot of the fitted equation,  $E_{1/2} = -43.3 \ln (I_0) - 15.6$ . The scan rate is 50 mV s<sup>4</sup>.

The scan rate dependence on the cyclic voltammetry for ferrocene-functionalized poorly doped ntype silicon under a given light intensity were investigated, and the results are summarized in Figure 3 & S4. Firstly, as expected for a surface-attached redox couple, there is a linear relationship between the current density of redox peak and scan rate. Secondly in the ideal case, for which there are no interactions between the adsorbed molecules on a homogeneous surface, the redox peak potentials will be identical, the peak has a symmetrical shape and the width at mid-height of the redox peaks will be 90.6 mV at 298 K.<sup>45</sup> It can be seen the voltammetric studies for the ferrocene moieties on silicon in this work show comparable voltammetric behavior to that obtained on metallic electrode.<sup>46</sup> The peak-to-peak separation ( $\Delta E_{e}$ ) is close to zero (4-12 mV), until the scan rate is larger than 10 V s<sup>4</sup> (Figure S3), indicating the high quality of monolayer and the rapid interfacial electron transfer for the system.<sup>45</sup> This is more ideal electrochemical performance compared to previous works on ferrocene-functionalized semiconductor electrodes, such as silicon,<sup>47</sup> diamond,<sup>3</sup> and gallium.<sup>43</sup> The mid-height of the anodic peak is 100.3 mV for ferroceneterminated silicon in the present work, and the slight mid-height of the oxidation peak deviation is mainly attributed to the repulsive interactions between ferrocene moieties according to Laviron.48



**Figure 3.** (a) Cyclic voltammograms of the ferrocene-terminated silicon electrode in a 0.1 M HClO<sub>4</sub> solution at various scan rates; (b) the plot of anodic and cathodic peak current density *versus* scan rate,  $v : I_{\mu} = 1.82 + 0.134 v$ ; and  $I_{\mu} = -3.27 - 0.139 v$ . The light intensity is 94.2 mW cm<sup>3</sup>.

#### **Effect of Light Intensity on Interfacial Electron Transfer**

Despite numerous studies on the charge transfer at semiconductor-electrolyte interfaces having been performed over the past 60 years,<sup>(9, 9)</sup> most of these studies were aimed at stimulating the photo/dark current-voltage characteristics. Charge transfer kinetic studies between silicon and redox systems are very rare due to the complexity of the semiconductor-electrolyte system, such as its susceptibility to corrosion, or charge carrier recombination. The accomplished passivation, and further termination of ferrocene on silicon in the present work affords a much simpler case, and thus the quantification for the transfer kinetics is achievable using electrochemical impedance spectroscopy.

Figure 4a shows the Nyquist plot for ferrocene-terminated n-type silicon under illumination, which contains a semicircle portion and a linear portion. This is different with the prior impedance measurements on anthraquinone functionalized p-type silicon,<sup>37</sup> where the charge transfer at the interface as well as in space charge layer were represented as two representative semicircles in the Nyquist plots. In the present case the Nyquist plot on ferrocene-terminated n-type silicon is consistent with the Randles equivalent circuit for the redox-active monolayer on electrode surface.<sup>31</sup> A set of the fitted values for charge transfer resistance ( $R_{co}$  and capacitance ( $C_{ab}$ ) in the equivalent circuit under various light intensities are plotted in Figure 4b. It can be seen that the charge transfer resistance decreases, while the capacitance increases (Figure 4c), with increasing light intensity. Correspondingly, the electron transfer rate constant ( $k_{co}$ ) is obtained by

$$k_{et} = \frac{1}{2R_{ct}C_{ads}} \tag{1}$$

Thus, using the interpreted values noted in Figure 4b, the  $k_a$  obtained at light intensity of 94.2 mW cm<sup>3</sup> is 2470 ± 170 s<sup>4</sup>. This value is considerable higher than those measured on p-type silicon with the same surface chemistry (around 130 ± 40 s<sup>4</sup>).<sup>47</sup> A set of impedance measurements for ferroceneterminated n-type silicon under different light intensities were acquired, and the calculated  $k_a$  values are plotted in Figure 4d. As can be seen from figure 4d, the rate constant for electron transfer is rather high at the silicon-electrolyte interface, which is consistent with the well-behaved cyclic voltammetry at fast scan rates.<sup>45</sup> More importantly, it can be seen the  $k_a$  increases with the increase of incident irradiation intensity (with values from 690 ± 150 to 2470 ± 170 s<sup>4</sup>) according to a quadratic-polynomial relationship.



**Figure 4.** (a) Nyquist plot for ferrocene-terminated n-type silicon at light intensity 94.2 mW cm<sup>2</sup>; plot of (b)  $R_a$  and (c)  $C_{ab}$  under different light intensities, the data were obtained from Nyquist plots interpreted to the equivalent circuit (inset in Figure 4a) (d) plot of  $k_a$  versus light intensity as measured through impedance on  $k_{et} = 0.23I_0^2 - 3.65I_{0.} + 712.28$ ,  $R^2 = 0.999$ . Impedance data were measured under representative light intensity at applied potential  $E_{ac} = E_{az}$  and fitted to the

equivalent circuit, the refined  $k_{a}$  value in Figure 4a was 2470 ± 170 s<sup>-1</sup> (R<sub>a</sub> =8.9  $\Omega$ , C<sub>a</sub> = 0.8  $\mu$ F, C<sub>ab</sub> =23.13  $\mu$ F, R<sub>a</sub> = 8.75  $\Omega$ ).

#### DISCUSSION

In the study herein, by taking advantage of the established modification strategy for silicon(100)<sup>\*\*</sup> surfaces, the  $E_{12}$  for ferrocene moieties at a silicon surface was effectively tuned to more negative potential with increasing light intensity. Figure 5a illustrates the band diagram for the irradiated n-type silicon/ferrocene system, where the holes migrate from the bulk silicon to the interface where they can be captured by the ferrocene, and conversely the electrons will be driven into the bulk silicon. More electron-hole pairs will be generated with the increase of light intensity and as such the quasi-Fermi level of silicon moves to higher energy due to the increased occupancy of the conduction band. Therefore, the redox process of ferrocene is driven to more negative potentials

as observed in Figure 2. It has been noted that the observed  $E_{n2}$  shift with light intensity in this work is consistent with the expression for  $V_{\infty}$  previously reported in a theoretical study:<sup>55</sup>

$$V_{oc} \approx \frac{kT}{q} ln \frac{J_{ph}}{J_0} + \frac{E_g}{q}$$
(2)

where  $J_{\mu}$  is the photocurrent density,  $J_{0}$  is the dark current density,  $E_{s}$  is the band gap, and at room temperature kT/q is approximately 25 mV. Equation (2) indicates the  $V_{\infty}$  increases logarithmically with the photocurrent, and in the ideal case, with photon flux. This trend is revealed by the results in Figure 2, as  $V_{\infty}$  is represented by the difference between  $E_{1/2}$  on poorly and highly doped silicon; although the obtained slope of 43 mV deviates from the theoretical value of 25 mV.

In addition to the change in thermodynamics of the electron transfer process between the silicon electrode and the ferrocene moieties with light intensity, it has been demonstrated the light intensity also alters the charge transfer kinetics of the system. To gain more insights into the light intensity effect on the charge carrier changes at silicon electrode, the real capacitance per unit area  $(C_n)$  obtained at different light intensities is shown in Figure 5b. The real capacitance was calculated from the impedance data using:<sup>57,58</sup>

$$C_{re} = \frac{-Z''}{2\pi f A(Z'^2 + Z''^2)}$$
(3)

where Z' and Z'' are the real and imaginary parts of the impedance, A is the area of silicon electrode, and f is the frequency. In this case, the dependence of  $C_{\pi}$  on frequency and light intensity differs in three regions as indicated. In the high frequency range (f > 10K Hz), the capacitance is independent of both light intensity and frequency, which is assigned to the bulk silicon region.<sup>57,59</sup> In the intermediate frequency region (from 100 to 1K Hz), the capacitance increases either with

the decrease of frequency or with the increase of light intensity. The frequency dependence could be attributed to the charge carrier distribution that is influenced by the depth of light penetration into the silicon.<sup>57,66</sup> For a given light intensity, Figure 5b gives direct evidence that the concentration of charge carriers in this frequency regime decreases with the increase in the depth of the light penetration depth. The light intensity dependence is associated with an increase in hole concentration in the silicon with the increase in overall photon flux. In the low frequency regime (f < 100 Hz), the capacitance becomes insensitive to frequency, but very sensitive to increasing light intensity. We attribute the constant capacitance value to the space charge layer at the silicon/electrolyte interface,<sup>57</sup> where the charge carrier density is relatively constant across a broad frequency range for a given light intensity. An increase in light intensity however will directly regulate the amount of photogenerated charge carriers in this region and hence alter the capacitance.

As predicted from the cyclic voltammetry data, ferrocene moieties at silicon electrode here showed well-defined, almost ideal, reversible redox peaks until the scan rate is higher than 10 V s<sup>4</sup>, which is comparable to those observed on metallic electrodes and indicates rapid electron transfer rate. A quantification of experimental  $k_a$  values with light intensity were hence obtained from the impedance measurements and given in Figure 4b, whereas the increase of  $k_a$  with light intensity followed a quadratic-polynomial. Two main effects are proposed for the  $k_a$  varying with light intensity. Considering the density of holes for an n-type semiconductor electrode are limited, the increase in photogenerated charge carrier density would explain the observed faster electron transfer kinetics with light intensity. That is, the minority charge carrier will increase in concentration linearly with photon flux if charge recombination is neglected. Second, the driving force for holes transfer can be expressed in terms of the difference between the valence band

potential and the redox potential of ferrocene, and this difference is expected to increase logarithmically with light intensity based on the above voltammetry data. The light intensity dependence of the impedance data was consistent with the hypotheses. As shown in Figure 4c, with an increase in light intensity, the capacitance dominated by the charge carrier concentrations is increasing, while the charge transfer resistance decreases due to a greater driving force with the negative shift of  $E_{u2}$ . Therefore, the obtained  $k_{e}$  values is enhanced by increasing the light intensity.



**Figure 5.** (a) Band diagram for ferrocene-terminated n-type silicon under illumination; (b) real capacitance ( $C_{\alpha}$ ) *versus* frequency under different light intensities as indicated.

## CONCLUSIONS

By taking advantage of passivation and 'click' chemistry, an effective approach to tune the thermodynamics and kinetics of ferrocene moieties at poorly doped n-type silicon surface has been developed. Specifically, more cathodic redox-peak potentials were obtained at higher light intensities, and the maximum  $V_{sc}$  obtained at the highest light intensity is ~600 mV, this is attributed to the reduced band bending and correspond negative shift of quasi-Fermi level of silicon. A simple analytical expression for the  $E_{II2}$  with light intensity was given based on the theoretical model for  $V_{sc}$ . It has been demonstrated that the  $k_{sc}$  for ferrocene moieties at illuminated silicon are comparable

with those obtained at metallic electrodes, which is indicated in cyclic voltammetry behavior as well. Moreover, the  $E_{in}$  altering by light intensity in a way that also brings changes of  $k_a$ , which can be facilitated by increasing the irradiated light intensity of the incoming light. The increase of photogenerated holes inside silicon and the driving force account for the promoted electron transfer rate. Overall, the study built a simple case for pure redox processes on semiconducting silicon in aqueous electrolyte, and experimentally quantified the changes for  $E_{in}$  and  $k_a$  with light intensity, and lead to an understanding of how to tune the thermodynamics and kinetics for the redox-active molecules at n-type silicon electrodes.

## ASSOCIATED CONTENT

## **Supporting Information.**

The Supporting Information is available free of charge on the ACS Publications website at Synthesis of azidomethylferrocene, XPS data for alkyne-terminated silicon, Mott-Schottky plot, and cyclic voltammetry of ferrocene-terminated silicon under different scan rates.

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