MECHANISTIC UNDERSTANDING OF WATER OXIDATION DYNAMIC ON CuWO₄ PHOTOANODE: IDENTIFYING THE ROLE OF ELECTROCATALYST AND SURFACE INTERMEDIATES

By

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ABSTRACT

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Copper tungstate (CuWO₄) has been realized as a promising photoanode material for driving oxygen evolution reaction (OER), also called water oxidation, a half-reaction of water splitting. It has been shown that surface state recombination limits the performance of the $CuWO_4$ for photoelectrochemical (PEC) water oxidation. The integration of an electrocatalyst with a semiconductor photoanode is a well-adopted approach to eliminate surface recombination and improve the efficiency of water oxidation process. Unlike most demonstrated photoanodes for OER, the integration of an electrocatalyst with a $CuWO_4$ electrode has been observed to be usually detriment, or at most, do not affect the photocatalytic water oxidation activity of this material. Because the interfacial processes control the overall reaction, unraveling the dynamic of the interface is an essential step for the principle design of the electrocatalyst for enhanced PEC water oxidation on CuWO₄ photoanode. In this dissertation, I am seeking to gain a fundamental understanding of the role of surface states as well as the influence of electrocatalysts on the behavior of CuWO₄ thin-film electrodes for PEC OER. Here we present results that deepen the understanding of the energetics and electron-transfer processes at the CuWO₄/electrolyte and CuWO₄/electrocatalyst interfaces, which controls the performance of such systems. Ni_{0.75}Fe_{0.25}O_{ν} was chosen as a model electrocatalyst to investigate the CuWO₄/electrocatalyst interface due to the high electrocatalytic activity. Through dual-working electrode experiments, current transient, and impedance spectroscopy measurements, we have been able to gain significant insight into the

role of the electrocatalyst and the electron-transfer at the CuWO₄/electrocatalyst interface. Our results indicate that the lack of efficiency improvement after deposition of electrocatalyst on CuWO₄ is due to water oxidation on the CuWO₄ surface kinetically outcompetes the electrocatalyst oxidation. Thus, water oxidation occurs primarily from the CuWO₄ surface rather than the electrocatalyst. For the investigation of the role of CuWO₄ surface states, we employed the operando ATR-IR spectroscopy under PER OER condition. Our results show growing of absorption peaks at 750 and 1100 cm⁻¹, which can be attributed to the formation of surface *oxo* and *superoxo* water oxidation intermediates on the CuWO₄ surface, respectively.

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KEY TO ABBREVIATIONS

AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
ATR	Attenuated Total Reflectance
cat	Electrocatalyst
CB	Conduction Band
CE	Counter Electrode
CRR	Carbon Dioxide Reduction Reaction
CS	Charge Separation
CV	Cyclic Voltammetry
DWEP	Dual Working Electrode Photoelectrochemistry
E _{cat}	Electrocatalyst Potential
ED	Electrodeposition
$E_{\rm sc}$	Semiconductor Potential
EIS	Electrochemical Impedance Spectroscopy
Eredox	Solution Redox Potential
FTO	Fluorine-Doped Tin Oxide
HAADF	High-Angle Annular Dark-Field
НС	Hole Collection
HER	Hydrogen Evolution Reaction
IMPS	Intensity Modulated Photocurrent Spectroscopy
IR	Infrared Spectroscopy

KBi	Potassium Borate
LH	Light-Harvesting
$Ni_{0.75}Fe_{0.25}O_y$	Ni75
Ni _{0.25} Fe _{0.75} O _y	Ni25
OER	Oxygen Evolution Reaction
PEC	Photoelectrochemical
PMOD	Photochemical Metal-Organic Deposition
РРО	Poly (Phenylene Oxide)
PV	Photovoltaic
RHE	Reversible Hydrogen Electrode
sc	Semiconductor
SEM	Scanning Electron Microscope
SS	Surface States
ТСО	Transparent Conductive Oxide
TEM	Transmission Electron Micrograph
UV	Ultraviolet
VB	Valence Band
$V_{\rm ph}$	Photovoltage
W	Depletion Region
WE2	Second Working Electrode
WE1	First Working Electrode
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

Chapter 1:

Introduction

1.1 Motivation

The world energy demand has been significantly increasing due to economic and technological development with the expectation to approach 28 TW by the year 2050.¹ Fossil fuel has been the primary source of energy and is expected to remain as a main energy source for the next several decades. Although humanity has been relying on fossil fuel to supply power to society for centuries, a future continuation of this path clearly is not a wise choice. Fossil fuel combustion emits a significant amount of carbon dioxide and has been considered the main contributor to global warming. On top of that is the emission of toxic pollutants, such as nitrogen dioxide and sulfur dioxide, into the atmosphere. These compounds are known for their contribution to acidic rain and severe respiratory damage in humans. Moreover, fossil fuels are a non-renewable and unstable energy source that takes millions of years to form deep in the earth. Therefore, there is an urgent demand for replacing fossil fuel sources with alternative carbon-free sources of energy. This research effort started more than four decades ago, and despite substantial progress, it is yet to be continued!

1.2 Approach

Sunlight is the largest free and accessible energy source with a power capacity of 120000 TW that strikes the earth surface. Harvesting solar energy is a viable approach to satisfy the terawatt scale world energy demand. However, the low energy density of the sunlight compared to liquid and fossil fuels has been a hurdle for replacing carbon-based fuel with this sustainable and renewable alternative of energy resources. Sun energy can be stored in photovoltaic (PV) systems in the form of electricity. Si-based solar cells are one of the examples of PV cells that have been used for decades.² However, their relatively high cost for electricity production (\$ 0.35/kW-hr) compared to that generated from traditional fossil fuel combustion (\$ 0.02-0.05/kW-hr) has limited

their popularity for widespread application among society and ordinary consumers. Besides, energy production from solar cells is intermittent and depends on the weather and time of the day; their efficiency drops during the night or on rainy days. The development of the PV cells is currently limited by the lack of inexpensive methods for storing electricity on a large scale.

An alternative solution to PV systems is to collect and store the solar energy in chemical bonds; nature accomplishes this through photosynthesis. Two of the most studied approaches are photoelectrochemical (PEC) carbon dioxide reduction reaction (CRR) and hydrogen production.^{2–} ⁶ In photoelectrocatalytic CRR, carbon dioxide can be reduced to carbon monoxide and higher hydrocarbons using the energy of incident photons. While this approach provides a possible way for the utilization of solar energy, capturing the carbon dioxide from the atmosphere remains a challenge. Besides, the combustion of the products of CRR produces CO₂. In contrast, solar-tofuel energy conversion through PEC water splitting is an attractive and the most studied approach for conversion of solar energy that utilizes the cheap and abundant source of water to generate clean and energy-dense hydrogen fuel that is storable on a global scale.

1.3 PEC water splitting

The overall water splitting reaction is described by equation 1-1. Splitting water to O_2 and H_2 is an uphill reaction and requires a Gibs free energy change of + 237 (kJ/ mol H_2) under the standard condition that corresponds to 1.23 V potential difference between two half-reactions of water splitting. These two half-reactions of water splitting are called hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), and in the alkaline condition, are shown by equations of 1-2 and 1-3.

$$2H_2O \rightarrow 2H_2 + O_2$$
 $\Delta G = +237 \frac{kJ}{mol}$ $1-1$

1.7

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$
 (*HER*) $E^0_{red} = -0.83 \text{ V vs. NHE}$ $1-2$
 $4OH^- \rightarrow O_2 + 4e^- + 2H_2O$ (OER) $E^0_{ox} = -0.4 \text{ V vs. NHE}$ $1-3$

The main component of the PEC devices for water splitting is semiconductor photoelectrode. For a single photoelectrode material to be used for PEC water splitting, it must meet the following requirements:

- The valance band potential must be positive than the water oxidation potential (1.23 V vs. RHE) and the conduction band must be more negative than the water reduction potential (0.0 V vs. RHE) to drive each half-reaction efficiently.
- The bandgap should be reasonably small to absorb a substantial fraction of incident sunlight flux in the visible region.
- The semiconductor material should be stable during harsh PEC water splitting conditions.
- Finally, the semiconductor should be ideally composed of earth-abundant elements.

Since the photoelectrode bandgap should straddle the water reduction and water oxidation standard potential for a complete water splitting, a bandgap of 1.23 eV is necessary. Considering the overpotential required (600-900 mV) due to the kinetic loss to drive the two half-reactions efficiently, the ideal bandgap of a single photoelectrode for overall water splitting should be 1.8 - 2.2 eV.⁷ However, the relatively large bandgap limits the photon absorption in the visible region. Unfortunately, no single photoelectrode can be used for overall water splitting, mainly due to the limited light absorption and the photoelectrode stability in PEC conditions.

An attractive alternative to a single photoelectrode is the photoelectrochemical tandem cell, a combination of an n-type semiconductor (photoanode) and a p-type semiconductor

(photocathode).⁸ In PEC tandem cells, a photoanode with a wider bandgap is typically used to absorb photons at higher energy and perform the water oxidation reaction, and a narrow bandgap is typically used as a photocathode to drive water reduction reaction (Figure 1-1). This tandem configuration allows for using a broader range of the solar spectrum for PEC water splitting. OER is the rate-limiting step of the overall water splitting process due to the multi proton-electron coupling to yield two bond making steps (sigma and pi bonds in O₂). Besides, OER is the general half-reaction of other important reactions, *e.g.*, carbon dioxide reduction. Since the discovery of PEC water splitting by Fujishima and Honda in 1972,⁹ the pursuit of highly active and stable yet inexpensive and earth-abundant photoanode catalysts for OER has become an essential frontier for the practical development of PEC water splitting.



Figure 1-1. Configuration of PEC water splitting tandem cell. The overview of water splitting process using a PEC tandem cell with each half-reaction is shown

1.4 Photoanode materials

To drive PEC OER, the photogenerated holes within the n-type semiconductor materials must reach the electrode surface for injection into the water molecules. Effective water oxidation is achievable if the photoanode electrode possesses the following requirements:

- A reasonably small bandgap to absorb a large fraction of the incident sunlight flux in the visible region.
- The position of the valance band must be sufficiently positive with respect to the water oxidation potential (1.23 V *vs.* RHE) to avoid a large overpotential to initiate OER.
- It should have long term stability under harsh PEC water oxidation condition.
- The photoanode material should be composed of earth-abundant elements for large scale production.
- The charge transport properties must favorably outcompete the recombination losses processes to produce high quantum yields with minimal applied bias.

Metal oxides or metal oxide anions (in pure or doped forms) are likely the largest class of photoanode materials that have been investigated for OER in large part owing to their high stability under the reaction environment. The metal is usually in its highest oxidation state with the valence band (VB) consist of O 2p orbitals, and the conduction band (CB) is formed by the valence orbitals of one or more metals. Binary oxides such as TiO₂, hematite (α -Fe₂O₃), and WO₃ have been extensively studied as photoanodes to drive water oxidation reaction.^{9–16} Historically, titanium dioxide (TiO₂) is known as the first reported photoanode material used for PEC water oxidation.⁹ The application of TiO₂ for stable water oxidation was shown without any need for further surface modification.¹⁰ However, the wide bandgap of 3.2 eV limits the visible light-capturing by TiO₂ for efficient solar-to-fuel energy conversion. This issue has been recently addressed by introducing

the surface disordered black TiO₂ with mid-gap states for boosting visible light absorption and thus improving the efficacy of TiO₂-based photoanode for visible-light-driven water oxidation.¹¹ Hematite (α -Fe₂O₃) photoanode has also been the subject of extensive investigations.^{12,13,17} A combination of the small bandgap of 2.1 eV (absorption edge of 590 nm) and high stability under severe oxidizing conditions place the hematite as a highly suitable material for integration into PEC water oxidation devices.¹⁸ However, its application has been hampered due to the very short minority carrier lifetime and mobility and a low absorption coefficient (from an indirect bandgap) for capturing the incident photons.^{19,20,21,22}

In contrast, tungsten oxide (WO₃) exhibits relatively high electron mobility and long minority career diffusion length that are beneficial for the separation and transport of the charge carriers. However, WO₃ suffers from limited stability in alkaline media and low optical absorption in the visible spectrum owing to its large bandgap.^{15,16} Other photoanode materials, including Ta₃N₅ ^{23,24}, BaTaO₂N₅ ^{25,26}, GaAs²⁷, and CdTe²⁸ were also reported, but their application is also hindered because of a low efficiency associated with a number of factors, including a lack of chemical stability in the electrolyte medium for OER, poor charge-carrier transport, fast surface recombination, and a slow reaction kinetics.

Ternary and quaternary oxides material are the emerging alternative to binary oxide photoanodes and have garnered substantial interest for water oxidation reaction owing to the extent of their diversity and tunability.^{29,30} Bismuth Vanadate (BiVO₄) with a bandgap of 2.4 eV is a promising example of ternary oxide with a conversion efficiency that outperforms a large number of binary oxide photoanodes.^{31,32} This semiconductor shows high chemical stability in a neutral environment and has a favorable band-edge position to drive water oxidation reaction. This

promising activity of BiVO₄ caused searching for other ternary oxide materials such as CuWO₄ with an even smaller bandgap (2.3 eV) to further promote the PEC efficiencies.

1.5 Copper tungstate (CuWO₄)

CuWO₄, as a ternary oxide, emerges as an interesting photoanode material for PEC OER. CuWO₄ with distorted wolframite structure contains WO₆ octahedral and corner linked CuO₆.³³ It is composed of earth-abundant elements with a relatively small bandgap of 2.3 eV,³⁴ which allows absorbing photons shorter than 539 nm, making it suitable for harvesting a large portion of incident photons in the visible region for carrier generation to drive OER. In terms of catalyst stability, CuWO₄ has proven to be highly stable in neutral and slightly basic conditions that are favorable for OER.^{35–37} The integration of AM 1.5 solar spectrum based on the semiconductor with a bandgap of 2.3 eV results in a maximum photocurrent density of 9 mA cm⁻² (Figure 1-2). However, the reported overall water oxidation efficiency on CuWO₄ is relatively low with a best-reported photocurrent density of only 0.5 mA cm⁻², and a photocurrent onset potential that is several hundred millivolts positive with respect to the material's flat band potential.^{35,38–40}



Figure 1-2. AM 1.5 solar spectrum. A maximum photon flux that can be absorbed by CuWO₄ under 1 sun illumination (yellow area). The black vertical line shows the wavelength that corresponds to the CuWO₄ bandgap.

1.5.1 PEC water oxidation on CuWO4 surface

The photocurrent density (J_{photo}) that can be obtained from a photoanode material, e.g., CuWO₄, is determined by three different processes, including light-harvesting (LH), charge separation (CS), and hole collection (HC) that are summarized in equation 1-4:

$$J_{\text{photo}}(V) = q\Phi \left[\eta_{\text{LH}}(\lambda) \times \eta_{\text{CS}}(V) \times \eta_{\text{HC}}(V)\right]$$
 1-4

where q is the electron charge, and Φ is incident photon flux. The light-harvesting efficiency (η_{LH}) at a given wavelength (λ) depends on the material absorption coefficient (α), and thickness (l), as described by $\eta_{LH} = 1 - e^{-\alpha l}$. The thickness of a semiconductor material must be 3/ α to absorb 95% of the incident light. CuWO₄ has a weak absorption coefficient,⁴¹ and thus a several hundred nanometers to several microns of its thickness are required to absorb a decent amount of the incident photons for carrier generation. Following light absorption, electrons and holes are being generated in the conduction band (CB) and the valance band (VB) of the semiconductor, respectively (Figure 1-3). For a photoanode material, electrons are generally collected at the back ohmic contact, while photogenerated holes are transferred to the photoanode surface to drive the water oxidation reaction.

Meanwhile, charge carriers may also undergo unfavorable recombination within the bulk or the depletion region (W) near the surface. A portion of charge carriers that can reach the semiconductor/electrolyte interface is defined as charge separation efficiency (η_{CS}). Upon reaching the interface, photogenerated holes are either injected into the water molecule to produce oxygen through the OER or they may follow a recombination path with electrons from the conduction band through the surface states (SS). The fraction of holes at the photoelectrode surface that contributes to the oxidation of water is described by the hole collection efficiency (η_{HC}).

The low PEC OER activity of CuWO₄ can mainly be attributed to a limited η_{CS} and η_{HC} . ^{35,40,42} Strategies such as nanostructuring⁴³ and doping⁴⁴ have proven to slightly improve the η_{CS} and, thus, the overall performance for OER. By contrast, the poor hole collection efficiency originates from a slow reaction kinetics on the CuWO₄ surface due to increased carrier recombination in midgap surface states.^{40,45,46} It has been generally shown that electrocatalyst, once integrated with photoanode material, can improve the hole collection efficiency for the water oxidation reaction. However, reports, including work by our group, show that the presence of electrocatalysts on the CuWO₄ electrode surfaces generally does not improve the electrode performance or, in some cases, may even worsen it. In only one report, the presence of the manganese phosphate (MnPO) catalyst resulted in a slight improvement of the CuWO₄ electrode performance, although the reproducibility of the experiment has been a question to the best of our knowledge.⁴⁵



Figure 1-3. An overview of charge carrier generation and transfer for PEC water oxidation condition on the CuWO₄ photoanode. The pink arrow indicates light absorption (charge carrier generation). Green arrows indicate charge separation, including diffusion in the quasi-neutral region (bulk) and drift in the depletion region (W) due to the electric field. Red arrows indicate charge recombination in the bulk, depletion region, or surface states (SS). The blue arrow represents hole collection at the CuWO₄/electrolyte interface to oxidize water to oxygen.

1.6 Influence of electrocatalyst on water oxidation process

The semiconductor/electrolyte interface plays a determining role in surface-related phenomena in PEC devices, including charge separation and transfer to the electrolyte. The integration of an electrocatalyst onto the photoanode surface is an attractive way to modify the interface for improved PEC OER. These improvements are reflected in a cathodic shift of photocurrent onset potential, enhancement of the fill factor and/or an increase in photocurrent density. However, the origin of these enhancements has not been fully understood. Various experimental techniques have been developed and applied to the semiconductor/electrocatalyst system to investigate the role of the electrocatalyst for enhanced OER. Figure 1-4 shows the possible behaviors of an electrocatalyst layer on the semiconductor photoanode for the enhanced OER. Passivation of surface states through modification with a co-catalyst can reduce the rate of charge carrier trapping and recombination to improve the photoelectrode performance (Figure 1-4a). The formation of surface states arises from a truncation of the crystal lattice at the surface, and their presence can induce Fermi-level pinning, which increases the rate of surface recombination, and thus negatively affects the PEC performance of photoanode. Krol and coworkers demonstrated the role of Cobalt phosphate (CoPi) co-catalyst as a surface state passivator on BiVO₄ photoanode that led to an improved performance for the PEC OER.⁴⁷

Another suggested mechanism for the improved performance of the electrode after electrocatalyst deposition is based on the accumulation of photogenerated holes from the semiconductor valance band in the electrocatalyst layer that results in an enhanced charge separation efficiency (Figure 1-4b). Studies by Hamann and coworkers supported this mechanism by conducting impedance spectroscopy of the α -Fe₂O₃/Co-Pi photoanode that suggested the role of electrocatalyst overlayer as a hole collector.⁴⁸ The electrocatalyst may improve the charge separation efficiency by increasing the degree of band bending, which leads to a decrease in the electron concentration at the photoelectrode surface (Figure 1-4c). Barroso et al. ⁴⁹ reported that the presence of cobalt oxide overlayer on the hematite photoanode could enhance its PEC performance for OER due to increased band bending and the retardation of electron/hole recombination. Recent operando investigation of the hematite interfaced with the Ni_{1-x}Fe_xO_y via the advance dual working electrode (DWE) PEC technique developed by Boettcher and coworkers unambiguously suggested that the electrocatalyst can serve as both the hole storage layer and a water oxidation catalyst during PEC OER.⁵⁰



Figure 1-4. Influence of electrocatalyst on the activity of semiconductor photoanode for OER. (a) the electrocatalyst acts as a surface passivator to decrease electron/hole recombination, (b) accumulation of photogenerated holes in the electrocatalyst improves the charge separation efficiency, (c) increase of band bending causes the decrease of the carrier recombination. Black arrows indicate the favorable processes of charge transfer, and the red arrows represent the unfavorable processes of recombination. [Parisa Shadabipour, Hamed Hajibabaei, and Thomas W. Hamann *springer book chapter, in press*]

1.7 Dual working electrode photoelectrochemistry (DWEP)

DWEP, developed by Lin and Boettcher, is a valuable technique that enables the direct probe of semiconductor interface with electrocatalyst and provides insights into the role of the electrocatalyst on driving OER. Figure 1-5 shows the schematic illustration of the energy diagram and wiring of the DWE PEC setup. A thin electrolyte-permeable gold layer deposited at the surface of the electrocatalyst serves as a second working electrode (WE2) to independently probe the potential of electrocatalyst (E_{cat}) (or the current flowing through the electrocatalyst (J_{cat})) *in situ*. In contrast, the semiconductor potential (E_{sc}) /current (J_{sc}) can be simultaneously monitored and controlled through the first working electrode (WE1) with respect to a common reference electrode. However, the material choice to serve as a second working electrode in this technique has some limitations. First, the metal (gold in here) in contact with the electrocatalyst should be much less electrochemically active than the electrocatalyst itself for catalyzing the reaction (OER). It means that metal should equilibrate with electrocatalyst and the electrolyte. Second, it should be porous such that the contact between the electrocatalyst must remain intact during the electrochemical reaction. Gold is a very reasonable choice since it has slow kinetics for water oxidation reaction compared to typical water oxidation catalysts and remains highly stable during the chemical reaction.

Using DWEP, one can obtain the reaction overpotential from the difference between the solution redox potential and the measured electrocatalyst potential ($\eta = (E_{cat} - E_{redox}) / q$). Thus, probing the E_{cat} through the gold layer at the semiconductor surface quantifies the PEC system loss due to a kinetic barrier. On the other hand, controlling the E_{cat} via the potentiostat and then monitoring the E_{sc} under illumination allows for direct measurement of the photovoltage ($qV_{ph} = E_{sc} - E_{cat}$). Boettcher and coworkers applied DWEP to various semiconductor/electrocatalyst systems and found that electrocatalyst can serve as both a hole collector layer, which improves charge separation efficiency, and a water oxidation catalyst.⁵¹ The accumulation of holes in the electrocatalyst overlayer results in oxidation of the electrocatalyst to a sufficient potential to drive the water oxidation reaction.



Figure 1-5. Schematic diagram and wiring of DWE PEC setup.

1.8 Objectives

The overall objective of this dissertation is to provide a high-level fundamental understanding of the interfacial phenomena at the CuWO₄/electrocatalyst/electrolyte interface and to ultimately describe the origin of the unusual synergy between the CuWO₄ and electrocatalyst that fails to promote the photoanode performance for PEC OER. The integration of electrocatalyst with semiconducting photoelectrodes is a well-adopted approach to boost the efficiency of the watersplitting process. However, unlike the majority of demonstrated photoanodes for OER, the integration of electrocatalyst to the CuWO₄ electrode has been observed to be usually a detriment to, or at most do not affect, the photocatalytic water oxidation activity of this material. Despite previous reports, the lack of proper understanding of the energetics and carrier-transfer processes at the electrocatalyst/CuWO₄ interface has been a significant obstacle for developing an efficient co-catalyst for CuWO₄ photoanode. Developing new and novel electrocatalyst material for promoting the performance of the CuWO₄ photoanode can only be achieved once the fundamental understanding is reached. To accomplish this goal, I will use an arsenal of electrochemical measurements and material characterization techniques for photoelectrode characterization. A heavyweight will be placed on developing a platform based on the DWEP system for mechanistic description of charge carrier generation and their fate at the interface.

Chapter 2 demonstrates the preliminary investigation of the effect of various water oxidation catalysts on the performance of CuWO₄ photoanode for PER OER and a major issue in those systems caused by the shunting recombination. Chapter 3 introduces a simple strategy to overcome the shunting recombination, recombination of electrons instigated by the conductive underlying substrate and holes accumulated in the conductive catalyst, in mesoporous photoelectrodes in contact with conductive electrocatalyst. Chapter 4 demonstrates developing the DWEP platform to interrogate the dynamic of CuWO₄/electrocatalyst/electrolyte interface during PEC OER. Chapter 5 focuses on the application of electrochemical impedance spectroscopy (EIS) to evaluate the variation in the electrocatalyst capacitance during PEC OER and to correlate the finding with the result obtained from DWEP measurements. Chapter 6 presents the results of the operando ATR-IR spectroscopy measurements aiming at the detection of the water oxidation intermediates on the CuWO₄ surface. I envision the outcome of this thesis will pave the way for elucidating the unusual synergy between electrocatalyst and CuWO₄ electrode and provide significant insight for the future design of the proper electrocatalysts for highly efficient PEC water oxidation on this earth-abundant photoanode. The future promise of CuWO₄ as a water-splitting photoanode will be discussed in Chapter 7.

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Chapter 2:

Water oxidation on electrocatalyst-

modified CuWO₄

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2.1 Abstract

The evaluation of hole collection efficiency at the surface of CuWO₄ for water oxidation reaction suggests an improvement of the electrode performance after deposition of an electrocatalyst. Here, $Ni_{1-x}Fe_xO_y$ was chosen as a model electrocatalyst due to the high electrocatalytic activity to investigate the effect of electrocatalyst on photoelectrochemical (PEC) activity of CuWO₄ for the water oxidation reaction. We applied two compositions of the $Ni_{1-x}Fe_xO_y$ electrocatalyst, Fe-rich (Ni25) and Ni-rich (Ni75), to the CuWO₄ surface. Deposition of a thin film of Ni25 and Ni75 electrocatalyst on the CuWO₄ electrode does not cause any noticeable change in the electrode performance. It was also found that deposition of a higher thickness of Ni25 does not improve the CuWO₄ performance, similar to what we observed after applying a thin film of Ni25. However, an increase in Ni75 thickness results in a dramatic decay of the CuWO₄ performance due to the shunting recombination. This shunting recombination happens only when the conductive electrocatalyst, here Ni75, is in direct contact with the underlying conductive substrate due to incomplete coverage of the substrate by the semiconductor. Elimination of this such shunting recombination is vital for a systematic study of semiconductor/electrocatalyst to elucidate the role of electrocatalyst on the water oxidation activity of the CuWO₄.

2.2 Introduction

In chapter 1, CuWO₄ was introduced as a promising photoanode material, mainly due to a relatively small bandgap of 2.3 eV, earth-abundant composition, and high chemical stability in neutral and slightly basic conditions during photoelectrochemical (PEC) water oxidation.^{1–3} Also, as discussed in chapter 1 that CuWO₄ exhibits relatively low water oxidation efficiency with the best-reported photocurrent density of only 0.5 mA cm⁻² at water oxidation standard potential (1.23 V *vs.* RHE).^{1,4–6} Previous studies attributed the low water oxidation efficiency of CuWO₄ to a combination of inefficient charge separation in the bulk and hole collection at the surface.^{1,6,7} Li et al. demonstrated the improved charge separation efficiency of CuWO₄ through nanostructuring of the photoelectrode.⁸ Also, it has been recently shown that the Fe-doping of CuWO₄ can improve the charge separation efficiency of this material for PEC water oxidation.⁹

Hamann and a coworker evaluated the hole collection efficiency of CuWO₄ utilizing Na₂SO₃ as a suitable hole scavenger, and the results indicated a quantitative hole collection efficiency at potentials more positive than 1.23 V *vs.* RHE.¹ Deposition of an electrocatalyst on CuWO₄ surface, therefore, offers a possible route to improve hole collection efficiency at the lower applied potentials. However, unlike nearly all other photoanodes, the addition of electrocatalysts on the CuWO₄ surface has not shown a promise to improve PEC water oxidation efficiency. With that being said, there are a few reports that suggest moderate performance improvement of CuWO₄ photoanode upon deposition of an electrocatalyst.^{4,10–12} To improve hole collection efficiency at the surface of CuWO₄ by developing an efficient electrocatalyst, we need to fundamentally understand the charge carrier dynamics at the interface. The enhancement of the PEC activity of a photoelectrode upon deposition of an electrocatalyst has been attributed to different causes, including a decrease of surface state recombination^{13,14}, increased band bending^{15,16}, and improving charge separation.^{17,18} Recently, Boettcher and coworkers, using advanced dual

working electrode (DWE) photoelectrochemistry, unambiguously demonstrated the role of electrocatalyst overlayers as both water oxidation catalyst and hole storage layer. ¹⁹

In this chapter, we investigate the effect of electrocatalyst on the CuWO₄ performance for PEC water oxidation reaction. Thin films of CuWO₄ were prepared by atomic layer deposition (ALD) and modified with two compositions of $Ni_{1-x}Fe_xO_y$ electrocatalyst via photochemical metal-organic deposition (PMOD) method. The deposition of a thin film of Fe-rich (Ni25) and Ni-rich (Ni75) phases of $Ni_{1-x}Fe_xO_y$ on CuWO₄ does not show any noticeable change in the electrode performance. The higher thickness of Ni75, however, causes a dramatic decay of the CuWO₄ performance for PEC water oxidation.

2.3 Experimental

2.3.1 CuWO₄ thin-film preparation

CuWO₄ thin films were prepared on Fluorine-doped tin oxide (FTO)-coated glass substrate (Hartford Glass, TEC 15, 12Ω cm⁻²) via atomic layer deposition (ALD) using the previously reported procedure.¹⁰ FTO substrates were cleaned by sequential sonication in soap, water, and isopropyl alcohol for about 15 min, followed by drying in an N2 stream. The precursors for deposition of WO₃ and CuO were bis(tert-butylimido) bis(dimethylamido)tungsten (VI) $((tBuN)_2(Me_2N)_2W)$ Chemicals Inc., >97%) and (Strem Copper(I)-N,N'-di-secbutylacetamidinate ([Cu(sBu-amd)]₂) (Dow Chemical Co., >99.0%), respectively. First, 2000 ALD cycles of WO₃ were deposited on the FTO substrate using the modified reported procedure.²⁰ During the deposition, the W cylinder was heated to 75 °C and pulsed for 2 s, followed by 10 s underexposure mode and 6 s nitrogen purge. A 0.5 s pulse of deionized water (millipore, 18 M Ω cm) was then introduced as an oxidant, followed by 15 s of exposure mode and 6 s of the purge to oxidize the W precursor. Then, 340 cycles of CuO were deposited on WO₃ according to the

previous work calculation to have a 1:1 ratio between two metals.²¹ The copper cylinder was heated to 150 °C, and in each ALD cycle was pulsed for 3 s. The oxidation was performed after purging for 6 s. Then 10 cycles of ozone (~10% by weight O_3 in ultrahigh purity O_2 produced by Yanco Industries ozone generator) were used as an oxidant and pulsed for 2 s then followed by a 3 s purge to have enough generation of ozone. After the deposition of CuO on WO₃, the binary oxides were annealed at 550 °C in air for 30 min with a ramping rate of 2 °C / min. The thickness of CuWO₄ was calculated to be 200 nm according to the cross-sectional scanning electron microscope (SEM) image and ellipsometry (Horiba Jobin Yvon, Smart-SE).

2.3.2 Electrocatalyst deposition

The Ni_{1-x}Fe_xO_y electrocatalyst was deposited on 1 cm² of freshly prepared CuWO₄ photoanode through a spin coating from the metal precursor solution.^{22,23} Prior to the electrocatalyst deposition, the freshly prepared CuWO₄ film was rinsed with deionized water and dried with N₂. Precursor stock solution was prepared from 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) by dissolving an appropriate amount of metal precursor in hexane to give a total concentration of 15% w/w metal complex, and further the stock solution was diluted with hexane to obtain a total metal concentration of 50 mM. Approximately 0.25 ml of the stock or diluted precursor solution was placed on the substrate to prepare two different thicknesses of the electrocatalyst, and followed by spinning at 3000 rpm for 60 s. The as-prepared catalyst/CuWO₄ photoelectrode was treated with UV light to decompose organic residue (254 nm, 4 W) for 2 h followed by annealing in preheated furnace at 100 °C in air for 1 h.

2.3.3 Material characterization

SEM images were taken using Carl Zeiss Auriga, Dual Column FIBSEM. The X-ray diffraction (XRD) was measured with Bruker Davinci Diffractometer operating at 40 kV and 40 mA using Cu K α radiation. The X-ray photoelectron spectroscopy (XPS) analysis was performed at a takeoff angle of 45° using a Perkin Elmer Phi 5600 ESCA system with a magnesium K α X-ray source.

2.3.4 (Photo)electrochemical measurements

All electrochemical and photoelectrochemical measurements were carried out in a threeelectrode system with an Eco Chemie Autolab potentiostat (Nova electrochemical software) in back illumination configuration (photons passing through the glass before reaching the electrode surface). A homemade saturated Ag/AgCl and high surface area Pt mesh were used as a reference and counter electrode, respectively. The CuWO₄ electrodes were examined at room temperature and in contact with 1.0 M potassium borate (KB_i) buffered at pH 9.0 using KOH pellets and 1.0 M H₃BO₃ (Fisher Scientific Accumet pH meter). We prepared the aqueous solutions with ultrapure water (resistivity 18 M Ω cm) from a Milli-Q water purifier.

We used a 450 W Xe arc lamp (Horiba Jobin Yvon) as a white light source with an AM 1.5 solar filter to obtain a simulated solar spectrum with 100 mW cm⁻² (1 sun) intensity. All electrochemical potentials were converted to the reversible hydrogen electrode (RHE) by the equation $E_{\text{RHE}}=E_{\text{Ag/AgCl}}+0.197+\text{pH}$ (0.0591).

2.4 Results and discussion

CuWO₄ thin films were prepared via atomic layer deposition (ALD) on fluorine-doped tin oxide (FTO) substrates following a previously reported procedure.²¹ The prepared CuWO₄ thin films were characterized using various techniques. The existence of CuWO₄ crystal was confirmed using X-ray diffraction (XRD), Figure A2-1. The X-ray photoelectron spectroscopy (XPS) analysis shows W 4f, Cu 2p, and O 1s peaks of the CuWO₄ film (Figure A2-2). The top-view SEM image (Figure A2-3a) shows the surface morphology of the continuous film and CuWO₄ crystallites. The thickness of the prepared film was 200 nm, according to the cross-sectional SEM image and the spectroscopic ellipsometry measurement (Figure A2-3b).

Recently, Hamann and Gao demonstrated the use of Na₂SO₃ as a suitable sacrificial hole scavenger for quantitative hole collection with CuWO₄.¹ Therefore, we evaluated the hole collection efficiency ($\eta_{\rm HC}$) of CuWO₄ for water oxidation by comparison of the photocurrent density as a function of the applied potential $(J_{photo}-E)$ responses of the electrode for both water oxidation and Na₂SO₃ oxidation (Figure 2-1). The J_{photo} of the electrode was obtained by subtracting the dark current density (J_{dark}) from the total current density (J_{total}) under illumination since the CuWO₄ has a significant dark current in contact with Na₂SO₃. The J_{total} -E responses of the electrode for Na₂SO₃ oxidation under both illumination and in the dark are provided in the Appendix (Figure A2-4). Figure 2-1 shows that upon the addition of Na₂SO₃ hole scavenger to the electrolyte, the photocurrent onset potential exhibits a cathodic shift of about 200 mV. Consistently, the measured photocurrent is higher for the electrode in contact with the hole scavenger, particularly at lower applied biases. However, as the potential is scanned toward more anodic biases, the difference between the measured photocurrent in these two systems becomes less significant, and ultimately two curves meet each other at potentials more positive than 1.6 V vs. RHE.



Figure 2-1. Surface state recombination limits the hole collection efficiency of CuWO₄ for the water oxidation reaction. J_{photo} -E responses of CuWO₄ for water oxidation (pink) and Na₂SO₃ oxidation (blue) under 1 sun illumination and the scan rate of 20 mV s⁻¹.

The improvement of the photocurrent onset potential for Na₂SO₃ oxidation implies that the $\eta_{\rm HC}$ at the surface of CuWO₄ is limited by surface state recombination. The integration of an electrocatalyst ought to improve the $\eta_{\rm HC}$ of the photoelectrode for the water oxidation reaction, which would be reflected in an improved photocurrent onset potential.^{17,24–26} Based on the obtained results, the integration of a proper electrocatalyst to the CuWO₄ electrode, if can efficiently collect the photogenerated holes, should cause about 200 mV cathodic shift of the onset potential for water oxidation. However, the electrocatalyst deposition so far did not significantly affect the onset potential of CuWO₄ for water oxidation. ^{4,10–12} This provides an opportunity to study the dynamic of the electrocatalyst/electrode interface during water oxidation on CuWO₄ photoanode. A better understanding of the hole collection and transfer processes at the electrocatalysts to improve the CuWO₄ performance for water oxidation.

Ni_{1-x}Fe_xO_y was chosen as a model electrocatalyst for probing the electrocatalyst/electrode interface because it is one of the most active electrocatalysts for water oxidation in an alkaline environment, and its intrinsic activity can be tuned by Fe content. ^{27,28} It should be noted that the electrical conductivity of Ni_{1-x}Fe_xO_y depends on Fe concentration. While pure FeOOH is an insulator, an Fe concentration below 25 percent can improve the electrical conductivity. We chose two compositions of Ni_{1-x}Fe_xO_y to study the interface of electrocatalyst/CuWO₄; the Fe-rich electrocatalyst (Ni_{0.25}Fe_{0.75}O_y) refers to Ni25, and Ni-rich electrocatalyst (Ni_{0.75}Fe_{0.25}O_y) refers to Ni75. The electrocatalysts were deposited on the bare FTO and CuWO₄ thin films via the PMOD method (see the experimental section for more details). Ni75 is much more active than Ni25, as indicated by more cathodic onset potential (1.5 V vs. RHE) of the Ni75 on bare FTO (Figure 2-2). This higher activity is due to the higher percentage of electrochemically accessible Ni sites in Ni75 compared to Ni25, as is noticeable by the large redox wave of Ni75 on FTO. The observed redox wave is due to Ni²⁺ oxidation at 1.60 V vs. RHE and the Ni³⁺ reduction at 1.38 V vs. RHE.



Figure 2-2. Electrocatalytic activity of Ni25 and Ni75 films. *J-E* responses of bare FTO (black) and Ni75 (green) and Ni25 (red) on the FTO substrate were measured in 1.0 M KB_i and a scan rate of 20 mV s⁻¹.

Figure 2-3 shows the influence of the applied electrocatalyst with two representative $Ni_{1-x}Fe_xO_y$ compositions (Ni25 and Ni75) on the *J-E* response of the CuWO₄ electrode under dark and light conditions. As can be seen, for both cases, there is no noticeable change in the water oxidation performance after modifying the electrode compared to the bare CuWO₄. Indeed, the performance of the electrode under illumination even slightly decreases after Ni75 deposition. To unravel whether the thickness of the electrocatalyst plays a role in the observed behavior of CuWO₄ after electrocatalysts deposition, we also applied a higher electrocatalyst thickness (~220 nm); Figure 2-4 (see Appendix for the characterization of the electrocatalyst thickness). In the case of Ni25, an increase of the electrocatalyst thickness did not improve the performance of CuWO₄ photoanode, similar to what was observed for the thin Ni25 layer. However, in the case of Ni75, an increase in the catalyst thickness led to a dramatic decay of the performance. We hypothesized that the decreased performance could be due to the shunting recombination from the direct contact of Ni75 and the underlying FTO substrate.



Figure 2-3. Effect of electrocatalyst $(Ni_{1-x}Fe_xO_y)$ deposition on performance of CuWO₄ photoelectrode for water oxidation. *J*-*E* responses of CuWO₄ (a) before (solid pink) and after (solid violet) deposition of a thin layer of Ni25 (Ni_{0.25}Fe_{0.75}O_y) under illumination, (b) before (solid pink) and after (solid green) deposition of a thin layer of Ni75 (Ni_{0.75}Fe_{0.25}O_y). Representative *J*-*E* responses in the dark are

shown with a dashed line. The scan rate was 20 mV s⁻¹.



Figure 2-4. Impact of the higher thicknesses of $Ni_{1-x}Fe_xO_y$ on CuWO₄ activity for water oxidation. *J-E* responses of CuWO₄ (a) before (solid pink) and after (solid violet) deposition of a thick layer of Ni25 under illumination, (b) before (solid pink) and after (solid green) deposition of a thick layer of Ni75. Representative *J-E* responses in the dark are shown with a dashed line. The scan rate was 20 mV s⁻¹.

To test our hypothesis, we collected the dark *J-E* response of the bare CuWO₄ electrode in 10 mM ferrocyanide solution (fast electron transfer) and compared it to the *J-E* response measured for the bare FTO in the same electrolyte. When bare FTO is in contact with the ferrocyanide solution, a redox wave is observed due to the electron transfer between the solution and FTO. We observed a similar redox wave when CuWO₄ was in contact with ferrocyanide, albeit with lower peak height and higher peak separation. The observance of the redox wave for CuWO₄ in contact with ferrocyanide solution suggests that a large fraction of FTO remains exposed after CuWO₄ deposition. This result agrees with the result previously reported for porous hematite and BiVO₄.^{28,29}

Figure 2-6 shows the proposed model for the shunting phenomena on CuWO₄ photoelectrode. The deposition of a thin layer of Ni75 on CuWO₄ sparsely coats the semiconductor surface and is not in direct contact with the underlying substrate (Figure 2-6a). As the Ni75 thickness increases, the exposed FTO of CuWO₄ becomes filled with Ni75, leading to significant recombination of accumulated photogenerated holes in Ni75 with electrons in the FTO substrate. These shunting recombinations happen only when a conductive electrocatalyst is in direct contact with the underlying conductive substrate. As shown in Figure 2-4a, applying a higher thickness of Ni25 with a lower conductivity than Ni75 on the CuWO₄ surface does not lead to shunting recombination, and the performance of the CuWO₄ remains nearly the same as the bare electrode (Figure 2-4a). Therefore, we can conclude that the PEC activity of a system depends on both photoelectrode morphology and electrocatalyst properties such as conductivity and thickness. Elimination of such shunting recombination is vital for the investigation of charge carrier dynamics at the interface of CuWO₄/electrocatalyst and is the subject of the next chapter of this thesis.



Figure 2-5. The coverage of FTO substrate by the CuWO₄ film. Dark *J-E* responses of bare FTO (black) and CuWO₄ (pink) in 1.0 M KB_i buffer containing 10 mM k₄[Fe(CN)₆]. The scan rate is 20 mV s⁻¹.



Figure 2-6. Impact of the electrocatalyst thickness on CuWO₄ **activity.** (a) Deposition of a thin layer (or low loading) of Ni75 on CuWO₄ does not significantly shunt to the underlying conductive FTO substrate (b) deposition of a higher thickness (or high loading) of Ni75 cause a direct contact of the electrocatalyst to the underlying FTO substrate and leads to shunting recombination.

2.5 Conclusions

The PEC activity of the CuWO₄ photoanode was studied after the deposition of two compositions of $Ni_{1-x}Fe_xO_y$, Ni25 and Ni75, electrocatalyst by cyclic voltammetry. The deposition of a thin layer of electrocatalyst on the CuWO₄ surface does not show an improvement of the performance similar to other metal oxide photoanodes. Also, we observed that the modification of CuWO₄ with high thickness of the conductive electrocatalyst, here Ni75, causes shunting recombination due to the direct contact to the underlying substrate, which further leads to a decrease of the electrode performance for PEC water oxidation. This study suggests that selective deposition of an insulator into the pinholes of the photoelectrode while leaving the photoelectrode surface exposed would eliminate shunting recombination. The elimination of this such shunting recombination is vital for the systematic study of the CuWO₄ interface with an electrocatalyst to find the possible causes for the lack of performance improvement.

APPENDIX



Figure A2-1. XRD pattern of CuWO₄ prepared via the ALD method. Experimental data of CuWO₄ are shown as black curves, and peak positions from the database are shown as a vertical red dash. Diffraction peaks from FTO are labeled with a star.



Figure A2-2. XPS spectrum of CuWO₄ synthesized by the ALD method.



Figure A2-3. Scanning electron micrographs images of the CuWO₄ photoelectrode. (a) Cross-section view, and (b) top-view. The white dashed line shows the border of FTO with CuWO₄.



Figure A2-4. Hole scavenger oxidation with CuWO₄ photoanode. *J*-*E* responses of CuWO₄ for Na₂SO₃ oxidation under illumination (solid line) and in the dark (dashed line) in 1.0 M KB_i buffer containing 0.5 M Na₂SO₃. The scan rate of 20 mV s⁻¹.



Figure A2-5. The thickness of Ni75 electrocatalyst on CuWO₄. Cross-sectional SEM image of Ni75coated CuWO₄.

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Chapter 3:

Interface Passivation to Overcome Shunting in Semiconductor-Catalyst

Junctions

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3.1 Abstract

Most high-performance semiconductors used for photoelectrochemical water splitting applications are mesoporous. The deposition of cocatalysts, therefore, can result in direct contact with the underlying conductive substrate. This shunting can significantly inhibit performance as well as the understanding of semiconductor – catalyst junctions. Here we show high-performance mesoporous α -Fe₂O₃ photoanode modified with a conductive water oxidation catalyst, Ni_{0.75}Fe_{0.25}O_y, for photoelectrochemical oxygen evolution reaction are limited by shunting recombination. We propose a simple method to overcome shunting recombination via electrodeposition of thin film of poly (phenylene oxide) (PPO) insulating layer selectively to the exposed transparent conductive oxide substrate before deposition of the electrocatalyst. Elimination of the shunting recombination resulted in a significant improvement of the hematite performance for photoelectrochemical water oxidation. We envision the proposed strategy can be widely used to passivate interfaces, prevent shunting, and improve performance in a variety of other mesoporous systems for photoelectrochemical applications.

3.2 Introduction

In chapter 1, we discussed the integration of an electrocatalyst as a possible route to enhance the photoelectrochemical (PEC) activity of the semiconductor.¹⁻⁷ The use of electrocatalyst for boosting the performance of photoanodes has been successfully demonstrated through various suggested mechanisms, including enhanced charge separation,^{3,8} an increase of band bending^{9,10}, and surface passivation.^{11,12} However, the PEC activity of the electrocatalystmodified photoelectrode is dictated not only by the electrocatalyst nature but also by structural features of the photoanode layer. In other words, the integration of electrocatalyst could be detrimental to the performance of certain photoanodes. This has often been the case where a mesoporous photoanode electrode is interfaced with a conductive electrocatalyst. For example, the efficiency of mesoporous hematite and BiVO₄ photoanodes, extensively studied for PEC OER, showed a notable decrease after modification with the conductive electrocatalyst, such as Co-Pi, NiOOH, and Ni (Fe)O_xH_v (Ni-rich).¹³⁻¹⁶ Consensus supports an increase in the rate of carrier (electron and holes) recombination at the electrocatalyst/photoanode interface as a plausible reason for the deteriorated performance of the reported photoanodes upon modification with the conductive electrocatalysts.

Recently, Boettcher and coworkers proposed, based on the Dual working electrode (DWE) experiment, that the decrease in the electrode performance is indeed due to the possibility of shunting recombination.¹⁵ The porosity of the photoanodes layer deposited onto the transparent conductive oxide (TCO) may directly contact the top conductive electrocatalyst layer and the underlying TCO that provides a significant recombination path for otherwise spatially separated photogenerated electrons and holes in the photoelectrode architecture. The porosity of the photoanode layer deposited onto TCOs is, therefore, an important but generally overlooked design parameter for realizing efficient PEC water splitting. Indeed, the existence of such shunting

recombination in many prior reports of mesoporous photoelectrodes can also be inferred based on findings of performance improvement by (i) increasing the photoanode thickness,¹⁶ (ii) improving the surface morphology (e.g., fabrication of a pinhole-free photoanode using atomic layer deposition (ALD))¹³, and (iii) the incorporation of an additional non-conductive catalyst layer.⁵ However, mesoporous semiconductor photoanodes are particularly attractive due to their high surface area while also benefit from simple preparation methods, such as spray pyrolysis or electrodeposition. Therefore, developing approaches to address the shunting recombination in porous photoelectrodes without compromising the morphological characteristics or adopting a complicated fabrication is critical to their performance. However, this issue is not generally understood for PEC water splitting, and methods to overcome shunting are lacking in the literature.

In this chapter, we propose a simple strategy based on selective electropolymerization of poly (phenylene oxide) (PPO) onto the exposed fluorine-doped tin oxide (FTO) to eliminate the shunting recombination in mesostructured hematite interfaced with electrically conductive $Ni_{0.75}Fe_{0.25}O_y$ (Ni75) catalyst for OER. PPO serves as an organic blocking layer between the catalyst layer and FTO to prevent the recombination of the spatially separated charge carriers that consequently result in a significant improvement of the electrode performance for OER under illumination conditions.

3.3 Experimental

3.3.1 Hematite thin film preparation

Hematite thin films were prepared via two different methods of electrodeposition (ED), and atomic layer deposition (ALD) on Fluorine-doped tin oxide (FTO) coated aluminoborosilicate glass substrate (Solaronix, $10 \Omega/sq$) using the procedure reported previously.^{17,18} Before deposition of the thin film of hematite, FTO substrates were cleaned by sequential sonication in soap, water,

and isopropyl alcohol for about 15 min, followed by drying in an N₂ stream. The electrodeposition of hematite thin film was performed by applying a constant potential of 1.2 V *vs*. Ag/AgCl to the FTO substrate in a solution of 0.1 M FeCl₂.4H₂O (pH~4.3) at 60 °C for 30 min under gentle stirring. Then, amorphous FeOOH film was converted to crystalline Fe₂O₃ by annealing at 800 °C for 10 min.

Hematite film was also deposited via the ALD method on 2 nm Ga₂O₃ underlayer. Ga₂O₃ underlayer was deposited on FTO substrate by ALD using a modified version of the previously reported procedure.¹⁹ The Ga₂O₃ was deposited using tris-(dimethyl amido) gallium (III) (Ga₂(NMe₂)₆) (Strem Chemical Inc.) as the metal precursor and H₂O as an oxidant. The Ga cylinder was heated to 150 °C during the deposition of Ga₂O₃ and pulsed for 0.2 s under exposure mode for 8 s, followed by a 12 s purge. A 0.015 s pulse of H₂O was then introduced to oxidize gallium precursor under the same exposure time. Using spectroscopic ellipsometry (Horiba Jobin Yvon, Smart-SE), the growth rate of ~1.1 A° Ga₂O₃ underlayer. The precursor for the deposition of ALD-hematite was ferrocene, and wet ozone was used as the oxidation source. During the deposition, the ferrocene cylinder was heated to 70 °C and pulsed for 20 s, followed by a 2 s ozone pulse where each sub-cycle was separated by a 5 s purge. In the end, ALD-Fe₂O₃ film was annealed at 500 °C for 2 h and followed by annealing in a preheated furnace at 800 °C for 4 min.

3.3.2 Electrodeposition of poly (phenylene oxide) (PPO)

PPO blocking layer was selectively electrodeposited onto the exposed FTO of the semiconductor thin film. The electrodeposition of PPO was performed according to the previous report.²³ Briefly, the electrodes were submerged in a solution containing 60 mM phenol, 90 mM

2-allylphenol, and100 mM LiClO₄ in 10/10/1 water/ethanol/2-butoxyethanol. The solution was adjusted to pH 9 by the addition of 10 mM tetrabutylammonium hydroxide in methanol. The electrode potential was then scanned in the dark with the scan rate of 100 mV s⁻¹ from 0.1 to 1.5 V versus Ag/AgCl for 75 cycles. In order to remove unreacted monomers and oligomers, the electrode was soaked in 10 mM tetrabutylammonium hydroxide in methanol for 10 min. In the end, the electrode was rinsed with ethanol and cured in the air at 150 °C for 30 min. We measured the thickness of the PPO layer to be 12 nm using ellipsometry (Horiba Jobin Yvon, Smart-SE) on a silicon wafer coated with gold subjected to the same polymerization treatment as described above.

3.3.3 Catalyst deposition

Ni_{0.75}Fe_{0.25}O_y (Ni75) catalyst was deposited on 1 cm² of bare FTO and freshly prepared and PPO-modified ED-hematite photoanodes through the spin coating of the metal precursor solution.²⁴ Before catalyst deposition, thin films were rinsed with deionized water and dried with N₂. Iron (III) 2-ethyl hexanoate (50% w/w in mineral spirits, Strem Chemicals), and nickel (II) 2ethyl hexanoate (78% w/w in 2-ethyl hexanoic acid, Strem Chemicals) were used as a precursor. An appropriate amount of metal precursor was dissolved in hexane to obtain a total concentration of 15% w/w metal complex. Approximately 200 μ L of the precursor solution was placed on the substrate, and spinning was performed at 3000 rpm for 60 s. The as-prepared catalyst/semiconductor photoelectrodes were treated with UV light for 2 h to decompose organic residues (254 nm, 4 W) followed by annealing in a preheated furnace at 100 °C in air for 1 h. The thickness of Ni75 was measured using atomic force microscopy (AFM), cross-sectional scanning electron microscopy (SEM), and spectroscopic ellipsometry (SE) and is provided in the Appendix (Table A3-1).

3.3.4 (Photo)electrochemical measurements

A11 (photo)electrochemical measurements were done in made а custom photoelectrochemical cell setup with an Eco Chemie Autolab potentiostat (Nova electrochemical software) in back illumination configuration (photon passing through the glass before reaching the electrode surface). A homemade saturated Ag/AgCl and high surface area Pt mesh were used as reference and counter electrode, respectively. (Photo)electrochemical measurements were performed at room temperature in 1.0 M KOH. Aqueous solutions were prepared with ultra-pure water (resistivity 18 M Ω cm) from a Milli-Q water purifier. A 450 W Xe arc lamp (Horiba Jobin Yvon) was used as a white light source with an AM 1.5 solar filter to obtain a simulated solar spectrum with 100 mW cm⁻² (1 sun) intensity. All electrochemical potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) by using equation 1:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + (0.059 \text{ V}) \times pH$$
 eq.1

The Ni75 film on the hematite surface was conditioned by a series of cyclic voltammograms between 0.5 and 1.6 V *vs.* RHE under illumination until the Ni reduction peak remains constant. The *J-E* data shown for the catalyst-modified electrodes are from the final measurement.

3.3.5 Material characterization

Scanning electron microscope (SEM) images were taken using JEOL 7500F (field emission emitter). The cross-sectional sample for scanning transmission electron micrograph (STEM) was prepared using Thermal Fisher Helios 650 Nanolab SEM/FIB. Gold and platinum were deposited at the surface of the sample to protect it during the sample preparation. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-

dispersive x-ray (EDX) analysis were taken on a Thermo Fisher Scientific Talos F200X operated at 200 kV.

3.4 Results and discussion

In this study, the hematite photoanode electrodes were prepared through the electrodeposition from a 0.1 M FeCl₂.4H₂O solution onto the FTO substrate (see experimental for the fabrication details). The hematite photoanode prepared via electrodeposition (ED-hematite hereafter) is known to have mesoporous surface morphology and thus serves as an excellent platform to evaluate the effect of shunting and methods to overcome it.¹⁵ Because of the mesoporous structure, when the electrode is immersed in the electrolyte, there are areas of the FTO substrate that are directly in contact with the solution. We evaluated the mesoporous characteristic of the ED-hematite by comparing its dark cyclic voltammetric (CV) response to that of bare FTO in 10 mM ferrocyanide (fast electron transfer) solution (Figure 3-1). The reversible redox wave appears on the bare FTO (black line in Figure 3-1) corresponds to the charge transfer between the ferrocyanide and the electrode. Likewise, the reversible redox wave, albeit with a smaller peak height and increased peak separation, also observed for the ED-hematite (pink line in Figure 3-1), suggesting that a portion of the FTO remains exposed to the electrolyte after hematite electrodeposition. It should be noted that it is not likely to identify the exposed FTO through the hematite layer by looking at the scanning electron micrographs of the hematite film (Figure 3-2). However, the presence of pinholes in the ED-hematite layer was identified through cross-sectional imaging of the sample using high-angle annular dark-field scanning transmission electron micrograph (HAADF-STEM) and energy-dispersive X-ray (EDX) analysis (Figure 3-3, also see Figure A3-1).



Figure 3-1. The role of PPO on insulating the exposed FTO. Dark CV response of the bare FTO (black), ED-hematite (pink), and PPO-modified ED-hematite (blue) in 1.0 M KOH containing 10 mM k₄[Fe(CN)₆] solution. The scan rate is 10 mV s⁻¹.

Considering that ferri/ferrocyanide redox couples can penetrate the hematite film, we thought that organic monomers could also penetrate hematite films and reach the FTO substrate, and be selectively polymerized to form an insulating film. The PPO modification was carried out by introducing electrodes to the solutions containing phenol and 2-allylphenol, which were anodically electropolymerized to form PPO insulating films following the previous procedure 23 (Figure 3-4). The self-limiting growth mechanism results in very thin (~ 12 nm) films of PPO being selectively deposited on the FTO substrates. The insulating nature of the electrodeposited PPO blocks the direct charge transfer between the FTO layer and ferri/ferrocyanide species, which is evidenced by the lack of a redox wave for this system (blue line in Figure 3-1). The absence of the ferri/ferrocyanide redox wave after treating the ED-hematite with PPO suggests that PPO sufficiently covers all the exposed FTO, and a pinhole-free film is obtained.



Figure 3-2. Scanning electron microscopy images of ED-hematite on FTO substrate. (a) top view (b) cross-sectional view.



Figure 3-3. HAADF-STEM and EDX elemental mapping of the PPO-modified ED-hematite. (a) HAADAF-STEM image and (b-h) EDX mapping of tin (b), iron (c), oxygen (d), carbon (e), platinum (f), gold (g) and their overlay (h).



Figure 3-4. Current density measurements during the electrodeposition of PPO into the ED-hematite pinholes. The progressive decrease in the current density indicates the growth of the insulating PPO film. Scan rates are 100 mV s⁻¹.

To determine if the PPO electrodeposition occurs selectively on exposed FTO, we also attempted to deposit PPO on the hematite photoanode fabricated via atomic layer deposition (ALD). The ALD yields a pinhole-free hematite thin film with nearly no exposed FTO as previously determined²⁵ and further evidenced by the dark CV measurement in ferrocyanide solution (Figure 3-5a). The electropolymerization of PPO onto the ALD-hematite led to almost no measurable current compared to the current measured during PPO electropolymerization on the bare FTO and ED-hematite (Figure 3-5b). This result provides evidence that the hematite surface is electrocatalytically inactive for the deposition of PPO. Thus, the current measured during PPO deposition on the ED-hematite photoanode should originate from the deposition process selectively occurred on the exposed FTO through mesoporous hematite film. The absence of the exposed FTO can also be confirmed from the comparison of X-ray photoelectron spectroscopy (XPS) measurements of bare and PPO modified ED-hematite (Figure 3-6). The peak related to the



Figure 3-5. Evidence of selective PPO deposition on FTO. (a) Dark CV response of the bare FTO (black), ED-hematite (pink), and ALD-hematite (orange) in 1.0 M KOH containing 10 mM k_4 [Fe(CN)₆] solution. The scan rates are 10 mVs⁻¹ (b) The measured current density during the first scan of PPO electrodeposition on different surfaces, including bare FTO (black), ED-hematite (pink) and ALD-hematite (orange). The scan rates are 100 mVs⁻¹.



Figure 3-6. PPO blocks the exposed FTO of hematite film. XPS measurement of (a) bare ED-hematite and (b) PPO modified ED-hematite.

Tin (Sn) element coming from the FTO substrate disappeared for the PPO modified EDhematite film. More importantly, we found that modification of the ED-hematite photoanode with PPO, while insulates the underlying FTO, does not compromise the hematite surface area and thus the performance of the ED-hematite photoanode for water oxidation. Figure 3-7a compares the
performance of the bare and PPO-modified ED hematite for the PEC OER, where the measured current remains identical. Likewise, we observed the same performance for the pinhole-free ALD-hematite before and after the PPO modification (Figure 3-7b). These observations suggest that PPO electrodeposition is unlikely to happen on the hematite surface.



Figure 3-7. PPO deposition does not compromise the hematite performance for PEC OER. The comparison of the *J*-*E* responses for the (a) ED-hematite before (pink) and after PPO modification (blue) and (b) ALD-hematite before (orange) and after deposition of PPO (violet). Measurements were executed at a scan rate of 10 mV s⁻¹ under 1 sun illumination in 1.0 M KOH.

We then demonstrate the role of the PPO blocking layer in preventing the shunting recombination in the ED-hematite photoanode when interfaced with the electrically conductive electrocatalyst. Ni_{0.75}Fe_{0.25}O_y (Ni75) was chosen as the model electrocatalyst as the Ni-rich phase is known for its high electrical conductivity compared to the Fe-rich phase.^{26,27} Figure 3-8 shows the dark and light current density *vs.* applied potential (*J-E*) responses of an ED-hematite in 1.0 M KOH before and after deposition of a smooth layer of ~220 nm thick Ni75 electrocatalyst (see Appendix for the characterization of the electrocatalyst thickness). As shown, the deposition of the

Ni75 resulted in a large dark current along with the appearance of cathodic peaks at 1.3 V (vs. RHE) under both dark and illumination conditions. This peak, which also existed when the electrocatalyst directly deposited on the bare FTO corresponds to the reduction of Ni⁺³ to Ni⁺² on exposed FTO, and thus suggests a direct contact between the conductive electrocatalysts and the FTO layer underneath the hematite (Figure A3-3). ¹⁵ The resulted shunting from this direct contact, which can also be inferred by the significant increase of the dark current upon catalyst deposition, severely deteriorated the PEC performance of the electrode, leading to only a slight increase of the measured photocurrent during OER. Notably, an additional redox wave centered at 0.8 V vs. RHE has also appeared upon illumination of the catalyst modified-photoanode. This peak is also related to the Ni⁺³/Ni⁺² redox couple but occurs at the hematite surface. The generation of photovoltage in hematite under illumination resulted in about 0.5 V cathodic shift of Ni⁺³/Ni⁺² redox wave on the hematite surface compared to the same redox process on exposed FTO. Similar observations were previously reported where porous semiconductors were modified with an electrically conductive catalyst such as CoPi and Ni_{0.8}Fe_{0.2}O_y. ^{15,16}

Figure 3-8b shows the *J-E* behavior of ED-hematite electrodes with PPO blocking layers in contact with 1.0 M KOH aqueous electrolyte. As noted above, the addition of the PPO film does not affect the PEC performance without a catalyst. There is a striking difference in performance upon the deposition of a Ni_{0.75}Fe_{0.25} O_y electrocatalyst, however. Once the shunting pathway has been passivated through the addition of the PPO layer, there is no significant dark current and the reduction peak on FTO (Ni⁺³ to Ni⁺² at 1.3 V *vs.* RHE) is eliminated. Blocking the shunting pathway also results in a significant improvement in the PEC performance, where a ~200 mV cathodic shift of the photocurrent onset potential is observed on the catalyst-deposited electrode compared to the bare electrode, along with a significant increase in the photocurrent density. This improved behavior is similar to the improvement reported many times for compact hematite electrodes with a variety of catalysts, which is now well understood.



Figure 3-8. Impact of PPO electrodeposition on the elimination of shunting recombination. (a) *J-E* curves of the bare ED-hematite under illumination (solid pink line), in the dark (dashed pink line) and after deposition of Ni75 catalyst under illumination (solid violet line) and in the dark (dashed violet line). (b) *J-E* curves of ED-hematite after electrodeposition of PPO under illumination (solid blue line), in the dark

(dashed blue line), and after deposition of Ni75 under illumination (solid green line) and in the dark (dashed green line). All measurements were done in 1.0 M KOH, the scan rate of 10 mV s⁻¹.

Hematite is well known for its high photoelectrochemical stability in an alkaline environment during water oxidation reaction.^{28–30} In the meantime, the PPO layers are also expected to be stable under anodic conditions; indeed, they are deposited by applying potentials significantly more positive than expected at the hematite photoelectrode surface. To ascertain the robustness of the PPO layer under PEC water splitting conditions, we measured the photocurrent for the ED-hematite+PPO| Ni75 photoanode in 1.0 M KOH under 1 sun illumination at a constant applied potential of 1.26 V *vs.* RHE (Figure 3-9). The measured photocurrent density of 0.72 mA/cm² shows remarkable stability over 15 hours of measurement, proving the long-term stability of the PPO layer with no sign of photobleaching or degradation under the measurement conditions.



Figure 3-9. Photostability measurement of ED-hematite+PPO|Ni75 for PEC OER. *J-t* plot measured at 1.26 V *vs.* RHE in 1.0 M KOH under 1 sun illumination.

3.5 Conclusions

Here, we presented an approach based on the selective electrodeposition of PPO into porous photoelectrode to eliminate the shunting recombination that emerges from interfacing the electrode with an electrically conductive catalyst. The shunting, while its degree depends on photoelectrode morphology and catalyst conductivity, can severely limit the performance in PEC processes. We demonstrate that the integration of PPO results in a pronounced improvement in the performance of ED-hematite | Ni75 for PEC OER with remarkable stability. This approach should generally be applicable to other photoelectrode systems for improving their efficiencies in solar-energy applications, an open area for future research.

APPENDIX

The thickness of Ni75 was measured using atomic force microscopy (AFM), cross-sectional scanning electron microscopy (SEM), and spectroscopic ellipsometry (SE), which is ~ 220 nm.

Table A3-1. The measured and calculated thickness of the Ni75 on hematite: using AFM and SEM, and on a silicon wafer using SE.

Measured	thickness	with	Measured	thickness	with	SE	Measured	thickness	with
AFM (nm)			(nm)				cross-sectio	onal SEM (nr	n)
	220			210				220	



Figure A3-1. HAADF-STEM and EDX elemental mapping of the PPO-modified ED-hematite. (a) HAADAF-STEM image and (b-h) EDX mapping of tin (b), iron (c), oxygen (d), carbon (e), platinum (f), gold (g) and their overlay (h).



Figure A3-2. The thickness of Ni75 on hematite photoelectrode. Cross-sectional scanning electron microscopy image of ED-hematite modified with Ni75.



Figure A3-3. Electrocatalytic activity of Ni75 film. *J-E* response of the Ni75 electrocatalyst deposited on the FTO substrate.

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Chapter 4:

Charge Carrier Dynamics at the CuWO₄/Electrocatalyst Interface for Photoelectrochemical Water Oxidation

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4.1 Abstract

The integration of electrocatalysts with CuWO₄ electrodes generally results in comparable or worse performance compared to the bare electrode for photoelectrochemical (PEC) water oxidation. This is despite the fact that surface state recombination limits the water oxidation efficiency with CuWO₄ electrode, and an electrocatalyst ought to bypass this reaction and improve performance. Here we employ dual working electrode (DWE) technique and current transient measurements to directly probe the CuWO₄/electrocatalyst interface. The obtained results deepen the understanding of the energetics and electron-transfer processes at the CuWO₄/electrocatalyst interface, which controls the performance of such systems.

4.2 Introduction

Here, we employ the dual working electrode photoelectrochemistry (DWEP) technique pioneered by Boettcher and coworkers¹³ to investigate the unusual behavior of CuWO₄ after electrocatalyst deposition. This technique allows independent characterization of an electrocatalyst (cat) at the surface of the semiconductor (sc) and provides invaluable information about the role of electrocatalyst. In this technique, a thin electrolyte-permeable gold film at the surface of the electrocatalyst serves as a second working electrode (WE2), and the semiconductor photoanode serves as a first working electrode (WE1). The WE2 enables an independent probe of the potential or the current passing through the electrocatalyst, while the semiconductor potential/current is monitored and controlled through the WE1 simultaneously. Qiu and Boettcher employed the DWE technique to investigate the role of electrocatalyst overlayer as both water oxidation catalyst and hole storage layer.

In this chapter, we provide a systematic study into the charge-carrier dynamics at the interface of CuWO₄/electrocatalyst. Ni_{0.75}Fe_{0.25}O_y (Ni75) was chosen as a model electrocatalyst due to the high electrocatalytic activity to probe the interface. CuWO₄ thin films were prepared via atomic layer deposition (ALD) and modified with poly (phenylene oxide) (PPO) prior to the electrocatalyst deposition to eliminate shunting pathways.¹⁵ The electrocatalyst-coated CuWO₄ was then subjected to DWE and current transient measurements. Through the DWE technique, we could directly measure the electrocatalyst potential and the current flowing through the electrocatalyst. We demonstrate that the transport of the photogenerated holes to the electrocatalyst layer is not efficient, and the electrocatalyst cannot drive the water oxidation reaction. Current transient measurements reveal that the charging of the electrocatalyst is a slower process compared

to CuWO₄ surface states. These combined results provide new insight regarding the dynamic of CuWO₄/electrocatalyst interface and allow for further development and mechanistic investigation of this important system.

4.3 Experimental

4.3.1 CuWO₄ thin film preparation

CuWO₄ thin films were prepared on Fluorine-doped tin oxide (FTO)-coated glass substrate (Hartford Glass, TEC 15, 12Ω cm⁻²) via atomic layer deposition method using a previously reported procedure and described in chapter 2.¹⁶ Briefly, 2000 ALD cycles of WO₃ were deposited from its precursor (bis(tert-butylimido) bis(dimethylamido)tungsten (VI) ((tBuN)₂(Me₂N)₂W) (Strem Chemicals Inc., >97%)) on the FTO substrate using the modified reported procedure.¹⁷ Then, 340 cycles of CuO were deposited on WO₃ according to the previous work calculation to have a 1:1 ratio between two metals.¹⁸ The precursor for CuO deposition was Copper(I)-N,N'-disec-butylacetamidinate ([Cu(sBu-amd)]₂) (Dow Chemical Co., >99.0% also synthesized by our group). After the deposition, the binary oxides were annealed at 550 °C in air for 30 min with a ramping rate of 2 °C / min. The thickness of CuWO₄ was calculated in chapter 2 to be 200 nm according to the cross-sectional SEM image and ellipsometry (Horiba Jobin Yvon, Smart-SE).

Synthesis of ([Cu(sBu-amd)]₂): Sec-butylamine (99 %) and La(OTf)₃ were purchased from Oakwood Chemical, and sec-butylamine was dried over activated 3A molecular sieves for 3 days and La(OTf)₃ was activated by heating to 190 °C for 3 days under vacuum. Diethyl ether was purchased from Fisher Scientific and was prepared by drying over activated 3A molecular sieves for 3 days, degassing, and storing in a nitrogen-filled glove box for use. CuCl (\geq 99.995 %) and MeLi (1.6 M in diethyl ether) were purchased from Sigma Aldrich and were used as received. Deuterated benzene-*d6* was purchased from Cambridge Isotopes and used as received. N,N'Disec-butylacetamidine was prepared as reported previously.¹⁹ ([Cu(sBu-amd)]₂) was prepared by modifying a previously reported procedure as described below.²⁰

8.40 g (49 mmol) of N,N'-Di-sec-butylacetamidine was dissolved in 100 mL of dry diethyl ether in a 200-mL round bottom flask under nitrogen. The flask was cooled to -30 °C and then allowed to stir at -30 °C for 30 minutes. 3.85 mL of MeLi (1.6 M in diethyl) was added dropwise to the solution. The flask was allowed to warm to room temperature and was then stirred for 2 hours. The solution was then canula transferred to another 200-mL round-bottom containing 4.88 g of CuCl (49 mmol) and 30 mL of dry diethyl ether. The solution was allowed to stir for 18 hours and was then filtered under nitrogen and then dried by vacuum. The resulting brown solid was then collected inside a nitrogen-filled glovebox and was then sublimated onto a cold finger under vacuum at 95 °C. A white crystalline powder was collected from the cold finder (4.8024 g, 41.6 %). ¹H NMR (500 MHz, Benzene-*d*₆) δ 3.13 (m, 2H), 1.73 – 1.57 (m, 5H), 1.50 (m, 2H), 1.17 (dt, *J* = 6.3, 1.6 Hz, 6H), 0.95 – 0.86 (m, 6H).

4.3.2 Electrocatalyst deposition

 $Ni_{0.75}Fe_{0.25}O_y$ (Ni75) electrocatalyst was deposited on 1 cm² of PPO modified CuWO₄ photoanode via photochemical metal-organic deposition (PMOD) method from the metal precursor solution.^{21,22} Prior to electrocatalyst deposition, CuWO₄ films were rinsed with deionized water and dried with N₂. The precursor solution was prepared from iron (III) 2-ethyl hexanoate (50% w/w in mineral spirits, Strem Chemicals), and nickel (II) 2-ethyl hexanoate (78% w/w in 2-ethyl hexanoic acid, Strem Chemicals) by dissolving the appropriate amount of each precursor in hexane to give a total concentration of 15% w/w metal complex. Approximately 250 μ L of the precursor solution was placed on the substrate, followed by spinning at 3000 rpm for 60 s. The as-prepared CuWO₄/Ni75 electrode was treated with UV light to decompose organic

residues (254 nm, 4 W) for 2 h followed by annealing in a preheated furnace at 100 °C in air for 1 h. The thickness of Ni75 film was measured to be ~ 220 nm same as chapter 2 using spectroscopic ellipsometry (SE) and cross-sectional scanning electron microscopy.

4.3.3 Electrodeposition of poly(phenylene oxide) (PPO)

The PPO electrodeposition was performed according to a previous report and described in chapter 3.²³ The prepared CuWO₄ electrodes were submerged in a solution consisting of 90 mM 2-allylphenol, 60 mM phenol, and100 mM LiClO₄ in 10/10/1 water/ethanol/2-butoxyethanol. 10 mM tetrabutylammonium hydroxide in methanol was added to the solution to adjust the pH at 9.0. Then electrodeposition of PPO was done by scanning the electrode potential in the dark with the scan rate of 100 mV/s from 0.1 to 1.5 V versus Ag/AgCl for 60-80 cycles. The electrodes were then soaked in 10 mM tetrabutylammonium hydroxide in methanol, and cured in the air at 150°C for 30 min. We used ellipsometry (Horiba Jobin Yvon, Smart-SE) to measure the thickness of the PPO layer on a silicon wafer coated with gold and subjected to the same polymerization treatment as described above, which was~12 nm.

4.3.4 Material characterization

Scanning electron microscope (SEM) images were obtained using Carl Zeiss Auriga, Dual Column FIBSEM. Raman spectrums were collected via Raman microprobe (Renishaw) equipped with a 45W Cobalt DPSS laser (532 nm line) laser and a 100× mag. objective to focus the laser on the film surface. The roughness of the surface was examined by atomic force microscopy (AFM) using MFP-3D from Asylum Research.

4.3.5 Fabrication of dual-working electrode devices

To fabricate CuWO₄+PPO|Ni_{0.75}Fe_{0.25}O_y|Au DWE device, the electrical contact was made to the FTO|CuWO₄+PPO substrate coated with Ni75 film using silver paste and copper wire to make the first working electrode (WE1). Then, electrical connections were covered with epoxy (Loctite Hysol 1C) for keeping them isolated from the electrolyte during the measurement. Then 12 nm-thick Au was evaporated from Au metal in the aluminum boat using a vacuum thermal evaporator (rate = 2 Å·s⁻¹) on to the catalyst surface and epoxy around the electrode. The second electrical contact was made to the Au using silver paste and copper wire to make the second working electrode (WE2) and covered with epoxy again. The first wire was placed inside a glass tube. The second wire was coiled around the glass tube, and then it was inserted into the second glass tube and sealed with hot glue. The voltages and current densities of FTO|CuWO₄+PPO, and the Ni75 film were controlled and measured via WE1 and WE2, respectively. The gathered *E*_{WE2} and *J*_{WE2} hence give a measure of the potential of the electrocatalyst layer (*E*_{cat}) and current density flowing through the electrocatalyst layer (*J*_{cat}), respectively. Scheme 4-1 shows the structure and the digital image of CuWO₄+PPO|Ni_{0.75}Fe_{0.25}O₉|Au device.



Scheme 4-1. The structure and the digital image of CuWO₄ |Ni75|Au DWE device.

4.3.6 (Photo)electrochemical measurements

All electrochemical and photoelectrochemical measurements were conducted in a custom made photoelectrochemical cell setup with an Eco Chemie Autolab potentiostat (Nova electrochemical software) in back illumination configuration (photon passing through the glass before reaching the electrode surface). A homemade saturated Ag/AgCl and high surface area Pt mesh were used as reference and counter electrode, respectively. All (photo) electrochemical measurements were conducted at room temperature and in 1.0 M potassium borate (KB_i) buffered at pH 9.0. We used the same source of white light, as described in chapter 2. All (photo) electrochemical potentials were converted to the reversible hydrogen electrode (RHE) by the equation $E_{RHE}=E_{Ag/AgCl}+0.197+pH$ (0.0591).

4.4 Results and discussion

200 nm thin films of CuWO₄ were prepared on fluorine-doped tin oxide (FTO) substrates by ALD following the previously reported procedure.¹⁴ We choose Ni_{0.75}Fe_{0.25}O_y (Ni75) as a model electrocatalyst to investigate the CuWO₄/electrocatalyst interface for OER, as Ni-rich phases of Ni_{1-x}Fe_xO_y are known for their fast electrocatalytic activity and high electrical conductivity compared to the Fe-rich phases of the electrocatalyst.²⁴ Prior to the electrocatalyst deposition, CuWO₄ thin films were modified with PPO according to the described procedure in chapter 3 to block the exposed underlying FTO substrate. For this purpose, the CuWO₄ electrodes were submerged in the solution containing phenol and 2-allylphenol, where the potential of the electrodes was scanned anodically to electrodeposit PPO to the exposed FTO (Figure A4-1). The absence of the exposed FTO on PPO-modified CuWO₄ was confirmed by measuring the current density *vs.* applied potential (*J-E*) responses of the electrode before and after PPO modification in 0.5 M of Na₂SO₃ (hole scavenger solution) (Figure 4-1). The bare CuWO₄ has a significant dark current when it is in contact with the hole scavenger solution which is due to the electron transfer between conductive substrate, FTO, and the electrolyte. This such dark current is absent when CuWO₄ is modified with PPO. The lack of exposed FTO on CuWO₄ after PPO electrodeposition was also confirmed by comparison of the dark *J-E* responses of the electrode before and after PPO modification in a 10 mM ferrocyanide solution (Figure A4-2).



Figure 4-1. The lack of exposed FTO on CuWO₄ after PPO electrodeposition. *J*-*E* responses of CuWO₄ before and after PPO electrodeposition when the electrode is in contact with 1.0 M of KB_i containing 0.5 M Na₂SO₃ under illumination and in the dark. The scan rate is 20 mV s⁻¹.

After PPO modification, a smooth ~220 nm thick Ni75 electrocatalyst was deposited via the PMOD method from its precursor solution at the surface of the CuWO₄ photoanode (see chapter 2 appendix for the characterization of the electrocatalyst thickness). In the PMOD method, the annealing time is vital to decompose all organic residues. We used Raman spectroscopy to track the organic residues at the surface of the electrode. We found 2-hour illumination of the film with UV light can decompose all organic precursors. Figure 4-2 shows the comparison of Raman spectrums of the CuWO₄ modified with Ni75 before and after UV treatment with bare FTO. Before UV treatment, the Ni75- coated CuWO₄ (green line) shows a peak in the C-H stretching region $(2800-3100 \text{ cm}^{-1})$. This peak is absent for the same sample after UV illumination (blue line), which confirms the decomposition of organic residues from the electrocatalyst composition.



Figure 4-2. The UV treatment of Ni75-coated CuWO₄ decomposes organic residues from Ni75 composition. Raman spectra of bare FTO (black line), Ni75-coated CuWO₄ before UV treatment (green line), and after UV treatment (blue line).

The deposition of Ni75 electrocatalyst on CuWO₄ reduces the root-mean-squared surface roughness and provides a smooth surface (Figure A4-3). This smoothness is necessary for the systematic study of the CuWO₄/Ni75 interface. The *J-E* responses of the PPO modified CuWO₄ before and after the addition of Ni75 were measured to investigate the effect of electrocatalyst on electrode performance. As shown in Figure 4-3, the electrocatalyst deposition does not improve the CuWO₄ performance for PEC OER. We have shown even the deposition of a very thin layer of Ni75, although it does not cause shunting but still does not improve the CuWO₄ performance (Figure A4-4). Our results are in contrast with the result of other metal oxide photoanodes such as hematite and BiVO₄, where deposition of electrocatalyst improves the performance for PEC OER; however, it is in agreement with literature on $CuWO_4$.^{25–27} We, therefore, attribute the lack of improvement to a unique aspect of CuWO₄ in controlling the electron dynamics at the interface of semiconductor with an electrocatalyst.



Figure 4-3. The PEC activity of PPO-modified CuWO₄ after Ni75 deposition. *J*-*E* responses of CuWO₄ after modification with PPO (blue) and then deposition of Ni75 (green) under illumination. All measurements were done in 1.0 M KB_i, the scan rate of 20 mV s⁻¹.

For a more in-depth understanding of the charge carrier dynamics at the interface of the CuWO₄ with an electrocatalyst, we fabricated dual working electrode (DWE) devices developed by Boettcher and coworkers. ¹³ In the DWE technique, a thin electrolyte permeable gold at the surface of the electrocatalyst serves as a second working electrode (WE2), whereas the semiconductor photoanode serves as a first working electrode (WE1) (Figure 4-4). Such a configuration allows independent probing of the electrocatalyst potential (E_{cat}) or the current passing through the electrocatalyst (J_{cat}) via WE2 while simultaneously controlling semiconductor potential (E_{sc}) or monitoring the current density (J_{sc}) via WE1. The deposition of crack-free

electrocatalyst is essential to prevent any short between the gold layer and the underlying substrate. As mentioned earlier, the deposition of electrocatalyst via the PMOD method can provide smooth and pinhole-free film; thus, we applied a 220 nm smooth film of Ni75 at the surface of the CuWO₄ using this method. This smoothness help for the deposition of an interconnected gold film on the electrocatalyst surface. Further, we applied a 12 nm film of gold at the electrocatalyst surface using a thermal evaporator to make CuWO₄|Ni75|Au device.



Figure 4-4. Schematic diagram of CuWO₄|Ni75|Au device for PEC OER. Au at the surface of the electrocatalyst serves as WE2 to independently probe E_{cat} or J_{cat} while controlling E_{sc} or monitoring J_{sc} from WE1 simultaneously.

For the PEC characterization of the DWE device, the illumination was performed from the back contact (photons were passing through the glass side of the FTO substrate) to eliminate light absorption by the electrocatalyst. The electrocatalyst was conditioned by measuring a series of cyclic voltammograms (CVs) from WE1 under illumination and from WE2 in the dark to make it electrolyte permeable. Figure 4-5 shows the post conditioned *J-E* response of the Ni75 overlayer (dark red line), which is measured from WE2. The *J-E* response of the Ni75 electrocatalyst measured through the gold layer is the same as the *J-E* response of the Ni75 deposited on bare

FTO, which confirms the porosity of the gold layer (electrolyte is accessible to the electrocatalyst) (Figure A4-5). The *J*-*E* response of the electrocatalyst shows a redox wave with the Ni²⁺ oxidation peak at 1.65 V (*vs.* RHE) and the Ni³⁺ reduction peak at 1.45 V (*vs.* RHE). The *J*-*E* response of CuWO4 under illumination (solid black line Figure 4-6a) shows a Ni³⁺ reduction peak on the CuWO4 surface at 0.85 V (*vs.* RHE) and is similar to the *J*-*E* response of the electrode without the gold layer because of the backside illumination (Figure A4-6). This similarity confirms that the gold layer electrocatalyst surface does not have any measurable effect on water oxidation activity. However, the dark current remains negligible in the studied range of potential (dashed black line in Figure 4-5). From the *J*-*E* response of CuWO4 (Figure 5-4 black line), we can see that the net current is positive for E_{sc} > 0.9 V (*vs.* RHE). This positive net current at steady-state can oxidize water molecules at the surface of the CuWO4 as well as the electrocatalyst layer. For the latter to occur, the electrocatalyst should reach a sufficiently positive potential from the transfer of photogenerated holes.



Figure 4-5. DWE PEC characterization of the electrocatalyst. (a) *J-E* curves of the CuWO₄ (sc) (solid black line) under illumination and in the dark (dashed black line) and Ni75 (cat) (dark red line) that are separately collected through WE1 and WE2, respectively.

The *J-E* response of the CuWO₄ exhibits a capacitive wave at 0.85 V vs. RHE, which implies that at least some of the current go towards oxidizing the Ni75 electrocatalyst overlayer. To be more quantitative, we measured the potential of Ni75 on CuWO₄ while controlling the semiconductor potential. Figure 4-6 shows the steady-state potential of Ni75 (E_{cat}) on the CuWO₄ surface while stepping the potential of CuWO₄ (E_{sc}) under illumination and in the dark. In the dark, the electrocatalyst film can only be oxidized at anodic biases through the leakage current of the CuWO₄. Due to the negligible leakage current across the CuWO₄, potential of the electrocatalyst remains nearly constant up to E_{sc} =1.7 V vs. RHE (Figure 4-7 blue line). Under illumination, however, the transfer of photogenerated holes from the CuWO₄ valance band to the electrocatalyst causes oxidation of Ni active sites and leads to the sharp transition of the electrocatalyst potential from 0.6 to 1.3 V vs. RHE. The transition of the electrocatalyst potential under illumination is happening at $E_{sc} \sim 0.7$ V vs. RHE.

The decrease in the applied potential for oxidizing the electrocatalyst under illumination compared to the dark is due to the photovoltage build up at the interface of CuWO₄/Ni75. Interestingly, however, the E_{cat} transition stops at a potential of 1.3 V vs. RHE, which is not as positive as the current onset potential of the electrocatalyst (1.6 V vs. RHE). These results suggest that while some of the photogenerated holes transfer to the electrocatalyst, the potential of the electrocatalyst somehow becomes pinned at a potential insufficient to drive water oxidation and that in parallel, water oxidation must occur from the CuWO₄ surface. Figure 4-7a and b show the superimposition of E_{cat} and steady-state current density of the semiconductor and the representative *J*-*E*s under illumination and in the dark, respectively. The agreement between the steady-state J_{sc} s, which is measured from WE1 of the DWE device during the *in-situ* measurement and the *J*-*E*s, confirms the validity of the DWE measurement.



Figure 4-6. *In-situ* measurement of the electrocatalyst potential. E_{cat} measurement under illumination (red line) and in the dark (blue line) while stepping the potential of semiconductor (E_{sc}) (black line).



Figure 4-7. Superimposition of E_{cat} , steady-state current density, and *J-E* curve of the CuWO₄. (a) under illumination and (b) in the dark.





To investigate the fate of accumulated photogenerated holes in the electrocatalyst, we measured the current density through WE1 and WE2 (J_{sc} and J_{cat}) of CuWO₄+PPO|Ni75|Au device simultaneously. The potential-dependent current densities of the device under illumination and in the dark are composed of J_e (electron current density) and J_h (hole current density) (Figure 4-8) and can be described by the following equations:

In the dark:

 $J_{\rm sc} = J_{\rm e}$ $J_{\rm WE2} = J_{\rm cat} - J_{\rm e}$

Under illumination:

$$J_{\rm sc} = J_{\rm h} + J_{\rm e}$$
$$J_{\rm WE2} = J_{\rm cat} - J_{\rm h} - J_{\rm e}$$

If the hole transfer from the semiconductor valance band to the electrocatalyst be 100 percent efficient, the difference between the dark and illuminated currents measured of both working electrodes will be equal to the magnitude of $J_{\rm h}$. For the *in-situ* measurement of the current densities, we held the potential of the WE1 constant at 1.23 V *vs*. RHE while stepping the potential of WE2 (Figure A4-7).



Figure 4-8. Photogenerated hole transfer at the interface of semiconductor/electrocatalyst. Band bending diagram of the CuWO₄|Ni75|Au (a) in the dark and (b) under illumination.

Figure 4-9a shows the steady-state current density of CuWO₄ measured via WE1 under illumination and in the dark. Under illumination, J_{sc} is the anodic current generated by CuWO₄ photoanode and is equal to 0.15 m Acm⁻² at E_{sc} =1.23 V vs. RHE. However, in the dark, due to the lack of electron transfer at 1.23 V vs. RHE, the current remains negligible. Also, we measured the current density of the electrocatalyst under illumination and in the dark via WE2 (Figure 4-10b). The electrocatalyst current density in the dark remains negligible up to E_{sc} =1.6 V vs. RHE, which is the current onset potential of the electrocatalyst for water oxidation. By increasing the applied potential, the current density increases. Similar behavior is observed under illumination with a small difference compared to the electrocatalyst current density in the dark. Since the potential of the electrocatalyst is controlled via WE2 at a constant value, any photogenerated holes injected into the electrocatalyst from the semiconductor valance band should be artificially reduced by the potentiostat to maintain the constant potential. This results in a decrease of the measured current through WE2 under illumination by the magnitude of the semiconductor generated photocurrent. Our results show a small difference between J_{cat} under illumination and the dark, which suggests inefficient hole transfer from the semiconductor to the electrocatalyst.

We also measured the *in-situ* J_{sc} and J_{cat} under chopped illumination at various applied E_{cat} while E_{sc} held at 1.23 V vs. RHE (Figure 4-9c). Upon turning the light on, there is an anodic spike in J_{sc} that slowly reaches steady-state. The observance of an anodic spike after turning the light on is attributed to the charging of the electrocatalyst. However, after turning the light off, there is nearly zero current passing in the system. Figure 4-9d shows the zoom-in of the J_{cat} under chopped illumination with a negligible difference between J_{cat} under illumination and in the dark. The difference between the J_{sc} under illumination and the dark (ΔJ_{sc}) indicates the generated photocurrent density at the CuWO4 surface. By contrast, the ΔJ_{cat} , the difference between J_{cat} under illumination and in the dark, indicates the quantity of the photogenerated holes transferred from the semiconductor to the electrocatalyst. The ratio of $\Delta J_{cat}/\Delta J_{sc}$ then can be used to calculate the hole transfer efficiency from the semiconductor valence band to the electrocatalyst, which is a small number (~7%). These results suggest that the water oxidation reaction occurs almost exclusively at the surface of the CuWO4. This is consistent with the nominally identical *J-E* curves for the bare and catalyst modified electrodes displayed in Figure 4-3.



Figure 4-9. Photogenerated hole transfer at the interface of CuWO₄/Ni75. (a) The J_{sc} was measured under illumination, and in the dark from WE1, (b) the J_{cat} was measured under illumination and, in the dark from WE2 (c) the *in-situ* measurement of J_{sc} and J_{cat} under chopped illumination (d) zoom-in of J_{cat} under chopped illumination. All measurements were done by applying different catalyst potentials, while the semiconductor potential was held at 1.23 V vs. RHE.

Current transient measurements were also carried out to assess the charge transfer and recombination processes at the CuWO₄/Ni75 interface. The anodic and cathodic current transient for both bare and catalyst-coated CuWO₄ were measured in response to turning the light on and off, respectively, at constant E_{sc} 's stepped from 0.78-1.13 V vs. RHE (Figure A4-8). Examples of anodic and cathodic current transients for PPO modified CuWO₄ before and after the deposition

of Ni75 at an applied bias of 0.83 V (*vs.* RHE) are provided in Figure 4-10. Previous work on bare CuWO₄ photoelectrodes showed that, under illumination, such transient behavior upon turning the light on, which quickly decay to the steady-state current, is due to the accumulation of the photogenerated holes at the electrode surface before being transferred to the electrolyte.²⁰ Upon switching the light off, the accumulated holes at the surface recombine with the electrons from the conduction band, causing a cathodic spike that eventually reaches the steady-state level.

We observe similar behavior for the CuWO₄ electrodes modified with Ni75. However, it takes a longer time for CuWO₄ integrated with Ni75 to reach a steady-state current, and the total amount of charge that passes in the transient increases. The anodic transients are attributed to the oxidation of Ni²⁺ to Ni³⁺ by photogenerated holes in the valance band. This assignment agrees with the *in situ* measurement of the Ni75 potential under illumination via the DWE experiment, where the transfer of photogenerated holes from the semiconductor oxidizes the electrocatalyst. The cathodic transient, after turning the light off, is attributed to the reduction of Ni³⁺ to Ni²⁺ by electrons from the electrode conduction band, which takes a relatively long time to reach a steady-state. From current transient and DWE measurements, we conclude that surface state trapping and water oxidation from these states kinetically outcompetes oxidation of the electrocatalyst. This is surprising since previous reports have suggested slow water oxidation from the CuWO₄ surface.^{16,17,20}



Figure 4-10. Current transient measurement of the PPO modified $CuWO_4$ before and after Ni75 deposition. (a) Anodic current transients measured for a PPO modified $CuWO_4$ electrode (blue line) and after deposition of Ni75 (green line) in response to turning the light on. (b) Cathodic current transients after switching the light off. Electrodes were in contact with 1.0 M KB_i buffer at pH 9.0 at an applied bias of 0.83 V vs. RHE.

Figure 4-11 summarizes the charge transfer processes taking place at the interface of CuWO₄/electrolyte and CuWO₄/electrocatalyst. For the bare CuWO₄, the photogenerated holes

can be transferred from the valance band to the surface of the semiconductor, leading to the oxidation of surface states (ss) (1). These species may serve as intermediates to catalyze the water oxidation analogous to hematite (3). ^{21,50} Water oxidation from these surface states is in kinetic competition with surface state recombination (2), which results in suboptimal current onset potential. It has been generally shown that in the presence of an electrocatalyst, a direct hole transfer from the semiconductor to the electrocatalyst (4) can outcompete the kinetics of hole transfer to the surface, i.e., the oxidation of ss species, which in turn results in an improvement of the electrocatalytic performance.^{24,26} Storage of holes in the electrocatalyst introduces an additional recombination pathway for conduction band electrons (5). In contrast, we found that in the case of CuWO₄, a direct hole transfer from the semiconductor to the transfer from the semiconductor surface. ^{24,26} Storage of holes in the electrocatalyst introduces an additional recombination pathway for conduction band electrons (5). In contrast, we found that in the case of CuWO₄, a direct hole transfer from the semiconductor to the electrocatalyst layer is likely not an efficient process and thus cannot activate the electrocatalyst to drive water oxidation reaction. This suggests that the water oxidation process is likely to proceed directly at the underlying semiconductor surface. This suggestion is a highly plausible scenario considering that the Ni75 layer is permeable to the electrolyte solution.



Figure 4-11. Simplified illustration of charge transfer pathways at the interface. (a) bare and (b) Ni75coated CuWO₄ under illumination. Green arrows represent the favorable processes (hole transfer to surface stats (ss) (1) and to the electrocatalyst (4)), the dashed red arrows represent the unfavorable processes

(recombination of electrons with holes in ss (2) and with holes accumulated in the electrocatalyst (5)), and the blue arrow indicates hole collection at the interface for water oxidation from ss (3) and from the electrocatalyst (6). For simplicity, the $E_{F,p}$ under illumination, is not shown.

4.5 Conclusions

In this chapter, we presented a systematic study to understand the charge carrier dynamics at the interface of CuWO₄ with the electrocatalyst. Thin films of CuWO₄ were modified with PPO to eliminate shunting pathways and further integrated with Ni75 electrocatalyst. The DWE technique and transient current measurements were employed to study the interface of CuWO₄/Ni75. The DWE measurement demonstrated that the Ni75 catalyst at the surface of the CuWO₄ collects photogenerated holes from the semiconductor valance band and oxidize it to a positive potential. However, the electrocatalyst potential is not sufficient to drive the water oxidation reaction. The *in-situ* measurement of the current density in both semiconductor and the electrocatalyst demonstrated the fate of the photogenerated holes and provided evidence that the water oxidation reaction is likely happening at the surface of CuWO₄.

APPENDIX


Figure A4-1. Current density measurements during the electrodeposition of PPO into the CuWO⁴ **pinholes.** The progressive decrease in the current density indicates the growth of the insulating PPO film. Scan rates are 100 mV s⁻¹.



Figure A4-2. The role of PPO on insulating the exposed FTO of CuWO4. Dark CV responses of the bare CuWO4 (pink), and PPO-modified CuWO4 (blue) in 1.0 M KB_i containing 10 mM k4[Fe(CN)6] solution.



Figure A4-3. Surface roughness measurements of CuWO₄. (a) bare CuWO₄ and (b) CuWO₄ deposited with Ni75 via AFM.



Figure A4-4. PEC activity of CuWO₄ before and after deposition of a thin film of Ni75. *J*-*E* responses of bare CuWO₄ (pink line) and coated with a thin film of Ni75 (green line) measured in 1.0 M KB_i buffered at pH 9.0, and the scan rate is 20mVs⁻¹.



Figure A4-5. Electrocatalytic activity of Ni75 on FTO substrate. *J-E* response of the Ni75 electrocatalyst deposited on the FTO substrate in 1.0 M KB_i buffered at pH 9.0, and the scan rate is 20mVs⁻¹.



Figure A4-6. *J-E* responses of the Ni75-coated CuWO₄ before and after Au deposition. Before Au deposition (green line) and after Au deposition (blue line) measured in 1.0 M KB_i buffered at pH 9.0, and the scan rate is 20mVs⁻¹.



Figure A4-7. In-situ measurement of the catalyst and semiconductor current density. Esc held at 1.23

V vs. RHE while E_{cat} stepped from 0.93 to 1.7 V vs. RHE (a) Steady-state current density of the semiconductor under illumination (red) and in dark (black) (b) catalyst steady-state current density under illumination (red) and in the dark (black).



Figure A4-8. Anodic and cathodic current transients at different applied potentials *vs.* **RHE**. (a) PPO modified CuWO₄ and (b) PPO modified CuWO₄ deposited with Ni75.

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Chapter 5:

Photoelectrochemical and impedance spectroscopy investigation of water oxidation with catalyst coated electrodes

5.1 Abstract

The modification of semiconductor photoelectrodes with an electrocatalyst layer is a wellestablished approach to improve the electrode performance for the photoelectrochemical water oxidation process. However, unlike most metal oxide photoanode materials, including α -Fe₂O₃, this approach has not yet led to performance improvement for water oxidation at the CuWO₄ surface. To unravel the reason for this unusual behavior, in this chapter, we investigate and compare the charge carrier dynamics during water oxidation at the interface of α -Fe₂O₃ and CuWO₄ with the $Ni_{0.75}Fe_{0.25}O_{\nu}$ (Ni75) model electrocatalyst using dual working electrode photoelectrochemistry and photoelectrochemical impedance spectroscopy measurements. Our results revealed that the charge carrier recombination at the semiconductor/electrocatalyst interface limits a performance improvement for water oxidation at the electrocatalyst-modified electrode. We show that the deposition of Ni75 on the α -Fe₂O₃ results in a decrease of the interfacial carrier recombination. In sharp contrast, measurements showed an increase of the charge recombination at the CuWO₄ / Ni75 interface compared to that on the bare electrode. Our results shed light on the previously unknown role of charge carrier dynamics at the CuWO₄ / Ni75 interface and will be valuable to the future design of electrocatalysts materials for enhancing the performance of the CuWO₄-based photoanodes for PEC water oxidation.

5.2 Introduction

Photoelectrochemical impedance spectroscopy (PEIS) is a non-destructive technique where a small potential perturbation is applied to the system under illumination, and the phase shift and the amplitude of the resulting current are measured. This technique has been used extensively to characterize photoelectrode materials for photoelectrochemical (PEC) water oxidation, such as hematite (α -Fe₂O₃),¹⁻⁵TiO₂,^{6,7} BiVO₄,^{8,9} and CuWO₄¹⁰⁻¹². Recently this technique extended to study the charge carrier dynamic at the interface of photoelectrode with a cocatalyst.^{13–15} Hamann and coworkers have suggested a well-established equivalent circuit model for the interpretation of the PEIS result of hematite photoanode modified with Co-Pi cocatalyst.¹³ This equivalent circuit model comprises capacitance and resistance elements in parallel to model the system under study. Based on the PEIS results, the authors suggested the role of Co-Pi electrocatalyst on hematite photoanode as a hole storage layer, which enhances the charge separation in hematite and results in a cathodic shift of the photocurrent onset potential.

PEIS technique can also be used to get information about the kinetics of charge transfer and recombination at the photoelectrode interface with an electrolyte or a cocatalyst.^{15–18} Bisquert and coworker suggested a simple model to study the charge transfer and trap assisted recombination kinetics in a thin photoelectrode system under water splitting condition.¹⁸ Using this model, Gamelin and coworker demonstrated that upon deposition of Co-Pi on hematite photoanode, the kinetic of the water oxidation slows down, and the resulting performance enhancement is due to the even slower electron-hole recombination at the interface.¹⁹

PEIS has proven to be very useful for the mechanistic understanding of interfacial phenomena at the electrode/electrolyte and electrode/electrocatalyst interfaces toward designing advanced photoelectrode systems with higher efficiency for PEC water splitting. However, it is also essential to note that the interpretation of PEIS results heavily relies on the suggested model

for fitting the data. This often results in a substantial discrepancy in understanding the underlying charge transfer phenomena between reports in the literature. Here we show that combining dual working electrode (DWE) with EIS can address this critical challenge to provide an accurate picture of interfacial phenomena in the electrode/electrocatalyst system.

In this chapter, we study the charge carrier dynamics at the interface of α -Fe₂O₃ and CuWO₄ with Ni_{0.75}Fe_{0.25}O_y (Ni75) electrocatalyst using PEIS and DWEP measurements. Comparing these two important systems can boost understanding of the charge carrier dynamics at the interface of a photoelectrode with an electrocatalyst and will allow us to elucidate possible causes of the lack of improvement in PEC activity of CuWO₄ following the electrocatalyst deposition.

5.3 Experimental

5.3.1 Film preparation

Copper tungstate (CuWO₄) thin films were prepared on fluorine-doped tin oxide (FTO) substrate via atomic layer deposition (ALD) using a procedure reported previously and included in chapter 2.²⁰ 320 cycles of CuO were deposited on 2000 cycles of WO₃ according to a previous calculation to maintain 1:1 ratio of Cu and W. After deposition, the prepared film was annealed at 550 °C in air for 30 min with a ramping rate of 2 °C/min. The prepared film was then modified with poly (phenylene oxide) (PPO) to block the shunting pathways of the CuWO₄ film following the procedure reported in chapter 4.²¹

Hematite thin films were deposited on 2 nm Ga_2O_3 under layer via atomic layer deposition (ALD) (Savannah 100, Cambridge Nanotech Inc.) using the procedure described in chapter 3.²² Ga_2O_3 underlayer deposited on FTO substrate via ALD using a procedure described previously and is included in chapter 3.²³ The precursor for the hematite deposition was ferrocene, and wet

ozone was used as an oxidant. After deposition of 650 cycles of the ferrocene, the prepared film was annealed at 500 °C for 2 h and followed by annealing in the preheated furnace at 800 °C for 4 min.

5.3.2 Catalyst deposition

Ni_{0.75}Fe_{0.25}O_y (Ni75) catalyst was deposited at the surface of α -Fe₂O₃ and PPO modified CuWO₄ via spin coater from the precursor solution. Before the catalyst deposition, the CuWO₄ and α -Fe₂O₃ thin films were rinsed with water and dried with N₂. The precursor solution for catalyst deposition was consist of Iron (III) 2-ethyl hexanoate (50 % w/w in mineral spirits, Strem Chemicals), and nickel (II) 2-ethyl hexanoate (78% w/w in 2-ethyl hexanoic acid, Strem Chemicals), which was diluted with hexane to obtain a total metal concentration of 50 mM. Approximately 200 µL of the precursor solution was added at the substrate surface, and then spinning was performed at 3000 rpm for 60 s. The prepared films were illuminated under UV light (254 nm, 4W) for 2 h and further annealed at a preheated furnace at 100 °C for 1 h.

5.3.3 DWE fabrication

Two types of DWE devices were prepared after catalyst deposition, CuWO₄|Ni75|Au and α -Fe₂O₃|Ni75|Au.²⁴ The copper wire was connected to the underlying substrate via silver paste to make it the first working electrode (WE1). Then, all the electrical connections were covered with epoxy (Loctite Hysol 1C) to keep them isolated from the solution during the measurements. A 12 nm Au film was evaporated on the electrocatalyst surface and the epoxy around the electrode using a vacuum thermal evaporator. The second working electrode (WE2) was made by connecting the copper wire via silver paste to the gold at the epoxy surface. The first working electrode was inserted inside a glass tube, and then the second working electrode coiled around it and kept in a second glass tube.

5.3.4 (Photo)electrochemical measurements

DWE devices and bare electrodes were assembled and measured in a custom-made electrochemical cell. All (photo) electrochemical measurements were done in 0.5 M KB_i buffered at pH 11.0. Electrodes potentials were scanned with respect to the Ag/AgCl reference electrode, and a platinum mesh was used as a counter electrode. All electrochemical potentials were converted to the reversible hydrogen electrode (RHE) by the equation $E_{RHE} = E_{Ag/AgCl} + 0.197 + pH (0.059)$. Current density *vs.* applied potential (*J-E*) responses were measured by a scan rate of 20 mVs⁻¹. The white light source was the same as described in chapter 2. All photoelectrochemical measurements were performed in a back-illumination configuration (photons were passing the glass side of the FTO substrate before reaching the electrode surface). Photoelectrochemical impedance spectroscopy (PEIS) was performed with 10 mV amplitude perturbation and frequency range from 0.04 Hz to 15 kHz in the same supporting electrolyte solution under 1 sun illumination. Zview software (Scribner Associates) was used for data analysis and fitting.

5.4 Results and discussion

CuWO₄ and α -Fe₂O₃ thin films were deposited on fluorine-doped tin oxide (FTO) substrate via atomic layer deposition (ALD) followed by deposition of about 220 nm of Ni_{0.75}Fe_{0.25}O_y (Ni75) thin films electrocatalyst. We chose Ni75 as an electrocatalyst because of its high electrocatalytic activity for water oxidation reaction.²⁵ Current density (*J*) responses of bare and Ni75-coated α -Fe₂O₃ and CuWO₄ photoelectrodes were measured as a function of applied potential (*E*) in contact with 0.5 M KB_i buffered at pH 11.0 under illumination. Figure 5-1a shows the comparison of *J*-*E* responses for α -Fe₂O₃, where catalyst modification causes a 400-mV cathodic shift of the photocurrent onset potential and a photocurrent enhancement. This result is consistent with the result in chapter 3 (Figure 3-8b) and literature,^{13,24,26,27} where electrode modification with an electrocatalyst can improve the electrode performance for PEC water oxidation. In contrast, the deposition of Ni75 does not improve the PEC performance of the CuWO₄ electrode (Figure 5-1b). Indeed, the anodic feature of the *J-E* response of the Ni75-modified CuWO₄ remains nearly the same as the bare electrode. However, the cathodic scan shows a capacitive peak at 0.9 V *vs*. RHE, which can be assigned to the reduction of Ni³⁺ to Ni²⁺.



Figure 5-1. Effect of an electrocatalyst on PEC performance of α -Fe₂O₃ and CuWO₄. *J*-*E* responses of (a) bare α -Fe₂O₃ (red line) and after Ni75 deposition (black line), (b) bare CuWO₄ (red line), and after Ni75 deposition (black line). The scan rates are 20 mVs⁻¹.

The lack of performance improvement of CuWO₄ photoanode after deposition of Ni75 electrocatalyst was studied in chapter 4 using DWEP and current transient measurements, and it was attributed to the inefficient hole transfer from the photoelectrode valance band to the electrocatalyst. We hypothesized that water oxidation on CuWO₄ surface kinetically outcompetes electrocatalyst oxidation, and surface state recombination limits water oxidation efficiency on this material. However, a more detailed analysis of this system is necessary to support our hypothesis.

A systematic comparison between CuWO₄ and α -Fe₂O₃ photoelectrodes can provide useful insights regarding the role of electrode/electrocatalyst interface on the PEC performance for water oxidation. This can also help to elucidate the origin of lack of activity improvement on CuWO₄ following the electrocatalyst deposition.

Our approach for studying the electrode/electrocatalyst interface in CuWO₄ and α -Fe₂O₃ photoelectrodes is based on dual working electrode (DWE) technique as described in the previous chapter. Additionally, we performed electrochemical impedance spectroscopy (EIS) on α -Fe₂O₃|Ni75|Au and CuWO₄|Ni75|Au in DWE configuration. Figure 5-2a shows the post conditioned *J*-*E* responses of the α -Fe₂O₃|Ni75|Au device. The *J*-*E* response measured via working electrode 1 (WE1) under back illumination condition (solid black line) is similar to that obtained for the regular electrode without the Au layer, suggesting the validity of α -Fe₂O₃|Ni75|Au device for DEW experiment (see the previous chapter for more details). Likewise, the *J*-*E* response measured via WE2 is similar to that of Ni75 on the FTO substrate (Figure A5-2a) with the Ni^{2+/3+} redox wave centered at 1.5 V vs. RHE. This indicates that the gold film at the electrocatalyst surface is sufficiently porous and allows the free movement of ions in the electrolyte.

Next, we measured the steady-state potential of the Ni75 electrocatalyst at the surface of α -Fe₂O₃ photoelectrode via WE2 in the dark and under illumination conditions and a stepwise potential increase of the WE1. In the dark, the electrocatalyst overlayer can only be oxidized at anodic biases through the leakage current from α -Fe₂O₃. However, due to the lack of leakage current in the studied range of potential, the electrocatalyst potential remains nearly constant (dashed blue line). In contrast, the transfer of photogenerated holes under illumination from the α -Fe₂O₃ valance band to the electrocatalyst film can oxidize Ni²⁺ to Ni³⁺. The oxidized Ni75 is electrically conductive, and therefore, its potential can be sensed via WE2. Figure 5-2b (solid blue

line) shows a sharp transition of electrocatalyst potential (0.8 V to 1.45 V vs. RHE) that occurs at E_{sc} =0.8 V vs. RHE. The difference between the electrocatalyst potential under illumination and the dark is due to the photovoltage build-up at the α -Fe₂O₃/Ni75 interface. A recent DWE study of the α -Fe₂O₃|Ni_{0.8}Fe_{0.2}O_x system by Boettcher and coworkers suggested that the kinetic of hole transfer to the electrocatalyst overlayer outcompetes direct water oxidation on α -Fe₂O₃.²⁴ The transfer of the photogenerated holes from the α -Fe₂O₃ valence band can sufficiently oxidize the electrocatalyst overlayer, thus making it suitable to perform water oxidation. Our DWE results for α -Fe₂O₃ in Figure 5-2, thus agree well with the results presented by the Boettcher group.²⁴ However, the results of the DWE characterization obtained from the CuWO₄|Ni75|Au, as described below, suggest a different dynamic of the charge carrier transfer could likely exist at the interface of the CuWO₄|Ni75| electrolyte for water oxidation.

Figure 5-3a shows the post conditioned *J-E* responses for the CuWO₄|Ni75|Au. Direct measurement of the Ni75 potential via WE2 under illumination (Figure 5-3b) shows a sharp transition from 0.9 to 1.43 V vs. RHE at CuWO₄ potential of 0.9 V vs. RHE, similar to what observed for the α -Fe₂O₃|Ni75|Au albeit at different potential (Figure 5-2b). Based on the measured steady-state catalyst potentials (Figure 5-4), we conclude a lower degree of catalyst charging on CuWO₄ at the cathodic range compared to that on α -Fe₂O₃. The results suggest that in the case of CuWO₄, the kinetic of hole transfer to the surface states likely outcompete the electrocatalyst oxidation, in sharp contrast with the hole transfer dynamic at the α -Fe₂O₃/Ni75 interface. They also suggest significant recombination of charge carriers at the interface of CuWO₄/Ni75 at lower applied potentials. In other words, there is a high chance for photogenerated holes to recombine with conduction band electrons in CuWO₄ before transferring to the electrocatalyst layer.



Figure 5-2. DWE PEC characterization of α -Fe₂O₃|Ni75|Au. (a) *J*-*E* responses of α -Fe₂O₃ measured under illumination (solid black line) and in the dark (dashed black line) and the Ni75 at the surface of the α -Fe₂O₃ (blue line) measured from WE1 and WE2, respectively. (b) *E*_{cat} measurement under illumination (solid blue line) and in the dark (dashed blue line) while stepping the potential of semiconductor (*E*_{sc}) (black line).



Figure 5-3. DWE PEC characterization of CuWO₄|Ni75|Au. *J*-*E* responses of CuWO₄ measured under illumination (solid black line) and in the dark (dashed black line), and the Ni75 at the surface of the α -Fe₂O₃ (blue line) measured from WE1 and WE2, respectively. (b) E_{cat} measurement under illumination (solid blue line) and in the dark (dashed blue line) while stepping the potential of semiconductor (E_{sc}) (black line).



Figure 5-4. Superimposition of E_{cat} that is measured via WE2 (blue sphere), steady-state current density (black sphere), measured via WE1 during the *in-situ* measurement of E_{cat} , and their representative *J-E* curves. (a) α -Fe₂O₃|Ni75|Au, (b) CuWO₄|Ni75|Au.

To gain a better understanding of the interfacial charge carrier dynamics, we complemented the direct potential measurements of the electrocatalysts above with EIS measurements in the DWE configuration. EIS can provide information about the capacitance related to surface state and electrocatalyst for bare and electrocatalyst-modified photoelectrode, respectively. Thus, we performed EIS measurements of bare α -Fe₂O₃ and CuWO₄ electrodes for the evaluation of surface state capacitance and charge transfer resistance to their interfaces with the electrolyte. Also, we performed EIS measurements of the DWE devices from both WE1 and WE2 as a function of applied potential to the semiconductor and the electrocatalyst, respectively. This way, we can proceed to analyze the electrocatalyst capacitance from both WEs.

Figure 5-5 displays examples of illuminated Nyquist plots at an applied potential of 0.93 V vs. RHE for both bare and Ni75-coated α -Fe₂O₃ (examples of Nyquist plots at higher applied potentials are provided in the Appendix, Figure A5-1). Two capacitive elements are visible for the bare electrode around the photocurrent onset potential (Figure 5-5a). According to the previous studies,^{5,28} these two capacitive elements can be attributed to the space charge capacitance and chemical capacitance due to the build-up of holes on the surface, i.e., surface states capacitance, C_{ss} . Likewise, the obtained Nyquist plot for the Ni75 coated α -Fe₂O₃ electrode exhibits two capacitive elements (Figure 5-5b, also see Figure A5-1). However, the measured low-frequency semicircles are much smaller for the electrocatalyst coated electrode compared to the bare ones. Hamann and coworkers assigned the low-frequency capacitive features for α -Fe₂O₃/Co-Pi to the electrocatalyst capacitance, evidenced by observing an increase in the electrocatalyst capacitance with an increase of the Co-Pi thickness.¹³ The obtained Nyquist plots under illumination from the bare and electrocatalyst coated CuWO₄ electrodes also show two capacitive features (Figure A5-2). The Bode plots of the CuWO₄ electrodes are also presented in Figure A5-2.



Figure 5-5. Nyquist plots of α -Fe₂O₃ before and after electrocatalyst deposition. (a) bare α -Fe₂O₃ electrode and (b) with Ni75 at 0.90 V *vs*. RHE in 0.5 M of KB_i, pH 11.0, under 1 sun illumination.

We used a previously established equivalent circuit model^{10,13} to fit the EIS data of the bare photoelectrodes with two capacitive features (Figure 5-6). The proposed equivalent circuit model consists of the bulk capacitance (C_{bulk}), the series resistance from the bulk of the photoelectrode, electrical contacts, and electrolyte (R_s), the resistance related to the rate of holes trapping in the surface states (R_{trap}), the capacitance of the surface states (C_{ss}), and the charge transfer resistance from surface states ($R_{ct,ss}$). Additional electrical components are added to the equivalent circuit when the semiconductor photoanode comes in contact with the Ni75 electrocatalyst, including the capacitance of the Ni75 overlayer (C_{Ni75}), and the charge transfer resistance from the Ni75 overlayer to the electrolyte ($R_{ct, Ni75}$). Figure 5-6a shows the full equivalent circuit for the interpretation of the EIS data from our DWE devices. Because of its complexity, this equivalent circuit cannot properly be used to fit the EIS data. Therefore, we use a simplified version of the equivalent circuit shown in Figure 5-6b. We used a Randles circuit model to fit the EIS data in the dark and under illumination with only one capacitive feature (Figure 5-6c).



Figure 5-6. Proposed equivalent circuit model for interpretation of EIS results of bare electrodes. The model was used for fitting the EIS result of bare α -Fe₂O₃ and CuWO₄ electrodes under illumination when two semicircles were visible.



Figure 5-7. Proposed equivalent circuit models for fitting the EIS results of catalyst-coated electrodes. (a) the full equivalent circuit for DWE device, (b) simplified equivalent circuit for interpretation of EIS results when two semicircles are visible in the Nyquist plot, and (c) Randal circuit when there is only one semicircle is visible or in the dark.

Figure 5-8a and b show plots of C_{ss} and C_{Ni75} vs. applied potentials for the bare and Ni75coated α -Fe₂O₃ and CuWO₄, respectively. C_{Ni75} was also measured via WE2 as a function of applied potential to the electrocatalyst overlayer (Figure 5-8a, blue spheres). As shown in Figure 5-8a, both C_{ss} (extracted from the EIS result of the bare α -Fe₂O₃) and C_{Ni75} (extracted from the EIS result of WE1) show a peak with maxima around the photocurrent onset potential (Figure 5-1a). An increase of the C_{ss} as a function of applied potential can be assigned to the accumulation of the photogenerated hole at the electrode surface that contributes to the formation of the water oxidation intermediates.¹ This is followed by the participation of the intermediate species in the oxidation process that can be inferred from a decrease of the C_{ss} at anodic potentials. In Figure 5-8a, a similar trend is observed after deposition of the catalyst, an increase of the C_{Ni75} followed by its decrease at anodic potentials. However, the overall capacitance values substantially increased after the catalyst deposition (C_{Ni75} is substantially larger than the C_{ss} at all applied potentials). The increase of capacitance values for α -Fe₂O₃ after electrocatalyst deposition can be assigned to the direct transfer of photogenerated holes from the valance band to the electrocatalyst, which agrees with the result of DWE measurement.¹³

For the α -Fe₂O₃|Ni75|Au, the measured C_{Ni75} values from the WE2 also show a peak with the maxima around the current onset potential of the electrocatalyst for water oxidation (Figure 5-8a, blues spheres; also see Figure 5-2a). For reference, we also measured C_{Ni75} from the Ni75|FTO electrode, which showed a trend similar to that observed for the WE2 in α -Fe₂O₃|Ni75|Au (Figure A5-3). In Figure 5-8a, the peak maxima value for the C_{Ni75} measured from the WE1 (data shown in black spheres) and WE2 (data shown in blue spheres) are almost equal. This implies that the electrocatalyst is fully oxidized by the accumulation of photogenerated holes from the α -Fe₂O₃ valance band and reaches sufficient potential to drive water oxidation reaction. The capacitance (C) values were also calculated for the CuWO₄|Ni75|Au and bare CuWO₄ electrodes from fitting the Nyquist plot and plotted as a function of applied potential (Figure 5-8b). Interestingly, in contrast to the α -Fe₂O₃ case, the obtained C_{Ni75} values (black spheres in Figure 5-8b) remain close to the C_{ss} (red spheres in Figure 5-8b), suggesting that the transfer of photogenerated holes from CuWO₄ valance band to the electrocatalyst is not efficient. This can also be inferred by comparing the peak maxima for the C_{Ni75} values obtained from the WE1 to that obtained from the WE2 (blue sphere in Figure 5-8b). In other words, a larger value for the C_{Ni75} peak maxima from WE2 compared to that from the WE1 indicates that the kinetics of hole transfer to the surface outcompetes oxidation of the electrocatalyst, thus supporting our hypothesis (in Chapter 4) that water oxidation should primarily proceed on CuWO₄, rather than the electrocatalyst, surface.



Figure 5-8. Plots of parameters extracted from fitting the EIS data. (a, b) C_{Ni75} , and (b, c) $R_{\text{ct, Ni75}}$ obtained from fitting EIS response of bare catalyst coated electrode (a) C_{ss} and $R_{\text{ct, ss}}$ are shown for comparison.

We have also obtained the values for the $R_{ct,Ni75}$ (Figures 5-8c-d) for WE1 and WE2. The $R_{ct, ss}$ values are also included for the comparison, showing a decrease of the charge transfer resistance after the integration of the electrodes with Ni75. The decrease of the charge transfer, however, is more evident for the α -Fe₂O₃. As expected, the potential at which the maximum C_{Ni75} has observed matches that of the minimum charge transfer resistance from Ni75 overlayer (R_{ct} ,

Ni75). As a cross-check, the total resistance (R_{tot}) was calculated from PEIS, ($R_s+R_{ct,ss \text{ or Ni75}}+R_{trap}$), and was compared to the resistance derived directly from *J-E* curves. There is an agreement between these two independent data sets (Figure A5-4).

Bisquert and the coworker suggested a simple model for the kinetic of the hole and electron transfer in a thin film of the semiconductor under the water oxidation condition.¹⁸ According to their model, the ratio of $R_{\text{trap}}/R_{\text{ct, ss}}$ for bare electrodes, and $R_{\text{trap}}/R_{\text{ct, Ni75}}$ for the Ni75-coated electrodes are proportional to the ratio of charge transfer to recombination rate constants. Figure 5-9a and b show the comparison of the ratio of $R_{\text{trap}}/R_{\text{ct, Ni75}}$ to the ratio of $R_{\text{trap}}/R_{\text{ct, ss}}$ as a function of applied potentials. Improvement of the photocurrent onset potential for Ni75-coated α-Fe₂O₃ can be ascribed to a faster charge transfer to the electrocatalyst compared to the bare electrode, which outcompetes the interface recombination. For Ni75-coated CuWO₄, on the other hand, the $R_{\text{cat}}/R_{\text{ct}}$ ratio is low and essentially constant compared to the bare electrode, which indicates that fast recombination at the CuWO₄/Ni75 interface can inhibit an improvement of the electrode performance for PEC water oxidation. These results are also in agreement with the results of DWE measurements and explain the lack of performance improvement for the CuWO₄ following the deposition of an electrocatalyst on its surface. Based on our results, we hypothesize that deposition of a very thin layer of surface passivator, such as Al₂O₃, at the interface of CuWO₄/Ni75 could potentially contribute to a performance improvement through passivation of surface states and reducing recombination of charge carrier.



Figure 5-9. The comparison of $R_{trap}/R_{ct,ss}$ for bare and $R_{trap}/R_{ct,Ni75}$ for electrocatalyst coated electrodes. (a) α -Fe₂O₃ (b) CuWO₄.

5.5 Conclusions

In this chapter, we investigated the interfaces of α -Fe₂O₃ and CuWO₄ with Ni75 electrocatalyst using DWEP and PEIS techniques. *In-situ* analysis of the electrocatalyst potential via DWEP measurements demonstrated the transfer of the photogenerated holes in α -Fe₂O₃ and CuWO₄ to the electrocatalyst, which oxidizes the Ni75 overlayer to a suitable potential for driving water oxidation reaction. However, the PEIS results revealed a difference in the rate of interfacial carrier recombination in these two systems. We found an increase in the rate of charge carrier recombination for the CuWO₄ photoelectrode following the electrocatalyst deposition. In sharp contrast, the rate of recombination is much slower for the Ni75-coated α -Fe₂O₃ comparing to the bare system. Based on these results, we conclude that interfacial charge carrier recombination at CuWO₄ /electrocatalyst interface is the major factor that largely limits efficient hole transfer to the catalyst, thus leading to a lack of performance improvement for water oxidation on the electrocatalyst-modified electrode compared to that on the bare CuWO₄ photoanode. APPENDIX



Figure A5-1. Nyquist plots of α -Fe₂O₃ before and after electrocatalyst deposition at 1.1 V vs. RHE. The Nyquist plots of (a) bare α -Fe₂O₃ (b) α -Fe₂O₃ |Ni75 were measured under illumination.



Figure A5-2. Nyquist and Bode plots of CuWO₄ before and after electrocatalyst deposition at 0.93 V vs. RHE. The Nyquist plots of (a) bare CuWO₄ (b) CuWO₄|Ni75 and Bode plots of (c) bare CuWO₄ (d) CuWO₄|Ni75 measured at 0.93 V vs. RHE under illumination.

Figure A5-2. (cont'd).



Figure A5-3. *J-E* and EIS results of Ni75 on FTO substrate. (a) *J-E* response of the Ni75 electrocatalyst on FTO substrate (b) C_{Ni75} (c) $R_{\text{ct, Ni75}}$ obtained from fitting EIS data of the Ni75 on FTO substrate.



Figure A5-4. The agreement between R values extracted from PEIS and *J*-*E* curves. R_{tot} calculated from PEIS data (black circles) and *J*-*E* curves (dashed lines) for bare and Ni75 coated electrodes.

Table A5-1. Parameters extracted from fitting EIS data of bare α -Fe₂O₃. The measurements were done in 0.5 M KB_i, pH 11.0 under illumination. Surface area, 0.062 cm².

E / V vs.	E / V vs.	$R_{ m s}$ / Ω	C_{bulk}/F	$R_{ m trap}/\Omega$	$C_{\rm ss}/{ m F}$	$R_{ m ct,ss}/$ Ω
Ag/AgCl	RHE					
-0.249	0.598	245.8	1.28E-07	3551	9.09E-07	7.56E+06
-0.083	0.764	240.1	1.12E-07	4668	5.81E-06	1.62E+06
0.083	0.930	242.6	1.02E-07	6967	4.91E-06	2.00E+05
0.25	1.097	240.4	9.39E-08	7815	3.82E-06	43606
0.416	1.263	227.6	8.59E-08	6548	3.27E-06	6652

Table A5-2. Parameters extracted from fitting EIS data of WE1 of α -Fe₂O₃|Ni75|Au. The measurements were done in 0.5 M KB_i, pH 11.0 under illumination. Surface area, 0.024 cm².

E / V vs.	E / V vs.	$R_{ m s}$ / Ω	$C_{\rm bulk}/{ m F}$	$R_{ m trap}/\Omega$	$C_{ m Ni75}/ m F$	$R_{ m ct, Ni75}/ \ \Omega$
Ag/AgCl	RHE					
-0.25	0.597	459.6	2.94E-07	2878	1.01E-06	5.97E+05
-0.0832	0.764	429.9	2.07E-07	2626	1.04E-05	22498
0.0832	0.930	424.2	1.85E-07	3557	3.12E-05	4360
0.25	1.097	422	1.71E-07	4796	1.38E-05	3736
0.416	1.263	413.6	1.49E-07	5209	1.57E-06	4605
0.58	1.427	426.1	1.41E-07	6676	1.44E-06	6034

Table A5-3. Parameters extracted from fitting EIS data of bare CuWO₄. The measurements were done in 0.5 M KB_i, pH 11.0 under illumination.

E / V vs.	<i>E</i> / V <i>vs</i> .	$R_{ m s}$ / Ω	$C_{ m bulk}/ m F$	$R_{ m trap}/\Omega$	$C_{\rm ss}/{ m F}$	$R_{ m ct,ss}/$ Ω
Ag/AgCl	RHE					
-0.25	0.609	207.1	1.06E-05	1408	1.15E-05	1448
-0.083	0.776	215.9	6.89E-06	4935	1.59E-05	15536
0.083	0.942	215.7	4.44E-06	3009	2.23E-05	5539
0.25	1.109	213.2	3.52E-06	5339	9.63E-06	6086
0.416	1.273	211.9	3.08E-06	7024	6.08E-06	7401

Table A5-4. Parameters extracted from fitting EIS data of WE1 of CuWO₄|Ni75|Au. The measurements were done in 0.5 M KB_i, pH 11.0 under illumination.

E / V vs.	E / V vs.	$R_{ m s}$ / Ω	$C_{\rm bulk}/{ m F}$	$R_{ m trap}/\Omega$	$C_{\rm ss}/{ m F}$	$R_{ m ct,ss}/$ Ω
Ag/AgCl	RHE					
-0.25	0.60892	213.5	3.59E-06	1080	6.65E-06	5552
-0.083	0.77592	215.7	2.57E-06	2336	3.32E-06	43136
0.083	0.94192	217.8	2.16E-06	2391	5.09E-06	9001
0.25	1.10892	212.7	1.67E-06	1735	2.44E-06	10564
0.416	1.27492	212	1.46E-06	1587	2.04E-06	9022

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Chapter 6:

Investigation of photoelectrochemical

water oxidation intermediates on CuWO₄ surface via operando ATR-IR

spectroscopy

6.1 Abstract

Understanding the nature of surface states is highly essential for developing a mechanistic picture of water oxidation on the semiconductor surface. There are only a few reports with different perspectives on the nature of CuWO₄ surface species. Here, we study the water oxidation reaction on the CuWO₄ surface employing operando ATR-IR spectroscopy to identify the role of surface states unambiguously. We performed the *in-situ* experiment as a function of illumination and applied potential. We found an absorption peak growing at 750 cm⁻¹ and 1100 cm⁻¹ under water oxidation condition, which can be attributed to the *oxo* and *superoxo* species, respectively. These results provide evidence regarding the nature of surface states as water oxidation intermediate on CuWO₄ photoelectrode.

6.2 Introduction

The CuWO₄/electrolyte interface plays an essential role in surface-related phenomena, charge carrier separation, and transfer to the electrolyte. For example, the recombination of electrons and photogenerated holes at the surface of the CuWO₄ is one of the significant efficiency losses that competes with hole transfer to the electrolyte.¹ Therefore, a clear understanding of the surface electrochemistry of CuWO₄ is vital for improving water oxidation efficiency. There are only a few reports on the role of CuWO₄ surface states with different perspectives. Bartlett and coworkers demonstrated the nature of CuWO₄ surface states as intrinsic states composed of Cu-(3d) orbitals.² However, recent work based on photoelectrochemical (PEC) and electrochemical impedance spectroscopy (EIS) measurements demonstrated the role of the CuWO₄ surface states with charging the surface states with photogenerated holes accounts for the first oxidative step of water oxidation. However, direct evidence of this intermediate species yet to be provided.

Recently, Hamann and Zandi demonstrated the implementation of operando ATR-IR PEC as a novel approach for chemical detection of intermediate surface species during water oxidation on hematite photoanode.⁴ Employing this technique, the first experimental observation of high valent iron oxo (Fe^{IV}=O) as water oxidation intermediate with an absorption feature at 898 cm⁻¹ was provided. Later, the subsequent rate-determining step of O-O bond formation was identified by observation of superoxide species via FT-IR analysis. ⁵ These superoxide intermediates have an IR absorption at 1100 cm⁻¹ and only are produced at near-neutral pH (8-10).

In this chapter, we employed the operando ATR-IR PEC approach to identify the nature of CuWO₄ surface states under PEC water oxidation condition. For the *in-situ* measurement, we probed the electrode surface as a function of illumination and potential. Under the PEC water

oxidation condition, IR absorption peaks are growing at 730 cm⁻¹ and 1100 cm⁻¹, which can be attributed to the *oxo* and *superoxo* surface species, respectively.

6.3 Experimental

6.3.1 CuWO₄ thin-film preparation

CuWO₄ thin films were prepared on fluorine-doped tin oxide (FTO)-coated glass substrate (Hartford Glass, TEC 15, 12 Ω cm⁻²) via spray pyrolysis method using a modified procedure from the literature.⁶ For the *in-situ* measurement, FTO substrates were cut in 1.5×6 cm. Two small holes were made on both sides of the substrate for holding the reference and counter electrode during the (photo)electrochemical measurement. FTO substrates were cleaned by sequential sonication in soap, water, 0.1 M HCl in ethanol, isopropyl alcohol, and acetone for about 15 min each and followed by drying in an N₂ stream. An aqueous precursor solution consists of 0.01 M of Cu (II), and 0.01 M of W (VI) was prepared from CuCl₂.2H₂O (Sigma-Aldrich, \geq 99.0%,) and (NH₄)₆H₂W₁₂O₄₀ (Alfa Aesar, metal impurity \leq 0.1%). For CuWO₄ thin film deposition, the FTO substrate was placed on a hot plate at a distance of 31 cm from the nozzle and heated to 275 °C. The precursor solution was then sprayed onto the substrate for a deposition pulse of 1 s and a resting pulse of 5 s. The as-prepared film was then annealed at 550 °C in air for 1 h with 1 h ramping time. Scheme 6-1 shows the experimental setup for CuWO₄ preparation by the spray pyrolysis method.



Scheme 6-1. Experimental setup for CuWO₄ preparation by spray pyrolysis method.

6.3.2 Film characterization

The composition of prepared films was determined by employing the energy-dispersive Xray (EDX) analysis. EDX spectra were collected using Ametek-EDAX Apollo X. The accelerating voltage for the EDX measurement was 20 kV, with 8 mm working distance. The X-ray photoelectron spectroscopy (XPS) analysis was performed at a takeoff angle of 45° using a Perkin Elmer Phi 5600 ESCA system with a magnesium K α X-ray source. The thickness of the CuWO₄ film was determined to be 1.5 µm by cross-sectional scanning electron microscopy (SEM) (Carl Zeiss Microscopy).

6.3.3 (Photo)electrochemical measurements

CuWO₄ electrodes were prepared by connecting a copper wire to the underlying FTO substrate (sandpaper was used to remove the CuWO₄ film) using a silver paste, and then the electrical connection was covered with an insulating epoxy. Because the penetration depth of the ATR beam is only a few microns, a thin layer of the electrolyte (20µL of 0.1 M KCl in D₂O (pH=7.3), or 1.0 M KB_i in H₂O (pH=9)) was introduced between ZnSe ATR crystal and CuWO₄ photoanode. A homemade Ag/AgCl and a Pt wire were used as reference and counter electrodes (CE), respectively. The reference and CE were mounted through the small holes (contained a droplet of electrolyte) from the backside of the CuWO₄ working electrode to be electrically in

contact through the thin electrolyte layer. A Teflon holder was used to hold the CuWO₄ electrode tightly in place. A UV LED flashlight (395 nm) was used as a source of light for the PEC measurement. Scheme 6-2 and 6-3 show the experimental setup for operando PEC infrared (IR) measurements. All electrochemical potentials in KB_i buffer were reported with respect to the reversible hydrogen electrode (RHE) by using the equation $E_{RHE} = E_{Ag/AgC1} + 0.197 \text{ V} + (0.059 \text{ V}) \times pH$



Scheme 6-2. Schematic of the experimental setup for operando PEC infrared (IR) measurements. The setup depicts the CuWO₄ working electrode (WE), platinum counter electrode (CE), Ag/AgCl reference electrode (RE), and ZnSe ATR crystal. A thin layer of electrolyte between the CuWO₄ and the ATR crystal was introduced.



Scheme 6-3. 3D view of the electrochemical setup.

6.3.4 In-situ PEC-IR measurements

IR spectrums were measured using a Magna-IR 550 Spectrometer using a Gateway Flow-Through Top-plate cell multi reflection ATR setup (Specac). A 45° angle ZnSe crystal was used with the cut-off energy of ~ 625 cm⁻¹. We performed the *in-situ* measurement as a function of illumination and potential. Each IR spectrum was obtained by averaging 64 scans at the resolution of 4 cm⁻¹ and corrected for background before each measurement. For the *in-situ* electrochemical measurements, we used a micro-Autolab potentiostat.

6.3.5 Results and discussion

The prepared CuWO₄ thin films via the spray pyrolysis method were characterized using various techniques. The elemental compositions were mapped using energy-dispersive X-ray spectroscopy (EDX) with the measured tungsten to copper ratio of approximately 1:1, as expected (Figure A6-1). The X-ray photoelectron spectroscopy (XPS) analysis shows W 4f, Cu 2p, and O 1s peaks of the CuWO₄ film (Figure A6-2). Cross-section scanning electron micrograph (SEM) of CuWO₄ shows a film thickness of about 1.5 μ m (Figure 6-1a). The top-view SEM images (Figure 6-1b) shows the surface morphology of the continuous film and CuWO₄ crystallites. The current density (*J*) *vs.* applied potential (*E*) responses of the CuWO₄ photoanode was measured for water oxidation reaction under illumination and in the dark (Figure 6-2a). The *J-E* response of the electrode here is in good agreement with the *J-E* response of electrodes prepared via ALD, which is presented in previous chapters.



Figure 6-1. Scanning electron micrographs images of the CuWO₄ **photoelectrode.** (a) Cross-section view, and (b) top-view.

We performed electrochemical impedance spectroscopy (EIS) measurement of CuWO₄ electrode under PEC water oxidation at various applied potentials. Figure 6-2b shows an example of a Bode plot that is measured under illumination at 0.9 V vs. RHE. We display the Bode plot instead of the Nyquist plot for better clarity, as in some cases, the semicircles in Nyquist plots are merged (Figure A6-3). The Bode plots under illumination exhibit two capacitive elements around the photocurrent onset potential. These capacitive elements correspond to the space charge capacitance, and chemical capacitance due to the build-up of holes on the surface, i.e., surface states capacitance, C_{ss} .⁷ We used a previously established equivalent circuit model^{8,3} to fit the EIS data (Figure A6-4, the parameters extracted from fitting the EIS data are provided in the Appendix).

Figure 6-2c shows the C_{ss} at various applied potentials. The C_{ss} exhibits a Gaussian peak with the maxima around the photocurrent onset potential (1.05 V vs. RHE), which was attributed to the surface hole accumulation.⁹ We also measured charging and de-charging of surface states by cyclic voltammetry (CV) (Figure 6-2d). The CVs were recorded in the dark immediately after applying a constant potential of 1.6 V vs. RHE for 60 s to the CuWO₄ electrode under illumination. At this potential, holes get trapped at the surface and oxidize the surface states. Then scanning the electrode potential negatively in the dark reduces these states, resulting in a negative peak in current at their specific energy, which disappeared in the second scan. The results of C_{ss} from EIS measurement and the reduction peak in CV measurement suggest the role of surface states as build-up intermediates at the surface of CuWO₄ during PEC water oxidation and agrees with previous work.⁹



Figure 6-2. The investigation of the role of CuWO₄ surface states during water oxidation. a) *J-E* responses of CuWO₄ electrode measured in 1.0 M KB_i (pH=9) in the dark (dashed black line) and under illumination (solid red line). b) the Bode plot measured at 0.9 V vs. RHE under illumination. c) Surface states capacitance is measured at various applied potentials under illumination. d) CV curves scanned in the dark at 100 mV s⁻¹ immediately after holding the electrode potential at 1.6 V vs. RHE under illumination.

Since water has a strong absorption at the expected window for *oxo* and *peroxo* vibrational modes (600-850 cm⁻¹)¹⁰, we opted to use D₂O as a first solvent for studying the possible intermediates through operando IR measurements (Figure 6-3). For the *in-situ* measurement, approximately 20 μ L electrolyte (0.2 M KCl in D₂O) was sandwiched between the ZnSe ATR crystal and CuWO₄ working electrode. The *J-E* responses of the electrode were measured under illumination and in the dark to ensure the feasibility of the electrochemical setup. IR spectrums were then collected under various applied potentials. The measurements were initiated with a 100 s delay to ensure the system was stable. Each spectrum was corrected for the background at a reference potential of 0.0 V *vs*. Ag/AgCl (flatband potential), as in this potential hole trapping is not happening at the CuWO₄ surface.



Figure 6-3. The transmittance of the ZnSe ATR element in contact with H₂O (black line) and D₂O (red line).

Figure 6-4c and d show the IR absorption of the CuWO₄ electrode at various applied potentials under illumination and in the dark, respectively. Under illumination, a peak is growing at 750 cm⁻¹. In the dark, this IR absorption still exists, albeit with lower intensity. The fact that absorption peaks at 750 cm⁻¹ are observed positive of the water oxidation current onset potential suggests that these absorptions are related to the water oxidation reaction. As the peak at 750 cm⁻¹ grows, the signal of weakly surface adsorbate D₂O centered at 1200 cm⁻¹ decreases. The absorption feature at 1500 cm⁻¹ may be due to the HOD production due to the proton exchange between D₂O and residual water. Table 6-1 shows the possible intermediates that can be detected at the surface of the CuWO₄ during the water oxidation reaction and their expected absorption window. These species could be *oxo*, *peroxo*, or *superoxo*, such as W=O, W–O–O–W, W– O–O–D, W–O–O–Cu, Cu–O–O–Cu, W–O–O[•], or Cu–O–O[•].^{11–15} We do not expect copper oxo to be formed at the electrode surface since copper is beyond the oxo wall. The vibrational frequency of W=O is expected to fall in 870-970 cm^{-1,} and the stretching mode of O–O in peroxide lies in the 740-920 cm⁻¹.^{10,15,16} The observed IR peak at 750 cm⁻¹, therefore, can be likely attributed to either W-O-O-W/D or Cu-O-O-Cu/D species.



Figure 6-4. *In-situ* PEC-IR Measurements of CuWO₄ in contact with 0.2 M KCl in D₂O for water oxidation. a) *J-E* responses of a CuWO₄ electrode measured *in-situ* in contact with 0.2 M KCl in D₂O. b) The IR spectrum of the ZnSe IR element in contact with 0.2 M KCl in D₂O. *In-situ* IR spectra scanned at a constant applied potential (c) under monochromatic 395 nm illumination (d) in the dark. IR spectra are corrected for the background at a reference potential of 0.0 V vs. Ag/AgCl.

		-	
Species	Wavenumber (cm ⁻¹)	Species	Wavenumber (cm ⁻¹)
W=O	870-970 12,17	Cu-O-O-Cu	832 18
W-O-O-D/Cu-O-O-D	740-920 13	W-O-O*/ Cu-O-O*	1100-1300 ¹⁵
W-O-O-W	900-950 ¹³	W-O-O-Cu	

Table 6-1. Expected surface species that can be detected at the surface of CuWO₄ during water oxidation.

Since D_2O has a strong absorption at 1100-1300 cm⁻¹ region, where the stretching vibration of *superoxo* species located, we performed the *in-situ* measurement also in water, which provides more transparency at this window.¹⁵ Figure 6-3a shows the *J-E* responses of the CuWO₄ electrode in the *in-situ* experimental setup under illumination and the dark in 1.0 M KB_i (pH=9). The resistive shape of the J-E curve under illumination is due to the series resistance mostly imposed by the geometry of the *in-situ* setup. In general, however, the J-E response is in good agreement with the *ex-situ* measurement. It should be noted that KB_i has an absorption in 1300-1700 cm⁻¹, and, therefore, the investigation of surface species at this window is limited. Figure 5-3c and d show IR spectrums of CuWO₄ electrode under photoelectrochemical and electrochemical water oxidation, respectively. There is an absorption peak growing at 1100 cm⁻¹ under illumination, which is absent in the dark. The fact that this absorption peak is only evolving under illumination indicates that these peaks are associated with surface species during water oxidation at the surface of the CuWO₄. The observed IR vibration at 1100 cm⁻¹ under PEC water oxidation lies in the expected window for stretching vibration of superoxide species (1070-1200 cm⁻¹). Therefore, the observed peaks can be assigned to either W-O-O• or Cu-O-O• groups forming during water oxidation.



Figure 6-5. *In-situ* PEC-IR Measurements of CuWO₄ in contact with 1.0 M KB_i in H₂O for water oxidation. (a) *J-E* curves of a CuWO₄ electrode were measured *in-situ* in contact with D₂O (1.0 M KB_i, pH 9.0). (b) The IR spectra of the ZnSe IR element in contact with 01.0 M KBi in H₂O. *In-situ* IR spectra scanned at a constant applied potential (c) under monochromatic 395 nm illumination (d) and in the dark. IR spectra are corrected for the background at a reference potential of 0.6 V vs. RHE.

We note that it will be difficult to clearly distinguish between W-O-O-W/D or Cu-O-O-Cu/D, and W-O-O• or Cu-O-O• species. To solve this issue, we will prepare CuWO4 photoelectrodes with W and Cu rich surfaces to elucidate the subtle difference in vibration bands. Oxygen isotope labeling will also be utilized to confirm the chemical nature of the evolved species and differentiate between M–O–O–M from M–O–O–D/H species. Future work will extend these

preliminary results to a more detailed investigation of water oxidation intermediates at the surface of CuWO₄.

6.4 Conclusions

In this chapter, we examined the CuWO₄ electrode by operando ATR-IR spectroscopy under (photo)electrochemical water oxidation condition. The potential and light-dependent IR absorption peaks were measured and correlated to the photoelectrochemical measurements. These measurements are provided valuable pieces of evidence related to the nature of the surface state for PEC water oxidation on CuWO₄ photoanode. Further investigation of the CuWO₄ system is necessary to differentiate between possible intermediates and unambiguously detecting the chemical nature of the surface species. APPENDIX



Figure A6-1. EDX spectrum of CuWO₄ synthesized by spray pyrolysis method.



Figure A6-2. XPS spectrum of CuWO₄ synthesized by spray pyrolysis method.



Figure A6-3. EIS measurement of CuWO₄ photoanode for water oxidation reaction. The Nyquist plots were measured at (a) 0.93 V *vs.* RHE (b) 1.03 V *vs.* RHE. (c) the Bode plot was measured at 1.03 V *vs.* RHE. All measurements were done in 1.0 M of M KB_i under illumination.



Figure A6-4. The equivalent circuit used for fitting the EIS results of CuWO₄ for water oxidation reaction under illumination.

Table A6-1. Parameters extracted from fitting the EIS data of CuWO₄**.** The measurements were done under 1 sun illumination in 1.0 M KB_i buffer.

<i>E /</i> V <i>vs.</i> Ag/AgCl, pH 9	<i>E</i> / V <i>vs</i> . RHE	C _{bulk} /F	$R_{ m trap}/\Omega$	$C_{\rm ss}/{ m F}$	$R_{ m ct,ss}/$ Ω
0.1	0.83	1.06E-05	23105	1.97E-05	34097
0.15	0.88	9.21E-06	8032	1.44E-05	17719
0.2	0.93	7.82E-06	3735	1.80E-05	9045
0.25	0.98	6.83E-06	2687	2.53E-05	5293
0.3	1.03	6.17E-06	2481	3.17E-05	3854
0.35	1.08	5.79E-06	2596	3.74E-05	3245
0.4	1.13	5.41E-06	2736	3.58E-05	3043
0.45	1.18	5.09E-06	2963	3.21E-05	2938
0.5	1.23	4.61E-06	2955	2.08E-05	3244
0.55	1.28	4.08E-06	2662	1.09E-05	3865

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Chapter 7:

Conclusions and future directions

7.1 Conclusions

CuWO₄ is a promising candidate photoanode for water oxidation, mainly due to the small bandgap (2.3 eV) and high stability in neutral to slightly basic solutions.¹⁻⁴ The integration of solar spectrum with this bandgap gives a maximum photocurrent density of 9 mA cm⁻¹. However, the overall water oxidation efficiency with CuWO₄ has been low, and the best photocurrent density achieved to date with this semiconductor is only 0.5 mA cm⁻² at water oxidation standard potential (1.23 V vs. RHE).^{2,5-7} The limited hole collection efficiency at the surface of CuWO₄ for water oxidation compared with Na₂SO₃ oxidation, as a suitable hole scavenger,² implies that surface state recombination limits the electrode performance for water oxidation reaction. Usually, integrating an electrocatalyst with a semiconductor photoanode can improve the hole collection efficiency and lead to a performance improvement. In the case of CuWO₄, however, there is not any report of significant improvement of the electrode performance after electrocatalyst deposition. In this dissertation, we have done systematic studies of charge carrier dynamics at the interface of the CuWO₄ with electrolyte and electrocatalyst to elucidate the unusual synergy between electrocatalyst and CuWO₄ electrode and also to better understand the water oxidation mechanism with this semiconductor.

• CuWO₄ thin films were synthesized via atomic layer deposition (ALD) and further integrated with Ni_{1-x}Fe_xO_y model electrocatalyst to investigate the effect of electrocatalyst on PEC performance of CuWO₄ for water oxidation. We found that electrocatalyst deposition does not improve the CuWO₄ performance for water oxidation reaction. This result is in contrast with what is generally reported with other metal oxide photoanodes such as hematite and bismuth vanadate, where electrocatalyst deposition improves the electrode performance. We also found that deposition of a conductive electrocatalyst at the surface of CuWO₄ causes a dramatic decrease in the electrode performance due to the shunting recombination.

- In chapter 3, we reported a general method based on polyphenylene oxide (PPO) electrodeposition to overcome shunting recombination. This such shunting recombination comes from direct contact of conductive electrocatalyst with an underlying conductive substrate. Thin films of hematite were prepared by electrodeposition method and were used as a model semiconductor photoanode due to the porous structure. Elimination of shunting pathways of the ED-hematite through PPO electrodeposition led to improving the performance after the deposition of Ni_{0.75}Fe_{0.25}O_y (Ni75) electrocatalyst.
- In chapter 4, thin films of CuWO₄ were prepared via ALD and were modified with PPO to block the exposed FTO. Ni75 was used as a model electrocatalyst for the investigation of the interface of CuWO₄ with an electrocatalyst. We employed the dual working electrode photoelectrochemistry (DWEP) pioneered by Boettcher and coworkers to study the CuWO₄/ Ni75 interface.⁸ Through the DWEP characterization of the CuWO₄/ Ni75, it was found that the potential of the electrocatalyst overlayer is not reaching sufficient potential to drive the water oxidation reaction. Instead, the reaction predominantly proceeds on the surface of CuWO₄, as revealed by *in situ* current density measurements.⁹
- DWEP and photoelectrochemical impedance spectroscopy (PEIS) were employed to study the interface of two important systems with Ni75 electrocatalyst, namely hematite and copper tungstate. The deposition of Ni75 electrocatalyst onto hematite thin film induces a cathodic shift of the photocurrent onset potential. In contrast, as

also discussed in chapter 4, the deposition of the same thickness of the Ni75 electrocatalyst does not improve the CuWO₄ performance for the water oxidation reaction. The comparison of these two systems provided invaluable information about the lack of performance improvement of CuWO₄ after electrocatalyst deposition. The capacitance of the electrocatalysts and charge transfer resistances to the respective interfaces were evaluated through the PEIS measurements. The comparison of the ratio of $R_{trap}/R_{ct,ss}$, and $R_{trap}/R_{ct,cat}$ from PEIS measurements is indicated fast recombination of accumulated photogenerated holes in the electrocatalyst overlayer with electrons from the CuWO₄ conduction band at the interface. In contrast, this ratio is smaller for the hematite photoanode modified with Ni75 compared to that of the bare electrode. These results indicate that water oxidation is directly proceeding at the CuWO₄ surface rather than electrocatalyst overlayer and agrees with the result of chapter 4, and explains the lack of CuWO₄ performance improvement after electrocatalyst deposition.

• The surface properties of the CuWO₄ photoanode play a key role in determining the hole collection efficiency for water oxidation reaction. Recently, it has been shown that water oxidation on CuWO₄ surface is associated with the oxidation of the surface states, which further proceed to evolve oxygen.¹⁰ In chapter 6, we employed an *in-situ* PEC-IR method to study the evolved intermediate species at the surface of CuWO₄ during water oxidation reaction. The preliminary results show the growth of IR peaks under PEC condition, which can be attributed to the formation of peroxide and superoxide species.

7.2 Future directions

In the future, we intend to employ Intensity-modulated photocurrent spectroscopy (IMPS) measurements to study the mechanism and kinetics of charge extraction and recombination at the interface of CuWO₄ with both electrocatalyst and electrolyte. A detailed understanding of these processes is highly beneficial for the future design of electrocatalyst(s) with highly efficient hole extraction and transfer to the water for enhanced PEC water oxidation on CuWO₄. In IMPS, the phase shift in photocurrent is measured in relation to the sinusoidal frequency modulation of the light source.¹¹ Any changes of the photocurrent response to the illumination intensity can be monitored based on the assumption that a small variation in the illumination intensity only affects the concentration of the surface charge, but not the degree of band bending. At the low modulation frequencies, the produced photocurrent refers to the actual steady-state water oxidation process, whereas high modulation frequencies that lead to a transient spike in photocurrent is an indication of total hole flux reaches to the electrode surface. The outcome is comparable to the current transient, yet IMPS provides more precise and conclusive results.

We will carry out IMPS measurements at various applied potentials for both bare and electrocatalyst-coated CuWO₄ photoanodes. The challenging step will be to calculate and interpret the charge transfer (k_{tran}) and recombination (k_{rec}) rate constants based on the previously established model.¹² k_{tran} and k_{rec} are limiting factors that determine the efficiency of water oxidation process, and we aim to provide an assessment of the role of electrocatalysts on their contribution for PEC water oxidation. We also suggest performing IMPS measurements with the DWE techniques even further to strengthen our future findings on charge transfer and recombination rate constants at both CuWO₄/electrocatalyst and electrocatalyst/electrolyte interfaces.

The nature of CuWO₄ surface states has been investigated by *in-situ* PEC-IR measurements, and the preliminary results provided in chapter 6. More work is required to unravel the details of this exciting result so it can be further exploited. The results will help us to establish the mechanism of H_2O oxidation on CuWO₄ and reconciling the long-lasting controversy as to the role of surface states in water oxidation with this material.

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