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Nanowire-based Integration for Artificial Photosynthesis

By

Chong Liu

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

Committee in charge:

Professor Peidong Yang, Chair Professor Gabor Somorjai Professor Junqiao Wu

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by

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Abstract

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Professor Peidong Yang, Chair

Artificial photosynthesis, the biomimetic approach to converting sunlight's energy directly into chemical fuels, offers an attractive way to address the need for a clean, renewable source of energy. In plants, chloroplasts store the sun's energy using a system of integrated photosynthetic nanostructures including light-absorbing pigments, electron-transport chains, and chemical catalysts. However, neither such integration of nanostructures nor energy conversion efficiency suitable for practical applications has been achieved in artificial photosynthesis. In this context, the subject of my graduate research is to develop an integrated system using nanowire-based nanostructures to imitate natural photosynthesis. This centers on two themes: (1) constructing novel integrated nanostructures for solar-to-fuel conversion, and (2) developing next-generation materials and catalysts for improved photoelectrochemical (PEC) performance.

Although natural photosynthesis organizes its active components at the nanometer scale to better control the process of energy conversion, this level of integration had not been realized until recently for artificial photosynthesis. Here the construction of a nanowire-based integrated system to realize such a nanoscopic control is demonstrated.

Since all of the processes in PEC relate to the interfaces among semiconductor light-absorbers, electrocatalysts, and the electrolyte, the first to realize an integrated nanosystem was to under how photo-excited carriers would transfer within these interfaces. By using kelvin probe force microscopy (KPFM), the local electrostatic potential of an asymmetric nanowire composed of Si and a TiO_2 shell, which was covered in a layer of water. Different local potentials were observed in dark and under illumination, which provides the knowledge that the heterojunction of Si and TiO_2 could function as a Z-scheme system for solar water splitting.

After obtaining this piece of information, we moved forward to develop an integrated nanosystem for artificial photosynthesis. Taking the concept of Z-scheme, we used Si and TiO₂ nanowires as building blocks to construct a tree-shaped heterostructure. In this structure, the positions of the reduction and oxidation components were predefined to mimic the spatial control found in chloroplasts. The integrated standalone device splits H_2O into H_2 and O_2 under simulated sunlight, with an efficiency of solar-to-fuel conversion comparable to that of natural photosynthesis. This first demonstration

paves the way for using nano-sized building blocks to achieve efficient solar-to-fuel conversion.

The nanowire-based integration allows individual building blocks to be replaced with newly developed ones. In this dissertation advanced building blocks for artificial photosynthesis is also demonstrated.

We have explored new materials and methods to improve the energy conversion efficiency of semiconductor light-absorbers. Solution-phase synthesis of III-V semiconductor nanowires was successfully demonstrated for photocatalytic reactions, and the nanowires' electronic properties could be fine-tuned to fit the needs of device integration. Also we demonstrated enhancement of the photoanodic activity of hematite (Fe_2O_3) using the surface plasmon resonance of exquisitely controlled Au nanostructures.

Additionally, new electrocatalysts suitable for practical applications are developed. We first looked into the lower limit of platinum (Pt) loading as a catalyst for the H₂ evolution reaction (HER). Using the atomic layer deposition (ALD) technique, it is possible to quantitatively controlled the Pt loading down to about 0.2% of a monolayer (~10 ng/cm²), which is sufficient for some PEC applications. Cobalt sulfide, an earth-abundant catalyst, was also synthesized by electrodeposition. It acted as a HER catalyst in water at neutral pH and could be coupled with a Si photocathode for solar H₂ production. Moreover we are developing an effective CO₂ reduction catalyst of near unity selectivity for acetate production, which could be added into the integrated nanostructure.

In conclusion, my graduate research focuses on the integration of nanowire-based structures to achieve more efficient artificial photosynthesis. This is demonstrated in this dissertation not only at system level for an integrated nanostructure, but also at component level for advanced building blocks. This research can serve as a foundation for the efforts of other researches in the field of artificial photosynthesis.

I dedicate this dissertation to my parents, for their love and unwavering support.

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Chapter 1

Introduction

1.1 Fundamentals of photoelectrochemical (PEC) devices

1.1.1 Overall picture: utilization of solar energy

Industry, electricity, heating, air-conditioning, computers, cars, planes-the hallmarks of modernity are synonymous with energy consumption. Since much of the world's ever-growing population lives in societies striving to modernize, the world's need for clean and renewable energy sources is more urgent than ever. Although the sun offers more than enough power to satisfy humanity's appetite for energy, solar energy conversion technologies remain too costly to compete with fossil fuels on a worldwide scale. Research into new and improved technology is part of the solution, and photovoltaics and artificial photosynthesis are two approaches with much potential for practical implementation. Photovoltaics convert sunlight into electricity: small installations can power individual homes or solar farms can light up cities. Nevertheless, storing the sun's energy as a fuel to balance out daily or seasonal solar fluctuations or for transportation remains an important demand of modern life. Artificial photosynthesis uses photoelectrochemistry (PEC) to transform sunlight directly into chemical fuels for these applications. Both of these approaches have a promising future as part of the portfolio of renewable energy technologies that will be needed to wean the world from its dependence on fossil fuels. For this breakthrough to occur, however, these technologies will need to be more efficient and less costly, two challenges that nanomaterials can help overcome.

My Ph. D research project focuses on the application of nanowire-based structures to facilitate artificial photosynthesis, the biomimetic approach to store the solar energy into the chemical bonds of fuels. However, for a deeper understanding of the PEC devices, it is needed to first understand its close relative, solar cells. In this chapter, we will first go through a brief description of the function of photovoltaics (section 1.1.2), and then a detailed description of PEC devices, in the context of similarity and difference with solar cells (section 1.1.3). This will lead into a discussion of the approaches for practical application of artificial photosynthesis, particularly the dual light-absorber "Zscheme" approach (section 1.2.1), along with current limitations and problems (section 1.2.2). The description of limitations of current solar-to-fuel process endows a good opportunity for the introduction of nanomaterials, nanowires in particular, and its merits in the context of artificial photosynthesis (section 1.3). Based on this, the objective of present thesis is centered on two themes: (1) constructing novel integrated nanostructures for solar-to-fuel conversion, and (2) developing next-generation materials and catalysts for improved PEC performance (section 1.4). With these discussions, detailed research work will be described in the following chapters.

1.1.2 Starting point: photovoltaic

Photovoltaics is the conversion of sunlight into electricity using solar cells. In conventional semiconductor solar cells, a p-n junction establishes a built-in electric field within the material (Figure 1.1a). At the contact point 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. The extent of the area devoid of carriers, or 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 an electronhole pair. The built-in electric field at the junction, or band-bending, separates the electron and hole and accelerates them toward the solar cell's contacts to be collected as current. This current and the built-in field's voltage transform the sun's energy into electrical energy. If the photogenerated carriers originate in the semiconductor 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.



Figure 1.1 a, Schematics of how a photovoltaics function. **b**, The spectrum of AM 1.5G sun light. **c**, Metrics the PV performance evaluation.

Several metrics are used to evaluate and compare the performance of solar cells. The current density-voltage (J-V) curve is measured under illumination from a solar simulator, which is a light source that produces 1-sun intensity (100 mW/cm^2) with an AM1.5G spectral profile (Figure 1.1b). It provides the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}) , and the fill factor (FF); the product of these three metrics is the maximum power produced by the solar cell (Figure 1.1c). If the material properties of the solar cell are known, the thermodynamic limits for these metrics can be calculated (27, 28) to analyze the solar cell's experimental performance and diagnose areas for improvement. Efficiency (η) , which is the maximum power produced by the solar cell divided by the power of the light incident on it, is the most important metric of performance. Since the two primary processes in a solar cell are generation of electronhole pairs and their collection, measuring both the wavelength-dependent absorption of the solar cell and its efficiency at each wavelength, referred to as the external quantum efficiency (EOE), 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. These measurements are performed most accurately by illuminating the solar cell with a solar simulator and using lock-in detection to measure the response to an AC-modulated monochromatic light source.

1.1.3 Description of a PEC device

Photovoltaics converts sunlight into electricity, but transforming solar energy directly into chemical fuels is also important. The direct conversion of sunlight into energy stored within chemical bonds, termed artificial photosynthesis, (29-33) mimics natural photosynthesis that occurs in plants. (34) This concept was originally demonstrated in the 1970s, using TiO₂ as a photocatalyst to split water into H₂ and O₂.(35)

The classic operation of a PEC cell used for artificial photosynthesis takes advantage of the semiconductor/electrolyte interface and resembles a photovoltaic: a photocatalytic semiconductor is immersed in an electrolyte, which forms a built-in electric field at the semiconductor/electrolyte interface (Figure 1.2a). Light absorbed by the semiconductor produces electron-hole pairs, and the built-in field at this junction separates the charges so they can perform separate chemical reactions: an oxidation and a reduction. Typically, the minority carrier reacts at the surface of the semiconductor while the majority carrier travels through the bulk of the semiconductor electrode and performs the complementary reaction at a counter electrode (Figure 1.2b).

In contrast with a photovoltaic cell, the efficiency of a PEC cell can be benchmarked in different ways.(36) For an individual photoelectrode that facilitates a redox half-reaction, e.g. reducing H^+ to H_2 or oxidizing H_2O to O_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 this context, this calculated efficiency is in accord with the efficiency of the sunlight-to-fuel conversion process, however, can also be defined as the overall energy stored in the chemical bonds of the produced fuel, normalized to the energy density of the incident photons. Here the efficiency is defined in the context of the overall chemical reaction rather than a redox half-reaction; this method is relevant to the full process of artificial photosynthesis.

Artificial photosynthesis shares similarities with photovoltaics, but it has additional flexibilities as well as restrictions. Both processes require absorption of light and use a junction's built-in electric field(37) to separate photogenerated charges; however, since in artificial photosynthesis a liquid electrolyte facilitates the electrochemical reactions,(32) the electric field is created by semiconductor/electrolyte interfaces(36, 37) or embedded solid junctions.(38, 39) The materials used must also be stable against photocorrosion in the electrolyte under illumination. Additionally, unlike photovoltaics, which aims simply to maximize overall power output, a minimum voltage is required to produce fuels from sunlight, which is imposed by the energetics of the desired chemical reaction. Driving reactions such as splitting water into hydrogen and oxygen or reducing carbon dioxide into organic fuels requires thermodynamic potentials

greater than 1V. To overcome the kinetic barrier to achieve a high reaction rate, an electrochemical overpotential is also required. (40) This voltage restriction limits the choice of materials to semiconductors with wide band gaps if only one light-absorber is used. (41) Because of this, variable approaches have been designed to realize efficient solar-to-fuel conversion, including using a different number of light-absorbers to realize an overall chemical reaction. (41-44) This is going to be discussed in the following section.



Figure 1.2 a, Energetics of a semiconductor-electrolyte interface, with the density of states of redox couple plotted. Under illumination, the bandbending at interface induce charge transfer of photo-excited carrers into the redox in the electrolyte. **b**, Complete circuitry of a single light-absorber PEC device with a metal counter electrode. **c**, Schematics of a dual light-absorber PEC device for unassisted solar-fuel production.

1.2 Z-scheme approach for solar-to-fuel conversion

1.2.1 Single light-absorber vs. dual light-absorber (Z-scheme)

Because of the presence of overpotential and other loss terms in the solar-to-fuel conversion process, the choice of materials to semiconductors with wide band gaps if only one light-absorber is used.(41) Alternatively, two light-absorbing semiconductors can be used in the biomimetic "Z-scheme": one semiconductor acts as a photocathode for reduction and the other as a photoanode for oxidation (Figure 1.2c).(17, 31, 42, 45, 46) In each of these electrodes, photoexcited minority carriers move to the solution for the half-reactions, while majority carriers recombine at the interface connecting the light absorbers. Often the surfaces of the electrodes are decorated with co-catalysts to facilitate the chemical reactions. To achieve high efficiency, two light-absorbers with small band gaps can provide the voltage for the chemical reaction in the "Z-scheme" (Figure 1.3). (41, 47) This design means that many materials with small band gaps developed in photovoltaic research could be used, provided they are stable in the electrolyte. The additional flexibility of the "Z-scheme" design makes it a promising approach for converting solar energy into chemical fuels.

In terms of the structure for the artificial photosynthesis, since the product of a PEC cell is a chemical fuel rather than electricity, the entire structure can be miniaturized into powder form. This version is particularly attractive because it is extremely low cost: powder is mixed into electrolyte and, upon exposure to sunlight, produces chemical fuels.

The "Z-scheme" approach mimics the natural photosynthetic process of twophoton absorption to drive the overall electrochemical reaction. In chloroplasts, the components of photosynthesis are carefully arranged(30, 34, 39): photosystems I and II are arranged side by side on the thylakoid membrane with the electron transport chain between them for efficient charge transfer, while the reduction and oxidation catalytic centers are spatially separated to minimize the undesirable back-reaction of the photosynthetic products. Comparatively in the "Z-scheme" the photocathode and photoanode are inorganic analogues of photosystem I and II, and the electrocatalysts function as the reduction and oxidation centers. Therefore the "Z-scheme" is an integrated system that combines multiple different processes(48), and mimics the function of natural photosynthesis. However in general the spatial control at nanometer scale in the chloroplast is not present in a typical "Z-scheme" device. As shown later, achieving such nanoscale integration in artificial photosynthesis is one of the centerpieces in this Ph. D. thesis.

1.2.2 Present limitations of Z-scheme approach

For the practical application of solar fuels as a renewable energy resource, high solar-to-fuel conversion efficiency is necessary (3, 44, 47, 49). The energy input requirement for such a process is fundamentally limited by the nature of the chemical reactions involved. As show below, the thermodynamic potential needed to drive the reaction of interest is typically greater than 1V.





Figure 1.3 Maximum theoretical solar-to-hydrogen efficiency for a dual stacked light-absorber configuration plotted as a function of the top and bottom photo-absorber band gaps. The figure is cited from reference (*2*, *3*).

H₂O → H₂ +
$$\frac{1}{2}$$
O₂, ΔE = 1.23V
CO₂ + H₂O → HCOOH + $\frac{1}{2}$ O₂, ΔE = 1.40V
CO₂ + H₂O → HCHO + O₂, ΔE = 1.34V
CO₂ + 2H₂O → CH₃OH + $\frac{3}{2}$ O₂, ΔE = 1.21V
CO₂ + 2H₂O → CH₄ + 2O₂, ΔE = 1.06V

In addition to the thermodynamic potential, an electrochemical overpotential is needed to overcome the kinetic barriers for a high reaction rate(40). This voltage restriction limits the choice of materials to wide band gap semiconductors if only one light-absorber is applied(41). As discussed above, the application of "Z-scheme" approach could provide large photovoltage with the use of two small band gap semiconductors, which are capable to capture the visible region of the solar spectrum.

Due to the integrated nature of the components in artificial photosynthesis, an efficient solar-to-fuel device should operate under a harmonic state such that there is no significant bottleneck hindering the charge flux. Under the "Z-scheme" approach there are two major issues that should be addressed: i) matching the flux between current-

generating light-absorbers and the current-consuming electrocatalysts, *i.e.*, is the electrocatalyst capable of handling the chemical reactions efficiently and selectively under the flux of photo-excited carriers? ii) matching the flux between different light absorbers, *i.e.*, could both the photoanode and photocathode provide the necessary photocurrent flux for practical applications, while maintaining a desirable voltage output? These two questions are currently not fully answered, due to the inadequacy of catalyst and material development, and the lack of structural design based on a device integration approach. The introduction of nanomaterials and nanostructures, particularly a one-dimensional nanowire morphology(*50*, *51*), could contribute to tackle these issues from various aspects.

1.3 Advantages of nanowires for artificial photosynthesis

1.3.1 Nanowires for studying the electrocatalyst/light-abosrber interface

To address the issue of flux matching between the electrocatalyst and lightabsorbers, nanowire array electrodes can provide a reduced overpotential for solar-to-fuel conversion, and are an ideal platform for a quantitative investigation of the interface between electrocatalysts and light-absorbing semiconductor junctions. It has been proposed that to be economically viable, a solar-to-fuel energy efficiency of between $5 \sim 10\%$ is desired (3, 44, 49). This corresponds roughly to a photo-generated carrier flux of $\sim 10 \text{ mA/cm}^2$ under one-sun irradiation, which is equivalent to approximately 620 $el/(nm^2 \cdot sec)$ (electrons per square nanometer per second). Typical materials have a surface atom density of $\sim 10^{15}$ atom/cm⁻², or equivalently ~ 10 atom/nm⁻². This sets a ~ 62 sec⁻¹ lower limit of turn-over frequency (TOF) for the electrocatalyst on a planar electrode, assuming that all surface atoms are electrochemically active. Practically, a higher TOF is needed because not all surface atoms are catalytic centers, and a reduced co-catalyst loading may be desirable to avoid blocking the photon flux. To achieve a higher current density (and therefore a higher TOF), an increased overpotential is required based on the Butler-Volmer equation(40), which leads to a reduced energy conversion efficiency.

Upon examining several electrocatalysts studied for the hydrogen evolution (HER)(4-9), oxygen evolution (OER)(10, 11, 14, 15, 18-20), and CO_2 reduction(21-23), a non-negligible overopotential loss may be present owing to an inadequate TOF (Figure 1.4). This implies that increased effort is necessary to develop advanced electrocatalysts, especially for the OER and CO_2 reduction. One actively studied approach is to develop biomimetic structures as catalytic centers(14, 52, 53). Alternately, with presently available electrocatalysts, the introduction of large surface area electrode such as nanowire arrays can alleviate this mismatch. As shown in Figure 1.4, the increase of roughness factor (the ratio between surface area and the projected electrode area) reduces the required overpotential by decreasing the surface flux of charge carriers. While an increased surface area could be accomplished in many forms, the nanowire morphology provides a well-controlled platform for quantitative investigation of the catalyst requirements, while also providing a direct current path for charge collection. This sheds light on the fundamental properties of the interface between the electrocatalyst and semiconductor light absorber beyond previous investigations.



Figure 1.4 An examination for the flux matching between electrocatalysts and light-absorbers. For affordable application, a charge flux of 10 mA/cm² from light-absorbers is desired. Here the required overpotential η (left y-axis) to satisfy such a flux is plotted against the exchange current density i₀ (x-axis) of a planar electrode. The dashed blue curve represents a simulation for one electrode with 100% surface coverage of an electrocatalyst, assuming a 59 mV/dec Tafel slope in the Bulter-Volmer equation. The solid yellow curve represents the same electrode but with only 10% surface coverage. In the same figure some of electrocatlysts are displayed for HER (Pt(4, 5), NiMo(6, 7), $MoS_{x(8, 9)}$ and OER (IrO_x/RuO_{x(10, 11)}, CoPi and its derivatives(14, 15), amorphous NiCoFe oxide(18-20)). CO₂ reduction electrocatalysts have such a high η to satisfy the flux that they are out of the figure under present scale(21-23). The merits of nanowire are evident as shown by the solid red curve, which is the simulation for one electrode with 10% electrocatalyst coverage, but with a roughness factor of 1000. The required η is significantly reduced, also illustrated by the percentage of voltage loss between the η and 1.23V, the thermodynamic energy required to split water (right y-axis). Notably the electrochemical activities for catalysts listed here are meant to be planar monolayers for fair comparison and fundamental analysis. However this is not available for every electrocatalysts under 10 mA/cm². Therefore some extrapolation and approximation are carried out. Please see individual references for detailed information.

1.3.2 Nanowires for semiconductor light-absorbers

The second major issue facing present solar-to-fuel conversion devices is matching the flux between different light absorbers in the "Z-scheme". This requires a well-designed choice of material pairs with suitable band gaps, and a low-resistance charge transfer pathway between the two light absorbers(12). According to theoretical calculations that take into account overpotentials and other losses(3, 47), the target band gaps for a pair of electrodes are around 1.1eV and 1.7eV for optimized efficiency. However, upon examining several typical semiconductors for PEC applications (Figure 1.5), the choice of available materials with band gaps ranging between 1.5eV to 2.0eV is limited. In addition, unlike photovoltaic cells, which aim to maximize power output, the nature of the chemical reactions in artificial photosynthesis requires a minimal voltage output to drive the reaction. Therefore, not only the band gap of the materials but also the band alignment and the resultant photovoltage output of the junction are important.

For the photocathode, Si(54, 55) ($E_g = 1.1eV$) and InP(56) ($E_g = 1.3eV$) have been reported to generate high current density with photovoltages of greater than 500mV. Therefore, the development of photocathodes can focus on reducing the raw material usage and fabrication costs, for example via solution-phase synthesis of semiconductor nanomaterials(1, 2). Comparatively, the photoanode deserves more attention(57). Presently there is no stable photoanode device capable of providing a photocurrent of greater than 10 mA/cm², while at the same time providing 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 valance band(58). Novel materials, including compound semiconductors with junction engineering and corrosion protection, should be developed for photoanode research using advanced synthesis techniques.

The introduction of a nanowire morphology could help to improve the performance of existing photoanode materials. The nanowire morphology provides a large surface area for co-catalyst loading and electrochemical reaction sites, while at the same time leading to enhanced charge collection efficiency, especially for indirect band gap semiconductors with short minority carrier diffusion lengths(36, 51, 59). For example, TiO₂ rutile nanowire photoanodes have been well studied, and the nanowire morphology has proven to be beneficial(13, 60, 61). In particular, when care was taken to improve the surface properties of the nanowires by a thin epitaxial coating, significant improvement was observed (Figure 1.6a) (13).

As an extension of the nanowire morphology, core-shell structures demonstrate unique advantages (25, 62). Although single-composition nanowire electrodes improve charge separation within the band-bending region, charge transport through the electrode may still be restricted by a large resistivity of the bulk material in the core of nanowire. A core-shell configuration can alleviate this issue, by designing a photoactive shell for charge separation and a conductive core for charge collection. This could further benefit from light scattering and trapping in the shell material due to the nanowire geometry (63). Additionally, the heterojucntion between two materials can provide extra photovoltage (Figure 1.6b), which is crucial for the successful application of a "Z-scheme" approach (25, 64). It is likely that with appropriate structures of the nanowire



Theoretical photocurrent density under one-sun illumination

Figure 1.5 theoretical photocurrent densities of semiconductors under one-sun illumination. The blue curve is the integrated photon flux at different cut-off energies, based on the AM1.5G solar spectrum. Some of the semiconductors used in solar-tofuel conversion are also listed, along with their band gaps in bulk phases. The arrows at the bottom indicate the regions of ultraviolet (UV) (below 400nm), visible (400nm \sim 750nm), and infrared (IR) spectra.

morphology(59), oxide or nitride based photoanodes can generate high photocurrent densities with satisfying photovoltage outputs.

The progress in novel material development could also benefit from the nanowire structure. Facile synthesis techniques for nanowire materials, using either gas-phase (65,66) or liquid-phase(1) approaches, could help to produce materials with unique properties. Despite the limited number of materials available with band gap between 1.5eV and 2.0eV (Figure 1.5), this band gap range overlaps with compound III-V semiconductor alloys that have tunable band gaps. III-V semiconductor nanowires, for example GaAs(66), GaP(1, 2) (Figure 1.6c), and $In_xGa_{1-x}N$ alloys(67), have been prepared and applied for PEC applications. The versatility of nanowire synthesis provides a unique pathway of low-cost III-V materials for solar-to-fuel application, which can be extended to other compound semiconductors with tunable material properties.



Figure 1.6 a, Epitaxial TiO₂ ALD coating on TiO₂ rutile nanowire resulted in enhanced photocurrent for OER(13). **b**, The heterojunction within core-shell Si/TiO₂ nanowire leads to additional photovoltage output for photoanode application(25). **c**, GaP nanowire could be synthesized in large quantity via solution-phase approach, and function as a low-cost photocathode material(1, 2).

1.4 Objectives of graduate research

1.4.1 Achieving integration at nanoscale for artificial photosynthesis

In the above discussion, we considered individual components for artificial photosynthesis, with a focus on the constraints of current matching and corresponding improvements needed. An integrated system with interconnected components is the key concept to be addressed(48). In addition to the efforts to improve individual components, it is critical to assemble all the pieces together and demonstrate overall solar-to-fuel conversion under such an integrated system. This also acts as the final milestone for consideration of a solar-to-fuel application for commercialization. Furthermore, an integrated standalone system is fundamentally intriguing, in order to mimic the nanoscopic spatial control of natural photosynthesis. In chloroplasts, the components of photosynthesis are carefully arranged(30, 34, 39): photosystems I and II are arranged side by side on the thylakoid membrane with the electron transport chain between them for efficient charge transfer, while the reduction and oxidation catalytic centers are spatially separated to minimize the undesirable back-reaction of the photosynthetic products. Achieving such microscopic spatial control is a crucial aspect of our pursuit for artificial photosynthesis.

One of the goals for my graduate research is to realize a nanoscale control of active components in artificial photosynthesis. This contains two parts: (1) understanding the photo-induced local charge transfer within a nanowire-based heterojunction under conditions of solar-to-fuel process, and (2) taking the knowledge of local charge transfer

to construct an integrated system composed of nanowires as building blocks for unassisted solar-to-fuel conversion.

Since all of the processes in PEC interfaces relate to the among semiconductor light-absorbers, electrocatalysts, and the electrolyte, it is of importance to under how photo-excited carriers would transfer within these interfaces. Using a variation of scanning probe microscopy, kelvin probe force microscopy (KPFM), we are able to probe the local electrostatic potential distribution for a nanowire heterojunction embedded in a layer of water. Additionally we are capable to observe the photo-response of the local electrical potential using different wavelengths of light source, and derive the motion of photo-excited carriers with nanometer scale spatial resolution. Using Si and TiO_2 as a model material combination, we investigated the charge transfer of photo-excited carriers in an asymmetric Si/TiO₂ nanowires (Figure 1.7a)(12), and obtained valuable information that this material combination could act as a "Z-scheme" system for artificial photosynthesis (Chapter 2).

Taking that piece of information in mind, I moved forward to develop an integrated nanosystem for artificial photosynthesis. Using Si and TiO₂ nanowires as building blocks, a proof-ofconcept solar-to-fuel conversion nanodevice was demonstrated for solar water splitting(17) (Figure 1.7b and 1.7c). Equipped with knowledge of the various interfaces involved(12, 25), a tree-shaped



Figure 1.7 a, KPFM was applied to study the photoresponse of local electronic potential in an asymmetric Si/TiO₂ nanowire.(*12*) **b** & **c**, a nanowire-based integrated device was constructed for unassisted solar watersplitting.(*2*, *17*)

nanowire-based heterojunction device was constructed and loaded selectively with HER and OER electrocatalysts. Compared with the Si nanowire photocathode, the smaller feature size of the TiO₂ nanowire photoanode is motivated by the design principles of nanowire photoelectrodes(59), owing to the smaller minority carrier diffusion length in the photoanode and the slower reaction kinetics of OER. As discussed above, the bottleneck of the constructed system is the TiO₂ photoanode, whose band gap is in the UV region. Despite this limitation, unassisted solar water splitting was observed with 0.12% solar-to-fuel efficiency, comparable with natural photosynthesis(30, 34).

1.4.2 Defining new building blocks for solar-to-fuel processes

This proof-of-concept device leaves much room for improvement and welcomes performance enhancements by updating individual components with the latest improvements, allowing for a modular design approach(48). By implementing the advantages of nanowire morphology discussed in earlier sections, continued efficiency improvement is expected. Specifically, the balance between electron flux from the light-absorber and the TOF of the electrocatalyst requires development of electrocatalyst materials, especially for the OER and CO₂ reduction. Ideally, an overptential of less than 100mV at 10 mA/cm² is desired. Nanowire electrodes can help accomplish this by providing a large surface area for catalyst loading. They can also provide a well-controlled system for fundamental studies such as tuning the interface between electrocatalyst and underlying semiconductor light-absorber.

Additionally, the requirements for high photocurrent and photovoltage output rely



Figure 1.8 a, GaP nanowires were synthesized with tunable electronic properties for photocatlytic applications.(*1*, *2*) **b**, Au nanostructures promote the PEC activity of a hematite photoanode via their surface plasmon resonance.(*16*) **c**, ALD techniques allow for sub-monolayer deposition of Pt as a HER catalyst.(*24*) **d**, cobalt sulfide acts as an efficient HER catalyst for solar-to-fuel conversion.(*26*)

heavily on photoanode research, which can be further supplemented by improvement of photovoltage output in the photocathode. Nanowire structures provide opportunities for new material discovery, as well as improving the performance of existing materials. Also it is possible to use nanostructured metal substrate to further enhance the PEC performance via surface-plasmon.

The second goal of my graduate research is to develop advanced building blocks, including electrocatalyst and semiconductor light-absorbers, for enhanced solar-to-fuel conversion efficiency under the theme of integrated nanostructures. This includes several distinct approaches, which are briefly discussed below and will be elaborated in the following chapters.

We have explored new materials and methods to improve the energy conversion efficiency of semiconductor light-absorbers. Solution-phase synthesis of III-V semiconductor nanowires was successfully demonstrated for photocatalytic reactions, and the nanowires' electronic properties could be fine-tuned to fit the needs of device integration (Figure 1.8a).(1, 2) Also we demonstrated enhancement of the photoanodic activity of hematite (Fe₂O₃) using the surface plasmon resonance of exquisitely controlled Au nanostructures (Figure 1.8b).(16)

Additionally, we developed new electrocatalysts suitable for practical applications. We first looked into the lower limit of platinum (Pt) loading as a catalyst for the H₂ evolution reaction (HER). Using the atomic layer deposition (ALD) technique, we quantitatively controlled the Pt loading down to about 0.2% of a monolayer (~10 ng/cm²), which is sufficient for some PEC applications (Figure 1.8c).(24) Cobalt sulfide, an earth-abundant catalyst, was also synthesized by electrodeposition. It acted as a HER catalyst in water at neutral pH and could be coupled with a Si photocathode for solar H₂ production (Figure 1.8d).(26) Moreover we are developing an effective CO₂ reduction catalyst of near unity selectivity for acetate production, which could be added into the integrated nanostructure.

1.5 Summary

Artificial photosynthesis, a renewable energy approach that stores solar energy in chemical bonds, is an interesting research field for both fundamental research and practical applications. While nature has evolved for millions of years to tackle the challenges of photosynthesis, we are just beginning our journey. At present there are many challenges and limitations for practical application of solar-to-fuel conversion. The purpose of my graduate study is to take the advantages of nanomaterials, in particularly one-dimentional nanowires, to tackle these issues. As proved later in this thesis, the application of the nanowire structure has its merits for solar-to-fuel conversion, particularly when emphasizing on design principles that are based on integrated artificial photosynthesis architecture. Nanostructures are powerful tools for the design and realization of integrated microscopic systems, and it is possible that their use will enable practical applications of efficient and affordable solar-to-fuel conversion. Once realized, this will drastically change our use of energy resources, the life that we enjoy, and foremost the planet that we call home.

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Chapter 2

Light-Induced Charge Transport within a Single Asymmetric Nanowire

2.1 Importance of local surface potential mapping in nanostructures for "Z-scheme"

A semiconductor used for direct solar water splitting (1, 2) is required to be photo-electrochemically stable, to have an appropriate band gap that can support broad absorption of the solar spectrum as well as band edges at suitable potentials for the water reduction/oxidation half reactions, and to perform fast charge transfer at the semiconductor/electrolyte interface and efficient evolution of hydrogen and oxygen.(1, 3)Because of the stringent requirements on the band gap and band edge energies, early research efforts have focused on semiconductors with relatively large band gaps, which are mostly UV-absorbing semiconductors.(4-7) On the other hand, the dual-band gap approach (Z-scheme) enables the usage of smaller band gap materials for much better coverage of the solar spectrum,(8) and it was predicted that such a scheme could lead to a PEC system with energy conversion efficiency as high as $\eta = 27\%$.(9)

In natural photosynthetic systems, (10) a process involving two photons is in operation for the oxidation of water and storage of the solar energy in sugar. Similarly, in an ideal dual-band gap PEC cell, (8) two photons could be used to excite the two semiconductors that are in close contact. The minority carriers of the two semiconductors will oxidize and reduce water, while the majority carriers recombine at the semiconductor junction. Chemical redox mediators or metal can be introduced for fast electron transfer between the two semiconductors.(1, 11)

Although under the "Z-scheme" a typical solar-to-fuel device functions similarly as the natural photosynthesis, the structure similarily under nanoscale is largely missed. It is scientifically intriguing to construct a nanostructure that integrates the function of natural photosynthesis, at the same time maintain the structure control at nanometer scale as what has been realized in chloroplast. Additionally, as discussed in Chapter 1, the introduction of nanostructures, nanowire morphology in particular, would help to tackle the challenges faced by artifical photosynthesis. But how can we construct such an integrated nanostructure? What sort of knowledge is needed before we start to design and synthesize such a nano-enabled device?

One requirement is the detailed information of charge transport among the interfaces of semiconductor light-absorbers, electrocatalysts, and the electrolyte. It is only possible to construct the device when knowledge of charge transport kinetics is known for certain material combination. Here an asymmetric Si/TiO_2 core/shell nanowire

heterostructure was designed (Figure 2.1a) to as a model system to understand the charge transport of photo-excited carriers inside, and to explore the feasibility of such a dualband gap scheme for direct solar water splitting.(12)

In this study, charge separation within an asymmetric structure of Si and TiO_2 is observed at the single nanowire level.(12) Using KPFM(13) under conditions that mimic the environment of real water splitting, the light-induced local surface potential change within a single asymmetric nanowire is mapped to demonstrate the proposed spatial charge separation mechanism. These experiments suggest that a dual-band gap



Figure 2.1 a, Schematic illustration of the asymmetric nanowires, with silicon core (yellow) and TiO_2 shell (red). **b**, Corresponding tilted SEM image of the asymmetric nanowires grown vertically on a Si(111) substrate, and **c**, a cross-sectional SEM image of the asymmetric nanowires, showing the contrast difference between the top Si (bright) and the bottom Si/TiO₂ (dark) parts. **d-f**, TEM images of asymmetric nanowires, indicating the sharp Si/TiO₂ junctions (**e**), and core-shell TiO₂/Si structure (**f**).

asymmetric configuration with exposed anode and cathode surfaces induce charge separation at semiconducotor/electrolyte interface, which is consistent with what is expected based on the band gap alignment of two materials. Based on this, it is possible to use the combinatio of Si and TiO_2 as a model system to realize an integrated nanostructure for unassisted solar water-splitting.

2.2 Experiment Setup and Procedure

2.2.1 Synthesis of Si/TiO₂ asymmetric nanowire

The asymmetric Si/TiO₂ core-shell nanowire structures were synthesized with one part consisting of a Si nanowire and the other part consisting of a Si/TiO₂ core-shell structure (Figure 2.1a). This asymmetric structure ensures large contact area and charge separation/collection efficiency across the semiconductor/semiconductor and the semiconductor/electrolyte junction.(*14-17*) A detailed synthesis scheme is illustrated in Figure 2.2. Si nanowires were grown vertically on a Si (111) substrate via the vaporliquid-solid (VLS) mechanism,(*18*) and the amorphous TiO₂ shell was conformally coated by atomic layer deposition (ALD) at 80 °C. With the bottom half of the structures protected by photoresist, the top part of the TiO₂ shell was removed by HF etchant, which resulted in arrays of asymmetric Si/TiO₂ core/shell nanowires (Figure 2.1b). Additional annealing at 600 °C transformed amorphous TiO₂ into the anatase structure, which was



Asymmetric catalyst/Si/TiO₂ nanowire

Figure 2.2 A generalized scheme for fabrication of the asymmetric nanowires. The Si VLS nanowire in the first step was synthesized using either 80 nm Au nanoparticles or Au thin film deposited on the soft-lithographically patterned substrate.

confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Scanning electron microscopy (SEM) and TEM images show that these asymmetric Si/TiO₂ nanowires are typically 5~6 μ m in length, with a Si core of 120 nm in diameter and a TiO₂ layer of 30 nm in thickness (Figure 2.1c-f). A sharp junction between the Si and Si/TiO₂ core/shell parts was generated, and the nanowires remained vertical on the Si substrate after all the processing steps. The TiO₂ layer often had single-crystalline domains of up to 100 nm.(*15*)

In the rest of this chapter, we are going to use KPFM to detect the local electrostatic potential distribution of such an asymmetric nanowire, and observe the photo-induced charge transport under the same environment as solar water splitting.

2.2.2 Experimental setup of kelvin probe force microscopy (KPFM)

KPFM measurements were performed in an Asylum MFP-3DTM stand-alone AFM equipped with AEK 2002 acoustic isolation hood. The experimental setup is shown in Figure 2.3. In detail, an asymmetric nanowire was transferred to a fused silica substrate patterned with Au lines to minimize the effect of static charge. The quartz substrate was placed on top of an aluminum sample stage. 2.5 mW, a 365 nm UV LED (T-1 ³/₄ package, NICHIA Inc.) or 20mW 465 nm LED (T-1 ³/₄ package, Thorlabs Inc.) was positioned ~0.5 mm underneath the quartz substrate to realize diffusive illumination.



Figure 2.3 Schematic illustration (a) and photograph (b) of the KPFM setup with backside LED illumination.

KPFM measurements were carried out in AC mode using the technique reported before(13), with 50 nm lift distance. A typical 512-by-512 pixel scan was run at 0.5 Hz over $10 \times 10 \text{ }\mu\text{m}^2$ with a Nanoworld PointProbeTM EFM cantilever under the controlled humidity at 60~70% r.h. Changing the light intensity was achieved by controlling the current through the LED with an external circuit, and the light intensity was measured based on the ratio of overall optical power passing through the hole of sample stage (measured by a calibrated photodiode from Newport Inc.) to the area of the hole.

2.3 Photo-response of local surface potnetial in asymmetric nanowire

For such asymmetric nanowire heterostructures with the dual-band gap configuration, electron-hole pairs can be generated in the silicon and TiO_2 using photons of different wavelengths. Because of the band-bending of the space-charge layer at the semiconductor/electrolyte interface,(3) solar illumination would leave positively charged holes on the n-TiO₂ side (anode behavior) and negatively charged electrons on the p-Si side (cathode behavior), with the recombination of majority carriers between the two semiconductors (Figure 2.4a). As the result, a dipole along the asymmetric nanowire is expected with more positive electrical potential in the n-TiO₂ part relative to that of the p-Si part when both the Si and TiO₂ absorb light (Figure 2.4a and 2.4b). The minority carriers of both semiconductors, with proper energetics, are ready to perform a complete water splitting reaction.



Figure 2.4 a, Schematic energy diagram of charge separation for the Si/TiO_2 dualband gap configuration. The Fermi level in dark (dashed blue) and quasi-Fermi levels under illumination (dashed red) are shown. For simplicity, a uniform distribution of quasi-Fermi level is assumed within each part of the asymmetric nanowire. **b**, Schematic of the spatial charge distribution within an asymmetric nanowire under illumination according to (**a**). **c**, Topographical AFM image of the asymmetric nanowire and measured surface potential mapping of an asymmetric nanowire in the dark (**d**) and under 365 nm UV illumination with 4.5 mW/cm² intensity (**e**). **f**, Surface potential profiles along an asymmetric nanowire from Si (distance 0 µm) to Si/TiO₂ measured under the same light intensity as in **e**. The curves are offset for clarity. The data were collected sequentially from bottom to top, switching between dark and UV illumination.

An asymmetric Si/TiO₂ nanowire was transferred onto an insulating fused silica substrate and 365 nm UV light was applied to excite both Si and TiO₂.(19) Controlled humidity was applied to condense water onto the nanowire surface and to establish semiconductor/electrolyte interfaces. In the dark, the surface potential of the Si/TiO₂ core/shell part is about 15 mV higher than that of the Si-only part (Figure 2.4d), mainly due to the work function difference between these two materials(13). Under UV illumination, the local surface potential of the Si/TiO₂ part is significantly more positive (by 60 mV) than that of the Si (Figure 2.4e), indicating positive charge buildup on the Si/TiO₂ part as expected. This photoresponse of the surface potential is reversible (Figure 2.4f), suggesting that the change of the surface potentials originates from UV illumination. Control experiments with both pristine Si nanowires and complete Si/TiO₂ core/shell nanowires showed no comparable surface potential changes (See Supplementary Figure S3 and Figure S4 in reference (12)). Changing the wavelength of illumination to 465 nm also gave no significant change in the surface potential's profile (See Supplementary Figure S5 in reference (12)). Photo-excitation of both semiconductors, and in this case UV-activation of TiO₂, was necessary for effective charge separation and dipole formation.



Figure 2.5 a, Surface potential profile of an asymmetric nanowire measured at different light intensities. The potential profiles are offset for clarity. **b**, Averaged surface potential difference between the Si/TiO₂ core-shell region and the Si region, and its dependence on the intensity of the 365 nm UV light. The error bars on the data indicate the spatial variation of the surface potential of the Si/TiO₂ core-shell region as compared to the averaged value of the Si region caused by the heterogenity of the photoresponse among TiO₂ domains. The average was calculated from multiple samples with different scan parameters performed at the same light intensity.

2.4 Light intensity dependence of local surface potential

By changing the output power of incident light, the light intensity dependence of the local surface potential could be measured. The surface potential difference between the Si and Si/TiO₂ increased gradually as the light intensity was increased (Figure 2.5). The surface potentials on the Si/TiO₂ part were not uniform under illumination (Figure 2.5a), probably because of the domain structure of the TiO₂ shell. Despite this non-uniform profile, the trend of saturation at high light intensity (Figure 2.5b) is in accordance with the expected behavior of the dual-band gap configuration, with flatting of the band at the semiconductor/electrolyte interface.(8, 9) The result also suggests that photo-generated minority holes in the TiO₂ layer and electrons in the Si core can be efficiently separated in our asymmetric core/shell nanostructures.

Based on above observation, it could be derived that the light-induced charge transport produces a redistribution of the local surface potential, which is consistent with what is expected for a "Z-scheme" device that comprises of one p-type photocathode and n-type photoanode. Therefore, the measurement of KPFM implies that the material combinatio of p-type Si and n-type TiO_2 could function for "Z-scheme" solar water splitting.

2.5 Conclusion

As a powerful technique to resolve the surface potential of materials spatially, KPFM has been widely applied in surface chemistry, light emitting diodes, and solar cells.(13, 19) In the study described in this chapter, we applied this technique to a photoelectrochemically relevant nanostructure, and examined the photo-responses of the surface potential at the semiconductor/electrolyte and semiconductor/semiconductor heterojunctions. The light-induced charge transport within an asymmetric nanowire was observed through KPFM in a dual-band gap configuration, indicating that the minority carriers of the semiconductors are separated while the majority carriers of the semiconductors recombine at the interface. The construction of such a nanowire-based heterostructure could help to achieve integration at nanoscale for artificial photosynthesis. Moreover, the design that applies dual-band gap configuration is applicable to other semiconductors, and the overall solar energy conversion efficiency can potentially be improved by coupling two visible light absorbers which balance the photo-excited carrier generation rate upon solar irradiation.

2.6 References

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Chapter 3

A Fully Integrated Nanosystem of Semicondcutor Nanowires for Direct Solar Water Splitting

3.1 Importance of achieving integration at nanoscale for artificial photosynthesis

Artificial photosynthesis(1-4), the biomimetic approach to converting sunlight's energy directly into chemical fuels, offers an attractive way to address the need for a clean, renewable source of energy. In plants, chloroplasts store the sun's energy using a system of integrated photosynthetic nanostructures including light-absorbing pigments, electron-transport chains, and chemical catalysts(5, 6). Artificial photosynthesis aims to imitate nature by using a system of integrated nanostructures, each of which plays a specific role in the sunlight-to-fuel conversion process. Here we describe a fully integrated photoelectrode nanosystem fabricated from inorganic nanowires for direct solar water splitting. Similar to the photosynthetic system in a chloroplast, our artificial photosynthetic system comprises two large surface-area semiconductor light absorbers, an interfacial layer for charge transport, and spatially separated cocatalysts to facilitate the water reduction and oxidation(7, 8). Under simulated sunlight, a 0.12% solar-to-fuel conversion efficiency is achieved, which is comparable to that of natural photosynthesis (6, 9). These integrated nanostructures clearly demonstrate the possibility of integrating material components into a functional system (10) that mimics the nanoscopic integration in chloroplasts. The results here also provide a conceptual blueprint towards better solar-to-fuel energy conversion efficiency using a modular approach, where newly discovered components can be readily plugged in.

In natural photosynthesis the energy of absorbed sunlight produces energized carriers that execute chemical reactions in separate regions of the chloroplast. The electrons used to produce NADPH are excited via the "Z-scheme" of photosystems I and II, which absorb light in different energy regions (5, 6). The energy of the photoexcited charge carriers is then used to overcome the thermodynamic barrier and to provide any kinetic overpotential needed to drive the photosynthetic reactions. Compared to excitation of a single light absorber, excitation of the two ligh-absorbers or "Z-scheme" system allows capture of lower energy photons and thus a larger part of the solar spectrum(9), which can potentially lead to a higher efficiency(11). Moreover, photosystems I and II are arranged side by side on the thylakoid membrane with the electron transport chain between them for efficient charge transfer. In addition, the spatial separation of the reduction and oxidation catalytic centers minimizes the undesirable back-reaction of the photosynthetic products. This careful arrangement of photosynthetic

constituents results in a fully integrated system that facilitates conversion of solar energy into chemical fuels(12). The average rate of energy captured by this photosynthetic process approaches 130 terawatts, about 6 times larger than the current worldwide power consumption.

The same concept of an integrated functional system of nanostructures can be applied to artificial photosynthesis. A general path for mimicking natural photosynthesis is to generate O_2 and H_2 separately via the "Z-scheme"(13)_ using two inorganic semiconductors loaded with cocatalysts. Upon exposure to light, the minority carriers in two semiconductors will be used to carry out the individual half reactions, while the majority carriers recombine at an ohmic contact between the materials. Such ohmic contact is designed to be the inorganic analog of the electron transport chain in a chloroplast. Previous studies of solar water splitting without any applied bias employed either electrode-based macroscopic devices(13-17) or a mixture of two semiconductor powders(18, 19). Here we demonstrate a fully integrated functional system for direct solar water splitting, where all the individual components, e.g. two high surface-area nanowire photoelectrodes, ohmic contact and two co-catalysts, are carefully positioned in order to maximize the energy conversion efficiency(20). Such module-integration-towards-system approach demonstrates system-level materials design and integration(10) at the nanoscale for efficient and cost-effective solar-to-fuel conversion.

3.2 Design of a nanowire-based integrated system

A model "Z-scheme" system with two light-absorbing materials is chosen here to demonstrate the capability of an integrated nanostructure to use sunlight to split water(δ). Earth-abundant and stable semiconductors, silicon (Si) and titanium dioxide (TiO₂), were chosen as the hydrogen-generating photocathode and oxygen-generating photoanode, respectively (Figure 3.1). Moreover the nanowire morphology of both materials was applied here because of its large surface area and the shorter distances that carriers must travel to reach the semiconductor-electrolyte surface(21). Upon illumination photoexcited electron-hole pairs will be generated in Si and TiO₂ by absorbing different regions of the solar spectrum. Because of the electric field at the semiconductor-electrolyte interfaces(2) (Figure 1b), the minority carrier electrons in the Si nanowires migrate to the surface and reduce protons to generate H_2 ; meanwhile the photo-generated holes in the TiO₂ nanowires oxidize water to evolve O₂. The holes from Si and electrons from TiO₂ recombine at the ohmic contact, completing the relay of the "Z-scheme", similar to that of natural photosynthesis(8). Owing to the difference of the two materials in catalytic and electrical transport properties, a hierarchical nanoscale tree-like light-harvesting architecture is employed to maximize the performance (Figure 3.1a). As compared to Si nanowires, TiO₂ nanowires with smaller diameters and higher surface area are preferred because of TiO₂'s shorter carrier diffusion length and slower O₂ evolution kinetics(22). An ohmic contact was created between the Si/TiO_2 interface where majority carriers can recombine. Cocatalysts for both reactions are loaded to reduce the reactions' overpotential. The overall system resembles a nanoscale tree where the Si nanowire serves as the trunk and the TiO_2 as the branches (Figure 3.1a). Such nanotree system possesses large surface area that is favorable for catalytic reactions. At the same time the spatially separated photoelectrodes with a local ohmic contact help to segregate the products to mitigate back-reactions(7).

3.3 Results of linked electrode configuration

To realize this artificial photosynthetic nanoscale tree architecture, we started by optimizing the individual components of the integrated system. Substrates with highly ordered array of Si nanowires 800 nm in diameter were tested as H₂-generating photocathodes. For O₂ evolution, the photoanodes consisted of single-crystalline rutile TiO₂ nanowires with diameters about 80-100 nm made using a hydrothermal synthesis(23) (Figure 3.2a). Both Si (24-26) and TiO_{2 (1, 27, 28)} nanowires have been well studied as model systems for H_2 and O_2 evolution, but they function under aqueous electrolytes of different pH for materials stability and optimal performance. In addition the cocatalyst used in one half reaction may either damage the other cocatlyst or induce the back-reaction of the other half reaction(19, 29). In this work Si nanowire photocathodes loaded with platinum nanoparticles and TiO₂ nanowire photoanodes loaded with iridium oxide nanoparticles were tested to ensure they could function in acidic electrolyte together (see Supplementary Information of reference (20)). The optimized J-V photocurrent data of both Si and TiO₂ nanowire photoelectrodes under simulated sunlight are plotted in Figure 2b. A current density intersection of 0.35 mA/cm² suggests a non-zero current flow under illumination when the Si nanowire photocathode and TiO₂ nanowire photoanode are directly wired together. This result is confirmed by the system's transient current response under chopped illumination (Figure



Figure 3.1 a, Structural schematics of the nanotree heterostructure. The small diameter TiO_2 nanowires (blue) were grown on the upper half of a Si nanowire (gray), and the two semiconductors absorb different regions of the solar spectrum. The two insets display the photoexcited electron-hole pairs that are separated at the semiconductor-electrolyte interface to carry out water splitting with the help of cocatalysts (yellow and gray dots on the surface). **b**, Energy band diagram of the nanotree heterostructure for solar-driven water splitting. The photogenerated electrons in Si and holes in TiO_2 move to the surface to perform water splitting, while the holes in Si and electrons in TiO_2 recombine at the ohmic contact between the two semiconductors.

3.2c), implying that solar-driven water splitting without applied bias is possible for Si and TiO₂ nanowires when they are externally linked.

Prolonged testing of the two illuminated nanowire photoelectrodes under shortcircuit conditions was also evaluated. Figure 2d shows that the photocurrent first decreased and then stabilized at 70% of its original performance, rendering a stabilized photocurrent of about 0.7 mA/cm² under simulated three-sun illumination. Under illumination, gas bubbles were evolved from the surface of both electrodes; gas chromatography measured a stoichiometric 2:1 hydrogen-to-oxygen ratio, as is expected for water splitting (Figure 3.2e). Moreover, comparison of the quantities of gases produced and the amount of charge that passed through the circuit shows that these nanowire electrodes exhibits a 91% charge-to-chemical faradic efficiency.



Figure 3.2 a, SEM characterization of Si (top) and TiO₂ (bottom) nanowire electrodes. Nanowires of different length scales for the two semiconductors are shown. When the two semiconductor nanowire electrodes were electrically connected, immersed in water, and illuminated, a nonzero photocurrent flowed from the TiO₂ to the Si to carry out the water-splitting reaction. **b**, Photocurrent density (mA/cm²) of Si and TiO₂ nanowires in 0.5M H₂SO₄ solution *versus* the applied voltage (V) referenced to a reversible hydrogen electrode (RHE). Simulated one-sun illumination was used, and the absolute value of the photocurrent density is shown here. **c**, Current density (mA/cm²) of externally short-circuited Si and TiO₂ nanowire photoelectrodes under the same conditions as **b** but using chopped light exposure. The measurement scheme is shown in **a**. **d**, Photocurrent measurement to test the stability of the short-circuited nanowire photoelectrodes as shown in **a**, under simulated three-sun illumination. **e**, Comparison of the evolved H₂ and O₂ gases and the charge through the circuit in **d**; the ratio close to 4:2:1 for charge, H₂, and O₂ proves water splitting with few losses. The scale bars in **a** are 10 µm (top) and 1 µm (bottom).

3.4 Experiment details of integrated nanosystem

3.4.1 Fabrication of integrated nanostructure

Silicon (Si) nanowire arrays were fabricated using reactive-ion etching of patterned single-crystalline Si wafers. P-type boron-doped 4" Si wafers (<100> oriented, 0.1~0.2 Ω •cm) were first patterned with a photoresist dot array using a standard photolithography stepper. Then the wafer underwent inductive-coupled plasma deep reactive-ion etching (Surface Technology Systems, Inc.) to produce nanowire arrays with uniform diameter ~850 nm and length ~30 µm. After removing the residual photoresist by an O₂ plasma, 50 nm of dry thermal oxide was grown on the nanowires at 1050 °C for 40 min. After a 5:1 buffered HF etch and critical point drying (Tousimis, Inc.), Si nanowire arrays with wires whose diameters were about 800 nm were obtained.

To optimize the Si nanowire photocathode, a thin, highly doped n^+ layer was formed on the surface of the Si nanowires for enhanced photovoltage, similar to the approach reported in reference 24. A Si handle wafer was spin-coated with arseniccontaining spin-on dopant (SOD) (Filmtronics, Inc.) at 3000 rpm for 1 min and then baked at 150 °C on a hotplate for 30 min. This handle wafer was used as a local arsenic source for proximity doping to form the n^+ layer on the silicon nanowire surface. The HFvapor treated Si nanowire substrate was then placed on the SOD-coated handle wafer and subjected to rapid thermal annealing at 900-1000 °C for 1-3 min in argon. The formation of an n^+ layer on the nanowire's surface was confirmed when the onset potential of the silicon nanowire photocathode shifted cathodically 150-250 mV as compared to that of the untreated nanowire photocathode; a similar result was reported in reference 24.

The synthesis of the Si/TiO_2 heterostructures combined the synthesis of the Si and TiO_2 nanowires, in which all components were compatible and retained their



Figure 3.3 Synthetic scheme for the Si/TiO_2 nanotree heterostructures, starting from a p-type Si nanowire array.

photoactivity. A detailed synthetic scheme is displayed in Figure 3.3. After fabrication of the silicon nanowire array as described above, a conformal polymer coating of parylene-N was applied at room temperature (Specialty Coating Systems, Inc.) to embed the n^+/p Si nanowire array. The polymer-coated array was then treated with an O₂ plasma to expose the top half of the Si nanowires. An aqueous solution of potassium hydroxide (20 wt%) was applied for 1-2 min to remove the n^+ layer on the top half of Si nanowires, resulting in asymmetric nanowire structures with p-type tops and n^+/p core-shell bottoms. A parylene coating was applied again to embed the nanowires in polymer and then etched by an O_2 plasma. To avoid reducing the shunt resistance between the n⁺ Si layer and the ohmic contact formed later between the Si and TiO₂, a gap was left between the first and second parylene etches. Then 5-10 nm of platinum was sputtered onto the substrate (Edwards, Inc.) and a seed layer for TiO₂ nanowire growth was deposited either by atomic layer deposition or by vacuum sputtering before being treated with rapid thermal annealing at 400 °C for 15 sec in argon. After removal of the residual parylene polymer by either an O₂ plasma or annealing in O₂ at 450 °C for 30 min, the nanowire substrate was then used for hydrothermal TiO₂ nanowire synthesis to produce the Si/TiO₂ nanotree heterostructures after a subsequent 450 °C anneal for 30 min.

3.4.2 Measurement setup for overall solar water splitting

For optimization of the individual components of the nanotree heterostructures, photoelectrochemical measurements of individual electrodes were performed using a Gamry reference 600 potentiostat. All measurements were performed under an inert helium environment and in a 0.5 M sulfuric acid electrolyte (pH = 0.52). Ag/AgCl in 3 M NaCl (ALS, Corp.) was used as the reference electrode when needed, and all voltages reported were calculated *versus* the reversible hydrogen electrode (RHE) using the following equation:

V vs RHE (volt) = V vs Ag/AgCl (volt) + 0.234 (volt)

The light source used for simulated sunlight in this report was a 300-Watt xenon lamp equipped with an air mass 1.5G filter (Newport). Before each measurement, a calibrated silicon photodiode determined the light intensity at the position of the electrode being measured. All photoresponses were measured right after the cocatalyst loading procedures described above.

The J-V photocurrent data for individual photoelectrodes were measured using a standard three-electrode setup under simulated one-sun illumination, with a scan rate of 10 mV/sec. The dark currents were orders of magnitude lower than photocurrent in all cases within the voltage ranges measured.

The short-circuit measurements of externally wired Si and TiO_2 nanowire electrodes were performed using a two-electrode setup, in which the potentiostat remained short-circuited and behaved as an ammeter. The two photoelectrodes were in the same reaction chamber and placed side by side in the region of light exposure.

To measure the amount of gas evolved in the photoelectrochemical process, the system was designed as a batch reactor in a helium environment. A bubbler purged the electrolyte in the reactor to bring the evolved gases into a gas chromatograph for analysis. After that, the gas was fed back into the reactor via a recirculation pump. The gas chromatograph (SRI Instrument, Inc.) was equipped with a molecular sieve 13X packed

column and a helium ionization detector. Before each reaction the system was calibrated with H_2 and O_2 gases of known concentration.

In order to test the photoactivity of the Si/TiO₂ nanotree heterostructures, a similar system as the one used for externally wired electrodes was applied, except that there were no ports for the electrodes. After loading of the cocatalysts, Si/TiO₂ nanowire heterostructures were removed from the substrate and dispersed in electrolyte. The dispersion was loaded into the reactor and exposed to simulated sunlight after constant gas purging to remove O_2 in the reactor. After every 90 min while the photocatalytic reaction continued, the system was purged with helium to remove evolved gas product. A schematic of the circulated batch reactor is shown in Figure 3.4.

3.5 Unassisted solar water splitting of integrated

nanostructure

As described in previous section, we synthesized the nanotree heterostructure that combines the optimized photocathode and photoanode. Figure 3.5a shows a scanning electron microscope (SEM) image of a large area of the substrate that contains many nanotree heterostructures with Si nanowire trunk and TiO_2 nanowire branches. We prepared silicon nanowire arrays by the reactive ion etching (RIE) process(26) since it is



Figure 3.4 Schematics of the circulated batch reactor for the measurement of overall solar water splitting with in-line gas chromatography detection of H₂ and O₂.



Figure 3.5 Structural characterization of the nanotree heterostructures. **a**, Falsecolored, large-scale SEM image of a Si/TiO₂ nanotree array. **b**, Comparison of the optical images of a TiO₂ nanowire substrate, a Si nanowire substrate, and a Si/TiO₂ nanotree substrate. **c**, SEM image of the details of a nanotree heterostructure. **d** Magnified SEM image showing the large surface area of the TiO₂ segment used for water oxidation. The scale bars are 10 μ m (**a**) and 1 μ m (**c**, **d**).

readily available for wafer-scale fabrication, but the same process can also be applied to Si nanowires prepared by vapor-liquid-solid (VLS) growth(24) or electroless etching(25). As shown in Figure 3.5b, a uniform and large-scale array of nanotree heterostructures can be synthesized. The color of the nanotree array combines the white scattering of TiO_2 nanowires and the visible-light absorption of the silicon nanowire array. Closer examination of an individual nanotree (Figure 3.5c) shows a core-shell heterostructure with the photoanode of TiO_2 nanowires on the top and a photocathode of Si nanowires on the bottom. The high surface area of the TiO_2 nanowires (Figure 3.5d) provides abundant reactive sites for the sluggish O_2 evolution. The Si nanowire embedded underneath the TiO_2 nanowire photoanode provides an ohmic contact for recombination of majority carriers and serves as a charge collector, which takes advantage of the high carrier mobility of single-crystalline Si nanowires. As a fully integrated nanosystem, the whole nanotree heterostructure captures all the essential features of natural photosynthesis.

Solar-driven water splitting without any applied bias is achieved under simulated sunlight using the nanotree heterostructures. Figure 4a displays the evolution of H₂ and O₂ gases from the Si/TiO₂ nanotree heterostructures dispersed in electrolyte. The 2:1 stoichiometry between H₂ and O₂ confirms the water-splitting photoactivity, and the linear increase of gas concentrations (2.1 and 1.1 µmol/hr for H₂ and O₂ from 2.4 mg of nanotree heterostructures) reveals stable catalytic performance. Since no direct water splitting is observed from dispersions of Si nanowires, TiO₂ nanowires, or their mixture (see Supplementary Information), the solar-driven water splitting does result specifically from the integrated nanosystem design. Additionally, system-level optimization(*10*) for the nanotree heterostructure is carried out. Because of the current-matching requirement in a "Z-scheme" system, the overall rate of water splitting is limited by the photoelectrode that produces the smaller photocurrent output(*3*). By varying the percentage of the nanotree's length that is TiO₂, an optimized water-splitting photoactivity can be found. Figure 4b compares the experimental results of nanotree



Figure 3.6 Solar-driven water splitting of the nanotree heterostructures. **a**, The evolution of H_2 and O_2 gases measured by gas chromatography under simulated sunlight of 150 mW/cm² (1.5 suns). Nanotree heterostructures were dispersed in 0.5M H_2SO_4 solution. After every 90 minutes of measurement, the gas in the reactor was purged and refilled with helium. The 2:1 ratio of H_2 versus O_2 confirmed the watersplitting reaction. **b**, Measured energy conversion efficiency of suspensions of nanotree heterostructures (left axis) with different percentages of TiO₂ covering the Si nanowires. The estimation for the normalized relative photoactivity of the nanotrees (right axis) is displayed for comparison (yellow curve).

water splitting activity at different TiO₂ percentages (see Supplementary Information), with the estimation based on the J-V data of the separate Si and TiO₂ nanowire photoelectrodes in Figure 2b (see Supplementary Information). As expected, both data sets show the best performance from a geometry in which TiO_2 is 50 ~ 80% of the heterostructure's total length. The optimized nanotree geometry allows these heterostuctures to reach an energy conversion efficiency of 0.12% under simulated sunlight, which is comparable to that of photosynthesis in plants(6, 9). The weightnormalized photoactivity of the nanotree heterostructures (about 875 µmol/hr H₂ for 1 gram of material) is higher than that for both electrode and powder approaches (see Supplementary Information), demonstrating that the nanotree heterostructures use less material to achieve comparable photocatalytic performance. Future improvements in the material quality and the synthetic methods, along with using earth-abundant cocatalysts(12, 26), would make this nanotree material more efficient and cost-effective. Also an ion-conductive membrane could be incorporated between the silicon nanowires and the TiO₂ nanowires to realize macroscopic separation of H₂ and O₂(7, 30, 31). These integrated nanostructures reported here clearly demonstrate the possibility of integrating material components into a functional system that mimics the nanoscopic integration in chloroplasts. The system design principles in this work also provide a conceptual blueprint towards better solar-to-fuel energy conversion efficiency using a modular approach, where newly discovered components can be readily plugged in.

3.6 Conclusion

From both a scientific and social viewpoint, the conversion of solar energy into fuels has become one of the important topics that people are trying to address. By taking the advantage of large surface area and effective charge collection, nanowire could be applied as efficient building blocks for a fully integrated system of solar-to-fuel conversion. In this chapter, it is shown that precise control of the construction and optimization for nanowire-based structures could be achieved. The idea of nanowirebased structure demonstrates an advance to mimic the natural photosynthesis by spatially control the whole photosynthetic process at microscopic level, at the same time achieving a solar-to-fuel conversion efficiency comparable to that of natural photosynthesis. Based on such concept, further performance improvement could be achieved when advanced building blocks of artificial photosynthesis are developed. The building blocks include advanced elecrocatalysts to reduce the overpotential of charge transfer at electrode interface, and advanced semiconductor light-absorbers that could generate increased photocurrent output with reduced cost. Both directions will be presented later in this thesis.

3.7 References

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Chapter 4

Developing Advanced Integrated Nanosystem

Electrocatalysts for

4.1 Introduction

In previous chapters (Chapter 2 and 3) the focus of my graduate research is to achieve integration at nanoscale for artificial photosynthesis, via using nanowire-based heterostructures under the "Z-scheme". Applying such a intergrated nanostructure, overall solar-to-fuel conversion efficiency comparable to that of natural photosynthesis had been achieved(I). For improved performance based on such an integrated concept, advanced building blocks, including electrocatalysts and semiconductor light-absorbers, should be developed. In this chapter, some of my graduate studies for advanced electrocatlyst building blocks are described.

One of the issues during the solar-to-fuel process is the sluggish kinetics of the hydrogen evolution reaction (HER) at the semiconductor surface, which requires the incorporation of a co-catalyst material on the surface to reduce the reaction overpotential(2). Among the various co-catalyst materials, noble-metals such as Pt have been shown to provide the highest electrochemical activity towards the HER. However, the high cost of precious metal co-catalysts limits the economic viability of an artificial photosynthesis scheme. As elaborated in the following, there are two approaches to tackle such issue. One approach to reduce the co-catalyst cost is to dramatically reduce the loading of Pt on the electrode surface, while maintaining sufficient catalytic activity for the chemical reaction(3); On the other hand, alternate co-catalyst materials based on earth-abundant elements should be explored to reduce the costs associated with the use of Pt for solar-to-fuel applications(4-8).

4.1.1 Reducing the use of precious metal electrocatalyst

The first approach to reduce the co-catalyst cost is to dramatically reduce the loading of Pt on the electrode surface, while maintaining sufficient catalytic activity for the chemical reaction(3). Additionaly, the required catalytic activity for a given overpotential could be further reduced via the use of high surface area photoelectrodes(9). In particular, one dimensional semiconductor microwire and nanowire (NW) arrays are being explored for solar-to-fuel applications(10, 11) owing to a large semiconductor/electrolyte interfacial area, in addition to other beneficial properties including enhanced light scattering and trapping(12-14) and efficient transport of charge carriers to the electrodes(15, 16). However, the ability to coat these high-aspect ratio structures with a uniform coating of co-catalyst particles remains challenging using

traditional deposition techniques such as electrodeposition or physical vapor deposition, which can lead to a poor utilization of the expensive Pt material(17). Therefore, a technique is needed to uniformly coat the surface of high aspect ratio structures with precise control of the catalyst loading and size to minimize the overall raw material cost. One technique which meets this requirement is atomic layer deposition (ALD)(18). ALD is a modified chemical vapor deposition (CVD) technique capable of conformal coating of ultra-high aspect ratio structures with sub-nm precision in material thickness due to self-limiting surface reactions and the separate introduction of material precursors in a cyclic manner. While many ALD processes lead to the formation of a dense thin film, certain reaction chemistries result in nucleation of isolated islands on the growth surface, which grow larger with increasing ALD cycle number and eventually coalesce into a film. This process has been explored for direct deposition of catalysts(19) and quantum dots(20) with diameters below 10-nm on nanostructured surfaces.

As shown in this chapter, by using a Si NW array photocathode as a model system with large surface area, we demonstrated that ALD of Pt nanoparticles can serve as an efficient co-catalyst for photoelectrochemical water reduction utilizing as little as 1 cycle of ALD(3). Pt nanoparticles with diameters ranging from 0.5-3 nm form during the initial 3 ALD cycles, leading to a uniform catalyst loading along the length of NW with a sub-monolayer Pt surface density. Electrochemical and photoelectrochemical measurements demonstrate that the HER catalytic activity of these Pt clusters on high surface area nanowire photoelectrodes is stable and sufficient for solar-to-fuel applications. The combination of highly uniform coating and precise control of nanoparticle size and loading in the ALD process is a powerful tool which can take advantage of the benefits of the NW geometry while minimizing the total volume of Pt required.

4.1.2 Alternative earth-abundant electrocatalyst

The second approach to reduce the cost of electrocatalyst for solar-to-fuel conversion is to develop alternate co-catalyst materials based on earth-abundant elements(4-8). Various materials have been explored as HER catalysts, including alloys(21), nitrides(22), borides(23), carbides(23), chalcogenides(6, 24, 25), and phosphides(26). Nevertheless, most of these catalysts were reported to function in strong acidic media. There is a strong need for HER catalysts composed of earth-abundant elements to work in neutral aqueous media. It will avoid the use of acids and potentially make the catalysts compatible with biological systems. Based on such logic, we extended our interests to heterogeneous electrocatalysts composed of first-row row transition metals for HER catalysis in neutral aqueous media. In the rest of the chapter it is shown that we are capable to use cobalt sulfide as an earth-abundant HER electrocatalyst, which is synthesized by electrochemical deposition. This catalyst exhibits a catalytic onset overpotential (n) of 43 mV, a Tafel slope of 93 mV/dec, and nearly 100% Faradaic efficiency in pH 7 phosphate buffer. The facile preparation also allows it to be easily coated on semiconductors, resulting in a water-compatible system for PEC hydrogen evolution under simulated one-sun irradiation.

4.2 Ultra-low Pt loading for proton reduction via ALD techniques

P-type Si NW arrays were selected as a photocathode material due to a suitable conduction band edge with respect to the HER potential and a sufficiently low bandgap for visible light absorption(2). The well-defined NW arrays (Same as shown in Figure 3.2) provide a high surface area structure suitable for quantitative analysis. То achieve a positive photovoltage and stabilize the Si surface, a p-Si/TiO₂ core-shell structure was formed by ALD of 10-12 nm TiO₂ on the nanowire surface, which was followed by deposition of Pt by ALD(27).

The morphology of the core-shell p-Si/TiO₂ NWs loaded with Pt NPs was observed using aberration-corrected scanning transmission electron microscopy (STEM), as shown in Figure 4.1. Nucleation of sub-nm scale islands on the NW surface was observed after only 1 ALD cycle (Figure 4.1c). A low-magnification STEM



Figure 4.1 STEM analysis of Pt nanoparticles deposited on core-shell Si-TiO2 NWs by ALD. HAADF images of (a) 10 cycles (b) 3 cycles and (c) 1 cycle of ALD Pt. (a) Low magnification image showing core-shell structure coated uniformly with Pt nanoparticles. (d) Histogram of particle size for various cycle numbers.

analysis demonstrated the excellent uniformity of the ALD coatings along the length of the NW surface (Figure 4.1a). This was further confirmed by a high magnification STEM analysis at different regions of a NW coated by 1 cycle. A high-resolution image of a single 2nm Pt NP shows a crystalline phase with a d-spacing of 2.3 Å. A histogram of the lateral dimension of the islands based on several images is shown in Figure 4.1d. We measure an average particle diameter of 0.8 nm after 1 cycle, with a standard deviation of 0.25 nm. The size and density of the Pt particles on the surface can be seen to increase with increasing cycle number, showing the ability to control the Pt loading and particle size by simply varying the number of ALD cycles. We note that the STEM images over-represent the absolute value of surface particle density due to the curved surface of the nanowires, and the fact that we observe nano-clusters on both sides of the nanowire in the image.

To provide a more quantitative measure of surface coverage, total-reflection x-ray fluoresecence (TXRF) was performed on a planar Si wafer coated with the same ALD conditions. After 1 cycle ALD of Pt, the surface coverage was measured to be 4.0 ± 0.5



Figure 4.2 Electrochemical performance of Pt co-catalyst loaded via ALD in 0.5M H_2SO_4 electrolyte. (a) Linear sweep voltammetry and (b) Tafel plots of ALD Pt with various cycles on FTO substrate coated with 12 nm TiO₂.

 $\times 10^{13}$ cm⁻², which corresponds to a surface density of about 2.7% compared to the Pt (111) surface (1.5 x 10¹⁵ cm⁻²), and a platinum mass loading of approximately 10 ng/cm², which is consistent with the STEM analysis. Therefore, while the atomic-scale distribution of Pt atoms on the surface is not homogeneous due to the formation of Pt clusters, the co-catalyst loading via ALD is in the deep sub-monolayer level. Furthermore, from shallow-angle x-ray photoelectron spectroscopy (XPS) measurements, an increase in the peak intensity can be observed with increasing the number of ALD cycles, showing an approximately monotonic increase in the Pt loading with increasing cycle number. Achieving these low levels of Pt loading uniformly over a high-aspect ratio surface would be extremely difficult by standard Pt deposition techniques, allowing us to efficiently explore the lower limits of Pt loading for catalytic activity of the HER reaction.

The electrocatalytic performance of the Pt NPs was tested using planar fluorinedoped tin oxide (FTO) substrates as an electrode. 12 nm of TiO₂ was first deposited on the FTO surface, followed by Pt of varying number of ALD cycles to replicate the conditions on the *p*-Si nanowires. The catalytic performance was measured using linear sweep voltammetry in 0.5M H₂SO₄ electrolyte with series resistance subtracted, under a standard three-electrode configuration. The measured onset of cathodic current for a potential negative of 0V vs. the reversible hydrogen electrode (RHE) (Figure 4.2a) and the observed formation of gas bubbles at high current density imply catalytic activity for the HER. With an increasing number of Pt ALD cycles the cathodic currents increase, consistent with the confirmed increase of Pt loading amount. From the Tafel plots shown in Figure 4.2b, all samples exhibit a current slope of about 60 mV per decade, and the apparent exchange current densities for substrates of different ALD cycles were obtained.

The data presented in the section indicates that the Pt loading for HER could be fine tuned at sub-monolayer level. The corresponding electrochemical HER activities are measured. This allows us to apply this technique on high surface-area nanowire PEC electrodes to determine the lower limit of Pt loading for solar-to-fuel conversion process.

4.3 Cobalt sulfide as an earth-abundant electrocatalyst for proton reduction

Although cobalt has been shown to promote the catalytic HER performance of molybdenum sulfide film prepared by electrodeposition in acidic media(28), scarce work has been devoted to cobalt sulfide itself as a HER catalyst. particularly in neutral aqueous media(29). The only precedent of electrodeposited CoS was used as a counter electrode for dye-sensitized solar cells(*30*). Using fluorine-doped tin oxide (FTO) as both working and counter electrode, cobalt sulfide deposited on FTO was electrochemically via cyclovoltammetric under a conventional scans. threeelectrode setup. Ag/AgCl reference electrode is applied and the electrolyte



Figure 4.3 SEM images (**a** and **b**) and typical EDX histogram (**c**) of annealed CoS/FTO.

contains 5 mM CoCl₂ and 0.5 M thiourea. 15 consecutive scans is typically used in a voltage window between -1.2 V and 0.2 V vs Ag/AgCl, with a scan rate of 5 mV/sec. During the deposition process, the exposed area of the transparent FTO working electrode in the electrolyte turned dark and became nearly black at the end of deposition. The scans of a typical potentiodynamic deposition of CoS film are shown in Figure S2 of reference (7). After thoroughly rinsed with copious water and acetone, the dried CoS/FTO electrode was annealed at 300 °C under argon for 2 h. Figure 4.3 displays the scanning electron microscopy (SEM) of the annealed CoS film showing its morphology with cracks. The presence of Co and S in the film was identified by energy dispersive x-ray spectroscopy (EDX) (Figure 4.3c) and further confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES). It is worth noting that the Co/S ratio maintains at ~1.4 for both of the as-prepared and annealed CoS films. The Co/S ratio of 1.4 indicates the original composition of the film is not purely CoS, but likely contains CoO/Co(OH)2 as well. This is also confirmed by the x-ray photoelectron spectroscopy (XPS) data. It should be noted that the 2 h annealing under argon does not alter the oxidation states of either Co or S, given the similarity of the XPS spectra of the film before and after annealing.

It appears that the annealed CoS film is a competent HER catalyst as illustrated in Figure 4.4. In a neutral phosphate buffer when employing CoS/FTO as the working electrode, a catalytic current takes off at an onset overpotential of 43 mV accompanied with hydrogen bubbles evolving on the electrode surface. The catalytic current density approaching nearly 50 mA/cm² at η = 397 mV. In contrast, the blank FTO electrode does not exhibit appreciable current density until scanning to more negative potentials than η = 500 mV under the same condition. The Tafel plot of the CoS film is included in the inset of Figure 4.4a. Linear fitting in the region of η = 50 – 110 mV results in a Tafel



Figure 4.4 a, Polarization curves of annealed CoS/FTO (solid) after controlled potential electrolysis at = 287 mV for 3 hours and a blank FTO electrode (dotted) in 1.0 M KPi of pH 7 (scan rate: 5 mV/s). Inset: Tafel plot of the CoS/FTO electrode under the same condition (black dotted) and linear fitting curve (red solid) within η of 50 to 110 mV, rendering a Tafel slope of 93 mV/dec. **b**, Extended controlled potential electrolysis shows the accumulated charge versus time for annealed CoS/FTO (solid) and a blank FTO electrode (dotted) in 1.0 M potassium phosphate buffer of pH 7 at η = 187 mV. Inset: current versus time during the long-term controlled potential electrolysis of CoS/FTO (solid) and a blank FTO electrode (dotted).

slope of 93 mV/dec. This Tafel slope value does not match any of the three principle steps for hydrogen evolution, which would result in a Tafel slope of 29, 38, or 116 mV/dec. However, this 93 mV/dec slope is comparable to those of amorphous M-MoS₃ (M = Fe, Co, or Ni) films (86-96 mV/dec) at pH 7 (28).

The durability of the CoS film was further assessed in an extended long-term controlled potential electrolysis experiment. Still in a 1.0 M potassium phosphate buffer of pH 7, an external potential of $\eta = 187$ mV was applied. As depicted in Figure 4.4b, the catalyst affords a robust and essentially linear charge build-up over time, with no substantial loss in activity over the course of 40 h. In contrast, negligible charge was passed when a blank FTO electrode was used as the working electrode under the same condition. The slight current decrease during the first two hours of electrolysis may be due to surface reorganization, mechanical damage, or possible detachment of catalyst from the FTO surface. To estimate the turnover frequency (TOF) and turnover numbers (TON) for HER during the 40 h electrolysis, we assumed all of the loading catalysts contributed to the overall catalysis. Based on the ICP-measured catalyst loading (Co = 1.35 µmol/cm², Table S2), a TOF of 0.017 s⁻¹ and a TON of 2420 per cobalt center were calculated for this long-term bulk electrolysis. However, these values represent an underestimated activity of the CoS film, since only the surface active sites are expected to be responsible for catalysis.

The good activity and durability of cobalt sulfide represents a good candidate of HER co-catalyst for practical solar-to-fuel conversion at neutral pH electrolyte. In the next section, the application of such an earth-abudant electrocatalyst for solar hydrogen production was described, in the case of Si photocathode.

4.4 Integrating advanced electrocatalysts for solar-to-fuel conversion

As shown above, to reduce the cost of precious metal as electrocatalyst for solarto-fuel process, two distinct approaches have been explored. We had developed ALD of Pt to quantitatively control the loading amount of Pt down to ~10 ng/cm²; On the other hand we also had synthesized cobalt sulfide via electrochemical deposition as an earthabundant HER catalyst. Both approaches are promising to reduce the cost for artificial photosynthesis, and here we describe some tentative results to integrate these advanced HER electrocatalysts with a Si photocathode, a model material that could be used for the integrated nanosystem(1).

A well-defined large surface area Si NW array electrode was synthesized via gasphase deep reactive ion etching (DRIE) method (described in section 3.4.1). The PEC performance of these photocathodes was tested under the same condition as the above electrochemical measurement. It was empirically found that the thin TiO₂ interlayer was required to achieve positive photovoltages with these ALD Pt catalysts on the Si surface. A similar phenomenon has been observed in e-beam evaporated Pt catalysts on bare Si, which was attributed to the formation of an ohmic contact between Si and Pt, which determined the energetics of the Si-Pt-electrolyte interface(*31*). However, the presence of an intermediate TiO₂ barrier layer allowed for the observation of a characteristic photocathode *J*-V curve with as low as 1 ALD cycle, despite the ultralow Pt loading under these conditions. As shown in Figure 4.5a, the absence of Pt co-catalyst gives no photoactivity of the Si NW photocathode. For all samples measured, an onset voltage of 0.15-0.25 V vs. RHE and current densities of ~30 mA/cm² was observed under 100 mW/cm² simulated AM 1.5 irradiation.

Moreover, the slope of this J-V curve was seen to increase with increasing number of ALD cycles from 1 to 10, leading to an increase of the current density from 7 - 20



Figure 4.5 Photoelectrochemical performance of Pt co-catalyst loaded via ALD in $0.5M H_2SO_4$ electrolyte. **a**, H_2 evolution performance of Si NW array photocathode synthesized via gas-phase etching under 1 sun illumination, loaded with ALD Pt co-catalyst. **b**, H_2 evolution performance of Si NW photocathode via electroless etching, under the same condition as (**a**).

no. of cycles	surface Pt loading (ng/cm ²)	$j_0 (\mu A/cm^2)$	$j_{\rm sc} ({\rm mA/cm^2})^a$	
1	13 ± 3	27 ± 4	7.1	
2	24 ± 5	59 ± 9	8.3 12.5	
3	34 ± 7	85 ± 10		
10	105 ± 21	130 ± 20	20.7	
^a Current der	sity at 0 V vs RHE.			

Table 4.1 Summary of electrochemical and photoelectrochemical performance of ALD Pt catalysts

mA/cm² at 0V vs. RHE, which are comparable to previous results for *p*-Si wires using standard Pt processing techniques(31). From the values of photocurrent density at 0V vs. RHE, the actual surface current density can be compared to the electrochemical data as a function of ALD cycles (Table 4.1). For each ALD cycle number and corresponding current density, a roughly constant overpotential of ~100 mV can be calculated from the electrochemical data. This indicates that the HER catalytic activity of the Pt atoms on the NW surface determines the slope of the J-V curve.

The result also illustrates an important balance between the required catalytic activity (and therefore raw material loading) of Pt, vs the surface area of a nanowire electrode structure. While the use of sub-monolayer quantities of Pt leads to an increased overpotential for a given current density compared to larger mass loadings, the use of nanostructured surfaces reduces the required catalyst loading by distributing the charge transfer reaction over a larger surface area. To further illustrate this point, the ALD TiO₂/Pt coatings were deposited on electrolessly-etched NW arrays (synthesis in Support Info) with a higher surface roughness factor than the gas-phase etched nanowires. Due to the high surface area of these structures, the J-V behavior of the arrays (Figure 4.5b) did not vary significantly even when the number of ALD cycles was reduced to 1. On the other hand, the electroless-etch nanowire arrays led to a decrease in photocurrent, which could be due to increased surface recombination for these larger surface areas. Therefore, while further decreasing the NW diameter may decrease the catalyst loading and material purity requirements due to an increased surface area and decreased minority carrier diffusion length requirement, an optimization exists after which point additional surface area will begin to detrimentally affect the performance of NW array photoelectrodes.

Besides reducing the Pt loading via ALD techniques, we can also try to integrate the electrochemically deposit CoS on Si photocathode to assemble a system for PEC hydrogen evolution. Figure 4.6a compares the photocurrent densities of the n^+/p -Si electrodes coated with CoS which were prepared by different cycles of potentiodynamic deposition. Indeed, the presence of CoS significantly enhances the photocurrent densities of the planar n^+/p -Si electrodes under simulated one-sun irradiation in pH 7 buffer. With increasing cycles from 2 to 6, the photocurrent density rises from ~1 to ~11 mA/cm² at 0 V vs RHE, and the onset also shifts to ~320 mV vs RHE. It should be noted that further increase in preparation cycles of CoS deposition does not improve the photocurrent response, probably due to the diminishing light absorption of Si coated by the catalyst film which itself absorbs a wide range of the solar spectrum (Figure 4.6b). Indeed the application of CoS onto Si nanowire array electrodes leads to a photocurrent density less than 1 mA/cm² for 2 cycles of electrodeposition. This emphasizes a very important piece of message for an integrated nanostructure: the introduced electrocatalyst should not



Figure 4.6 a, Polarization curves of CoS deposited on planar n^+/p -Si photoelectrodes with different preparation cycles in 1.0 M potassium phosphate buffer of pH 7. Light source: 100 mW/cm² AM 1.5 G illumination via a 300W Xenon lamp. Scan rate: 10 mV/s. **b**, Absorbance of electrodeposited CoS film on FTO with different cyclic voltammetry cycles between 0.2 V and -1.2 V vs Ag/AgCl

compete to absorb photons with the semiconductor light-absorber. These criteria should be noted for future design of the integrated nanosystem for artificial photosynthesis.

4.5 Conclusion

In this chapter, some progress was introduced in the direction of developing advanced electrocatalysts for solar-to-fuel conversion, particularly proton reduction. Two distinct approaches were developed: (1) reducing the Pt loading amount via ALD techniques, and (2) developing earth-abundant cobalt sulfide electrocatalyst to replace Pt. Both approaches yields desirable electrochemical performance of the corresponding electrocatalysts, however different effects showed up when attempting to apply these HER catalysts onto a Si photocathode.

For the case of ALD techniques for reduced Pt loading amount, the results demonstrated the ability to tune the catalytic activity of the Pt nanoparticles based on simply varying the number of ALD cycles, while maintaining very low levels of Pt loading. For an affordable application of overall water-splitting by coupling two light-absorbing semiconductors, a current density on the order of 10 mA/cm² is expected(2). The photocathode of 1 cycle ALD Pt provides a current density about 7 mA/cm² at 0V vs. RHE, indicating that ALD Pt for co-catalyst loading is applicable for an affordable integrated water-splitting system.

For cobalt sulfide for hydrogen generation at neutral pH, appealing HER activity was observed. However when applying CoS onto Si photocathode, the strong absorption of electrocatalysts prevented the use of high surface-area nanowire electorde, and the resultant photocurrent is not as high as expected even on planar photoelectrode. This delivers the note that a transparent or weakly-absorbing layer of electrocatalyst should be preferred for an integration solar-to-fuel device, and further improvement is needed for those sulfide-based transition metal electrocatalysts.

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Chapter 5

Developing Advanced Semiconductor Lightabsorbers for Integrated Nanosystem Part I: III-V Semiconductor Nanowires via Solution Phase Synthesis

5.1 Introduction: advantages of solution-processable

semiconductor light-absorbers

Compared to other available semiconductors, III-V semiconductors, including gallium phosphide (GaP)(1, 2) and indium phosphide (InP), are considered highly promising photocathode materials for solar-fuel conversion(3-5). The large photovoltage enables it to be coupled with photoanode materials for complete water-splitting under zero external bias, and its high conduction band edge (for example, -0.6V vs. NHE at pH = 0 for GaP) (6) allows it to reduce not only water into hydrogen (0V vs. NHE)(7-10) but also CO₂ into chemical fuels (-0.17V vs. NHE to generate CH₄) (11, 12) with incident photon-to-current efficiency (IPCE) up to 30% at 400nm (10); however, the conventional planar geometry from a single-crystalline wafer is not ideal for inexpensive or large-scale processing. It also poses an obstacle to exploring the potential of III-V semiconductors fully. Take GaP as an example, in the planar geometry most of the photons absorbed by GaP (9, 10, 13, 14) do not fall within the charge collection layer, as is required for an efficient photoelectrode (15).

Recent progress indicates that this issue could be solved when the photoelectrode is composed of semiconductor micro- or nanowires (16-20). Compared to a planar electrode, the larger surface area and relative band-bending volume of a wire geometry not only allows more efficient charge separation but also reduces the current density and therefore the overpotential at the surface (21, 22). These advantages, properly applied to III-V semiconductor light-absorbers, could lead to higher charge separation efficiency.

So far, synthesis of III-V semiconductor NWs is dominated by high-temperature vapor-phase approaches (23-27), which generally suffer from the scalability problem. In contrast, solution-based synthesis of colloidal NWs may be readily scaled up (28-30) but often requires use of organic surfactants/ligands to achieve desired morphology control (31-36), which necessitates additional efforts to remove the organic molecules covalently bound to nanostructure surfaces before they can be used for solar water splitting. In this chapter, to address the absence of synthesis approach for III-V semiconductor, we took GaP as a model material system to start with, and described a surfactant-free, self-seeded, solution-liquid-solid (SLS)(37, 38) approach to grow high-quality GaP NWs on a large



Figure 5.1 Proposed nanowire-based mesh concept for solar-to-fuel conversion, from the point of the systems materials engineering.



Figure 5.2 Synthesis and purification of colloidal GaP nanowires. The NWs are grown by a surfactant-free, self-seeded, solution-liquid-solid (SLS) method in squalane.

scale. To the best of our knowledge, this is the first time that colloidal semiconductor NWs have been grown by a SLS method in the absence of surfactants/ligands, which allows us to demonstrate visible-light-driven hydrogen production from water reduction using these as-made NWs.

In a bigger picture, the introduction of scalable solution synthesis approach for III-V semiconductors offers new design concept for the nanowire-based integrated system. The solution-dispersed nanowires could be applied as a unique building block to affordable solution-processed solar-to-fuel devices, for example the nanowire-based mesh concept shown in Figure 5.1 (39). In this concept, solution-dispersed nanowires of photocathode and photoanode materials are contacting with each other through the microscopic interfaces among them, which function as an ohmic contract based on the "Z-scheme". The effort described in this chapter is in consistent with the theme of my overall graduate research for integrated nanosystem in artificial photosynthesis.

5.2 Synthesis of surfactant-free gallium phosphide (GaP) nanowires

Our SLS syntheses of GaP NWs used triethylgallium (TEG) tris(trimethylsilyl)phosphine and (TMSP) as precursors. In addition, we used saturated hydrocarbons having high boiling points as noncoordinating solvents to synthesize straight GaP NWs. Squalane was empirically found to be the best solvent. The wire growth in squalane was found to be a selfseeded SLS process: the precursor first thermally decomposes in situ to generate Ga nanoscale droplets, which then subsequently promote the growth of GaP NWs via the SLS mechanism (Figure 5.2).

In the absence of surface ligands, small Ga nanodroplets tend to grow rapidly and aggregate, resulting in highly tapered wires. To achieve better control over the wire growth, synthetic conditions including the precursor ratio, concentration and stirring were optimized. In a typical synthesis, the Ga and P precursors (molar ratio of 1:1) were quickly injected into hot squalane solvent at 290



Figure 5.3 GaP nanowires synthesized using a surfactant-free, self-seeded solution-liquid-solid method. (a) and (b) Low- and high-magnification TEM images of as-prepared wires; (c) HRTEM image of a single nanowire, the inset shows the indexed fast-Fourier-transform (FFT) pattern of the image, indicating that the wire grows along the [111] direction; (d) TEM image of GaP nanowires after treatment in 1 M hydrochloric acid solution.

°C. The mixture was vigorously stirred for 30 seconds to form a homogeneous solution. After stirring was stopped, the color of the solution changed to yellow in 15-20 seconds due to the generation of Ga nanodroplets and then quickly to dark brown as the NWs grew. We note that although the initial precursor ratio was 1:1, the P precursor was in slight excess during wire growth because a portion of the Ga precursor was first consumed to generate Ga nanoparticles. The product yield reached ~80% at optimized conditions.

Representative low- and high-magnification TEM images of the as-synthesized GaP NWs showed that the wires were relatively uniform, having length of ~1-2 μ m (Figure 5.3a) and diameter of ~30 nm (Figure 5.3b). Detailed TEM study showed that the wires were slightly tapered at the nanoparticle-free end (Supporting Information, Figure S2), indicating that the initially generated Ga nanoparticles grew during the wire growth until a steady state was achieved. The single-crystalline nature of the NWs was

clearly seen in a lattice-resolved high-resolution TEM (HRTEM) image (Figure 5.3c). The fast-Fourier-transform (FFT) pattern of the image was indexed to the zincblende structure (inset, Figure 5.3c) and indicated a [111] wire growth direction. The spacing of the lattice fringes perpendicular to the growth direction was measured to be 0.316 nm, consistent with the d spacing of (111) planes in zincblende GaP (JCPDS 12-0191). The zinc-blende structure of the GaP NWs was also confirmed by powder X-ray diffraction.



Figure 5.4 Photograph of a large GaP nanowire membrane on a PVDF filter membrane (white), a quarter-dollar coin in the image is for comparison.

To remove the viscous squalane solvent and any unreacted precursors and byproducts, the as-synthesized GaP NWs were thoroughly washed with toluene, methanol, and DI water in sequence. The purified wires could be readily dispersed in aqueous solutions. We next sought to effectively remove the Ga nanoparticles attached to NW tips without damage to the wires. Since Ga reacts with hydrochloric acid (2Ga + 6HCl \rightarrow 2GaCl₃ + 3H₂) while GaP does not (40), the purified GaP NWs were then dispersed in 1 M HCl with stirring. Bubbles were observed due to formation of hydrogen gas. TEM image after the HCl treatment (Figure 5.3d) showed that all Ga NPs were completely etched away and no diameter change of the NWs was noticed.

Our surfactant-free synthesis of GaP NWs can be easily scaled up. To demonstrate this, ~75 mg of purified, Ga-removed wires were prepared using 300 ml of squalane according to the general procedure described above and in Figure 5.2. A large NW membrane (Figure 5.4) was then made by filtration of an aqueous NW suspension through a commercial PVDF filter membrane.

5.3 Fine-tuning doping properties of GaP nanowires from solution synthesis

For practical and large-scale fabrication of nanowire photoelectrodes, in general there are three major requirements. First, the synthesis of the material should be scalable and inexpensive. This condition implies that for GaP, solution-phase synthesis(28) is potentially preferred to gas-phase synthesis(23) because of the small yield of the latter approach. Second, the surface of the nanowires should be free of insulating organics that hinder charge transfer across the semiconductor-electrolyte interface, so conventional solution synthesis that often requires surfactants/ligands(41, 42) is not desirable. Finally, the electrical properties of the synthesized nanowires should be tunable. The advantages of nanowire photoelectrodes will diminish unless their diameter, doping level, and minority carrier diffusion length can be systematically controlled(21, 43). Although doped semiconductor nanocrystals(44) and nanowires(45, 46) from solution-phase



Figure 5.5 Structural and optical properties of Zn-doped GaP nanowires (0.19 at% Zn vs. Ga). (a) TEM image of a Zn-doped GaP nanowire after the removal of Ga droplets. (b) HRTEM image indicates that the nanowire is single-crystalline and grows along the <111> direction. (c) SEM image of the same nanowires when prepared as a photoelectrode by drop casting (64 μ g/cm²). (d) Photograph of the GaP nanowire dispersion and GaP photoelectrode. (e) UV-vis absorption spectrum of GaP nanowires dispersed in acetone. The positions of the direct (E_{g, direct}) and indirect (E_{g,indirect}) band gaps of bulk GaP are shown. The absorption tail in longer wavelengths is due to the strong scattering of the nanowires.

synthesis have been reported, there have been no studies that correlate the electrical properties of solution-grown nanowires to their PEC performance.

Here it is shown that the electrical properties of GaP nanowires could be modified by in-situ Zn doping during their synthesis, which was based on the surfactant-free solution-liquid-solid (SLS) synthetic method developed above(*37*, *47*, *48*); p-type GaP nanowires of various doping levels were obtained. In principle this approach could also be applied to other semiconductor materials for the fabrication of large-scale photoelectrodes with high surface area.

The nanowires' growth follows a self-seeded SLS mechanism(47), in which Ga metal nano-droplets are first generated and then function as catalytic sites for further growth. Prolonged stirring after injection of the precursor helps the Ga nano-droplets merge with each other before the growth of the GaP nanowire takes place, therefore allowing control of the diameter of the nanowires. After growth, removal of the Ga nano-droplets by hydrochloric acid yields clean GaP nanowires.



Figure 5.6 Electrical properties of Zn-doped GaP nanowires (0.19 at% Zn *vs* Ga). (a) SEM image of a single-nanowire FET device. The source (S) and drain (D) are colored in yellow, and the top gate (G) is colored in pink. (b) Plot of the current within the nanowire channel (I_{DS}) vs. the gate voltage (V_g), indicating p-type conductivity ($V_{DS} = 1V$). (c) Open-circuit photovoltage measurements of the nanowire photoelectrode in pH 5.2 buffer under simulated one-sun conditions (AM1.5G). (d) Mott-Schottky measurement of a nanowire photoelectrode in pH 5.2 buffer. The intercept of the dashed line indicates the flat-band potential of the GaP nanowires.

To optimize the electrical properties of the GaP nanowires, a p-type shallow dopant, typically Zn(49), is necessary to control the acceptor concentration. Diethylzinc (DEZn) was added as the source of Zn(50) during the synthesis. Because of the weaker Zn-C bond strength (35 kJ/mol) as compared to that of the Ga-C bond (59 kJ/mol)(50), most of the DEZn decomposes into metallic zinc during formation of the metal droplets, yielding Ga-Zn alloy droplets that can catalyze the growth of the GaP nanowires. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was applied to determine the elemental composition of the resultant nanowires. Despite the fast decomposition of DEZn, only 5-10% of the zinc precursor added to the reaction was introduced into the GaP lattice during growth (Table 5.1). The Zn doping of GaP nanowires may occur from the Ga-Zn alloy droplets in a process similar to the incorporation of Al from metal droplets during GaAs growth, which results in Al_xGa_{1-x}As

nanowiskers (51). The concentration of Zn in GaP nanowires could be quantitatively controlled up to 2 atomic percent (at%) vs. Ga by changing the amount of DEZn (Table 5.1), while the nanowire geometry and optical absorption features of gallium phosphide were retained. Transmission electron microscope (TEM) and scanning electron microscope (SEM) images show that the nanowires' morphology remains the same upon Zn-doping (Figure 5.5a and 5.5c), and highresolution TEM (HRTEM) images (Figure 5.5b) reveal that the GaP lattice grows along the <111> direction with lattice spacing of 0.31 nm (48). The UV-vis absorption spectrum of a suspension of Zn-doped nanowires (Figure 5.5e) is the same as that of undoped nanowires(48), the implying that introducing Zn does not alter the band gap of GaP(13).

Several approaches were used to demonstrate the p-type behavior of the Zn-doped GaP nanowires (Table 5.1). Singlenanowire field effect transistors



Figure 5.7 GaP nanowires for hydrogen production under visible-light illumination. **a**, Hydrogen evolution as a function of illumination time for both as-made and Pt-loaded (2 wt.%) wires (1 mg) dispersed in methanol-water solution (1:5 by volume, 3 ml). The visible light was obtained by placing a 400-nm longpass filter in front of a 450 W Xe lamp. **b**, HRTEM image of a Pt-loaded (5 wt.%) GaP NW. **c** & **d**, HRTEM images of GaP NWs before (**c**) and after (**d**) visible-light illumination for 18 hours.

(FET) were constructed to determine the carrier type and concentration (Figure 5.6a). For a 0.19 at% Zn-doped GaP nanowire (Figure 5.6), the negative transconductance (I_{DS}/V_g) was measured to be -4.5 nA/mV at $V_{DS} = 1V$, which corresponds to an acceptor concentration of 1×10^{19} cm⁻³. This measured acceptor concentration corresponds well with the 0.19 at% zinc concentration (equivalent to 4×10^{19} cm⁻³) from elemental analysis, implying that the included Zn does contribute to p-type behavior of the GaP nanowires. In addition, open-circuit photovoltage and Mott-Schottky measurements were performed to test the band bending at the semiconductor-electrolyte interface (Figure 5.6c and 5.6d). Larger open-circuit photovoltage (up to 280 mV) was found for Zn-doped GaP nanowires (Table 5.1), indicating that the increased acceptor concentration prevents full depletion of the nanowire and allows a barrier of greater height to form at the semiconductorelectrolyte interface. Besides the p-type behavior, the Mott-Schottky measurement gives the flat-band potential of GaP nanowires at around 0.52 V vs. the reversible hydrogen electrode (RHE), which is consistent with the literature on planar substrates(*6, 12*). Overall, the photovoltage and Mott-Schottky measurements that these Zndoped GaP nanowires possess desirable band bending at the semiconductor-electrolyte interface to act as a photocathode for hydrogen evolution.

5.4 Photocatalytic performance of GaP nanowires

5.4.1 Solar H₂ production when using a hole-scavenger

The capability of our GaP NWs to drive hydrogen evolution from water reduction under visible-light illumination at neutral pH was demonstrated by gas chromatography (GC) (Figure 5.7a). Methanol was used as hole-scavenger. Using 1 mg of GaP wires, hydrogen was produced at a rate of ~9 nmol/h. In a control experiment conducted in the absence of NWs, hydrogen was not detected. HRTEM images before (Figure 5.7c) and after (Figure 5.7d) 18-hour GC measurement under continuous illumination confirmed that there was no noticeable change of the wire surfaces, indicating that our GaP NWs were stable under the GC measurement conditions investigated.

It's well known that surface-bound electrocatalysts can significantly improve the water splitting performance of semiconductors.(15). As a proof-of-concept, we photochemically deposited small Pt nanoparticles onto the GaP NW surfaces using H_2PtCl_6 precursor dissolved in a methanol-water solution. The size of the deposited Pt NPs was found to be related to the Pt loading amount (determined from the initial H_2PtCl_6/NW ratio) at fixed illumination conditions. Higher Pt loading amount yielded relatively larger Pt NPs. HRTEM of GaP NWs with 5 wt.% Pt loading (Figure 3b) showed 1-2 nm NPs anchored on the surface of a single wire. The spacing of the lattice fringes in a lattice-resolved NP was measured to be 0.22 nm, consistent with the *d* spacing of (111) planes in cubic Pt (JCPDS 04-0802). When the Pt loading amount was

DEZn/TEGa	D	Zn	NA	j _{ph}	Voc,ph	η
(%) ^a	$(nm)^{b}$	at% ^c	$(cm^{-3})^{d}$	$(\mu A/cm^2)^{e}$	$(mV)^{T}$	(%) ^g
0	25±5			11	145	75
0	89±24			23	195	81
1	90±27	0.19	4×10^{19}	29	220	
5	86±22	0.57	1×10^{20}	33	280	
10	93±33	0.98	2×10^{20}	61	247	79
15	91±29	1.3	3×10^{20}	43	226	
20	87±27	1.6	4×10^{20}	25	141	

Table 5.1 Photoelectrochemical performance of GaP nanowire photoelectrodes. ^a The molar ratio between diethylzinc (DEZn) and triethylgallium (TEGa) precursors in the SLS synthesis. ^b Average diameter of the GaP nanowires. ^c Atomic concentration of Zn dopant vs. Ga, measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). ^d Carrier concentration calculated from ICP-AES measurement ^e Photocurrent of nanowire photocathodes in pH 5.2 buffer at 0.1V vs. RHE, under simulated one-sun conditions (AM1.5G). ^f Open-circuit photovoltage of GaP nanowire photocathodes in the same conditions as for the photocurrent measurements. ^g Faradic efficiency of hydrogen evolution, measured by gas chromatography.

reduced to 2 wt.%, the deposited NPs could not be clearly imaged by TEM. However, Pt signals were detected by X-ray photoelectron spectroscopy, suggesting that only extremely small Pt clusters (<1 nm) were deposited at low Pt loading. GC measurements were also conducted using these Pt-loaded GaP NWs at the same conditions used for the as-made GaP NWs described above. The hydrogen production rate was significantly enhanced (up to ~40 nmol/h) using Pt-loaded GaP NWs at low Pt loading of 2 wt.% (Figure 5.7a). More systematic studies of GaP NW decorated with various water-reduction electrocatalysts are currently underway.

5.4.2 Photocathode fabricated from GaP nanowires

To test the photoelectrochemical performance of the doped GaP nanowires, a solution of nanowires was drop cast onto a conductive substrate. After annealing to improve the electrical contact between the substrate and the nanowires, a uniform electrode was obtained (Figure 5.5a). The volume of the nanowire dispersion applied



Figure 5.8 Photoelectrochemical performance of the GaP photocathode in pH 5.2 buffer. **a**, I-V scans of GaP nanowire (blue) and planar (yellow) photocathodes under chopped illumination. The illumination is simulated one-sun conditions (AM1.5G). The nanowire electrode is made of 0.98 at% Zn-doped GaP nanowire with loading amount of 64 μ g/cm². When close to 0 V vs. RHE, the planar electrode yields higher photocurrent density, mostly because of its greater thickness and increased depletion layer; however, it should be noted that the performance at more anodic regions (larger than 0.2V vs. RHE) is of greater importance because only in this region can the GaP photocathode be coupled with a photoanode to realize a complete water-splitting reaction without external bias(*3*, *4*) **b**, The correlation of photovoltage (blue) and photocurrent data was measured at 0.1V vs. RHE and normalized with the photocurrent of planar GaP electrode at the same bias. The photovoltage is measured as the difference of open-circuit potential between dark and simulated one sun illumination (AM 1.5G).



Figure 5.9 a, Comparison of the absorbed photon-to-current efficiency (APCE) spectra between GaP planar (blue) and nanowire (yellow) photocathodes of $64 \mu g/cm^2$ loading amount. **b**, APCE spectra of GaP nanowire photocathodes at different loading amounts. In both figures the GaP nanowires were doped with 0.98 at% Zn vs. Ga, and the spectra were measured at 0.1V vs. RHE under simulated one-sun conditions (AM1.5G).

during drop casting controls the thickness of the nanowire film. Typical loading amount was about 60 μ g/cm², which is about 1/3000 of the amount of material used in a planar wafer electrode (0.2 g/cm²). After preparation, the nanowire electrodes were tested in pH 5.2 buffer solutions under chopped, one-sun illumination (AM1.5G) using a conventional three-electrode configuration (Figure 5.8a, Table 5.1). For comparison, the performance of a single crystalline p-type GaP wafer was also examined under the same conditions. The planar p-type GaP electrode exhibits comparable photocurrent density with other reports (10, 12). All nanowire electrodes showed onset potentials at about 0.5V vs. RHE, consistent with the flat-band potential from the Mott-Schottky experiment (Figure 5.6d). Compared to other recently studied photocathode materials (for example, silicon (17)), this relatively anodic onset potential (0.5V vs RHE) is advantageous, potentially allowing GaP to couple with a wider selection of photoanode materials to realize complete watersplitting using two semiconductors photoelectrodes. Another noticeable feature is that the nanowire electrode shows much smaller transient photocurrent than the planar electrode (Figure 5.8a). Since the transient photocurrent arises from photogenerated carriers that accumulate at the semiconductor-electrolyte interface because of slow reaction kinetics or surface state traps(52), the nanowire electrode's small transient current suggests that its large surface area reduces its current density and required overpotential.

A systematic study was performed to investigate factors affecting the photoelectrochemical properties of the nanowires. Although all GaP nanowires studied generated cathodic photocurrent, larger diameter wires corresponded to larger photovoltages and higher photocurrent densities (Table 5.1). When keeping the diameter of the nanowires constant and increasing the doping concentration of Zn, an optimal doping level ($0.6 \sim 1$ at%) was achieved for the photoactivity of the GaP nanowires with



Figure 5.10 Schematic illustration of the electrostatics of a GaP nanowire in electrolyte with varying diameters and doping levels. *W* is the width of band-bending or depletion at the semiconductor-electrolyte interface, ΔV is the band-bending between the nanowire core and the interface, $E_{\rm fb}$ is the flat-band potential of GaP, and $E_{\rm F}$ is the Fermi level of the system. The nanowire of small diameter suffers small band-bending. Large diameter alleviates this issue however it was not completely solved until Zn was introduced.

average diameter of 90 nm (Figure 5.8b). For undoped nanowires of about 25 nm diameters, the relatively large depletion region width (~30 nm, calculated as planar abrupt junction with 0.5V barrier height) from low doping level (at most 10¹⁸ cm⁻³ based on FET data, Table 1) leads to complete depletion within the semiconductor. This depletion yields low photovoltage and photocurrent because of the reduced band bending at the semiconductor-electrolyte interface and the large ohmic resistance along the length of the wire (Figure 5.10)(21, 43). Larger diameter nanowires (~90 nm) alleviate this issue, but the depletion width is still too large until extra Zn dopant is introduced to increase the acceptor concentration and reduce the depletion region width (~10 nm for 10^{19} cm⁻³). Zn doping prevents the complete depletion of the nanowire, leading to a larger photovoltage (Figure 5.10). Additionally, a narrower band-bending region means a stronger electric field close to the semiconductor-electrolyte interface, yielding higher charge separation efficiency and photocurrent density (43). On the other hand, the introduction of dopants also increases recombination within nanowire, meaning that an excessively high Zn concentration would be detrimental for efficient charge separation. This trade-off leads to an optimal Zn concentration for the best photocathode performance, as observed in our current study (Figure 5.9b).

When the properties of GaP nanowires were optimized, the photocurrent density of Zn-doped GaP nanowires was about 85% to that of the single crystalline wafer at 0.1V vs RHE (Figure 5.8a). In addition, 80% Faradic efficiency of H_2 evolution was observed,

affirming that most of the photocurrent contributes to reduce protons (Table 5.1). Because a comparable photocurrent density was achieved while using much less material, these results demonstrate that solution-synthesized surfactant-free Zn-doped GaP nanowires are a promising photocathode material for water splitting.

Even though its photocurrent is only comparable to that exhibited by a planar GaP electrode (Figure 5.8a), the GaP nanowire photocathode has much higher charge separation efficiency, as could be seen from the APCE spectrum (Figure 5.9a). Closer examination of the APCE spectrum of the nanowire photoelectrodes with different loading amounts of nanowires shows that the APCE increases with reduced loading amount (Figure 5.9b) and reaches a maximum with less than a monolayer of GaP nanowires. This result indicates that charge transport to the electrode from nanowires lacking direct contact with the underlying substrate is difficult because of the semi-insulating native oxide at the GaP surface(53). By removing the necessity of charge transport through the nanowire/nanowire interface, the submonolayer of Zn-doped GaP nanowires reaches 57% efficiency at 400 nm (0.1V vs RHE) (Figure 5.9b). By improving the contact between wires, the overall photocurrent of the GaP nanowire films could be further improved.

5.5 Using GaP nanowires as building blocks for "Z-scheme"

As demonstrated above, GaP nanowires synthesized via SLS method is capable to function as photocathode for solar hydrogen evolution. As shown in Figure 5.8, GaP does



Figure 5.11 a, photocurrent generated when linking GaP nanowire photocathode with TiO_2 nanowire photoanode, in 0.5 M phosphate buffer solution (pH 5). 100mW/cm^2 simulated sun-light is the light source, realized by 300W Xenon lamp equipped with AM 1.5G filter. **b**, Comparison between the charge generated by the photocurrent, and charge transferred to evolved H₂ gas that is measured by gas chromatography. O₂ detection is not feasible owing to the comparatively large O₂ leakage of the reaction setup.
have enough photovoltage to couple with a photoanode material, TiO_2 for example, for unassisted solar-to-fuel conversion. In the following the idea of coupling a GaP nanowire photocathode and TiO_2 photoanode is tested.

The fabrication of GaP nanowire photocathode are described above, and the TiO₂ nanowire photoanode is synthesized according the procedure described in section 3.3. These two photoelectrodes are assembled same as the linked-electrode configuration in section 3.3, with GC in-line sampling to determine the amount of evolved H₂ and O₂. The results are shown in Figure 5.11. Non-zero photocurrent was observed when coupling GaP with TiO₂ nanowires (Figure 5.11a), and the charges generated from photocurrent corresponded well with the evolved H₂ observed by GC (Figure 5.11b). However the activity of the linked-electrodes are not high enough to get signal-noise ratio for O₂ detection, making the claim of solar water splitting inclusive. In spite of that incompleteness, the result shows that the III-V semiconductor nanowires synthesized via SLS method is a promising candidate for the integrated system of artificial photosynthesis.

5.6 Conclusion

Semiconductor nanowire photoelectrodes have the potential to be scaled up for practical conversion of solar energy to fuels. Gallium phosphide, a very promising material for both hydrogen evolution and CO_2 reduction(6, 15), has been tested as one example. Based on the requirements of scalability and a clean semiconductor-electrolyte interface, GaP nanowires of different diameters were synthesized by a surfactant-free solution approach via the SLS mechanism (48). The electrical properties of these nanowires were engineered by introducing p-type Zn dopant during the synthesis. Using only 1/3000 of the amount of GaP in a single crystalline wafer and a scalable dropcasting process for electrode preparation, the photocurrent density of the Zn-doped GaP nanowires was comparable to that of a single crystalline wafer, with higher APCE value over the spectrum. These findings not only demonstrate the advantage of nanowire electrodes but also enrich our understanding of nanowire photoelectrochemistry. Moreover, some preliminary experiment was performed to combine GaP nanowire photocathode with TiO₂ photoanode for unassisted solar water splitting. The versatility of the SLS synthesis (47), and the capability to control the electrical properties by introducing dopants during synthesis (50), suggest that our approach could be generalized to other III-V and II-VI semiconductors, and III-V semiconductor nanowires from solution phase synthesis could act as an advanced building block for the integrated nanostructures in artificial photosynthesis.

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Chapter 6

Developing Advanced Semiconductor Lightabsorbers for Integrated Nanosystem Part II: Plasmon-enhanced Photocatalytic Activity of Fe₂O₃ on Au Nanopillars

6.1 Introduction: plasmon-enhancement for soalr energy application

In this chapter one more approach to develop advanced building blocks of semiconductor light-absorbers for integrated nanosystem was described. Contrary to finding novel methods to synthesize promising semiconductor nanowires as shown in Chapter 5, it is also interesting to use available materials and apply nanostructures to extract more photocurrent output. One way to realize this is to take advantages of surface plasmon on metal surfaces. Here we demonstrate enhancing the photocurrent of iron oxide (hematite) photoanode by coating the semiconductor thin films on Au nanopillars(1). The enhancement can be attributed to the increased optical absorption originating from both surface plasmon resonances and photonic-mode light trapping, with a net enhancement as high as 50% was observed over the solar spectrum. This provides a general, widely applicable solution to concentrating light in the active regions of semiconductors. Such optical engineering methods are fully compatible with and independent to efforts on material quality optimization, which together can lead to improved performance of solar-to-fuel conversion in a nanowire-based integrated system.

As shown previously, for optimal optical absorption, it is desirable to use materials with smaller bandgap (e.g. Eg < 2.5 eV) so that the significant part in the visible range of solar radiation can be utilized(2). Hematite Fe₂O₃ has been identified an excellent candidate for photoanode in water splitting because it is earth abundant, cost-effective, photoelectrochemically stable, and most importantly, has the desirable band gap(3-9). Unfortunately, severe bulk recombination was reported in Fe₂O₃ so that only the charge carriers generated in a very thin layer (a few nanometers without bias (10) and tens of nanometers with bias (11, 12)) near the interface against the electrolyte can contribute effectively to the reactions on the surface of the Fe₂O₃ electrode. Plasmonic and photonic nanostructures have shown promises in manipulating and concentrating light in photocatalytic and photovoltaic devices, which can lead to enhanced photon absorption in the thin, effective layer of the semiconductors (13-18). Here we use arrays of Au nanopillars as dual functioning substrates—electrical contact and plasmonic coupler—to achieve enhanced efficiency of Fe₂O₃ photoanode. Compared to metal

nanoparticles that exhibit extremely confined localized plasmon resonances (17, 19, 20), the nanostructured continuous Au substrates sustain surface plasmon modes with much longer decay length of the evanescent fields (21). Therefore, pronounced enhancement can be achieved with the Au nanopillars buried under the Fe₂O₃ layer, avoiding issues such as metal-interfered chemical reaction processes and loss of incoming light shadowed by metal particles placed near semiconductor-electrolyte interfaces (22).

6.2 Fabrication of Au/Fe₂O₃ nanostructured photoanode for

plasmonic enhancement

Fe₂O₃ Electrodes on large-area arrays of Au nanopillars were fabricated based on nanoimprinting techniques (23). 200-nm Au, with a thin Ti adhesion layer, was deposit onto quartz substrates using electron beam evaporation. A layer of nominally 500-nm polymethylmethacrylate (PMMA) thin film was spin-coated onto Au and being imprinted against a polyurethane mold at about 130 C for 20 minutes. The polyurethane mold was replicated from a silicon master (homemade using photolithography), which contained square arrays of 300-nm diameter cylindrical rods on 700-nm pitches. The imprinted PMMA has the inverted nanostructures (i.e. cylindrical holes). 5-nm chromium was then evaporated from a glancing angle (ca. 80 degree) onto the patterned PMMA as an etching mask. The holes in the PMMA thin film were deepened using reactive ion etching (50 Watt for 5 min in 90 mTorr Oxygen, Plasma-Therm PK-12) until the Au surface was exposed. After directional Au deposition using electron beam evaporation at slow rate (1 A/s) followed by PMMA liftoff in acetone, arrays of Au nanopillars were obtained on a continuous Au substrates. The photoanode material Fe₂O₃ was coated on the Au surface using electron beam evaporated metallic Fe followed by annealing in pure oxygen at 550 C for about one hour.

The resultant arrays of Au nanopillars were 300 nm in height, and had a base diameter of about 300 nm, approximately equal to the diameter of the nanorodes in the polyurethane molds (Figure 6.1). The top of the nanopillars had smaller diameter due to the aperture shrinking effect in masked electron beam evaporation. The Au nanopillar patterns were made highly uniform on a centimeter scale (Figure 6.1a inset), and can be potentially further scaled up owing to the prominent scalability of nanoimprinting techniques. Conformal coating of the Fe₂O₃ layer can be seen in the tilt-angle scanning electron microscopy (SEM) image (Figure 6.1b). The annealed Fe₂O₃ layer resembled the typically cauliflower morphology reported previously (24) (Figure 6.1c). The x-ray diffraction indicated complete conversion from Fe to hematite Fe₂O₃.

6.3 Plasmon-enhanced photoanodic performance of Fe₂O₃

A net enhancement of photocurrent under AM1.5 simulated solar illumination was observed from the Fe_2O_3 nanopillar photoanode compared to a planar control sample (Figure 6.2a). The measurement was carried out in 1M NaOH electrolyte using a three-electrode configuration with Ag/AgCl reference electrode and platinum mesh counter electrode. The Fe_2O_3 electrode was illuminated by 100 mW/cm² light from a 300W Xenon lamp through an AM1.5 solar simulation filter. A photocurrent enhancement

higher than 40% was achieved at 1.5 V vs RHE (reversible hydrogen electrode) (Figure 6.2a). The dark current remained low even beyond 1.6 V vs RHE, which indicated high quality conformal coating of the Fe_2O_3 on the Au nanopillars. Interestingly, the onset voltage of the photocurrent remained nearly the same between the planar and the pattered photoanodes. In photoelectrochemical reactions, the total quantum efficiency is limited recombination of by photogenerated charge carriers in both the semiconductor bulk and on the semiconductor-electrolyte interfaces. Under low bias, surface recombination, which is originated from surface states and interface barriers, is the dominant effect in the oxygen evolution reaction on Fe_2O_3 photoanode. Such surface barriers become less effective under higher bias, where the bulk recombination turn to be the major limiting factor and the photocurrent approaches the plateau (25). The fact that constant onset voltage was observed regardless the surface nanopatterning indicated that the nanopillar structures had minimal influence on the chemical processes occurring at the semiconductorelectrolyte interface. Therefore, the significant enhancement of photocurrent under high bias was contributed mainly by enhanced optical absorption in the Fe₂O₃ thin film that led to increased number of photogenerated charge carriers.

incident photon-to-current The efficiency (IPCE), obtained via spectral photocurrent measurements, resolved showed clear wavelength dependence of the photocurrent enhancement (Figure 6.2b). Well defined peaks in visible wavelengths were observed with а magnitude higher than 2.5. While the enhancement spectrum reaches the maxima at long wavelength, the peaks are





Figure 6.1 a, The geometry of the Au nanopillars is shown schematically. The nanopillars are 300-nm diameter at the base and 300-nm in height. Connected by a 200-nm thick planar Au thin film, the nanopillars were patterned in square arrays on 700-nm pitches. Inset: photograph of a 1.5×1.5 cm² sample uniformly patterned with Au nanopillars. 30° tilted (b) and top view (c) scanning electron microscopy (SEM) images of 90-nm Fe₂O₃ coated on Au nanopillar array.

so broad that significant enhancement occurs starting from 500 nm around the band gap

of Fe₂O₃. In contrast, the photocurrent enhancement was much lower at wavelengths shorter than 500 nm where the intrinsic interband transitions in Au suppress the surface plasmon resonances(26). Although the higher photocurrent enhancement locates in the spectral region where the incident photon to current efficiency is low, light in visible region comprises a great portion of the solar radiation power, which together accounts for the considerable net enhancement of photocurrent under solar simulated illumination.

These spectral features of the IPCE enhancement can be attributed to the electric field of the plasmonic resonances that originated from the modulated Fe₂O₃-Au interface and resulted in enhanced optical absorption. The mechanisms were verified by numerical electromagnetic simulations (Figure 6.3). Optical absorption spectra of the Fe₂O₃ layer on patterned and planar Au substrates calculated using were threedimensional full-field finite difference time domain methods (Lumerical® FDTD Solution 7.5). Large increase in the absorption was observed with peaks at 624 and 681 nm (Figure 6.3a), matches which well with the experimentally measured **IPCE** enhancement spectra. When surface plasmons resonances are generated, the collective charge oscillations at the metal surface cause increased Ohmic loss of electromagnetic energy, which can thus be visualized as peaks in spectral resolved absorption in the metal (27). While the absorption in the semiconductor and in the metallic distinguish. sections is hard to simulations provide a theoretical



Figure 6.2 a, The I-V curves shows enhancement of the photocurrent from the patterned Fe_2O_3 electrode compared to the planar control under AM1.5 simulated solar illumination. **b**, The IPCE spectra (circles and squares) were obtained using spectral resolved photocurrent measurement. Distinct enhancement can be observed as peaks (triangles) in visible wavelengths.

powerful tool to gain more microscopic insights. By integrating the absorption only in the Au regions, the electromagnetic energy dissipated in Au was obtained theoretically (Figure 6.3a). The two plasmonic resonances at longer wavelengths (> 600 nm) in the absorption spectrum of Au nanopillars coincide with the peak wavelengths of the enhancement absorption in Fe₂O₃, which verified that generation of the surface plasmons with Au nanopillar arrays was responsible for the calculated absorption enhancement and the measured photocurrent enhancement. It is worth noting that the peaks in the measured enhancement spectrum were much broader than the calculated plasmonic resonances. Such discrepancy was very often observed between experiments and simulations, which can be attributed to a variety of factors such as the variation of the unit cell geometry, the

surface roughness inevitable in reality but not considered in theory, and imperfectly collimation of optical illumination. However, the broadening effect turns out to be quite important to the enhanced photocurrent achieved here. Significant contribution arises from the enhancement in the spectral range from 500 to 600 nm.

As a further evidence for plasmonic nature of the measured enhancement, the plasmonic characteristics at both enhancement peaks (624 and 681 nm) can be observed in the electric field distribution maps provided by the FDTD simulations (Figure 6.3b). The plasmonic evanescent waves featured with spatially confined and highly intense electromagnetic fields show maximum amplitudes around the nanopillars at the Fe₂O₃-Au interface, which decay exponentially into the bulk of Fe₂O₃. The effective optical



Figure 6.3 a, Well-defined peaks are observed in the simulated absorption enhancement spectra of Fe_2O_3 at 624 and 681 nm (solid curve), which agree well with the measured enhancement in IPCE. Peaks at the same wavelengths are also found in the simulated absorption spectrum of Au nanopillars (dashed curve), indicating that the photocurrent enhancement obtained in nanopatterned Fe_2O_3 electrodes are induced by surface plasmon resonances. **b**, Electric field distribution maps from the FDTD simulations verified the plasmonic resonances at 624 and 681 nm with the characteristic evanescent field patterns near the Fe_2O_3 -Au interfaces. Moreover, the field map at non-resonant wavelength (e.g. 451 nm) indicates that photonic-mode light trapping is responsible for the enhancement in a broader spectral range.

absorption coefficient of the Fe_2O_3 in principle decreases as the distance to the Fe₂O₃-electrolyte interface increases. Because of the bulk recombination, only the photogenerated charge carriers within a thin layer of the active material close the to semiconductor-electrolyte interface can reach the aqueous solution and contribute to the electrochemical reaction. Therefore, the photocurrent enhancement **b** measured on 90-nm thick Fe₂O₃ showed smaller magnitude than the calculated absorption enhancement around the plasmonic resonances.

In addition the to evanescent field patterns around the nanopillars, photonic-mode light trapping is another important factor for the enhanced photocurrent in Fe₂O₃ coated on Au nanopillars. This light trapping effect can be identified by the intense electric field in the planar region in-between adjacent nanopillars in the simulated field distribution maps (Figure 6.3b). Different from plasmonic modes which have the most intense field amplitude the at Fe₂O₃-Au interface, the electric field of the photonic-mode light trapping maximizes in the middle of the Fe_2O_3 layer (28). The photonic-



Figure 6.4 Photoanodes of Fe_2O_3 on Au nanopillars with different thicknesses were investigated. The surface plasmon resonances shifted to (a) shorter wavelengths with 50-nm Fe_2O_3 and (b) longer wavelengths with 140-nm Fe_2O_3 are shown in the simulated absorption in Au nanopillars (dashed curves) and absorption enhancement in Fe_2O_3 (solid curves). The shifted peaks are also observed in the measured IPCE spectra (triangles).

mode light trapping is responsible for the enhanced optical absorption in much broader spectral regions. At wavelengths other than the plasmonic resonances (e.g. 450 nm), photonic-mode trapping can be observed both between and around the nanopillars while the evanescent field is not present (Figure 6.3b). Compared to the simplified, extremely smooth surfaces in theoretical simulations, the samples in the experiments benefit from substantial surface roughness which resulted in more significant photonic-mode light trapping – an effect that has been taken advantage of in solar cells with intentionally roughened back electrodes (29). Therefore, the measured photocurrent enhancement is generally higher than the calculated absorption enhancement at non-plasmon-resonance wavelengths.

The wavelengths of enhanced photocurrent can be tuned by changing the thickness of the Fe₂O₃. Surface plasmon resonances are dependent upon the electric permittivity dielectric environment surrounding the metallic nanostructures (21). The effective refractive index of the plasmon resonances takes the average between the refractive index of the Fe₂O₃ layer and the aqueous solution due to the small thickness of the Fe₂O₃ layer isn our experiments (30-32). By reducing the Fe₂O₃ thickness to 45 nm, the effective refractive was reduced (Fe_2O_3 has a higher refractive index than water), and the plasmon resonances shifted to shorter wavelengths (Figure 6.4a). Consistently, the spectrum of photocurrent enhancement also shows blue-shifted peaks (Figure 6.4a). Although the surface plasmon resonances in the case of 45-nm thick Fe₂O₃ exhibited smaller amplitude in the simulated absorption spectrum of Au nanopillars, the blueshifted resonances led to higher enhancement at wavelengths with higher IPCE in Fe₂O₃, which yielded a net photocurrent enhancement of about 50% at 1.5 V vs RHE. Oppositely, we also demonstrated that by increase the thickness of the Fe_2O_3 , the peak of photocurrent enhancement shifted to longer wavelength, which agreed well with the redshifted plasmonic resonances predicted by the FDTD simulation (Figure 6.4b).

6.4 Conclusion

The intrinsic absorption coefficient of semiconductor materials, the photoactivity of electrodes, the resonances of surface plasmons, and the power density of the solar radiation are all wavelength dependent. It is, thus, critical to match the spectral profile of these properties for optimized photocurrent enhancement by improving effective photon absorption. The significant photocurrent enhancement observed here takes advantage of both the surface plasmon resonances in visible range sustained by Au nanopillars and the relatively low bandgap (about 2.2 eV) of the active semiconductor Fe₂O₃. The effects demonstrated here, however, should not be limited to the Fe₂O₃-Au combination. Plasmonic metals such as Ag, Al and Pd sustain resonances in UV region (33) and can be selected to pair with photoactive materials with wider bandgap including WO_3 (34) and TiO₂ (35). Recent advances in alloved plasmonic metals can be particularly interesting because they are more chemically stable while retaining pronounced plasmonic resonances (36, 37). Furthermore, the thickness of the thin semiconductor layer provides an extra dimension to tune the plasmon resonances. Together with the nanoimprinting based fabrication processes, the metallic nanopillar arrays offer a controllable and scalable platform with rationally tailored plasmonic and photonic resonances for solar water splitting.

In the context of intergrated nanosystem, the experiment performed within this chapter implies that the presence of metal nanostructures could not only function as ohmic contact between two semiconductor light-absorbers in the "Z-scheme", but also could have additive benefit of concentrating the incident illuminations by the presence of surface plasmon. It serves as a good reminder for the idea of system materials engineering: the components within a system may be convoluted together and additional merits could be gained by an excellent design (*38*).

6.5 References

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Chapter 7

Concluding Remarks

As shown in this dissertation, the research goal of my graduate study has been to demonstrate nanowire-based integration for artificial photosynthesis, by taking advantage of the benefits offered by the nanowire morphology. Starting from the fundamentals of charge transport in a nano-sized "Z-scheme" structure, I achieved integration of solar-to-fuel conversion at the nanoscale using nanowire building blocks. Additionally I developed advanced components for future use in integrated nanosystems, including electrocatlaysts and semiconductor light-absorbers. For electrocatalysts, two approaches were demonstrated for practical applications: reducing the loading of a precious metal and developing alternative earth-abundant catalysts. For semiconductor light-absorbers, also two distinct methods were explored: developing solution-phase-synthesized III-V semiconductor nanowires for photocathodes and enhancing the photocurrent output on metal nanostructures via their surface plasmon resonances. These distinct approaches demonstrate the versatility and huge potential of integrated nanosystems, and I hope that what I have done will serve as a foundation for the efforts of other researches in the field of artificial photosynthesis.

In the following I want to comment on two topics beyond the experimental data of my research. The first one is some general trends in the field of solar-to-fuel conversion, and the second one is my understanding of how to apply nanotechnologies for practical applications. In my opinion, my graduate research is also a journey for me to develop a suitable opinion of how to think about these two topics, and they are also results of my Ph. D. study, which I treasure at least equally with the experiments that I did.

A very common question concerning the concept of solar-to-fuel conversion is how it relates to other solar-based technologies, particularly photovoltaics. It is apparent that they are closely related. In this dissertation, the first part of the introduction discusses the basics of solar cells because a solar cell is a suitable introductory concept with fewer complications. Recently there is a trend of using the techniques of photovoltaics to address issues in the field of artificial photosynthesis, and the border between these two fields has become vague. So what are the ways that artificial photosynthesis is distinctive from solar cells? In my view there are two: (1) the electrocatalysts, and (2) the control of the photosynthetic components at nano-scale.

The need for electrocatalysts is unique to solar-to-fuel conversion because photovoltaics does not deal with the formation and breaking of chemical bonds. Based on its current research status, CO_2 reduction is the focus because at present it suffers from high overpotentials, poor selectivity, and poor stability. The presence of the selectivity issue implies that the research in CO_2 reduction resembles conventional catalysts, and the solution to solve this issue should be versatile. On the other hand, the control of photosynthetic components at the nano-scale is also unique. Originally artificial photosynthesis is a biomimetic term and in biology photosynthesis proceeds with spatial control at the nanometer scale. Because artificial photosynthesis does not need to be connected to the grid, an integrated device at nanoscale is possible with additional benefits, as discussed in this dissertation. Therefore achieving such control not only is desirable to mitigate many adverse effects for practical application, but also should be appreciated via mimicking nature by using building blocks of small molecules or nanomaterials.

Then how does nanotechnology fit into such a context? Although at present in the literature there are numerous reports of applying nanomaterials to solar-to-fuel conversion, I think we should be humble at first since nanotechnology is not a panacea. The introduction of nanomaterials brings pros and cons, so careful design of the nanostructures and nanomaterials should be implemented at the beginning of experiment; otherwise, the resultant performance may be worse. Moreover, the proliferation of applying nanomaterials to various research directions without careful thought can create doubt in the credibility of nanotechnology, which is an unwanted side effect. Therefore when trying to apply the advantages of nanostructures onto solar-to-fuel conversion, I personally would prefer always to ask myself the following questions: is nano really needed here? Can it be better with nano? Initially the answer may be disappointing. But the purpose of scientific research is to challenge yourself with critical thinking and to achieve innovative accomplishments with elegant experiment design, otherwise why should we spend that many years in a Ph. D. program?

To conclude, I hope that I can pass the baton onto future scientists in the field of nanotechnology, through not only the experimental results that I have demonstrated but also through the courage and optimism to challenge oneself in science.

"After all, tomorrow is another day." ---- Scarlett O'Hara

Appendix

List of Publications

([#]Authors contributed equally)

- <u>C. Liu</u>[#], J. Tang[#], H. M. Chen, B. Liu, P. Yang, "A Fully Integrated Nanosystem of Semiconductor Nanowires for Direct Solar Water Splitting", *Nano Lett.*, **2013**, *13*, 2989-2992
- <u>C. Liu</u>, J. Sun, J. Tang, P. Yang, "Zn-doped p-type Gallium Phosphide Nanowire Photocathodes from a Surfactant-free Solution Synthesis", *Nano Lett.*, 2012, 12, 5407-5411
- 3. <u>C. Liu</u>[#], Y. J. Hwang[#], H. E. Jeong, P. Yang, "Light Induced Charge Transport within a Single Asymmetric Nanowire", *Nano Lett.*, **2011**, *11*, 3755-3758
- 4. <u>C. Liu</u>, N. P. Dasgupta, P. Yang, "Semiconductor Nanowires for Artificial Photosynthesis", *Chem. Mater.*, In press (DOI: 10.1021/cm4023198) (Invited review)
- Y. Sun[#], <u>C. Liu</u>[#], D. C. Grauer, J. Yano, J. R. Long, P. Yang, C. J. Chang, "Electrodeposited Cobalt-Sulfied Catalyst for Electrochemical and Photoelectrochemical Hydrogen Generation from Water", *J. Am. Chem. Soc.*, In press (DOI: 10.1021/ja4094764)
- N. P. Dasgupta[#], <u>C. Liu</u>[#], S. Andrews, F. B. Prinz, P. Yang, "Atomic Layer Deposition of Platinum Catalysts on Nanowire Surfaces for Photoelectrochemical Water Reduction", *J. Am. Chem. Soc.*, **2013**, *135*, 12932-12935
- 7. H. Gao[#], <u>C. Liu[#]</u>, H. E. Jeong, P. Yang, "Plasmon Enhanced-Photocatalytic Activity of Iron Oxide on Gold Nanopillars", *ACS Nano*, **2012**, *6*, 234-240
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- J. Vura-Weis, C. M. Jiang, <u>C. Liu</u>, H. Gao, J. M. Lucas, F. de Groot, P. Yang, A. P. Alivisatos, S. R. Leone, "Femtosecond M_{2,3}-Edge Spectroscopy of Transition-Metal Oxides: Photoinduced Oxidation State Change in α-Fe₂O₃", *J. Phys. Chem. Lett.*, **2013**, *4*, 3667-3671
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