### Photoelectrochemical Synthesis Hot Paper

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## **Photoelectroreduction toward Chemical Building Blocks**

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Abstract: Conventional photoelectrochemical cells utilize solar energy to drive the chemical conversion of water or CO<sub>2</sub> into useful chemical fuels. Such processes are confronted with general challenges, including the low intrinsic activities and inconvenient storage and transportation of their gaseous products. A photoelectrochemical approach is proposed to drive the reductive production of industrial building-block chemicals and demonstrate that succinic acid and glyoxylic acid can be readily synthesized on Si nanowire array photocathodes free of any cocatalyst and at room temperature. These photocathodes exhibit a positive onset potential, large saturation photocurrent density, high reaction selectivity, and excellent operation durability. They capitalize on the large photovoltage generated from the semiconductor/electrolyte junction to partially offset the required external bias, and thereby make this photoelectrosynthetic approach significantly more sustainable compared to traditional electrosynthesis.

 $\mathbf{P}$ hotoelectrochemical synthesis is the process where photogenerated electrons and holes in semiconductor electrodes are utilized for chemical fuel production.<sup>[1,2]</sup> The process mimics what Mother Nature does through photosynthesis, and may potentially enable efficient solar-to-chemical conversion on a wide scale. In typical PEC devices, photogenerated electrons are used to drive the reduction of water to H<sub>2</sub> or the reduction of CO<sub>2</sub> to organic feedstocks (for example, CO, formic acid, and CH<sub>4</sub>) at the cathode; photogenerated holes are used to drive the oxidation of water to O2 at the anode.<sup>[1,2]</sup> Most light-adsorbing semiconductor materials (such as Si) have limited intrinsic electrocatalytic activities toward the aforementioned reactions. They often require the assistance of cocatalysts (sometimes made of precious metals) to expedite the charge transfer kinetics at the surface.<sup>[3,4]</sup> However, the introduction of an additional semiconductor/ cocatalyst interface not only adds new design complexity to existing devices, but may also risk creating adverse surface states that trap electrons or holes. Another well-recognized challenge with photoelectrochemical (PEC) water splitting or  $CO_2$  reduction is that the products (for example,  $H_2$  or CO) are often in the gaseous state. Their storage and trans-

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portation would incur considerable extra cost, rendering the use of these solar fuels less attractive.  $^{[5,6]}$ 

We reason that, in addition to splitting water or reducing  $CO_2$ , photogenerated carriers can also be used to drive the electrochemical transformation of organic molecules and produce value-added chemicals that have industrial significance.<sup>[3,7]</sup> The ideal scenario would be to combine a photo-anode and -cathode, and make use of both the anodic and cathodic processes with zero external bias. Recently, Choi et al. reported the PEC oxidative transformation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid on a BiVO<sub>4</sub> photoanode with a high yield and Faradaic efficiency.<sup>[7]</sup> However, as far as we are aware, there is no demonstration on the possible PEC reductive production of industrial building-block chemicals.

An experimental proof of concept is provided, which shows that two industrially significant molecules-succinic acid and glyoxylic acid-can be selectively produced on PEC photocathodes. Succinic acid is listed as one of the top valueadded chemicals by the US Department of Energy.<sup>[8,9]</sup> It is the precursor of many key chemicals (including 1,4-butanediol, tetrahydrofuran, 2-pyrrolidinone, and N-methylpyrrolidinone) and an important ingredient in food and pharmaceutical products, surfactants and detergents, green solvents, and biodegradable plastics.<sup>[9]</sup> The annual production volume of succinic at present is between 30 and 50 million tons, and its global market potential is projected to reach 7-10 billion USD per year.<sup>[10]</sup> In industry, succinic acid is mainly produced from the liquid-phase hydrogenation of maleic anhydride at a temperature ranging from 120 to 180°C under a hydrogen pressure between 5-40 atm.<sup>[11]</sup> This method is typically energy-intensive and costly. A milder approach is to electrochemically reduce maleic acid in acidic medium on high hydrogen overpotential metals such as lead and titanium (Equation 1).<sup>[12]</sup> The second target molecule-glyoxylic acid-is also an important intermediate in pharmaceutical, perfumery, and fine chemical industries.<sup>[13,14]</sup> Its production by electrochemical reduction of oxalic acid has been known for about a century (Equation 2). Even though the electrosynthesis of both compounds has been well-documented, their PEC synthesis using renewable solar energy is unexplored.

$$\begin{array}{l} \text{HOOC-HC=CH-COOH} + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \\ \text{HOOC-CH}_2 - \text{CH}_2 - \text{COOH} \end{array} \tag{1}$$

$$HOOC-COOH + 2H^+ + 2e^- \rightarrow HOOC-COOH$$
 (2)

Herein, we report for the first time the PEC reductive transformation of maleic acid to succinic acid and oxalic acid to glyoxylic acid. We use chemically etched Si nanowire arrays without any cocatalyst as the model photocathode, and study

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 Supporting information and the ORCID identification number(s) for

their potential-dependent reaction rate and Faradaic efficiency. A positive onset potential up to approximately 0.2 V versus a reversible hydrogen electrode (RHE), a large saturation photocurrent density of about 37 mA cm<sup>-2</sup>, and a Faradaic efficiency close to 100% were successfully attained.

P-type Si was selected as the light-absorbing semiconductor electrode material for its relatively low cost and commercial availability. Herein, large-area vertically aligned Si nanowire arrays (Si NWs) were fabricated by metal-assisted chemical etching of p-type (100) Si wafers (see Supporting Information for details).<sup>[15,16]</sup> By carefully controlling the reaction time between 10 to 60 min, we obtained Si NWs with varying lengths up to approximately 3 µm. Figure 1 a shows



**Figure 1.** Vertically aligned Si NWs from the metal-assisted chemical etching of Si wafers. a) SEM image of 2.8  $\mu$ m Si NWs. b) TEM images of a Si NW at different magnifications.

the scanning electron microscopy (SEM) image of Si NWs etched to a specific length of  $2.8 \mu m$ . They grew vertically with respect to the substrate underneath. When examined under transmission electron microscopy (TEM), these NWs were revealed to have diameters in the range of 80–150 nm. High-resolution transmission electron microscopy (TEM) analysis confirmed the single-crystalline nature of each NW (Figure 1b). Their long-axial orientation was determined to be along the [100] direction, consistent with the surface orientation of starting Si wafers.

Compared to planar electrodes, previous studies have established that NW array electrodes are advantageous for PEC applications in that they possess long optical paths for efficient light absorption (because of substantial internal light scattering) and short transport distances across the NW diameter for efficient charge collection.<sup>[17,18]</sup> Moreover, the enlarged surface area of NW arrays dilutes the distribution of photogenerated electron/hole flux over their entire surfaces, and therefore relaxes the electrocatalytic turnover requirement of the electrode and lowers the reaction overpotential.<sup>[18]</sup> This becomes particularly important if photogenerated electrons or holes are used to drive kinetically sluggish reactions.<sup>[19]</sup> We envisaged that a process similar to PEC water splitting took place on the Si NW photocathode (Figure 2a). Immediately following light absorption, photogenerated electrons migrated to the NW/electrolyte interface, as driven by the built-in potential, and were subsequently injected into nearby organic electron acceptors in the electrolyte. Meanwhile, photogenerated holes moved through the outer circuit to the counter electrode and participated in an



Figure 2. PEC reduction of maleic acid to succinic acid. a) Schematic showing the PEC process on the Si NW photocathode. b) Polarization curve of PEC maleic acid reduction on Si NWs in the light ( $\square$ ) or dark (
) in comparison with that of PEC maleic acid reduction on planar Si in the light (0), HER on Si NWs (•) and electrochemical maleic acid reduction on p<sup>++</sup>-Si (■). c) Polarization curves of electrochemical maleic acid reduction on Ti/TiO2 and lead electrodes in comparison with that of PEC maleic acid reduction on Si NWs in the light. d) Chronoamperometric responses of the Si NW photocathode at selected potentials as indicated. e) Potential-dependent Faradaic efficiency for succinic acid on Si NW photocathode in comparison with Ti/TiO2 and lead electrodes. f) Concentration increase of succinic acid in the catholyte for the first 6 h during the long-term stability study. Gray curve indicates the prediction assuming 100% Faradaic efficiency. Inset: the corresponding chronoamperometric response of Si NW photocathode held at 0 V.

oxidation reaction. In this process, the hydrogen evolution reaction (HER) presented an obvious competing reaction channel. Depending on their relative interfacial charge transfer rates, if photogenerated electrons weren't rapidly scavenged by organic electron acceptors, they would instead be captured by solution protons, resulting in a lower reaction Faradaic efficiency.

We first studied the PEC reductive transformation of maleic acid to succinic acid. The electrochemical reduction of maleic acid to succinic acid is a two-electron process with a standard reduction potential of 0.62 V (vs. RHE). Lead and titanium are common electrode materials for the electrosynthesis of succinic acid with typical Faradaic efficiencies in the range of 70–90 %.<sup>[12,20]</sup> Our PEC experiments were carried out in a custom-built two-compartment electrochemical cell using the standard three-electrode system (Supporting Information, Figure S1). The electrolyte was  $0.3 \text{ M} \text{ Na}_2\text{SO}_4$  and 0.3 M maleic acid (pH 2.0). As displayed in Figure 2b, no current flowed in dark conditions. Under 100 mW cm<sup>-2</sup> of simulated AM 1.5 G

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illumination, the J-V curve of 2.8 µm Si NWs exhibited an onset potential (defined as the potential to reach  $1 \text{ mA cm}^{-2}$ ) of 0.18 V versus RHE, beyond which the cathodic photocurrent density quickly took off and reached a saturation value of approximately  $37 \text{ mA cm}^{-2}$  at about -0.6 V. The observed cathodic photocurrent density quantitatively corresponds to the reduction of maleic acid to succinic acid (see proceeding text). The large saturation photocurrent density of the Si NW electrode agreed well with the ideal value for Si photoelectrodes, suggesting that there was no optical loss and that all the photogenerated electrons were fully utilized.<sup>[21]</sup> A control experiment with a planar Si electrode revealed a more negative onset potential (0.06 V) and a smaller saturation photocurrent density (ca.  $34 \text{ mA cm}^{-2}$ ). We also compared the PEC maleic acid reduction performance of Si NW electrodes with different NW lengths (Supporting Information, Figure S2). Moreover, electrochemical reaction of maleic acid on degenerately doped planar Si wafer (p++-Si, not p++-Si NWs because their NWs could not be prepared by the same metalassisted chemical etching process) showed that the reaction did not initiate until a very negative potential of -0.60 V was reached on the Si surface. To a certain degree, the approximately 770 mV difference in the onset potential between Si NWs and  $p^{++}$ -Si reflected the considerable photovoltage generated from the Si NW/electrolyte junction under 1 sun illumination.

To shed light on and contrast the different interfacial charge transfer rates between maleic acid reduction and HER, PEC experiments in the absence of maleic acid were also carried out. The electrolyte was 0.3 M Na<sub>2</sub>SO<sub>4</sub> with its pH adjusted to 2.0 with H<sub>2</sub>SO<sub>4</sub>. Under these circumstances, only HER could possibly occur in the cathodic potential regime. Mott-Schottky analysis indicated a similar flat band (ca. 0.17 V; Supporting Information, Figure S3). However, the onset potential of the Si NW electrode was displaced to -0.07 V, and its saturation photocurrent density was not reached until about -1.2 V (Figure 2b). In the presence or absence of maleic acid, the required potential to sustain a photocurrent density of  $10 \text{ mA cm}^{-2}$  ( $V_{i=10}$ ) differed by approximately 460 mV. Such a drastic difference emphasizes the much facilitated reduction rate of maleic acid over the competing HER process. As a result, we can reasonably deduce that HER was fully suppressed in the presence of maleic acid (see proceeding discussion).

To highlight the advantage of PEC photosynthesis relative to conventional electrosynthesis, we subsequently investigated the electrochemical reduction of maleic acid on heattreated titanium  $(Ti/TiO_2)^{[22]}$  and lead—two common electrode materials used widely in previous studies with reported Faradaic efficiencies typically in the range of 70–90%.<sup>[12,20]</sup> As depicted in Figure 2 c, the polarization curves on Ti/TiO<sub>2</sub> and lead exhibited more negative onset potentials of -0.21 V and -0.30 V, respectively; and their potentials required to reach a cathodic current density of 10 mA cm<sup>-2</sup> were -0.68 V and -0.48 V, respectively. The Si NW photocathode displayed markedly improved performance in solar-assisted maleic acid reduction relative to Ti/TiO<sub>2</sub> and lead. By capitalizing on the large photovoltage generated at the semiconductor/electrolyte junction, the Si NW photocathode was able to drive this reductive transformation at substantially more positive potentials (ca. 700 mV based on  $V_{j=10}$ ), thereby reducing the required external bias.

Subsequently, we analyzed the potential-dependent reduction product and its Faradaic efficiency on the Si NW photoelectrode. To do so, bulk photoelectrolysis was performed at a few selected potentials between -0.9 and 0.1 V. All the recorded chronopotentiometric curves  $(i \sim t)$  remained highly stable for at least 1 h (Figure 2d). At the conclusion of each photoelectrolysis experiment, the liquid product in the catholyte (ca. 125 mL) was collected and characterized by nuclear magnetic resonance (NMR). Succinic acid was determined to be the only liquid product (Supporting Information, Figure S4). Based on its concentration in the catholyte, we calculated the Faradaic efficiency for succinic acid (Figure 2e). Faradaic efficiency was close to 100% within the entire potential range, suggesting that HER was largely overwhelmed by maleic acid reduction on the Si NW photocathode. In stark contrast, electrochemical reduction of maleic acid on both Ti/TiO<sub>2</sub> and lead was accompanied by significant cogeneration of H<sub>2</sub>. The Faradaic efficiency for succinic acid on Ti/TiO2 was around 90% between -0.9 and -0.4 V, and within the range of 70–90% on lead, which is consistent with previous studies.<sup>[12,22]</sup> The very high Faradaic efficiency for the quantitative transformation of maleic acid to succinic acid on the Si NW photocathode therefore presents another advantage over conventional electrosynthesis.

Furthermore, we assessed the operation durability of the Si NW photocathode. Its photocurrent density at 0 V was monitored continuously for about 17 h, and there was no sign of activity loss (Figure 2 f inset). The slight initial photocurrent decline was probably caused by the decreasing local concentration of maleic acid, and a gradual rise in photocurrent thereafter was probably due to increasing wetting of the Si NW photocathode. Postmortem SEM and TEM examinations showed that there was no obvious change in the electrode morphology after prolonged photoelectrolysis (Supporting Information, Figure S5). Additionally, we extracted the catholyte every 30 min for the first 6 h during photoelectrolysis and analyzed the concentration of succinic acid. The measured concentrations were in perfect accordance with what was predicted by assuming all the cathodic photocurrent resulted from the two-electron reduction of maleic acid (Figure 2 f,  $\blacksquare$ ). These results suggest that the Faradaic efficiency for succinic acid is retained at about 100% during prolonged photoelectrolysis.

The aforementioned results corroborate that the conversion of maleic acid to succinic acid was efficiently achieved on Si NW photocathode under light illumination. Furthermore, we demonstrated that the idea of PEC reductive transformation was not specific to succinic acid, but also applicable to other industrial building-block chemicals. In the proceeding text, we describe a second example in which glyoxylic acid was photoelectrosynthesized on a Si NW electrode.

The electrochemical reduction of oxalic acid is a wellestablished approach to synthesize glyoxylic acid in industry.<sup>[13,23]</sup> The process has a standard reduction potential of -0.08 V, which is very close to that of HER. As a result,

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reaction selectivity was a general concern. Herein, the PEC reduction of oxalic acid was carried out in the same experimental setup. The electrolyte was 0.3 M K<sub>2</sub>SO<sub>4</sub> and 0.1M oxalic acid (pH 1.85). Under 1 sun illumination, the polarization curve of 2.8 µm Si NW electrode exhibited an onset potential of -0.063 V and reached a saturation photocurrent density of approximately 37 mA cm<sup>-2</sup> at about -1.2 V (Figure 3a). Both the onset potential and curve fill factor were noticeably inferior to those of maleic acid reduction, but still slightly better than those of HER (control experiment in  $0.3 \text{ M} \text{ K}_2 \text{SO}_4$  with pH adjusted to  $1.85 \text{ by } \text{H}_2 \text{SO}_4$ ). Considering that the light absorption and charge separation steps were essentially identical for all the three PEC reactions, the aforementioned difference therefore reflected their dissimilar interfacial charge transfer rates; oxalic acid reduction was not as facile as maleic acid reduction, but still more kinetically favorable than HER on the Si surface. Ion chromatography (IC) was used to confirm glyoxylic acid as the sole reduction product in the catholyte (Supporting Information, Figure S6). Quantitative analysis showed that the Faradaic efficiency for glyoxylic acid on the Si NW electrode was between 70-80% within the potential range of -0.9 to -0.3 V (Figure 3b). At more negative potentials, it is probable that the PEC reduction of oxalic acid became diffusion-limited, and consequently Faradaic efficiency was slightly decreased. The operation durability of the Si NW photocathode for oxalic acid reduction at -0.5 V was monitored for 6 h (Figure 3c). Photocurrent density initially decreased and then leveled off at approximately 14 mA cm<sup>-2</sup>. Slight fluctuations were due to the interference of H<sub>2</sub> bubbles generated on the electrode surface. Glyoxylic acid concentration was analyzed every 30 min (Figure 3 d). The black and gray curves in this Figure



**Figure 3.** PEC reduction of oxalic acid to glyoxylic acid. a) Polarization curves for PEC oxalic acid reduction on Si NWs in the light ( $\square$ ) or dark ( $\square$ ) in comparison with those of HER on Si NWs in the light ( $\square$ ); electrochemical oxalic acid reduction on p<sup>++</sup>-Si ( $\blacksquare$ ) and lead ( $\bigcirc$ ). b) Potential-dependent Faradaic efficiency for glyoxylic acid on the Si NW photocathode and lead electrode. c) Long-term chronoamperometric stability held at -0.5 V. d) Corresponding concentration increase of glyoxylic acid in the catholyte. Black and gray curves indicate the prediction assuming 100% and 75% Faradaic efficiencies, respectively.

present theoretical predictions that assume 100% and 75% of the cathodic photocurrent was used for oxalic acid reduction, respectively. The measured concentrations of glyoxylic acid were in quantitative agreement with the latter, suggesting the PEC reductive transformation of oxalic acid proceeded at about 75% Faradaic efficiency.

In summary, we used chemically etched Si NW arrays as the model photocathode, and for the first time demonstrated the photoelectrosynthesis of succinic acid and glyoxylic acid with positive onset potential, large saturation photocurrent density, high reaction selectivity and excellent operation durability. This PEC process was substantially more advantageous compared to conventional electrosynthesis because the large photovoltage (ca. 700 mV) supplied from the semiconductor/electrolyte junction partially offset the required external bias, rendering such a photoelectrosynthetic approach significantly more sustainable. Reduction products could be isolated following established industrial protocols. In the present study. Si was used as a model system for a conceptual demonstration; it is far from the ideal p-type semiconductor material since its valence band edge is too high in energy. If other semiconductor materials (for example, GaAs and CdS) were developed, they might reduce maleic acid at an even more positive potentials. When combined with proper photoanodes, they may achieve spontaneous photosynthesis of a wide range of valuable organic compounds.

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#### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** building-block chemicals · glyoxylic acid · photoelectrosynthetic synthesis · reduction · succinic acid

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Photoelectrochemical Synthesis

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Photoelectroreduction toward Chemical Building Blocks



A photoelectrochemical approach was used to drive reductive production of industrial building-block chemicals, such as succinic and glyoxylic acids, on Si nanowire array photocathodes. No cocatalyst was required and the process was performed at room temperature with a positive onset potential, large saturation photocurrent density, high reaction selectivity, and excellent operational durability.

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