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Silicon nanowires for solar-to-fuel conversion

By
Yude Su

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate Division of the University of California, Berkeley

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Abstract

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Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Peidong Yang, Chair

Photoelectrochemistry is one of several promising approaches for the realization of efficient solar-to-fuel conversion. Recent work has shown that photoelectrodes made of semiconductor nanowires can have better photoelectrochemical (PEC) performance than their planar counterparts for several reasons including the enhanced light absorption efficiency, release of the high requirement on the minority carrier diffusion length and providing much more catalytic sites for the electrochemical oxidation/reduction reactions to happen. Owing to its earth-abundance, biocompatibility, suitable band structure and stability in aqueous condition, Si nanowire is widely considered as a promising photocathode candidate. Though Si nanowire has been studied for both solar hydrogen evolution and CO₂ reduction, our understanding on this photocathode is still not comprehensive, from both fundamental and practical perspectives. Under this context, the subject of my graduate focuses on investigating the properties, understanding the benefits and improving the efficiency of Si nanowire photocathode.

Although much effort has been focused on studying Si nanowire arrays, inhomogeneity in the geometry, doping, defects and catalyst loading present in such arrays can obscure the link between these properties and the nanowires’ PEC performance; correlating the performance with the specific properties of individual wire is difficult because of ensemble averaging. Here, we show that a single-nanowire-based photoelectrode platform can be used to reliably probe the current-voltage (I-V) characteristics of individual nanowires. We found that the photovoltage output of ensemble array samples can be limited by poorly performing individual wires, which highlights the importance of improving the nanowire homogeneity within an array. Furthermore, this platform allows the flux of photo-generated electrons to be quantified as a function of the lengths and
diameters of individual nanowires, and the flux over the entire nanowire surface (7-30 electrons/ (nm\(^2\)·s)) is found to be significantly reduced as compared to that of a planar analogue (~1,200 electrons/ (nm\(^2\)·s)). Such characterization of the photo-generated carrier flux at the semiconductor/electrolyte interface is essential for designing nanowire photoelectrodes that match the activity of their loaded electrocatalysts.

Based on the information obtained from single-nanowire photoelectrode, we moved forward to develop approaches to improving the energy conversion efficiency of Si nanowire photocathode. First, we demonstrate the resonant absorption effect of Si nanowire photoelectrode. Strongly dependent on the nanowire’s diameter, such resonant effect provides guidance to design proper nanowire geometry for maximized light absorption. Second, we try to use Cu to replace Au for the vapor-liquid-solid (VLS) Si nanowire growth. It shows that Cu-catalyzed VLS Si nanowire photocathode outperforms the Au-catalyzed counterpart. Such result highlights the importance of improving the material’s quality, especially avoiding the metal contamination, to realize efficient nanowire-based solar-to-fuel conversion. Third, we use a commercial chemical vapor deposition (CVD) system for wafer-scale Si nanowire growth. Attributed to the capability of precisely-controlled in-situ boron doping, the CVD yields Si nanowire arrays with decent PEC performance. Our approach opens up the opportunities for scale-up production of high-quality Si nanowire photocathode.

Recently the inorganic/microorganism hybrid systems have attracted a lot of interests in the field of microbial electrosynthesis and artificial photosynthesis. However, the electron transfer pathway from electrode to microorganism is still elusive. With Si nanowire/Ni/S. Ovata hybrids as a model system, the last part of my graduate research used sophisticated electrochemical methods to investigate the cathodic electron transfer mechanism in the bacteria-catalyzing CO\(_2\)-reducing process. The Tafel plot on biotic condition yields fast kinetics (low Tafel slope) at lower over-potential region and slow kinetics (high Tafel slope) at higher over-potential region. Comparison with the abiotic Tafel plot suggests that H\(_2\)-mediated electron transfer dominates at higher over-potential. The charge transfer resistance extracted from the EIS measurement is consistent with the information obtained from the Tafel plot. The comparison between Ni-based hybrids and Pt-based hybrids system indicate that Ni plays an important role in such kinetics transition. At lower over-potential, the Ni species is oxidized into Ni(OH)\(_2\), which is proposed here to bind with the conductive protein complexes on the membrane of S. Ovata bacteria. Such binding would induce the direct electron transfer from Si cathode to the intracellular environment and thus facilitate the kinetics. Our results provide the guidance to design the efficient bio-inorganic interface in the field of microbial electrosynthesis and artificial photosynthesis.
I dedicate this dissertation to my parents, for their everlasting love.
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Chapter 1

Introduction

1.1 Fundamentals of PEC devices

1.1.1 Utilization of solar energy

Electricity and lightening, heating and cooling, computers, cars and planes, the hallmarks of modern life are synonymous with consumption of energy. The world’s population increase, along with the rapid growth of many developing economies, indicates that the demand for energy may double in the following fifty years. Even though they are a finite energy resource, fossil fuels can still meet this energy demand. However, the increasing concentration of CO\textsubscript{2} in the atmosphere, as a result of the combustion of these carbon-based fossil fuels, is forecast to lead to severe climate change and the rise of the sea level. For these reasons, the world’s need for sources of clean and sustainable energy is more urgent than ever. As the most abundant and universally available renewable energy source, sun offers more than enough power to satisfy humanity’s appetite for energy. As a result, finding a viable and cost-effective way to utilize solar energy is urgently needed. During the past decades, the techniques and thus efficiency of photovoltaic cells have been steadily increasing, however, it remains too costly compared with fossil fuels on a worldwide scale. In addition, the solar electricity is not easy to store and transport, considering the inhomogeneous sunlight distribution all over the world and the daily or seasonal sunlight fluctuation. Since fuels account for more than 70% of current energy consumption, there is urgent need to convert solar energy to fuels, ideally liquid fuels that are easy to store and transport. The direct conversion of sunlight into the energy stored in chemical bonds, termed as artificial photosynthesis, mimics the natural photosynthetic process occurring in plants. To realize efficient solar-to-fuel conversion, several approaches have been proposed and used, including the photovoltaic-electrolyzer system, the photoelectrochemistry system and the self-supported photocatalysts. Although the photovoltaic-electrolyzer system potentially can reach very high efficiency, the high cost of such system makes it difficult for practical implementation. In contrast, PEC devices, in which the light-absorbing semiconductor is simply immersed in the electrolyte, represent a cost-effective method to realize solar-to-fuel conversion. In recent years, semiconducting nanomaterials, especially nanowires, have attracted a lot attention in the field of photoelectrochemistry, for the purpose of improving efficiency with less material. Photoelectrodes made of semiconductor nanowires have demonstrated better
PEC performance than their planar counterparts, however, questions still remain at fundamental level. For example, although much effort has been focused on studying the nanowire arrays, inhomogeneity present in such arrays obscures the link between the nanowire’s properties and its PEC performance; quantitative understanding of the nanowire’s native advantages is still missing because of the ensemble average. To make the nanowire-based PEC device a competitive candidate for future solar-to-fuel conversion applications, these fundamental questions will need to be fully answered.

My Ph.D research exploited nanowires made of Si, a model semiconducting material, to investigate and unravel the existing issues about the nanowire-based PEC systems. Before we talk through the research details, we will need to glance at the background of the nanowire-based PEC systems. In this chapter, we will first go through a brief description of PEC devices, including the physics, the materials, efficiency calculation and limitations and problems (1.1.2). The description of limitations and problems of current PEC systems endows a good opportunity for the introduction of semiconductor nanowires, and their strengths in the field of photoelectrochemistry (section 1.2.1). As a promising photoelectrode material and the model material used over my Ph.D career, the fundamentals of Si nanowire photocathode will be introduced next (section 1.2.2). Based on this model material, the objective of my graduate research is to investigate the properties, quantitatively understanding the benefits and improving the efficiency of Si nanowire photocathode (section 1.3). With these introductions, detailed research work will be described in the following chapters.

### 1.1.2 Introduction to PEC devices

Always described as the extension of photovoltaic devices, PEC devices utilize the photo-generated charge carriers for electrochemical reactions. Notably, a PEC device share similarities with a photovoltaic device, including the band energetics, efficiency calculation and material choice. As a result, before we introduce the PEC device, we will need to take a glance at its relative-the photovoltaic device. p-n junction is the key component in a conventional photovoltaic device. At the junction between the p-type and n-type semiconductors, excess holes and electrons recombine until the chemical potential difference is counterbalanced by an electrical potential difference (figure 1a). The width of the area devoid of carriers, termed as depletion region, depends upon the doping levels of the two sides of junction and the materials’ dielectric constants. When a semiconductor absorbs photons, electrons are excited from its valence band to conduction band, producing electron-hole pairs within the material. The built-in electric field at the junction, or band-bending, separates the electron-hole pairs and drives them towards the solar cell’s contacts to be collected as electrical current. This current and the built-in field’s voltage transform the photon energy into electrical power. If the photo-generated carriers are far from the p-n junction, the minority carriers must diffuse to the depletion
region to be separated. Recombination during this diffusion process is one of the main loss mechanisms that reduce a solar cell’s efficiency.

Several metrics are used to evaluate the performance of a photovoltaic device. The current density-voltage (J-V) curve is typically characterized under illumination from a solar simulator, which is a light source that produces one-sun intensity (100 mW/cm²) with an AM1.5G spectral profile (Figure 1b). The J-V curve yields the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}) and the fill factor (FF)-three important metrics to evaluate the solar cell’s performance (Figure 1c). If the material properties of the solar cell are known, the thermodynamics limits for these metrics can be calculated to analyze the solar cell’s experimental performance and diagnose areas for improvement\textsuperscript{23}, \textsuperscript{24}. Efficiency (\eta), which is the maximum power produced by the solar cell divided by the power of the incident light intensity, is the most important metric and determines how efficient the solar cell is. In addition, measuring both the wavelength-dependent absorption of the solar cell and its efficiency at each wavelength, referred to as the external quantum efficiency (EQE), allows the calculation of the wavelength-dependent internal quantum efficiency (IQE). While EQE provides the net performance of the solar cell that comprises effects from both absorption and charge collection, IQE indicates how well the solar cell collects charges once they are generated.

Sixteen years after Bell labs exhibited the first Si photovoltaic device, photoelectrochemistry was demonstrated by Fujishima and Honda in 1970, using TiO\textsubscript{2} as a photocatalyst to split water into H\textsubscript{2} and O\textsubscript{2}\textsuperscript{25}. The classic operation of a PEC cell takes advantage of the semiconductor/electrolyte interface and resembles a photovoltaic device. Specifically, when a photocatalytic semiconductor is immersed in an electrolyte, at equilibrium, a built-in electric field will be established at the interface to balance the fermi level difference between the semiconductor and the electrolyte (Figure 2). Similar to the photovoltaic device, the width of the electric field is determined by the doping level and dielectric constant of the semiconductor and the ionic intensity in the electrolyte. Upon illumination, extra minority carriers are generated, resulting in a quasi-fermi level splitting. The built-in electric field at the junction separates the charge carriers so that
they can perform separate chemical reactions: an oxidation reaction and a reduction reaction, respectively. Typically, the minority carriers react at the surface of the semiconductor while the majority carriers travel through the bulk of the semiconductor electrode and carry out the complementary reaction at a counter electrode.

The efficiency of a PEC device can be benchmarked in different ways\textsuperscript{15}. For an individual photoelectrode that facilitates a redox half-reaction, e.g. reducing H\textsuperscript{+} to H\textsubscript{2} or oxidizing H\textsubscript{2}O to O\textsubscript{2}, the efficiency of the PEC device can be calculated in the same way as that of a solar cell, taking the thermodynamic electrochemical potential of the redox species as the short-circuit condition. This measured efficiency can be interpreted as the efficiency of the photon’s assistance in driving the redox reaction, neglecting the additional energy required for the other half-reaction to maintain charge neutrality. In the context, this calculated efficiency is in accord with the efficiency of conventional electrochemistry, which uses a three-electrode setup. On the other hand, the efficiency of the sunlight-to-fuel conversion process can be defined as the overall chemical energy stored in the chemical bonds of the products, divided by the energy density of the incident photons. Here the efficiency is defined based on the overall chemical reaction rather than a redox half-reaction.

In contrast with the photovoltaic device, a PEC device is operated in the electrolyte so that there is additional requirement on the functioning material. Particularly, the semiconductor materials must be stable against photocorrosion and electrochemical-corrosion in the electrolyte. Protection against corrosion is typically realized by coating a conductive oxide protective layer on the semiconductor surface\textsuperscript{26, 27}. Additionally, unlike a photovoltaic device, which aims simply to maximize power output, a minimum driving voltage is required for PEC devices, which is determined by the energetics of the overall chemical reaction. Driving reactions such as water splitting and CO\textsubscript{2} reduction requires thermodynamic potentials greater than 1V.

Furthermore, to overcome the kinetic barrier and achieve a high reaction rate, an electrochemical over-potential is also required, especially for relatively sluggish electrochemical reactions, such as CO\textsubscript{2} reduction and N\textsubscript{2} reduction. This voltage restriction limits the choice of materials to semiconductor with wide band gaps if only one light-absorber is used\textsuperscript{28}, leading to the inefficient utilization of the solar energy and thus low theoretical efficiency. To improve the theoretical solar-to-fuel efficiency, the biomimetic Z-scheme approach has been proposed recently\textsuperscript{10, 11, 29, 30}. In such Z-scheme, two semiconductor materials are utilized: one works as a photocathode for reduction and the other as a photoanode for oxidation. In each of these electrodes, photo-excited minority carriers move to the electrolyte for the half-reactions, while majority carriers recombine at the interface between the two light absorbers. Usually the surfaces of the electrodes are decorated with co-catalysts to facilitate the chemical reactions. In principle, two light-absorbers with appropriately small band gaps can provide enough voltage to drive the overall chemical reaction. Most importantly, the use of relatively small bandgap semiconductors allows the absorption of longer wavelength photons, and thus
theoretically can reach efficiency as high as 10%\textsuperscript{11}. In addition, such duel light-absorber system allows the combination of different semiconductors and thus increases the flexibility of the material choice.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{The band energetics of a $p$-type semiconductor/electrolyte interface are displayed in three conditions. \textbf{a}, before equilibrium between the two phases. \textbf{b}, after equilibrium is established, but in the dark. \textbf{c}, under sunlight illumination. In \textbf{b}, $q\Phi_{bi}$ is known as the barrier height, and $W$ is the depletion width. In \textbf{c}, $E_{F,n}$ is the electron quasi-fermi level, and $E_{F,p}$ is the hole quasi-fermi level. The splitting of the two fermi levels is the open-circuit voltage.}
\end{figure}

In nature, the solar-to-fuel efficiency of the photosynthesis process is typically low than 1\%\textsuperscript{8}. If artificial photosynthesis is aimed at practical implementation, the solar-to-fuel efficiency should be at least larger than that of the natural photosynthesis systems. In theory, the Z-scheme approach can provide enough thermodynamic driving force for the reaction to happen, and at the same time allow the absorption of a large portion of the sunlight. But practically, in order to reach desirable efficiency, the kinetics over-potential and the interfaces between different functional components need to be taken into consideration. Due to the integrated nature of the components in artificial photosynthesis, an efficient Z-scheme PEC device should operate in harmony so that there is no significant bottleneck hindering the overall charge flux\textsuperscript{11}. Under the context of the Z-scheme approach, there are two major issues that may lower the overall efficiency should be addressed: 1) matching the flux between current-generating light-absorbers and the current-consuming electrocatalysts, i.e., under an acceptable over-potential, is the electrocatalyst capable of handling the photo-generated carrier flux efficiently and operating the chemical reaction selectively 2) matching the flux between different light absorbers, i.e., could both the photoanode and photocathode provide enough photocurrent for practical application, while maintaining a desirable voltage output? These two questions are currently not fully answered, due to the inadequacy of efficient and earth-abundant electrocatalyst, and the lack of structural design based on a device integration.
approach. The introduction of nanomaterials, particularly the one-dimensional nanowire morphology, could contribute to tackle these issues from various perspectives.

1.2 Semiconductor nanowires for photoelectrochemistry

1.2.1 Advantages of semiconductor nanowires in photoelectrochemistry

Taking advantage of the unique properties, semiconductor nanowire is a potential solution to addressing the two flux matching issues incurred in the Z-scheme PEC process. Frist of all, semiconductor nanowire photoelectrodes serve as an ideal platform to quantitatively investigate and significantly alleviate the flux matching issue between the current-generating light-absorber and the current-consuming electrocatalysts. To make the solar-to-fuel devices economically viable, an energy conversion efficiency of ~5% is preferable. This corresponds roughly to a photo-generated carrier flux of ~10 mA/cm² under one-sun illumination, which is equivalent to approximately a flux of 620 electron/(nm².s). Typically materials have a surface atom density of ~10¹⁵ atoms/cm² or equivalently ~10 atom/nm². This sets a ~62 s⁻¹ lower limit of turnover frequency (TOF) for the electrocatalyst coated on a planar electrode. Practically, a higher TOF is needed because not all surface atoms are catalytic centers, and a reduced cocatalyst loading may

Figure 3. Nanowire geometry alleviates the flux matching issue in PEC device. The over-potential to satisfy a carrier flux of 10 mA/cm² is plotted vs. the exchange current density ($i_0$) for three kinds of photoelectrode: planar electrode with 10% cocatalyst coverage (yellow), planar electrode with 100% cocatalyst coverage (dashed blue) and nanowire electrode with 10% cocatalyst coverage (red). It shows that the nanowire geometry with a large roughness factor can significantly reduce the required over-potential. Reprinted with permission from reference 11. Copyright © 2013 American Chemical Society.
be desirable to avoid blocking the sunlight and to reduce cost. Based on the Butler-Volmer equation and Tafel plot, an increased electrochemical over-potential is needed to achieve a higher TOF, which will in turn decrease the energy conversion efficiency correspondingly. One approach to reducing the incurred over-potential is to develop efficient and low-cost electrocatalysts. However, the existing electrocatalysts for electrochemical reactions of interests are either less-efficient or too expensive, or both. And a non-negligible over-potential is always present owing to an inadequate TOF of the electrocatalysts, i.e. for hydrogen evolution (HER), the most widely-studied earth-abundant electrocatalyst-MoS$_2$ needs ~200 mV over-potential to reach ~62 s$^{-1}$ TOF$^{31-33}$; for more sluggish reaction such as CO$_2$ reduction, the Cu nanoparticles need ~600 mV over-potential to reach ~62 s$^{-1}$ TOF$^{31,34}$. As a result, such inefficient catalytic activity makes it difficult to handle the photo-generated carrier flux in a low-over-potential manner. Indeed, the biological catalyst, including extracted enzymes and microorganism, potentially can be utilized in the artificial photosynthetic systems. However, the integration between the biological systems and the solid-state materials is still challenging. Alternatively, with presently available electrocatalysts, the introduction of a large surface area electrode such as nanowire arrays can alleviate this flux mismatch. Based on the theoretical calculation, the increase of roughness factor (the ratio between surface area and the projected area) reduces the required over-potential by decreasing the surface flux of charge carriers (figure 3). Specifically, nanowire photoelectrodes with a roughness factor of 1000 can reduce the over-potential by ~200 mV, provided a 59 mV/decade Tafel slope. Experimentally, recent work has also demonstrated the nanowire photoelectrodes outperform the planar photoelectrode because of the reduced over-potential. Furthermore, although most of the current studies focus on the semiconductor nanowire arrays, inhomogeneity in doping, geometry, defects and catalyst loading present in such arrays can obscure the link between these properties and the nanowire’s PEC performance; correlating the performance with the specific properties of individual nanowire is difficult because of the ensemble averaging. As a result, it is necessary to study the nanowire’s benefits at the single-nanowire level, which circumvents the inhomogeneity present in nanowire arrays. With a well-defined single-nanowire PEC system, an improved and quantitative understanding of the reduced over-potential can be unveiled.

The second major issue of the current Z-scheme PEC devices is matching the flux between different light absorbers, i.e. photocathode and photoanode. Indeed, such flux matching would require a well-designed combination of semiconductor materials with suitable band gaps and a low resistance charge transfer pathway between the two light absorbers. From the perspective of the material’s structure, the nanowire morphology can help address this issue in two aspects: the enhanced light absorption and more efficient charge carrier collection. For the semiconductor materials with indirect bandgap, particularly some promising photocathode materials such as Si, Cu$_2$S and GaP, the absorption coefficient is quite low at longer wavelength. Such low absorption coefficient correspondingly requires a considerable thickness of material to absorb a large portion of
the solar spectrum and thus provide enough photocurrent, i.e. thickness of 100 μm is needed for planar Si photoelectrode to absorb most of the solar spectrum. In addition, even if the longer-wavelength photons get absorbed in the deep region of the material, the charge carriers may not be able to diffuse to the solid/electrolyte interface for electrochemical reactions, given the limited minority carrier diffusion length. The nanowire geometry potentially can contribute to enhance the light absorption and reduce the required material thickness, by providing a rough surface and inducing the light trapping effect. Both Si nanowire and GaP nanowire arrays have demonstrated enhanced photocurrent with less material used\textsuperscript{35, 36}. Moreover, owing to the similar length scale with the photon wavelength, the nanowire morphology can also induce the resonant absorption, which can further increase the absorption beyond the Shockley-Queisser limit\textsuperscript{37}. Compared with the several promising photocathode materials such as Si and InP\textsuperscript{26, 38, 39}, which have been reported to generate high current densities with photovoltages of greater than 500 mV, the photoanode deserves more attention in terms of the photocurrent. Presently, there is no stable photoanode device capable of providing a photocurrent of larger than 10 mA/cm\textsuperscript{2}, while at the same time providing an adequate photovoltage to couple with the photocathode. This is typically observed in the use of conventional oxide or nitride materials, which intrinsically have low hole mobility due to the localized p-orbital nature of the valence band. The introduction of nanowire morphology decouples the light absorption direction with the minority carrier diffusion length. As a result, the photo-generated charge carriers only need to diffuse a short distance along the radial direction to reach the interface for electrochemical reactions. Such design has been reported to significantly improve the photocurrent of some photoanodes materials such as Hematite and BiVO\textsubscript{4}\textsuperscript{30, 40}.

1.2.1 Si nanowire photocathode

Taking advantage of its earth-abundance, suitable bandgap and band edge, biocompatibility and stability in aqueous condition, Si has been intensively investigated as a photocathode material\textsuperscript{20, 27, 31, 41, 42}. Compared with the planar Si, Si nanowire photocathodes attract particular research interests, because of their unique properties such as large surface area, strong light absorption and low-cost synthesis. Notably, they have demonstrated better performance than their planar counterparts for different PEC reactions, including the heterogeneous reactions such as solar hydrogen evolution\textsuperscript{27, 31, 41} and solar CO\textsubscript{2} reduction\textsuperscript{42}, and the homogeneous reactions with organic molecules involved\textsuperscript{20}. For HER, the required over-potential is typically acceptable even with earth-abundant electrocatalyst such as MoS\textsubscript{2} and CoS\textsubscript{2}, owing to the relatively simple reaction kinetics of HER\textsuperscript{32, 33}. As a result, the reduced over-potential and the benefits from the Si nanowire’s large surface area are not appreciable as expected. In contrast, for more sluggish reactions such as CO\textsubscript{2} reaction, a big improvement of the PEC performance and product selectivity has been observed on the Si nanowire photocathode, compared with the planar counterparts. The Yang group reported the directed assembly of Au\textsubscript{3}Cu
nanoparticles on the Si nanowire photocathode with flexible tunability of the particle’s density. A reduction of 120 mV over-potential compared to the planar counterpart was observed resulting from the optimized spatial arrangement of nanoparticles on the high surface area nanowire arrays. Although the benefits of the large surface area and reduced over-potential have been observed on Si nanowire arrays, inhomogeneity in the geometry, doping, defects and catalyst loading present in such arrays can obscure the link between these properties and the nanowires’ PEC performance; correlating the performance with the specific properties of individual wire is difficult because of ensemble averaging. As a consequence, to achieve a more quantitative understanding on the Si nanowire’s benefits, a single-nanowire model is needed, where the inhomogeneity present in nanowire arrays is circumvented.

The good PEC performance of Si nanowire photocathode is also attributed to its good charge collection. Because of the orthogonalization between the light absorption and the charge collection in Si nanowires, the charge carriers only need to diffuse a short distance to the solid/electrolyte interface before they recombine. The Wang group claims that Si nanowire geometry can improve the onset potential by 110 mV for solar CO₂ reduction, owing to the improved charge transfer kinetics. Remarkably, the above mentioned Si nanowire photocathodes are all fabricated by the top-down method, which use gas-phase or liquid-phase etchant to etch the Si wafer into aligned nanowires. On the other hand, the VLS method represents a more cost-effective way to scale up the synthesis of Si nanowires, provided that SiCl₄, a precursor for VLS Si nanowire synthesis, is an inexpensive chemical used in industry. However, the PEC performance of the synthesized VLS Si nanowire is significantly lower than the etched counterpart and the planar Si, presumably because the Au contamination introduced during the VLS growth acts as a deep trap and damages the electronic properties of Si nanowire. As a result, people have proposed to use other metal seeds, such as Cu and Ti, for the VLS Si nanowire growth to get better material quality. If high-quality VLS Si nanowire photocathode can be produced on a wafer scale, it will open up opportunities for scale-up solar-to-fuel conversion applications.

The excellent biocompatibility makes Si nanowire a good model material to investigate the solid/biological interface as well. Recently the inorganic/microorganism hybrid systems have attracted a lot of interests in the field of microbial electrosynthesis and artificial photosynthesis. The Yang group demonstrated that by interfacing Si nanowire photocathode with a kind of acetogen, Sporomusa Ovata, CO₂ can be selectively reduced into acetic acid with sunlight as the sole energy source. Using bacteria as the CO₂ reduction catalyst, this study represents a major breakthrough in the field of artificial photosynthesis. However, the electron transfer pathway from the Si photocathode to microorganism is still elusive and attracts a lot of attention recently. Understanding such fundamental process is not only scientifically but also practically important, given that an efficient semiconductor/biological interface is critical for the overall process. Furthermore, provided the special interaction between Si nanowire and microorganisms, such inorganic/bio hybrids systems can be applied to other reactions...
such as the solar N₂ fixation. Under mild temperature and pressure, such method may provide an alternative way to synthesize ammonia instead of using the energy-consuming Harbor-Bosch process.

1.3 Objectives of my graduate research

Under this context, my graduate research mainly utilize Si nanowire photocathode as a model material to investigate the benefits and limiting factor of the nanowire-based PEC process. Specifically, I carry out three novel projects during my Ph.D. career: 1) Study the PEC phenomena at the single-nanowire level. Circumventing the inhomogeneity present in nanowire arrays, single-nanowire platform quantitatively reveals the nanowire photoelectrode’s benefits and limiting factor. 2) Based on the information obtained from single-nanowire photoelectrochemistry, I used different approaches to improving the PEC performance of Si nanowire array. These approaches include light management, material quality improvement and scale-up nanowire growth. 3) With Si nanowire/Ni/S. Ovata hybrids as a model system, the last part of my graduate research used sophisticated electrochemical methods to investigate the cathodic electron transfer mechanism in the bacteria-catalyzing CO₂-reducing process. Such study provides the guidance to design the efficient bio-inorganic interface in the field of microbial electrosynthesis and artificial photosynthesis.

1.4 References

Chapter 2

Single-nanowire photoelectrochemistry

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2.1 Introduction

Energy crisis and the resulting environment issues represent a major challenge facing mankind in the 21st century. To replace the traditional fossil fuels, tremendous efforts have been put into developing renewable energy sources, in particular solar energy1, 2. Although the photovoltaic techniques have been well-established, it is expensive to store and transport the electricity, considering the world-distribution and intermittent nature of the sunlight. As a result, the direct conversion of solar energy into chemical fuels that can be stored, transported and used upon needed, is a desirable approach to solve the energy problems. Photoelectrochemistry3-5 is one of several promising approaches to realize efficient solar-to-fuel conversion6, 7. Since Fujishima and Honda demonstrated that TiO2 photoelectrode can harvest the light and carry out solar water-splitting in 19728, photoelectrochemistry has attracted a lot of research interests. In a typical PEC process, the semiconducting photoelectrode absorbs photons and generate electron-hole pairs, which are subsequently separated at either a semiconductor/electrolyte interface or an embedded solid junction5, 9. The charge carriers then move to a catalytic center and carry out oxidation/reduction in the solution. As a result, photoelectrochemistry is an integrated process containing multiple steps, and an efficient PEC system would require the optimization of different components9. With dimensions much smaller than visible materials, nanomaterials possess a lot of unique and unexpected advantages over the bulk analogs in many different research fields including photoelectrochemistry. Recent work has shown that photoelectrodes made of semiconductor nanowire arrays9-14 can have better PEC performance than their planar counterparts for three reasons as following. First, the semiconductor nanowire can induce strong light trapping effect, leading to significantly reduced reflection and enhanced light absorption efficiency15, 16. Second, the nanowire geometry decouples the path of light absorption with the path of minority
carrier diffusion. As a consequence, the semiconductor nanowires would release the high requirement on the minority carrier diffusion length and thus the material’s quality. Last but not least, the nanowire geometry exposes larger surface area than bulk materials, and thus provides much more catalytic sites for the oxidation/reduction reaction to happen. For these reasons, much effort has been focused on understanding and improving the PEC performance of semiconductor nanowire arrays, which are typically grown by the VLS method or etched with gas/liquid etchant. However, in nanowire array samples, inhomogeneity in the geometry, doping, defects and catalyst loading always exist, and such inhomogeneity can obscure the link between these properties and the nanowires’ PEC performance. Furthermore, correlating the performance with the specific properties of individual wire is difficult because of ensemble averaging. As a result, the information achieved from nanowire arrays is the ensemble averaged value and can’t represent the nanowire’s native properties. Instead of the nanowire arrays, single-nanowire device circumvents the inhomogeneity issue and represents a useful platform to quantitatively understand the nanowire’s advantages. Notably, single nanowire platform has been successfully applied to a lot of research fields. Back to 2001, the Lieber group fabricated a single-nanowire-based field effect transistor to probe different kinds of biological molecules. Yang group reported that a Tin oxide single-nanowire device can penetrate the cell membrane to probe the intracellular phenomena. In addition, people investigated the single-nanowire-based photovoltaic devices and found that they can reach surprisingly high energy-conversion efficiency. Moreover, people also applied single-nanowire device to electrochemistry to probe the nanoscopic electrochemical

**Figure 1.** a, Schematics of the single Si nanowire for the PEC process. Under illumination, the photoexcited electron-hole pairs are produced and subsequently separated at the nanowire/electrolyte interface because of the band bending. The electrons then move to the Pt catalytic sites and carry out the proton reduction. b, SEM image of the individually addressable single nanowires. The Si layer of the SOI substrate is patterned into nine electrically isolated, oxide-passivated electrodes, with an oxide layer underneath. The single Si nanowires are vertically grown on these isolated Si electrodes by the VLS mechanism. The scale bar is 10 μm.
phenomena. Here, we show that a single-nanowire-based photoelectrode platform can be used to reliably probe the $I$-$V$ characteristics of individual nanowires (Figure 1a). We found that the photovoltage output of ensemble array samples can be limited by poorly performing individual wires, which highlights the importance of improving the nanowire homogeneity within an array. Furthermore, this platform allows the flux of photo-generated electrons to be quantified as a function of the lengths and diameters of individual nanowires, and the flux over the entire nanowire surface (7-30 electrons/ (nm$^2$∙s)) is found to be significantly reduced as compared to that of a planar analogue (~1,200 electrons/ (nm$^2$∙s)). Such characterization of the photo-generated carrier flux at the semiconductor/electrolyte interface is essential for designing nanowire photoelectrodes that match the activity of their loaded electrocatalysts.

2.2 Fabrication and measurement of single-nanowire-photoelectrode devices

2.2.1 Fabrication of single-nanowire-photoelectrode devices

As a model system, silicon (Si) and platinum (Pt) are selected as the light-absorbing semiconductor and the proton-reduction electrocatalyst respectively. Si nanowires were grown epitaxially on the pre-patterned, degenerately-doped Si <111> device layer of a silicon-on-insulator (SOI) substrate, as shown in the scanning electron microscope (SEM) image (Figure 1b). The detailed fabrication and nanowire growth process is described as

![Figure 2. Schematic illustrations of the fabrication and measurement processes. a, Outline of the post-growth fabrication process. Devices with two kinds of doping profiles (p-Si and n⁺p-Si) were fabricated for comparison. b, The PEC measurement scheme. A two-electrode configuration was used to characterize the I-V properties of single nanowires. While the Si nanowire serves as the working electrode, a Pt wire functions as the counter/reference electrode whose electrochemical potential was calibrated. The reactor volume in which the PEC processes occur is defined by a polydimethylsiloxane (PDMS) chamber. A probe makes electrical contact to each nanowire through the outside pads, while the chamber is illuminated from above.](image-url)
following. Initially, the heavily doped (ρ of 0.01-0.05 Ω cm) p-type (boron) SOI wafers with 3 μm device layer oriented <111> and 2 μm buried oxide layer were obtained from WRS Materials. The device layer was first thinned down to 1.5 μm by thermal oxidation and subsequent etching in buffered hydrofluoric acid (BHF). Then the device layer was further doped with boron (Techneglas GS-139) at 1,050 ºC for 10 hours, followed by a second thermal oxidation and BHF etching. The resulting device layer was ~1 μm thick with a resistivity < 0.002 Ω cm. The Si electrodes were patterned by photolithography and anisotropic plasma etching (Surface Technology Systems), and then thermally oxidized to form a 300 nm thick oxide. With an oxide layer underneath, the patterned Si electrodes are electrically isolated from each other, enabling the characterization of each nanowire individually. The bonding pads were defined by photolithography and anisotropic plasma etching of the oxide (Plasma-Therm PK-12 RIE). The catalysts for VLS growth were defined by photolithography, anisotropic plasma etching of the oxide, and subsequent electron-beam evaporation of gold (150 nm). The isolated Si nanowires were grown at 875 ºC for 10-15 minutes with SiCl₄ as the precursor and 10% hydrogen in argon as the reducing agent. Moreover, the VLS growth allowed control over the nanowire’s dimensions, which facilitated studying the effects of the nanowire’s geometry. In this work, the as-grown single Si nanowires were 8-20 μm long and 500-800 nm in diameter.

The post-growth fabrication process yielded nanowires with two types of doping profiles (Figure 2a). In one case, the as-grown Si nanowires were doped into p-type only. In the second case, after the p-type doping, an n⁺ shell was added to yield an n⁺p buried junction in each single nanowire. The detailed doping process is elaborated as following. The as-grown isolated Si nanowires were etched in BHF for 30 seconds and subsequently soaked in gold etchant (Transene) for 30 minutes. Then the nanowires were thermally oxidized at 1,000 ºC for 1 hour, followed by etching in BHF. The boron doping process was split into two parts. First, boron was pre-deposited at the nanowire surface at 750 ºC for 1 hour, with 1% BCl₃ in argon as the precursor and 10% hydrogen in argon as the reducing agent. Second, the boron atoms at the nanowire surface were driven into the nanowire at 1,000 ºC for 5 hours in vacuum. The resulting boron doping level of the single nanowires was estimated to be ~2 × 10¹⁷/cm³. Such estimation is based on the resistivity of the SOI control chip, which was approximated by four-probe measurement. The key steps used in the n⁺ layer fabrication are given below. First, the p-Si nanowires were thermally oxidized at 1,000 ºC for 1 hour, then coated with ~1 μm of I-line photoresist at the base of the nanowires. Second, BHF was used to etch the oxide on the nanowire upper exposed part, followed by I-line removal in acetone. Third, a Si handle wafer was spin-coated with arsenic-containing spin-on dopant (SOD) (Filmtronics, Inc.) and baked at 150 ºC for 30 minutes. Then the device chip was placed on the SOD coated Si wafer, and annealed at 900 ºC for 4 minutes in an N₂ atmosphere to form an n⁺ layer at the nanowire’s surface. Fourth, SU-8 dissolved in ethyl acetate was drop-cast onto the device chip, resulting in a ~3 μm thick SU-8 layer at the base of the device chip. With the SU-8 at the bonding pad scratched to expose the electrode’s surface, the chip was baked
in order to harden the SU-8. Finally after a quick etching in BHF, the device chip was soaked in the solution containing 0.1 M HF and 0.2 mM K$_2$PtCl$_6$ for 3 minutes to carry out the platinum deposition on the nanowire surface. The SEM images before (Figure 3a) and after (Figure 3b) the Pt loading shows that the Pt nanoparticles are successfully loaded on the nanowire’s surface. The high-resolution TEM images (Figure 3c, 3d) reveal that there is an amorphous SiO$_2$ layer at the Si nanowire/Pt interface. This SiO$_2$ layer serves as a protective layer to prevent further oxidation. In addition, such native oxide layer also prevents the formation of the ohmic contact at the Si nanowire/Pt interface$^{24}$.

**2.2.2 Measurement techniques**
Figure 4. PEC performance of the single-Si-nanowire devices. a, I-V characteristics of single-nanowire devices. The measurement was carried out in 0.1 M K₂SO₄ solution adjusted to pH ~ 2 with H₂SO₄. Under simulated sunlight (100 mW/cm², AM 1.5G), both the p-Si device (L = 8 μm, D = 620 nm) and n⁺p-Si device (L = 12.5 μm, D = 530 nm) have significant photoresponses. b, Repeated scans of the n⁺p-Si device displayed in a.

To characterize the PEC behavior of single-nanowire devices, a specialized PEC measurement setup was developed (Figure. 2b). The complete description of the measurement is as following. A 150 W Xenon arc lamp (Newport Corporation) with an AM1.5G filter was used to characterize the PEC response of the single-nanowire devices. As a top-illumination measurement, the angle between the incident light and the axis of the single nanowire is smaller than 3º. The light intensity was calibrated using a Si photodiode referenced to an NREL calibrated Si photodiode. All PEC measurements were carried out in a two-electrode configuration. A platinum wire worked as the counter electrode, whose electrochemical potential was immediately calibrated with Ag/AgCl (0.1 M KCl) after the PEC measurement. A PDMS chamber was used to define the reactor space, where the nanowire device was immersed in 0.1 M aq. K₂SO₄ adjusted to pH ~ 2 using H₂SO₄. I-V characterization was performed with a Keithley 2636 source-measure unit (SMU), and the typical potential sweep rate was 10 mV/s. The open-circuit instrumental noise current level is less than 0.5 pA. This unique measurement platform can be further applied to other light-driven redox reactions that require high sensitivity.

2.3 Statistical analysis of photovoltage of single-nanowire-photoelectrode device and the comparison with nanowire arrays

2.3.1 Statistical analysis of photovoltage of single-nanowire-photoelectrode device
Figure 5. Schematic illustration of the band diagram for (a) a $p$-Si nanowire and (b) an $n^+p$-Si nanowire in contact with acidic electrolyte. After contact, the Fermi level ($E_F$) of the Si will equilibrate with the Fermi level ($E'_F$) in the acidic electrolyte, leading to the band bending in the Si. For the case of an $n^+p$-Si nanowire, the $n^+/p$ buried junction will significantly increase the built-in potential ($\phi_{bi}$). Despite the upward band bending at the $n^+$/electrolyte interface, the photo-generated electrons can tunnel through such a barrier, given the thin depletion layer (~5 nm) resulting from the high arsenic concentration (~$10^{20}$/cm$^3$).

These aforementioned techniques provide us with a nanowire photoelectrode platform that is individually addressable and enable the first observation of single-nanowire photoelectrochemistry. The photocurrents of devices were characterized with pA sensitivity. In the dark, devices show negligible current ($|I| < 1$ pA). The slightly increased current at potentials negative of 0 V vs. the reversible hydrogen electrode (RHE) implies a proton-reduction reaction catalyzed by the loaded Pt nanoparticles (Figure 3b). Under one-sun illumination (100 mW/cm$^2$, AM 1.5G), a significant photoresponse was
observed with the photocurrent reaching a plateau under negative bias, indicative of a light-activated process limited by the number of incident photons (Figure 4a). Such PEC behavior is consistent with that of the reported ensemble systems24, 25, confirming the observation of PEC phenomena at the single-nanowire level. Additionally, the performance of the device was consistent for multiple scan cycles (Figure 4b), indicating the robustness of our single-nanowire platform.

The photovoltage distribution statistics of the single-nanowire devices was analyzed next. For Si photocathodes, a previous study on ensemble systems proposed that the $n^+p$-buried junction increases the degree of band bending at the interface and consequently leads to a 250-350 mV improvement in photovoltage24. This concept was also implemented in our single-nanowire photoelectrodes. The onset potentials and standard deviations of $p$-Si and $n^+p$-Si devices are 280±110 mV and 530±120 mV vs. RHE, respectively (Figure 6). The ~250 mV difference between the average onset potentials demonstrates that the single-nanowire photoelectrode’s doping profile and photovoltage can be reproducibly modulated. And the improvement of photovoltage of the $n^+p$ device can be clearly explained by the band diagram illustration in Figure 5. In addition, for devices that underwent the same growth and doping process, the broad photovoltage distribution implies individual variance among single nanowires. Such individual variance, most

Figure 6. The statistical distribution of onset potentials for seven $p$-Si and nine $n^+p$-Si devices. To evaluate the photovoltage response of the single-nanowire devices, the onset potential is defined as the potential vs. RHE where $\Delta I$ is -0.5 pA. Here $\Delta I$ is the difference between the photocurrent and the dark current. The pink band shows the difference in the average onset potential between $p$-Si and $n^+p$-Si devices.
likely resulting from the nanowire’s intrinsic properties, could have a significant impact on the performance of the nanowire array samples, where many individual nanowires are connected in parallel. To investigate the impact of such individual variance, we subsequently carried out PEC measurements on ensemble Si nanowire arrays.

### 2.3.2 Fabrication and PEC measurement of Si nanowire array devices

The $p$-Si (boron) wafers ($\rho \approx 1.7$-$2.8$ $\Omega\cdot$cm) were obtained from Addison Engineering, Inc. The wafers were thermally oxidized at 1,050 °C for 8 hours to form a SiO$_2$ layer with a thickness of $\approx 350$ nm. The catalysts for vapor-liquid-solid growth were defined by photolithography, anisotropic plasma etching of the oxide, and subsequent electron-beam evaporation of gold (150 nm). The Si nanowire arrays were grown at 875 °C for $\approx 40$ minutes with SiCl$_4$ as the precursor and 10% hydrogen in argon as the reducing agent. The resulting Si nanowires are $\approx 15$ μm long and $\approx 700$ nm thick (Figure 7). The as-grown Si nanowire arrays were etched in BHF for 30 seconds and subsequently soaked in gold etchant (Transene) for 30 minutes at 85 °C. Then the nanowire arrays were thermally oxidized at 1,000 °C for 1 hour, followed by etching in BHF for 3 minutes. Subsequently, the Si nanowire arrays were soaked in gold etchant (Transene) again for 30 minutes at 85 °C. The silicon nanowire array samples went through the same boron doping process as used with the single nanowires, as follows. First, boron was pre-deposited at the nanowire surface at 750 °C for 1 hour, with 1% BCl$_3$ in argon as the precursor and 10% hydrogen in argon as the reducing agent. Second, the boron atoms at the nanowire’s surface were driven into the nanowire at 1,000 °C for 5 hours in vacuum, followed by an hour’s thermal oxidation at 950 °C. As a result, presumably the silicon nanowire arrays have the same radial boron doping profile with the single nanowires in this work. After the boron doping, for $p$-Si nanowire array devices, the chip was directly coated with 5 nm of TiO$_2$ by atomic layer deposition (Picosun ALD) after the thermal oxide was etched in BHF solution. For $n^+p$-Si nanowire array devices, the nanowire arrays were $n^+$ doped using a
Figure 8. $J$-$V$ characteristic comparison between the single-nanowire devices and nanowire arrays devices. Both (a) $n^+p$-Si and (b) $p$-Si samples are compared. Generally, the photocurrent onset potential of the array devices is comparable with the worst single-nanowire devices.

Method similar to that applied to the single nanowires. A silicon handle wafer was spin-coated with arsenic-containing spin-on dopant (SOD) (Filmtronics, Inc.) and baked at 150 °C for 30 minutes. After the thermal oxide was etched in BHF solution, the device chip was placed on the SOD-coated handle wafer, and annealed (rapid thermal annealing) at 900 °C for 3-4 minutes in a N$_2$ atmosphere to form an $n^+$ layer at the nanowires’ surface. Then the device chip was soaked in BHF solution for 30 seconds to remove the thin oxide formed during the $n^+$ doping process. Subsequently, the $n^+p$-Si nanowire array device was coated with 5 nm of TiO$_2$ by atomic layer deposition (Picosun ALD). Both types of nanowire array devices were sputtered with platinum as the HER catalyst. For the electrode fabrication, ohmic contact to the device chip was made by rubbing Ga-In eutectic on its back side. Then the chip was fixed on Ti foil with conductive silver paint and carbon tape, resulting in good electrical connections. After that, the Si nanowire array samples were sealed using the nail polish. PEC measurements were carried out in 0.5 M H$_2$SO$_4$ under one-sun illumination (AM 1.5G, 100 mW/cm$^2$) with a 20 mV/s sweep rate (single sweep, from positive to negative). Multiple scan cycles were repeated in order to get reproducible PEC behavior. The $V_{oc}$ of the Si nanowire array device was determined relative to the RHE potential in acidic electrolyte. For single-nanowire devices, the photocurrent onset potential ($V_{oc}$) is defined as the potential vs. RHE where $\Delta I$ is -0.5 pA, considering the instrumental noise. Here $\Delta I$ is the difference between the photocurrent and the dark current of the single nanowire device. For both array and single nanowire devices, the $V_{oc}$ drifts slightly among multiple scan cycles, and the median value is selected as the representative to report here.

The PEC performance of the Si nanowire array samples is compared with that of the single-nanowire-photoelectrode devices in Figure 8. It was found that the $V_{oc}$ of the array device is comparable with that of the single nanowire with the lowest photovoltage output, and this observation applied to both $p$-Si and $n^+p$-Si devices. These results suggest that the photovoltage of the ensemble array photoelectrode is largely affected by
the worst-performing individual nanowire, and this conclusion is further supported by our calculation based on an equivalent circuit model (Figure 9). Since the single nanowires and the nanowire arrays studied in this work have similar physical dimensions and go through the same doping process, such observed individual variance should be related to the heterogeneity of the material quality introduced during either the VLS growth\textsuperscript{29,30} or the fabrication process, or both. As a result, our report emphasizes the importance of controlling material quality not only in the averaged value but also the sample homogeneity, in order to produce efficient nanowire-based solar-to-fuel devices.

2.3.3 Equivalent circuit modeling

The photoelectrochemical proton-reducing Si cathode is analyzed under the framework of an equivalent circuit model as applied in photovoltaic devices\textsuperscript{31}. In such a model, the band-bending and subsequent generation of photocurrent is modeled as a standard diode
junction with an apparent ideality factor \( n \), along with the reverse saturation current density \( j_s \) and photocurrent density \( j_{ph} \). In addition, the electrochemical reaction is considered as a series resistance \( R_s \), which is dictated by the classic Butler-Volmer equation \(^{32} \). In summary, the governing equation for current density \( j \) in the photocathode is:

\[
j = j_s \left\{ \exp \left[ \frac{q(V - j_R)}{n k T} \right] - 1 \right\} - j_{ph}
\]

Here we assume that the differences in PEC performance of individual single nanowires, in particular the photovoltage \( V_{oc} \), originate from the differences in \( n \). This is reasonable given the variation of unintentional dopants that might exist, as noted in previous literature \(^{29,30} \). Moreover, we assume that among all of these single nanowire devices, \( V_{oc} \) follows a truncated normal distribution, which means that the value of \( V_{oc} \) follows a normal distribution within the range that its photovoltage \( V_{oc} \) is physically reasonable, i.e. \( V_{oc} \) \( \in \) (0,1.1):

\[
f(V_{oc}|\bar{V}_{oc}, \sigma_v) = A \cdot \exp \left[ -\frac{(V_{oc} - \bar{V}_{oc})^2}{2\sigma_v^2} \right], V_{oc} \in (0,1.1)
\]

Here \( A \) is the normalization coefficient, which in practice is close to the one for a normal distribution. The upper bound of 1.1 is chosen based on the 1.1 eV band gap of silicon.

The above assumptions lead to the relationship between \( n \), an implicit parameter, and \( V_{oc} \), a value that has been reliably measured experimentally in this report:

\[
V_{oc} = \frac{kT}{q} \cdot n \cdot \ln \left( \frac{j_{ph}}{j_s} + 1 \right)
\]

Subsequently, \( n \) follows the similar distribution as \( V_{oc} \) does:

\[
n = \frac{n}{\bar{V}_{oc} \cdot V_{oc}}, \text{ in which } n = \frac{q}{kT \cdot \ln \left( \frac{j_{ph}}{j_s} + 1 \right)} \cdot \bar{V}_{oc}
\]

The ensemble array devices, each of which is composed of a large number of single nanowire devices linked in parallel, can be considered mathematically as the probability-weighted integration of every possible configuration of single nanowires. Therefore, the \( j-V \) characteristics of an ensemble device could be written as:

\[
\int_0^{1.1} dx \cdot f(x|\bar{V}_{oc}, \sigma_v) \cdot \left\{ \exp \left[ \frac{q(V - j_R)}{kT \cdot \bar{n} - \bar{V}_{oc}} \cdot \frac{\bar{n}}{\bar{V}_{oc}} - 1 \right] \right\}
\]

At open circuit condition \( (j = 0) \), the above expression transforms into:
\[
\frac{I_{ph}}{J_s} + 1 = \int_0^{1.1} dx \cdot f(x|\bar{V}_{oc}, \sigma_v) \cdot \exp \left[ \ln \left( \frac{I_{ph}}{J_s} + 1 \right) \cdot \frac{V_{oc, array}}{x} \right]
\]

Here, \( V_{oc, array} \) is the observed open-circuit potential of the array devices. Therefore, a correlation between \( V_{oc, array} \) of ensemble devices with the distribution of \( V_{oc} \) in single nanowire devices is established (Supplementary Fig. 9). With known statistics of \( V_{oc} \) in single nanowire devices, it is possible to calculate the theoretical \( V_{oc, array} \) of an array devices, assuming that the measured statistics from single nanowire devices faithfully represent the properties wires within the array samples.

### 2.4 Quantitative understanding of the nanowire geometry’s benefits in photoelectrochemistry

#### 2.4.1 Quantification of photo-generated electron flux through the nanowire’s surface area

Semiconductor nanowire arrays have demonstrated better PEC performance over their planar counterparts because the nanowires provide a larger surface area, allow for much more electrocatalysts loading and lead to a much lower over-potential. However, our previous understanding on such advantage is based on the nanowire array samples, and the inhomogeneity present in array samples can’t provide us quantitative information. Here, owing to the high-sensitivity photocurrent measurement and the well-defined geometry of a single nanowire, the photo-generated electron flux through the nanowire’s entire surface (\( Flux_{wire} \)) was quantified. Because of the nanowire’s large surface area, \( Flux_{wire} \) was much reduced compared to a planar analogue. In order to quantitatively evaluate how the large surface area functions to dilute the electron flux, the roughness factor of a single nanowire (\( \gamma_{rough} \)) is introduced in the following equation. Here the nanowire is considered as a cylinder whose length and diameter are \( L \) and \( D \), respectively.

\[
\gamma_{rough} = \frac{\text{actual surface area of a single nanowire}}{\text{cross section area of a single nanowire}} = \frac{4L}{D} + 1
\]

Subsequently, as shown in the following equation, \( Flux_{wire} \) can be correlated with \( Flux_{geo} \), which is the photo-generated electron flux normalized to the geometric cross-sectional area.

\[
Flux_{wire} = \frac{Flux_{geo}}{\gamma_{rough}}
\]
Therefore $ Flux_{wire} $ can be expressed as a function of $ L $ and $ D $, which allows for a quantitative calculation of $ Flux_{wire} $ for each single-nanowire device. For a representative device (Figure 10), $ I $ reaches a plateau of -43 pA when cathodic bias is applied. Correspondingly, $ J $ and $ Flux_{geo} $ are -22 mA/cm$^2$ and 1,350 electrons/ (nm$^2$·s), respectively (-1 mA/cm$^2$ = 62 electrons/ (nm$^2$·s)). When normalizing to the nanowire’s actual surface area, the corresponding $ Flux_{wire} $ is dramatically reduced to 13 electrons/ (nm$^2$·s), because of the large $ \gamma_{rough} $. The trend of such a reduced electron flux is elucidated when values of saturated $ Flux_{wire} $ for individual nanowires were plotted against their $ L $ and $ D $ (Figure 11a). Here we take advantage of the fact that the dimensions of each single nanowire are not only highly tunable but also can be reliably measured, in contrast to the inhomogeneity that typically occurs for ensemble devices. Ranging from 30 to 7 electrons/ (nm$^2$·s), $ Flux_{wire} $ follows a generally decreasing trend as $ L $ becomes longer or $ D $ becomes smaller. Such dependence can be clearly seen when $ Flux_{wire} $ is correlated with $ \gamma_{rough} $, which incorporates the impact of both $ L $ and $ D $ (Figure 11b). $ Flux_{wire} $ tends to decrease as $ \gamma_{rough} $ increases.
To elucidate the nanowire’s advantage, we fabricated planar $n^+p$-Si photoelectrode and subsequently carried out its PEC performance. The fabrication and measurement detailed are described as following. The $p$-Si (boron) wafers ($\rho \sim$10-30 $\Omega \cdot$ cm) were obtained from Addison Engineering, Inc. The wafer’s surface was $n^+$ doped using a method similar to that applied to the single nanowires. A silicon handle wafer was spin-coated with arsenic-containing spin-on dopant (SOD) (Filmtronics, Inc.) and baked at 150 °C for 30 minutes. Then the device wafer was placed on the SOD-coated handle wafer, and annealed (rapid thermal annealing) at 1,000 °C for 1.5 minutes in a N$_2$ atmosphere to form an $n^+$ layer at the wafer’s surface. Subsequently, the wafer was conformally coated with 5 nm of TiO$_2$ by atomic layer deposition (Picosun ALD). After that, the wafer was diced into small chips ($1\text{cm} \times 1\text{cm}$), which were subsequently sputtered with platinum as the HER catalyst. For the electrode fabrication, ohmic contact to the chip was made by rubbing Ga-In eutectic on its back side. Then the chip was fixed on Ti foil with conductive silver paint and carbon tape, resulting in good electrical connections. After that, the planar Si samples were sealed using the nail polish. PEC measurements were carried out in 0.5 M H$_2$SO$_4$ under one-sun illumination (AM 1.5G) with a 20 mV/s sweep rate (single sweep, from positive to negative). The resulting PEC characterization shows that the current density and the corresponding surface photo-generated electron flux of the planar $n^+p$-Si are -20 mA/cm$^2$ and 1,240 electrons/ (nm$^2 \cdot$ s) at 0V vs. RHE (Figure 12). As a result, compared to the photo-generated electron flux of a planar $n^+p$-Si electrode, $\text{Flux}_{\text{wire}}$ is diluted by about 100 times.
2.4.3 Over-potential estimation and quantitative understanding of the nanowire geometry’s benefits

In the PEC process, the electrocatalysts should have a certain TOF to handle the photogenerated electron flux at the surface of the photoelectrode. To reach a certain TOF for a specific electrocatalyst, an electrochemical over-potential is necessary based on the Butler-Volmer equation. Typically, a large photo-generated electron flux will require a large TOF and thus a large over-potential. Because of the well-defined nanowire geometry, $Flux_{wire}$ can be quantified precisely. Take the specific single-nanowire device mentioned in Figure 10 for example. $Flux_{wire}$ reaches 13 electrons/ (nm$^2$·s) at 0 V vs. RHE. In comparison, for the planar $n^+p$-Si, $Flux_{planar}$ is 1,240 electrons/ (nm$^2$·s) at 0 V vs. RHE. As a result, loading electrocatalysts on the Si-nanowire will lead to a lower TOF requirement and a reduced over-potential compared to loading electrocatalysts on the planar-Si. Figure 13 lists several reported typical electrocatalysts with quantitative TOF measurements, and summarizes the electrochemical over-potentials needed for these electrocatalysts to reach different TOFs. Here we assume that all the reported electrocatalysts cover the surface of semiconductor photoelectrodes, and the density of

Figure 12. The PEC characteristics of $n^+p$ planar Si. The PEC measurement was carried out in 0.5 M aqueous H$_2$SO$_4$ solution (20 mV s$^{-1}$, single sweep from positive to negative potential). Under one-sun illumination (100 mW/cm$^2$, AM 1.5G), the current density and the corresponding photogenerated electron flux are -20 mA/cm$^2$ and ~1,240 electrons/ (nm$^2$·s) at 0 V vs. RHE.
the surface catalytically active atom is $\sim 10^{15}$ atom/cm$^2$ or equivalently $\sim 10$ atom/nm$^2$ for all listed electrocatalysts. So for the single-nanowire photoelectrode, the photo-generated electron flux of 13 electrons/(nm$^2$·s) will correspond to a $1.3/n$ s$^{-1}$ TOF (n being the number of electrons for a particular catalytic reaction) requirement on the electrocatalysts. In comparison, for the planar-Si, the photo-generated electron flux of 1,240 electrons/(nm$^2$·s) will correspond to a $124/n$ s$^{-1}$ TOF requirement on the electrocatalysts. As a result, our calculation results show that the nanowire geometry can reduce the necessary over-potential by about 40 mV for platinum$^{33}$, one of the best proton reduction electrocatalysts. For more earth-abundant but less active proton reduction electrocatalysts, like the MoS$_2^{34,35}$, the nanowire geometry can reduce the over-potential by more than 100 mV, indicating a large benefit. For more complicated and sluggish reactions, like the CO$_2$ reduction$^{36}$, the reduced over-potential due to the nanowire’s large surface area can be much more significant.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Tafel slope (mV/decade)</th>
<th>$\eta$ (mV) for TOF = 1.3 s$^{-1}$</th>
<th>$\eta$ (mV) for TOF = 124 s$^{-1}$</th>
<th>$\Delta \eta$ (mV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (100)</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>34</td>
<td>6</td>
<td>45</td>
<td>39</td>
<td>33</td>
</tr>
<tr>
<td>[MoS$_2$]$^2$ nanoclusters</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>57</td>
<td>&lt; 160</td>
<td>&gt; 280</td>
<td>&gt; 120</td>
<td>34</td>
</tr>
<tr>
<td>Amorphous MoS$_2$ thin film</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>47</td>
<td>180</td>
<td>&gt; 280</td>
<td>&gt; 100</td>
<td>35</td>
</tr>
<tr>
<td>Au$_3$Cu nanoparticles</td>
<td>0.1 M KHCO$_3$</td>
<td>0.1</td>
<td>&lt; 550</td>
<td>&gt; 890</td>
<td>&gt; 340</td>
<td>36</td>
</tr>
</tbody>
</table>

**Figure 13. Over-potential calculation.** The electrochemical over-potentials are calculated and compared between loading electrocatalysts on Si-nanowire surface and planar-Si surface. The results show that the over-potential can be reduced if loading electrocatalysts on the nanowire’s surface. And this is especially significant for less active electrocatalysts.

2.5 Conclusion

Take advantage sophisticated fabrication, doping and measurement techniques, we demonstrate a single-nanowire-based photoelectrode platform that can be used to reliably probe the current-voltage (I-V) characteristics of individual nanowires. In terms of the photovoltage, we discovered that there is a broad photovoltage distribution among individual nanowires, even if these single-nanowire devices underwent the same growth and doping process. Furthermore, we found that the $V_{oc}$ of the array device is comparable with that of the single nanowire with the lowest photovoltage output, and this observation applied to both $p$-Si and $n^{+}$ $p$-Si devices. These results suggest that the photovoltage of the ensemble array photoelectrode is largely affected by the worst-performing individual nanowire, and this conclusion is further supported by our calculation based on an equivalent circuit model. Since the single nanowires and the nanowire arrays studied in this work have similar physical dimensions and go through the same doping process, such observed individual variance should be related to the heterogeneity of the material quality.
introduced during either the VLS growth or the fabrication process, or both. As a result, our report emphasizes the importance of controlling material quality not only in the averaged value but also the sample homogeneity, in order to produce efficient nanowire-based solar-to-fuel devices. Moreover, this platform allows the flux of photo-generated electrons to be quantified as a function of the lengths and diameters of individual nanowires, and the flux over the entire nanowire surface (7-30 electrons/ (nm$^2$∙s)) is found to be significantly reduced as compared to that of a planar analogue (~1,200 electrons/ (nm$^2$∙s)). The characterization of $Flux_{wire}$ provides quantitative insight into the nanowire geometry’s benefits in photoelectrochemistry. In principle, the loaded electrocatalyst should have a sufficiently high TOF to handle the photo-generated electron flux. As a result, the much reduced $Flux_{wire}$ (7-30 electrons/ (nm$^2$∙s) under 1 Sun illumination measured in this study, compared to typical ~1,200 electrons/ (nm$^2$∙s) for a planar photoelectrode) can significantly alleviate the requirement on the TOFs of loaded electrocatalysts and consequently reduce the necessary over-potential as compared with a planar counterpart. This is especially critical for more complicated and sluggish electrochemical reactions such as CO$_2$ reduction$^{37,38}$, where the electrocatalyst typically needs a large over-potential to reach an appreciable TOF$^{39-41}$. In addition, the systematic trend of $Flux_{wire}$ introduces the possibility to design specific nanowire geometries to match the activities of different loaded electrocatalysts in different PEC reactions. This single-nanowire photoelectrode represents a model system that can be used to study and design nanowire photoelectrodes for next-generation solar-to-fuel conversion devices.
2.6 References


Chapter 3

Approaches to improving the energy conversion efficiency of Si nanowire photocathode

3.1 Introduction

In natural photosynthesis the energy of absorbed sunlight produces carriers that operate different chemical reactions in separate regions of chloroplast. The electrons used to produce NADPH are excited via the “Z-scheme” of light absorbing photosystems I and II\(^1,2\). The energy of the photo-excited charge carriers is subsequently utilized to overcome the thermodynamic barrier and kinetic over-potential needed to drive the photosynthetic reactions. In contrast to the excitation of a single light absorber, excitation of the two light absorbers, or a “Z-scheme” system, allows capture of lower energy photons and thus a larger part of the solar spectrum, which can potentially result in high energy-conversion efficiency\(^3,4\). Such “Z-scheme” concept also can be applied to artificial photosynthesis, where two semiconductor materials harness different portion of solar spectrum to drive the overall electrochemical reaction. Within such a process, one semiconductor acts as a photocathode for reduction reactions, while the other works as a photoanode for water oxidation reaction. Upon exposure to sunlight, the minority carrier in the two semiconductor electrodes will move to the electrolyte and carry out electrochemical reactions facilitated by electrocatalysts, while majority carriers recombine at the interface between photocathode and photoanode. The flexibility of material choices, along with the use of visible wavelength for light absorption, makes such “Z-scheme” system one of the most promising approaches for solar-to-fuel conversion application\(^5,6\).

Among all the candidates for photocathode material, Si is considered a promising one\(^7-13\). Si is earth-abundant and relatively cathodically stable, thus potentially can be scaled up for sustainable solar-to-fuel applications. In addition, Si has a suitable bandgap for visible light absorption, and in principle can produce a significant portion of the total photovoltage needed for the overall reaction\(^5,7\). Furthermore, Si also possesses a proper conduction band edge to carry out different reduction reactions including HER and CO\(_2\) reduction\(^14\). Compared with the bulk Si, Si nanowires have attracted a lot of attentions for the solar-to-fuel applications because of several reasons. First, the nanowire geometry induces the light trapping effect and potentially can enhance the light absorption efficiency\(^15, 16\). Second, the use of nanowire arrays allows orthogonalization of light absorption and minority carrier collection, alleviating the high requirement on the material quality and minority carrier diffusion length\(^7,13\). Third, the nanowire geometry
provides a larger surface area and allows for more catalyst loading, leading to a reduced electrochemical over-potential\textsuperscript{6, 17-20}. Notably, a lot of efforts have been focused on developing efficient Si nanowire photocathode for different reactions such as HER and CO\textsubscript{2} reduction. However, the energy-conversion efficiency of Si nanowire photocathode is still far from satisfaction. The low efficiency can be attributed to several aspects, such as the surface recombination\textsuperscript{21}, the poor material quality\textsuperscript{22} and the sluggish electron transportation at the semiconductor/electrolyte interface\textsuperscript{14}. This chapter will cover the approaches that we have been using in the past few years to improving the energy-conversion efficiency of Si nanowire photocathode. These approaches include light management, improving material quality and precisely-controlled \textit{in-situ} boron doping method.

### 3.2 Understanding and improving the light absorption of Si nanowire photocathode through the wavelength dependent photocurrent measurement

#### 3.2.1 The importance of studying the light absorption of a single-nanowire photoelectrode

Efficient light management is crucial for achieving desirable energy conversion efficiency in light harvesting process. One of the strategies to enhance the light absorption and simultaneously reduce the material cost is to use the nanostructured semiconductors\textsuperscript{23}. As one of the well-defined nanostructures, nanowires have demonstrated unique optical properties, such as the light trapping effect and the resonant absorption. Although a lot of work has been reported to study the light scattering and trapping effect of the nanowire arrays\textsuperscript{24-27}, the inhomogeneity typically present within the arrays convolutes our basic understanding on the resonant absorption of individual nanowires, considering such resonant effect is highly dependent on the nanowire’s size\textsuperscript{23, 28}. Taking advantage of the well-defined dimensions, single-nanowire device represents a unique platform to study the fundamental phenomenon at the nanoscopic level and correlate the experimental observations with the specific properties of individual nanowires. Indeed, some pioneer work has studied the single-nanowire devices for photovoltaic and photodetectors, and characterized the optical resonances that can increase the nanowire’s absorption at various wavelengths\textsuperscript{29-32}. However, to date most of the work reported the nanowire devices lying on the substrate, and few work investigated the resonant absorption of a standing single-nanowire device. Compared with the device lying on the substrate, the standing single-nanowire theoretically may yield more enhanced absorption efficiency\textsuperscript{32} and thus can be scientifically significant. In this work, we fabricated the standing single-Si-nanowire photoelectrode and reliable probed the wavelength-dependent photocurrent with pA sensitivity. The calculated external quantum efficiency (EQE) spectra exhibited distinguished peaks and is highly dependent on the
nanowire’s diameters, which is consistent with the wave-guiding theory established by previous work. As the nanowire’s diameter decreases, the peak EQE can reach as large as 1.5, even if the Si nanowire’s length is only nine microns. Such experimentally observed resonant modes also match well with the three-dimensional finite-different time domain (FDTD) simulation results. In addition, it was found that thinner nanowires yield larger photocurrent compared with thicker nanowires, after integrating the incident photon conversion efficiency (IPCE) with the solar spectrum. The demonstrated ability to modulate the absorption by changing the nanowire diameter represents a new consideration for designing the future nanowire photoelectrodes.

3.2.2 Experiment setup and procedure

The device fabrication procedure is similar to that described in Chapter 2. Initially, the heavily doped (ρ of 0.01-0.05 Ω cm) p-type (boron) SOI wafers with 3 μm device layer oriented <111> and 2 μm buried oxide layer were obtained from WRS Materials. The device layer was first thinned down to 1.5 μm by thermal oxidation and subsequent etching in BHF. Then the device layer was further doped with boron (Techneglas GS-139) at 1,050 ºC for 10 hours, followed by a second thermal oxidation and BHF etching. The
The comparison of EQE among planar Si, Si nanowire array sample and single-nanowire device

resulting device layer was ~1 μm thick with a resistivity < 0.002 Ω cm. The Si electrodes were patterned by photolithography and anisotropic plasma etching (Surface Technology Systems), and then thermally oxidized to form a 300 nm thick oxide. With an oxide layer underneath, the patterned Si electrodes are electrically isolated from each other, enabling the characterization of each nanowire individually. The bonding pads were defined by photolithography and anisotropic plasma etching of the oxide (Plasma-Therm PK-12 RIE). The catalysts for VLS growth were defined by photolithography, anisotropic plasma etching of the oxide, and subsequent electron-beam evaporation of gold (150 nm). The isolated Si nanowires were grown at 875 ºC for 10-15 minutes with SiCl₄ as the precursor and 10% hydrogen in argon as the reducing agent. The VLS growth allowed control over the nanowire’s dimensions especially diameter, which facilitated studying the influence of the nanowire’s geometry on the resonant absorption. The as-grown single Si nanowires were 15 μm long and 500-800 nm in diameter.

The as-grown nanowires subsequently underwent a careful doping process, yielding an $n^+p$ buried junction in each single nanowire. The detailed doping process is elaborated as following. The as-grown isolated Si nanowires were etched in BHF for 30 seconds and subsequently soaked in gold etchant (Transene) for 30 minutes. Then the nanowires were thermally oxidized at 1,000 ºC for 1 hour, followed by etching in BHF. The boron doping process was split into two parts. First, boron was pre-deposited at the nanowire surface at 750 ºC for 1 hour, with 1% BCl₃ in argon as the precursor and 10% hydrogen in argon as
Figure 3. The normalized EQE obtained from experiments and numerical FDTD simulations of (a) a 560 nm-diameter device and (b) a 370 nm-diameter device.
Corp.) was coupled to a monochromator (Newport Corp.) to obtain monochromatic illumination (Figure 1). A mirror and a lens are also precisely positioned along the illumination direction in order to obtain strong light intensity and thus high signal-to-noise ratio. The output of the source was measured using a Si photodiode reference referenced to a calibrated Si photodiode (Newport Corp.). To achieve the greatest precision between measurements, devices were positioned using a micrometer driven translation probe station. The potential of the single-nanowire device is set to be negative enough (-1.8 V vs. Pt counter electrode) to achieve an incident-photon-limited PEC process. The photocurrent measurement was carried out with a Keithley 2636 source-measure unit (SMU). The open-circuit instrumental noise current level is less than 0.5 pA. The current density and absolute EQE are calculated based on the measured saturated photocurrent and the cross-section area of the Si nanowires, which was measured by the SEM. The simulations were carried out using the commercial FDTD software package. In the simulation, the cross-section of the nanowire is estimated to be a circle to reflect the experimental structures. The optical properties of Si and water are obtained from the FDTD software. In the simulation, the absorption efficiency is defined as the ratio of absorption area to the physical cross-section area. The simulated EQE is calculated by multiplying the absorption efficiency by the internal quantum efficiency (IQE), where IQE is assumed to be unity in the simulation.

3.2.3 The incident photon-to-current efficiency (IPCE) of single-nanowire photoelectrodes

Thanks to the above mentioned fabrication and measurement techniques, for the first time the wavelength dependent EQE was obtained from a vertical single-nanowire photoelectrode. A curve of the absolute EQE spectrum acquired for a representative single-nanowire device is compared with that of a nanowire array sample and a planar Si sample (Figure 2). The EQE spectrum of single-nanowire device shows apparent absorption peaks at specific wavelengths, presumably because of the resonant absorption modes. Such absorption peaks are not observed in the EQE spectrum of the nanowire array sample, which is consistent with the previous reports. Such featureless EQE spectrum of nanowire array is owing to the broadened and merged resonant peaks resulting from the inhomogeneity of dimensions among individual nanowires in the array. At shorter wavelength, the EQE of the representative single nanowire is larger than unity because of the optical antenna effect, where the absorption area is larger than the physical cross-section area. However, at longer wavelength where the extinction coefficient is low for Si, the absorption and thus EQE are limited by the finite length of the single nanowire (~ 9 μm). For planar Si, the thickness can be considered infinite, leading to a larger EQE at longer wavelength than the single-nanowire device. In addition, the EQE of nanowire array sample is comparable with that of the single-nanowire device at longer wavelength, even if the nanowire array’s packing fraction is only 10%. Such observation
can be explained by the strong light trapping effect in the nanowire array at longer wavelength.

To further understand the absorption peaks in EQE spectrum of single nanowire, we carried out the FDTD simulation. The simulated EQE is normalized and compared with the experimental EQE of single-nanowire device (Figure 3). Several important points are observed. First, for both 560-nm diameter and 370-nm diameter device, the simulation results agree well with the experimental EQE in terms of the peak position and the relative peak intensity. From the analysis of the simulation, such absorption peaks can be assigned to the previous reported leaky waveguide mode. Second, the number of peaks increases as the nanowire’s diameter increases, indicating that larger diameter nanowire can support more absorption modes. Third, in the experimental EQE spectrum, the resonant peaks tend to merge together and don’t separate distinguishably as the simulated EQE spectrum, in particular at shorter wavelength region. Such significant merge of peaks can be attributed to the broad spectral bandwidth of our monochromator as well as the tapering structure of the single-nanowire device.

To further investigate the EQE’s dependence on the nanowire size, particularly the diameter, we carried out the IPCE measurement on the nanowires with different geometries. The EQE spectrums of four representative devices with different diameters are compared in Figure 4a. As the nanowire diameter decreases, the absolute EQE increases significantly, especially at shorter wavelength. For the 370 nm-diameter single-nanowire device, the peaking EQE can reach 1.5. Such phenomenon is owing to the increasing ratio of the absorption cross section to the physical cross section as the diameter decreases to subwavelength region. When the diameter increases to a 800 nm, the EQE spectrum of the single nanowire is similar to the planar device, which suggests that the resonance enhancement is much weaker compared to the thinner nanowire. In
addition, for nanowires with different diameters, the position of the peaks shift correspondingly particularly at longer wavelength. Such position shift is consistent with the simulation based on the leaky waveguide mode\textsuperscript{33}.

Furthermore, we integrate the EQE over the solar spectrum, and calculate the photocurrent density under sunlight for nanowires with different diameters. Compared with the planar counterpart, the photocurrent density enhancement is obtained for nanowires with different diameters (Figure 4b). The photocurrent enhancement percentage would follow the general increasing trend as the nanowire diameter decreases. And this is consistent with the previous study on the horizontal nanowires\textsuperscript{23}. Though experiments on the even thinner nanowires (diameter < 200 nm) need to be further carried out, such already existing trend provides important information for the geometry design of nanowire-based photoelectrode. Previous works claim both the benefits and loss resulting from the large aspect ratio of semiconductor nanowire photoelectrode. Generally speaking, the large aspect ratio can decrease the overpotential, but at the same time would reduce the photovoltage because of the strong charge recombination at the surface\textsuperscript{21}. Our study here provides another important evidence of the thinner nanowire’s advantage, and potential can be a guidance for designing more efficient nanowire photoelectrode.

3.3 Improving the energy conversion efficiency of Si nanowire photocathode by optimizing the material’s quality

3.3.1 Improve the material quality during the VLS growth

Since R. S. Wagner introduced the concept of VLS growth in 1964\textsuperscript{34}, it has been the most widely used method to synthesize the bottom-up semiconductor nanowires on the substrates, because of its simplicity and versatility. With the capability to control the semiconductor nanowire’s morphology, size, composition and doping\textsuperscript{35}, the VLS growth has opened up substantial opportunities in several research fields, such as photovoltaic, electronics and artificial photosynthesis\textsuperscript{22, 28, 30}. As one of the most important semiconductor materials, Si nanowire synthesized by VLS method especially attracts a lot of research interest. Typically, metal nanoparticles, particularly Au nanoparticles act as the catalyst during the VLS growth of Si nanowire. Specifically, during the VLS growth, the Au particle forms a liquid metal-semiconductor eutectic alloy at an elevated temperature by absorbing the vapor reactant such as SiCl\textsubscript{4}. Continuous incorporation of the Si Vapor reactant in the Au-Si alloy through the vapor-liquid interface eventually leads to the supersaturation of the Si material. It then drives the precipitation of Si at the liquid-solid interface, to form the one-dimension Si nanowire on the substrate\textsuperscript{36}. 
Figure. 5. The Cu-catalyzed VLS growth of Si nanowire arrays (a) before and (b) after the Cu removal. The scale bar is 1 μm.

However, the Au atoms tend to be incorporated into the nanowires during the VLS growth, which has been evidenced by TEM and atomic-probe techniques. Such Au contamination is known to introduce deep level trap states and can act as a recombination center in Si. And the incorporated Au atoms have demonstrated to be deleterious for Si nanowires’ performance, particularly in photovoltaic and PEC applications. As a result, people have proposed to use other metal seeds, such as Cu and Ti, for the VLS Si nanowire growth to get better material quality.

Here, we seek to use Cu to replace Au to synthesize Si nanowire arrays with better PEC performance. The method for growing the Cu-catalyzed VLS Si nanowire is similar to that of the Au-catalyzed samples mentioned in chapter 2. In detail, the p-Si (boron) wafers (ρ ~1.7-2.8 Ω. cm) were obtained from Addison Engineering, Inc. The wafers were thermally oxidized at 1,050 ºC for 8 hours to form a SiO₂ layer with a thickness of ~350 nm. The catalysts for vapor-liquid-solid growth were defined by photolithography, anisotropic plasma etching of the oxide, and subsequent electron-beam evaporation of Cu (150 nm). The Si nanowire arrays were grown at 905 ºC for ~40 minutes with SiCl₄ as the precursor and 10% hydrogen in argon as the reducing agent. The resulting Si nanowires are ~15 μm long and ~700 nm thick (Figure. 5a). The as-grown Si nanowire arrays were etched in BHF for 30 seconds and subsequently soaked in copper etchant for 30 minutes at 75 ºC. Then the nanowire arrays were thermally oxidized at 1,000 ºC for 1 hour, followed by etching in BHF for 3 minutes (Figure 5b). These silicon nanowire array samples went through the same boron doping process as used with the Au-catalyzed samples, as follows. First, boron was pre-deposited at the nanowire surface at 750 ºC for 1 hour, with 1% BCl₃ in argon as the precursor and 10% hydrogen in argon as the reducing agent. Second, the boron atoms at the nanowire’s surface were driven into the nanowire at 1,000 ºC for 5 hours in vacuum, followed by an hour’s thermal oxidation at 950 ºC. After the boron doping, the nanowire arrays were n⁺ doped for form an n⁺p buried junction. A silicon handle wafer was spin-coated with arsenic-containing spin-on
Figure 6. a, Comparison of PEC performance between Au-catalyzed and Cu-catalyzed VLS Si nanowire array samples. b, J-V characteristics of Si nanowire photocathode and BiVO$_4$ photoanode shows that the overall current density can reach 1.9 mA/cm$^2$ if linking these two materials to form a Z-scheme tandem system.

dopant (SOD) (Filmtronics, Inc.) and baked at 150 °C for 30 minutes. After the thermal oxide was etched in BHF solution, the device chip was placed on the SOD-coated handle wafer, and annealed (rapid thermal annealing) at 900 °C for 3-4 minutes in a N$_2$ atmosphere to form an $n^+$ layer at the nanowires’ surface. Then the device chip was soaked in BHF solution for 30 seconds to remove the thin oxide formed during the $n^+$ doping process. Subsequently, the $n^+p$-Si nanowire array device was coated with 5 nm of TiO$_2$ by atomic layer deposition (Picosun ALD). After that the nanowire array devices were sputtered with platinum as the HER catalyst. For the electrode fabrication, ohmic contact to the device chip was made by rubbing Ga-In eutectic on its back side. Then the chip was fixed on Ti foil with conductive silver paint and carbon tape, resulting in good electrical connections. After that, the Si nanowire array samples were sealed using the nail polish. PEC measurements were carried out in 0.5 M H$_2$SO$_4$ under one-sun illumination (AM 1.5G, 100 mW/cm$^2$) with a 20 mV/s sweep rate (single sweep, from positive to negative).

The PEC performance of Cu-catalyzed VLS Si nanowire array sample is compared with that of the Au-catalyzed sample (Figure 6a). The Cu-catalyzed sample significantly outperforms the Au-catalyzed one, in terms of the onset potential, fill factor and energy conversion efficiency. Specifically, the Au-catalyzed sample exhibits onset potential = 0.32 V vs. RHE, fill factor = 10% and energy conversion efficiency = 0.39%. In contrast, the Cu-catalyzed sample exhibits onset potential = 0.55, fill factor = 53% and energy conversion efficiency = 2.3%. Because both samples underwent the same doping process, such remarkably different PEC performance is owing to the difference of intrinsic material quality originating from the VLS growth. And such decent PEC performance of Cu-catalyzed sample demonstrates that Cu contamination doesn’t impair the quality of Si.
nanowire, in contrast with the Au contamination. Such high-performance, Cu-catalyzed Si nanowire photocathode, in principle, can play an important role in the Z-scheme tandem system. Assuming that such Si nanowire photocathode is linked with the BiVO_4 which is a promising photoanode material, unassisted solar water splitting can be realized without adding external bias (figure 6b). Provided that the voltage loss at the Si/BiVO_4 interface is negligible, the overall photocurrent density and energy conversion efficiency theoretically can reach 1.9 mA/cm\(^2\) and 1.2%, respectively. The 1.2% solar-to-fuel conversion efficiency, if can be realized, is the record efficiency for Z-scheme PEC system\(^{39}\). Though such efficiency is lower than then photovoltaic-electrolyzer system (~10%), the Z-scheme PEC system indeed represents a cost-effective approach. As a result, we show that the readily-grown, Cu-catalyzed VLS Si nanowire photocathode can be a promising candidate for Z-scheme solar-to-fuel applications. In addition, we also demonstrate that the metal contamination during the semiconductor material synthesis can impact the material quality significantly and thus needs to be paid more attention, especially in the field of artificial photosynthesis.

3.3.2 Commercialized chemical vapor deposition (CVD) for scale-up production of Si nanowire photocathode

Given the growing importance of nanomaterials especially in semiconductor industry, the uniform growth of single-crystal high-quality nanomaterials over wafer-scale areas has attracted a lot of research interests. Taking advantage of the CVD method, recently people realized the wafer-scale growth of monolayer graphene\(^{40}\) and Si microwires\(^{41}\), both of which can be flexibly transferred to other substrates for various applications. As one of the most widely-used and intensively-studied one-dimensional nanomaterials, Si nanowires potentially have a lot of applications including photovoltaic, artificial photosynthesis, field effect transistor and bioelectronics. However, the wafer-scale growth of high-quality Si nanowires has never been realized. Here, we report using a commercial CVD system (Figure 7a), it is feasible to accomplish uniform growth of Si nanowire arrays over a 3-inch wafer area. Such large-area Si nanowires open up opportunities for scale-up solar-to-fuel conversion applications.
Figure 7. a, the commercial CVD system. b, a photo of the as-grown VLS Si nanowire arrays on a 3-inch substrate. c, the SEM images of Cu-catalyzed VLS Si nanowire arrays. d, close-up SEM image shows the Cu catalyst at the nanowire’s tip. The scale bars in c and d are 10 µm and 1 µm, respectively.

The substrate fabrication and nanowire growth procedure are similar to the previously mentioned methods. Specifically, the p-Si (boron) wafers (ρ ~1.7-2.8 Ω cm) were obtained from Addison Engineering, Inc. The wafers were thermally oxidized at 1,050 ºC for 8 hours to form a SiO₂ layer with a thickness of ~350 nm. The catalysts for VLS growth were defined by photolithography, anisotropic plasma etching of the oxide, and subsequent electron-beam evaporation of Cu (150 nm). After that, the wafer is diced into 3×3 inch² size that can be accommodated into the CVD chamber. The Si nanowire arrays were grown on such prepared substrate at 905 ºC for 2 hours, with SiCl₄ as the precursor and 10% hydrogen in argon as the reducing agent. The as-grown 3-inch substrate appears black (Figure 7b), suggesting the reduced reflection owing to the light trapping effect of the grown Si nanowire arrays. The Cu-catalyzed VLS Si nanowire arrays are well arranged with a ~2 µm pitch, resulting in a ~10 packing fraction (Figure 7c). The zoom-in image shows that the Cu particles sit on top of the Si nanowires (Figure 7d).

In addition to the wafer-scale growth, this commercial CVD is capable of in-situ doping the Si nanowires with boron. Specifically, the CVD is equipped with a diluted BCl₃ gas
delivery system, which can provide BCl$_3$ with precisely controlled flow rate. With hydrogen as the reducing agent, BCl$_3$ is reduced into boron atoms, which will *in-situ* dope the Si nanowires during the VLS growth. Compared to the *ex-situ* doping method mentioned in chapter 2, such *in-situ* doping represents a more flexible and convenient approach, and at the same time ensures relatively homogeneous dopant distribution along the nanowire radial direction$^{42}$. In order to test the effect of the *in-situ* boron doping, we carried out the PEC measurements on both doped sample and undoped sample (Figure 8a). The doped sample exhibits onset potential = 0.34 V vs. RHE, fill factor = 30% and energy conversion efficiency = 1.15%. On the other hand, the undoped sample exhibits onset potential = 0.3, fill factor = 11% and energy conversion efficiency = 0.16%. The more positive onset potential of the doped sample suggests that the boron doping increases the degree of band bending and thus the quasi fermi level splitting under illumination. The superior energy conversion efficiency and fill factor of the doped sample is attributed to the more efficient carrier separation, which is consistent with the previous study on gallium phosphide nanowire photocathode$^{43}$. The effect of boron doping is further evidenced by the Mott-Schottky characteristic (figure 8b), which shows that the carrier concentration is larger in the doped sample. Though the performance of such *in-situ* doped sample is still far from satisfaction, we believe that it can be further improved by systematically tuning the BCl$_3$ flow rate. Our CVD system opens up the opportunities to synthesize the efficient large-area Si nanowire photocathode for scale-up solar-to-fuel applications.

Figure 8. a, PEC performances of Si nanowire photocathode samples with and without *in-situ* Boron doping. b, Mott-schottky plot of Boron-doped sample and undoped sample.
3.4 Conclusion

In this chapter, we show three different methods for improving the PEC performance of Si nanowire photocathode. First, we demonstrate the resonant absorption effect of Si nanowire photoelectrode. Strongly dependent on the nanowire’s diameter, such resonant effect provides guidance to design proper nanowire geometry for maximized light absorption. Second, we try to use Cu to replace Au for the VLS Si nanowire growth. It demonstrates that Cu-catalyzed VLS Si nanowire photocathode outperforms the Au-catalyzed counterpart. Such result highlights the importance of improving the material’s quality, especially avoiding the metal contamination, to realize efficient solar-to-fuel conversion. Third, we use a commercial CVD system for wafer-scale Si nanowire growth. Attributed to the capability of precisely-controlled \textit{in-situ} boron doping, the CVD yields Si nanowire arrays with decent PEC performance. Our approach opens up the opportunities for scale-up production of high-quality Si nanowire photocathode for future solar-to-fuel conversion applications.

3.5 References


Chapter 4

New insights into the electron transfer mechanism in S. Ovata/Si nanowire hybrids: A study by Tafel plot and impedance spectroscopy

4.1 The importance for studying the charge transfer process at the electrode/microorganism interface

The direct conversion of sunlight into energy stored in chemical bonds, termed as artificial photosynthesis\(^1\)\(^-\)\(^4\), mimics the natural photosynthesis process occurring in plants\(^5\). The overall process consists of two parts: light absorption and generation of excited charge carriers, and the utilization of photo-excited carriers to drive catalytic reactions. The former process typically uses semiconductors to absorb photons and generate carriers, which are subsequently separated at either a semiconductor/electrolyte interface\(^6\),\(^7\) or an embedded solid junction\(^8\),\(^9\). The photo-generated carriers subsequently move to a catalytic center to drive oxidation/reduction reactions in the solution. Therefore, artificial photosynthesis is an integrated system that combines multiple different processes\(^10\). For efficient solar-to-fuel conversion it is important to have robust light-capture materials, efficient electrochemical catalysts and an efficient interface between these two for swift charge transfer.

One of the major challenges in the field of the artificial photosynthesis is the catalyst for CO\(_2\) reduction and its integration into a functional artificial photosynthetic system\(^11\). Because the electrochemical CO\(_2\) reduction itself is much more complex than the related hydrogen evolution reaction (HER)\(^12\) and oxygen evolution reaction (OER)\(^13\) to date the synthetic CO\(_2\) reduction catalyst suffers several limitations\(^14\),\(^15\). First, as multiple electron and proton coupling steps are typically involved in several different reaction pathways, electrochemical CO\(_2\) reduction typically produces several possible final products, leading to a low selectivity and Faraday efficiency\(^16\)\(^-\)\(^20\). Second, most of the synthetic materials studied as CO\(_2\) reduction catalysts to date require large over-potentials and typically are also active for HER, which results in low turnover rates (TOR) to CO\(_2\) reduction products at moderate over-potentials\(^16\). Furthermore, synthetic CO\(_2\) reduction catalysts always degrade slowly over time, which is not desirable for sustained production of fuels from CO\(_2\)\(^16\). On the other hand, nature has evolved over billions of years to have an arsenal of powerful enzymes to catalyze CO\(_2\) reduction to selective products\(^14\),\(^20\)\(^-\)\(^22\), under relatively low over-potential. As a consequence, interfacing these natural CO\(_2\)-reducing enzymatic
systems with semiconductor light absorbers represent a promising way to unblock the CO\textsubscript{2}-reducing bottleneck in artificial photosynthetic systems. Such a combination between biology and materials science separates the demanding dual requirements for catalytic activity and light-capturing efficiency, respectively, and provides a route to bridge the high catalytic activity of enzymes in living cells with efficient solar conversion in robust solid-state devices.

As a proof of concept, recently Yang group have demonstrated that a hybrid semiconductor nanowire-bacteria system can reduce CO\textsubscript{2} photoelectrochemically to a wide array of value-added chemicals\textsuperscript{23}. Specifically, the high-surface-area silicon nanowire array efficiently harvests light energy to provide reducing equivalents to the anaerobic bacterium, \textit{Sporomusa ovata}, for photoelectrochemical production of acetic acid under aerobic conditions (21\% O\textsubscript{2}) with low overpotential and high faraday efficiency. The resulting acetate can be activated to acetyl coenzyme by genetically engineered \textit{Escherichia coli} and used as a building block for a variety of value-added chemicals. Such results, for the first time, demonstrated the capability to interface acetogen with semiconductor photoelectrodes for solar-powered CO\textsubscript{2} reduction. However, questions still remain at both application and fundamental levels.

First, the 0.4\% solar-to-chemical efficiency of this hybrid system, despite comparable with that of the natural photosynthesis system, is still one order of magnitude lower than the desired value\textsuperscript{2}. One possible explanation for such low efficiency is that the integrated components in this PEC system don’t operate in a perfectly harmonious way so that there is bottleneck hindering the charge flux\textsuperscript{10}. In particular, if the TOF of the bacteria can’t match the electron flux over the nanowire’s surface, charge carrier wouldn’t flow swiftly through the Si nanowire-bacteria interface\textsuperscript{24}. As a result, the quantification of the TOF of bacteria at different overpotential regions is important to optimize the material design, such as the density of loaded bacteria, so as to improve the efficiency of the overall system. However, the exact TOF of bacteria is still not clear, mainly because it is difficult to \textit{in-situ} quantify the number of bacteria\textsuperscript{23}. 
Second, besides the demonstration of a photoelectrochemical CO$_2$-reduction system integrating the biocatalysts with semiconductor nanowires, fundamental questions remain regarding how the charge transfer happens between a CO$_2$-reducing microorganism and a solid-state device. In biology the charge carrier is in the form of redox molecules involving proton-couple electron transfer (PCET) reactions$^{25}$. However in solid-state physics quasi-particles with certain wavefunctions are typically considered. Such a drastic difference of how people describe a “charge” intrigues the question that in what way the “charge” is transferred through the interface, and furthermore how to describe it in both spatial and temporal dimensions. At present, two kinds of mechanisms for such electron transfer have been proposed: these are direct and indirect transfer$^{26}$. The direct electron transfer is defined as “not requiring the diffusion of a mobile component to and from the cell for electron transport”$^{27-30}$. Briefly, direct electron transfer typically involves at least a series of periplasmic and outer-membrane complexes, which are responsible for transporting electron from or to the cell. And such direct electron transfer has been widely studied in *Geobacter sulfurreducens* and *Shewanella oneidensis* str. MR-1 for the microbial fuel cell (MFC) applications$^{31}$. Different from the direct method, the
indirect electron transfer involves the production or use of the so-called electron shuttles, which transport electrons between the cells and the electrodes. Examples of electron shuttles produced as secondary metabolites by organism are phenazines and flavins. In addition, primary metabolites of bacteria such as Sulphur species and H₂, are also very important shuttles to convey electrons towards electrodes. Although these two electron transfer mechanisms have been proposed and evidenced at some point, they are both based on the MFC system, where electrons are transferred from the microbial systems to the solid-state electrodes. However, during the artificial photosynthetic process that we are interested, the electrons are typically transferred from the solid-state electrodes to the bacteria. Such opposite electron transfer pathway indicates that the information achieved from MFC may not apply here, and more systematical investigations are needed to unveil the mechanism of the electron transfer from electrodes to bacteria. Previous report has suggested that on graphite electrode acetogens (including S. ovata) require a direct physical contact for charge transfer based on the observation that there are no planktonic cells in the bulk electrolyte. However the evidence is not direct and the molecular basis for this charge transfer is not established. Recently, Yang group reported that transient absorption spectroscopy can be employed to study the semiconductor-to-bacterium electron transfer based on the reported CdS/M. thermoacetica system. It was found that the lifetime of photo-generated electrons in CdS is related to the activity of the membrane-bound hydrogenase enzyme. As the hydrogenase enzyme is more active, the lifetime of photo-generated electron is shorter. Such results suggest that the hydrogenase enzyme as well as the H₂-mediated electron transfer mechanism indeed plays an important role in this electrochemical process. However, this study didn’t provide evidence for the direct electron transfer mechanism when the hydrogenase enzyme is inactive, especially at the molecular level. In addition, it is still illusive that how these two mechanisms compete with each other at a specific condition (Figure 1). Such fundamental knowledge is crucial for engineering the interface and potentially improving the efficiency of artificial photosynthesis system. To untangle these unsolved questions, other sophisticated characterization techniques are needed.

4.2 Using Tafel plot and impedance spectroscopy to investigate the electron transfer mechanism in S. Ovata/Si nanowire hybrids

As a classical electrochemical characterization technique, Tafel plot correlates the electrochemical overpotential with the rate of the heterogeneous electron transfer, and thus sheds light on the reaction kinetics at the solid-electrolyte interface. As a consequence, Tafel plot is regarded as an important method to probe the reaction mechanism, and it has been applied to study a number of electrochemical reactions. Furthermore, Tafel plot is also employed to investigate the electron transfer kinetics in the MFC. Previous work reported that by modifying the anode in MFC, the exchange current density extracted from Tafel plot can be improved, so as the kinetics at the bi-
In addition, people used Tafel plot and relative equations to quantitatively correlate the internal resistance and power density with the surface area and conductivity of different electrodes in MFC. Such study gives insights on the different electrodes’ strength and weakness and provides guidance to optimizing the MFC efficiency. Although Tafel plot has been widely used in MFC, notably, Tafel plot has been rarely used in the field of microbial electrosynthesis, in particular bacteria-catalyzed CO₂ reduction.

Electrochemical impedance spectroscopy (EIS) is another powerful tool to characterize the dynamics and kinetics at the electrochemical interfaces. EIS is a method that allows investigating electrical signal of an electrochemical system by measuring its response in current or voltage after imposing a small AC perturbation to a stationary state and obtaining the impedance through the equation as followed.

\[ Z = \frac{dV}{dl} \]

The measurement is performed in a wide range of frequencies, which reveals different time constant related to the processes and reactions occurring at different electrochemical components. The obtained impedance spectra allow interpretation of the electrochemical characteristic of the system through the use of the appropriate equivalent circuit model. As a result, EIS is widely regarded as a sophisticated and quantitative electrochemical method to characterize the internal resistance components (Ohmic resistance, charge transfer resistance, mass transport resistance) as well as the double layer capacitance. Notably, EIS has been applied to the bioelectrochemical process, in particular MFC. Previous work has demonstrated that the charge transfer resistance as well as the biofilm capacitance of MFC system can be characterized through EIS method. Indeed, the fact that many microorganisms form biofilms on electrodes places complication of a series of distinct intracellular cell reactions, which represents a more complex system than reactions on one or more catalyst sites on a planar or porous electrode in typical fuel cells. And a simplified equivalent circuit model typically allows the reasonable mimetic expression of the real bioelectrochemical system. Although EIS has been widely applied to the anode in MFC, very few reports utilize it to study the biocathode, where the electrons are transferred from the cathode to the bacteria and carry out reducing reactions, such as CO₂ reduction.
Here we combine Tafel plot with EIS method to investigate the electron transfer mechanism at the biocathode. Tafel plot yields two different slopes at two electrochemical over-potential regions: 150 mV/decade from -0.1 V to -0.3 V (vs. RHE), and 330 mV/decade from -0.4 V to -0.8 V (vs. RHE). The Tafel slope (360 mV/decade) on abiotic condition suggests that H₂-mediated electron transfer dominates at high over-potential, while the direct electron transfer mechanism dominates at low over-potential. EIS measurement was carried out and an equivalent model was built correspondingly to mimic the electrochemical system. The quantitative data extracted from EIS measurement indicates that the charge transfer resistance is crucial for the kinetics switch. The presumably direct electron transfer is very likely due to the binding of cytochrome-c to the cathode surface at low over-potential.

Taking advantage of the large surface area, p⁺ Si nanowire arrays are used as the cathode material. And a 10 nm conformal-coated TiO₂ layer was deposited at 300°C on the Si surface by atomic layer deposition (ALD, Picosun), in order to maintain stable performance in a neutral pH electrolyte for prolonged period of time. In addition, to facilitate the electron transfer, about 10 nm Nickel (Ni) was quasi-conformal sputtered (Edwards, Inc) onto the cathode (citation). As mentioned above, the bacteria used here is S. Ovata, a kind of Acetogen that can specifically reduce CO₂ and produce acetic acid. In detail, an inoculum of S. Ovata was grown under strict anaerobic conditions in a Balch tube at 30°C. For autotrophic growth of S. Ovata, hydrogen was used as the electron source.
donor (80% \( \text{H}_2 \)& 20% \( \text{CO}_2 \)) in brackish water medium modified from the DSMZ-recommended medium. To achieve higher acetic acid concentrations, a slightly modified M9-MOPS minimal medium was used. S. Ovata was gradually adapted to growth in M9-MOPS medium before incorporated with the electrode. Incorporation of bacteria into the electrode was accomplished within the electrochemical cells using organic-free minimal medium, similar to precious report\(^{27}\). 10% inoculation was conducted in the cathode chamber of assembled electrochemical cell (Figure 2), where the cathode was constantly biased at -0.1 V vs. RHE at the initial stage. Such dispersion was cultured for 12 hours under 80%\( \text{H}_2 \)& 20%\( \text{CO}_2 \) environment, and 2/3 of the electrolyte was replaced with fresh medium. Then the culture was incubated for 24 hours under 20%\( \text{CO}_2 \)& 80%\( \text{N}_2 \) environment, and again 2/3 of the electrolyte was replaced with fresh medium. After two more cycles of this medium exchange procedure, the nanowire/bacteria hybrids could be obtained in the cathode chamber with minimal planktonic cells suspended in the bulk solution. Such nano-bio hybrids are ready for subsequent detailed characterization (Figure 3).

All electrochemical measurements were performed within a set of custom-built electrochemical cells (Figure 2). The setup is a two-chamber cell, with the working electrode and reference electrode (Ag/AgCl, 1M KCl, CH Instruments, Inc) in one chamber and a Pt wire as counter electrode in the other chamber. A Nifion 212 membrane

![Figure 3. SEM image of the Si nanowire/S. Ovata hybrids system. \( p^+ \) Si nanowire array serves as the cathode material, and S. Ovata bacteria interface with Si nanowires and catalyze the electrochemical \( \text{CO}_2 \) reduction reaction. The scale bar is 10 \( \mu \text{m} \).](image-url)
The electrochemical characterization was performed using Gamry Interface 1000 potentiostats. The reversible hydrogen electrode (RHE) potential is defined as:

\[ V \text{ vs. RHE (V)} = V \text{ vs. Ag/AgCl (V)} + 0.209 \text{ (V)} + 0.059 \times \text{pH} \]

The over-potential \( \eta \) for CO2 reduction is defined as the voltage difference between the applied electrochemical potential and the standard potential for CO2 reduction into acetic acid:

\[ \eta \text{ (V)} = V \text{ vs. RHE (V)} + 0.143 \text{ (V)} \]

Chronoamperometry was carried out to obtain the Faraday efficiency and the Tafel plot of the Si nanowire/S. Ovata hybrids system (Figure 4a). To measure the Faraday efficiency at different over-potentials, chronoamperometry runs for at least 24 hours to collect enough acetic acid products. And the Faraday efficiency is calculated based on the following equation:

\[
\text{Faraday efficiency} = \frac{96485 \times 8 \times \text{incremental mole of acetic acid}}{\int I \text{ dt}}
\]

The decent Faraday efficiency of acetic acid demonstrates that S. Ovata bacteria indeed play an important role in this electrochemical CO2-reducing process. As current becomes larger, Faraday efficiency decreases correspondingly, but the specific current of acetic acid tends to reach a plateau (Figure 4c). Given that the number of bacteria S. Ovata that

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**Figure 4.**

**a.** Tafel plot and acetic acid Faraday efficiency of Si/S. Ovata inorganic-organic hybrid system. The Tafel plot yields two distinct regions with different Tafel slopes \((n=3)\). At each over-potential, the Faraday efficiency of the produced acetic acid is also quantified. During the electrochemical measurements, the system was purged with 80% CO2 & 20% N2 mixture gas. **b.** Tafel plot comparison between biotic condition and abiotic condition with Si nanowire/Ni cathode.
are interfaced with the cathode does not fluctuate after stabilization, such result reveals that the average turnover rate of the bacteria is stable over time and is not dependent on the over-potential. Such consistent behavior of bacteria as well as the acetic acid production is largely owing to the biocompatibility of the materials used in this hybrids system, including Si nanowire, TiO$_2$ coating as well as the Ni particles$^{23,43}$.

In the Tafel plot (Figure 4a), each data point represents a stable current density at a specific electrochemical potential ($n=3$). Interestingly, we observed an apparent Tafel slope transition at about -0.35 V vs. RHE. Specifically, at lower over-potential, Tafel slope is about 150 mV/decade. In contrast, Tafel slope is about 330 mV/decade at higher over-potential, indicating a relatively sluggish kinetics. Such slope transition suggests

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**Figure 5.** EIS characterization of Si nanowire/$S. Ovata$ hybrids system. a. Nyquist plot obtained by Gamry Interface 1000 Potentiostats. b. An equivalent circuit model is built to mimic the electrochemical CO$_2$-reducing reaction. For the Faradic process, two possible pathways are proposed. c. The extracted charge transfer resistance of the two possible Faradic pathways.
that the electron transfer pathway from Si cathode to *S. Ovata* may change for different over-potential regions. In order to investigate the involvement of bacteria in such slope transition, we also characterize the Tafel plot under abiotic condition, as a control experiment (Figure 4b). Different from the biotic case, no obvious transition was detected, and the slope is about 360 mV/decade, which is similar to the Tafel slope at higher over-potential region for the biotic case. Under abiotic condition, the sputtered Ni particles work as electrocatalyst of hydrogen evolution reaction (HER), and the kinetics is dominated by the HER. As a consequence, the correspondence of the Tafel slopes indicates that for the biotic case the kinetics is governed by the HER at higher over-potential (from -0.4 V vs. RHE to -0.8 V vs. RHE), provided that the subsequent homogenous reaction happening within the bacteria (Wood-Ljungdahl pathway) doesn’t contribute significantly to the Tafel slope. Our experiment result plausibly shows that the H₂-mediated electron transfer mechanism dominates in bio-inorganic hybrids system, as the electrochemical potential becomes negative enough.

In order to uncover the kinetics transition as well as the electron transfer mechanism at lower over-potential region, we moved forward and carried out the EIS characterization on the hybrids system. The EIS measurements were performed via Gamry Interface 1000 Potentiostas, with frequency ranging from 0.1 Hz to 1000000 Hz. The resulting Nyquist plot (Figure 5a) displays that the impedance (including $Z_{\text{imaginary}}$ and $Z_{\text{real}}$) changes significantly with the applied electrochemical potential. To extract the quantitative impedance value and explain the correlation between the impedance and the applied potentials, an equivalent circuit model has been established (Figure 5b). In this model, three electron pathways are connected in parallel, and the double-layer capacitance represents the non-faradic process. For the faradic process, two branches exist in this model, corresponding to the two different electron transfer mechanisms that are demonstrated in the Tafel plot. Because one of the electron transfer pathway demonstrates to be governed by HER, the heterogeneous charge transfer resistance, catalyst resistance and catalyst capacitance of this branch are annotated with $R_{\text{ct, Ni-proton}}$, $R_{\text{Ni, HER}}$ and $C_{\text{Ni, HER}}$, respectively. For the other branch, the counterparts are annotated with $R_{\text{ct, Ni-bacteria}}$, $R_{\text{bacteria}}$, and $C_{\text{bacteria}}$, respectively. Based on this equivalent circuit model, the heterogeneous charge transfer resistance are extracted as a function of the applied electrochemical potential (Figure 5c). The two charge transfer resistances follows different trends. $R_{\text{ct, Ni-proton}}$ tends to decrease as over-potential increases, consistent with the trend for a typical HER catalyst (citation). In contrast, as over-potential becomes larger, $R_{\text{ct, Ni-bacteria}}$ first increases, reach a peak at -0.5 V vs. RHE, then decreases. Notably, at lower over-potential (-0.2 V vs. RHE to -0.4 V vs. RHE), $R_{\text{ct, Ni-bacteria}}$ is significantly smaller than $R_{\text{ct, Ni-proton}}$. While at higher over-potential (-0.4 V vs. RHE to -0.8 V vs. RHE), $R_{\text{ct, Ni-bacteria}}$ becomes larger than $R_{\text{ct, Ni-proton}}$. Provided that the heterogeneous charge transfer resistance is crucial for the kinetics at the electrode/electrolyte interface, these quantitative results obtained from the impedance spectroscopy further support that H₂-mediated mechanism dominates at higher over-potential and another mechanism dominates at lower over-potential. In addition, the electrochemical potential where the
two resistances are equal (-0.4 V vs. RHE) is consistent with the kinetics transition (-0.35 V vs. RHE) observed from the Tafel plot.

Previous work has shown that metal nanoparticles, particularly Ni particles, are capable of enhancing electrode-microbe electron exchange\textsuperscript{43, 45}. To investigate whether the specific Ni particles are responsible for the facile kinetics at lower over-potential, we fabricated Si nanowire/Pt/S. Ovata hybrids system and compare its performance with the above discussed Ni-based system. Comparison of the Tafel plot (Figure 6a) reveals that the current produced by Pt-based hybrids is much higher than that of the Ni-based system, which is presumably due to the excellent HER catalytic activity of Pt particles\textsuperscript{46}. However, the Faraday efficiency of acetic acid of Pt-based system is several folds lower than that of the Ni-based hybrids (Figure 6a), in spite of the applied electrochemical
potential. The low faraday efficiency leads to relatively low acetic acid production (figure 6c), even if the overall current of Pt-based system is high. This observation is consistent with the previous work that Pt nanoparticle can be toxic for microbe and may inhibit the proper biological metabolism. Our results highlight the importance of optimizing the biocompatibility of the electrode surface, to produce the robust bio-inorganic hybrids system for artificial photosynthesis. Most interestingly, we don’t observe the Tafel slope transition for the Pt-based hybrids, in contrast to the clear transition probed from the Ni-based hybrids system. Furthermore, by comparing the Tafel plot between biotic condition with abiotic condition for the Si nanowire/Pt cathode, we found that these two plots almost overlap with each other. Provided that Pt particles specifically catalyze the HER reaction under abiotic condition, the indistinguishable Tafel plots indicate that the H₂-mediated electron transfer mechanisms always dominate for the Si/Pt/S. *Ovata* hybrids system regardless of the applied over-potential. As a consequence, the transition of the kinetics and the electron transfer mechanism is specified for Ni-based system and not applicable generally to other noble metal particles such as Pt.

Back to early 1990s, metal ions, such as Zn²⁺, Cu²⁺ and Ni²⁺, have been intensively studied for affinitive binding with specific proteins. Similar to the classical coordination chemistry, here the metal ions serve as the coordination center and Lewis acid which accept electrons, while proteins act as the ligand and provide electrons. In particular, Ni²⁺ can form very strong binding with different kinds of proteins, especially proteins terminated with Histidine, Cysteine and Tryptophan amino acids. In our Si nanowire/Ni/S. *Ovata* hybrids system, Ni is likely to be oxidized into Ni²⁺ under neutral pH, governed by the following Nernst equation:

\[
\text{Ni(OH)}_2 + 2e^- = \text{Ni} + 2\text{OH}^- \quad \text{E} = -0.3 \text{ V vs. RHE, when pH = 7}
\]
Figure 7. Schematic illustration of the proposed Ni(OH)$_2$-induced direct electron transfer mechanism. The three kinds of protein complexes (MtrA, MtrB and MtrC) cross the bacteria membrane and bind with Ni(OH)$_2$. The electrons transfer directly from Si to the intracellular environment through the Ni(OH)$_2$-protein channel.

As a consequence, when the electrochemical potential is more positive than -0.3V vs. RHE, the Ni species at the surface of the Ni particles exist in the form of Ni(OH)$_2$, which allows for the specific binding of protein. Because the required electrochemical potential to form Ni(OH)$_2$ (-0.3 V vs. RHE) is consistent with the kinetics transition in Tafel plot and EIS measurement, Ni(OH)$_2$ is arguably responsible for the facile kinetics at low over-potential. Therefore, here we propose a direct electron transfer mechanism for our Si/Ni/S. Ovata hybrids system (Figure 7). In the proposed model, Ni(OH)$_2$ would bind with the protein complexes on the membrane of S. Ovata bacteria. These protein complexes, such as cytochromes, have been well studied and proposed to be responsible for transporting electrons from/to the bacteria. As a result, the electrons can transfer direct from the Si
nanowire cathode to the intracellular environment via the Ni-protein channel, without H₂ as the electron shuttle. In such process, the Ni species work as a conductive channel instead of a modest HER catalyst. In addition, the diffusion limitations of H₂ and proton are also circumvented, leading to a facile kinetics.

4.3 Conclusion

With Si nanowire/Ni/S. Ovata hybrids as a model system, we use Tafel plot and EIS method to investigate the cathodic electron transfer mechanism in the bacteria-catalyzing CO₂-reducing process. The Tafel plot on biotic condition yields fast kinetics (low Tafel slope) at lower over-potential region and slow kinetics (high Tafel slope) at higher over-potential region. The Tafel slope on abiotic condition is similar to that of high over-potential region on biotic condition, which suggests that H₂-mediated electron transfer dominates at this region. The charge transfer resistance extracted from the EIS measurement is consistent with the information obtained from the Tafel plot, and further support that the kinetics and thus the electron transfer mechanism would switch at about -0.35 V vs. RHE. The comparison between Ni-based hybrids and Pt-based hybrids system indicate that Ni plays an important role in such kinetics transition. Through the calculation via the Nernst equation, we found that Ni species is oxidized into Ni(OH)₂ at -0.3 V vs. RHE. The Ni(OH)₂ species are proposed here to bind with the conductive protein complexes on the membrane of S. Ovata bacteria. Such binding would induce the direct electron transfer from Si cathode to the intracellular environment and thus facilitate the kinetics. Our results provide the guidance to design the efficient bio-inorganic interface in the field of microbial electrosynthesis and artificial photosynthesis.

4.4 References


Appendix

List of publications

(† Authors contributed equally)


