Understanding the Limitations of Photoelectrochemical Water Splitting

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Understanding the Limitations of Photoelectrochemical Water Splitting

James E. Thorne

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James E. Thorne

Advisor: Professor Dunwei Wang

Artificial photosynthesis is achieved by placing a semiconductor in water, where photoexcited charges generate a photovoltage at the surface of the semiconductor. However, solar to fuel efficiencies of earth abundant metal oxides and metal nitrides remain limited by their low photovoltages. Many different treatments have been used to improve the photovoltages of semiconductors, such as photocharging, surface regrowths, or the addition of heterogeneous catalysts. However, in these treatments, it remains unclear whether the enhanced photovoltage arises from improved kinetics or energetics. In many of the following studies, the surface kinetics of different semiconductors are measured in order to quantify how surface kinetics are related to the photovoltage of these materials. Different spectroscopic measurements are made along with detailed analysis of the Fermi level and quasi Fermi level in order to corroborate the kinetic data with energetic data. Together, this dissertation explores a multitude of methods and procedures that demonstrate how the photovoltage of semiconductors can be understood and manipulated for photoelectrochemial artificial photosynthesis.

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ABBREVIATIONS

ALD – Atomic layer deposition AM – Air mass CB – Conduction band E_F – Fermi level EIS – Electrochemical impedance spectroscopy EXAFS – Extended X-ray absorption fine structure FTIR-ATR – Fourier transform infrared spectroscopy – attenuated total reflectance FTO – Fluorine doped tin oxide HER – Hydrogen evolution reaction IMPS – Intensity modulated photocurrent spectroscopy JV – Current density voltage LSV – Linear sweep voltammetry krec – Recombination rate constant k_{tran} – Charge transfer rate constant NHE – Normal hydrogen electrode OER – Oxygen evolution reaction RHE – Reversible hydrogen electrode PEC - Photoelectrochemistry RIXS – Resonant inelastic x-ray spectroscopy SCLI - Semiconductor liquid interface SEM – Scanning electron microscopy

STH – Solar to hydrogen

sXAS – soft X-ray absorption spectroscopy

TE – Transfer efficiency

TEM - Transmission electron microscopy

VB - Valence band

Von – onset potential

 $V_{ph}-photovoltage$

XAS – X-ray absorption spectroscopy

XPS – X-ray photoemission spectroscopy

XRD – X-ray diffraction

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Dedication

The author wishes to dedicate this dissertation to his Father, Richard Charles Thorne. Fair winds, calm seas and smooth sailing...

LIST OF PUBLICATIONS

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INTRODUCTION

1.1 THE GLOBAL ENERGY DEMAND

The global energy demand is nearly18 terrawatt hours per year, with projections showing that this value could very well double by $2050.^{1,2}$ At the moment, fossil fuels provide more than 80% of this energy.² When fossil fuels, such as methane, are oxidized the product is carbon dioxide (CO₂), which can remain in the atmosphere for well over a century.³

$$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$$

As evidenced by the Keeling curve and ice core isotope samples (Fig. 1), the burning of fossil fuels has contributed to a massive increase in the amount of atmospheric CO_2 (from 280 ppm to 410 ppm). This is quite alarming since carbon dioxide is a potent greenhouse gas that contributes to global warming, which in turn will result in significant agricultural changes, population relocations, and societal turmoil. Evidence already supports that the conflicts in Syria since 2011 were in at least in part initiated by anthropogenic related climate changes.⁴ However, replacing fossil fuels is not a trivial task, and the options that can satisfy a terrawatt hours energy demand are limited.



Figure 1. The concentration of carbon dioxide in the atmosphere plotted against thousands of years. The red arrows indicate the sharp increase in modern day (2018) atmospheric CO_2 since the Mauna Loa measurements were started by Charles Keeling in 1958. Prior to that, data comes from ice core samples. This figure is reproduced with permission from the Scripps Institution of Oceanography.

The nuclear fusion reaction taking place in the sun emits an enormous amount of energy. The amount of this energy that reaches the earth is 100,000 terrawatt hours per year, enough to meet our global energy needs in less than two hours. Even with modern day commercial solar cells, only a small fraction of the land area on the planet would be needed to produce enough energy to meet the global energy demands. However, with costs aside, the diurnal and intermittent nature of sunlight is a major hurdle preventing wide scale solar implementation. Finding a means of energy storage on the terrawatt scale must be realized in order for solar energy to be used as a reliable source of energy. Creating this technology is a grand challenge for the 21st century researchers. Unfortunately, current battery technologies do not offer the energy densities or stabilities that will be required for this task. However, storing solar energy in the form of chemical bonds can meet these requirements.

1.2 NATURAL AND ARTIFICIAL PHOTOSYNTHESIS

Nature's photosynthesis provides a roadmap for large scale energy storage. Simply speaking, photosynthesis combines water and carbon dioxide to form carbohydrates. Nearly all of the planet is directly or indirectly fueled by this reaction. The photosynthetic process involves two light absorbers driving two different reactions, in what is known as the Z scheme (Fig. 2). At the first light absorber, photosystem II (PSII), a photon is absorbed to generate an electron. This results in the activation of the oxygen evolving complex, where water is broken apart (oxidized) to form oxygen gas. This is the reason why plants "breath" oxygen. At the second light absorber, photosystem I (PSI), a photon is absorbed to generate an electron, which is used to reduce NADP⁺ and ADP to NADPH and ATP, respectively.



Figure 2. A simplified schematic view of the charge transfer processes that occur during photosynthesis. *This figure is reproduced with permission from "Nature Photonics, 2012, 6, 511–518"*

A similar design scheme has been proposed to enable artificial photosynthesis, and is commonly known at photoelectrochemical (PEC) water splitting. In many cases, two light absorbers, semiconductors or dyes, are used in place of PSII and PSI. These light absorbers are submerged into a solution, light is shone on them, water is oxidized oxygen at the photoanode, and hydrogen ions are reduced to hydrogen gas at the photocathode (hydrogen evolution) (Fig 3).

Water Oxidation:
$$2 H_2 O \rightarrow O_2 + 4 H^+ + 4 e^-$$
1.23 VHydrogen Evolution: $4 H^+ + 4 e^- \rightarrow 2 H_2$ $0 V$

Indeed, artificial photosynthesis was demonstrated by Fujishima in 1972.⁵ However, this was done with a single wide band gap semiconductor, TiO_2 , that absorbs very little solar light making the efficiency of this device very low (<1%). In a simplified ideal case, with two light absorbers, PEC water splitting could be 42% efficient.⁶ Where the solar to hydrogen gas (STH) efficiency is defined by:

$$\eta = \frac{J_{SC}(1.23V - V_{app})}{P_{in}}$$

Here, J_{SC} equals the short circuit photocurrent and is equivalent to the rate of electrons being generated by absorbed photons, V_{app} is a measure of any additional applied voltage between the oxygen evolving photoanode and the hydrogen evolving photocathode, and P_{in} is the power density of the light shone on to the light absorbers.



Figure 3. A schematic example of an artificial photosynthetic device using two light absorbers, a photocathode and a photoanode. Typically, low energy red light (>600 nm) is absorbed by the photocathode and higher energy blue light (<600 nm) is absorbed by the photoanode. To prevent crossover of the generated products, an ion exchange membrane is introduced between the cathode and anode. *This figure is reproduced with permission from "J. Phys. Chem. Lett. 2015, 6, 4083-4088" Copyright 2015 American Chemical Society*

In an ideal case, the photoanode and photocathode produce the same photocurrent with near zero V_{app} (Fig. 4). In the decades since Fujishima, a large amount of research has gone into exploring, understanding, and optimizing the artificial photosynthesis process in order to maximize the STH efficiency. Today dual absorbing PEC devices, with true semiconductor liquid interfaces, are only a few percent efficient. There are several factors that have limited the STH efficiencies of PEC devices. Often the J_{SC} values are far too small. This is due to poor charge separation and transport through semiconducting materials, namely metal oxides.⁷ Typically metal oxide semiconductors are required for stability reasons, however there is a serious lack of metal oxide semiconducting materials available to the community. While a great deal of effort has gone in to combinatorial research of new stable metal oxide semiconductors,⁸ there has yet to be a "game changing"

discovery on this front. In order to maximize the J_{SC} performance of current metal oxide materials, TiO₂, WO₃, BiVO₄, α -Fe₂O₃, nanostructuring has proven effective in circumventing the poor charge separation and transport of these materials.⁷ Conversely, minimizing the V_{app}, thus maximizing the photovoltage, has received much less attention in the literature. As seen in the following section, there has been a fair amount of debate on how to improve the photovoltage of PEC devices. In order to help settle this debate it will require a fundamental exploration of how the semiconductor liquid interface and semiconductor catalyst interface are operating.



Figure 4. A) an ideal band diagram on a photocathode and photoanode. **B)** the JV curve of an ideal dual absorbing PEC device. J_{op} represents the operating photocurrent of the device and defines the STH efficiency. *Reproduced with permission from "Chem. Rev., 2010, 110, 6446–6473" Copyright 2010 American Chemical Society*

1.3 THE SEMICONDUCTOR LIQUID INTERFACE

When a semiconductor is submerged into water, a built-in field near the surface of the semiconductor is developed due to the differences between Fermi level and the redox potential of water. When light is absorbed by the semiconductor, this field separates charges by driving electrons and holes toward opposite directions. Once the charges reach the catalytically active sites on the surfaces, they participate in the desired chemical reactions (Fig. 4).⁹ To measure the overall performance of a PEC system, it helps to study half reactions, in the hope that the anodic and cathodic reaction metrics can be matched for optimized complete water splitting.¹⁰ For most of this dissertation the anode will be discussed, however the same discussions can be had for cathode (as found in Chapter 4). Under the ideal situation of 100% Faradaic efficiencies (all photoexcited holes are used for water oxidation), the anodic current measures the effectiveness of charge separation by the photoanode. The anodic current is collectively controlled by the quality of the Schottky-type diode formed at the photoelectrode surface and the charge transfer across the electrode/electrolyte interface, as described in Equations (1) and (2).¹¹

$$\frac{P_s}{P_s^0} = \exp\left(-q\Phi/kT\right) = \exp\left[-q\left(V_{app} + V_{ph} - V_{CB}\right)/kT\right]$$
(1)
$$i_p = i_p^0 \left\{\frac{P_s}{P_s^0} \exp\left(q\alpha_p \eta/kT\right) - \exp\left[-q\left(1-\alpha_p\right)\eta/kT\right]\right\}$$
(2)

Here P_s is the surface hole concentration; P_s⁰ is the equilibrium surface hole concentration; q is the charge of electrons (1.6 x 10⁻¹⁹ C); ϕ is the magnitude of the band bending as defined by the difference between the combination of applied potential (V_{app}) and photovoltage (V_{ph}) and the conduction band edge (V_{CB}), where V_{ph} is defined as the difference in the Fermi levels between dark and light. α_p is the hole transfer coefficient; η is the overpotential, which is the difference between the quasi-Fermi level of holes and the electrochemical potential of the solution; k is the Boltzmann constant (1.38 x 10⁻¹⁸ J/K); T is temperature; i_p^0 is the exchange current in dark; and i_p is the hole current in light. In essence, Eq. 1 describes how the steady-state hole concentration on the photoelectrode surfaces (P_s) depends on the degree of surface band bending (ϕ). Because only energetic terms (the differences among various energy levels, including the applied potential, Fermi level, and band edge positions) are concerned in Eq. 1, it is considered to mainly describe the influence of thermodynamic factors on the overall performance of a PEC system. For the remainder of this dissertation the term "surface energetics" will be used when referring to these thermodynamic factors. Eq. 2 is derived from the Butler-Volmer relation under the likely assumption that the charge transfer kinetics are dependent on the surface hole concentration (P_s) as P_s tends to be significantly lower on semiconductor surfaces than metal ones. It is important to note that Eq. 2 relates to the overpotential (η) needed to drive the water oxidation reaction and therefore is mainly describing the influence of the kinetic factors.



Figure 5. JV curves of hematite photoanodes with and without a surface catalyst. The addition of a catalyst results in a large cathodic shift in the V_{on} , which ultimately reduces the V_{app} and maximizes the STH efficiency.

Experimentally, the most frequently employed technique, to quantitatively characterize an electrode, is to measure the steady-state current density against the applied voltage (J-V). However, we see from equations 1 & 2 that both energetics (ϕ) and kinetics (η) influence the J-V curves in an intertwined fashion. When the surfaces of a photoelectrode are modified by, for instance, by a catalyst, the degree of band bending (i.e., surface energetics) and charge transfer rates (i.e., kinetics) may be changed, and each can alter the J-V curves. In the case of the photoanode, the desired effect is a cathodic shift in the turn-on voltages (Von, photocurrent onset potentials) as shown in Fig. 5. Between these two factors, surface energetics reduce the Von by increasing the voltage supplied by light (V_{ph} in Eq. 1) with better charge separation and hence higher surface hole concentration (P_s). Whereas, kinetics reduce the V_{on} by decreasing the needed overpotential (η in Eq. 2). Knowing what the true reasons are for changes in the Von has important implications. For a given system, if the reduction in η is the main or only reason for the improved V_{on}, future research should be directed toward discovering new catalysts with better turn-over characteristics in order to minimize n. If, however, the changes in Von are caused by surface energetics, efforts in finding better catalysts will have little if any impact on further improvement of Von, and research should instead be directed towards controlling the photoelectrode/catalyst interface for better charge separation. To further illustrate this understanding, we next evaluate how surface energetics change the J-V curves in greater detail, within the framework of a photoanode.

As shown in Figure 6, under ideal conditions, the band edge positions of a photoanode should be pinned relative to the electrochemical potentials of the solution (H_2O oxidation in the current discussion) so that the entirety of the applied potential will be used

to build a field within the semiconductor for charge separation (Figure 6A). Non-ideality factors, such as surface states, can partially unpin the band edge positions. As a consequence, the band edge positions (V_{CB} in Equation 1) move with the applied potentials (V_{app} in Equation 1; also see Figure 6B). Under such a circumstance, the relative position of the Fermi level and the band edge positions at the surface appear to be fixed, a phenomenon more commonly referred to as surface Fermi level pinning.¹² As a result of Fermi level pinning, the degree of surface band bending would not change when the V_{app} is increased. It means that a portion if not all of the applied potential is "wasted" in the sense that it does not contribute to charge separation. Fermi level pinning is an important reason for late turn-on characteristics of photoanodic reactions. Now if we turn our attention back to Eq. 1 & 2, we see that measuring higher currents at a reduced V_{app} may also be caused by mitigating the influences of Fermi level pinning.



Figure 6. Band diagrams showing the desired band edge pinning (A) and undesired Fermi level pinning (B) effects in a photoelectrochemical system for a photoanode. With Fermi level pinning the band edges become dislocated, resulting in "wasted" applied potential in that increased V_{app} does not lead to better charge separation. It is noted that although band bending, as depicted here, may not be fully developed for thin film-based photoelectrodes, the discussion of the influence of surface Fermi level pinning remains valid as it only concerns the energetics at the surface.

The influence that both energetics and kinetics exert on J-V characteristics of photoelectrodes is probably best exemplified by the prototypical material of hematite (α - Fe_2O_3). With a bandgap of ca. 2.0 eV, hematite represents a photoanode material that absorbs in the right range within the solar spectrum, is abundant in the crust of the earth, and is stable against photocorrosion in neutral and basic solutions.^{9,13,14} As one of the most researched photoanode materials, however, hematite also presents a host of critical challenges. For instance, the hole diffusion distance within hematite is notoriously short, on the order of only a few nanometers.¹⁵ Forming nanostructures with at least one dimension within the nanometer range has proven effective in mitigating the negative impact of the short charge diffusion problem.^{16,17} More recently, research attention on hematite has been shifted to issues connected to the late photocurrent turn-on characteristics (high Von, typically ~1.0 V vs. reversible hydrogen electrode, or RHE). Although the positive band edge positions relative to water redox potential may help partially explain the high Von's, the previously reported Vph, as defined by Vph=1.23-Von (where 1.23 V vs. RHE is the equilibrium water oxidation potential), falls in the range of 0.2-0.4 V, well short of the expected 0.6-0.8 V as calculated from the reported Fermi levels of hematite ($V_f = 0.4-0.6 \text{ V vs. RHE}$).^{18,19} To address this issue, Grätzel et al. deposited a layer of Co^{II} onto hematite and observed an 80 mV cathodic shift of Von, which they attributed to hole trapping by Co. Later, Gamlin et al. applied a Co phosphate (Co-Pi) water oxidation catalyst onto hematite and found a ca. 200 mV cathodic shift of Von. This shift was attributed to improved kinetics. That is, a reduction in the required overpotential was considered the key reason for the shift. Soon after, the same effect was observed on

other photoelectrodes as well, including on BiVO₄ by Gamelin et al. and on WO₃ by Choi et al.^{20,21}

Dynamic transient optical absorption studies performed by Durrant et al., however, revealed that hole transfer kinetics from hematite to water does not seem to change with or without the Co-Pi catalyst.²² Instead, the Co-Pi functions to improve the performance by serving to "store" electrons within itself. As such, its role is to reduce electron-hole recombination on hematite surface by increasing the band bending. Although not explicitly stated by Durrant et al., the effect is equivalent to increasing P_s/P_s^0 ratios as shown in Eq. 1, which is essentially to improve surface energetics. This evidence is against the understanding that the observed V_{on} reduction is due to a decrease in the required overpotential, and it raises the question whether the applied Co-Pi actually functions as a catalyst, which, by definition, is to change chemical reaction kinetics. The debate was partially answered by detailed electrochemical studies reported by Hamann and Bisquert et al., which suggests that Co-Pi functions both as a catalyst and to improve the surface energetics.²³

More recently, there have been several works that have further clarified the role of a surface catalyst to influence the surface energetics of semiconductors, albeit on different material platforms. For instance, Boettcher et al. demonstrated that when coupling TiO_2 photoanodes with an ion-permeable electrocatalyst, such as $Ni(OH)_2$, an "adaptive" semiconductor/electrocatalyst interface was formed.²⁴ They describe this as an instance when the potential of the catalyst is independent of the semiconductor potential. The permeability of the catalyst becomes important in order to maintain charge balance within the catalytic film. In their study, they found that dense electrocatalyst, such as IrO_x , placed

on TiO₂ followed the potential of the semiconductor, as expected for a Schottky junction. Similarly, Hamann et al. studied the ion-permeable Ni(OH)₂ film on hematite films and found a cathodic shift in photocurrent onset potential by as much as 300 mV.²⁵ Together, these studies underline the importance of reducing recombination rates rather than focusing solely on improving water oxidation kinetics, which aligns well with our understandings of the semiconductor-catalyst interface.

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1.4 INTENSITY MODULATED PHOTOCURRENT SPECTROSCOPY

In order to directly measure the recombination rates and surface kinetics of semiconductors used for artificial photosynthesis, intensity modulated photocurrent spectroscopy (IMPS) is often employed throughout this dissertation. The theory behind IMPS was developed by Laurence Peter from Bath University.²⁷⁻³¹ As in the name, this technique uses a small AC modulation in the light intensity shone onto a light absorber. As seen in Figure 7, a Si diode is used to reference the incident light. The incident light and outgoing photocurrent from the photoelectrode are compared with a frequency response analyzer (FRA), which can detect any impedance between the incident light and the photocurrent.



Figure 7. A schematic of an IMPS set up. *This figure is reproduced with permission from "Chem. Sci., 2017, 8, 3712–3719."*

The frequency of the light is typically modulated from kHz down to Hz, or μ s down to seconds, where these time scales relate to slow surface processes within the semiconductor. This technique is essentially the measurement of the transient recombination spikes that appear when steady state lighting is turned on and off, as seen in Figure 8. By tuning the frequency of light modulation the time constant of these transient spikes can be measured, then with a few simple equations, the recombination rate constant and forward charge transfer rate constant of the photoelectrode can then be determined. The derivation of the rate constants is detail in the following chapters. In short, the steady state photocurrent of an electrode, j_{ss} , is defined by the ratio of forward charge transfer (k_{tran}) to the sum of the k_{tran} and surface recombination (k_{rec}). IMPS allows k_{tran} and k_{rec} to be quantitatively measured.

$$\frac{j_{ss}}{j_{t=0}} = \frac{k_{tran}}{k_{rec} + k_{tran}}$$



Figure 8. A normalized current vs time plot of a photoanode for water oxidation, where the incident light is periodically blocked. When the light is turned on, a transient spike is formed before it decays to a steady state value that is defined by the transfer efficiency. IMPS measures the time constant of the transient decay. *This figure is reproduced with permission from "Phys. Chem. Chem. Phys., 2014,16, 24610-24620"*

Before this dissertation, Peter's group was one of the few to have used IMPS to measure the rate constant of photoelectrodes for water oxidation.³²⁻³⁴ Since most potentiostats come equipped with the instrumentation necessary to make EIS measurements, EIS has been more commonly utilized in the literature. However, equivalent circuit models required for a semiconductor's surface can be complex and subjective. Therefore, for our studies we chose IMPS as a primary method to quantify the surface kinetics of semiconductors used for water splitting, as seen in chapters 2-4.

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2.0 UNDERSTANDING THE ONSET POTENTIAL OF REGROWN AND NIFEO_X PASSIVATED HEMATITE ELECTRODES

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Using intensity modulated photocurrent spectroscopy (IMPS), we determined the rate constants of water oxidation and recombination at the surface of three different hematite-based photoanodes. It was found that the best performing electrodes, in terms of photocurrent onset potential, exhibited the slowest water oxidation rate constants, which was a surprise. The performance of these photoelectrodes were enabled by the slow surface recombination. When amorphous NiFeO_x, a water oxidation catalyst, was present, the rate of surface hole transfer actually slowed down; what was slowed more was the recombination rate at the hematite surface, resulting in better water oxidation performance. As such, this study supports that the primary role of the added heterogeneous catalyst NiFeO_x is to act as passivation layer rather than a catalytic layer.

2.1 EXPERIMENTAL DETAILS

2.1.1 Hematite Preparation

For the sdH and rgH syntheses, β -FeOOH was first grown on fluorine-doped tin oxide (FTO) substrates (~7 Ω /sq, Sigma) in a solution containing 0.15 M iron (III) chloride hexahydrate (FeCl₃, 97%, Alfa Aesar) and 1 M sodium nitrate (NaNO₃, 99%, Alfa Aesar). The deposition was carried out at 100 °C for 1 h. After rinsing, the electrodes were annealed in a tube furnace at 800 °C for 5 minutes to convert β -FeOOH into hematite. For the rgH electrodes they were subjected to the same procedure two more times.

For aH (ALD) samples a Cambridge Nanotech, Savannah 100 atomic layer deposition apparatus was used. Iron tert-butoxide (heated to 125 °C) and water (25 °C) were used as the precursors for hematite and were pulsed alternatingly into the deposition chamber (heated to 180 °C) with a 10 cm³/min flow of N₂ as carrier gas. 500 cycles was used to produce films between 20-30 nm thick, grown onto FTO.¹ Following the deposition, the samples were annealed at 500 °C for 15 minutes in air to assure all samples were completely converted into hematite.

2.1.2 NiFeO_x/GaO_x Deposition

To deposit NiFeO_x, Iron (III) 2-ethylhexanoate (50% w/w in mineral spirits, Strem Chemicals) and nickel (II) 2-ethylhexanoate (78% w/w in 2-ethylhexanoic acid, Strem Chemicals) were mixed in hexane to give a concentration of 15% w/w metal complex solution. The solution was further diluted 10 times with hexane and approximately 10 μ L/cm² of this solution was directly drop-casted onto the hematite electrodes. After drying in air for 5 minutes, the electrode was irradiated with UV light for 5 minutes.

GaO_x depositions were done following a previously reported procedure with slight adjustments.² Hematite films were immersed in 50 mL of water at approximately 348 K. 0.209 g Ga(NO₃)₃·nH₂O (99.9%, Aldrich) and 3.01 g of urea (99%, Aldrich) were added sequentially with an interval of 2 minutes under mild stirring. 20 min after the urea addition, the samples were rinsed with deionized water and annealed in a tube furnace at 1073 K for 5 minutes to improve crystallinity and stability.

2.1.3 Electrochemical Characterization

To characterize the hematite films a Solartron Modulab XM potentiostat with a photoelectrochemical accessory was used for all current-voltage, IMPS, and IMVS measurements. Measurements were made in 1 M NaOH. A 3-electrode configuration was used with a platinum counter electrode, with a Hg/HgO reference electrode (CHI-152), and the hematite samples used as the working electrode. For the H₂O₂ study, 100 µL of 31 wt % H₂O₂ was added to 18 mL of 1 M NaOH. A 405 nm LED (ThorLabs) was used as the light source for all measurements, at 90% of its maximum power (134 mW/cm²). For IMPS and IMVS measurements a 10% modulation intensity was used, and the frequency was swept from 10 kHz down to 0.1 Hz. During the JV measurements a scan rate of 20 mV/s was used. All samples were measured using front side illumination.

2.2 BACKGROUND OF HEMATITE-CATALYST INTERFACE

Solar water splitting is an important first step in photosynthesis. Plants utilize the harvested solar energy to extract electrons from H₂O, providing enough thermodynamic energy to reduce carbon dioxide during the dark reactions.³ Given the vast availability of H₂O and sunlight, solar water splitting holds great potential for direct solar energy conversion and storage.⁴ For complete water splitting, two fundamentally important processes, the reduction reaction and the oxidation reaction, need to be balanced. Due to the complex 4-electron/4-proton nature, the water oxidation reaction tends to be more difficult and slower than the reduction reaction. This highlights the necessity for the addition of catalysts to facilitate hole transfer to H₂O for O₂ evolution.⁵ A number of materials, including IrO_x, CoO_x, RuO_x, NiFeO_x, Co-phosphate, NiOOH, and more recently a molecular heterogenized Ir, have been confirmed as active catalysts toward the O2 evolution reaction (OER).⁵⁻¹² However, when integrated with light absorbers, the role of these catalysts is often a source of confusion and debate (vide infra). This is because the presence of catalysts on a photoelectrode surface not only changes the charge transfer kinetics, but they can also alter the surface energetics that define the charge separation capabilities near the photoelectrode surface.¹³ Further development of the water splitting field will require a detailed understanding of the mechanisms that underpin the observed performance, which in turn depends on the quantitative measurement of surface energies and charge transfer kinetics. Using hematite as a prototypical photoelectrode system, we show that surface modifications of hematite by either a re-growth strategy or with an amorphous NiFeO_x catalyst serve to reduce surface recombination. Whereas, the charge transfer kinetics are either slower or remain unchanged for all scenarios studied here,

strongly supporting that a surface passivation effect is the key reason for the observed improvement in water oxidation by hematite.

Hematite was chosen as the material for the present study as it has been at the center of a recent debate about how catalysts alter the photoanodic characteristics of water oxidation.^{14,15} Despite the appeals of low cost and good stability, hematite faces great challenges as a photoelectrode material due to its low photovoltages and poor catalytic activities.¹⁶⁻¹⁸ The slow hole transfer kinetics across the hematite/water interface, in particular, has been considered a key reason for the low photovoltages.^{19,20} Therefore there have been numerous attempts targeted at reducing the kinetic overpotentials in hopes to overcome the issues connected to the slow surface kinetics and improve the onset potential to more cathodic potentials. For example, Grätzel et al. applied Co^{II} onto hematite's surface and observed appreciable cathodic shift of the steady-state current-voltage relationship (~80 mV), which was thought as a direct proof of how fast hole transfer improves the photoelectrochemical (PEC) performance.²¹ A more pronounced effect was observed by Gamelin et al. with a Co-phosphate OER catalyst (Co-Pi; 200 mV),²² with similar phenomena having been reported on other catalyst/photoelectrode combinations.²³⁻ ²⁵ However, the view that the change in the PEC performance was due to better charge transfer was challenged by Durrant et al.'s transient absorption measurements, where longer surface hole lifetimes, rather than faster hole transfer kinetics, were concluded to be the reason for the cathodic shift.²⁶ Subsequent detailed electrochemical studies by Hamann and Bisquert et al. suggested that Co-Pi on hematite may serve dual functionalities of promoting charge transfer and building up hole concentrations.²⁷ Their results, nevertheless, do not fully settle the debate as a quantitative understanding of the system is
still missing. In parallel, the Wang group has conducted studies on combining amorphous NiFeO_x with hematite and attributed the cathodic shift in onset potential to better charge separation.^{1,28} Where the key experimental evidence comes from the measurement of the surface energies of the system under equilibrium or pseudo-equilibrium conditions. With the addition of a-NiFeO_x to the surface of our regrown hematite samples, our group achieved the best turn on potential observed for hematite (0.45 V vs. RHE).²⁹ However, our initial studies indicate that the cathodic shift in onset potential is mostly, if not entirely, due to surface energetics rather than improved water oxidation kinetics. Again, for a complete understanding of the system, quantitative measurements of the surface charge transfer kinetics are necessary. The results reported herein fill in this knowledge gap.

On a fundamental level, the key driving force of a photoanodic reaction is the accumulation of energetic holes on the photoelectrode surfaces. While the detailed dependence of the reaction rate on the hole concentration may be intricate, as revealed by several recent studies, a high steady-state surface hole concentration is generally desired,³⁰ where a higher concentration of surface holes results in higher photovoltages that help reduce the need for externally applied potentials. To the first order approximation, the rate at which the holes are generated depends on the light absorption and charge separation of the photoelectrode, as well as the light intensity. The rate at which the holes disappear depends on the rate of surface recombination and hole transfer into the solution. Note that contributions by bulk recombination may be regarded as part of the photoelectrode charge separation and is not considered here. We see from this simplified argument that, for a given system under fixed lighting conditions, detailed knowledge of surface recombination may be

inferred by probing hole concentrations using, for instance, spectroscopic methods, or by fitting electrochemical impedance data,³¹⁻³³ a direct measure of these kinetic parameters is of great value. For this purpose, we employed a technique pioneered by Peter et al., known as intensity modulated photocurrent spectroscopy (IMPS).³⁴ In using IMPS, we are presented with an opportunity to systematically compare samples of different surfaces that feature different PEC performance. This information leads to a better understanding of the kinetics at the photoelectrode/water interface that has been missing in the literature. By examining hematite prepared by three different methods (atomic layer deposition (denoted as aH), solution synthesis (denoted as sdH), and re-growth treated (denoted as rgH); see experimental section for details) with and without surface modifications (amorphous NiFeO_x catalysts), we show that in all cases the cathodic shift of PEC water oxidation is only driven by the suppression of surface recombination, while no contribution by faster hole transfer kinetics was observed.

As briefly introduced in the previous chapter, IMPS is a form of impedance spectroscopy that measures the phase shift in photocurrent in relation to a sinusoidal modulation of the light source.³⁴ By assuming that the small changes in the light intensity only alter surface charge concentrations but not the degree of band bending, IMPS probes how the photocurrent of a PEC system responds to these changes in light intensity. The complex photocurrent, as a function of the light modulation frequency, may be presented in a Nyquist plot (Fig. 2A). In this plot, at the high-frequency intercept with the real photocurrent axis, the surface recombination rate is insufficient to match the rate at which the surface hole concentrations change as a result of light intensity modulations. This value provides a measure of the hole flux moving toward the photoelectrode surface. Note that

in hematite samples the bulk recombination kinetics are much faster than the surface recombination kinetics, and a separate technique is needed in order to study bulk recombination rates. At the low frequency intercept, it reports on the steady-state photocurrent, which measures the rate at which the charges are transferred to the solution for water oxidation. The ratio of the photocurrents between the low-frequency intercept and the high-frequency one provides the charge transfer efficiency (TE), defined as $k_{tran}/(k_{tran} + k_{rec})$, where k_{tran} and k_{rec} are the surface charge transfer and recombination rate constants, respectively. The rate constants at the apex of the semicircle, where the maximum phase shift is measured, reports on the combined rate of charge transfer and recombination $(k_{tran} + k_{rec})$, where the effective hole transfer from the semiconductor is the measured ktran. The theoretical basis for IMPS was developed by Peter et al. in a series of publications,^{34,35} and has been recently applied to study hematite.^{36,37} By extending the technique to a systematic study of a series of photoelectrodes with the same crystal structure but different surfaces, we unambiguously confirm that the passivation effect, rather than better surface catalytic activities, is the true reason for the observed PEC performance improvement. As such, the results presented here are new and significant.

2.3 RESULTS AND DISCUSSION

2.3.1 Summary of Samples Studied

A total of 6 types of samples were studied here. They were based on three different synthesis methods, (1) atomic layer deposition (ALD) grown hematite (aH); (2) solution

derived hematite (sdH); and (3) hematite subjected to surface regrowth (rgH; note that here rgH refers to hematite that has been subjected to regrowth treatments twice). The details of their syntheses have been recently reported elsewhere and are summarized in the experimental section.²⁹ Among these samples, aH features a high degree of surface states and the highest turn-on voltages (V_{on}, as defined by the lowest applied potential at which appreciable photocurrents are measured). The rgH samples exhibit the lowest V_{on}'s. In addition to samples with bare surfaces, studies were performed on samples coated with amorphous NiFeO_x and GaO, where examples of the former two can be seen in Figure 1.



Figure 1. The JV curves shown are all under 405 nm light at 134 mW/cm^2 . The left image shows the three hematite samples without NiFeO_x on the surface. Where the right figure is after the NiFeO_x has been added.

2.3.2 IMPS Data and Validation of the Technique for the Present Study

A set of representative Nyquist plots for bare hematite are shown in Fig. 2A, from which the surface charge transfer efficiencies ($TE = k_{tran}/(k_{tran} + k_{rec})$) were extracted. The hole flux into the photoelectrode surface can be calculated following the Gärtner relation (eq. 1). Here the Gärtner equation is employed for its simplicity. A more complete

treatment that considers the recombination in the space charge region and back flow of electrons to the electrolyte has been developed by Reichman.³⁸ Intriguingly, when the charge transfer efficiency is combined with the Gärtner model, a close match with the experimental data is already obtained, raising a question as to how significant the recombination in the space charge region is in limiting the performance of hematite. Here we assume the depletion width (W_{SC}) changes with the applied potential (V_{app}) following, Wsc= $(2\epsilon\epsilon_0(V_{app}-V_{fb})/N_D)^{1/2}$. Both V_{fb} and N_D were measured by the Mott-Schottky method, where further discussion of these measurements can be found in section 1.3.4. The measurable photocurrent was then obtained by combining the Gärtner hole flux with TE, as is described in equation 1:

$$J = J_0 \left(1 - e^{\frac{\alpha W_{sc}}{(1 + \alpha L_p)}} \right) \times TE$$
(1)

At λ =405 nm, an absorption coefficient (α) of 1.0×10^5 cm⁻¹ was used. The hole diffusion distance of 3 nm was used, as hematite typically has a value of 2-4.³⁹ Guided by our previous research, a reflection of 20% was considered for the light intensity (J_{θ}).²⁹ Finally, the potential drop within the Helmholtz layer was compensated for (see 1.3.4). As seen in Fig. 2B, a close match between the simulated photocurrent, based on the TE obtained from the IMPS data, and the experimental data was obtained. Importantly, since all parameters have physical significance, the match was achieved without adjusting any parameters. Seeing how the TE can correct the Gärtner current for surface processes shows the power of IMPS as a tool to examine surface kinetics, and encouraged us to employ it in a systemic study of hematite's surfaces.



Figure 2. Representative IMPS and PEC data for hematite under monochromic illuminations (λ =405 nm; intensity: 134 mW/cm²). (A) Nyquist plots of the three bare samples, aH, sdH, and rgH, at an applied potential of 0.7 V vs. RHE (reversible hydrogen electrode). The sample IDs are explained in the main text. The two key parts in the plots used for data analysis are highlighted by arrows. The real and imaginary photocurrents are normalized to the high frequency intercept, which represents the hole flux toward the surface. (B) Using transfer efficiency extracted from IMPS data and the Gärtner equation, we obtained the photocurrent for ALD hematite (light green between squares), which is in agreement with the experimental steady-state current-voltage curve (dark green).

2.3.3 Gärtner Analysis of Hematite Samples

Mott-Schottky analysis was used in order to determine the flat band potential and the doping density of aH electrodes. The measurements were made in the dark with a CH Instruments (CHI604C) potentiostat, in 1 M NaOH while stirring the solution. Both 100 Hz and 1000 Hz were sampled from 0.5 V to 1.1 V, where the 1000 Hz data can be seen in Figure 3. The data set obtained was plotted using the following relation:

$$\frac{1}{c_s^2} = -\frac{N_D e}{2A^2 \varepsilon \varepsilon_0} \left[V_{sc} - V_{fb} \right]$$
(2)

A linear line was found and the donor density of aH was determined to be 2.65 x 10^{19} cm³. For the flat band potential, a value of 0.73 V_{RHE} was obtained, consistent with other aH electrodes tested and previous values reported for aH.



Figure 3. A Mott-Schottky plot of aH at 1000 Hz.

Next the width of the space charge region was calculated using the following equation:

$$W_{sc} = \sqrt{\frac{2\epsilon\varepsilon_0 (V_{app} - V_{fb})}{N_D q}}$$
(3)

Where $\varepsilon = 60$, $\varepsilon_0 = 8.85 \text{ x } 10^{12} \text{ F/m}$, $V_{app} - V_{fb}$ is the magnitude of the space charge region assuming that all applied potential contributes to increased band bending, where $V_{fb} = 0.73$ V vs. RHE, and $N_D = 2.65 \text{ x } 10^{19} \text{ cm}^{-3}$ for the aH sample used here. With the space charge region, we were now able to fully calculate the Gärtner current in our aH electrodes. Where the Gärtner current is defined by:

$$J = q J_0 \left(1 - e^{\frac{\alpha W_{SC}}{1 + \alpha L_p}} \right) \tag{4}$$

Here J is the Gärtner current, $J_0 = 2.2 \times 10^{17}$ photons/cm² with a 405 nm LED (where the elementary charge, q, on an electron is used to convert the absorbed photons into an amperage), α is the absorption coefficient where a value of 1.00 x 10⁵ cm⁻¹ at 405 nm was used. A minority carrier length of 3 nm was employed here. After calculating the Gärtner current, we then measured the IMPS response of the same aH electrode in order to obtain the transfer efficiency of the electrode. For the electrode shown in section 1.3.2 (Fig. 2B) the values are shown in the table 1.

Potential (VRHE)	Transfer Efficiency (ktr/(ktr + krec))
0.9	0.003
1	0.0314
1.1	0.302
1.2	0.746
1.3	0.899
1.4	0.961
1.5	0.973

Table 1. Transfer efficiency values measured for aH samples as abstracted from the IMPS measurement at each applied potential (V_{RHE})

Our initial steady state currents, as modeled by equation 1, were cathodically shifted by $\sim 100 \text{ mV}$. This mismatch in between the IMPS calculated steady state current and the DC steady state current has previously been reported.^{35,40} Here we attribute this shift to the charging of the Helmholtz layer under steady state conditions that will be less prominent under AC incident lighting.



Figure 4. The Gärtner current, aH experimental JV data, and the Gärtner current multiplied by the transfer efficiency, not corrected for the potential drop across the Helmholtz layer.

In order to more closely fit our model, the potential drop across the Helmholtz layer across the studied potential range was corrected, 0.5 - 1.2 V vs. RHE. This can be done by calculating the change in potential across the Helmholtz layer with the following equation:

$$\Delta V = \frac{q p_{surf}}{c_H + c_{SC}} \tag{5}$$

Where q is the elementary charge, C_H is the Helmholtz capacitance, 100 μ F was used here. C_{SC} is the space charge capacitance, as taken from the Mott-Schottky analysis and was on the order of 0.1-0.3 μ F. Lastly, p_{surf} is the surface concentration of holes. In order to calculate the surface concentration of holes, the Gärtner current is divided by the recombination and transfer rates, as shown below.

$$p_{surf} = \frac{J}{k_{tran} + k_{rec}} \tag{6}$$

J here is the calculated Gärtner current, and $k_{tran} + k_{rec}$ is determined by the apex of the upper quadrant IMPS semicircle, as seen in Fig. 2A. Ultimately a surface hole concentration of 1-10 x 10¹³ holes/cm² was determined. After plugging all of the values into equation 5 and 6 the light induced potential drop across the Helmholtz layer was determined. For the aH sample shown in Fig. 2B, Table 2 shows the determined values.

Potential	ΔV across		
(Vrhe)	Helmholtz		
	layer		
0.9	0.0343		
1.0	0.107		
1.1	0.126		
1.2	0.112		
1.3	0.124		
1.4	0.168		

Table 2. Calculated potential drop across the Helmholtze layer for aH samples used to correct TE values obtained from IMPS.

When applying the potential drop across the Helmholtz layer to the original Gärtner + transfer efficiency (as seen in section 1.3.2), the fit becomes much closer to the experimental values that were observed for the same aH electrode (Fig. 2B). This analysis was limited to aH electrodes, since the Mott-Schottky analysis is less straight forward for nanostructured materials.

2.3.4 Rate Constants of Charge Transfer and Surface Recombination for Bare Hematite

The charge transfer rate constant (k_{tran}) and surface recombination rate constant (k_{rec}) were obtained by combining the TE at the low-frequency intercept with $k_{tran} + k_{rec}$,

as determined by the apex of the semicircle in Fig. 2A. The raw IMPS data for each of the six samples studies in this chapter are shown in Fig. 5, with the calculated k_{tran} values being shown in Table 3. Note that a first order dependence of the reaction rate on the hole concentration is assumed here. The assumption is consistent with experimental results reported to date. Recently, Durrant et al. observed that at 1.5 V a transition from 1st to 3rd order reactions took place at high light intensities.³⁰ The third order reactions would indeed make the data interpretation more difficult. Nevertheless, a close correlation between our measured water oxidation rate constants with previously reported values was found, confirming that the water oxidation as measured in our experiments is likely first order. As shown in Fig. 6, a monotonic decrease of k_{rec} is observed for all three bare hematite samples studied here. Notably, the recombination rate constants across the entire potential range are much higher for aH than sdH or rgH. This trend agrees with our previous observation by X-ray absorption that greater defect densities are present on aH and lowest for rgH.²⁹ The second notable feature of this set of data is the k_{tran} for aH is on the rising curve at V>V_{on}, whereas k_{tran} 's for sdH and rgH plateau at ~120 s⁻¹ and ~35 s⁻¹, respectively. The results suggest that the mechanisms involved in water oxidation may be different for hematite with different surfaces. This is consistent with literature reports that water oxidation by hematite is mediated by surface-adsorbed species (also denoted as "surface



Figure 5. IMPS measurements of all six samples tested for this study. The high frequency crossing point with the real photocurrent axis was used to normalize the imaginary and real axes. This allows for an easy comparison between samples at different applied potential, and for the transfer efficiency to be easily determined. The black trace represents a 0.4 V_{RHE} applied potential for each graph with 0.1 V steps up to 1.4 V_{RHE} . The order of the traces goes, black, red, green, blue, cyan, magenta, dark yellow, olive green, orange, purple, pink. Each color represents the same applied potential in each graph.

	Water Oxidation Rate Constant							
	aldH		sdH		rgH2			
V _{RHE}	No	With	No	With	No	With		
	NiFeO _x	NiFeO _x	NiFeO _x	NiFeO _x	NiFeO _x	NiFeO _x		
	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)		
0.5	6.97	15.9	9.21	140	1.52	13.9		
0.6	1.91	74.5	12.9	168	3.66	25.5		
0.7	1.82	116	44.9	174	16.2	28.8		
0.8	4.44	143	72.4	141	30.0	30.9		
0.9	14.8	147	94.1	95.6	35.4	27.2		
1.0	48.2	122	118	113	50.9	26.6		
1.1	135	137	133	103	37.8	23.2		
1.2	226	136	123	102	25.4	17.5		
1.3	286	140	122	91.3	19.6	15.5		

Table 3. The numerical values obtained from k_{tran} values in Figure 5. The blue shaded regions show where the k_{tran} values are higher for the sample without NiFeO_x than without.



Figure 6. Rate constants extracted from IMPS data at different applied potentials. (**Top panel**) aH, (**Middle panel**), sdH and (**Bottom panel**) rgH. Rate constants of recombination are shown as black symbols; rate constants for surface charge transfer are shown as green symbols. The error bar is the standard deviation between different samples (typically 4 to 5 samples are measured for each group of data).

states").^{28,41} Thirdly, k_{rec} for aH is considerably higher near the turn-on potential (167 s⁻¹ at 1.1 V) than that for sdH (110 s⁻¹ at 0.9 V), which is still higher than that for rgH (27 s⁻¹ at 0.8 V). This supports that surface regrowth treatment indeed reduces surface recombination, as we previously concluded by open-circuit potential measurements.²⁹ Lastly, the potential at which k_{tran} surpasses k_{rec} coincides with the V_{on}, further proving that IMPS provides a valid measure of the surface kinetic constants.

It is further noted that for a PEC system, a higher light intensity is expected to lead to a greater degree of quasi-Fermi level splitting. The corresponding driving force for hole transfer would increase, as well. Consequently, faster charge transfer (i.e., greater k_{tran}) is expected as light intensity is increased. This trend is indeed observed, where k_{tran} increases with light intensity monotonically (Fig. 7).



Figure 7. IMPS measurements made at 5 - 90% of the LED intensity, where 90% is 134 mW/cm². The samples tested here are bare electrodes. The figure on the left shows the transfer rate constant, which increases monotonically with light intensity. The figure on the right shows the recombination which remains nearly constant at all light intensities probed. All measurements were made on rgh2 at 0.6 V vs RHE, which is slightly after the onset of the photocurrent for these photoelectrodes.

2.3.5 Rate Constants of Hematite Photoelectrodes with NiFeO_x catalysts

With the presence of NiFeO_x as an OER catalyst, a distinctly different trend of k_{rec} and k_{tran} was observed than when compared to the bare hematite photoelectrodes. As shown in Fig. 8, k_{tran} appeared to be independent of V_{app}. A similar phenomenon has been previously observed by Peter et al. on Co-treated hematite photoelectrodes.³⁶ However, there are several features of this set of data that deserve further discussion. First, k_{tran}'s for all photoelectrodes decorated by NiFeO_x are equal to or smaller than those without the catalyst. This is a surprise since the presence of a catalyst was expected to increase water oxidation rates. Rather, a significant suppression of the krec's was found, as shown in Fig. 8. It is therefore concluded that the main function of $NiFeO_x$ is to passivate the hematite surfaces against recombination by reducing the surface Fermi pinning, effectively increasing the band bending at the surface, rather than activating the surface for water oxidation. Note that the smaller k_{tran} measured here on NiFeO_x does not suggest water oxidation is slower. After all, NiFeO_x has been confirmed as a good water oxidation catalyst.⁵ k_{tran} , as measured by IMPS, likely reports on the rate determining steps (RDS) of the complex charge transfer processes from the photoelectrode to water. These results agree with Durrant et al. measurements of Co-Pi coated hematite photoelectrodes.^{19,42} They also agree with our open-circuit potential measurements.^{1,28,43} Second, the k_{tran}'s for



Figure 8. Rate constants for hematite photoelectrodes with NiFeO_x surface decorations. (**Top panel**) Recombination rate constants for photoelectrodes by three different preparation methods. (**Bottom panel**) Surface charge transfer rate constants for the same photoelectrodes. The error bars are standard deviations between different samples.

aH and sdH are comparable when NiFeO_x is present on the surfaces across the entire voltage range (Fig. 8). It supports that the water oxidation processes are now governed by NiFeO_x. But the k_{tran} 's for rgH photoelectrodes are considerably lower, by almost a factor of 5. A possible reason is that the NiFeO_x employed here is ca. 10 nm in thickness. Its functionality may be influenced by the interface between hematite and NiFeO_x. Another reason is that k_{tran} as measured here is the apparent charge transfer rate constant of the RDS that follows a first order dependence on the hole concentration, which may be an

oversimplification of the complex water oxidation process. More research is needed to fully understand the differences. Despite rgH's slow k_{tran} 's, the k_{rec} 's for the rgH photoelectrodes are much slower than k_{rec} 's for sdH or aH, by more than 10 times across the entire voltage range, further highlighting the importance of measuring photocurrent is a high TE but not necessarily a high k_{tran} (vide infra).

The large decrease in k_{rec} led to rgH photoelectrodes having the best measured TE (Fig. 9), consistent with the observation that the best PEC performance, in terms of photovoltages and photocurrents, was measured on rgH. It highlights that as far as PEC performance is concerned, it is equally, if not more, important to consider k_{rec} as well as k_{tran} , as defined by the TE. Examining Equation 1, we see that so long as the light absorption and charge separation by the photoelectrode are fixed, the determining factor for the measurable photocurrent is the TE. In other words, under the likely assumption that the main mechanisms to dissipate surface holes are charge transfer for water oxidation and surface recombination, fast water oxidation kinetics is not a prerequisite for good anodic PEC performance, so long as surface recombination can be minimized. This understanding has major implications for water oxidation reactions because, as the overall reactions are multi-electron, multi-proton in nature, they are considered inherently slow, with the characteristic rate constants in the range of millisecond (ms) or longer.^{33,36} Our data in Figs. 6 & 8 support such an estimate. By comparison, charge lifetimes within the bulk of semiconductors are typically in the microsecond (μ s) or shorter time scales. This disparity of time scales creates a major challenge. In order to beneficially balance the effects of the solid state and water oxidation processes it is necessary to consider their resulting interactions. It is known that the thermodynamic energy of holes on the surface of a photoanode is connected to the hole concentration by: V_{ph} =(k_BT/q)ln(P_s/P_s^0), where V_{ph} is the photovoltage as defined by the difference between the quasi-Fermi level of holes (E_{*f*,*h*}) and flatband potential (V_{*f*b}): V_{ph} =E_{*f*,*h*}-V_{*f*b}; k_B is the Boltzmann constant, T is the temperature, q is the fundamental charge of electrons, P_s is the steady-state surface hole concentration under light, and P_s⁰ is the equilibrium surface hole concentration under dark. It is seen that greater steady-state surface hole concentration, which is determined by the transfer efficiency, translates to higher V_{*ph*} and is desired for greater oxidation power. From this standpoint, the slow kinetic constants in both recombination and charge transfer, but more so in the slow recombination, is desired as it contributes to the build-up of surface hole concentrations, which translates to greater photovoltages. The interplay between V_{*ph*} and TE has been confirmed by our earlier work, where V_{*ph*} of 0.56 V and 0.8 V was measured on rgH without and with NiFeO_x, respectively.²⁹ As a comparison, only 0.24 V was measured on bare aH, whereas 0.42 V and 0.66 V was measured on sdH without and with NiFeO_x, respectively.²⁹



Figure 9. Charge transfer efficiencies for various hematite photoelectrodes without (**Top panel**) and with (**Bottom panel**) NiFeO_x decorations at different applied potentials.

2.3.6 Rate constants of hematite photoelectrodes decorated with GaO_x passivation

As a control experiment, IMPS characterizations on GaO_x -treated hematite photoelectrodes (sdH was studied here) were performed. GaO_x was chosen here as it has previously been shown by Grätzel et al. to passivate the surfaces of hematite,² and Durrant et al. have also shown that GaO_x behaves similarly to Co-Pi on hematite when they studied the transient decay kinetics.⁴² No known catalytic effects of water oxidation were reported on GaO_x . The IMPS data as shown in Fig. 10 are to be compared with those in Fig. 8 and Fig. 6. It is seen that within the range of 0.6 and 1.0 V vs. V_{RHE} , k_{tran} 's for both hematite with and without GaO_x only increased marginally. In contrast, k_{rec} 's are significantly reduced due to the application of GaO_x. The trend is consistent with that in Fig. 6 for bare sdH. These data further support Grätzel's proposition that GaO_x improves the PEC performance of hematite by passivating the surfaces.²



Figure 10. Rate constants for hematite treated with GaO_x passivation. (**Top panel**) charge recombination rate constants. (**Bottom panel**) charge transfer rate constants.

2.3.7 IMPS Studies of PEC Systems with H₂O₂ as Hole Scavengers

As a hole scavenger that features fast charge transfer, H_2O_2 has been frequently used in studies on photoanodes.⁴⁴⁻⁴⁵ For instance, it is so efficient in receiving holes that in its presence the charge collection efficiency has been considered unity. The next task was to carry out IMPS studies with H_2O_2 present, and the purpose was to measure charge transfer efficiencies (TE). As expected, near unity TE was obtained (Fig. 11) when 0.05 M H_2O_2 was added to the electrolyte. Under these conditions, because k_{tran} is significantly greater than k_{rec} , the same analysis as outlined above in extracting k_{tran} and k_{rec} is no longer suitable. For this reason, no quantitative rate constant calculations were performed using IMPS.



Figure 11. Characterizations with H_2O_2 as hole scavengers. (A) Steady-state currentvoltage curves for sdH with (red) and without (black) H_2O_2 . (B) IMPS data of sdH with (red) and without (black) H_2O_2 at 0.7 V vs. RHE.

2.3.8 Intensity Modulated Photovoltage Characterizations with and without Hole Scavengers

An alternative measurement enabled by the varying light intensities is IMVS (intensity modulate photovoltage spectroscopy). Different from IMPS, IMVS probes the how the photovoltage changes as a function of the frequency of the perturbation to the light intensity under open circuit conditions. Since the external circuit is open, the net exchange current is expected to be zero. Changes in the surface hole concentration as probed by the



Figure 12. Intensity modulate photovoltage spectroscopy (IMVS) of various hematite photoelectrodes in H_2O (Top panel) and in H_2O_2 (Bottom panel). Data presented as Bode plots, where the Y axis shows the imaginary component of the complex photovoltage, and the X axis shows the rate constants converted from the modulation frequencies.

photovoltage are expected to chiefly respond to surface recombination. When presented in Bode plots (Fig. 12), the peak frequencies report on the characteristic rate constants of surface charge recombination. In the absence of H_2O_2 , two peaks are observed (top panel, Fig. 12). The first peak, at the higher rate constant, corresponds to a rate constant of approximately 1000 s⁻¹ or faster for all three electrodes studied. When understood as surface recombination rate constants, these values agree with those obtained by analyzing IMPS data (Fig. 6). The corresponding processes are likely connected to states due to H₂O adsorption onto hematite. This agrees with our previous research that these states are due to chemical adsorption rather than structural defects.²⁸ It is also consistent with a recent EIS study by Hamann et al. on hematite for methanol oxidation.⁴¹ That the peak positions by and large remain the same for all three types of hematite electrodes further supports this understanding. Furthermore, the addition of H₂O₂ does not shift these peaks (Fig. 12, bottom panel) because the majority chemicals are still H₂O in the latter case. It is noted that the measured steady-state open circuit potentials under the same lighting conditions for this set of experiments were 0.53 V, 0.52 V, and 0.49 V (vs. V_{RHE}) for aH, sdH, and rgH, respectively. These values need to be taken into account when comparing the rate constants obtained in Fig. 12 and with those in Fig. 6.

The second peak, only observed in the absence of H_2O_2 , appears at much lower frequencies. At 5 s⁻¹ or slower, this rate constant likely corresponds to recombination by states directly connected to water oxidation. Under open circuit conditions, although the net exchange current is zero, charge transfer to oxidize H_2O still takes places, albeit in a transient fashion as a continued H_2O oxidation cannot be sustained. That is, the transferred

charges will be annihilated by processes akin to back electron transfer that has been observed in studies on dye-sensitized solar cells.^{46,47} As such, it is reasonable to understand the second rate constants as water oxidation kinetics. There are two pieces of evidence that support this understanding. First, the peak rate constant for aH is the highest, followed by that of sdH. The peak for rgH is still developing, and the corresponding rate constants are likely slower than 0.1 s^{-1} . The trend and the rate constants quasi-quantitatively agree with those presented in Fig. 6. Second, while the first group of peaks remains unchanged in the presence of H₂O₂, the second group disappeared completely, supporting that the second peaks are indeed connected to water oxidation (but not H₂O₂ oxidation). Taken as a whole, we understand the IMVS data as an additional proof that measurements under modulated lighting conditions can provide valuable surface kinetic information.



Figure 13. Surface decorations on hematite improves the overall PEC performance by reducing surface recombination. Compared with bare hematite (left), NiFeO_x does not change k_{tran} (right). Instead, it reduces the recombination rate constant (k_{rec}) greatly.

2.4 CONCLUSIONS

In conclusion, we measured the surface charge recombination and transfer rate constants in a quantitative fashion. As summarized in Fig. 13, our key results are that the regrowth procedures and surface decorations by NiFeO_x OER catalyst improve the PEC performance by reducing surface recombination. Charge transfer rate constants remained unchanged for all samples studied. It was understood that slower surface recombination rates help to increase surface hole concentrations, which is measured as greater surface photovoltages. Together, with a higher charge transfer efficiency, more holes with higher energies are transferred to the solution for water oxidation. As such, for all surface decorations studied here, a passivation effect prevails. We envision that while maintaining a slow surface recombination rate, faster charge transfer should indeed lead to even better PEC performance.

2.5 **REFERENCES**

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3.0 UNDERSTANDING THE PHOTOCHARGING EFFECTS OBSERVED ON BISMUTH VANDATE PHOTOANODES

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Bismuth vanadate (BiVO₄) is a promising material for photoelectrochemical water oxidation. Recently, it has been shown that "photocharging" BiVO₄ results in an improved water oxidation performance. However, the understanding of how BiVO₄ is being improved has been lacking. Here the surface kinetics of BiVO₄ were studied using IMPS and show that photocharging BiVO₄ results in both surface and bulk improvements. This result sheds light on how the surface charge transfer and bulk charge transport of BiVO₄ respond to illumination.

3.1 EXPERIMENTAL DETAILS

3.1.1 Synthesis of Bismuth Vanadate

BiVO₄ was synthesized electrochemically using a slightly modified version of a previously reported procedure.¹ Here, a solution of 0.04 M Bi(NO₃)₃ was prepared by

dissolving Bi(NO₃)₃·H₂O in 50 mL of 0.4 M KI adjusted to pH 1.7 by adding HNO₃. This was mixed with 0.23 M p-benzoquinone in 20 mL of absolute ethanol. The resulting solution was placed in a three-electrode cell with fluorine-doped tin oxide as the working electrode, Ag/AgCl (4 M KCl) as the reference electrode, and a platinum counter electrode. Cathodic deposition was performed at -0.1 V vs. Ag/AgCl at room temperature for 80-90 seconds corresponding to passing a total charge of 0.13 C/cm² and a uniform orange film of BiOI was obtained. Afterwards, the electrodes were washed with copious amounts of deionized water. Next, 0.2 M vanadyl acetylacetonate in dimethyl sulfoxide was drop casted onto the BiOI electrode. Approximately 0.10-0.15 mL/cm² of the DMSO solution was used. The electrodes were placed into a 1 M NaOH bath for 30 min with mild stirring to dissolve any excess V₂O₅. At this point, BiVO₄ remained and the films were bright yellow in color.



Figure 1. Photograph of BiVO₄. All samples were grown onto FTO and had the bright yellow color consistent with the band gap of BiVO₄.

3.1.2 Characterization of Uncharged and Photocharged Bismuth Vanadate



Figure 2. SEM images of uncharged (A, C, E) and photocharged (B, D, F) BiVO₄ samples. A and B have a scale bar of 100 nm. C and D have a scale bare of 1 micron. E and F have a zoomed out scale bar of 1 micron. No noticeable morphology difference is observed between the uncharged and charged samples.

SEI

10.0kV



Figure 3. Raman Spectra of BiVO₄. The peaks at 206, 328, 368,709 and 824 all correspond with previously reported BiVO₄ Raman shifts.² The strong peak at 824 cm⁻¹ represents the symmetric V-O stretch.



Figure 4. X-ray diffraction pattern of BiVO₄. The pattern closely matches the previously reported peaks for BiVO₄ using the same deposition method.¹ This diffraction pattern also closely matches previous photocharging studies.³⁻⁴

3.1.3 Representative IMPS Plots of Bismuth Vanadate



Figure 5. Representative IMPS measurements for samples tested before and after photocharging.

As in the previous chapter, during the IMPS measurements a 405 nm LED light is modulated from 10 kHz down to 0.1 Hz at a fixed potential. To determine the rate constants
three points are needed from the IMPS plots. First the low frequency (LF) and high frequency (HF) intercepts are determined. Then the frequency of light modulation at ω_{max} (see top panel of Figure 5) is determined and multiplied by 2π . With this information the transfer efficiency (TE) can be determined by dividing LF/HF. The transfer efficiency represents the ratio of the k_{tran} to the $k_{tran} + k_{rec}$ (as seen in the bottom panel of Figure 5) The TE is then multiplied by the ω_{max} which gives the k_{tran} . k_{tran} is then subtracted from the ω_{max} to give k_{rec} . This is performed at each applied potential to plot the changes in the rate constant versus the applied potential.

3.1.1 Electrochemical Characterization of Bismuth Vanadate

For electrochemical characterization, the BiVO₄ electrodes were studied in pH 7 0.5 M phosphate buffer with a Ag/AgCl (4 M KCl) reference electrode and a platinum wire counter electrode. A Solartron Modulab XM with a photoechem attachment was used for all current-voltage, IMPS, and Mott-Schottky measurements. For the photocharging process, the electrodes were placed in the pH 7 phosphate buffer under 1 sun illumination for 3 h. An AM 1.5 solar simulator (100 mW/cm², Solarlight Model 16S-300-M Air Mass Solar Simulator) was used as the light source for all photocharging procedures. For the IMPS measurements and current-voltage measurements, a 405 nm LED was used. The illumination was set to 90% corresponding to a power of 134 mW/cm² with a 10% modulation. All IMPS measurements were made from 10 kHz down to 0.1 Hz. All experiments were performed with backside illumination. For hole scavenger experiments, a 0.05 M solution of H₂O₂ was made by adding 30 wt% H₂O₂ to the phosphate buffer.

3.2 BACKGROUND OF BISMUTH VANADATE PHOTOCHARGING EFFECT

Metal oxides have been widely studied, owing to their relative stability and abundance.⁵ The high electronegativity of oxygen often creates a valence band position that can withstand the highly oxidative conditions needed for water oxidation. Among the studied materials, bismuth vanadate (BiVO₄) as a promising photoanode material has received significant attention.^{1,6-10} Thanks to the favorably positioned band edge positions and a reasonable band gap of 2.4 eV, BiVO₄ has become a model platform for studying the PEC water oxidation reactions. Indeed, significant progress has been made. For instance, record-high photocurrent densities have been measured on BiVO₄ through improved charge collection by forming nanostructures to minimize charge transport distance.^{1,8} Doping and elevating the temperature of BiVO₄ has been shown effective to improve its conductivity.¹¹⁻¹³ These treatments effectively address the issues connected to the small polaron formation.⁶ Similarly, a number of strategies have been developed using various overlayers to mediate surface kinetics including Co-Pi, NiOOH, and FeOOH.^{1, 14} These surface treatments resulted in a dramatic increase in the water oxidation performance by BiVO₄.

Of these approaches, the "photocharging" effect is particularly unique as it has only been reported on BiVO₄. It was first reported by Smith et al., where the authors observed a dramatic increase in performance by AM 1.5 illumination.³ Similar phenomenon was also reported by Berlinguette et al. using UV curing.⁴ In both cases the authors claim that the surface is being improved through the process of light. While their understandings are reasonable, quantitative information on the effect of the photocharging procedure is missing. The lack of information leaves an important gap in the understanding of the detailed role of the photocharging process, making it difficult to further improve the performance of this widely studied material when one tries to combine the various developments in terms of doping, nanostructuring, photocharging, surface catalyst applications and passivation. Here, we aim to fill in this knowledge gap by providing the missing information in a quantitative fashion. Using IMPS, we quantitatively demonstrate that photocharging improves charge separation, surface charge transfer, and reduces surface recombination.

3.3 **RESULTS AND DISCUSION**

3.3.1 Using IMPS to Understand the Photocharging Effect



Figure 6. (A) Current density-voltage curves of bismuth vanadate before and after photocharging. Photocharging was performed in the 0.5 M, pH 7.0 phosphate buffer with AM 1.5 illumination for 3 h. (B) Transfer Efficiencies extracted from IMPS.

Fig. 6A shows the effect of the photocharging treatment. After illumination under AM 1.5 1 sun conditions for 3 h, a clear increase in photocurrent was observed. The improvement (from 0.5 mA/cm² to 1 mA/cm² at 1.23 V vs. RHE) was highly reproducible across all samples tested for this work. To rule out possibilities that the effect could originate from doping or catalyst decorations, we investigated bare BiVO₄ electrodes in this study. The SEM, XRD, Raman, and photograph of BiVO₄ can be seen for the samples studied in this chapter in Figures 1-4, respectively. The morphology and crystal structure remained unchanged after photocharging (Fig. 2 -4). These results are consistent with previous reports by Smith et al. and Berlinguette et al., separately. At least two sources of improvements, namely the bulk and the surface, could be responsible for the effect, however. While previous evidence appears to support that surface effect is the main reason,^{3.4} no quantitative information is available to measure whether the effect is due to slower surface recombination or faster charge transfer or a combination of both. Our main research goal for this body of work is to provide the missing information quantitatively.

We measured the rate constants of surface recombination and charge transfer using IMPS. The theory behind IMPS as established by Peter et al, is well suited to study bismuth vanadate electrodes.¹⁵⁻¹⁶ Previously, IMPS has been primarily used to understand the surface passivation/treatment effects on the surface on hematite.¹⁷⁻²¹ This study presents one of the first studies published that uses IMPS to study BiVO4.²² In the case of BiVO4, it is reasonable to assume that the reaction is pseudo first order since the concentration of electrons will not be effected by the recombination process. It is also reasonable to assume that the bands will remain unchanged during the light modulation, as a small 10% light

modulation is used. Lastly, since the bulk recombination processes are taking place on a much faster time scale (ps - ns) than the measured IMPS rate constants (ms - s), it is fair to assume that there is negligible contribution from charges coming from bulk of BiVO₄.

In Fig. 6B, we plot how the transfer efficiency (the fraction of charges at the surface being used for water oxidation) depends on applied potentials. In general, transfer efficiencies of both $BiVO_4$ samples increased with increasing applied potentials, consistent with studies performed on other n-type semiconductors. This intuitively makes sense since the transfer efficiency should closely track the measured photocurrent. The second feature in this group of data worth noting is the increase in transfer efficiency due to photocharging. It confirms previous hypotheses that photocharging is primarily a surface-related effect. However, the increase in transfer efficiency (e.g., 38% at V=1.2 vs. RHE) does not fully



Figure 7. The black and red traces use the photocurrent values from Figure 6 at each of the 4 potentials from the typical untreated and photocharged sample, respectively. The blue trace shows the untreated photocurrent that has been corrected using the transfer efficiency increase seen in Figure 6B.

account for the increase in PEC performance (91% at V=1.2 vs. RHE). We attributed this mismatch to an important nature of IMPS because the technique only reports on processes occurring on the surface. As such, we concluded that the improvement of the bulk properties also contributes to the PEC performance increase.

This improvement can be seen in Figure 7, where the blue squares would represent the improved photocurrent densities due to surface effects. Specifically, the blue trace is achieved from multiplying the original photocurrent by the ratio of transfer efficiencies after and before photocharging. If the photocharging effect were entirely due to changes on the surface, the photocurrent densities would match those of the measured data (red



Figure 8. Rate constants for (A) charge transfer (k_{tran}) and (B) recombination (k_{rec})

trace). That the blue trace is lower than the red trace as shown in Fig. 7 indicates that there are changes in the bulk of $BiVO_4$ during the photocharging. This change will be further explored later in this chapter. It is important to note here that the improvement of the TE after photocharging confirms either the rate constant of charge transfer or the rate constant of recombination at the surface or both is indeed affected during the photocharging process.

Next, we analyzed the rate constants for surface recombination, k_{rec} , and surface charge transfer, k_{tran} , and present the results in Fig. 8. By comparing the data for samples before and after photocharging we intend to determine whether photocharging reduces the k_{rec} or increases k_{tran} . Two important trends are seen from this set of data. First, photocharging generally suppresses surface recombination as indicated by the smaller k_{rec} (Fig. 8B). This effect is expected and consistent with previous analysis by other authors.^{3,4,23}



Figure 9. Study of the bulk properties of $BiVO_4$ by photoelectrochemistry and electrochemistry. (A) Photocurrent density-voltage relationship with and without H_2O_2 as hole scavenger. (B) Mott-Schottky plots of $BiVO_4$ before and after photocharging.

In the meanwhile, photocharging also improves surface charge transfer as supported by the greater k_{tran} (Fig. 8A). Such an effect is unexpected. It supports that the photocharging effect should not be simply attributed to a single cause, but rather a complex interplay of improved charge transfer and reduced surface recombination, both of which favor higher charge transfer efficiencies. Second, the degree of improvements in k_{rec} and k_{tran} depends on the applied potentials. The general trend is that at higher applied potentials, the

suppression of surface recombination is more prominent than improvement in charge transfer. Further research is needed to fully understand this voltage dependence.

3.3.2 Measuring Bulk Improvements from Photocharging

To investigate the charge separation characteristics in the bulk, PEC measurements were performed with and without H_2O_2 as a hole scavenger. It has previously been shown that H_2O_2 oxidation by BiVO₄ has a near-unity catalytic efficiency.⁹ Thus any photocurrent enhancement in the presence of H_2O_2 can be attributed to increases in charge separation. We observed here, as shown in Fig. 9, that the photocurrent of BiVO₄ increased after photocharging and with addition of H_2O_2 . The results strongly support the conjecture that



Figure 10. Photocharging improves k_{tran} and charge separation, but reduces k_{rec} . The result is a significant increase in PEC performance.

the charge separation in the bulk is indeed improved by photocharging. We next used the Mott-Schottky technique to quantify donor densities before and after photocharging. Under the same experimental conditions, photocharging yielded a donor density increase of \sim 2.1 times (Fig. 9B). These results suggest that better charge transport within BiVO₄ is

enabled by photocharging due to increased carrier concentration. The understanding supports previous predictions that V^{5+} is reduced to V^{4+} through photocharging,³ thereby increasing the concentration of mobile electrons as the majority charge carrier. We also note that the onset potential of the photocharged and uncharged samples with H_2O_2 remain nearly unchanged, as seen in Figure 9A. This result is somewhat surprising due to the change in the flatband potential seen in Figure 9B. It is expected that surface trap states are leading to a nonideal space charge region at the semiconductor liquid interface, which can account for the difference in the flatband potential and the observed onset potential.²⁴ Together these data show that photocharging BiVO₄ photoelectrodes results in a threefold effect: the surface recombination is reduced, the charge transfer is increased, and the donor density is increased all by simply exposing BiVO₄ to irradiation for an extended period of time. The various effects can be quasi-quantitatively characterized as following, using data obtained at 1.2 V vs. RHE (Fig. 6). Of the 91% increase of the photocurrent density, 45% is due to improved charge transfer efficiency (surface effect, as measured by IMPS) and 46% is due to better charge behaviors (bulk effect, as measured by the addition of H_2O_2).

3.4 CONCLUSIONS

In summary, we have measured charge transfer and recombination constants to understand quantitatively the effect of "photocharging" enhancement. As shown in Fig. 10, PEC performance of photocharged BiVO₄ is the sum of a synergistic effects of charge transfer, surface recombination, and charge separation. This serves as one of the first quantitative measurements of the surface kinetics of BiVO₄ and offers further understanding of the surface of BiVO₄ that will help guide future studies of BiVO₄ and other photoanodes used for water oxidation.

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4.0 UNDERSTANDING THE ROLE OF CO-CATALYSTS ON SILICON PHOTOCATHODES

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The addition of a co-catalyst onto the surface of a photocathode often greatly enhances the harvested photovoltage of the system. However, the true nature of how the catalyst improves the onset potential remains poorly understood. As a result, how to best utilize effective co-catalysts is still a limiting factor in achieving high performance earth abundant photoelectrochemical hydrogen evolution. Using IMPS, the charge behaviors at the photoelectrode co-catalyst interface were probed. It was found that Pt drastically reduces charge recombination at the semiconductor liquid interface (SCLI). Further studies reveal that the onset potentials can be improved either by accelerating the reaction kinetics or reducing the recombination at the SCLI. The knowledge permits us to understand how earth abundant HER catalysts, such as CoP, behave at the SCLI. It is found that CoP is more effective at accelerating the reaction kinetics than reducing recombination.

4.1 EXPERIMENTAL DETAILS

4.1.1 Preparation of Si-GaN Photocathodes

The preparation of the p-n - Si homojunction, and the growth of the n-GaN nanowires onto the Si, follows a previously reported procedure.¹ Furthermore, the platinum deposition onto the GaN followed previous reports.¹ For the addition of Ag, a AJA International Orion 8 sputtering system with a Ag target was used for the deposition of ca. 2 nm of Ag. A modified electrochemical deposition was used for the deposition of CoP.² Here a solution of 0.15 M H₃BO₃, 0.1 M NaCl, 0.33 M Na₂H₂PO₂, and 0.2 M CoCl₂ was employed. Electrodes were biased at -1.2 V vs. reference for 10 s under 1 sun illumination. A Solartron XM potentiostat was used for all electrochemical and photoelectrochemical experiments. A solar simulator (Solar Light 300M) with a AM 1.5 filter was used for all 1 sun condition experiments.



Figure 1. SEM image of the photocathode used for this study. The dark park on the bottom of the image shows the Si substrate. The white pillars show the n-GaN nanowires that were grown on top of silicon.

4.1.2 Details of IMPS Measurements

For the IMPS experiments, a 405 nm LED (ThorLabs) was used at a power of 26 mW/cm². A 10% light modulation was used for all experiments, and the frequency of the modulation was swept from 10 kHz down to 0.1 Hz. A 30 s relaxation time was used between each potential step. A 0.1 M phosphate buffer (pH 6.97) was used for all JV and IMPS experiments. The error bars for all IMPS data is determined by taking the standard deviation of the rate constants measured from at least three different electrodes in the same electrolyte and lighting conditions.

As expected, the bare electrode is dominated by recombination as nearly no photocurrent is observed at all applied potentials. When the electron scavenger is added to the bare electrode the radial frequency is not changed. However, the low frequency intercept is greatly increased at higher applied potentials as compared with the bare electrode. This indicates that the k_{tran} is being increased while the k_{rec} remains unchanged. The addition of Pt to the surface of the photocathodes greatly reduces the recombination rate constant Figure 2. Additionally, as the charge transfer increases so does the low frequency intercept. With CoP on the surface of the GaN NWs the recombination does not change at low allied potentials, but at high applied potentials the recombination rate constant drastically decreases and the charge transfer begins to increase, as seen by the increase in the low frequency intercept. The addition of Ag to the photocathodes looks much like the bare electrode. However, the Bode plot (Figure 3) shows that the resonant frequency is much lower. Since the low frequency intercept is essentially zero for the bare and electrode with Ag, the resonant frequency can be associated with the recombination rate constant.



Figure 2. Representative raw IMPS data of each of the systems tested for this study. **A**) a bare photocathode **B**) a photocathoe with a $Na_2S_2O_4$ electron scavenger **C**) a photocathode with platinum **D**) a photocathode with silver **E**) a photocathode with CoP



Figure 3. Representative Bode plots as measured by IMPS at 0.65 V vs RHE. In A and C it can be seen that the addition of Pt or Ag, respectively, decreased the rate constant for surface recombination. However, in **B** and **D**, the use of an electron scavenger or the addition of CoP do not change the surface recombination rate constant, yet they still shift the onset potential for HER to more anodic values.

4.1.3 Electrochemical Characterization

A SCE reference electrode was used for all measurements, and a Pt wire was employed as the counter electrode. The Nernst equation was used to adjust the potential scale from SCE to RHE based on the pH of the solution. During the experiments that required Na₂S₂O₈, 100 mM of Na₂S₂O₈ was added to the pH 7 solution. During all tests, the solutions were stirred and purged with N_2 to remove O_2 from the solution, eliminating the possibility of oxygen reduction, which would otherwise complicate the data analysis.

4.1.4 Faradaic Efficiency Measurements

 H_2 detection was carried out in a sealed three-neck flask under 0 V vs. RHE applied potential with different working electrodes. Three electrode configuration was employed similar to the PEC tests. UHP-grade He was used to purge the cell for at least 60 min in order to remove residual gases in the electrolyte before the measurement. A gas sample of 100 µL, from the head space of the flask, was injected manually to GC-MS (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column at 35°C) every 20 min. UHP-grade H₂ was used to calibrate the instrument.



Figure 4. Faradaic efficiency plots of the photocathodes modified with CoP and Ag.

The electrode with Ag did not show 100% Faradaic efficiency. However, since it is known that Ag will capacitively accept charges, the differences between the detected product and

the charge passed could come from the charging of the Ag nanoparticles. Regardless of the product, Ag forms a Schottky junction with n-GaN and will reduce recombination and shift the onset potential.

4.2 BACKGROUND OF PHOTOCATHODE-CATALYST INTERFACE

Solar fuel production is a promising route toward large scale renewable energy implementation.³ Similar to natural photosynthesis, the artificial process oxidizes water to harvest electrons from H_2O . These electrons can then be utilized to reduce H^+ , CO_2 , or N_2 into a storable fuel.⁴⁻⁶ Photoelectrochemical (PEC) water splitting (the generation of molecular oxygen and molecular hydrogen from water) has been widely studied as a practical way to produce solar fuels.⁷⁻⁹ PEC utilizes a SCLI where the chemistry takes place on the surface of the semiconductor. However, to achieve high performance, light absorption, charge separation, and surface charge transfer all need to operate efficiently, which has proven exceedingly difficult.¹⁰ In order to understand the limiting factors in the PEC system, it is necessary to characterize each of these processes in detail. Recently, there have indeed been efforts toward this direction by studying H₂O photooxidation by methods such as IMPS, photoelectrochemical impedance spectroscopy (PEIS) and timeresolved transient absorption spectroscopy (TAS).¹¹⁻¹⁶ Useful information on the detailed processes has been reported, which is expected to play positive roles toward further understanding and optimization of these processes. The relatively simpler hydrogen evolution reaction (HER) under PEC conditions has often been studied.¹⁷⁻¹⁹ However, the detailed quantitative information on the various processes remains unknown. This lack of

information has become an important limiting factor that prevents further optimization of the system for efficient and stable solar hydrogen generation. To correct this deficiency, here we report a systematic study on a photocathode. Our primary goal is to elucidate the detailed roles of co-catalysts in the PEC configuration. More specifically, we aim to enable high-performance solar hydrogen generation using earth abundant catalysts. For this purpose, we show that quantitative measurements of the surface processes reveal that the suppression of surface recombination is as critical as the improvement in charge transport. The broad context of this present study concerns the nature of the SCLI with co-catalyst modifications, particularly the earth abundant co-catalysts for HER. While the performance of these materials, such as CoPS,²⁰ is approaching the performance of Pt, their performance when incorporated as co-catalysts on a photocathode surface remains lower than Pt by a considerable margin.²¹⁻²³ Most importantly, detailed understandings of their effects on the SCLI remains limited, whereas parallel studies of the cocatalysts/photoanode SCLI have revealed that such understandings are of critical importance.^{11, 15, 25-26} The present study was carried out to fill in this knowledge gap. We found that Pt improves the performance of a Si/GaN nanowire photocathode by not only increasing charge transfer, but also reducing the rate of charge recombination. Similar effects on charge recombination can be obtained by replacing Pt with Ag, and those on charge transfer is measured by using CoP to replace Pt.

The photocathode material chosen for this study was a high-performance system that has been recently developed by Mi et al., which features a buried Si homojunction with a coating of n-GaN nanowires (NWs), as seen in Figure 5.^{1, 27, 28} The key novelty of this photocathode lies in the n-GaN NWs that are grown atop of the Si absorber. Advantages

offered by the GaN NWs include better stability of the underlying Si in aqueous media, greater surface area for enhanced charge transfer, and reduced reflectivity of the incident light. As the best recognized HER catalyst, Pt has been shown effective in shifting the onset potentials of photocathodes to more anodic values, improving the photovoltage and overall performance of the systems.^{22, 29, 30}



Figure 5. A) Schematic view of the photocathode explored in this study and the experimental configuration used. This photocathode uses a buried p-n junction in Si with n-GaN nanowires grown on top of the Si. Here, a platinum wire is used at the anode, as we focus our studies on understanding the onset potential for HER. B) A band diagram of the p-n-Si/n-GaN photocathode. k_{rec} represents electron hole recombination rate constant taking place at interfacial trap states. k_{tran1} , k_{tran2} , and k_{tran3} , all represent possible charge transfer rate constants within this photocathode.

It has been commonly assumed that Pt provides these functionalities by facilitating HER charge transfer because it features one of the lowest overpotentials for HER (directly connected to the activation energy, G^{\ddagger}). However, the same effect of improved PEC HER performance could also be explained by improved band bending and reduced charge recombination that are not necessarily due to better catalytic properties of Pt.^{31, 32} Such a case has been observed on a large number of photoanode systems involving the applications of OER catalysts such as NiFeO_x, IrO_x, and CoPi.^{11,15, 33, 34} As a matter of fact, only a handful of OER catalysts studied to date improve the overall performance of the system by offering better charge transfer kinetics, including a heterogenized Ir molecular catalyst (het-WOC) and the Co₃O₄ grown by atomic layer deposition (ALD).^{15, 35} It is therefore imperative to understand to what extent Pt addition changes the surface charge recombination. To the best of our knowledge, similar studies have not been performed in detail on the Pt-photocathode interface.

Here IMPS was again employed to correct this important deficiency by probing the kinetic information on the various surface processes, primarily the charge separation under PEC HER conditions. This is one of the first IMPS studies performed on a photocathode under HER conditions.³⁶ The quantitative kinetic information was critical to the insights that led us to propose to replace Pt with Ag or CoP, which are far less costly than Pt but exhibit similar effects. The study presented here further demonstrates how the detailed understanding of the surface processes can help accelerate research on developing high-efficiency, low-cost photoelectrode systems for practical solar fuel synthesis.

4.3 **RESULTS AND DISCUSSION**

4.3.1 Using IMPS for Photocathode Studies

IMPS was employed to probe the detailed kinetic information on the surface charge behaviors. The theoretical basis for IMPS and experimental treatments of the data have been reported previously and are suitably for this present photocathode platform.³⁷⁻³⁹ Briefly, the technique assumes that the surface charge concentration (electrons for a photocathode system) tracks the changes in light intensity. How the reaction rates change due to the change of light intensities (and hence the carrier concentrations) can then be used to extract quantitative information such as the rate constants of charge transfer (k_{tran}) and recombination (k_{rec}) . For the photocathode examined here, the depletion region of the p-n homojunction is calculated to be ca. 400 nm, significantly longer than the optical penetration depth of Si at λ =405 nm (ca. 100 nm), meaning that bulk recombination is expected to be minimum. This understanding further supports the suitability of using IMPS for the present study. A representative IMPS Nyquist plot of the photocathodes is shown in Fig. 6, from which the k_{tran} and k_{rec} were obtained. The semicircle in the negative imaginary quadrant is expected for a photocathode system near the onset potential, where recombination is competing with the forward charge transfer. The high frequency intercept is at a more negative photocurrent than the low frequency intercept because at high frequencies the rate at which the light intensities vary are expected to surpass the surface recombination rate, effectively suppressing charge recombination.



Figure 6. A representative IMPS Nyquist plot showing the imaginary (Im) photocurrent versus the real photocurrent at a fixed potential. 10% of the light is modulated from 10 kHz down to 0.1 Hz. The semicircle in the lower quadrant forms due to the recombination across the Si homojunction. From these data, the charge transfer rate constant (k_{tran}) and the charge recombination rate constant (k_{rec}) can be determined.

It is important to note that the system studied here does present a challenge to the IMPS technique because it is based on a mathematical model for a simple SCLI featuring a single junction, in which case the k_{tran} and k_{rec} correspond to well-defined surface processes. As shown in Fig. 5B, the system studied here features three interfaces, namely Si/GaN, GaN/co-catalyst and co-catalyst/H₂O. Because the characteristic lifetimes of charge behaviors at the Si/GaN interface are typically on the order of microseconds or faster, whereas the charge processes studied by IMPS are in the millisecond range, we consider the kinetics obtained here are not connected to the Si/GaN interface but mostly report on the nature of the GaN/catalyst/H₂O interface. Further distinguishing whether the information reports on the GaN/catalyst or catalyst/H₂O interface is beyond the scope of this present study. Nevertheless, it is worth noting that the true value generated by IMPS analysis lies in the insights into what the influences may be when modifications are made

to the photoelectrode surfaces, charge transfer or charge recombination or both, as has been shown by previous efforts focused on photoanodes with and without co-catalysts.^{11,15} Similar insights for a photocathode system are missing in the literature and are the primary target of this study.

4.3.2 Comparing Photocathodes with and without Platinum

It can be seen in Fig 7A, that the addition of a catalyst, such as Pt, greatly enhances the turn-on potential for HER. This is consistent with previous studies that have explored the addition of Pt to a photocathode's surface.^{22, 30} As seen in Fig. 7B (black squares), the photocathodes without co-catalysts feature fast recombination. Such an observation is expected because low HER catalytic activities have been reported on GaN.⁴⁰ While photogenerated electrons may transfer from Si to GaN fast, a significant portion of the charges will recombine, most likely within GaN near the H₂O interface. The increased surface area by GaN may be another important reason for the fast recombination rates.

Irrespective, the fast recombination reduces the steady-state electron concentration at the surface and, hence, the photovoltage. Combined with the fact that a high overpotential is necessary to drive the HER reaction, fast recombination and slow charge transfer contribute to the low onset potentials (-0.16 V vs. RHE; see Fig. 7A). The addition of Pt to the GaN NWs greatly improves the performance of the photocathode. When compared to the bare electrode (black line Fig. 7A), the one with Pt enabled a large shift in the onset potential (from -0.16 V to 0.56 V; the onset potential is defined by the potential where 100 μ A/cm² is observed). Well recognized as an effective HER catalyst, Pt is expected to enable fast HER kinetics. One could conclude with confidence that improved charge transfer kinetics should be a reason for the observed performance enhancement. What was not known, however, is whether the introduction of Pt also changed the recombination rates.



Figure 7. A) A photocurrent versus potential measurement (J-V curve). The black line represents the bare n-p - Si/n-GaN photocathode. The gold line shows the photocathode with platinum on the surface of the GaN. **B)** The measured recombination rate constant (k_{rec}) versus applied potential using IMPS, with Pt (gold down triangles) and without Pt (black squares).

The IMPS data as shown in Fig. 7B strongly suggested so, where we observed a significant reduction in k_{rec} (by more than >10 times). The observation is understood as following. Upon generation, the photogenerated charges are separated by the built-in field within the Si homojunction. n-type GaN facilitates the charge separation but is not the main driving force. The photogenerated electrons quickly diffuse to GaN where they may be either annihilated by recombination or transferred to the solution for H⁺ reduction. The presence of Pt serves as a trap to facilitate charge separation by preventing electrons from diffusing back to Si. In addition, Pt also serves as a catalyst to facilitate charge transfer for HER. While similar functionalities of metal co-catalysts have been reported in studies from Kamat et al., their studies focused on the TAS of nanoparticles,⁴¹⁻⁴³ whereas quantitative information on the effect in a PEC configuration was previously missing. Our data reported here are therefore new.

4.3.3 Separating Improved Recombination from Improved Charge Transfer

The quantitative measurement of the surface kinetic processes raised several important questions. First, is fast forward charge transfer alone sufficient to improve the overall performance? Second, is reduced charge recombination itself alone sufficient for the same purpose of improving the PEC performance? Third, can we find systems with similar overall effects as Pt based on earth-abundant materials? Our following efforts were guided by these questions. We first carried out experiments to test whether fast charge transfer alone is sufficient to improve the overall PEC performance.



Figure 8. A) J-V curves of a bare photocathode with and without 100 mM of the electron scavenger Na₂S₂O₈. B) The measured k_{rec} with (purple circles) and without the electron scavenger (black squares) does not change.

For this purpose, we chose to study the system in the presence of the electron scavenger, sodium persulfate $(Na_2S_2O_8)$.⁴⁴⁻⁴⁵ As seen in Fig. 8A, the addition of 100 mM of $Na_2S_2O_8$ greatly enhanced not only the photocurrent densities, but also the onset potential (purple line), bringing the overall performance comparable to that with Pt in the absence of $Na_2S_2O_8$. Different from the sample with Pt, however, the krec as measured by IMPS

remained nearly identical with (purple circles) and without (black squares) the sodium persulfate (Fig. 8B). The data clearly demonstrated that fast charge transfer alone is indeed sufficient for significant improvement of the overall performance. Quantitatively, this understanding makes sense because what matters in a PEC system is the charge transfer efficiency as defined by $TE = k_{tran}/(k_{tran}+k_{rec})$. So long as $k_{tran} \gg k_{rec}$ (e.g., by >10 times), high TE is expected.

4.3.4 Comparing Photocathodes with and without Silver

The above experiments clearly demonstrate the importance of improving surface charge transfer. Next, we designed experiments to study a system where only surface recombination was suppressed. For this purpose, we sputtered Ag nanoparticles (NPs) on the surface of the photocathode. With a work function of ca. 4.5 eV, Ag is expected to form a Schottky barrier with n-GaN and trap electrons on the GaN NWs (Figure 10) but is not expected to exhibit significant HER activity since it binds protons too weakly for efficient HER.^{28, 46} It has previously been shown that Ag can act as an electron acceptor from TiO₂, which has a similar conduction band edge with GaN.⁴² Indeed, as shown in Fig. 9A, the presence of Ag NPs was found to shift the onset potential by ca. 230 mV toward the anodic direction. This shift is significant given that Ag is a poor HER catalyst. It highlights that the shift must be due to higher photovoltages. As expected, the measured krec was reduced by an order of magnitude, similar to when Pt was added to the photocathode (Fig. 9B).



Figure 9. A) J-V curves of a bare photocathode and one with sputtered Ag on the surface of the GaN. B) The measured k_{rec} shows that the addition of Ag results in nearly a 10 times reduction in recombination.

Nevertheless, it is noted that the onset potential of the electrodes with Ag NPs remained lower than that with Pt NPs. This is because Pt improves the performance of the bare photocathode by enhancing not only the photovoltage (with reduced recombination) but also by improving the charge transfer (as a good HER catalyst).



Figure 10. Schematic band diagram of the Schottky junction that forms with the addition of Ag to the surface of n-GaN nanowires. The Schottky barrier will act as an electron trap for electron that transfer to Ag. This explains the large decrease in the recombination rate constant with the addition of Ag. Pt will also form a Schottky junction with n-GaN and since its work function is well above 5 eV the barrier will be much larger. This is also consistent with the recombination rate constants that we measured in this study, where recombination was typically lower with Pt rather than Ag.

This understanding has significant implications to the design of future photocathodes. For the purpose of reducing surface charge recombination, a low-cost material, such as Ag, can be as effective as a rare and expensive metal, such as Pt. Naturally, we were motivated to study whether the catalytic activity of Pt could be replaced by another earth-abundant material. This is the focus of the next section.

4.3.5 Photocathodes with and without Cobalt Phosphide

For this set of experiments, we studied CoP, which has been reported as a promising HER catalyst over a wide pH range.^{2,4,47} Using a previously reported simple photoelectrochemical deposition method, we deposited the CoP catalysts onto the surface of our photocathode.² It was found that, for the same electrode, the onset potential shifted by ca. 550 mV, Fig.11A. When the k_{rec} was measured, it was seen that the addition of CoP left the k_{rec} nearly unchanged at low applied potentials.



Figure 11. A) The J-V curves showing the addition of the HER catalyst CoP to the surface of the GaN. **B)** The k_{rec} shows that the addition of CoP (red hexagons) requires a minimum applied potential before CoP reduces the recombination rate constant.

It was not until a sufficiently large potential was applied that the k_{rec} was reduced. This large decrease in the k_{rec} is close to the measured onset potential for CoP, which we attribute to the charging of the CoP catalyst. While CoP improved the PEC performance by a large margin, it functions through fundamentally different mechanisms from Pt. As shown in Fig. 12, the inability of CoP to accept charges at low applied potentials now becomes a key factor in determining the onset potential for this system. At low applied potentials recombination will consume the majority of the charges, thus limiting the photovoltage that can build up. This stark difference with Pt highlights the importance of investigating the catalyst-semiconductor interface using impedance techniques, such as IMPS, in order to understand how to optimize the onset potential.



Figure 7. At low applied potentials the earth abundant catalyst CoP does not accept charges from the photocathode. Whereas high work function metals will accept charges due to the Schottky junction formed. This difference accounts for the lower onset potentials of the CoP co-catalyst.

Indeed, it was attempted to combine Ag and CoP to utilize their unique roles on the surface of the photocathode in order to maximize the onset potential for these photocathodes. However, while the onset potential did increase when CoP was added onto the Ag, the onset potential never exceeded the value that was observed with only CoP. The

recombination data, seen in Fig. 8B, show that the recombination is controlled by the Ag on the surface of the photocathode. This could support the fact that two charge transfer pathways are taking place. Charges moving to the Ag are trapped within the Ag and reduce the overall recombination rate constant. While the onset potential is controlled by the CoP,



Figure 8. A) JV curve of and electrode with Ag and the same electrode with CoP deposited on top. B) The recombination rate constant of the electrode with Ag before and after the CoP deposition.

where charges flow directly to the CoP and not first via the Ag nanoparticles. Further evidence for this hypothesis would be needed in order to confirm what is taking place when Ag and CoP are combined on these photocathodes. However, this further supports IMPS role in delineating how surface treatments affect the onset potential of photocathodes and further enables the combination of earth abundant materials to match the performance of costly Pt.

4.4 CONCLUSIONS

In conclusion, we have studied the catalyst-photocathode interface for the HER. Using IMPS, we have probed charge recombination at this interface and found that an interplay of faster kinetics and reduced recombination can contribute to improved onset potentials. This knowledge helps to reveal the unique and complex interaction that arises with each unique catalyst-semiconductor interface. Using impedance techniques, such as IMPS, can reveal this complexity and enables future research to characterize and optimize this interface in order to achieve high performance PEC, whether that is for HER, OER, CO_2 reduction, or N_2 fixation.

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5.0 WHAT LIMITS THE PERFORMANCE OF TA₃N₅ FOR SOLAR WATER SPLITTING?

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Tantalum nitride (Ta_3N_5) is a promising photoelectrode for solar water splitting. Although near theoretical limit photocurrent has already been reported on Ta_3N_5 , its low photovoltage and poor stability remain critical challenges. In this study, we used Ta_3N_5 nanotubes as a platform to understand the origins of these issues. Through a combination of photoelectrochemical and high-resolution electron microscope measurements, we found the self-limiting surface oxidation of Ta_3N_5 results in a thin amorphous layer (ca. 3 nm), which proves to be effective in pinning the surface Fermi levels and thus fully suppresses the photoactivity of Ta_3N_5 . XAS and XPS characterization confirmed the surface composition change resulting from the oxidation and also revealed a Fermi level shift toward the positive direction by up to 0.5 V.

5.1 EXPERIMENTAL DETAILS

5.1.1 Preparation of Ta₃N₅ Nanotubes Photoelectrodes

The Ta_3N_5 nanotubes were synthesized through the anodization of Ta foil to form tantalum oxide nanotubes followed by a post annealing in NH₃ to form tantalum nitride based on a modified procedure reported previously.¹ For the anodization procedure, tantalum foil (0.127 mm thick, Alfa Aesar) was firstly cut into 1 cm x 4 cm pieces. Then one side of the Ta foil was roughened using sandpaper for about 10 min. After the roughening, the Ta foil was cleaned by ultrasonication in acetone, methanol, isopropanol as well as deionized (DI) water and dried by flowing air. The electrolyte for anodization was made by mixing 38 mL sulfuric acid (95-98%, Sigma-Aldrich), 0.4 mL hydrofluoric acid (48%, Sigma-Aldrich) and 1.6 mL DI water with vigorous stirring during preparation. The Ta foil was anodized with a Pt gauze as the counter electrode at 60 V DC bias for 10 min without stirring. After thoroughly washing with ethanol and DI water, the as-prepared tantalum oxide nanotubes were naturally dried in air. The conversion of oxide to nitride was performed in a quartz tube furnace (Lindberg/Blue M). The temperature was raised from room temperature to 1000 °C at the rate of 10 °C/min and held at 1000 °C for 2 hours. After that, the furnace was naturally cooled down to room temperature. During the whole process, 75 sccm anhydrous NH₃ flowed through the quartz tube and the pressure in the tube remained as 300 torr. The Ta₃N₅ sample was scratched on the edge to expose the underneath conductive Ta. Tinned Cu wire was secured to the exposed Ta substrate by Ag epoxy (M.G. Chemicals Ltd.). Non-conductive hysol epoxy (Loctite 615) was used to seal the sample except for the exposed area for testing. Typical electrodes were ~ 0.05 cm² in area. NiFeOOH and CoFeOOH catalyst was deposited using a cathodic electrodeposition. For NiFeOOH deposition, a 0.09 M solution of nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6 H₂O, 98%, Alfa Aesar) was purged with N₂ for 20 min. Then 0.01 M of iron(II) chloride (FeCl₂, 98%, Sigma-Aldrich) was added. The deposition was carried out galvanostatically at -0.1 mA/cm² for 10 min while stirring. The electrodes were then washed thoroughly with DI water. For the CoFeOOH deposition, a 0.06 M of Co(NO₃)₂·6 H₂O and 0.04 M FeCl₂ solution was used and the deposition rate of -4 mA/cm² was used for 1 minute.

5.1.2 PEC Measurement

PEC measurements were carried out using a potentiostat (Modulab® XM, coupled with the Modulab® XM ECS soft-ware) in a three-electrode configuration. The light source was an AM 1.5 solar simulator (100 mW/cm², Solarlight Model 16S-300-M Air Mass Solar Simulator). There were three kinds of testing electrolyte, including 1M NaOH (pH 13.6), 1M NaOH with 0.1M H₂O₂ (pH 13.6), 0.1M phosphate solution (mixing of 0.1M K₂HPO₄ and 0.1M K₃PO₄) with 0.1M K₄Fe(CN)₆ and 0.1mM K₃Fe(CN)₆ (pH 10). The Ta₃N₅ photoanode served as the working electrode, with an Ag/AgCl electrode (for pH 10 testing electrolyte) or an Hg/HgO electrode (for pH 13.6 testing electrolyte) as the reference electrode, and a Pt wire as the counter electrode. The potential was corrected to RHE scale according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197$ or $E_{RHE} = E_{Hg/HgO} +$ 0.059pH + 0.098). In a typical linear sweep voltammetry (LSV) measurement, the potential was swept from negative to positive at a rate of 20 mV/s with stirring.

5.1.3 Material Characterization

Regular XPS measurements were performed using a PHI 5400 XPS system equipped with an Al X-ray source (incident photon energy 1486.7 eV). The aperture size was set to 1.1 mm in diameter. The binding energy of the obtained XPS spectra was calibrated with respect to the C1s peak of adventitious carbon at 284.4 eV. X-ray absorption spectroscopy (XAS) measurements were carried out at the wet-RIXS endstation at Beamline 8.0.1 and the ISAAC endstation at Beamline 6.3.1.2, both at the Advanced Light Source, Lawrence Berkeley National Laboratory. Fluorescence signals were collected using a Channeltron device, whereas total electron yield was measured as the drain current from the sample to the ground upon illumination, using a current amplifier. The energy scales of O 1s and N 1s XAS spectra were calibrated using a TiO₂ and a BN standard sample, respectively. All the XAS spectra were normalized by setting the pre-edge intensity to zero and the intensities well above the edge to unity, preceded by subtracting a linear background based on the slope of the pre-edge regions.

The fresh and tested Ta_3N_5 samples were imaged by the transmission electron microscope (TEM, JEOL 2010F) operated at an accelerating voltage of 200 kV. The nanotube samples were first scratched from Ta foils and dispersed in IPA by ultrasonication. Then the dispersion was dropcasted onto Cu grid for TEM measurement.

5.2 BACKGROUND OF TANTALUM NITRIDE FOR WATER OXIDATION

Ta₃N₅ features a direct bandgap of 2.1 eV and promises high photocurrent densities, which has been recently realized experimentally by Li et al.²⁻³ A record photocurrent current density of 12.1 mA/cm² at 1.23 V vs. RHE was reported.³ This impressive progress notwithstanding, Ta_3N_5 still faces two critical issues, namely low photovoltage and poor stability. The low photovoltage is manifested as the late turn-on potentials (Von; the lowest potential at which non-zero photocurrent is measured), typically >0.6 V.²⁻⁸ Given that the conduction band minimum (CBM) of Ta₃N₅ has been predicted by density functional theory (DFT) calculations to be more negative than water reduction potential, the reported Von's are unreasonably high.⁹⁻¹⁰ Significant efforts have been attracted to address the issue. For instance, Domen et al. recently improved the Von to 0.55 V through a combination of doping and surface treatment.¹¹ Nevertheless, the true reasons behind the poor performance in terms of photovoltages remain poorly understood. Similarly, little is known about the degradation mechanism. For instance, without passivation, the photocurrent of Ta₃N₅ would decrease >50% within the first few minutes of water splitting reactions.^{3,12} It has not been discussed previously in detail how the degradation is related to the photooxidation of Ta₃N₅.^{3, 12-14} Here we show that these two critical issues are intimately connected. Most strikingly, through systematic photoelectrochemical (PEC) and X-ray spectroscopic studies, we discovered that photooxidation of Ta₃N₅ is selflimiting and not the direct origin of the performance degradation. Instead, surface Fermi level pinning due to the thin oxidation formation plays a key role in defining the photovoltage and stability. A quantitative correlation between the extent of surface oxidation and the degree of Fermi level pinning was established.

5.3 **RESULTS AND DISCUSION**

5.3.1 Instability of Ta₃N₅

The PEC water oxidation performance of Ta_3N_5 was shown in the Figure 1A. With the help of electrodeposited nickel-iron (oxy) hydroxide (NiFeOOH) catalyst, the photocurrent density of Ta_3N_5 at 1.23 V can be increased from 0.8 to 6.3 mA/cm², showing the improvement of almost 8 times. In addition, the photocurrent onset cathodically shifted for almost 400 mV with the catalyst decoration. However, the onset potential of 0.65 V in our study was still unsatisfactory considering the negative flat-band potential of Ta_3N_5 and this phenomenon can be associated with the poor stability of Ta_3N_5 . In order to explore the true reason behind it, a detailed study about the degradation process of Ta_3N_5 during PEC water oxidation was conducted here.

Previous studies have shown poor stability of Ta_3N_5 during PEC water oxidation process was contributed to the self-oxidative decomposition of Ta_3N_5 . However, it is not clear about how severe the photocorrosion is when Ta_3N_5 is used for water oxidation and how it will affect the performance of Ta_3N_5 . To address these questions, we investigated the surface and bulk properties of Ta_3N_5 during the water oxidation process. Firstly, we tested the PEC performance of our bare electrodes in 1 M NaOH for water oxidation. We found that with cycling the performance of the Ta_3N_5 electrodes for water oxidation decreased both in terms of onset potential and photocurrent. As seen in Figure 2, after 25 scans the water oxidation performance of bare Ta_3N_5 NTs was nearly completely diminished under simulated sunlight conditions.



Figure 1. (A) The cyclic voltammetry (CV) curves of bare Ta_3N_5 electrode in 1M NaOH under light. **(B)** The photocurrent versus testing time curve of bare Ta_3N_5 electrode at 1.23 V in 1M NaOH. The TEM image of **(C)** fresh Ta_3N_5 surface, **(D)** Ta_3N_5 after one CV under light and **(E)** Ta_3N_5 after 3 hours photoelectrolysis at 1.23 V were listed. The scale bar was 1 nm in all three images.

When we tested our electrodes at a fixed potential we found that the photocurrent significantly decayed within the first few minutes of testing and after three hours that the water oxidation performance was completely diminished. The instability problem during PEC water oxidation was also reported for some other non-metal oxide materials such as

GaP and MoS₂, in which case the photoelectrodes were usually etched out. However, the severe oxidation of the electrode materials during photocorrosion was not observed in Ta_3N_5 case. The TEM images in Figure 1B-D showed that in comparison with the fresh Ta_3N_5 surface, the sample after initial PEC water oxidation test had a thin amorphous layer outside the original Ta_3N_5 . In addition, the thickness of the amorphous layer only increased from 0.5 nm to 1 nm after another 3 hours photoelectrolysis indicating that the formation of the amorphouse TaO_x layer is self-limiting.



Figure 2. (left) The cyclic voltammetry curves of bare Ta_3N_5 in 1M NaOH solution under 100 mW/cm² illumination. (**right**) The stability of bare Ta_3N_5 in 1M NaOH at fixed potential of 1.23 V_{RHE} under illumination.

5.3.2 XPS and XAS Measurements of Ta₃N₅

In collaboration with Jinghua Guo's group at the Advanced Light Source at Lawrence Berkeley National Lab, the composition of the amorphous film was investigated using XAS and XPS to probe the surface of fresh and tested Ta₃N₅ electrodes. The total electron yield (TEY) of O 1s and N 1s X-ray absorption were shown in Figure 4A and 4B,



Figure 4. The X-ray absorption spectrum of O 1s (A) and N 1s (B) were shown in the total electron yield. (C) to (E) corresponded to the XPS spectrum of O 1s, N 1s and Ta 4f of fresh sample and the sample after one light CV scan as well as three hours photoelectrolysis test.

which revealed the electronic structure on the surface of the samples. As the water oxidation time increased, the intensity of oxygen peaks became larger. In addition, the evolution of a small peak at 401 eV for N 1s absorption was observed for the tested samples. A previous study about the nitride and nitrogen doping has related this peak with

the intercalation of molecular N_2 , which indicated the surface oxidation indeed happened after the water oxidation. The surface oxidation was also confirmed in the XPS comparison of fresh and tested Ta_3N_5 samples. Even after the initial PEC test, the surface oxygen content has increased significantly, together with the decrease of nitrogen content and the evolution of TaO_x peaks. Noticeably, the shift of Ta 4f peaks after the PEC test was observed in the spectrum, which was not reported previously. This phenomenon was actually related with the surface Fermi level pinning after the oxidation of the surface and will be discussed in more detail in the following section.

5.3.3 Relating Photovoltage to Oxide Formation

To prevent the decay of our Ta₃N₅ electrodes we next tried to kinetically protect our Ta₃N₅ electrodes through the use of hole scavengers. Ideally, using a hole scavenger will prevent the self-oxidation of the material since the holes are transferred to the redox pair at a faster rate. The improved stability was indeed observed when Ta₃N₅ was tested in either H₂O₂ or Fe(CN)₆⁴⁻ as the hole scavenger, as shown in Figure 5A. Compared with the fast decay of photocurrent in 1M NaOH, a slower decay was observed in H₂O₂, while the photocurrent remained almost constant in Fe(CN)₆⁴⁻. When we explored the relation between our stability tests and the formation of the amorphous surface layer on our electrodes, we found that the formation of amorphous layer was not obvious in hole scavengers compared with that in just 1M NaOH (Figure 6).



Figure 5. (A) The stability test of bare Ta_3N_5 electrode in 1M NaOH, 1M NaOH with 0.1 M H₂O₂ and pH 10 0.1 M potassium phosphate buffer with 0.1 M K₄Fe(CN)₆ at 1.23 V under light. (B) The LSV scan of bare Ta_3N_5 electrode in the same solutions as in (A).

This correlation between stability and the formation of the amorphous layer further confirms that the oxidation of Ta₃N₅ is the cause of the instability. In comparing the hole scavengers, an interesting phenomenon was observed. The stability of Ta₃N₅ in H₂O₂ compared with that in Fe(CN)₆⁴⁻ is worse, which would not be expected since the oxidation potential of each scavenger is similar. However, the oxidation of H₂O likely proceeds through a peroxide intermediate, meaning that H₂O₂ oxidation and H₂O likely follow a similar 2 electron oxidation process. This led us to hypothesize that the intermediates being generated after H₂O₂ oxidation could be a source of Fermi level pinning, which would explain the limited stability of Ta₃N₅ in H₂O₂ can serve as the oxygen source for the Ta₃N₅ oxidation, which was absent during the oxidation of Fe(CN)₆⁴⁻. Lastly, a significantly better turn-on potential was observed in the presence of hole scavenger as shown in Figure 5B. While the initial values of the H₂O₂ and Fe(CN)₆⁴⁻ oxidation are the same, the H₂O₂

turn on potential quickly decays. Together, these observations led us to further explore the reason behind this enhancement and the effect of water oxidation on the turn on potential.



Figure 6. The TEM image of Ta_3N_5 sample tested for 3 hr in different hole scavenger solutions at 1.23 V_{RHE} under AM 1.5 light illumination. (A) Fe(CN)₆⁴⁻ (B) H₂O₂. The sample tested in 1M NaOH is used as comparison in (C).

Next we sought to investigate the photovoltage of Ta_3N_5 . The photovoltage of the PEC system should ideally be determined by the difference between the Fermi level position and the solution redox potential. A large photovoltage and early turn-on potential

is expected for Ta_3N_5 for water oxidation reaction due to its negative Fermi level position (< 0 V vs NHE) as reported previously. However, almost all the literature reported a late turn-on potential (>0.6 V) for Ta_3N_5 during water oxidation under light. While this phenomenon was usually explained as the poor transfer of photo-generated holes from semiconductor to electrolyte, adding OER catalyst on Ta₃N₅ surface still showed very limited improvement in the turn-on potential, which made the explanation less satisfactory. To investigate the Fermi level position of Ta₃N₅ in the aqueous solution and reveal the true reason behind the late turn-on potential, we tested the open circuit potential (OCP) under light and dark conditions and Mott Schottky (MS) measurements of the bare samples, after 1 CV and after three hours of PEC measurements with different hole scavengers. Ideally, the open circuit potential under dark and light illumination should be close to the corresponding Fermi level position. The difference between the dark and light OCP will give the photovoltage of the electrode. In addition, the open circuit potential under light should closely match the flat-band potential measured by MS and turn-on potential of the hole scavenger oxidation.

The OCP values of fresh Ta_3N_5 electrode in three different solutions were shown in Figure 7A. The light OCP in Fe(CN)6⁴⁻ was more negative compared with that in H₂O₂ and H₂O, while the dark OCP became closer to the light OCP in the absence of hole scavenger. The inability for the dark OCP to freely equilibrate with the water oxidation potential was indicative of Fermi level pinning, meaning that the Fermi level is equilibrating with surface states rather than the redox potential of the electrolyte under dark condition. The small photovoltage obtained by the OCP measurement in the absence of hole scavenger revealed the limited band bending at the surface of Ta_3N_5 , which can attribute to the late turn-on potential in the water oxidation. The existence of hole scavenger seems to passivate the surface states in some extent, which enabled a larger band bending and increased photovoltage. This was consistent with the early turn-on potential and higher photocurrent with hole scavenger observed in Figure 5B. However, it was still not clear how the PEC water oxidation or hole scavenger oxidation affected the surface Fermi level positions.



Figure 7. (A) The open-circuit potentials of fresh Ta_3N_5 in 1M NaOH solution with and without 0.1 M K₄Fe(CN)₆ and 0.1 M H₂O₂ under dark and light illumination (AM 1.5G, 100 mW/cm²). (B) The Mott-Schottky plot of the same Ta_3N_5 electrode in the solutions used in the OCP measurement.

To test the relation between the degradation and the Fermi level pinning we performed a series of stability tests with different redox pairs. As seen in Figure 8A, the OCP of Ta_3N_5 undergoing PEC oxidation of water and hole scavengers with different testing time was measured in the same solution with $Fe(CN)_6^{4-}$ for better comparison. After just one CV scan under light for water oxidation, the light OCP value already positively shifted by over 0.1 V. Similar shift was also observed for the sample tested in H₂O₂, while

the light OCP remains almost constant before and after the initial PEC test in $Fe(CN)_6^{4-}$. The LSV scans of those tested samples also showed similar trend in terms of turn-on potential and photocurrent, as shown in Figure 8B. In addition, the flat-band potential of Ta_3N_5 became more positive after the initial water oxidation test and the shifted value was consistent with the change for the light OCP (Figure 8C). Combined with previously described results for the surface oxidation observed in the XPS and the formation of thin amorphous layer from the TEM after PEC water oxidation, we can see a connection between the surface oxidation and change of Fermi level positions on the surface. It was reported that the oxidation of Ta₃N₅ was thermodynamically more favorable compared with the water oxidation. Therefore, during the water oxidation process, the surface oxidation of Ta₃N₅ became more competitive than the water oxidation, which resulted in the replacement of surface N by O as observed in XPS. The surface oxide layer further introduced the surface states and caused the shift of Fermi level to more positive value. With the presence of $Fe(CN)_6^{4-}$ as hole scavenger, the oxidation of Ta_3N_5 became less competitive and the shift of Fermi level was negligible. In the case of H₂O₂, as mentioned previously, some intermediates of H_2O_2 oxidation might be involved and served as the oxygen source for the surface oxidation, which resulted in the comparable shift of Fermi level as in the water oxidation case.



Figure 8. (A) The open-circuit potentials of three different Ta_3N_5 electrodes in pH 10 phosphate buffer with 0.1 M K₄Fe(CN)₆. Each electrode was tested in different solutions, including 1M NaOH, 1M NaOH with 0.1 M H₂O₂ and pH 10 phosphate buffer with 0.1 M K₄Fe(CN)₆ for one light CV and 3 hours photoelectrolysis at 1.23 V. The OCP values were recorded for each stage. (B) The J-V curves for LSV scans of each electrode from (A) in pH 10 phosphate buffer with 0.1 M K₄Fe(CN)₆. (C) The Mott-Schottky plot of Ta₃N₅ at fresh stage, after one light CV scan and 3 hours photoelectrolysis in 1M NaOH.



Figure 9. The J-V curves for bare Ta_3N_5 with different cycles of water oxidation test and the performance with re-deposited NiFeOOH were shown in (A), (B) and (C). (D) is the J-V curve of freshly prepared Ta_3N_5 with NiFeOOH or CoFeOOH as catalyst.

It was found that after the performance of Ta_3N_5 had been diminished it could be recovered with the addition of a water oxidation catalyst. This result is unexpected since the oxidation of Ta_3N_5 is an irreversible process. It can be seen in Figure 9 that once Ta_3N_5 has been cycled through one CV that the addition of the known OER catalyst, NiFeOOH,

resulted in a significant improvement of the water oxidation activity. Although the photocurrent was smaller compared with the freshly prepared Ta₃N₅/NiFeOOH electrode, the turn-on potential for each system was equal. Once Ta₃N₅ has been cycled 10 or 25 times though the extent to which the performance could be recovered was reduced. We hypothesize that initially the charges can tunnel through the oxide layer to the catalyst. As the oxidation of the surface becomes more severe (a thicker surface oxide layer) the tunnel barrier will become larger and the amount of charge that can be transferred to the catalyst will be reduced. While the addition of the NiFeOOH at earlier times can indeed temporarily stabilize the Ta₃N₅ surface and significantly shift the onset potential, the limited the turn-on potential at 0.65 V even for the freshly prepared sample. This is likely due to the porous nature of the NiFeOOH LDH material. Since water is still freely able to contact the surface of Ta_3N_5 a small amount of water oxidation will continue to take place on the Ta₃N₅ surface which will ultimately continue to limit the photovoltage through Fermi level pinning. If this is indeed the case, then in order to alleviate the Fermi level pinning in Ta₃N₅ a specific set of circumstances must be met.

5.3.5 Strategies for Improving Ta₃N₅

Based on the hypothesis that the evolution of surface tantalum oxide/hydroxide species is limiting the photovoltage of Ta_3N_5 , a very particular set of conditions must be met in order to effectively improve its photovoltage. In order to prevent the direct contact of Ta_3N_5 with aqueous electrolyte, the deposition of the catalyst must not include water. We have found that the deposition of catalyst such as NiFeOOH, CoFeOOH, Co-Pi and Co(OH)_x, all result in higher photocurrents, however they all fall short of further improving

the water oxidation turn-on potential. This is likely due to the inclusion of water during the deposition of these catalysts as well as the porosity of these catalysts. A protection layer could be incorporated onto the surface of Ta₃N₅ onto which a water oxidation catalyst could be deposited. However, commonly used protection layers, such as amorphous TiO_x and NiO_x, will oxidize the surface of Ta₃N₅ during the deposition procedure. Thus the process of adding a protection layer will create the detrimental Fermi level pinning states. This leads to non-oxide protection layers, such as GaN. While we have indeed explored the deposition of GaN onto our Ta₃N₅ by molecular beam expitaxy (MBE), we have found that the stability and the onset potential of our electrodes remain similar to that without the GaN protection layer. This could be due to the high aspect ratio of our samples, which will make it difficult to effectively protect. While moving to a low aspect ratio sample could be more easily tested for protection, it will also likely sacrifice the very high currents that are achievable with nanostructured Ta₃N₅ photoelectrodes. Well-constructed Ta₃N₅ nanostructures with high performance are needed for further investigation of protection strategies.

Doping Ta₃N₅ may also be an effective means to improving the photovoltage. Domen et al. have extensively attempted to dope Ta₃N₅, they have often used lower valent metals.^{2, 11} While this strategy does offer some small improvements in the photovoltage, the reason behind this improvement is not well understood and could be related to surface passivation just as well as doping. With a conduction band edge located at approximately -0.5 V vs NHE and the Fermi level between -0.1 to 0 V vs NHE, there is still plenty of room to further dope Ta₃N₅. The question is whether the already highly oxidized Ta⁵⁺ can be replaced with a higher valent metal such as Mo⁶⁺ or W⁶⁺ that would result in n-type doping. This may require a highly controlled growth of Ta_3N_5 in ultra-high vacuum conditions.

5.4 CONCLUSIONS

The reason behind the late turn-on potential and limited photovoltage for Ta₃N₅ as a photoanode for water oxidation was explored. We found that the hydrolysis of Ta₃N₅ surface in water as well as the self-oxidized surface during PEC water oxidation contributed to the limitation. This was confirmed by detailed analysis of the photoelectrochemical/electrochemical measurements in the aqueous solution that are corroborated with TEM and X-ray photoelectron/absorption spectroscopy. Together this provides insight into the limited photovoltage of Ta₃N₅ as a water oxidation material. This is also the first observation of Fermi level pinning in a nitride PEC photoanode and should provide a roadmap for future strategies to develop nitride materials for PEC applications.

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6.0 CONCLUSIONS AND OUTLOOK

6.1 MAXIMIZING THE PERFORMANCE OF EARTH ABUNDANT WATER OXIDATION CATALYSTS

In the previous chapters understanding the controlling factors of the photovoltage at the semiconductor liquid (catalyst) interface was the primary goal. It was shown that the addition of a heterogeneous catalyst to the surface of a photoelectrode can improve its surface energetics and thus the photovoltage. However, slow reaction kinetics, in particular for the water oxidation reaction, still necessitate the use of a catalyst, even with improved surface energetics. The kinetically slow water oxidation reaction requires hundreds of millivolts of overpotential to drive the reaction at meaningful current densities (>10 mA/cm²).^{1,2} Where the best known water oxidation catalyst, RuO₂, requires more than 200 millivolts of overpotential to generate 10 mA/cm². Not only does this catalyst require the extremely expensive ruthenium, but even as a state of the art catalyst it still requires a significant overpotential. To put this overpotential loss into perspective, with a 200 mV requirement the theoretical solar to hydrogen efficiency drops by nearly 20%. For the best earth abundant catalyst, NiFeOOH (used in Chapter 2 and 5), the overpotential requirements are even worse, as ~300 mV is needed to generate 10 mA/cm^{2.2} This highlights the need to further understand the limiting factors of these heterogeneous catalysts in order to further optimize their performances. For instance, if a key intermediate is being bound too strongly or weakly to the catalyst, the electronic structure of the catalyst can be tuned in order to improve the performance. Yet, understanding the mechanism of heterogeneous catalysts on the molecular level is an infamously arduous task.³ Spectroscopic methods that can be used to study these catalysts (FTIR, XAS, EXAFS, EPR, etc.) are difficult experiments to perform while the catalyst is being used under operating conditions, or *operando*. Also, these spectroscopic techniques generally suffer from very low signal to noise ratios, owing to the low concentration of the active sites relative to the bulk material. Because of this, the mechanism, and thus the limiting factors, of most heterogeneous catalysts are not well understood.

NiFeOOH has been the focus of intense debate in the literature in recent years, and is a prime example of the difficulties in studying heterogeneous catalysts. Since Boettcher et al. showed that the often reported NiOOH catalysts actually feature Fe impurities, there have been many different studies that have explored the role of Ni and Fe in this catalyst.⁴ Boettcher et al. through conductivity and thickness studies support that NiOOH is acting as a conducting framework for the active Fe.⁵ This is supported by *operando* Mössbauer experiments that show that Fe is indeed being oxidized as more potential is applied to the catalyst.⁶ Whereas, *operando* hard XAS and EXAFS experiments show that the Ni sites are primarily being oxidized during the water oxidation reaction.^{7,8} Coulometric titrations also support that Ni is the active site, again through the quantification of the oxidized nickel.⁹ Theoretical calculations of this material, albeit through different methods, also disagree about the active site. Norskov et al., showed that Fe is likely the active site based on their developed descriptor method that relates the binding energy of hydroxide to the activity of the catalyst.⁸ Whereas, Goddard et al. show, with more sophisticate methods that incorporate kinetic barriers, that the Ni is likely the active site and that Fe serves the role of withdrawing electron density from the Ni center.¹⁰ While these intense efforts have begun to unravel the roles of Ni and Fe within this catalyst, there remains no clear consensus on what the reaction mechanism of this catalyst looks like. Without this knowledge of the mechanistic limitations of NiFeOOH, improving its performance will be left to trial and error attempts based on phenomenological observations.

6.2 STUDYING HETEROGENEOUS CATALYSTS

However, developments in operando techniques have made mechanistic studies of heterogeneous catalysts more accessible. Time resolved-FTIR (tr-FTIR) and attenuated total reflectance-FTIR (ATR-FTIR) techniques have been used more frequently to study water oxidation catalysts.¹¹⁻¹⁵ While these experiments remain difficult to perform, researchers have found ways to maximize the signal from water oxidation intermediates by performing experiments in deuterated water, for instance. This has led to the unveiling of key intermediates of catalysts such as Co-Pi and hematite.^{12,13} Highly brilliant X-rays, generated from synchrotrons, also offer a wide range of operando techniques that can be used to study heterogeneous catalysts. Hard X-rays (2 keV - 20 keV) are often used to study the metal centers, as has been often used for NiFeOOH and CoPi water oxidation catalysts.^{7,8,16} Due to the very long X-ray path length of hard X-rays, these measurements are relatively easy benchtop experiments to perform. Whereas soft X-rays (50 eV - 1000eV) have been underutilized due to the increased difficulty of performing liquid operando measurements under ultra-high vacuum conditions. However, groups such as Jinghua Guo's group at the ALS at Lawrence Berkeley national lab, have been developing electrochemical operando liquid and gas cells to study heterogeneous catalysts using soft

X-rays (sXAS).¹⁷⁻¹⁹ These cells allow the electronic structure of lighter elements such as, O, N, C, to be measured, while still being able to measure transition metal L - edges ie. ~700 eV for Fe. Since solar fuel generation involves chemical transition of light elements, sXAS offers a powerful method to directly measure the electronic structure of these elements. Furthermore, XAS, unlike XPS, measures the unoccupied states of the element being measured, meaning that more detailed electronic structure information can be probed.



Figure 1. Schematic of a cell used for making operando sXAS of heterogeneous electrocatalyst. A silicon nitride window is used to separate the X-ray, traveling through an ultra-high vacuum, from the electrolyte. The X-rays penetrate the silicon nitride window and are then absorbed by the catalyst, where the element specific absorbance is reported on by both the total fluorescent yield and total electron yield. Pumps are used to constantly circulate the electrolyte through the electrochemical cell.

What's more, is that using X-ray fluorescent techniques, such as RIXS, allows the corresponding occupied states of the catalyst can be probed. As *operando* sXAS techniques further develop, XAS and RIXS will provide valuable mechanistic information on not only heterogeneous water oxidation catalysts, but heterogeneous catalysts for many different reactions such as carbon dioxide reduction or nitrogen reduction.

Preliminary studies were performed on NiFeOOH using sXAS and FTIR-ATR to understand the mechanistic pathway of this catalyst. Using the *operando* cell shown in Figure 1, the mechanistic pathway of NiFeOOH can be in part identified. While data of the *operando* sXAS and FITR experiments are still under analysis, the initial results support that the electronic and vibrational information are measuring the same reaction intermediate. Together, a new mechanistic pathway for NiFeOOH is being proposed that will indeed help future researchers improve heterogeneous water oxidation catalysts and reduce the overpotential, thus improving the solar to hydrogen efficiency. However, the coupling of these two operando techniques has further implications, as these studies provide a general framework for the use of multimodal studies in understanding heterogeneous catalysts.

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