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Boston College

The Graduate School of Arts and Sciences

Department of Chemistry

Nanostructured Semiconductors for High Efficiency

Artificial Photosynthesis

A dissertation

By

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Abstract

Nanostructured Semiconductors for High Efficiency Artificial Photosynthesis

A dissertation by Rui Liu Dissertation Advisor: Prof. Dunwei Wang

Photosynthesis converts solar energy and stores it in chemical forms. It is one of the most important processes in nature. Artificial photosynthesis, similar to nature, can provide us reaction products that can potentially be used as fuel. This process promises a solution to challenges caused by the intermitted nature of solar energy. Theoretical studies show that photosynthesis can be efficient and inexpensive. To achieve this goal, we need materials with suitable properties of light absorption charge separation, chemical stability, and compatibility with catalysts. For large-scale purpose, the materials should also be made of earth abundant elements. However, no material has been found to meet all requirements. As a result, existing photosynthesis is either too inefficient or too costly, creating a critical challenge in solar energy research. In this dissertation, we use inorganic semiconductors as model systems to present our strategies to combat this challenge through novel material designs of material morphologies, synthesis and chemical reaction pathways.

Guided by an insight that a collection of disired properties may be obtained by combining multiple material components (such as nanostructured semiconductor, effective catalysts, designed chemical reactions) through heterojunctions, we have produced some advanced systems aimed at solving fundamental challenges common in inorganic semiconductors. Most of the results will be presented within this dissertation of highly specific reaction routes for carbon dioxide photofixation as well as solar water splitting.

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Chapter 1: Introduction

An increasingly modernized world relies on a steady, dependable supply of energy. Currently, approximately 85 % of the global energy need is met by the burning of fossil fuel.^[1] However, the depletion of non-renewable fossil fuel is a well-known global challenge. To address this issue, alternative, renewable means of energy supply must be developed. Among those studied, solar energy as an abundant and free energy source stands out and has therefore attracted intense attention for many years. Indeed, the energy that arrives on the surface of the Earth from the Sun each hour is 4.3×10^{20} J, comparable to the total energy of 5.4×10^{20} J consumed by human activities in the entire year of 2012. There is no doubt that solar energy will play an important role in meeting our future energy needs. However, solar light is also diffusive, diurnal and sporadic, meaning direct usage of solar energy is not desired in most applications. To better utilize solar energy, we not only need to come up with methods to convert it into other energy forms with high efficiencies, but also need to devise technologies that can store solar energy for off-hour usage.

1.1 Natural Photosynthesis

Photosynthesis in nature converts solar energy and stores it as chemical energy. It is one of the most important processes on Earth. The light reaction of natural photosynthesis has a series of step-wise electron-transfer processes to produce

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sufficient energy that can power water splitting.^[2] The detailed mechanism is known as the "Z-scheme", which is illuminated in Figure. 1.1.^[3] In a simplified form, the photosynthesis machinery can be divided into two parts, photosystem I (PS I) and photosystem II (PS II). They both absorb solar light (with maximum absorption wavelength of 700 nm and 680 nm, respectively) through an assembly of light-harvesting chlorophylls and pump electrons to a higher electronic state (excitation) inside the reaction center.^[4,5] PS I contains photosystems in series with an electron transfer chain, which provides electrons to complete a series of reduction reactions, and finally produces the final product, nicotinamide adenine dinucleotide phosphate (NADPH). PS II involves a water oxidation reaction which takes place at a manganese calcium oxide cluster.^[6,7] Charge separation and charge collection within these processes are so effective under optimal conditions that there is almost no energy loss in natural photosynthesis.^[3] The dark reaction of natural photosynthesis incorporates carbon dioxide into the product of sugar, an important energy source for many biological reactions.



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Figure 1.1. Natural Photosynthesis charge-separation processes, including PS I and PS II reaction centres (simplified Z-scheme). (See all the abbreviation details in Appendix of Chapter 1.) Figure is adapted from reference 3.

Although not shown in Figure 1.1, NADP⁺ is ultimately used to reduce CO₂, making the CO₂ reduction reaction and water oxidation reaction (oxygen evolution reaction) on PS II the two key chemical processes in natural photosynthesis. Both reactions are complex because they involve multiple electrons and protons, and they usually exhibit slow kinetics and require high over potentials. The advantage of the complex "Z-scheme" is believed to lie in the capability to minimize side reactions and to improve overall efficiencies. This strategy is one of the most important aspects we have learned from nature.

1.2 Artificial Photosynthesis

Although natural photosystems present a highly inspiring platform for us to learn photosynthesis designs on a systematic level, they generally fail to provide a high overall incident photon-to-current efficiency because the light absorptions by PS I and PS II are too narrow. Starting from natural photosynthesis but working on improving solar energy conversion efficiency for large scale reactions, researchers have taken significant efforts to design artificial photosynthesis systems, such as photoelectrochemical cells (PEC). CO₂ photoreduction, similar to the dark reactions in natural photosynthesis that stores energy harvested by PS I, and solar water splitting, similar to PS II, are the two of the most important applications in PEC cells, and comprise the main contents of this dissertation. We are particularly interested in harvesting solar light and carrying out the

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reactions by inorganic semiconductor materials because they offer the promise of durability and low cost.

More specifically, semiconductors often possess the capabilities to absorb broadly in the visible light range, owing to existence of the band gap, pumping electrons from the valence band to the conduction band in the process. The depletion regions in semiconductors near the solid/electrolyte interface also offer a mechanism to separate photoexcited charges. Presently, the key challenge in the field is that no single semiconductor material can offers all desired properties in terms of light absorption, charge separation and catalytic activity simultaneously. Correspondingly, researchers have focused their efforts on improving the artificial photosynthesis efficiency by precisely controlling the materials synthesis, manipulating the materials morphologies, creating semiconductor/catalysts heterojunction systems, introducing homogenous reaction catalysts, and designing new reaction pathways. My thesis work covers this ground broadly.

1.2.1 CO₂ Photoreduction Related Study Based on Semiconductor

Photoelectrodes

Photoreduction of carbon dioxide by semiconductors promises a route to reduce CO_2 concentration in the atmosphere while producing useful molecules such as fuel. It has attracted significant research attention. The range of products that can be generated by photoreduction of CO_2 is broad, as can be seen from Table 1.1.

Table 1.1 Products of CO₂ reduction along with the number of electrons needed to

produce each one and their standard reduction potentials at pH 6.8. Table is adapted

from reference 8.



The potential (or energy required) to reduce CO_2 to different products (see Table 1.1^[8]) is generally within the range of what can be produced by many semiconductor photoelectrodes. Using semiconductors to harvest solar energy and to reduce CO_2 into the fuel is not only theoretically possible but also economically promising. The general details of PEC cells for CO_2 photoreduction through a semiconductor photoelectrode are schematically shown in Figure 1.2.^[9] At the photoanode the sequence of events is: 1) photon absorption, 2) excited state electron injection, 3) inter-electrode electron transport, 4) sequential hole transfer, 5) water oxidation, 6) light-driven CO_2 reduction at

the photocathode. In a simplified system, researchers usually focus on CO_2 reduction reaction and use sacrificial metal to replace the photoanode. Other approaches such as using catalyst decorated TiO₂ nanoparticles suspension to have CO_2 reduction and H₂O oxidation on the same particles are also being studied.^[10-11]



Figure 1.2 Tandem PEC configuration for CO_2 reduction to methane at a photocathode and light driven water oxidation at a photoanode. Figure is adapted from reference 9.

However, the subtle differences of energies in various CO_2 reduction products as shown in Table 1.1 also highlight a significant challenge. That is, it is difficult, if possible at all, to control which product is obtained when CO_2 is directly reduced by a photoelectrode. Consequently, CO_2 reduction by semiconductors usually suffers disadvantages such as low yield, low selectivity and high overpotential. The fundamental

reason is the multiple electrons transfer process required to fully reduce CO_2 .^[8,10-12] For instance, utilizing semiconductors such as TiO_2 or p-type Si in PEC cells to reduce CO_2 in aqueous solution by solar energy also has low faradic efficiency and significant production of byproducts, chiefly hydrogen and other hydrocarbons.^[13-14] It is our goal to address this particular issue and correct the deficiency, and our strategy will be further discussed later.

1.2.2 Solar Light Powered Water Splitting by Semiconductor

Another important PEC process is solar water oxidation on semiconductors, an analogy of PS II. To do so, we need an anode that can oxidize water to produce O_2 using harvested solar energy.



Figure 1.3. Principle of solar water splitting cells. The most important steps are illustrated as: (i) light absorption; (ii) charge transfer; (iii) charge transport; and (iv) surface chemical reactions. Figure is adapted from reference 15.

Similar to the CO₂ reduction PEC process discussed in 1.2.1, PEC water splitting also has following steps: light absorption and charge separation on semiconductor; charger transfer and transport inside semiconductor and circuit; surface chemical reactions (Figure 1.3). Those critical steps to achieve efficient water splitting are mainly associated with intrinsic properties of photoelectrodes such as its band gap, the energetic position of its conduction band and valance band, the electronic properties and surface catalytic properties. For example, the band gap of the semiconductor determines how much solar light that can be harvested. Only photons with equal or higher energy than the energy gap of semiconductor can be absorbed to excite electron-hole pairs. For water splitting, the standard free energy changes is 237 KJ mol⁻¹ or 1.23 eV. Therefore, for a single semiconductor to perform water splitting, its band gap should be larger than 1.23 eV.

The general requirements of a highly efficient electrode are summarized as follows. (1) The electrode must be stable in reaction solution for long term without corrosion. (2) The conduction band edge and valance band edge should be appropriate for both reduction and oxidation reactions (more negative conduction band edge to transfer photogenerated electrons for hydrogen evolution and more positive valence band edge to transfer to transfer holes for oxygen evolution, respectively). (3) The semiconductor should possess a suitable band gap to allow for light absorption and electronic excitation with sufficient energies. (4) Charge separation and collection should be efficient, without serious charge recombination which results in low energy conversion efficiency. (5) Because the number of incident photons received per unit area under standard conditions (e.g., solar simulator AM 1.5 with normalized intensities of 100 mW/cm²) is fixed, to match the kinetics, the material should be catalytically active for H_2O oxidation or reduction or both.^[15]

Since the first demonstration of photoelectrochemical water splitting by Fujishima and Honda^[16], intense research effort has been focused on searching for the ideal material that can meet all requirements discussed above. However, up to date, materials satisfying all criteria simultaneously have not been reported. Thus our research is guided to engineer materials for improved solar energy conversion efficiencies.

1.2.3 Development of Artificial Photosynthesis

In order to develop highly efficient artificial photosynthesis PEC cells, different strategies are introduced to simple photoanode or photocathode systems. Three of the strategies are most commonly studied: 1) introducing catalysts onto the effective photoanode or photocathode, which will reduce the reaction overpotential and increase the reaction kinetics;^[17-19] 2) fabricating high quality nanostructured semiconductors, such as nanoparticles^[20], nanowires^[21], nanotubes^[22], ultrathin films^[23] and nanonets^[24] etc., which improve the efficiency by increasing light absorption and reducing carrier transportation distance; 3) manipulating the materials by doping^[25], making homogenous p-n junction^[26], heterogenous p-n junction^[27], passivation, etc., which usually improve photovoltage by engineering the materials band structures.

Some outstanding work on artificial photosynthesis through PEC cells has been

demonstrated by designing adequate semiconductor/catalyst heterojunctions. For instance, Bocarsly *et al.* used pyridinium ion as a catalyst to selectively photoreduce carbon dioxide into methanol on a p-type GaP photocathode, measuring faradaic efficiencies close to 100 % at potentials well below the standard potential. The catalyst for CO₂ reduction not only reduces the reaction overpotential, but also increases the reaction selectivity by defining the reaction pathways.^[18]

Another example is water oxidation catalyst cobalt phosphate (CoPi), which has proved to be one of the most promising water oxidation catalysts, both on its intrinsic properties and in devices when applied onto semiconductors. As high as 350 mV cathodic shift of onset potential on α -Fe₂O₃ photoanodes for water oxidation is obtained when cobalt catalyst layer is deposited on it. ^[19] Recently, by combining atomic layer deposited MnO water oxidation catalyst with n-Si, Lewis et al. successfully demonstrate water oxidation (oxygen evolution reaction).^[29] MnO-coated n-Si photoanodes displayed open-circuit voltages of up to 550 mV and stable anodic currents for periods of hours at 0.0 V versus the solution potential.

Nanostructured materials take advantage of PEC cells from their morphology for better light absorption and less energy loss from shorter carrier transportation distance.^[22-24] Our group reported high external quantum efficiency using hematite deposited on TiSi₂ nanonets.^[24] Nanonets are highly conductive and have suitably high surface areas. The nanonets serve as a support with high surface area to hematite, which improves the light absorption of hematite. Also, nanonets serve as efficient charge collector, allowing for maximum photon-to-charge conversion. Moreover, for some PEC reactions, nanostructured materials may favor charge transfer due to their multifaceteds feature, meaning that a variety of crystal planes are present. It is reasonable to assume that charge transfer semiconductor/electrolyte interface are preferred on one of the

crystal planes in nanostructured materials, resulting in lower reaction overpotentials than the one on bulk materials for the same PEC reactions. For instance, SiNWs achieved better onset potential than planar Si when used on CO₂ photoreduction in aromatic ketone system and in alkyne system with catalyst existence.^[30-31]

Overall, synthesizing suitable nanostructured materials and rationally engineering semiconductor/catalyst heterojunctions for effective artificial photosynthesis is our goal. Appling energetically matched catalysts onto semiconductor can decrease reaction overpotential, increase selectivity. Nanostructured materials have advantages in PEC process for better light absorption, shorter charge transportation distances and sometimes lower charge transfer barrier due to their multifaceted nature. Manipulating multiple components with their unique functions into PEC device offers combinations of properties for high-efficiency artificial photosynthesis.

1.3 The Scope of This Dissertation

The motivation of this dissertation is to achieve highly efficient solar energy conversion in artificial photosynthesis processes of carbon dioxide photofixation and water splitting using nanostructured semiconductors. To achieve these goals, we focus on rational material design and synthesis for high-performance electrodes; we also design new chemical reaction routes for significantly improved product selectivity.

This dissertation mainly investigates artificial photosynthesis of PEC CO_2 reduction and PEC water oxidation. We start from artificial photosynthesis process of carbon dioxide photofixation by SiNWs. We designed a similar PEC reaction to the dark reaction of natural photosynthesis, which has improved PEC reactions selectivity and yields. Followed on this direction, we also broaden the reaction scope by introducing a CO_2 reduction catalyst onto SiNWs. The catalysts electrochemical properties are also studied to inspire people to optimizing energetic structure of semiconductor/catalyst heterojunctions. The water oxidation, as the other half reaction in natural photosynthesis, is also investigated in WO₃/Mn-oxo catalyst heterjunction in the last part of this dissertation.

In Chapter 2, we demonstrate a high selective and effective PEC carboxylation reaction achieved on Si nanowires (SiNWs) photocathode using CO₂ as carbon source. The reaction route optimization indeed helps to improve overall desired product yield by suppressing the chance of producing byproduct. Instead of directly reducing carbon dioxide, photogenerated electrons from SiNWs will reduce the aromatic ketone molecule, forming corresponding radical. The ketone radical will selectively bind with carbon dioxide in the solution and finally produce corresponding carboxylation acid. The reaction selectivity and yield are one of the best reported to date, and the reactions can be used to synthesize NSAIDs (non-steroidal anti-inflammatory drugs) such as ibuprofen and naproxen. As an earth abundant element, Si harvests solar energy to enable these reactions. The close resemblance to natural photosynthesis renders our work significant.^[30]

Further study of using SiNWs for organic reactions is investigated in Chapter 3. In order to expand PEC reactions types on SiNWs photoelectrode, we introduce a Ni catalyst into this system. It is a well-established catalyst for alkyne carboxylation reaction using CO₂ as the carbon source. SiNWs can reduce Ni catalyst under light illumination with photogenerated electrons, and the reduced form of Ni catalyst binds carbon dioxide and alkyne to finish the carboxylation reaction. This approach holds the potential to greatly broaden the reaction scopes as long as we choose the reaction suitable for Ni catalyst. ^[31]

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The ligand effect of Ni catalysts is discussed in Chapter 4. Energetic match of catalyst and semiconductor is crucial to design an effective PEC cell. By varying binding ligands with the Ni center, we are able to tune the reduction potential of the Ni catalysts by as much as 0.86 V. Consistently high photovoltages of 410-450 mV are measured on these catalysts when SiNWs are used as a photocathode for the cyclic voltammetry characterizations. This work is expected to inspire researchers to optimize energetic structures when applying catalysts onto semiconductors for PEC reactions. ^[32]

In Chapter 5, we successfully develop a new atomic layer deposition (ALD) process for the growth of WO₃ film and study its fundamental properties as a photoanode for water oxidation. Moreover, an effective water oxidation catalyst Mn-oxo is thermodeposited onto WO₃ to improve the oxygen evolution kinetics. The WO₃/Mn-oxo catalyst heterojunction has increased oxygen generation rate, and better stability in neutral solution.^[33]

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Appendix of Chapter 1

Abbreviation of Figure 1.1*

P680	pigment (chlorophyll) that absorbs 680 nm light in photosystem II (PSII)
P680*	excited state of P680
P700	pigment (chlorophyll) that absorbs 700 nm light in photosystem I (PSI)
P700*	excited state of P700
Mn	manganese calcium oxide cluster
Tyr	tyrosine in PSII
Pheo	pheophytin, the primary electron acceptor of PSII
Q _A	primary plastoquinone electron acceptor
Q _B	secondary plastoquinone electron acceptor
PQ	plastoquinone
FeS	Rieske iron sulphur protein
Cyt. f	cytochrome f
PC	plastocyanin
A ₀	primary electron acceptor of PSI
A ₁	phylloquinone
F_X, F_A, F_B	three separate iron sulphur centres
FD	ferredoxin
FNR	nicotinamide adenine dinucleotide phosphate (NADP) reductase

This Z-scheme process is driven by the absorption of two photons, one at PSII and the other at PSI. Light absorption at PSII creates P680, which provides an electron to reduce pheophytin, and the step-wise electron transfer occurs from pheophytin to P700* (the oxidizing species after the electron transfer from P700*). Following this initial electron transfer, P680* can oxidize tyrosine and subsequently the manganese calcium oxide cluster. Light absorption at PSI creates

P700^{*}, which provides an electron to reduce A_0 to FNR. A series of electron transfer pathways are indicated by black arrows.

Chapter 2:

Si Nanowires as Photoelectrodes for Carbon Dioxide Fixation

2.1 Introduction

Natural photosynthesis harvests the energy in solar light to power chemical reactions and uses CO₂ as the carbon source. Because light as an energy source is free and abundant, chemical reactions similar to photosynthesis have major fundamental and practical implications.^[1,2] Indeed, significant efforts have been attracted to this research goal. The majority of attention for photochemical reactions that transform CO₂ have focused primarily on conversion into *fuels*.^[3,4] How to learn from photosynthesis and devise reaction routes for the synthesis of useful organic compounds receives relatively underwhelmed considerations.^[5] Drawing inspiration from the mechanisms found in dark reactions of photosynthesis and using p-type Si nanowires as a photocathode, here we show that highly specific reactions can be readily carried out to produce α -hydroxy acids by photoreduction of aromatic ketones, followed by CO₂ fixation. Powered by solar light, this reaction is in close resemblance to natural photosynthesis, and different from its The carboxylation products of two of the substrates electrochemical analogues. examined in this work serve as precursors to nonsteroidal anti inflammatory drugs (NSAID), ibuprofen and naproxen.^[6]

In nature, photosynthesis is carried out in two distinct stages: light and dark reactions. During the light promoted stage, the energy in photons is harvested and stored in chemicals such as NADPH (nicotinamide adenine dinucleotide phosphate) and ATP

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(adenosine-5'-tiphosphate) are subsequently used to sequester carbon dioxide for the synthesis of complex sugar monomers. At the heart of the Calvin cycle (dark reactions) is the conversion of ribulose-1,5-bis-phosphate (RuBP) into an intermediate β -keto-acid (Scheme 1), which ultimately fragments to 3-phosphoglycerate (3PG), the core building block for sugars.^[7] By not directly reducing CO₂, this process avoids producing C in a variety of oxidation states and gains a critical advantage of high selectivity.^[8] This chemistry inspires us to propose a strategy to perform carboxylation reactions using light as a direct energy source and CO₂ as a carbon source. As shown in Schemes 2.1 and 2.2, our reaction route is in close resemblance to natural photosynthesis but different from existing approaches that seek to directly photoreduce CO₂. It solves a critical challenge of poor selectivity inherent to the direct photoreduction of CO₂ due to the nature of the multielectron transfer processes. Our strategy has the potential to meet the selectivity requirement necessary for more complex synthetic targets than fuels, opening up the doors to a wide range of light-powered chemical reactions^[9-12] that have not been previously studied.



Scheme 2.1. Comparison of the key carboxylation steps in natural photosynthesis and those in this work



Scheme 2.2. Proposed mechanism of the light-driven carboxylation reactions

2.2 Experimental

2.2.1 SiNWs synthesis

SiNWs were prepared following a previously reported method. A p-Si (100) (10^{15} cm⁻ ³ B doped; ρ :10~20 Ω •cm; Wafernet, CA, USA) was cleaned with acetone, methanol, and isopropanol sequentially and then oxidized in H₂O₂/H₂SO₄ (1:3) at 90°C for 15 min

to remove heavy metals and organic species. After rinsing with deionized (DI) water, the substrate was cut into approximately 1.0 cm×5.0 cm pieces and then immersed into an HF/AgNO₃ solution (4.6 M HF and 0.02 M AgNO₃) for 30 min at 50°C for a varying duration of time to produce SiNWs of varying lengths.

2.2.2 Photoelectrode fabrication

After thorough cleaning, the substrates containing SiNWs were immersed in HF (aqueous, 5 %) for 2 min and then dried in a stream of N₂. Al (300 nm) was then sputtered onto the backside of the substrates by radio frequency magnetron sputtering (AJA International, Orion 8, MA, USA). They were then annealed in Ar (flow rate: 5000 standard cubic centimeter per minute, SCCM) at 450 °C for 5 min. Afterward, tinned Cu wires were fixed to the Al film by Ag epoxy (SPI supplies, PA, USA). Lastly, non-conductive hysol epoxy (Loctite, OH, USA) was used to seal the entire substrates except the regions where SiNWs resided.

2.2.3 Photoelectrochemical (PEC) characterizations

PEC experiments were carried out using a CHI 609D Potentiostat/Galvanostat in a three-electrode configuration, the reference electrode being a Ag/AgI wire soaked in 0.1 M tetrabutylammonia iodine acetonitrile solution. A piece of high-purity AI foil (99.9995%, Alfa Aesar, MA, USA) served as the counter electrode. The electrolyte solution consisted of 0.025 M benzophenone (> 99.0%, Sigma-Aldrich, MO, USA), 0.1 M tertrabutyl ammonia bromide (\geq 99.0%, Sigma-Aldrich, MO, USA) in acetonitrile, into which CO₂ (Airgas, MA, USA; flow rate: 120 SCCM) was continuously bubbled. For all data reported here, a 150 W Xenon lamp (model 71228, CA, USA) equipped with an AM

1.5G filter was used as the light source and the light intensity was adjusted using a Si photodiode (UV 005, OSI, Optoelectronic, CA, USA). The scan rate was 50 mV s⁻¹.

2.2.4 Photoelectrochemical Synthesis

To a flame-dried, three-neck, 25-mL round-bottom flask equipped with magnetic stir bar was added tetrabutylammonium bromide (0.644 g, 2.00 mmol), benzophenone (0.22 M benzophenone in acetonitrile; 2.00 mL, 80.0 mg, 0.439 mmol) and acetonitrile (18 mL) in a dry box. One of the following was placed in each neck of the round-bottom flask: Si NWs working electrode, aluminum counter electrode, Ag/AgI/I⁻ reference electrode. The reaction vessel was brought out of the dry box and CO₂ was bubbled through the solution with an oil bubbler outlet. A constant potential of -1.2 V was applied to the reaction mixture and reaction current was monitored during the synthesis time. Light was shined onto the reaction with vigorous stirring overnight. Without illumination, the reaction current was negligible.

2.2.5 Procedure for determination of ¹H NMR yields of the products

The crude reaction mixture was transferred to a new 100 mL round-bottom flask and was concentrated *in vacuo* to remove acetonitrile. The reaction was quenched by the addition of 4N HCI (8 mL) and was extracted with diethyl ether (3 × 25 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was analyzed by the addition of 200 µL internal standard (0.719 M mesitylene in acetone- d_6). ¹H NMR analysis was carried out using acetone- d_6 as solvent.

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Unless otherwise noted, all reagents were obtained commercially and used without further purification. Flash column chromatography was performed using Silicycle SiliaFlash F60 silica gel and ACS grade solvents as received from Fisher Scientific. All reactions were performed with dry, degassed solvents dispensed from a Glass Contour Solvent Purification System (SG Water, USA LLC), unless otherwise noted. ¹H and ¹³C NMR were performed on a Varian VNMRS 500 MHz spectrometer. Deuterated solvents were purchased from Cambridge Isotope Labs and stored over 3 Å molecular sieves. All NMR chemical shifts are reported in ppm relative to residual solvent. Coupling constants are reported in Hz. All IR spectra were gathered on a Bruker Alpha FT-IR, equipped with a single crystal diamond ATR module, and values are reported in cm⁻¹.

2.3 Results and Discussion

2.3.1 Band Structure Investigation

We used Si nanowires (SiNWs) as the light-harvesting electrode because they have been shown to be efficient in converting solar energy into electrical forms, easy to make, and remarkably stable under reductive conditions.^[13-17] To examine their suitability for organic synthesis, we first conducted a reaction that has been previously performed electrochemically, the formation of benzilic acid through CO_2 fixation by benzophenone.^[18,19] The key difference of the result reported here is that light serves as an important source of energy input. Our goal for this initial set of experiments was to determine whether the energy levels of Si are aligned for reduction of benzophenone to the radical anion, the key step in the carboxylation reaction. We would then apply this knowledge to the CO_2 photofixation with ketone-based substrates. Information important to our considerations includes the electrochemical potential of the solution (determined by the Tafel technique in dark as -0.12 V; all potentials were relative to Ag/Agl/I⁻ reference, which was 0.60 V more positive than SCE, saturated calomel electrode) and the Fermi level of Si (measured by the Mott-Schottky plot as 0.74 V).

2.3.1.1 Equilibrium condition investigation with Tafel plot

The equilibrium potential is the point at which the cathodic current density and the anodic one are equal. At this potential, the electrochemical potential of the electrolyte solution aligns with the Fermi level of Si. As shown in Figure 2.1, the equilibrium potential of planar Si is -0.120 V in dark. When illuminated, the equilibrium potential shifts positively as a result of the photogenerated electron accumulation on the surface. Together with the Mott-Schottky plot (which will be discussed later), the energetic scheme of Si/ benzophenone junction can be generated.

Compared with planar samples, Si nanowires exhibit more positive equilibrium potential in dark or under illumination. This suggests that it requires less applied potential in order for the benzophenone reduction to take place on SiNWs. Importantly, the difference between the equilibrium potentials in dark and under illumination is larger (0.4 V) for SiNWs than for planar Si (0.22 V). It indicates that a higher build-in potential is obtained on SiNWs. This is likely caused by improved light absorption by SiNWs.


Figure 2.1 a. Tafel plot of planar Si sample in a benzophenone solution; b. Tafel plot of Si Nanowires sample in a benzophenone solution. All measurements were peformed with 25 mM benzophenone in 0.1 M TBAB acetonitrile solution with CO_2 bubbling. Xe lamp light intensity 100 mW cm⁻² was calibrated by a Si diode under AM 1.5 irradiation

condition. Scan rate was 0.1 mV/sec, and scan direction was from negative potential to positive potential. All the voltages are relative to reference electrode Ag/Agl/l⁻.

2.3.1.2 Mott-Schottky plot



Figure 2.2 Mott-Schottky plots of SiNW photoelectrode measured in CO_2 /benzophenone system at different frequencies. All the measurements were carried out in dark. The dotted lines are linear fitting curves.

In the reverse bias region, the space charge region capacitance (C_{sc}) of p-SiNWs can be described by the Mott-Schottky relation:

$$C_{SC}^{-2} = \frac{2}{A^2 q \varepsilon \varepsilon_0 N_A} \left(-V + V_{fb} - \frac{kT}{q} \right)$$
(2.1)

where ε_0 is the permittivity of free space; ε is the dielectric constant of silicon; *V* is the applied potential; *V*_{fb} is the flat-band potential; *N*_A is the dopant density of silicon; *A* is the surface area of the electrode; *k* is the Boltzmann constant; and *T* is the temperature.

The Mott-Schottky plots obtained at different frequencies are linear ($R^2>0.995$) and the flat-band potential is measured as 0.74 V (all potentials refer to Ag/AgI/I⁻ reference, which is 0.60 V more positive than SCE.).

2.3.1.3 Band structure build up

From this information and the known doping levels of Si (10^{15} cm⁻³ B-doped; ρ : 10-20 $\Omega \cdot$ cm), we constructed the energetics of the benzophenone system as shown in Figure 2.3. Under equilibrium conditions, a large degree of band bending (0.86 V in magnitude) on the surface creates a substantial depletion layer where photogenerated charges can be separated with high efficiencies when illuminated.

This understanding was indeed consistent with the photoelectrochemical (PEC) measurements (Figure 2.4, see later disscussion). We note that both p-type and n-type Si NWs with different doping levels were investigated in this work. Moderately doped p-type SiNWs were found to be the most suitable photocathodes.



Figure 2.3. Energetics of using p-type SiNWs for benzophenone reduction. Under equilibrium conditions in the dark, a substantial band bending (0.86 V in magnitude) forms, providing a basis for efficient charge separation. When illuminated, the separated charges create a build-in field to help power the benzilic acid formation by carboxylation.

2.3.2 Photoelectrochemical Performace

Several additional characteristics of the PEC data are noteworthy. First, in the absence of light, no photocurrent was detected for applied potentials up to -2.4 V, nor did we obtain any carboxylation products (Figure 2.4a). In contrast, when illuminated, a high saturation current density is measured at relatively low negative applied potentials (31.1 mA/cm² at -1.20 V, Figure 2.4). These results support that the reaction as shown in Schemes 2.1 & 2.2 is indeed powered by light. Control experiments where SiNWs

were replaced by Pt only measured 2.00 mA/cm² under identical applied potential and illumination conditions.

The current level also approaches what is theoretically possible by Si (43.0 mA/cm²) under the same lighting conditions,^[20,21] further highlighting the feasibility of using the system for high-efficiency PEC operations. Important to this discussion, the saturation current density scales with illumination intensity in a linear fashion, supporting that the charge separation mechanism agrees with that proposed in Figure 2.3, and that charge collection is effective.

Third, the sharp turn-on of the photocurrent density (a slope of 70.1 mA cm⁻² V⁻¹ was measured in the linear region between -1.00 and -1.20 V) was comparable to that measured on Si in the more extensively studied CoCp₂/CoCp₂⁺ system,^[22] where charge transfer resistance from Si to the electrolyte is known to be low, as well as that of Pt (a slope of 72.0 mA cm⁻² V⁻¹ between -1.15 and -1.50 V). The comparison indicates illuminated Si is a suitable candidate for aromatic ketone reduction. Indeed, under typical operation conditions (-1.20 V, 100 mW/cm² AM 1.5 illumination), benzophenone is carboxylated at a faradic efficiency of 94% and in >98% isolated yield of the α -hydroxy acid product (Figure 2.4c). We note that in order to avoid direct reduction of CO₂, which would alter the proposed reaction mechanism and produce undesired by-products, it is important to limit the operating potentials at or above -1.2 V. Additional control experiments also suggest that the reaction proceeds by a 2-step single-electron transfer process (see 2.3.4).^[23,24] Dimerization of the starting material as well as reduction to the secondary alcohol is often observed in electrochemical coupling of ketones with carbon dioxide. During the reaction, the product, in the form of an aluminum salt, would

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precipitate out of the solution and only a small portion left on the surface of aluminum anode. The solid product salt would not influence the charge transfer between Si NWs photocathode and the other organic substrate molecules. The observed photocurrent would not be disturbed as long as the aluminum anode was not consumed out. Analysis of the crude photoelectrochemical reaction mixture by ¹H NMR showed no signs of byproduct formation consistent with the high isolated yield.^[25]





negative turn-on voltages. Data obtained under 100 mW/cm² AM 1.5G illumination. (b) Light powered carboxylation of benzophenone.



Figure 2.5 a. photocurrent density of planar Si electrode at different light intensities; b. Photocurrent density vs. voltage plots under different illumination conditions. A cross

sectional view of the electrode is shown in the inset; scale bar: 1 μ m. All measurements were performed with 25 mM benzophenone in 0.1 M TBAB acetonitrile solution with CO₂ bubbling. Xe lamp was used as light source. All light intensity was calibrated by a Si diode under AM 1.5 irradiation condition.

The linear relationship between saturation photocurrents densities on planar Si and light intensities suggest effective electron transfer on the Si/ benzophenone junction. The photocurrent density of planar Si is slightly higher than Si NWs, which is due to the increased charge recombination on the larger surface area of Si NWs. But the turn-on potential is more negative than Si NWs. The turn-on photocurrent slop on Si NWs (68.7 mA cm⁻² V⁻¹) is also slightly lower than the planar Si (70.1 mA cm⁻² V⁻¹). This indicates improved electron transfer kinetics from multifaceted Si NWs to liquid electrolyte junction, leading to reduced overpotentials.

2.3.3 Photocurrent densities and turn-on voltages of different length SiNWs

Further analysis of the benzophenone carboxylation reaction showed that SiNWs exhibit a less negative turn-on (-0.52 V at >1 mA/cm²) than planar Si (-0.63 V) but lower saturation current density (32.1 mA/cm² vs. 34.4 mA/cm², Figure 2.4a). It has been reported that the high surface area of nanostructures such as SiNWs may result in increased charge recombination at the semiconductor/solution interface, leading to reduced saturation current densities without considering light trapping mechanisms.^[16,26,27] However, the recombination mechanism would also predict reduced open-circuit potentials, implying a more negative turn-on voltage should be measured on SiNWs than on planar Si.



Figure 2.6: Saturation photocurrent densities (a) and turn-on potentials (b) vs. p-SiNWs lengths.

To account for the apparent discrepancies, we suggest that the observed trend is indicative of improved charge transfer kinetics on SiNWs. That is, the multifaceted nature of SiNWs favors charge transfer from Si to benzophenone, resulting in lower overpotentials. Our hypothesis is supported by control experiments where the turn-on voltages were compared with the length of SiNWs (L varying between 0 and 10 μ m). Within a limited range (0 < L ≤ 6 μ m), the turn-on voltage changes with the surface roughening factor monotonically; the recombination-induced open-circuit reduction dominates for longer SiNWs (L > 6 μ m), and more negative turn-on voltages were measured. Similar effect has been observed on SiNWs-based water splitting reactions previously,^[28,29] although more details about the reasons remain unclear to the best of our knowledge.

Si NWs with different length were obtained by varying chemical etching time. All Si NWs photoelectrodes were measured in the CO_2 /benzophenone system in the same PEC setup and identical illumination condition. Photocurrent densities were determined from the saturate photocurrent densities (J_{sc}), and turn-on potentials (V_{on}) were identified at current density greater than 1 mA/cm² for comparison.

In order to interpret the observed trend of J_{sc} and V_{on} dependency on the nanowire lengths correctly, we need to consider several important factors. First, light absorption changes with the length (*L*) of Si NWs. Longer nanowires allows for more light absorption and, therefore, increases J_{sc} . Second, the probability for charge recombination increases with Si NWs length, too. Longer nanowires exhibit larger solid/liquid junction areas, which contain more surface states as charge recombination centers. As a result, for long NWs, J_{sc} is expected to decrease with increasing *L*. Taken as a whole, J_{sc} is likely to decrease for short Si NWs because the effect due to increased surface charge recombination dominates when light absorption is relatively weak. Indeed, we observed a monotonic decrease of J_{sc} for $L < 4 \mu m$. For longer Si NWs, however, the effect due to improved light absorption dominates, leading to an obvious increase of J_{sc} when $L>4 \ \mu m$ (Figure 2.6a).

Interestingly, V_{on} exhibited opposite trend for relatively short Si NWs (L≤4 µm). This observation suggested that additional factors have a significant effect on the V_{on} . In the literature, nanostructured semiconductor photoelectrodes have been shown to change the energetics of the solid/liquid interface and lead to reduced overpotentials.^{5¶} We suggest that the multifaceted nature of Si NWs improves the charge transfer kinetics and, hence, reduces the overpotentials.

For Si NWs longer than 10 μ m, the recombination effect would eventually dominate. As a result, lower V_{oc} is measured (Figure 2.6b).

2.3.4 Mechanistic studies of the reactions

To better understand the reaction mechanisms, we carried out control experiments using with p-Si NW photoelectrodes under illumination. For these experiments, the volume of solvent and concentration of supporting salt (tetrabutyl ammonia bromide) were kept constant. The results are summarized in Figure 2.7.



Figure 2.7 a. Si NWs photoelectrodes measured with or without the presence of CO_2 . b. Si NWs photoelectrodes measured without the presence of benzophenone. As a reference, the trace for typical carboxylation reactions is shown in red.

As shown in Figure 2.7, when CO_2 was absent, photogenerated electrons reduce benzophenone by a single-electron transfer process to produce ketyl radical anions or dimmer (see Scheme 1 in the main text for a drawing of the mechanism). The second electron transfer, which takes place after CO_2 fixation, is not observed. Supporting this understanding is currently density level of the observed plateau (14.6 mA/cm²), approximately half of that when CO_2 is present (29.4 mA/cm²). Under large negative bias condition (<-2.1 V), the solvent or supporting salt can be reduced and now the photocurrent density can be increased further.

In the absence of benzophenone, CO_2 is reduced to produce C of various oxidation states. This reaction competes with the carboxylation process and is undesired. To limit such side reactions, we typically chose the operating conditions in the green shaded area in Figure S5b. Lastly, we note that the reaction with the solvent only occurs at extremely negative potentials (*e.g.*, <-2.1 V) and no photocurrent due to solvent reduction could be observed under our photosynthesis conditions.

2.3.5 Photosynthesis Results

To demonstrate the synthetic utility of the reaction we applied the methodology to 2acetyl-6-methoxynaphthalene and 4-isobutylacetophenone, which are precursors for the anti-flammatory drugs naproxen and ibuprofen.^[19,24] We observed consistently high yield and selectivity for both new substrates (Figure 2.9); furthermore, the performance is comparable to what has been reported by electrochemical carboxylation techniques where electricity was the only source of energy input and graphite or mercury were the electrodes (see later discussion).

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For practical applications, the stability of the photoelectrodes against photo corrosion and other mechanisms that may degrade their performance such as oxidation is an important concern. For the reported process, the SiNWs are operating under reductive conditions, so we considered oxidation of SiNWs less likely and instead focused our attention on assessing the stability. Recycling of the photoelectrode made of SiNWs up to four times showed no measurable differences in the PEC performance (Figure 2.8). Importantly, the rate, yield, and selectivity were reproduced over each successive experiment, consistent with the fact that SiNWs remain intact over the course of the reaction (> 34 h). If we assume every Si surface atom as an active site, a peak turn-over frequency (TOF) of 25.8 s⁻¹ is estimated (detailed calculation see 2.3.6).

We emphasize that the photoelectrochemical syntheses reported here were carried out at potentials up to 670 mV less negative than what has been reported using electrochemical approaches, the difference provided by solar light. Our strategy showed that solar light photon energies can indeed be harnessed to promote the synthesis at lower applied potential.^[30]





Figure 2.8. Stability of Si NW photoelectrodes. No significant difference is observed for four consecutive runs under identical operating conditions.



Figure 2.9. Summary of selectivity and isolated yield for NSAID precursors.

2.3.6 Turnover frequency (TOF) calculation.

The TOF was calculated following the heterogeneous catalysis definition:

$$TOF = \frac{N_p}{N_{cat} \times t}$$
(2.2)

where N_p stands for the number of product molecules as measured by NMR; N_{cat} is the number of active sites, and we estimate it by assuming every surface Si atom is an active site (as such, the *TOF* calculated would be a conservative lower limit); *t* is the reaction time.

In a typical experiment, we detected 27% carbooxylation product of 0.44 mmol bezophenone starting material after 1 h reactions; the electrode area was 0.86 cm². From this information, we obtained a *TOF* of 25.8 s⁻¹.

2.3.7 Comparison of selectivity obtained by this work and those reported in the literature



* Yield of isolated product after purification; all the reactions of this work were carried out in acetonitrile at 25 °C with Si NWs cathode under an atmosphere of CO₂, reaction for 4-isobutylacetophenone was carried out at 4 °C. Applied potential was -1.2 V on benzophenone and 2-acetyl-6-methoxynaphthalene; -1.6 V on 4-isobutylacetophenone vs. Ag/Agl/l⁻ reference electrode.

[†] The reactions were carried out in N-methyl pyrrolidone at 20 °C with graphite cathode under an atmosphere of CO₂. ¹H NMR yield is based on converted starting material. ^{‡ 1}H NMR yield 97%.

[■] The reactions were carried out in N, N-dimethylformamide at 0 ^oC with mercury cathode under 1 atm CO₂. Reactions were done under constant current density: 10 mA cm⁻². ¹H NMR yield is based on converted starting material.

[§] The reactions were carried out in N, N-dimethylformamide at 25 °C with mercury cathode under 65 atm CO₂. Reactions were done under constant current density: 10 mA cm⁻². ¹H NMR yield is based on converted starting material.

2.4 Conclusion

In conclusion, we demonstrated a chemical reaction that is powered by light, the most abundant energy source on the surface of earth, and uses CO₂, an inexpensive and readily available source of carbon. Significantly, these reactions produce organic targets that can be readily used to synthesize NSAIDs such as ibuprofen and naproxen. Although the energy harvesting aspect of natural photosynthesis has been widely exploited in reactions such as H₂O splitting or CO₂ reduction for fuel production, how to learn from nature and use the harvested photo energy for complex molecule synthesis is an underdeveloped area. One of the most important merits offered by the reported reaction strategy is the ease with which electron exchange (donation for photocathode or withdrawal for photoanode) takes place between the photoelectrode and the organic substrates. It has the potential to greatly broaden the scope of photosynthesis. While in the present proof of concept demonstration an additional electrochemical potential is still necessary, the energy input from the harvested light plays a critically important role. As

such, our approach represents a step forward in the use of light to power complex organic molecule syntheses.

2.5 Reference

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2.6 Appendix

Substrate Characterization.

Substrate Syntheses

Benzophenone was obtained from Sigma-Aldrich and used without purification. 2-Acetyl-6-methoxynaphthalene was purchased from TCI America and was used without further purification.



1-(4-isobutylphenyl)ethanone. To a flame-dried, 250-mL, round-bottom flask was added AlCl₃ (9.38 g, 70.3 mmol) and CH₂Cl₂ (86 mL). The mixture was cooled to 0 °C, and acetylchloride (5.00 mL, 70.3 mmol) and isobutylbenzene (10.0 mL, 63.9 mmol) were added, sequentially, to the flask. The reaction was stirred at this temperature for 90 minutes. The mixture was poured into a mixture of ice water and CH₂Cl₂ (150 mL). The two layers were partitioned in a separatory funnel and the organic layer was washed with water (70 mL) and brine (50 mL). The organic layer was dried over MgSO₄ filtered, and concentrated *in vacuo*. The title compound was distilled to purity using a Kughelrohr and was isolated as a colorless oil (10.7 g, 95%). ¹H NMR ((CD₃)₂CO, 500 MHz) δ 7.89 (d, 2H, *J* = 8.3), 7.30 (3, 2H, *J* = 8.3), 2.55 (d, 2H, *J* = 7.3), 2.54 (s, 3H), 1.87 – 1.95 (m, 1H), 0.89 (d, 6H, *J* = 6.6); ¹³C NMR ((CD₃)₂CO, 125 MHz) δ 197.6, 148.2, 136.3, 130.3, 129.2, 45.9, 31.0, 26.8, 22.7; **IR**: 2956, 1680, 1605, 1357, 1265, 950, 596, 582 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₁₂H₁₇O₁ [M+H]⁺: 177.1279, found: 177.1280.

Product Characterization



2-hydroxy-2,2-diphenylacetic acid. To a flame-dried, three-neck, 25-mL, roundbottom flask equipped with magnetic stir bar was added tetrabutylammonium bromide (0.664 g, 2.00 mmol), benzophenone (0.22 M benzophenone in acetonitrile; 2.00 mL, 80.0 mg. 0.439 mmol) and acetonitrile (18 mL) in a dry box. One of the following was placed in each neck of the round-bottom flask: Si NWs working electrode, aluminum counter electrode, Aq/Aql/l⁻ reference electrode. The reaction vessel was brought out of the dry box and CO_2 was bubbled through the solution with an oil bubbler outlet. A potential -1.2 V was applied to the reaction mixture and a light was shined onto the reaction with vigorous stirring overnight. The crude reaction mixture was concentrated in vacuo, guenched with 6 N HCl (7.5 mL), and extracted with diethyl ether (3 x 20 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo to afford the title compound as a colorless solid (98 mg, 98%). ¹H NMR $((CD_3)_2CO, 500 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}, 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}; 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}; 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}; 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 - 7.52 \text{ (m. 4H)}; 7.29 - 7.37 \text{ (m. 6H)}; {}^{13}C \text{ NMR} ((CD_3)_2CO, 100 \text{ MHz}) \delta 7.49 + 7.52 \text{ (m. 4H)}; 7.49 + 7.52$ 125 MHz) δ 175.3, 144.1, 128.7, 128.5, 128.3, 81.6; **IR**: 3394, 2865, 1715, 1243, 1175, 1053. 697 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₁₄H₁₁O₂ [M+H-H₂O]⁺: 211.0759, found: 211.0758.



2-hydroxy-2-(6-methoxynaphthalen-2-yl)propanoic acid. To a flame-dried, threeneck, 25-mL, round-bottom flask equipped with magnetic stir bar was added tetrabutylammonium bromide (0.664 g, 2.00 mmol), 2-acetyl-6-methoxynaphthalene (0.0865 g, 0.432 mmol) and acetonitrile (20 mL) in a dry box. One of the following was placed in each neck of the round-bottom flask: Si NWs working electrode, aluminum counter electrode, Ag/Agl/l reference electrode. The reaction vessel was brought out of the dry box and CO_2 was bubbled through the solution with an oil bubbler outlet. A potential -1.2 V was applied to the reaction mixture and a light was shined onto the reaction with vigorous stirring overnight. The crude reaction mixture was concentrated in vacuo to remove the acetonitrile solvent. To the crude reaction was added 6 N NaOH (3 mL). The aqueous layer was washed with diethyl ether (15 mL). After separating the two layers, the organic layer was washed with an additional portion of 6 N NaOH (3 mL). The organic layer was discarded and the combined aqueous layers were acidified to pH = 2 with concentrated HCI. This aqueous layer was washed with diethyl ether (2 x 30 mL) and the combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo to afford the title compound as a colorless solid, which turns beige upon standing (89 mg, 84%). ¹H NMR (($(CD_3)_2CO$, 500 MHz) δ 8.05 (d, 1H, J = 1.5) 7.77 – 7.82 (m, 2H), 7.69 – 7.71 (m, 1H), 7.28 (d, 1H, J = 2.4), 7.13 – 7.15 (m, 1H), 3.91 (s, 3H), 1.81 (s, 3H); ¹³C NMR (((CD₃)₂CO, 125 MHz) δ 176.5, 158.8, 139.8, 134.8, 130.3, 129.3, 127.3, 125.0, 124.5, 119.5, 106.2, 76.0, 55.5, 27.4; **IR**: 3410, 2940, 1724, 1605, 1266, 1132, 851 cm⁻¹; **HRMS** (DART-TOF) calcd. for $C_{14}H_{13}O_3$ [M+H-H₂O]⁺: 229.0865, found: 229.0872.



2-hydroxy-2-(4-isobutylphenyl)propanoic acid. To a flame-dried, three-neck, 25-mL, round-bottom flask equipped with magnetic stir bar was added tetrabutylammonium bromide (0.664 g, 2.00 mmol) in a dry box. One of the following was placed in each neck of the round-bottom flask: Si NWs working electrode, aluminum counter electrode, Ag/Agl/I⁻ reference electrode. The reaction vessel was brought out of the glovebox and was purged with CO₂ three times. Acetonitrile (20 mL) was added to the flask under an atmosphere of CO_2 and the flask was then brought into a cold room (4 °C) where CO_2 was bubbled through the solution. During the course of sparging the solution, 4isobutylacetophenone (80.0 µL, 0.432 mmol) was brought out of the dry box and added to the reaction via syringe. Sparging with CO_2 was continued for an additional 20 minutes, after which time the inlet/outlet needles were replaced with a balloon of CO₂. A potential of -1.6 V was applied to the reaction mixture and a light was shined onto the reaction with vigorous stirring overnight. The crude reaction mixture was concentrated in vacuo to remove the acetonitrile solvent. To the crude reaction was added 6 N HCI (8 mL). The aqueous layer was washed with diethyl ether (3 x 20 mL). The combined organic layers were washed with 6 N NaOH (3 x 6 mL) and the organic layer was discarded. The aqueous layer was acidified to pH = 2 using concentrated HCI. The aqueous layer was extracted with diethyl ether (3 x 30 mL) and the organic layer was dried over MgSO₄, filtered, and concentrated in vacuo to afford the title compound as a colorless solid (62 mg, 65%). ¹H NMR ((CD₃)₂CO, 500 MHz) δ 7.53 (d, 2H, J = 8.1), 7.15 (d, 2H, J = 8.1), 2.47 (d, 2H, J = 7.3), 1.82 – 1.90 (m, 1H), 1.73 (s, 3H), 0.89 (d, 6H, J = 6.6); ¹³**C NMR** (((CD₃)₂CO, 125 MHz) δ 176.2, 142.0, 141.4, 129.4, 125.8, 75.9, 45.3, 30.7, 27.4, 22.5; **IR**: 3423, 2955, 2926, 2869, 1716, 1262, 1146, 1119 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₁₃H₁₇O₃ [M-H]⁻: 221.1178, found: 221.1175.

By-product Characterization



Diphenylmethanol. Purchased from Sigma-Aldrich and analyzed by ¹H NMR in acetone- d_6 . ¹H NMR ((CD₃)₂CO, 500 MHz) δ 7.44 (d, 4H, J = 7.6), 7.30 – 7.33 (m, 2H), 7.20 – 7.23 (m, 2H), 5.85 (d, 1H, J = 3.7), 4.87 (d, 1H, J = 3.9); ¹³C NMR ((CD₃)₂CO, 125 MHz) δ 146.5, 129.0, 127.7, 127.4, 76.2;. **IR**: 3275, 1493, 1454, 1032, 1017, 762, 739 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₁₃H₁₁ [M+H-H₂O]⁺: 167.0861, found: 167.0865.



1,1,2,2-tetraphenylethane-1,2-diol. Purchased from Sigma-Aldrich and analyzed by ¹H NMR in acetone- d_6 . ¹H NMR ((CD₃)₂CO, 500 MHz) δ 7.44 – 7.46 (m, 8H), 7.10 – 7.11 (m, 12H), 4.79 (s, 2H); ¹³C NMR ((CD₃)₂CO, 125 MHz) δ 147.0, 130.1, 127.4, 127.1, 84.1; **IR**: 3554, 3056, 1445, 1024, 741, 698 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₂₆H₂₁O₁ [M+H-H₂O]⁺: 349.1592, found: 349.1588.



1-(6-methoxynaphthalen-2-yl)ethanol. To a flame-dried, 15-mL, round-bottom flask was added NaBH₄ (134 mg, 3.00 mmol) and dry methanol (3.0 mL). The mixture was cooled to 0 °C and 2-Acetyl-6-methoxynaphthalene (500 mg, 2.50 mmol) was added to the flask, with stirring, as a solution in methanol (1.4 mL). After the addition was complete, the reaction was allowed to warm to room temperature over one hour. The reaction was quenched by the addition of 4 N HCl (10 mL), transferred to a separatory funnel, and extracted with dichloromethane (60 mL). The organic layer was dried over MgSO₄, filtered, and concentrated to yield a colorless solid (420 mg, 83%). ¹H NMR ((CD₃)₂CO, 500 MHz) δ ¹H NMR ((CD₃)₂CO, 500 MHz) δ 7.78 (s, 1H), 7.77 (d, 1H, *J* = 2.2), 7.75 (s, 1H), 7.50 – 7.52 (m, 1H), 7.27 (d, 1H, *J* = 2.4), 7.12 – 7.14 (m, 1H), 4.96 – 5.01 (m, 1H), 4.21 (d, 1H, *J* = 3.9), 3.90 (s, 3H), 1.48 (s, 3H, *J* = 6.6); ¹³C NMR ((CD₃)₂CO, 125 MHz) δ 158.5, 143.5, 134.9, 130.2, 129.8, 127.6, 125.7, 124.3, 119.5, 106.6, 70.1, 55.6, 26.2; **IR**: 3340, 2972, 1251, 1203, 760, 698 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₁₃H₁₃O₁ [M+H-H₂OI⁺: 185.0966, found: 185.0970.



1-(4-isobutylphenyl)ethanol. To a flame-dried, 25-mL, round-bottom flask was added NaBH₄ (129 mg, 3.40 mmol) and methanol (4 mL). The mixture was cooled to 0 °C, followed by the addition of 1-(4-isobutylphenyl)ethanone (500 mg, 2.84 mmol) as a solution in methanol (1 mL). The reaction was allowed to warm to room temperature over one hour, quenched by the addition of 4 N HCl (10 mL), transferred to a separatory funnel, and washed with dichloromethane (70 mL). The organic layer was dried over MgSO₄, filtered, and concentrated *in vacuo*. Isolation of the title compound was carried

out using silica gel column chromatography (20% EtOAc/Hex) to afford a colorless oil (429 mg, 84%). ¹H NMR ((CD₃)₂CO, 500 MHz) δ 7.28 (d, 2H, *J* = 7.8), 7.10 (d, 2H, *J* = 8.1), 4.78 – 4.82 (m, 1H), 4.0 (d, 1H, *J* = 4.2), 2.45 (d, 2H, *J* = 7.3), 1.82 – 1.87 (m, 1H), 1.38 (d, 3H, *J* = 6.4), 0.89 (d, 6H, *J* = 6.6) ¹³C NMR (((CD₃)₂CO, 125 MHz) δ 145.7, 140.7, 129.6, 126.1, 69.9, 45.7, 31.1, 26.3, 22.8; **IR**: 3342, 2954, 1094, 846, 799, 554 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₁₂H₁₇ [M+H-H₂O]⁺: 161.1330, found: 161.1331.



2,3-bis(4-isobutylphenyl)butane-2,3-diol (isolated as a mixture of *meso* and *dl* compounds). Prepared by the method of Banik, *et al.*¹ ¹**H NMR** ((CD_3)₂CO, 500 MHz) δ 7.23 (d, 4H, *J* = 8.3), 7.07 (d, 4H, *J* = 8.1), 6.95 (m, 8H), 4.07 (s, 2H), 3.92 (s, 2H), 2.42 – 2.44 (m, 8H), 1.81 – 1.86 (m, 4H), 1.51 (s, 6H), 1.50 (s, 6H), 0.87 – 0.89 (m, 24H); ¹³**C NMR** ((CD_3)₂CO, 125 MHz) δ 144.1, 143.5, 140.2, 140.0, 128.3, 128.2, 128.1, 128.0, 79.0, 78.7, 45.64, 46.63, 31.1, 31.0, 25.5, 25.2, 22.7, 22.6; **IR**: 3450, 2952, 1338, 1102, 1063, 1019, 907, 848, 798, 596 cm⁻¹; **HRMS** (DART-TOF) calcd. for C₂₄H₃₃O₁ [M+H-H₂O]⁺: 337.2531, found: 337.2519.

Chapter 3:

Si Nanowires Show Improved Performance as Photocathode for Catalyzed Carbon Dioxide Photofixation

3.1 Introduction

The ability to utilize sunlight, the most abundant form of energy on earth's surface, to power chemical reactions is a unique feature of natural photosynthesis.^[1] The process enables the storage of solar energy that is intermittent in nature. With carbon dioxide (CO_2) as a feedstock, it also produces highly specific organic chemicals that are the essential energy suppliers or building blocks for a wide range of important natural processes.^[2-4] Significant research efforts have been devoted to mimicking the process in artificial systems, and the major focus has been on how to improve the solar energy conversion efficiencies.^[5,6] Relatively underwhelming attention is paid to issues related to low product specificities when CO₂ is reduced. Inspired by the detailed mechanisms of the dark reactions in the Calvin cycle.^[7] we recently reported a strategy to combat this problem.^[8] Briefly, the key to our idea was to avoid direct CO₂ reduction, which is prone to produce carbons of varying oxidation states. Instead, we rely on the creation of an intermediate that subsequently reacts with CO₂ selectively. The idea is similar to Bocarsly *et al*'s approach of using pyradium for the production of methanol,^[6] although we seek to produce more complex, and hence synthetically relevant organic molecules. In principle, the scope of reactions can be significantly broadened if the intermediate produced by photoreduction is a catalyst that can be used to react with CO₂ to yield the

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desired product. Similar to photosynthesis, the carbon-carbon bond forming reactions are independent of photons (*e.g.* the dark reactions), allowing for improved control in selectivity. To test this hypothesis, here we report our success in performing CO₂ photofixation with the help of the Ni(bpy)₂ catalyst. To our surprise and delight, we observed that Si nanowire (SiNW) photoelectrode exhibited more than 300 mV turn-on potential reduction when compared with planar Si. We attributed this to the multifaceted nature of the nanowires.



Scheme 3.1. Proposed reaction mechanism of catalyzed CO₂ fixation by Si photoelectrodes.

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Our catalyzed CO_2 photofixation design is schematically shown in Scheme 1. SiNWs absorb solar energy and excite electrons to the conduction band. The excited electrons are transferred to the Ni(II)(bpy)₂²⁺ complex and produce Ni(0)(bpy)₂, which then binds with CO_2 and the alkyne substrate. Oxidative cyclization of the alkyne and CO_2 yields a Ni(II) metallacycle, which upon protonation releases the desired carboxylic acid, regenerating the Ni(II) catalyst. Overall, the Ni catalysed process provides an efficient and stereospecific synthesis of trisubstituted alkenes from CO_2 and an alkyne.

3.2 Experimental

3.2.1 Catalyst Synthesis

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

To a flame-dried, 100 mL, round-bottom flask was added, successively, $Ni(BF_4)_2 \cdot 6H_2O$ (1 eqiv.), EtOH (0.15 M), and 2,2'-bipyridine (3 equiv.). The reaction was stirred at room temperature for one hour. The resultant precipitate was filtered, washed with Et₂O, and dried overnight under reduced pressure.

3.2.2 SiNWs Synthesis

SiNWs were prepared by a previously reported method. A piece of p-Si (100) wafer, (10^{15} cm⁻³ B doped, p:10~20 Ω •cm, Wafernet, USA), sequentially cleaned with acetone, methanol, and isopropanol, was further cleaned using Piranha solution of H₂O₂/H₂SO₄ (1:3) (Sigma-Aldrich, USA) at 90°C for 15 min to remove heavy metals and organic species. Following rinsing with deionized (DI) water, the wafer was cut into approximately 1.0 cm× 4.0 cm pieces. Immersion of the pieces in an HF/AgNO₃ solution (4.6 M HF and 0.02 M AgNO₃, Sigma-Aldrich, USA) for 30 min at 50 $^{\circ}$ C resulted in SiNWs ca. 10 µm in length. The SiNWs substrate was then cleaned by an HNO₃ aqueous solution (Sigma-Aldrich, USA) to remove silver residue and finally was rinsed by DI water.

3.2.3 Photoelectrode fabrication

The SiNWs substrate was immersed in HF (aqueous, 5%) for 2 min and dried in a stream of N₂. Following AI (300 nm) sputtering onto the backside of the substrates by radio frequency magnetron sputtering (AJA International, Orion 8, USA), the substrate was annealed in Ar (flow rate: 5000 standard cubic centimeter per minute, SCCM) at 450°C for 5 min in rapid thermal processor (RTP-600S, Modular Process Tech., USA), and tinned Cu wires were fixed to the Al film by conductive epoxy (SPI supplies, USA) to form a back contact. Lastly, non-conductive hysol epoxy (Loctite, USA) was used to seal the substrate, allowing only the front surface where SiNWs reside to remain revealed.

3.2.4 Photoelectrochemical (PEC) and Electrochemical Impedance Spectroscopy (EIS)characterizations

PEC and EIS experiments were carried out using a CHI 609D Potentiostat. A threeelectrode configuration was used, in which a Ag/AgI wire soaked in 0.1 M tetrabutylammonium iodide acetonitrile solution was used as the reference electrode, a piece of high-purity AI foil (99.9995%, Alfa Aesar, USA) served as the counter electrode, and SiNW-based (or planar Si) photoelectrodes were used as the working electrode. The electrolyte solution was composed of 5 mM Ni(bpy)₃(BF₄)₂ catalyst and 0.1 M

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tetrabutyl ammonium bromide (TBAB) (\geq 99.0%, Sigma-Aldrich, USA) in 20 mL acetonitrile. CO₂ (Airgas, USA; flow rate: 120 SCCM) was continuously bubbled through the solution. A 150 W Xenon lamp (model 71228, Newport, USA) equipped with an AM 1.5G filter and illumination intensity calibrated to be 100 mW cm⁻² by a Si photodiode (UV 005, OSI, Optoelectronic, USA) was used as the light source. The scan rates for both CV and IV curves were 50 mV s⁻¹. EIS measurement was done with electrolyte solution of 5 mM Ni(bpy)₃(BF₄)₂ catalyst and 0.1 M tetrabutyl ammonium bromide in 20 mL acetonitrile without illumination. Frequency range was from 10⁵ Hz to 1 Hz.

3.2.5 Reference Electrode Calibration

All potentials shown hereafter in this dissertation are relative to the reference electrode of Ag/AgI/I⁻, which is -0.56 V relative to SCE, saturated calomel electrode).

This homemade reference electrode is made by soaking a silver wire into 0.1 M tertabutalammonium idiod acetonitrile solution in a glass tube with porous glass tip.

The potential of this electrode is calibrated with SCE based on testing same redox pair $(CoCp_2^0/CoCp_2^+/MeCN)$ potential with a Pt mesh. The cyclic voltammograms is recorded by using reference electrode of SCE or Ag/AgI/I⁻ electrode.



Figure 3.1. Reference electrode calibration by testing cyclic voltammograms in redox pair of $CoCp_2^0/CoCp_2^+$.

3.3 Results and Discussion

3.3.1 Polarization Curves Comparison of various electrodes and photoelectrodes

Although the process may be accomplished by electrochemistry^[9] using, for example, Pt as the working electrode, the advantage of performing the reaction on a Si photoelectrode is a significantly lowered requirement for externally applied potentials, as shown in Figure 3.2. Analysis of the crude reaction mixture shows the reaction proceeded at 81% faradaic efficiency for the carboxylated product.


Figure 3.2. Comparison of various electrodes and photoelectrodes. a) Cyclic voltammetry in acetonitrile with 0.1 M tetrabutylammonium bromide, 5 mM $Ni(bpy)_3(BF_4)_2$, and 0.05 M 4-octyne, saturated with CO₂. Scan rate: 50 mV/s. Both SiNW and planar Si photoelectrodes were under illumination of an Xenon lamp (light intensity adjusted to 100 mW cm⁻²). No measurable current was observed on SiNW and

planar Si photoelectrodes when they were not illuminated. b) Polarization curves in the same solution but with vigorous stiring (1000 rpm).

3.3.2 Mott-Schottky plots and the corresponding energy band diagrams of electrode made of SiNWs and planar Si

Most prominent of the features are that the peaks in the cyclic voltammetry (CV) corresponding to the reduction/oxidation of Ni(II)(bpy)₂²⁺/Ni(0)(bpy)₂ are anodically shifted, from -0.71 V for Pt to -0.37 V for planar Si photoelectrode, and -0.19 V for SiNWs (Figure 3.2a; all potentials shown hereafter in this chapter are relative to the reference electrode of Ag/Agl/I⁻, which is -0.56 V relative to SCE, saturated calomel electrode). The shift suggests the need for applied potentials is greatly reduced, with the additional power produced by the photoelectrode. It means that our approach allows one to effectively use the energy delivered by light for the reduction of CO₂, which is an important character of photosynthesis. We also note that there are no anodic peaks visible on all electrodes (Figure 3.2a), strongly indicating that electron transfer from Ni(0) catalyst to alkyne and CO₂ as proposed in Scheme 1. Without alkyne and CO₂, the anodic peaks were unambiguously observed.

There are several points we wish to highlight here, including the importance of light, the performance difference between electrodes made of SiNWs and planar Si, and a hypothesis for these unusual observations. We first focus on the effect of light on the reactions. Within the potential window that we measured (Figure 3.3), without light no

currents were observed on electrodes made of Si, either planar or SiNWs. The result suggests that light plays an important role in powering the reactions. The difference between the red/ox potentials of Ni(II)(bpy) $_{2}^{2+}$ /Ni(0)(bpy) $_{2}$ for Si and that for Pt was inferred as the photovoltage provided by Si.^[10] When Si is in equilibrium with the electrolyte system, a downward band bending occurs (see Figure 3.3c & 3.3d). This is because the Fermi level (as measured by the flatband potential, or V_{fb}) of Si is more positive than the equilibrium potential of the Ni(II)(bpy)₂²⁺/Ni(0)(bpy)₂ system. Here we emphasize that the exact equilibrium potentials of the electrolyte system relative to the Fermi levels of Si is unknown. The measurement of these values requires further It is likely to be different from the red/ox peak positions of research. $Ni(II)(bpy)_2^{2+}/Ni(0)(bpy)_2$ as measured by the CV peak positions in Figure 3.2a, which were obtained under stagnant conditions. This is because the equilibrium potential of $Ni(II)(bpy)_2^{2+}/Ni(0)(bpy)_2$ depends on the relative concentrations of the oxidized and reduced species. As such, our representation of the band-bending in Figure 3.3 is qualitative in nature.

The data presented in Figure 3.2a nonetheless allowed us to obtain a V_{ph} of 0.34 V for planar Si and one of 0.52 V for SiNWs. These values fall in the range of photovoltages observed on both n- and p-type Si previously^[11,12] and are therefore reasonable. What was intriguing, however, is the difference between photoelectrodes made of planar Si and SiNWs. To better present the difference, typical polarization curves for all three types of electrodes are plotted in Figure 3.2b. If we define the potential at which the currents (or photocurrents) reach 50 μ A cm⁻² as the turn-on voltage (V_{on}), the value for Pt is -0.46 V, and those for planar Si and SiNWs are -0.20 V and +0.04 V, respectively. Again, a greater reduction in V_{on} is observed on SiNWs (0.50

V as opposed to 0.26 V for planar Si), implying that photoelectrodes of SiNWs produce larger photovoltages. While reduced reflection and improved light harvesting by SiNWs might contribute to the greater photovoltage^[13], such an effect would fail to account for a significant difference like what we observe (0.24 V more photovoltage measured on SiNWs). It is noted that the same trend was observed on more than 6 pairs of photoelectrodes compared, with less than 0.02 V differences in the photovoltages measured. We therefore ruled out the possibilities of measurement artifacts.

We suggest the difference is a manifestation of how easy or difficult charge transfer can take place between Si and the catalyst. It is well documented that the impedance to the charge transfer process show up in polarization curves as a part of the *overpotential*.^[14] Because Ni(bpy)₂^{2+/0} is not known to form covalent bonds with Si, the electron transfer likely proceeds through an outer-sphere mechanism. The ease (or difficulty) of electron transfer from Si to Ni(bpy)₂^{2+/0} is dependent on which surfaces of Si is exposed to and how the molecules are arranged relative to Si surface atoms. The advantage of SiNWs is that each individual nanowire is multifaceted, meaning that a variety of crystal planes are present. It is reasonable to assume that electron transfer plane that favors the process, more so than on one that requires higher overpotentials, such as the (100) faces.

One way to test this hypothesis is to examine the electrochemical impedance spectroscopy. For this purpose, we plot how the capacitance varies with the applied potentials in dark. As shown in Figure 3.3a, a classical Mott-Schottky (M-S) relationship

$$C_{sc}^{-2} = \frac{2}{A_s^2 q \varepsilon \varepsilon_0 N_A} \left(V - V_{fb} - \frac{kT}{q} \right)$$
(3.1)

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is followed by SiNWs for frequencies ranging from 5000 Hz, 10000 Hz and 20000 Hz. Here, *C* represents the space charge capacitance in the semiconductor, N_A is the hole density, *q* is the electron charge, ε_0 is vacuum permittivity of a vacuum, ε is the dielectric constant of Si, *E* is the applied potential, V_{fb} is the flat band potential, *T* is the temperature, and *k* is the Boltzmann constant. The negative slope proves that the majority carrier is hole, consistent with the fact that p-type Si was used. From the M-S plots, a carrier concentration of N_A = 3.1×10^{15} cm⁻³ and V_{fb} =+0.69 V was obtained. The carrier concentration calculation is in excellent agreement with the information provided by the vendor of the Si substrate (resistivity: 10-20 Ω cm; N_A =10¹⁵ cm⁻³).

In stark contrast, a plateau shows up in the M-S plots for planar Si between -0.55 to -0.30 V. In the literature, a plateau like this is typically understood as a voltage region within which the applied potential drops within the Helmholtz layer instead of in the depletion region of the semiconductor.^[16] The most common cause for such a phenomenon has been regarded as surface states-induced Fermi level pinning.^[16] We, however, consider surface states trapping an unlikely mechanism for the phenomenon because the plateau was only observed on planar Si without chemical pre-treatments; it was absent on SiNWs produced by chemical etching which are far more likely to be of high surface states. We understand the origin of the plateau as the change of the Helmholtz layer on planar Si between -0.55 and -0.30 V. It is hypothesized that the arrangement of Ni(II)(bpy)₂²⁺ on Si surfaces is dependent on the surface potentials, and that the arrangement defines the impedance of charge transfer. For SiNWs, owing to the availability of a variety of facets, one that favors charge transfer between Ni(II)(bpy)₂²⁺ and Si is present within the entire potential window. For planar Si, on the other hand, the only available crystal plane is Si(100), which does not favor charge

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transfer between Ni(II)(bpy)₂²⁺ and Si above -0.30 V. Starting from -0.30 V, the negative potential induces molecular rearrangement for improved charge transfer, and the process is complete at -0.55 V. In other words, between -0.30 and -0.55 V, most of the applied potential drops at the Helmholtz layer instead of within the space charge region of Si. The understanding is depicted in Figure 3.3d. Close examinations of the M-S plots of planar Si revealed that if the data between $V_{applied}$ =0 and -0.30 V are used to extract the V_{fb} , a value of +0.66 V is obtained, which is only different from that obtained on SiNWs by 0.09 V (V_{fb} of SiNW is +0.69 V, as shown in Figure 3.3a). At applied potentials below -0.55 V, approximately 0.25 V drops within the Helmholtz layer that do not contribute to the formation of the space charge region. Note that all values discussed in this paragraph refer to steady-state conditions in dark.





Figure 3.3. Mott-Schottky plots and the corresponding energy band diagrams of electrode made of SiNWs (a & c, respectively) and that of planar Si (b &d, respectively). The insets in (a) and (b) show the legends of the frequencies used. The plateau observed on planar Si (b) is attributed to the charging of the Helmholtz layer. The understanding is shown in panel (d).

3.3.3 Electrochemical impedance spectroscopy (EIS) study of SiNWs and planar Si

To validate the hypothesis, we further examined the Nyquist plots at different applied potentials by fitting the data using equivalent circuits (Figure 3.4 and 3.5). Two distinct features of this group of data are noted.



Figure 3.4. Nyquist plots at 0 V (a), -0.600 V (b), -0.300 V(c) and -0.500 V (d) for SiNWs (red) and planar Si. The dotted lines are fitting data.

First, the capacitance attributed to the space charge region of SiNWs decreased monotonically between 0 V and -0.600 V. By comparison, the capacitance corresponding to the space charge region of planar Si remained unchanged between - 0.30 V and -0.50 V. This observation is consistent with the M-S plots as shown in Figure 3.3. It proves that within this potential window, the increased negative potential on planar Si drops within the solution but not in the space charge region, as indicated in Figure 3.3d.

Second, a clear difference between the data obtained on SiNWs and those on planar Si is observed in the low frequency region, where the characteristics of the Helmholtz layer and the solution dominate the features. For instance, at 0 V the fitting of the data for planar Si resulted in a resistor of $4.03 \times 10^6 \Omega$ while that for the SiNWs was $8.83 \times 10^4 \Omega$. At -0.60 V, the values were $1.49 \times 10^5 \Omega$ and $1.60 \times 10^5 \Omega$, respectively (see Table 3.1). The difference indicates that charge transfer from planar Si to Ni(II)(bpy)₂²⁺ at small applied potentials (*e.g.*, 0 V) was indeed more difficult than that from SiNWs to Ni(II)(bpy)₂²⁺, whereas the difference is negligible at high applied potentials (*e.g.*, -0.60 V).

Tabel 3.1a. EIS simulation results for planar Si at different applied potentials

	C_{sc}	R_{sc}	C_{ss}	R_{ss}	C _{dl}	R_{dl}	C _{n1}	R _{n1}
0 mV	7.46E-10	1.42E7	8.89E-8	1.15E5	2.82E-8	4.03E6	8.23E-7	9.05E4
-300 mV	5.60E-10	3.10E6	4.01E-8	2.15E5	4.17E-9	2.65E5	5.28E-8	2.43E5
-500 mV	5.87E-10	3.08E6	3.91E-8	2.12E5	4.50E-9	1.95E5	2.28E-8	3.90E5
-600 mV	5.31E-10	2.30E6	6.40E-8	2.42E5	2.60E-9	1.49E5	3.38E-8	4.00E5

Tabel 3.1b. EIS	simulation	results for	SiNWs at	different	ар	plied	potentials
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	C_{sc}	R_{sc}	C_{ss}	R_{ss}	C_{dl}	R_{dl}	C _{n1}	R _{n1}	C_{n2}	R_{n2}
0 mV	7.29E-10	1.58E6	2.17E-7	1.60E5	2.17E-8	8.83E4	7.72E-7	4.47E5	9.01E-8	9.94E4
-300 mV	5.89E-10	1.76E6	1.64E-7	1.69E5	1.71E-8	8.73E4	4.95E-7	2.87E5	9.80E-8	1.04E5
-500 mV	5.65E-10	2.46E6	1.33E-7	7.44E5	1.44E-8	1.35E5	2.14E-8	1.35E5	4.98E-8	1.31E5
-600 mV	5.39E-10	1.55E6	1.14E-7	2.55E5	1.12E-8	1.60E5	2.19E-8	4.72E5	2.19E-8	4.72E5





Figure 3.5. Nyquist plots of SiNWs at -600 mV with different fitting models respectively.

Taken as a whole, we understand the data as follows. When Ni(II)(bpy)₂ is in contact with SiNWs, a charge transfer pathway is established at relatively positive potentials due to the multifaceted nature of SiNWs. At similar potentials, a significant resistance between planar Si and Ni(II)(bpy)₂ exists, which disappears when the applied potential is negative enough (lower than -0.50 V, for example). The understanding also explains the photocurrent differences as shown in Figure 3.2b. At -0.20 V applied potential, a current density of -1.72 mA cm⁻² was observed on SiNWs while no photocurrent was measured on planar Si. In the diffusion-limited region (*e.g.*, -0.60 V), higher photocurrents were measured on planar Si than on SiNWs because of better diffusion on a planar electrode.

3.3.4 Ni catalysts turn over on SiNWs

The fact that Ni catalyst turns over on SiNWs was one of the most important pieces of information for the reaction. We used control experiment and the CV scans to prove the turning over of catalyst. In the control experiment, we continuously applied -0.3 V potential on SiNWs with light irradiation. But no substrate was added to the solution. As a result, photocurrent dropped continuously and quickly, maintaining less than 20 % when the 2n charge was passed through the PEC cell. The charge 2n means the equivalent amount of charge could reduce all catalyst in the solution. It implied that without substrate binding, the Ni catalyst cannot turn over on the SiNWs.

However, after the same amount of charge (2n), a very distinguish CV peak for Ni catalys was still obtained on SiNWs with substrates (4-octyne and CO₂) added to the solution. Overall, with the control experiment result, this was evidence to show that the Ni catalyst can turn over on SiNWs in the presence of substrates.



Figure 3.6. a) Control experiment with only 5 mM Ni catalyst in the acetonitrile solution with N_2 gas as protection gas; b) CV scans to show Ni catalyst was turning over on Si NWs. The electrolyte contained 5 mM Ni catalyst and 0.05 M 4-octyne acetonitrile

solution with CO_2 gas bubbling. In all electrolytes, 0.1 M tetrabutylammonium bromide was added in acetonitrile solution. SiNWs were illuminated with a 100 mW cm⁻² Xenon lamp.

3.3.5 Stability for SiNWs

The CV curve of SiNWs had good reproducibility (10 continuous CV scans overlapped well in Figure 3.7), suggesting that the stability of both SiNWs electrode and Ni catalyst were well maintained in this experimental condition.



Figure 3.7. CV stability of catalyst Ni(bpy)₃(BF4)₂ on SiNWs. SiNWs were illuminated with a 100 mW cm⁻² Xenon lamp.

3.3.6 Photosynthesis Results



Catalyst	Cathode/Conditions	Applied Potential	Faradaic Efficiency*
1	SiNWs / illuminated	-0.3 V	64 %
1	SiNWs / dark	-0.3 V	No product
1	Au	-0.8 V	74 %

*Faradaic efficiency is defined as one product mole per every 2 electron moles.

3.3.7 Characterization of Products

Carboylic Acid. The crude reaction mixture was transferred to a new 100 mL roundbottom flask and was concentrated *in vacuo* to remove acetonitrile. The reaction was quenched by the addition of 6N HCl (9 mL) and was extracted with diethyl ether (4 × 20 mL). The combined organic layers were dried over Mg₂SO₄, filtered, and concentrated under reduced pressure. ¹H NMR (CDCl₃, 500 MHz) δ 11.5 (s, 1H), 6.9 (t, 1H), 2.3 (t, 2H), 2.2 (q, 2H). 1.4-1,5 (m, 4H), 0.9-1.0 (m, 6H); ¹³C NMR [TBD]; HRMS (DART-TOF) calcd. for C₉H₁₇O₂ [M+H]⁺: 157.1233, found: 157.1229.

As Si is an earth abundant element, and a great deal of knowledge about its optoelectronic and photoelectrochemical properties has been accumulated, research on using Si-based materials for solar energy utilizations is of special interest. Within this

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context, our result is significant. It shows that SiNWs may exhibit advantages over planar Si in addition better light absorption. By reducing the overpotential due to charge transfer impedance, higher photovoltage is measured on SiNWs than on planar Si. Although similar observations have been made by earlier reports,^[17,18] little attention has been paid to the phenomenon. To the best of our knowledge, our report is the first to systematically compare photoelectrodes of SiNWs and planar Si in a synthetically useful system. A consistent trend, albeit in a much less pronounced magnitude, was observed in our proof-of-concept demonstration of the benzophonene system.^[8] Previous considerations^[13, 19, 20] about the trade-off between photovoltage reduction caused by surface states and better charge collection by the NW morphology are generally valid. We emphasize that cautions must be used when applying these considerations to specific chemical systems as these factors may be outplayed by those related to the detailed chemical mechanisms. With the intense research attention on solar energy utilization by photoelectrochemical processes, we envision that reactions similar to natural photosynthesis, that is, those seek to use solar energy to produce highly specific chemicals, will gain increasingly more attention. For these reactions, each system must be evaluated individually.

3.4 Conclusion

Communicating the point that the multifaceted nature of SiNWs may be advantageous for catalytic photoelectrochemical processes is our primary intention. To fully understand the nature of the interface between Si and the electron-receiving groups, more detailed research is needed. For instance, Si with different crystal faces exposed could be obtained or produced and the charge transfer characteristics could be measured to identify which facets favor charge transfer between Si and Ni(II)(bpy)₂²⁺. Detailed knowledge like this will contribute significantly to the goal of designing highly specific reactions that are powered by sunlight and produce useful chemicals in a way similar to natural photosynthesis but at much higher efficiencies.

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Chapter 4:

Tunable Redox Potential of Ni catalysts for carbon dioxide photoreduction on p-SiNW

4.1 Introduction

Converting solar energy into fuel through artificial photosynthesis is an attractive means to energy storage. ^[1-3] This process, analogous to natural photosynthesis, uses semiconductors to capture and convert solar irradiation to useful forms of energy. Carbon dioxide photofixation through semiconductors is, however, limited by the slow kinetics, ultrahigh overpotential, and extremely low yield. ^[4-6]

Recently, there has been an increase in work to introduce catalysts onto semiconductors to improve the light conversion efficiency in photoelectrochemical (PEC) cells. Nocera et al. used CoPi catalyst on Si based semiconductors to split water without external bias. ^[7] The Brudvig-Crabtree catalyst (Mn-oxo) has been thermally deposited on the surface of a WO₃ photoanode to improve the water oxidation efficiency. ^[8] Bocarsly et al. used pyridine as a catalsyt on p-type GaP to photoreduce carbon dioxide to methanol, obtaining yields as high as 96 %.^[9] These effectively show that catalysts can not only increase the efficiency when converting solar energy into chemical energy, but also increase the product selectivity by limiting the reaction pathway, especially for carbon dioxide photoreduction.

However, it is not always straightforward to apply catalysts onto semiconductor materials. The introduction of catalysts may cause stability issues, as well as introduce

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complexity to the energetic structure, which is a determining factor in the ability of photogenerated charges to flow from the semiconductor to the catalyst. The band position and Fermi level of the semiconductor must be appropriately placed relative to the redox potential of the catalyst. For reduction reactions, the redox potential of the catalyst is required to be more negative than the Fermi level of the semiconductor to allow for the flow of electrons from semiconductor to catalyst, a requirement that is met through the use of p-type semiconductors. Additionally, the overpotential of the charge transfer from semiconductor to catalyst should be sufficiently small. As a result, it is a challenge to find a suitable semiconductor/catalyst pair.

In this chapter, we look to address these issues by focusing on tuning the redox potential of Ni catalysts through the exchange of ligands. We began with Ni(bpy)₃(BF₄)₂ (bpy=2,2'-bipyridine, catalyst 1) as a model catalyst for the carboxylation of 4-octyne using CO₂ as a C1 source, which has previously been shown on carbon fiber.^[10] SiNWs are used as the photocathode to reduce these Ni catalysts. This work demonstrates the ability to tune the redox potential of a system simply by changing ligands on a catalyst, allowing for the selection of an appropriate catalyst/semiconductor pair.

In this chapter, we look to address these issues by focusing on tuning the redox potential of Ni catalysts through the exchange of ligands. We began with Ni(bpy)₃(BF4)₂ (bpy=2,2'-bipyridine, catalyst 1) as a model catalyst for the carboxylation of 4-octyne using CO_2 as a C1 source, which has previously been shown on carbon fiber.[10] SiNWs are used as the photocathode to reduce these Ni catalysts. This work demonstrates the ability to tune the redox potential of a system simply by changing ligands on a catalyst, allowing for the selection of an appropriate catalyst/semiconductor pair.

4.2 Experimental

Ni catalysts were prepared by the addition of Ni(BF_4)₂• $6H_2O$ and the appropriate ligand in a 1:3 ratio in ethanol for 1 hour.^[11] The resultant precipitate was washed with ether and dried overnight under reduced pressure. All ligands were obtained commercially, with the exception of ligand *3*, which was prepared according to literature. ^[12]

Electroless etched SiNWs were prepared following a reported method. ^[13] A p-type Si (100) substrate (Wafternet, 10^{15} cm³, B-doped; $10-20 \ \Omega$ •cm) was cleaned with acetone, methanol, and isopropanol sequentially and then oxidized in H₂O₂/H₂SO₄ 1:3 at 90 °C for 10 minutes to remove heavy metals and organic species. The cleaned substrate was immersed in an HF/AgNO₃ aqueous solution (4.6 M HF and 0.02 M AgNO₃) for 30 minutes at 50°C to produce SiNWs. Electrode fabrication was done after Al post-treatment to form ohmic contact as detailed in our previous work. ^[14]

Photoelectrochemical experiments were performed on a CHI 609D Potentiostat. A three-electrode configuration was used, in which Pt or SiNW electrodes were used as the working electrode, a piece of high-purity Al foil (99.9995%, Alfa Aesar, USA) served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte solution was composed of 5 mM Ni catalyst and 0.1 M tetrabutyl ammonium bromide (TBAB) (\geq 99.0%, Sigma-Aldrich, USA) in 20 mL acetonitrile. CO₂ (Airgas, USA; flow rate: 120 SCCM) was continuously bubbled through the solution. A 150 W Xenon lamp (model 71228, Newport, USA) equipped with an AM 1.5G filter and illumination intensity calibrated to be 100 mW cm⁻² was used as the light source. The scan rates of cyclic voltammetry curves were 50 mV s⁻¹. The resultant

product was analyzed by NMR and mass spectrometry.

4.3 Results and Discussion

4.3.1 Working principle

The proposed mechanism for the carboxylation is shown in Scheme 4.1. Ni(II)L₂ (L=ligand) receives photogenerated electrons from SiNWs under light illumination, and is reduced to Ni(0)L₂, the active catalyst in the reaction cycle. Ni(0)L₂ then couples with substrates, carbon dioxide and 4-octyne, forming an intermediate nickelacycle complex. With the help of the Al³⁺ ions generated at the anode by the holes from valence band of SiNWs, the carboxylate is released, regenerating Ni catalyst in the form of Ni(II)L₂. The catalytic cycle is maintained as long as SiNWs continuously reduce Ni(II)L₂ with assistance of light.



Scheme 4.1. Reaction mechanism of light promoted nickel catalyzed carboxylation of alkynes on SiNWs.

The electrochemical properties of this reaction were investigated to determine the effects of applying different ligands to the Ni metal center. This was done with the use of cyclic voltammetry (CV) scans, which are commonly used to investigate the electrochemical properties of metal complex redox reactions.

4.3.2 Photovoltage gained on SiNWs investigated by cyclic voltammetry

In the CV measurements, Pt or SiNW electrodes were employed as a photocathode, high purity aluminum was used as an anode, and the reference electrode was the saturated calomel electrode (SCE). The Ni catalyst *1* reduction peak on SiNWs with light irradiation is very distinct (Figure 4.1). In the absence of CO₂ and 4-octyne, symmetric CV peaks are obtained. This suggests that the redox pair Ni(II)(bpy)₂/Ni(0)(bpy)₂ has good reversibility. The reduction peak position is the most relevant information gained from this data, as it gives direct information about how much potential is required to reduce the Ni catalyst. Comparing these results to a conductive but non-photoeffective Pt cathode, the reduction peak position is shifted positively about 450 mV on SiNWs in light. This positive shift of reduction potential is due to photovoltage gained by SiNWs. It means Ni catalyst can be reduced easier with SiNWs due to the solar light contribution. It is worth mentioning here that the dark current on SiNWs is close to 0 mA/cm⁻² (about 3 orders smaller than light current), implying that all the current on SiNWs comes from solar light irradiation.





Figure 4.1. CV of Catalyst 1 on Pt and SiNWs under the conditions of: 5 mM Ni catalyst and 0.1 M Bu₄NBr in acetonitrile with N₂ as a protection gas.

We then looked to compare the results of our model catalyst with derivatives employing ligands alternative to 2,2'-bipyridine (Scheme 4.2). It has been shown that the introduction of electron withdrawing or electron donating groups can shift the redox potential of metal complexes.^[15] Overall, five additional Ni catalysts were synthesized (from catalyst *2* to catalyst *6*, with ligands of bathophenanthroline, 4,5-diazafluoren-9-one, 4,4'-dinitro-2,2'-bipyridine, 4,4'-di-tert-butyl-2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, respectively).



Scheme 4.2. Library of Ni catalysts used for CO_2 photofixation through alkyne carboxylation reaction.

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We see that, similar to our model catalyst, it is easier to reduce these catalysts on SiNWs relative to Pt due to the gained photovoltage. When looking at the effects of adding different substituents to the bipyridine ligand backbone, however, we see a marked change in the redox potential. When looking at the application of electron withdrawing groups, such as in catalyst *4*, we see a much more positive reduction peak position, at -0.51 V compared to that of catalyst *1* at -1.25 V (on Pt, see Figure 4.1).

Conversely, we see a relative negative shift in the reduction peak position with the introduction of electron donating groups, such as in catalyst 5. This could be expected, as the addition of electron withdrawing groups allows for a less electron rich metal center, and therefore a more easily reduced metal center. Similarly, a more electron rich metal center is less easily reduced. These affects demonstrate the ability to take advantage of the use of different ligands in order to obtain a desired reduction potential in a catalytic system.

In addition to the intrinsic reduction peak position of the catalysts, the respective reduction in the presence of substrate (CO₂ and 4-octyne) binding was also investigated, which presents the real artificial photosynthesis condition. When substrates are present in solution, they bind to the Ni(0) active catalyst species, and as a result the oxidation peak will be supressed. However, our primary focus is on the reduction peak and how it compares to the reduction peak without substrate. Reduction peak positions on a Pt electrode do not display a substantial difference with or without substrate binding in most catalysts. The exception to this is seen in catalyst *4*. The primary difference with this catalyst is the strongly electron withdrawing NO₂ groups. This makes the nickel species without substrates very easy to reduce. The species formed in the presence of substrates may not be as electron poor, and is therefore not as easily reduced as the

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original species, which is represented in the more negative potential required to reduce the species in the presence of substrates Again, with SiNWs as the photocathode, the reduction peak potentials consistently show about 400 mV to 450 mV shifts in a positive direction relative to those on Pt electrodes due to the energy gain from solar light. The detailed reduction peak positions of each catalyst on both Pt and SiNWs are summarized in Table 4.1.



Figure 4.2. Reduction peak potentials of Ni catalysts. All the solutions contain 5 mM Ni catalyst and 0.1 M tetrabutylammonium bromide in acetonitrile. For the conditions with substrate binding, 0.05 M 4-octyne was added with CO_2 gas bubbling. SiNWs are illuminated with a 100 mW cm⁻² Xenon lamp.

Catalyst	V_{RP} on	V _{RP} on Pt with starting	V _{RP} on SiNWs with	V _{ph} on
	Pt/ V	materials/ V	starting materials/ V	SiNWs
1	-1.25	-1.18	-0.73	450 mV
2	-1.26	-1.26	-0.83	430 mV
3	-1.09	-1.11	-0.71	400 mV
4	-0.51	-0.76	-0.33	430 mV
5	-1.37	-1.36	-0.95	410 mV
6	-1.35	-1.33	-0.90	430 mV

Table 4.1. Reduction potentials of the catalysts on Pt and potential shifts on SiNWs.

4.3.3 Stability

The alkyne carboxylation reaction on Ni catalysts requires good chemical stability and electrochemical stability of both catalyst and SiNWs in the reaction solution. Stability experiments were completed on SiNWs in the presence of catalyst 6, CO_2 and 4-octyne. The CV curve of the SiNWs had good reproducibility (10 continuous CV scans overlapped well, see Figure 4.3a), suggesting that the stability of both SiNWs and the Ni catalyst were well maintained under these experimental conditions. Most of the catalysts in Figure 2 had similar CV stabilities (except catalyst 4).

Long-term reactions were also completed with catalyst 6, CO_2 and 4-octyne in acetonitrile. The SiNWs were applied with constant potential (-0.90 V vs SCE), and the electrode showed no extensive photocurrent decay for more than 20 hours (Figure 4.3b).



Figure 4.3. a) CV stability of catalyst 6 on SiNWs. SiNWs were illuminated with a 100 mW cm⁻² Xenon lamp. *b)* Long-term experiment on SiNWs under light with constant applied potential shows very stable photocurrent. The solutions contain 5 mM Ni catalyst and 0.1 M tetrabutylammonium bromide in acetonitrile. 0.05 M 4-octyne is slowly added by a syringe pump with CO_2 gas bubbling.

4.4 Conclusion

In conclusion, we successfully show that we are able to tune the reduction potentials of nickel catalysts over a range of 0.86 V simply by changing the ligands on the catalyst. With SiNWs as the electrode, we consistently observe 400-450 mV photovaltage. The photogenterarted electrons can continously inject into the Ni catalysts from the SiNWs for more than 20 hours. With this work we hope to inspire people to use ligand effects as a viable design control in manupulating energetic structures when studying the application of catalysts on semiconductors.

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Chapter 5:

Water Splitting Using Tungsten Oxide Prepared by Atomic Layer Deposition and Stabilized by Oxygen-Evolving Catalyst

5.1 Introduction

When sunlight is used as direct energy input, water can be split into hydrogen and oxygen at conversion efficiencies similar to those of solar cells.^[1] This process offers a method for energy storage to address the problem that the sun does not shine continuously, and is a particularly appealing approach to solar-energy harvesting.^{[2-} ^{4]} Notwithstanding the intense research efforts, progress in this area is extremely slow. Efficient and inexpensive water splitting remains elusive. A key reason for the sluggish progress is the lack of suitable materials.^[5] The "ideal" material must absorb strongly in the visible range, be efficient in separating charges using the absorbed photons, and be effective in collecting and transporting charges for the chemical processes. Such a material has yet to be found.^[6] The difficulties in finding a suitable material stem from the competing nature of intrinsic material properties (e.g., optical depth, charge diffusion distance, and width of the depletion region, among others), which leaves limited opportunity for tunability.^[7] We recently demonstrated that heteronanostructures, a type of nanoscale material consisting of multiple components that complement each other, have a combination of properties which are not available in single component materials.^[8,9] For instance, we can add charge transport components to oxide semiconductors to solve the issue of low conductivity that oxide semiconductors generally suffer.^[8] In a similar fashion, one can add an effective catalyst to address the challenge that oxygen evolution is complex and tends to be the rate-limiting step.^[10-12] These new materials will likely lead to significant improvement in solar water splitting efficiencies. The success of a heteronanostructure design relies on the ability to produce high-quality components with interfaces of low defect density, and on the availability of various components. Here we show that crystalline WO₃ can be synthesized by the atomic layer deposition (ALD) method in the true ALD regime. When coated with a novel Mn-based catalyst, the resulting WO₃ survives soaking in H₂O at pH 7 and produces oxygen by splitting H₂O under illumination.

5.2 Experimental

5.2.1 Preparation of the Mn catalyst

The Mn catalyst was prepared by following published protocols.^[21] In a typical experiment, Mn(OAc)₂ (1.06 g, 4.29 mmol) and 2,2':6,2"-terpyridine (1.00 g, 4.29 mmol) were dissolved in 15 mL of H₂O, and then KHSO₅ (1.04 g, 3.21 mmol) in 15 mL of water was added dropwise with stirring, which turned the yellow solution dark green. After stirring at room temperature for 10 min, the solution was cooled to 0 °C. 20 mL of saturated KNO₃ solution was then added, resulting in a green precipitate of the oxobridged Mn dimer (2.31 g, 65.0%). Elemental analysis revealed a formula of $C_{30}H_{26}N_9O_{13}Mn_2$. More details of the elemental analysis are available in the table below.
Formula	Elemental analysis %
Mn2C30H26N9O13	Calcd C, 43.39; N, 15.18; H, 3.16; O, 25.05
	Found C, 42.52; N, 15.37; H, 2.68; O, 29.57

Table 5.1. Elemental analysis of the Mn-oxo dimmer

5.2.2 Fabrication of the electrodes

At room temperature, the Mn complex was redissolved in H_2O to make a 1 mm solution. When heated to 75 °C, the oxo-bridged Mn dimer underwent thermal decomposition to yield the Mn catalyst, which was received by the WO₃ film. The thickness of the catalyst coating was controlled by varying the concentration of the Mn complex. The deposition time was kept constant at 5 min. More details of controlling deposition thickness are available in the Supporting Information.

5.2.3 Photoelectrochemical (PEC) experiments

The resulting WO₃ (thickness: 180 nm) with or without the Mn catalyst was fabricated into a working electrode. A Pt mesh was used as counterelectrode, and the reference electrode was Ag/AgCl in 1m KCl solution. The electrolyte solution was 1m KCl with HCl added to adjust the pH from 2 to 7. A CHI 600C potentiostat was used. The voltage was swept between 0 and 1.3 V (vs. RHE) at a rate of 10 mVs⁻¹. The light source was a 150W Newport Mercury lamp, and the intensity was adjusted to 100 mW cm⁻². The incident photon-to-electron conversion efficiency (IPCE) and the absorbed photon-to-electron conversion efficiency was a Newport quantum efficiency measurement kit (QE-PV-SI).

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For the IPCE and the APCE experiments, the working electrode was biased at 1.23 V (vs. RHE). The absorption spectra were collected with an Ocean Optics spectrometer (USB 4000) and an integration sphere (Sphere Optics, RT-4Z).

5.2.4 GC analysis

To quantify the amount of oxygen and hydrogen generated by the water splitting process, the PEC apparatus was sealed in an N₂ environment. The working electrode bias was fixed at 1.23 V (vs. RHE). The gas phase was sampled periodically, and the samples were fed to an HP 5890 gas chromatograph equipped with an HP-PLOT MoleSeive column. The temperatures of the injector and the detector were set at 1008C. Helium and nitrogen were used as carrier gases for oxygen and hydrogen, respectively. For the GC-MS analysis, a Thermo Fisher Scientific ITQ 700 with a Focus GC was utilized.

5.2.5 Structural characterization

A transmission electron microscope (TEM, JEM-2010F, operating at 200 keV) was used to study crosssection samples of ALD-grownWO3, prepared by using a focused ion beam (FIB, JOEL 4500 Multibeam system). We used a focused ion beam microscope (FIB, JOEL 4500 Multibeam system) to prepare a cross-section transmission electron microscopy (TEM) sample. A carbon film (~ 2 µm thick) was pre-deposited onto the WO₃ film to reduce the ion beam damage. The sample was milled into thin slices (~15 µm × 5 µm span and 1.5 µm thick) with a 30-kV gallium (Ga) ion beam. A slice was cut off the substrate and transferred to a Cu support with a nano-manipulator S3 (Kleindiek Nanotechnik MM3A). After the slice was glued to the Cu support, it was further thinned

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to be e-beam transparent (< 100 nm thick). A final polish with low-energy ion beam (5 kV) was applied to remove or minimize ion beam damage introduced in the previous steps. 5.2.6 GCMS analysis of O_2 -34 and O_2 -36

GC-MS analysis was performed in a Thermo Fisher Scientific ITQ 700 with a Focus GC, which was equipped with Thermo TR-5MS SQC 30 m x 0.25 mm ID x 0.25 μ m fused silica capillary column. Helium gas served as the carrier gas with a constant flow rate of 1.5 mL/min. The oven temperature was held at 35 °C for 2.5 min and then ramped to 100 °C at the rate of 65 °C /min. Afterward the temperature was held at 100 °C for 2.5 min. Temperatures of the injector and detector were held for 200 °C through the analysis. The samples of 5.0 μ L headspace gas were injected, and the amount of ¹⁸O-labeled O₂ was quantified using the peak height in the resulting mass spectra by averaging three independent measurements.

5.3 Results and Discussion

We choose ALD to prepare WO₃ because of the following advantages: 1) a high degree of control over the resulting materials; 2) excellent step coverage to yield conformal coatings; and 3) process versatility to tailor the composition of the deposit. WO₃ was studied because it is one of the most researched compounds for water splitting. The widely available literature makes it easy to compare our results with existing reports^[13–15] and thus allows us to test the power of the heteronanostructure design. To avoid the production of corrosive byproducts during the ALD process^[16] and to ensure the reaction occurs in the true ALD regime, we used $(tBuN)_2(Me_2N)_2W$ as tungsten precursor and H₂O as oxygen precursor. Our first goal was to verify that the growth indeed takes place in the ALD regime. The dependence of the growth rate on the

precursor pulse times and on the substrate temperature unambiguously confirms this. In addition, the excellent linear dependence of the deposition thickness on the number of precursor pulses supports the ALD growth mechanism and shows the extent of control we can achieve (see Figure 5.1).

5.3.1 Atomic layer deposition (ALD) growth of WO₃

Figure. 5.1a and 5.1b show the growth rate dependence on the precursor pulse times. It is evident that the growth is self-limiting. The experimental data for both H₂O and $(tBuN)_2(Me_2N)_2W$ agree with a surface adsorption model (Langmuir model) fitting. Note that the optimum H₂O pulse time 40-100 ms is longer than what is used in typical oxide growths in a Savannah system, but was found necessary. We were unable to grow WO₃ thicker than 12 nm when shorter H₂O pulses (*e.g.*, 10 ms) were used. The slow oxidation of $(tBuN)_2(Me_2N)_2W$ is believed to be responsible for this observation.

The growth was also highly sensitive to the substrate temperatures. Little product was obtained for T < 300°C. No noticeable improvement was observed when T was raised above 350°C (Figure. 5.1c). Optimum growth conditions $(tBuN)_2(Me_2N)_2W$ pulse 2 s, N₂ purge 10 s, H₂O pulse 50 ms, N2 flow 5 s without pumping and then 10 s with pumping, T=350°C) yielded stable WO₃ growth (1.01 ± 0.05 Å/cycle) for at least up to 1600 cycles, Figure. 5.1d. For all data presented here, H₂O was kept at room temperature (25°C), and (tBuN)₂(Me₂N)₂W was heated at 75°C.





Figure 5.1. Characteristics of the WO₃ growth. The growth rate is sensitive to the precursor doses (a & b, H₂O and (tBuN)₂(Me₂N)₂W, respectively). The dependence can be fit by a surface adsorption model (blue lines in a and b). (c) The growth is also sensitive to the substrate temperature. (d) The thickness of WO₃ scales linearly with total number of precursor pluses.

5.3.2 Structure Characterization of ALD grown WO₃

That a long H₂O pulse time is necessary to initiate growth is a key finding of this work. Despite intentional strengthening of the oxidative conditions, as-grown WO₃ exhibited a tinted color, indicating the existence of oxygen deficiencies,^[17] which was then corrected by an annealing step in O₂ at 550 °C. The crystalline nature of the product is manifested in the high resolution (HR) TEM image in Figure 5.2a. We also synthesized WO₃ on two-dimensional TiSi₂ nanonets.^[18, 19] The uniformity and good coverage around the nanonet branches show that this deposition technique is suitable for the creation of heteronanostructures. Ready dissolution of WO₃ in aqueous solutions with pH=4 is a significant challenge that impedes its widespread use.^[20]



Figure 5.2. Microstructure of WO₃ by TEM after annealing. (a) Polycrystalline WO₃ on ITO substrate. (b) Conformal coating of WO₃ on TiSi₂ Nanonets.

The as-grown tungsten oxide film was annealed at 550°C in O₂ to achieve the desired stoichiometry and crystallinity. Consistent with the TEM result, formation of monoclinic tungsten oxide was confirmed by XRD after annealing.



Figure 5.3. XRD pattern of WO₃ after annealing. The crystal structure was identified as monoclinic tungsten oxide.

5.3.3 Thermal Deposit Mn-oxo Catalyst on to WO₃

Derived from the Brudvig–Crabtree catalyst, this coating was prepared by thermally decomposing $[(H_2O)-(terpy)Mn(O)_2Mn(H_2O)(terpy)](NO_3)_3$ (terpy=2,2':6',2''-terpyridine).^[21] Similar to the oxo-bridged dimanganese catalyst, the thermal decomposition product exhibits good catalytic properties when sacrificial oxidants are available.^[22]

The solid Mn-containing material is not manganese dioxide according to elemental analysis and EPR, FTIR, and atomic absorption spectroscopy.^[22] Although further study is needed to understand the exact structure of this catalyst and the nature of its working mechanism, its thermal stability, ease of fabrication, and unequivocal evidence for its catalytic properties compelled us to explore it in the heteronanostructure design.

The surface of WO₃ was coated with the catalyst by thermal treatment of a solution of the above Mn complex at 75 $^{\circ}$ C (see Experimental Section). This step was brief (typically 5 min) and did not cause noticeable colorization of WO₃.

Different Mn-oxo dimmer solution concentrations, different deposition temperatures and different deposition times were studied. The general trend was that more concentrated dimer solutions, lower temperatures and longer times tend to produce thicker film. The coating thickness was measured by TEM and spectroscopic ellipsometer (Vertical VASE, J. A.Wollam Co., Inc.). Important to the H₂O solar splitting functionalities, films thicker than 5 nm are undesired because charge transfer through the coating becomes hindered. Films thinner than 1 nm also exhibit detrimental effects because they fail to provide adequate protection for the WO₃. We identified the following optimum conditions to yield a continuous coating of 2 nm (Figure 5.4, the Mn-oxo dimmer concentration, 1 mM; deposition temperature: 75 °C; and deposition time: 5 min. Energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) confirmed the presence of Mn element in the amorphous layer.



Figure 5.4. TEM characterizations reveal the thin coating of the Mn-catalyst on the surface of WO₃.

No measurable differences were observed in the absorption spectra of WO₃ before and after this deposition, that is, solvation on the WO₃ surface was insignificant. This observation also suggests that the catalyst poses no appreciable competition to WO₃ in light absorption, which is an extremely important feature, because light absorbed by the catalyst would be wasted. WO₃ can be protected in non-acidic solutions by depositing other materials such as TiO₂ by, for example, ALD. However, deposition of the Mn catalyst is preferred for at least three reasons: 1) deposition is straightforward, 2) the coating does not compete with WO₃ in light absorption, and 3) the catalyst facilitates hole transfer from the semiconductor to the solution (see following discussion). 5.3.4 Working Principle



Figure 5.5. Proposed working principle of the MOC/WO₃ design for water oxidation. H_2O transfers electrons to Mn(IV,V) to produce O_2 and Mn(II, III), the latter of which then transfers the electrons to the semiconductor. The electrons are excited in the semiconductor by the absorbed light. With the assistance of the built-in field, they are collected and transported to the cathode for H_2O reduction to complete the artificial synthesis process.

Figure 5.5 illustrates the proposed working mechanism of the semiconductor/catalyst system. Light is absorbed by WO₃ to generate electrons and holes. The built-in field in WO₃ helps concentrate electrons away from the solid/liquid interface to be collected by the supporting substrate,^[23] which is indium tin oxide (ITO). Holes are driven by the built-in field toward the solid/liquid interface, where they transfer to the solution to oxidize H₂O. This schematic neglects the potential influence of the Mn catalyst coating on the

electronic energy of WO₃ because of the thinness of the former. The oxidation process is mediated by the catalyst, which we suggest works in a fashion similar to the oxobridged Mn₂ catalyst,^[24] that is, mixed-valent Mn^{III} and Mn^{IV} are oxidized by the photogenerated holes from the semiconductor, and the product of the oxidation process is reduced by H₂O to produce O₂. A distinguishing feature of the WO₃/Mn catalyst system is that no sacrificial oxidants are present for O₂ generation. H₂O oxidation by the Mn catalyst is effective and has fast kinetics.

5.3.5 Photoelectrochemical (PEC) Performance

When measured in an electrolyte at pH 4, electrodes with and without the Mn catalyst coating exhibited distinct but not significant differences in the photoelectrochemical (PEC) performance (photocurrent and onset potential, see Figure 5.6a). When the external and internal quantum efficiencies are compared for electrodes with and without the Mn catalyst coating, similar conclusions are reached (Figure 5.6b). When the catalyst coating is absent, deviation of the photocurrent and the dependence on light intensity from a linear relationship indicates that charge transfer from the semiconductor to the solution becomes a kinetically limiting step.^[25] The deviation from linearity is less obvious when the catalyst is present (Figure 5.7). This suggests that the presence of the catalyst facilitates charge transfer from the semiconductor to the solution, and the effect is more obvious when the charge density is high.





Figure 5.6. Photoelectrochemical properties of ALD-grown WO_3 and WO_3/Mn -catalyst. (a) In acidic solutions, the presence of the Mn-catalyst induces no significant change to the photocurrent (b)The differences between the APCE and the IPCE also highlight the room for improvement when absorption is improved without impairing the charge collection.



Figure 5.7. The photocurrent dependence on light intensity for WO3 with and without the Mn-catalyst at pH=4. For WO3, the photocurrent depends on the light intensity following a linear relationship; this dependence deviates at high light intensities (> 70 mW/cm²). The linear dependence is preserved when the catalyst coating is present.

5.3.6 Quantify the amount of O₂ and H₂ generated

To quantify the amount of O_2 and H_2 generated by the WO₃/Mn catalyst electrode, we conducted photocatalytic experiments with GC analysis. An HP 5890 GC instrument equipped with an HP-Plot MoleSeive column was used for this expierment. The injector and the detector temperatures were set at 100 °C. Helium was used as the carrier gas for oxygen measurements, and nitrogen was used for hydrogen. The flow rate of the carrier gases was 5.4 ml/min. For the stability test, the reaction veiscle was purged with N_2 every 7 h. All other test parameters were kept constant.

As shown in Figure 5.8, a stark difference is observed for the electrodes with and without the Mn catalyst. When the catalyst is present, the amount of O_2 increases with time, following a linear relationship for up to 5 h, after which the rate of O_2 generation slows down. The reduced rate of O_2 generation is caused by the experimental design.



Figure 5.8. When tested at pH=4, the oxygen generation rates by electrodes with and without the Mn-catalyst are drastically different.

When the vessel was purged with N_2 and the experiment was restarted, O_2 was produced at the same rate as in the original experiment (Figure 5.9). Without the Mn catalyst, the amount of O_2 measured was only approximately 50% of that with the Mn catalyst after 3 h. Thereafter, the electrode ceased to function, showed obvious colorization, and eventually peeled off from the ITO support.



Figure 5.9. Stability test of the Mn-catalyst coated WO_3 . Red arrows indicate where the reaction vesicle was purged by N_2 .

Better stability was observed when solutions with lower pH were used, and no obvious colorization was seen when WO₃ was tested in solutions of pH 2 for up to a day. The protecting effect of the Mn catalyst was more pronounced when the electrodes were tested in less acidic solutions. At pH 7, WO₃ without the Mn catalyst decayed more quickly than at pH 4 (60% after 1 h), whereas approximately 4% performance degradation was observed when the Mn catalyst was present (Figure 5.10) for up to 2 h. It took more than 19 h in the Mn/WO₃ case for the efficiency to drop to 50% of the initial value.



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Figure 5.10. The protection effect of the Mn-catalyst. The effect is more pronounced when tested in neutral solutions.

Various evidences support that the detected O_2 is the direct product of H_2O splitting. First, the amount of H_2 is approximately twice that of O_2 , consistent with complete decomposition of H_2O (Figure 5.11a). Second, control experiments with $H_2^{18}O$ confirmed that O in the gas phase comes from H_2O (Figure 5.11b).^[26] Third, the amount of O_2 far exceeds what would be available in WO_3 or the Mn catalyst. The rate of O_2 generation was measured by GC to be 13.6 mmol cm⁻² h⁻¹. The rate was also calculated from the measured photocurrent as 16.8 mmol cm⁻² h⁻¹ (based on a current density of 1.8 mA cm⁻²). The discrepancy originates from the GC measurements, which did not include O_2 dissolved in the solution or lost due to imperfections of the apparatus. Improvement of the GC method by, for example, using a flow-through system will correct this.



Figure 5.11. (a) The generations of O_2 and H_2 were measured simultaneously to verify the complete decomposition of H_2O . (b) When ¹⁸O isotope was used, the ratio of ³⁴O₂ to ³⁶O₂ was approximately 10:1, unambiguously confirming that the measured O_2 comes from H_2O splitting.

Using literature methods, we computed a peak energy-conversion efficiency of 1.1 % (at 0.80 V vs. reversible hydrogen electrode (RHE)), and the efficiency was 0.59 % at V=1.23 V (vs. RHE, Figure 5.12). Although the observed photocurrent at 1.23 V (vs.

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RHE) is among the highest for WO_3 , the efficiency is still low compared with solar cells. Weak absorption in the visible range is the primary reason for the low efficiency (Figure 5.6b). Nonetheless, the stability of the resulting material in neutral solutions is significant and has not been reported previously.

The energy conversion efficiency is calculated by the equation below,^[27]

$$\eta\% = \frac{(1.23 - V_{app})I_p}{P_{in}} \times 100\%$$

where η is the energy conversion efficiency, I_p is the photocurrent in A/m² and P_{in} is the total input power density in W/m². The maximum efficiency obtained is 1.10 % at 0.8 V (vs RHE).



Figure 5.12. Energy conversion efficiency at pH=4.

5.4 Conclusion

Efficiently and inexpensively converting solar energy by splitting H₂O is one of the most pressing issues we face today. Research in this area faces a multitude of challenges. Capabilities to design, make, and study novel materials that can perform this reaction with meaningful efficiency and at low cost have broad appeal. The results presented here will contribute significantly to this goal. The ALD growth of WO₃ without production of corrosive byproducts has not been reported elsewhere, and the synthetic technique makes it easy to form heteronanostructures. The Mn catalyst derived from the oxo-bridged Mn dimer is easy to prepare and exhibits good stability and catalytic properties. When interfaced with WO₃, it acts as a protecting layer without adverse effect on the water-splitting properties. To the best of our knowledge, this is the first time that WO₃ photoelectrodes stable in neutral solution have been prepared. The heteronanostructure design combines multiple components, each with unique complementary and critical functions, and offers combinations of properties that are not available in single-component materials. The versatility of this method will find applications in numerous areas where the availability of materials is the limiting factor.

5.5 Reference

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Chapter 6: Conclusions

In summary, this thesis is mainly focused on two most important reactions of photosynthesis, photoreduction of CO_2 and water oxidation. Photoreduction of CO_2 is a crucial reaction in natural photosynthesis because it stores harvested solar energy that is intermittent in nature, and water oxidation is important because it produces a molecule that is vital to the development of lives on this planet. Most of our efforts on artificial photosynthesis have been spent on designing chemical reactions or designing photoelectrode materials. Our strategy helped us define reaction pathways, improve photoelectrode stability, increase reaction kinetics on the semiconductor/electrolyte interface, and lower the reaction overpotentials.

Our aspirations are inspired by the detailed mechanisms of natural photosynthesis. To achieve highly specific reduction of CO_2 in a fashion similar to the dark reactions in natural photosynthesis, we demonstrated a chemical reaction route that does not directly pass electrons from the photoelectrode to CO_2 . Significantly, we realized this goal on Si nanowires (SiNWs) photocathode, which harvests solar energy. In an effort to show the usefulness of these reactions, we showed that these reactions produce organic targets that can be readily used to synthesize NSAIDs (non-steroidal anti-inflammatory drugs) such as ibuprofen and naproxen. We note the ease of electron exchange taken place between SiNWs and the organic substrates. It indicates that Si may be broadly used as a photoelectrode for a wide range of chemical reactions similar to photosynthesis. While in the present proof-of-concept demonstration an additional electrochemical potential is still necessary, the energy input from the harvested light plays an indispensable role. As

a result, our approach represents a critical step forward in the use of light to power complex organic molecule syntheses.

Further studies of using SiNWs for organic reactions were carried out by introducing a CO_2 reduction catalyst Ni(bpy)₃(BF₄)₂ in to the reaction electrolyte. The reduced form of the Ni catalyst (produced by photogenerated electrons from SiNWs) binds with CO_2 and alkyne to yield unsaturated carboxylic acids. To our surprise, SiNWs exhibited dramatically different reactivity from bulk Si in this reduction. The multifaceted nature of SiNWs was identified advantageous for the catalytic photoelectrochemical processes as it promotes charge transfer across the semiconductor/electrolyte interface. To fully understand the nature of the interface between Si and the electron-receiving groups, more detailed research is needed. For instance, Si with different crystal planes exposed could be obtained or produced and the charge transfer characteristics could be measured to identify which facets favour charge transfer between Si and Ni(II)(bpy)₂²⁺. Detailed knowledge like this will contribute significantly to the goal of designing highly specific reactions that are powered by sunlight and produce useful chemicals in a way similar to natural photosynthesis but at much higher efficiencies.

We also took efforts to tune the reduction potentials of nickel catalysts by as much as 0.86 V by simply changing the ligands on the catalyst. With SiNWs as the electrode, we consistently observed photovaltages of 400-450 mV. This result is expected to inspire researchers to design and manipulate energetic structures when applying catalysts onto semiconductors for photoelectronchemical reactions.

Similarly, solar water oxidation using a semiconductor photoelectrode was performed. We explored low-cost materials that can efficiently convert solar energy by splitting H_2O . For this goal, WO₃ has been successfully synthesized by an ALD method, which makes it possible to create heteronanostructures. To stabilize the photoelectrode in neutral solutions, we applied a Mn-oxo-based catalyst that was derived from the oxo-bridged Mn dimer on the surface of WO₃. The catalyst acts as a protecting layer without adverse effect on the water-splitting property. To the best of our knowledge, this is the first time that WO₃ photoelectrodes stable in neutral solution have been prepared. The heteronanostructure design combines multiple components, each with unique complementary and critical functions, and offers combinations of properties that are not available in single-component materials.