FUNDAMENTAL INVESTIGATIONS OF PHOTOELECTROCHEMICAL WATER SPLITTING WITH COPPER TUNGSTATE PHOTOANODES

By

Yuan Gao

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemistry – Doctor of Philosophy

2017

ABSTRACT

FUNDAMENTAL INVESTIGATIONS OF PHOTOELECTROCHEMICAL WATER SPLITTING WITH COPPER TUNGSTATE PHOTOANODES

By

Yuan Gao

An increasing global energy demand along with detrimental consequences of extensive usage of fossil fuel calls for the development of abundant, cost effective and carbon neutral alternative energy sources. Solar energy is well distributed and is the most abundant energy source available on Earth. This work focuses on using copper tungstate (CuWO₄) photoelectrode to harvest sunlight to oxidize water, which constitutes the rate limiting half reaction of photoelectrochemical water splitting to generate clean and carbon neutral energy dense fuel, hydrogen, and the byproduct, oxygen. CuWO₄ is a promising photoanode material for water splitting owing to its reasonably small bandgap, suitable band position, stability and abundance, but has received limited attention due to its reported poor bulk properties and low hole collection efficiency at the surface. A lack of fundamental insight into its limitations hinders rational design of strategies to improve its performance. We developed an atomic layer stack deposition-annealing (SDA) method derived from atomic layer deposition (ALD) to synthesize our CuWO₄ thin films. While keeping the benefit of precise thickness control of a uniform film as traditional ALD procedures, this new approach of ALD of ternary metal oxides allows for a wider selection of precursors since their ALD temperature windows do not have to overlap, and it allows for an easier control of stoichiometry. The hole collection efficiency at the electrode surface was quantified by comparing water oxidation and the oxidation of a suitable hole scavenger, as well as by intensity modulated photocurrent spectroscopy (IMPS). Our results showed that water oxidation with CuWO₄ is limited by surface recombination at low applied bias, but is essentially quantitative at higher potentials. A series of photoelectrochemical and electrochemical impedance spectroscopic measurements were employed to elucidate the role of surface state of CuWO₄ during water oxidation. Our results suggested that the surface state of CuWO₄ is related to a water oxidation intermediate species rather than intrinsic, as is opposed to previous literature. Relatively thick CuWO₄ electrodes were made by spray pyrolysis and the pores were back-filled with Al₂O₃ to produce compact films for bulk studies. Illumination direction and wavelength dependent photoelectrochemical measurements were employed to investigate the bulk properties of CuWO₄ for water oxidation, which suggested that the major problem of CuWO₄ is a short electron collection length.

ACKNOWLEDGEMENTS

When I look back on my five years' graduate life, I found that there are so many people I would like to express my gratitude. It was not only an experience of pursuing a PhD degree, but also an unforgettable experience living in a different country. It is all of these people who have helped and cared for me in my academic and personal life that got me through these years.

First of all, I would like to express my most sincere gratitude and appreciation to my advisor, Professor Thomas W. Hamann, for his patience, guidance, encouragement and support. Tom's wisdom and critical scientific insight has always helped, enlightened and inspired me throughout my research. He has always been a role model for his natural curiosity, passion and dedication in science. My completion of my PhD degree would not be accomplished without the help of my colleagues in Hamann Group. Many thanks to Ben, Kelley and Omid, who were the past members of the Water Splitting project, for mentoring me and sharing their inspiring thoughts and ideas about research. I would like to thank Yuling, who has graduated but has helped me a lot in my research and also personal life. I would like to thank Hamed, as another member in Water Splitting subgroup in the same year, for all the helpful discussions on our projects. I'd like to thank Yujue, Qiong, Mandal, Dan, Josh, Faezeh, Geletu, Austin and Parisa for all the joy and fun in Hamann Lab. I would also like to thank National Science Foundation for funding the research presented herein, and also MSU Dissertation Completion Fellowship (Summer 2017) which allowed me to complete this dissertation.

Many thanks to my committee members, Professor Gary Blanchard, Professor Rémi Beaulac and Professor Benjamin Levine for their valuable suggestions and advice. I would also like to express my thanks to my previous committee member and second reader, Professor Merlin Bruening, who has left MSU, for his help and advice during my PhD years.

I would like to thank my friends who cared for me. Many thanks to Chuanpeng Jiang, who has helped me in both my research and personal life. Thanks to Xiaoran Zhang, Shuang Liang, Ruiqiong Guo, Ruipeng Mu, Yiqing Yang and Zhihui Liu for their company in all these years. Thanks to Nan Du, Ningliang Li, Yang Shangguan, Li Ke and Keying Wen, for the wonderful time playing sports and games. Thanks to Yun Xian who is far away but gave me a lot of support.

I cannot express enough gratitude to my husband and best friend, Zhihao Jin, who is the most important person that has helped me through these years. Any of my achievements would not be possible without his patience, understanding, care and love. Many thanks to my relatives for helping my family in China while I am absent. Finally, I would like to thank my parents for their selfless love and support. No matter where I go, they are always the ones I care for.

TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	ix
Chapter 1: Introduction	1
1.1 Motivation	2
1.2 Approach	2
1.3 Performance Evaluation	6
1.3.1 Current Density - Voltage (J-V) Measurements	6
1.3.2 Quantum Efficiencies	
1.4 Copper Tungstate (CuWO ₄)	
1.5 Objectives	14
REFERENCES	
Chapter 2: Atomic Layer Stack Deposition-Annealing Synthesis of CuWO ₄	
2.1 Abstract	
2.2 Introduction	
2.3 Experimental	
2.3.1 Film Deposition	
2.3.2 Calculation of CuO Deposition Cycles	
2.3.3 Calculation of Film Thickness	
2.3.4 Film Characterization	
2.3.5 Photoelectrochemistry	
2.4 Results and Discussion	
2.5 Conclusion	
APPENDIX	
REFERENCES	56
Chapter 3: Quantifying Hole Collection Efficiency of CuWO ₄ for Water Oxidation	62
3.1 Abstract	
3.2 Introduction	64
3.3 Experimental	65
3.3.1 Film Preparation and Characterization	65
3.3.2 Characterization	65
3.3.3 Photoelectrochemical Measurements	
3.4 Results and Discussion	67
3.5 Conclusion	
APPENDIX	79
REFERENCES	
Chapter 4: Elucidation of Role of CuWO ₄ Surface States During Photoelectrochemical V	Water

4.1 Abstract	
4.2 Introduction	
4.3 Experimental	
4.3.1 Film Preparation	
4.3.2 Film Characterization	
4.3.3 Electrochemical / Photoelectrochemical Measurements	
4.3.4 Measurements in Aqueous Electrolytes	
4.3.5 Measurements in Non-aqueous Electrolytes	
4.4 Results and Discussion	
APPENDIX	107
REFERENCES	
Chapter 5: Investigations of Charge Separation Limitations of CuWO ₄	127
5.1 Abstract	
5.2 Introduction	129
5.3 Approaches and Methods	
5.4 Experimental	
5.4.1 Film Preparation	136
5.4.2 Film Characterization	
5.4.3 Sandwich Cell Preparation	
5.4.4 Photoelectrochemistry	
5.5 Results and Discussion	
5.6 Conclusions	153
REFERENCES	155
Chapter 6: Conclusions and Future Directions	158
6.1 Conclusions	159
6.2 Future Directions	
REFERENCES	164

LIST OF TABLES

Table 4-1.	Flat band potential and dopant density calculated from Mott-Schottky plots in the dark and under illumination
Table A4-1.	Parameters extracted from fitting EIS data in 0.5 M Na2SO3 electrolyte in the dark
Table A4-2.	Parameters extracted from fitting EIS data in 0.5 M Na ₂ SO ₃ electrolyte under 1 sun illumination
Table A4-3.	Parameters extracted from fitting EIS data in aqueous electrolyte (pH9 KB _i buffer) in the dark
Table A4-4.	Parameters extracted from fitting EIS data in aqueous electrolyte (pH9 KB _i buffer) under 0.1 sun illumination
Table A4-5.	Parameters extracted from fitting EIS data in aqueous electrolyte (pH9 KB _i buffer) under 1 sun illumination

LIST OF FIGURES

Figure 1-1.	Diagram of PEC water splitting tandem cell
Figure 1-2.	A three-electrode configuration for measuring the performance of a photoelectrode. Reference, working, and counter electrodes are labeled as "RE", "WE", and "CE", respectively. The green "V" and red "I" indicate where the voltage and current are measured, respectively
Figure 1-3.	Simulated <i>J-V</i> curves of a tandem PEC water splitting cell. The intercept of the <i>J-V</i> curves of the photocathode and photoanode determines the operating photocurrent
Figure 1-4.	Band edge energy levels and bandgaps of candidates for PEC water oxidation photoanodes
Figure 1-5.	Red curve: AM 1.5 solar spectrum; black vertical line: wavelength that corresponds to the bandgap of CuWO ₄ ; yellow area: maximum photon flux that can be absorbed by CuWO ₄ under 1 sun illumination
Figure 1-6.	Schematic diagram of PEC water oxidation at CuWO ₄ photoanode/electrolyte interface. The red arrow indicates light absorption (charge generation), green arrows represent charge separation, including diffusion in the quasi-neutral region and drift due to the electric field in the depletion region, and blue arrows indicate hole collection at CuWO ₄ /electrolyte interface to oxidize water. Meanwhile, the dark red arrows represent possible recombination pathways in the bulk or at the interface
Figure 2-1.	Schematic illustration of a) ALD reactor and b) one cycle of ALD process 23
Figure 2-2.	Experimental X-ray photoelectron spectroscopy (XPS) spectra of W 4f and O 1s peaks (black scatters) with fitting (red solid lines and dots) of as-deposited (top) and annealed (bottom) WO ₃
Figure 2-3.	X-ray diffraction (XRD) patterns of as-deposited (black) and annealed (red) WO ₃ .
Figure 2-4.	Raman spectra of as-deposited (black) and annealed (red) WO ₃
Figure 2-5.	Thickness of WO ₃ thin films vs number of deposition cycles using different metal precursor pulse lengths
Figure 2-6.	Experimental XPS spectra of Cu 2p and O 1s peaks (black scatters) with fitting (red solid lines and dots) of as-deposited (top) and annealed (bottom) CuO

Figure 2-7.	XRD patterns of as-deposited (black) and annealed (red) CuO
Figure 2-8.	Raman spectra of as-deposited (black) and annealed (red) CuO
Figure 2-9.	Thickness vs number of deposition cycles of CuO thin films with different metal precursor pulse length
Figure 2-10.	Total thickness of a) WO ₃ on 100 cycles of CuO and b) CuO on 100 cycles of WO ₃ as a function of number of deposition cycles
Figure 2-11.	Sequential ALD of WO ₃ /CuO and post-ALD annealing to make CuWO ₄ thin films via stack deposition-annealing (SDA) approach
Figure 2-12.	Cross-section SEM images of a) as-deposited WO ₃ and b) annealed CuWO ₄ thin films on Si substrate
Figure 2-13.	AFM surface morphology image of a) as-deposited WO_3 , b) as-deposited CuO on WO_3 , and c) annealed CuWO ₄ on Si substrate
Figure 2-14.	XPS survey spectra of as-deposited (bottom) and annealed (top) film of CuO on top of WO ₃
Figure 2-15.	Experimental XPS spectra of a) Cu 2p and W 4f peaks (black scatters) with fitting (red solid lines and dots) of CuO on top of WO ₃ as-deposited (top) and annealed (CuWO ₄) (bottom) and O 1s peaks (black scatters) with fitting (red solid lines and dots) of CuO on top of WO ₃ b) as-deposited and c) annealed (CuWO ₄)
Figure 2-16.	a) X-ray diffraction patterns and b) Raman spectra of CuO on WO_3 as-deposited (black) and annealed (CuWO ₄) (red). Peak positions of CuWO ₄ from literature are plotted as vertical dashed gray lines
Figure 2-17.	Images of CuWO ₄ thin films deposited on FTO substrates with varying ALD cycles of WO ₃ of 0, 500, 1000, 1500, 2000, and 2500
Figure 2-18.	Thickness of CuWO ₄ films with different deposition cycles of WO ₃ measured with AFM (black squares). Error bars represent the standard deviation of 10 different measurements on each film. Red dash shows the linear fit of thickness vs. number of cycles
Figure 2-19.	Top: a) Absorbance of CuWO ₄ thin films with ALD cycles of WO ₃ of 500 (red solid), 1000 (orange dash), 1500 (yellow short dash), 2000 (green dash dot), and 2500 (blue dot). Bottom: Absorbance of CuWO ₄ thin films at wavelength of b) 400 nm and c) 450 nm varying with different ALD cycles of WO ₃ . Error bars represent standard deviation of independent measurements on three different spots for each thickness

- Figure 3-2. a) Photocurrent densities measured with a CuWO₄ electrode in an aqueous electrolyte containing Na₂SO₃ with various concentrations at 0.88 (red squares), 1.23 (green triangles) and 1.53 (blue circles) V vs RHE under 1 sun illumination.
 b) Current transients measured under 1 sun illumination in 0.5 M Na₂SO₃ electrolyte at 0.88 (red solid), 1.23 (green dash) and 1.53 (blue dots) V vs RHE.70

- **Figure 3-7.** Calculated η_{HC} of water oxidation with CuWO₄ electrodes extracted from IMPS data at 116 mW cm⁻² with 470 nm LED (orange triangles) and from comparisons

of *J-V* curves of water oxidation and oxidation of a) Na₂SO₃ (purple solid) and b) H₂O₂ under 1 sun illumination (green solid)......77

Figure A3-1. SEM image	s of a) as-deposited Cu	uO on WO ₃ , and	CuWO ₄ annealed	at b) 550 °C
and c) 600 °	°C			80

- **Figure A4-1.** *J*_{dark}-*V* (black dash) and *J*_{total}-*V* (red solid) curves of CuWO₄ electrode measured in a) H₂O and b) 0.5 M Na₂SO₃ electrolytes in the dark and under 1 sun illumination. 108
- **Figure A4-3.** CV taken after holding potential at 2.3 V *vs.* RHE for 60 s in the dark. Scan rates varies from 200, 400, 600, 800, 1000, 1200 and 1500 mV s⁻¹ corresponding to red, orange, dark yellow, green, dark green, blue and purple solid. The peak intensity after the dark pretreatment is slightly smaller compared to the light pretreatment. 115

- **Figure A4-8.** Bode phase plots of SP-CuWO₄ at 0.93V *vs.* RHE in the dark (black squares) and under 1 sun illumination (red circles) measured in pH 9 aqueous (H₂O) electrolyte.

Figure A4-9.	C_{ss} obtained from fitting EIS measured in pH 9 aqueous (H ₂ O) electrolyte under 0.1 sun (blue triangles), 0.33 sun (green diamonds) and 1 sun (red circles) illumination with SP-CuWO ₄
Figure A4-10.	Mott-Schottky plots of SP-CuWO ₄ measured in the dark in pH 9 aqueous (H ₂ O) electrolyte
Figure A4-11.	CVs taken after holding potential at 2.3 V <i>vs.</i> RHE for 60 s under 1 sun illumination at scan rates from 200, 400, 600, 800, 1000, 1200 and 1500 mV s ⁻¹ corresponding to red, orange, dark yellow, green, dark green, blue and purple. Experiment was conducted in pH 9 aqueous electrolyte
Figure 5-1.	Scheme of charge separation in a) planar CuWO ₄ electrode and b) optimized nanostructured CuWO ₄ photoanode
Figure 5-2.	Schematic illustration of hole generation and charge separation in CuWO ₄ photoanode illuminated from a) electrolyte-electrode (front) side and b) substrate- electrode (back) side. The red arrows represent hole collection and green arrows represent electron transport
Figure 5-3.	Scheme of a) a nanostructured CuWO ₄ film, b) a nanostructured film with pores filled with excess Al_2O_3 and c) after etching the top Al_2O_3 layer with 1 M KOH to expose CuWO ₄ electrode to the electrolyte
Figure 5-4.	Schematic illustration of light absorption in CuWO ₄ electrode by a) front and b) back illumination. L_n is the electron collection length. The light red, orange, green, blue and purple arrows represent illumination from relatively long wavelengths to short wavelengths
Figure 5-5.	a) Absorption coefficient and b) Tauc plot of CuWO ₄ indicating its indirect bandgap. The red dashed line represents the fitting result of the linear region in Tauc plot. The blue dash represents the corrected baseline according to the plateau region in Tauc plot
Figure 5-6.	a) Calculated raw data and b) corrected absorptance of CuWO ₄ 140
Figure 5-7.	J_{photo} -V response of CuWO ₄ in a pH 9 KB _i electrolyte with 0.5 M Na ₂ SO ₃ (blue dash) and 200 mM KI / 5 mM I ₂ (red solid) under 1 sun illumination 141
Figure 5-8.	Dark <i>J-V</i> curves of CuWO ₄ measured in a) Na ₂ SO ₃ and b) I^{-}/I_{3}^{-} electrolyte 141
Figure 5-9.	Charge separation efficiency of CuWO ₄ electrode142

Figure 5-10.	SEM image of a) top-down and b) cross-section view of bare CuWO ₄ by spray pyrolysis, c) top-down and d) cross-section view of CuWO ₄ deposited with 1500 cycles (~150 nm) of Al ₂ O ₃ and etched in 1 M KOH for 40 min
Figure 5-11.	<i>J-V</i> curves of CuWO ₄ coated with ~150 nm of Al ₂ O ₃ (black dash) and etched in 1 M KOH for 30 min (red), 32 min (orange), 34 min (yellow), 36 min (green), 38 min (dark cyan), 40 min (blue), 42 min (purple) and 44 min (wine). These <i>J-V</i> curves are also compared with that of bare CuWO ₄ (pink dots). All measurements are done in pH 9 KB _i electrolyte under 1 sun illumination
Figure 5-12.	Schematic illustration of CuWO ₄ sandwich cell and light illumination146
Figure 5-13.	Absorptance of FTO-coated glass (black solid) and platinized FTO-coated glass (blue dash). Both were measured by illuminating from the glass side
Figure 5-14.	Absorbance of different concentrations of I ₂ in pH9 KB _i buffer with 200 mM KI at a) 350 nm, b) 405 nm and c) 470nm
Figure 5-15.	a) Absorptance of the integrated sandwich solar cell with (red solid) and without (black dash) electrolyte by illuminating from the front side. b) Absorptance of the electrolyte inside the sandwich cell
Figure 5-16.	a) J - V response of CuWO ₄ sandwich by illuminating from front (red dash) and back (blue solid) side under AM 1.5 1 sun illumination and in the dark (black dots). b) J_{photo} - V of CuWO ₄ sandwich cell illuminated from front (red dash) and back (blue solid) side
Figure 5-17.	a) <i>J-V</i> response, b) J_{photo} - <i>V</i> response and c) quantum efficiency of CuWO ₄ sandwich cell with front (red dash) and back (blue solid) illumination and in the dark (black dots). Light source was 470 nm LED with 218 mW cm ⁻² power density
Figure 5-18.	a) Original data and b) corrected IPCE of CuWO ₄ sandwich cell under front (red circles) and back (blue triangles) illumination
Figure 5-19.	Absorbed photon-to-current efficiency of CuWO4 sandwich cell under front (red circles) and back (blue triangles) illumination

Chapter 1: Introduction

1.1 Motivation

The world's total primary energy consumption rate in 2013 was estimated to be 18.0 TW (i.e. 5.67×10^{20} J/yr).¹ Due to the worldwide population increase, economic growth and industrialization, the energy demand is projected to increase to 27 TW by the year 2050.² So far, fossil fuels have been the major primary energy source, and are expected to remain the main source in the next several decades.^{1,2} The combustion of fossil fuels, however, releases excessive amount of carbon dioxide and has caused global warming, which is now widely accepted.³ Besides, the release of other harmful byproducts such as various forms of sulfur oxide and nitrogen oxide, toxic mineral particles, etc., has caused environmental issues especially in developing countries.⁴ In addition to these environmental concerns, fossil fuels are not always distributed where they are most needed, therefore causing geopolitical conflicts and economic issues. All these factors motivate development and utilization of carbon-neutral and easily distributable energy sources as an alternative to fossil fuels.

1.2 Approach

Sunlight strikes the earth with a power of ~120,000 TW, making it the largest energy source available. Utilizing only ~0.01% of solar energy would have the potential to meet the world's energy demand.² Being a carbon-neutral and clean energy source, it is also well-distributed over the most populous areas, which minimizes the transportation concerns of this energy source. These all make solar energy the most promising means of energy supply in the future.

One possible way to utilize solar energy is to harvest photons and convert them to electricity using photovoltaic (PV) systems, such as Si-based solar cells which have been investigated for decades. The purity requirements of these PV cells result in their relatively high cost, averagely \$0.35 / kW-hr for typical Si solar cells, comparing with traditional electricity

derived from combustion of fossil fuels (\$0.02-0.05 / kW-hr).² Another issue associated with PV cells is the storage of electricity. Current development in batteries is not sufficient to store electricity cost-effectively on a large scale, and scientists and engineers are working on improving the energy capacity and solving some stability and safety issues associated with battery technologies.

An alternative to PV cells is to store solar energy in chemical bonds (i.e. solar fuels), which is analogue to the photosynthesis process found in nature. Two of the most studied approaches are photoelectrochemical (PEC) hydrogen production and carbon dioxide reduction.^{2,5–7} While the conversion of CO₂ to CO or organic fuels provides an attractive way of solar energy utilization, capture of CO₂ from the atmosphere remains challenging. Besides, the combustion of these carboncontaining fuels generates CO₂, which raises the problem of capturing CO₂ efficiently. Alternatively, utilizing the solar energy to split water to get hydrogen appears an attractive and promising approach. Hydrogen can be used as a clean secondary energy source in fuel cells and other systems. The only combustion product of hydrogen is water, which is clean and carbonneutral, and hydrogen has a high mass energy density.⁸ Of course, water splitting can be accomplished by coupling a PV cell with an external electrolyzer,^{9,10} but the lack of long-term durability, toxicity and high cost of most high-performance excellent PV materials remain a problem. Instead, using earth abundant and robust semiconductors to harness solar energy and split water *in situ* would be more realistic.

The overall PEC water splitting reaction requires a Gibbs free energy change of +237 kJ/mol H₂ at standard temperature (298 K) and unit activities, which corresponds to 1.229 V potential difference between the reduction and oxidation half reactions. The overall reaction is described by the following equation:

$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2 \quad \Delta G=237 \text{ kJ/mol}$$
 (1.1)

For an alkaline environment, the reduction and oxidation half reactions can be written as:

$$4H_2O + 4e^- = 2H_2 + 4OH^- = E_{red}^0 = +0.000 \text{ V vs. RHE}$$
 (1.2)

$$4OH^{-} + 4h^{+} \rightleftharpoons 2H_{2}O + O_{2} \qquad E_{ox}^{0} = -1.229 \text{ V vs. RHE}$$
(1.3)

If a single material is to be used for photoelectrochemical water splitting, it has to meet the following requirements:

1) The conduction band (CB) edge and valence band (VB) edge should straddle the reduction and oxidation potentials of water to drive each half reaction effectively;

2) The bandgap should be reasonably small to harvest a sufficient portion of solar spectrum;

3) The semiconductor has to be composed of earth-abundant elements to scale up production;

4) The photoelectrode should be stable under harsh PEC water splitting conditions.

In reality, in order to provide fast kinetics to drive the two half reactions efficiently, an overpotential of 600 - 900 mV will likely be required in addition to the Nernstian potential difference of 1.23 V. Therefore, a bandgap energy of 1.8 - 2.2 eV would be ideal for a semiconductor to be used in a single photoelectrode configuration.^{11,12} Unfortunately, mainly due to the restriction in bandgap energy and band edge positions, as well as the instability of many III-V semiconductors in aqueous solutions under PEC conditions, no single material can fulfill all these requirements for efficient water splitting.¹³

An attractive alternative is to couple a n-type photoanode with a p-type photocathode to form a tandem cell and separate the two half reactions,¹³ as shown in Figure 1-1. In this configuration, one of the photoelectrode would absorb short wavelength light while the other one would absorb longer wavelengths. Apart from efficient utilization of solar spectrum, this

configuration allows us to investigate and optimize the two half reactions separately, and the usage of an ion-selective membrane would allow for the separation of H_2 and O_2 products to avoid potential explosion.



Figure 1-1. Diagram of PEC water splitting tandem cell.

According to equations 1.2 and 1.3, the generation of 1 mol of H₂ involves the participation of 2 mol of electrons (e⁻), while the evolution of 1 mol of O₂ involves 4 mol of holes (h⁺). The four-h⁺ process of water oxidation makes it a more challenging reaction than water reduction, suffering from sluggish kinetics and unfavorable recombination at photoanode/electrolyte interface.^{14–18} In addition to this, water oxidation is a universal oxidation half reaction for the production of many other solar fuels, *e.g.* CO₂ reduction. Therefore, the investigation of this half reaction would generally benefit the development of solar fuels. Thus, our research interest lies in searching for potentially promising photoanodes for water oxidation.

1.3 Performance Evaluation

1.3.1 Current Density - Voltage (*J*-*V*) Measurements

Current density - voltage (J-V) measurements are the most straightforward and important technique to evaluate the performance of photoelectrodes. The J-V measurements are usually measured in a three-electrode configuration as shown in Figure 1-2 in order to individually characterize and optimize single photoelectrodes (e.g. a photoanode) as polarization losses at the counter electrode can be neglected. The onset potential of photocurrent is related to the extra energy needed to initiate the corresponding reaction, and the photocurrent evaluates the rate of the reaction if the Faradaic efficiency of water oxidation reaction is 100%. Therefore, for water oxidation half reaction, low onset potentials and high photocurrents are desired.



Figure 1-2. A three-electrode configuration for measuring the performance of a photoelectrode. Reference, working, and counter electrodes are labeled as "RE", "WE", and "CE", respectively. The green "V" and red "I" indicate where the voltage and current are measured, respectively.

In a tandem PEC water splitting cell, assuming 100% Faradaic efficiency for each half reaction, if the *J-V* curves of the photocathode and photoanode have an intercept as shown in Figure 1-3, the operating photocurrent, J_{op} , would be the current at this matching point. If no external bias is needed to drive water splitting at this operating condition, the solar-to-hydrogen efficiency, h_{STH} , can be calculated using this equation:¹¹

$$\eta_{STH} = \frac{J_{op} \times 1.23 \text{ V}}{P_{in}} \tag{1.4}$$

Here, J_{op} is the operating current density of the cell, and P_{in} is the incident light power density (100 mW cm⁻² for 1 sun). According to calculations by Lewis and coworkers, a tandem PEC water splitting system exhibits a maximum h_{STH} of 29.7% with optimized band gap combination of 1.60 eV and 0.95 eV.¹⁹



Figure 1-3. Simulated *J*-*V* curves of a tandem PEC water splitting cell. The intercept of the *J*-*V* curves of the photocathode and photoanode determines the operating photocurrent.

1.3.2 Quantum Efficiencies

Apart from measuring the water oxidation *J-V* curves under simulated 1 sun illumination, the quantum efficiency under monochromatic illumination can be measured to assess the electrode performance. The *incident photon-to-current efficiency*, IPCE, also called the *external quantum efficiency*, is calculated by dividing the measured photocurrent by the number of incident photons at a certain wavelength using the following equation:

$$IPCE = \frac{J_{ph} \times hc}{\lambda P_{in} \times q} \tag{1.5}$$

Where J_{ph} is the measured photocurrent density, *h* is the Planck's constant, *c* is the speed of light, λ is the wavelength of incident light, P_{in} is the power density of the incident illumination, *q* is the elementary charge. IPCE considers all the incident photons, thus not correcting for the photons that are transmitted or reflected by the electrode. The *absorbed photon-to-current efficiency*, APCE, also called the *internal quantum efficiency*, can be calculated by dividing IPCE by the absorptance as in the following equation:

$$APCE = \frac{IPCE}{1 - T - R} \tag{1.6}$$

Where T and R are the transmittance and reflectance of the photoanode. APCE corrects for the photons that are transmitted and reflected by the electrode. Therefore, it is a more useful parameter to characterize and optimize a photoelectrode since APCE values lower than unity indicate recombination losses in the bulk or at the surface of the material.

1.4 Copper Tungstate (CuWO₄)

For an n-type semiconductor to be used as the photoanode material for water oxidation, it should meet several requirements:

1) It should possess a reasonably small bandgap to absorb a substantial fraction of sunlight;

2) The valence band edge potential should be positive enough to provide sufficient overpotential to drive water oxidation reaction;

3) The photoanode should facilitate efficient separation of photogenerated holes and electrons in the bulk of the material, and should oxidize water to oxygen at the photoanode/electrolyte interface selectively and efficiently;

4) The material has to be composed of earth-abundant elements for large scale production;

5) It should have long term stability under PEC water oxidation conditions.

Among various semiconductor materials, transitional metal oxides are on top of the candidate list because of their generally excellent stability. The band energy levels of promising water oxidation photoanodes^{20–25} are depicted in Figure 1-4. As the first photoelectrode used for water splitting, TiO₂ has a large bandgap of 3.2 eV.²⁰ Therefore, unfortunately, it is only able to absorb the UV portion of solar spectrum. WO₃ has been investigated as a promising water splitting photoanode due to its earth-abundant composition and stability in acidic solutions.^{26–29} However, it also suffers from a relatively large bandgap of 2.7 eV, so it only absorbs up to 460 nm. Besides, it is unstable in neutral and basic electrolytes, and it forms peroxide species during water oxidation which leads to photocorrosion. Even in acidic solutions, it tends to oxidize anions which leads to less-than-unity Faradaic efficiency, making it difficult to study its water oxidation performance.^{21,30,31} α -Fe₂O₃, known as "rust", has attracted extensive interest due to its small bandgap of 2.1 eV, its earth abundance, and stability in alkaline environment.^{32,33} In fact, α -Fe₂O₃ has been investigated extensively and systematically to understand its limiting processes in water oxidation, and various strategies have been designed to improve its performance.^{25,33–41} The lessons and investigation methods learnt from α-Fe₂O₃ can be applied to other systems to discover new promising materials for water oxidation and to better understand the general rules of tuning

the optoelectronic and catalytic properties of them. While there is a limited library of binary metal oxides as candidates of water oxidation photoanode, ternary and quaternary oxides have attracted emerging interest recently due to their diversity and tunability.^{23,42,43}



Figure 1-4. Band edge energy levels and bandgaps of candidates for PEC water oxidation photoanodes.

CuWO₄ has a distorted wolframite structure, which consists of corner-linked CuO₆ and WO₆ octahedra.¹⁸ It has an indirect bandgap of ~2.3 eV,¹⁹ which allows it to absorb photons up to 539 nm. The reduction of the bandgap compared with WO₃ is due to the valence band edge of CuWO₄ being more negative than that of WO₃, while the conduction band edge stays comparable.¹⁷ This is favorable because the holes in the valence band of WO₃ have more than sufficient energy for water oxidation. Integration of AM 1.5 solar spectrum with this bandgap gives a maximum photocurrent density of ~9 mA cm⁻² (Fig 1-5). Assuming that we could pair CuWO₄ with a suitable photocathode to operate the cell at the maximum photocurrent density of CuWO₄

and no additional overpotential is required, the maximum theoretical solar-to-hydrogen efficiency is ~11% based on calculation via equation 1.1. Besides, as mentioned above, $CuWO_4$ shows great stability over long periods of illumination in neutral and slightly basic electrolytes,¹⁶ and is made of earth abundant elements.



Figure 1-5. Red curve: AM 1.5 solar spectrum; black vertical line: wavelength that corresponds to the bandgap of CuWO₄; yellow area: maximum photon flux that can be absorbed by CuWO₄ under 1 sun illumination.

Despite all these favorable characteristics, the overall water oxidation efficiency with CuWO₄ has been low. The best photocurrent density achieved with CuWO₄ to date is only 0.3 mA cm⁻².⁴⁴ In addition, the photocurrent onset potential is several hundred millivolts positive of the flat band potential.^{45–47} The solar energy conversion efficiency of water oxidation with CuWO₄ is controlled by three factors: the light harvesting efficiency (η_{LH}), charge separation efficiency

($\eta_{\rm CS}$), and hole collection efficiency ($\eta_{\rm HC}$). Under the operating conditions of PEC water oxidation with CuWO₄ (Fig 1-6), light is absorbed by the photoanode, generating holes in the valence band (VB) and electrons in the conduction band (CB). The fraction of photons absorbed by the semiconductor determines the light harvesting efficiency, η_{LH} . This term is determined by the absorption coefficient (α) of CuWO₄ and the thickness of the electrode. Due to the weak absorption of this indirect semiconductor, a thickness of several hundred nm to several µm is needed to absorb 95% of incident light, depending on the wavelength and synthetic methods. After charge generation, electrons transport to the back contact, while holes go through diffusion in the quasi-neutral region in the bulk of the material and drift in the space charge region to reach the surface. Meanwhile, the charge carriers can undergo unfavorable recombination in the bulk. The portion of charge carriers that reach the interface is defined as $\eta_{\rm CS}$. For n-type semiconductors, since electrons are in large excess, usually the transport of holes limit their bulk properties. After the holes reach the CuWO₄/electrolyte interface, they either get collected by the electrolyte species to generate oxygen, or recombine with electrons from CB. The fraction of holes at the surface that contribute to water oxidation is described by η_{HC} .



Figure 1-6. Schematic diagram of PEC water oxidation at CuWO₄ photoanode/electrolyte interface. The red arrow indicates light absorption (charge generation), green arrows represent charge separation, including diffusion in the quasi-neutral region and drift due to the electric field in the depletion region, and blue arrows indicate hole collection at CuWO₄/electrolyte interface to oxidize water. Meanwhile, the dark red arrows represent possible recombination pathways in the bulk or at the interface.

The poor PEC performance of CuWO₄ has been attributed to both limited charge separation and hole collection efficiencies.^{45,47–49} Bohra *et al*⁵⁰ and Gaillard *et al*⁴⁵ compared the PEC performance by front (electrolyte) and back (substrate) illumination, and concluded that the electron transport is limiting the bulk property of CuWO₄. To overcome the opposing properties of a long light absorption depth^{48,51} and poor charge separation efficiency, strategies such as nanostructuring^{52,53} and doping⁴⁵ have been pursued. However, there has only been limited improvement through these modifications, mainly due to a lack of knowledge of its fundamental properties such as charge carrier collection length. Prior reports have also suggested that the hole collection efficiency is low, due to slow water oxidation kinetics and the presence of a mid-gap surface state which mediates the oxygen evolution reaction (OER) on CuWO₄.^{45,47,49,54} However, to date only one catalyst (MnPO)⁴⁷ has moderately improved the performance of CuWO₄, while other catalysts either make no change in its performance or make it worse. A limited number of previous work on the investigations of CuWO₄ indicates a lack of knowledge to direct scientists and engineers to effectively optimize its performance. Therefore, this motived us to conduct fundamental studies with this material to better understand its limits and properties.

1.5 Objectives

It is the purpose of this dissertation to deeply understand the limitations of CuWO₄ in terms of charge separation in the bulk of the material and charge transfer (hole collection) at semiconductor/electrolyte interface. Specifically, we mainly utilized atomic layer deposition (ALD) to deposit CuWO₄ electrodes⁴⁸ to conduct these fundamental studies. The self-limiting behavior of ALD allows for deposition of conformal flat films with precise thickness control.⁵⁵ This eliminates the complexity that nanostructured or porous films can cause in separating bulk and surface properties. A new ALD-based stack deposition-annealing method was used to deposit $CuWO_4$ as discussed in Chapter 2. In Chapter 3, we introduce using a suitable hole scavenger to quantify the hole collection efficiency which would benefit understanding the underlying reasons for the effect of water oxidation catalysts on CuWO₄ electrode.⁴⁶ In Chapter 4, complementary electrochemical and photoelectrochemical measurements were used to elucidate the nature of surface states of CuWO₄ which would enlighten understanding of the general role of surface states on other semiconductor photoanodes. In Chapter 5, spray pyrolysis was used to deposit thick CuWO₄ electrodes in order to determine the limiting charge carriers, which are the electrons. The future promise of CuWO₄ as water splitting photoanode was discussed in Chapter 6.

REFERENCES

REFERENCES

- (1) US. Energy Information Administration: eia.gov.
- (2) Lewis, N. S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci.* **2007**, *104*, 15729–15835.
- (3) Kerr, R. A. How Urgent Is Climate Change? *Science* 2007, *318*, 1230–1231.
- (4) United States Environmental Protection Agency: www.epa.gov.
- (5) Zhou, X.; Liu, R.; Sun, K.; Chen, Y.; Verlage, E.; Francis, S. A.; Lewis, N. S.; Xiang, C. Solar-Driven Reduction of 1 Atm of CO₂ to Formate at 10% Energy-Conversion Efficiency by Use of a TiO₂ -Protected III–V Tandem Photoanode in Conjunction with a Bipolar Membrane and a Pd/C Cathode. ACS Energy Lett. 2016, 764–770.
- (6) Sun, K.; Liu, R.; Chen, Y.; Verlage, E.; Lewis, N. S.; Xiang, C. Solar-Driven Water Splitting: A Stabilized, Intrinsically Safe, 10% Efficient, Solar-Driven Water-Splitting Cell Incorporating Earth-Abundant Electrocatalysts with Steady-State pH Gradients and Product Separation Enabled by a Bipolar Membrane. *Adv. Energy Mater.* **2016**, *6* (13), 1–7.
- (7) Shaner, M. R.; McDowell, M. T.; Pien, A.; Atwater, H. A.; Lewis, N. S. Si/TiO₂ Tandem-Junction Microwire Arrays for Unassisted Solar-Driven Water Splitting. *J. Electrochem. Soc.* 2016, *163* (5), H261–H264.
- (8) Thomas, G. Overview of Storage Development DOE Hydrogen Program eere.energy.gov.
- (9) Jingshan, L.; Jeong-Hyeok, I.; Mayer, M. T.; Schreier, M.; Nazeeruddfn, M. K.; Nam-Gyu, P.; Tilley, S. D.; Hong Jin, F.; Gratzel, M. Water Photolysis at 12.3% Efficiency via Perovskite Photovoltaics and Earth-Abundant Catalysts. *Science* 2014, 345, 1593–1596.
- (10) Khaselev, O.; Turner, J. A. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting. *Science* **1998**, *280* (1998), 425–427.
- (11) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* **2010**, *110*, 6446–6473.
- (12) Bolton, J. R.; Strickler, S. J.; Connolly, J. S. Limiting and Realizable Efficiencies of Solar Photolysis of Water. *Nature* 1985, *316*, 495–500.
- (13) Hamann, T. W. Splitting Water with Rust: Hematite Photoelectrochemistry. *Tetrahedron* **2011**, *67* (45), 8639–8647.
- (14) Dare-Edwards, M. P.; Goodenough, J. B.; Hamnett, A.; Trevellick, P. R. Electrochemistry

and Photoelectrochemistry of iron(III) Oxide. J. Chem. Soc. Faraday Trans. 1983, 79 (9), 2027.

- (15) Dotan, H.; Sivula, K.; Gr, M.; Warren, S. C. Probing the Photoelectrochemical Properties of Hematite (α-Fe₂O₃) Electrodes Using Hydrogen Peroxide as a Hole Scavenger. **2011**, 4, 958–964.
- (16) Cowan, A. J.; Barnett, C. J.; Pendlebury, S. R.; Barroso, M.; Sivula, K.; Grätzel, M.; Durrant, J. R.; Klug, D. R. Activation Energies for the Rate-Limiting Step in Water Photooxidation by Nanostructured α-Fe₂O₃ Nd TiO₂. J. Am. Chem. Soc. **2011**, 133 (26), 10134–10140.
- (17) Itoh, K. Thin Film Photoelectrochemistry: Iron Oxide. J. Electrochem. Soc. **1984**, 131 (6), 1266–1271.
- (18) Peter, L. M.; Upul, K. G.; Tahir, A. A. Kinetics of Light-Driven Oxygen Evolution at α-Fe₂O₃ Electrodes. *Faraday Discuss.* **2012**, *155*, 309–322.
- (19) Hu, S.; Xiang, C.; Haussener, S.; Berger, D.; Lewis, N. S. An Analysis of the Optimal Band Gaps of Light Absorbers in Integrated Tandem Photoelectrochemical Water-Splitting Systems. *Energy Environ. Sci.* **2013**, *6*, 2984–2993.
- (20) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.
- (21) Mi, Q.; Zhanaidarova, A.; Brunschwig, B. S.; Gray, H. B.; Lewis, N. S. A Quantitative Assessment of the Competition between Water and Anion Oxidation at WO₃ Photoanodes in Acidic Aqueous Electrolytes. *Energy Environ. Sci.* **2012**, *5*, 5694.
- (22) Seabold, J. a.; Choi, K. S. Efficient and Stable Photo-Oxidation of Water by a Bismuth Vanadate Photoanode Coupled with an Iron Oxyhydroxide Oxygen Evolution Catalyst. J. Am. Chem. Soc. **2012**, *134*, 2186–2192.
- (23) Park, Y.; McDonald, K. J.; Choi, K.-S. Progress in Bismuth Vanadate Photoanodes for Use in Solar Water Oxidation. *Chem. Soc. Rev.* **2013**, *42*, 2321–2337.
- (24) Lhermitte, C. R.; Bartlett, B. M. Advancing the Chemistry of CuWO₄ for Photoelectrochemical Water Oxidation. *Acc. Chem. Res.* **2016**, *49*, 1121–1129.
- (25) Riha, S. C.; Klahr, B. M.; Tyo, E. C.; Seifert, S.; Vajda, S.; Pellin, M. J.; Hamann, T. W.; Martinson, A. B. F. Atomic Layer Deposition of a Submonolayer Catalyst for the Enhanced Photoelectrochemical Performance of Water Oxidation with Hematite. *ACS Nano* 2013, 7 (3), 2396–2405.
- (26) Butler, M. A.; Nasby, R. D.; Quinn, R. K. Tungsten Trioxide as an Electrode for Photoelectrolysis of Water. *Solid State Commun.* **1976**, *19* (10), 1011–1014.

- (27) Liu, R.; Lin, Y.; Chou, L. Y.; Sheehan, S. W.; He, W.; Zhang, F.; Hou, H. J. M.; Wang, D. Water Splitting by Tungsten Oxide Prepared by Atomic Layer Deposition and Decorated with an Oxygen-Evolving Catalyst. *Angew. Chemie Int. Ed.* **2011**, *50*, 499–502.
- (28) Rodríguez-Pérez, M.; Chacón, C.; Palacios-González, E.; Rodríguez-Gattorno, G.; Oskam, G. Photoelectrochemical Water Oxidation at Electrophoretically Deposited WO₃ Films as a Function of Crystal Structure and Morphology. *Electrochim. Acta* **2014**, *140*, 320–331.
- (29) Weinhardt, L.; Blum, M.; Bär, M.; Heske, C.; Cole, B.; Marsen, B.; Miller, E. L. Electronic Surface Level Positions of WO₃ Thin Films for Photoelectrochemical Hydrogen Production. *J. Phys. Chem. C* 2008, *112* (8), 3078–3082.
- (30) Klepser, B. M.; Bartlett, B. M. Anchoring a Molecular Iron Catalyst to Solar-Responsive WO₃ Improves the Rate and Selectivity of Photoelectrochemical Water Oxidation. J. Am. Chem. Soc. 2014, 136, 1694–1697.
- (31) Hill, J.; Choi, K. Effect of Electrolytes on the Selectivity and Stability of N-Type WO₃ Photoelectrodes for Use in Solar Water Oxidation Cited by Me. J. Phys. Chem. C 2012, 116, 7612–7620.
- (32) Klahr, B.; Gimenez, S.; Fabregat-santiago, F.; Hamann, T.; Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. **2012**, 134, 4294-4302.
- (33) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Electrochemical and Photoelectrochemical Investigation of Water Oxidation with Hematite Electrodes. *Energy Environ. Sci.* **2012**, *5*, 7626–7636.
- (34) Klahr, B. M.; Hamann, T. W.; Klahr, B. M.; Hamann, T. W. Voltage Dependent Photocurrent of Thin Film Hematite Electrodes Voltage Dependent Photocurrent of Thin Film Hematite Electrodes. **2011**, *99*, 63508.
- (35) Klahr, B. M.; Hamann, T. W. Current and Voltage Limiting Processes in Thin Film Hematite Electrodes. **2011**, *115*, 8393–8399.
- (36) Klahr, B.; Gimenez, S.; Fabregat-santiago, F.; Hamann, T.; Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. J. Am. Chem. Soc. 2012, 134, 4294– 4302.
- (37) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation With "Co-Pi"-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **2012**, *134* (40), 16693–16700.
- (38) Zandi, O.; Beardslee, J. A; Hamann, T. W. Substrate Dependent Water Splitting with Ultrathin α -Fe₂O₃ Electrodes. **2014**, *118*, 16494-16503.
- (39) Zandi, O.; Hamann, T. W. Enhanced Water Splitting Efficiency Through Selective Surface

State Removal. J. Phys. Chem. Lett. 2014, 5 (9), 1522–1526.

- (40) Zandi, O.; Klahr, B. M.; Hamann, T. W. Highly Photoactive Ti-Doped α-Fe₂O₃ Thin Film Electrodes: Resurrection of the Dead Layer. *Energy Environ. Sci.* **2013**, *6* (2), 634–642.
- (41) Zandi, O.; Hamann, T. W. Determination of Photoelectrochemical Water Oxidation Intermediates on Haematite Electrode Surfaces Using Operando Infrared Spectroscopy. *Nat. Chem.* 2016, *8*, 778–783.
- (42) Benko, F. A.; MacLaurin, C. L.; Koffyberg, F. P. CuWO₄ and Cu₃WO₆ as Anodes for the Photoelectrolysis of Water. *Mat. Res. Bull.* **1982**, *17*, 133–136.
- (43) Guo, W.; Chemelewski, W. D.; Mabayoje, O.; Xiao, P.; Zhang, Y.; Mullins, C. B. Synthesis and Characterization of CuV_2O_6 and $Cu_2V_2O_7$: Two Photoanode Candidates for Photoelectrochemical Water Oxidation. *J. Phys. Chem. C* **2015**, *119*, 27220–27227.
- (44) Zhang, H.; Yilmaz, P.; Ansari, J. O.; Khan, F. F.; Binions, R.; Krause, S.; Dunn, S. Incorporation of Ag Nanowires in CuWO₄ for Improved Visible Light-Induced Photoanode Performance. J. Mater. Chem. A 2015, 3, 9638–9644.
- (45) Gaillard, N.; Chang, Y.; Deangelis, A.; Higgins, S.; Braun, A. A Nanocomposite Photoelectrode Made of 2.2 eV Band Gap Copper Tungstate (CuWO₄) and Multi-Wall Carbon Nanotubes for Solar-Assisted Water Splitting. *Int. J. Hydrogen Energy* 2013, 38, 3166–3176.
- (46) Gao, Y.; Hamann, T. W. Quantitative Hole Collection for Photoelectrochemical Water Oxidation with CuWO4. *Chem. Commun.* **2017**, *53*, 1285–1288.
- (47) Pyper, K. J.; Yourey, J. E.; Bartlett, B. M. Reactivity of CuWO₄ in Photoelectrochemical Water Oxidation Is Dictated by a Midgap Electronic State. *J. Phys. Chem. C* **2013**, *117*, 24726–24732.
- (48) Gao, Y.; Zandi, O.; Hamann, T. W. Atomic Layer Stack Deposition-Annealing Synthesis of CuWO₄. *J. Mater. Chem. A* **2016**, *4*, 2826–2830.
- (49) Hill, J. C.; Choi, K. Synthesis and Characterization of High Surface Area CuWO₄ and Bi₂WO₆ Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, *1*, 5006–5014.
- (50) Bohra, D.; Smith, W. A. Improved Charge Separation via Fe-Doping of Copper Tungstate Photoanodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9857–9866.
- (51) Yourey, J. E.; Bartlett, B. M. Electrochemical Deposition and Photoelectrochemistry of CuWO₄, a Promising Photoanode for Water Oxidation. *J. Mater. Chem.* **2011**, *21*, 7651–7660.
- (52) Ye, W.; Chen, F.; Zhao, F.; Han, N.; Li, Y. CuWO₄ Nanoflake Array-Based Single-Junction

and Heterojunction Photoanodes for Photoelectrochemical Water Oxidation. ACS Appl. Mater. Interfaces **2016**, 8, 9211–9217.

- (53) Hu, D.; Diao, P.; Xu, D.; Xia, M.; Gu, Y.; Wu, Q.; Li, C.; Yang, S. Copper (II) Tungstate Nanoflake Array Films: Sacrificial Template Synthesis, Hydrogen Treatment, and Their Application as Photoanodes in Solar Water Splitting. *Nanoscale* **2016**, *8*, 5892–5901.
- (54) Gaillard, N.; Changa, Y.; DeAngelis, A.; Higgins, S.; Braun, A. A Nanocomposite Photoelectrode Made of 2.2 eV Band Gap Copper Tungstate (CuWO₄) and Multi-Wall Carbon Nanotubes for Solar-Assisted Water Splitting Nicolas. *Int. J. Hydrogen Energy* 2013, 38, 3166–3176.
- (55) George, S. M. Atomic Layer Deposition: An Overview. 2009, 110, 111–131.

Chapter 2:

Atomic Layer Stack Deposition-Annealing Synthesis of CuWO₄

Adapted with permission from:

*Atomic Layer Stack Deposition-Annealing Synthesis of CuWO*₄, Yuan Gao, Omid Zandi and Thomas W. Hamann, *J. Mater. Chem. A*, **2016**, *4*, 2826–2830. Copyright 2016 The Royal Society of Chemistry.
2.1 Abstract

A stack deposition-annealing (SDA) approach was demonstrated for the synthesis of CuWO₄ via atomic layer deposition (ALD). Certain amount of CuO was deposited on WO₃, followed by annealing to produce CuWO₄. The resulted CuWO₄ shows a band gap of 2.3 eV. The resulted CuWO₄ shows an onset potential of 0.8 V vs RHE and a photocurrent density of 0.11 mA cm⁻² at 1.23 V vs RHE in pH 9 KB_i buffer, which is promising activity as a photoanode for photoelectrochemical (PEC) water splitting. The resulted photoelectrode shows great stability over 4 hours. This methodology can in principal, be utilized for the ALD of various ternary and quaternary oxides for different applications.

2.2 Introduction

Atomic layer deposition (ALD) is an ideal material synthesis technique to fabricate planar and nanostructured materials due to its self-limiting vapor-phase surface chemistry.^{1–3} These unique properties allow ALD to offer angstrom-level thickness and dimensional control of materials on high aspect ratio substrates with excellent reproducibility. Thus, ALD has become widely utilized for the fabrication of microelectronic devices and materials for energy applications.^{2,4–6} In typical ALD process of a binary oxide, the metal precursor and the oxidant are alternately introduced into the reaction chamber to react with the substrate in a self-limiting fashion. The simplified schematic illustration of the ALD instrument used in this study and ALD process is shown in Figure 2-1. While the ALD of binary oxides is relatively straightforward, the ALD of ternary oxides can be challenging. This is a major limitation since ternary oxides are widely used as electrochromic and transparent conductive materials,⁷ electrocatalysts,⁸ and photocatalytic materials.⁹



Figure 2-1. Schematic illustration of a) ALD reactor and b) one cycle of ALD process.

One method to prepare a ternary oxide via ALD is to use bimetallic single-source precursors.¹⁰ Limitations of this method are lack of suitable bimetallic precursors and the fixed stoichiometry defined by the molecular precursor, leaving little room for modification. Another method is to use metal alkoxides as the oxygen source instead of H₂O, O₂ or O₃, so that it provides two of the three elements of the ternary oxide.¹¹ This method also suffers from a lack of volatile and reactive precursors. The most straightforward and common way to deposit ternary metal oxides is alternating separate binary oxide deposition cycles, where the desired stoichiometry is obtained by adjusting the pulsing ratios of two binary oxides.^{12,13} This approach requires the two binary oxides to deposit at the same temperature, so an overlap of their ALD windows is necessary. Unfortunately, the ALD windows of many binary oxides have small to no overlap. Another limitation is that since ALD is a surface-sensitive process, the growth rate may vary on different surfaces, thus it is difficult to control the stoichiometry based on the growth rates of binary oxides.^{14,15} Further, some materials have surface-inhibited growth on certain substrates due to the seeding layer in the initial deposition stage,^{15,16} which prevents the realization of ternary metal oxides. As a consequence, there are no examples of the ALD of many promising ternary oxide materials, such as copper tungstate (CuWO₄), reported. In this work, we introduce a new methodology for the ALD of ternary metal oxide thin films via a stack deposition-annealing (SDA) approach and report the first ALD of CuWO₄ to demonstrate the promise of this approach. This approach of stacking layers followed by annealing has been widely used in material synthesis in fields besides ALD,^{17,18} including a solution-solid phase reaction to make CuWO₄,¹⁹ while ALD provides a better control over the film thickness and composition. We note that a similar method has been applied for synthesis of Cu₂ZnSnS₄ by stacking binary sulfides via ALD followed by annealing.²⁰ Ginestra et al. also utilized the same method, but their purpose was synthesis of Y_2O_3/ZrO_2 alloy.²¹ Yang *et al.* showed Mn-doping by depositing a thin layer of MnO_x on TiO₂ nanowires followed by annealing to allow for the solid state diffusion of Mn into TiO₂.²² The results reported herein, however, represent the first example of ALD of a pure phase ternary oxide material deposited by the SDA approach.

2.3 Experimental

2.3.1 Film Deposition

Atomic layer deposition was performed using a Savannah 100 reactor (Cambridge Nanotech Inc.) at a temperature of 250 °C. Fluorine-doped tin oxide (FTO) coated glass (Hartford Glass, TEC 15, 12Ω cm⁻²), Si wafer (University Wafer) and quartz (Technical Glass Products, 1/16 inch thick) were used as the substrates. The substrates were sonicated in soap water, distilled water and isopropanol, and blown dry with nitrogen prior to deposition. The precursors for the deposition of WO₃ and CuO were bis(tert-butylimido)bis(dimethylamido) tungsten (VI) ($(^{\prime}BuN)_{2}(Me_{2}N)_{2}W$) (Strem Chemicals Inc., >97%) and copper(I)-N,N'-di-sec-butylacetamidinate ([Cu(^sBu-amd)]₂) (Dow Chemical Co., >99.0%), respectively. The nitrogen carrier gas was kept at 5 sccm. WO₃ was deposited using a modified version of a reported procedure.²³ The precursor was heated up to 75 °C but the vapor pressure was too small to be detected by our pressure gauge. In each ALD cycle, the tungsten precursor was pulsed for 2 s, followed by 10 s under exposure mode and 6 s nitrogen purge. De-ionized water (millipore, 18 M Ω) was used as the oxidant and was pulsed for 0.5 s followed by 15 s of exposure mode and 6 s of purge. 2000 cycles of WO₃ (\sim 160 nm) was deposited for characterization. The CuO was deposited using a modified recipe suggested by Ultratech Inc. (unpublished). The precursor was heated to 150 °C but the vapor pressure was not detectable by the pressure gauge. The copper precursor was pulsed for 3 s in each ALD cycle. After purging for 6 s, the oxidation was performed. The oxidation was a 2 s ozone ($\sim 10\%$ by weight O₃ in ultrahigh purity O_2 produced by Yanco Industries ozone generator) pulse, followed by a 3 s purge to allow for enough generation of ozone, and performed for 10 times. A total of ~1500 cycles of CuO (~150 nm) was deposited for the ease of characterization. These binary oxide films were sintered at 550 °C at a ramping rate of 10 °C/min and heated for 2 h. CuWO₄ thin films were made by depositing suitable cycles of CuO on top of WO₃ followed by annealing at 600 °C in air for 30 min at a ramping rate of 2 °C/min.

2.3.2 Calculation of CuO Deposition Cycles

Equations used to calculate the thickness of CuO needed to produce desired 1:1 stoichiometry with WO₃:

$$n_{WO_3} = n_{CuO} \tag{2.1}$$

$$\frac{\Gamma_{WO_3} \land Area \land t_{WO_3}}{M_{WO_3}} = \frac{\Gamma_{CuO} \land Area \land t_{CuO}}{M_{CuO}}$$
(2.2)

$$t_{CuO} = t_{WO_3} \cdot \frac{\Gamma_{WO_3}}{\Gamma_{CuO}} \cdot \frac{M_{CuO}}{M_{WO_3}}$$
(2.3)

where n_{WO_3} , t_{WO_3} , r_{WO_3} and M_{WO_3} are the number of moles, thickness, density and molar mass of WO₃ (density 7.16 g/cm³, molar mass 231.84 g/mol), and n_{CuO} , t_{CuO} , r_{CuO} and M_{CuO} are the corresponding parameters of CuO (density 6.315 g/cm³, molar mass 79.545 g/mol). Since they are uniformly deposited on the same substrate, the area should be the same for both WO₃ and CuO. Thickness of WO₃ is measured by spectroscopic ellipsometry, and thus the thickness of CuO needed can be calculated.

2.3.3 Calculation of Film Thickness

Theoretical thickness of CuWO₄ is calculated using the following equations:

$$m_{WO_3} + m_{CuO} = m_{CuWO_4} \tag{2.4}$$

$$\rho_{WO_3} \times V_{WO_3} + \rho_{CuO} \times V_{CuO} = \rho_{CuWO_4} \times V_{CuWO_4}$$
(2.5)

$$\rho_{WO_3} \times A \times t_{WO_3} + \rho_{CuO} \times A \times t_{CuO} = \rho_{CuWO_4} \times A \times t_{CuWO_4}$$
(2.6)

$$\rho_{WO_3} \times t_{WO_3} + \rho_{CuO} \times t_{CuO} = \rho_{CuWO_4} \times t_{CuWO_4}$$
(2.7)

$$t_{CuWO_4} = \frac{\rho_{WO_3} \times t_{WO_3} + \rho_{CuO} \times t_{CuO}}{\rho_{CuWO_4}}$$
(2.8)

 Γ_{CuWO_4} and t_{CuWO_4} are the density and theoretical thickness of resulted CuWO₄. The density of CuWO₄ we used herein is 7.790 g cm⁻³, obtained by theoretical calculations based on the crystal structure in literature,²⁴ which is close to experimental values.^{24,25}

2.3.4 Film Characterization

The as-deposited and annealed films were characterized by X-ray diffraction (XRD), Xray photoelectron spectroscopy (XPS) and Raman spectroscopy. XRD was taken with Bruker Davinci Diffractometer operating at 40 kV and 40 mA using Cu K α radiation. XPS analysis was made using Perkin Elmer Phi 5600 ESCA system with a magnesium K α X-ray source at a takeoff angle of 45°. Survey scans of 0-1100 eV binding energy and detailed scans for C 1s, O 1s, W 4f and/or Cu 2p regions were scanned for all samples. Peaks were corrected with the C 1s peak set to 284.8 eV, and subsequent Shirley background subtraction was performed for fitting. Raman spectra were recorded using LabRam Armis, Horiba Jobin Yvon instrument equipped with 532 nm laser and a ×50 microscope to focus the laser on the film surface. The thicknesses of binary oxide films were obtained by ellipsometric measurements (Horiba Jobin Yvon, Smart-SE). Thickness of the ternary film and the surface morphology of the films were examined by atomic force microscopy (AFM) using MFP-3D from Asylum Research. Cross-section scanning electron microscopy (SEM) (Carl Zeiss Microscopy) was also used to determine the film thicknesses, as well as their morphology. Energy-dispersive X-ray (EDX) analysis spectra were collected using Ametek-EDAX Apollo X. Accelarating voltages used were 15 kV and 20 kV, with 8 mm working distance. Spectra were analyzed using TEAM EDS software. Cu K and W M emission lines were analyzed for 15 kV beam voltage and Cu K and W L were analyzed for 20 kV beam voltage. The error bar in the main text is the standard deviation of measurements on 10 different spots. Absorbance measurements were made using a Perkin-Elmer Lambda 35 UV-vis spectrometer with a Labsphere integrating sphere.

2.3.5 Photoelectrochemistry

Thin film electrodes were masked with a 60 μ m Surlyn film (Solaronix) with a 0.28 cm² hole to define the active area and to prevent scratching of the thin films which were clamped to a custom-made glass electrochemical cell. Surlyn films were adhered to the electrodes by heating to 120 °C. A homemade saturated Ag/AgCl electrode was used as a reference electrode, and high surface area platinum mesh was used as the counter electrode. All experiments shown used a pH 9 potassium borate (KB_i) buffer containing 0.2 M KCl as a supporting electrolyte. The buffer was prepared by adding an appropriate amount of KOH pellets into 0.1 M H₃BO₃ to adjust the pH. The pH was determined using a Fisher Scientific Accumet pH meter. All photoelectrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. The light source was a 450 W Xe arc lamp. An AM 1.5 solar filter (Sciencetech Inc.) was used to simulate sunlight at 100 mW cm⁻² (1 sun). The *J-V* curves were measured at a scan rate of 20 mV/s by shining light from the electrolyte-electrode (EE, front illumination) interface. The monochromatic photocurrents (IPCE) were measured at 1.23 V vs RHE using the same light source coupled with a grating monochromator with a 10 nm step.

2.4 Results and Discussion

WO₃ was deposited using a modified literature procedure at a substrate temperature of 250 °C.²³ According to the XPS data shown in Figure 2-2, the as-deposited film and annealed film both show W $4f_{7/2}$ and W $4f_{5/2}$ peaks at 35.6 eV and 37.8 eV, consistent with W⁶⁺ peaks in literature.²⁶⁻²⁹ The O 1s peak shows a main peak at 530.4 eV, corresponding to the metal oxide O 1s peak, with a small contribution from carbon bonded oxygen at 531.9 eV. According to the XRD (Figure 2-3) and Raman spectra (Figure 2-4), the as-deposited films appear to be amorphous since no peaks corresponding to WO_3 are present. After annealing, however, diffraction peaks at 23.0° , 24.3° and 34.1° clearly show the presence of WO₃. These peaks were assigned using the International Union of Crystallography (IUCr) database. Raman peaks at 272, 325, 713 and 808 cm⁻¹ also appeared with annealing, in agreement with Raman scattering from WO₃.^{30,31} Therefore, the as-deposited WO₃ was amorphous, and after annealing in air at 550 °C for 2h, it turned crystalline. As shown in Figure 2-5, ALD of WO₃ reaches saturation when the metal precursor pulse length is 2 s with a growth rate of 0.86 ± 0.03 Å/cycle. The growth rate is the average growth rate of four batches, including two batches pulsing 2 s and two batches pulsing 3 s. The error is calculated as the standard deviation of the four batches described above.



Figure 2-2. Experimental X-ray photoelectron spectroscopy (XPS) spectra of W 4f and O 1s peaks (black scatters) with fitting (red solid lines and dots) of as-deposited (top) and annealed (bottom) WO₃.



Figure 2-3. X-ray diffraction (XRD) patterns of as-deposited (black) and annealed (red) WO₃.



Figure 2-4. Raman spectra of as-deposited (black) and annealed (red) WO₃.



Figure 2-5. Thickness of WO₃ thin films vs number of deposition cycles using different metal precursor pulse lengths.

CuO was deposited at a substrate temperature of 250 °C, followed by annealing in air at 550 °C for 2 h. In the XPS spectra shown in Figure 2-6, the as-deposited film and annealed film both show Cu^{2+} peaks in the Cu 2p region. Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks are located at 933.9 and 953.8 eV, with their satellite peaks at 940.9, 943.4 (Cu $2p_{3/2}$ satellite) and 962.0 eV (Cu $2p_{1/2}$ satellite), respectively, which is the distinguishing feature of the XPS spectra of Cu^{2+} .^{32,33} The O 1s peak shows a main lattice oxide peak at 529.8 eV and a small contribution from carbon bonded oxygen at 532.1 eV. Also, there is a huge deconvoluted peak at 531.2 eV, which can be attributed to the defective oxygen CuO.³⁴ The XRD pattern and Raman Spectra of CuO films are shown in Figure 2-7 and 2-8. Both as-deposited and annealed CuO thin films are crystalline. All X-ray diffraction peaks agree with CuO diffractions according to the IUCr database, including CuO single crystals grown by different methods such as flux method^{35,36} and thermal decomposition of gerhardtite.³⁷ Raman spectra show three peaks which are all assigned to Raman scattering of CuO.^{38–40} The saturation growth rate with 1 s Cu source pulse length is 0.45 ± 0.04 Å/cycle, and 3 s pulse length was used in following experiments just to be conservative. This growth rate was calculated using the slope of the best fit line of the thickness vs number of cycles plot, but due to the surface-enhanced behavior^{41,42} of CuO on Si substrate, the intercept with the thickness axis is not zero (Fig 2-9). Thus, this growth rate is not reflecting the real growth rate of CuO on itself or in our case, on WO_3 . This experiment is only to show the self-limiting growth behavior of CuO. In the following demonstration of ALD of CuWO₄, we are using the growth rate of CuO on WO₃ for calculation.



Figure 2-6. Experimental XPS spectra of Cu 2p and O 1s peaks (black scatters) with fitting (red solid lines and dots) of as-deposited (top) and annealed (bottom) CuO.



Figure 2-7. XRD patterns of as-deposited (black) and annealed (red) CuO.



Figure 2-8. Raman spectra of as-deposited (black) and annealed (red) CuO.



Figure 2-9. Thickness vs number of deposition cycles of CuO thin films with different metal precursor pulse length.

Numerous attempts utilizing a variety of conditions to make the ternary oxide $CuWO_4$ by conventional approaches were unsuccessful. In order to determine the cause, we deposited WO_3

on CuO films and CuO on WO₃ films. Figure 2-10a shows the growth rate of WO₃ on as-deposited CuO. There is no significant increase in the total film thickness until after ~100 cycles of WO₃. This suggests that WO₃ has substrate-inhibited growth¹⁶ (blue line) on the CuO surface. After ~100 cycles, when the CuO surface is fully covered with WO₃, WO₃ grows linearly as expected (red line). This lack of growth of WO₃ on the CuO surface explains the failure of the conventional method to deposit CuWO₄ by alternating WO₃ and CuO deposition cycles. Figure 2-10b shows that CuO grows linearly on WO₃ (1.5 ± 0.1 Å/cycle), however, which means the WO₃ surface does not inhibit the deposition of CuO. While in principle, it may be possible to use a ~100:1 pulsing ratio of WO₃:CuO in each super cycle to deposit one layer of CuWO₄, this is impractical since it would waste 99% of the W precursor and a lot of time, and is not reproducible. Alternatively, new precursors could be identified, but that is a very time intensive process and not a general solution.



Figure 2-10. Total thickness of a) WO₃ on 100 cycles of CuO and b) CuO on 100 cycles of WO₃ as a function of number of deposition cycles.

Therefore, a stack deposition approach was utilized to grow $CuWO_4$ (Fig 2-11). A stoichiometric amount of CuO was deposited on WO_3 , followed by annealing. The advantages of this approach are numerous. Instead of empirically optimizing the pulse sequence, the precise number of cycles to produce a 1:1 stoichiometry of W:Cu for a given thickness is easily determined.

Since the materials are deposited sequentially, they can be grown at different temperatures and their ALD temperature windows do not have to overlap. This method should be general and applicable to a wide variety of ternary and potentially quaternary metal oxide materials.



Figure 2-11. Sequential ALD of WO₃/CuO and post-ALD annealing to make CuWO₄ thin films via stack deposition-annealing (SDA) approach.

1000 ALD cycles of WO₃ was deposited on Si, fluorine-doped tin oxide (FTO) coated glass and quartz substrates. The thickness of the WO₃ thin film was 65 nm, measured by spectroscopic ellipsometry and cross-section scanning electron microscopic (SEM) image (Figure 2-12a). To match the stoichiometry, the desired thickness of CuO was determined by considering the ratios of density and molar masses of WO₃ and CuO (see experimental for calculation details). Based on this calculation, 170 cycles of CuO was deposited on top of the 65 nm WO₃ film. The as-deposited films showed a brownish color, which is essentially the color of CuO. After annealing in air at 600 °C for 30 min, to allow for the solid-state reaction between CuO and WO₃, the thin film turned pale yellow, which agrees with the expected color of CuWO₄.^{43,44} The thickness of the resulted film was 83 nm measured by atomic force microscopy (AFM). The AFM image in Figure 2-13c shows that the annealed CuWO₄ film has an RMS roughness of 4 nm. Comparing this value with the roughness of as-deposited WO₃ and as-deposited CuO on WO₃ in Figure 2-13a and Figure 2-13b, which is 0.4 nm and 3 nm, respectively, we concluded that while the annealing process resulted in a slight increase in the roughness of our films, the resulted CuWO₄ film is overall smooth. Cross-section SEM image confirmed that the resulted film has a thickness of ~80 nm (Figure 2-12b). Considering the densities of WO₃, CuO and CuWO₄ and the thicknesses (or number of cycles) of WO₃ and CuO deposited, we should in principle obtain 80 nm of crystalline CuWO₄ (see experimental for details).



Figure 2-12. Cross-section SEM images of a) as-deposited WO_3 and b) annealed $CuWO_4$ thin films on Si substrate.



Figure 2-13. AFM surface morphology image of a) as-deposited WO₃, b) as-deposited CuO on WO₃, and c) annealed CuWO₄ on Si substrate.

Energy-dispersive X-ray (EDX) analysis spectra (see Appendix) gives W:Cu atomic ratio of 1.00 ± 0.05 using an accelerating voltage of 20 kV. A 15 kV beam voltage was also used to minimize the contribution from the underlying substrate, and the determined W:Cu ratio is $0.99 \pm$ 0.02. This agreement between the experimental and theoretical thicknesses/stoichiometry indicates that using this new SDA method, we can precisely control the thickness and composition of CuWO₄ thin films by varying the number of cycles deposited, which is essentially one benefit of ALD. The X-ray photoelectron spectroscopy (XPS) survey scans of as-deposited and annealed films (Fig 2-14) show W 4f, Cu 2p and O 1s peaks. Each of the peaks was further examined to determine the oxidation states of the metals (Fig 2-15). Both films showed W $4f_{7/2}$ and W $4f_{5/2}$ peaks at binding energy of 35.2 and 37.4 eV, consistent with W^{6+,27,28} Spectra showed the Cu $2p_{3/2}$ peak at 934.2 eV with its satellite peaks at 941.1 and 943.5 eV, and the Cu $2p_{1/2}$ peak at 954.1 eV with its satellite at 962.1 eV, respectively, which are unique to Cu^{2+,32,33} Figure 2-15b and Figure 2-15c shows the O 1s peaks of the as-deposited and annealed films, respectively, and both of them are fitted with three peaks. The peaks at 530.1 eV belong to the main lattice oxide peak. The peaks at 532.0 and 531.2 eV of as-deposited and annealed films are assigned to the defective oxygen.³⁴ Finally, the peaks at 533.2 and 532.2 eV in the as-deposited and annealed films are attributed to carbon-bonded oxygen.



Figure 2-14. XPS survey spectra of as-deposited (bottom) and annealed (top) film of CuO on top of WO₃.



Figure 2-15. Experimental XPS spectra of a) Cu 2p and W 4f peaks (black scatters) with fitting (red solid lines and dots) of CuO on top of WO₃ as-deposited (top) and annealed (CuWO₄) (bottom) and O 1s peaks (black scatters) with fitting (red solid lines and dots) of CuO on top of WO₃ b) as-deposited and c) annealed (CuWO₄).

X-ray diffraction (XRD) patterns and Raman spectra of the as-deposited stack and annealed films are shown in Figure 2-16. The XRD pattern of the as-deposited film does not show any diffraction peaks except those attributed to the FTO substrate. The diffraction peaks of CuO are not observed in XRD of the as-deposited stack because the amount of CuO at the surface is below its detection limit. The annealed film shows diffraction peaks of crystalline CuWO₄ well matched with literature.^{24,45} Raman spectra of the as-deposited films show a small peak around 290 cm⁻¹, which is assigned to the main Raman scattering peak of CuO. The small peak at 244 cm⁻¹ and humps around 600, 800 and 950 cm⁻¹ are due to the background scattering from the FTO substrate. This agrees with our results of binary oxides WO₃ and CuO, indicating that the underlying WO₃ is amorphous, while CuO is crystalline after deposition. Since only a thin layer of CuO (25 nm) was deposited, the other two peaks of CuO are not observed because of their low intensity. All the peaks from the annealed films match with Raman scattering from the crystal structure of CuWO₄ previously reported,^{45,46} except those from the substrate. The CuWO₄ Raman scattering peak at 550 cm⁻¹ overlaps with the wide FTO scattering peak around 600 cm⁻¹, but comparing this hump with that of the as-deposited film, this peak is sharper and more intense, with the peak position shifted toward smaller wavenumber, distinct from the hump from the substrate. Therefore, the peak at 550 cm⁻¹ is assigned to CuWO₄. Thus, we conclude that the as-deposited film essentially consists of a thin layer of crystalline CuO on top of amorphous WO₃, which is different from metal sulfide multilayers that can mix even at low deposition temperature (135 °C)²⁰; after annealing, the solid-state reaction between CuO and WO₃ produces pure crystalline CuWO₄.



Figure 2-16. a) X-ray diffraction patterns and b) Raman spectra of CuO on WO₃ as-deposited (black) and annealed (CuWO₄) (red). Peak positions of CuWO₄ from literature are plotted as vertical dashed gray lines.

Absorbance and AFM thickness measurements of CuWO₄ films with different thicknesses were further conducted to show the fine control of thickness using our SDA approach. In Figure 2-17 shows different CuWO₄ thin films deposited on FTO substrates. The thicknesses of resulted CuWO₄ films displayed in Figure 2-18 show a linear relationship with ALD cycles of WO₃, with a growth rate of 0.85 Å of CuWO₄/cycle of WO₃. The absorbance was calculated by correcting for the reflectance from the substrate using previously reported method.⁴⁷ Figure 2-19a shows that the absorbance increases with increasing deposition cycles, in agreement with the trend of color shown in Figure 2-17. Figure 2-19b and Figure 2-19c indicate a linear trend of absorbance of CuWO₄ using our SDA method. Considering the thicknesses of these films shown in Figure 2-18, the absorption coefficients of CuWO₄ at 400 nm and 450 nm are calculated to be 58370 cm⁻¹ and 29058 cm⁻¹, respectively. These values are higher than some reported values,^{43,45,48} and close to those measured with cosputtered films (~20000 cm⁻¹ at 450 nm) but still slightly higher.⁴⁹ One possible reason is that our film is more compact and uniform compared with films synthesized via other methods.



Figure 2-17. Images of CuWO₄ thin films deposited on FTO substrates with varying ALD cycles of WO₃ of 0, 500, 1000, 1500, 2000, and 2500.



Figure 2-18. Thickness of CuWO₄ films with different deposition cycles of WO₃ measured with AFM (black squares). Error bars represent the standard deviation of 10 different measurements on each film. Red dash shows the linear fit of thickness vs. number of cycles.



Figure 2-19. Top: a) Absorbance of CuWO₄ thin films with ALD cycles of WO₃ of 500 (red solid), 1000 (orange dash), 1500 (yellow short dash), 2000 (green dash dot), and 2500 (blue dot). Bottom: Absorbance of CuWO₄ thin films at wavelength of b) 400 nm and c) 450 nm varying with different ALD cycles of WO₃. Error bars represent standard deviation of independent measurements on three different spots for each thickness.

UV-vis of CuWO₄ electrodes was measured by illuminating from the FTO side. The absorptance of the films was calculated using absorptance = $T_{sub} + R_{sub} - T_{film} - R_{film}$, where T_{sub} ,

 R_{sub} , T_{film} , and R_{film} are the measured transmittance and reflectance of the quartz substrate and quartz coated with CuWO₄ thin film, respectively. As seen in Figure 2-20a, the absorption around 500 nm is weak due to the indirect bandgap of the semiconductor.⁵⁰ The absorbance was calculated by correcting for the reflectance from the substrate using previously reported method from which absorptivity and band gap are extracted.⁴⁷ The Tauc plot of resulted CuWO₄ (Fig 2-20b) shows an indirect band gap of 2.3 eV, in agreement with the other reports.^{43,45,50} The absorption coefficient shown in Figure 2-20c is slightly higher than previously reported values.^{43,48,49}



Figure 2-20. a) IPCE (red scatters) in pH9 KBi buffer at 1.23 V vs RHE and absorptance spectrum (black solid line), b) Tauc plot, and c) absorption coefficient of CuWO₄ thin film.

The photoelectrochemistry of the CuWO₄ films were examined under PEC water oxidation conditions. The current density, J, vs. applied voltage, V, curve of CuWO₄ under 1 sun illumination is shown in Figure 2-21. The CuWO₄ thin film electrodes exhibit excellent water oxidation activity with the photocurrent onset potential of 0.8 V vs RHE and photocurrent of 0.11 mA cm⁻² at 1.23 V vs RHE (the thermodynamic potential for water oxidation). The J-V curve under chopped light matches well with both dark current and the curve under illumination, except that at potentials close to the onset. These small spikes in the photocurrent transients suggest that surface recombination occurs at these potentials.⁵¹ To confirm that the *J*-V curve is attributed strictly to CuWO₄, it was compared to pure CuO (35 nm) and WO₃ (100 nm) films (Fig 2-22). The J-V curve of CuO under illumination shows a cathodic wave at potentials negative of 0.8 V vs RHE, which is due to the reduction of CuO to Cu₂O, and an anodic peak at 0.9 V vs RHE, which is assigned to the re-oxidation of Cu₂O.⁵² The oxidation of Cu₂O is a dark reaction because it is also observed in the dark J-V curve of the CuO electrode. The dark J-V curve of WO₃ shows no current within the applied potential range, and under 1 sun illumination, there is a hysteresis in the reverse scan, which might be attributed to the instability of the WO₃ under the operating conditions. While the initial J-V response of the WO₃ appears similar to the CuWO₄ electrode, the photocurrent quickly decays. The photocurrent at 1.23 V was measured as a function of time to assess the stability of CuWO₄ and WO₃ films in a pH 9 solution under 1 sun illumination (Figure 2-21b). Remarkable stability was observed for the CuWO₄ electrode over the 4 h experiment, while the current of WO_3 degraded quickly in less than an hour, likely due to the photo-corrosion of WO₃ in the basic electrolyte.53,54 Incident-photon-to-current efficiency (IPCE) measurements of the CuWO4 electrode exhibited an onset of photocurrent around 500 nm, which agrees with the absorptance measurements (Figure 2-20a). We note that the IPCE at wavelengths of 500–540 nm is very low

as a result of the minimal light absorption at these wavelengths due to the very thin film measured. In any case, we confirm that the photocurrent is strictly due to CuWO₄, not from either residual CuO or WO₃ impurities. The photocurrent from our CuWO₄ is comparable to many results in literature,^{44,55–57} but is lower than some reported by Bartlett *et al.*^{43,58} and Gaillard *et al.*⁴⁸ The electrodes examined herein are thinner than previously reported electrodes (80 nm vs 200 nm to several microns), so not as much light was absorbed. In addition, previously reported films were porous or had nanostructures, which possess a higher surface area that can facilitate overcoming the charge separation limitations. The comparable PEC results of our CuWO₄ film with previously reported thicker films with higher surface area suggest the promise of this synthetic method.



Figure 2-21. a) *J-V* curves of an 80 nm thick CuWO₄ electrode in the dark (black dash), under 1 sun illumination (blue solid) and chopped illumination (red solid). The vertical gray dash shows the thermal dynamic potential of water oxidation. b) Stability test of CuWO₄ (red) and WO₃ (black) at 1.23 V vs RHE under 1 sun illumination. Experiments were made in 0.2 M KCl in pH9 KBi buffer.



Figure 2-22. *J-V* curve of a) CuO and b) WO₃ electrode in the dark (black) and under 1 sun illumination (red) measured in 0.2 M KCl in pH9 KBi buffer.

2.5 Conclusion

Overall, the PEC performance shows that the SDA method produces high quality crystalline pure phase CuWO₄ films with promising photocatalytic performance. This advance enables fundamental studies of the limitations of such ternary oxide materials, such as charge carrier diffusion length, as well as strategies to overcome them. For example, optimized

nanostructured CuWO₄ photoanodes can in principle overcome a mismatch in light absorption and charge carrier diffusion length. This work will in theory be enabled by the new materials synthesis methodology described here.

APPENDIX



Figure A2-1. An example of an EDX spectrum of CuWO₄ on FTO-coated glass.

REFERENCES

REFERENCES

- (1) George, S. M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110*, 111–131.
- (2) Knez, M.; Nielsch, K.; Niinistö, L. Synthesis and Surface Engineering of Complex Nanostructures by Atomic Layer Deposition. *Adv. Mater.* **2007**, *19* (21), 3425–3438.
- (3) Puurunen, R. L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/water Process. J. Appl. Phys. 2005, 97, 121301.
- (4) Leskelä, M.; Ritala, M. Atomic Layer Deposition Chemistry: Recent Developments and Future Challenges. *Angew. Chemie Int. Ed.* **2003**, *42*, 5548–5554.
- Wang, T.; Luo, Z.; Li, C.; Gong, J. Controllable Fabrication of Nanostructured Materials for Photoelectrochemical Water Splitting via Atomic Layer Deposition. *Chem. Soc. Rev.* 2014, 43 (22), 7469–7484.
- (6) O'Neill, B.; Jackson, D. H. K.; Lee, J.; Canlas, C.; Stair, P. C.; Marshall, C. L.; Elam, J. W.; Kuech, T. F.; Dumesic, J. A.; Huber, G. W. Catalyst Design with Atomic Layer Deposition. *ACS Catal.* 2015, 1804–1825.
- (7) Granqvist, C. G. Electrochromics for Smart Windows: Oxide-Based Thin Films and Devices. *Thin Solid Films* **2014**, *564*, 1–38.
- (8) Zhang, C.; Fagan, R. D.; Smith, R. D. L.; Moore, S. a.; Berlinguette, C. P.; Trudel, S. Mapping the Performance of Amorphous Ternary Metal Oxide Water Oxidation Catalysts Containing Aluminium. *J. Mater. Chem. A* 2015, *3* (2), 756–761.
- (9) Kim, T. W.; Choi, K.-S. Nanoporous BiVO4 Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* **2014**, *343*, 990–995.
- (10) Vehkamäki, M.; Ritala, M.; Leskelä, M.; Jones, A. C.; Davies, H. O.; Sajavaara, T.; Rauhala, E. Atomic Layer Deposition of Strontium Tantalate Thin Films from Bimetallic Precursors and Water. J. Electrochem. Soc. 2004, 151 (4), F69.
- (11) Ritala, M. Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources. *Science* **2000**, 288 (2000), 319–321.
- (12) Pickrahn, K. L.; Garg, A.; Bent, S. F. ALD of Ultrathin Ternary Oxide Electrocatalysts for Water Splitting. *ACS Catal.* **2015**, *5*, 1609–1616.
- (13) Mullings, M. N.; Hägglund, C.; Tanskanen, J. T.; Yee, Y.; Geyer, S.; Bent, S. F. Thin Film Characterization of Zinc Tin Oxide Deposited by Thermal Atomic Layer Deposition. *Thin Solid Films* **2014**, *556*, 186–194.
- (14) Satta Alessandra, a.; Schuhmacher, J.; Whelan, C. M.; Vandervorst, W.; Brongersma, S. H.; Beyer, G. P.; Maex, K.; Vantomme, a.; Viitanen, M. M.; Brongersma, H. H.; et al. Growth Mechanism and Continuity of Atomic Layer Deposited TiN Films on Thermal SiO₂. *J. Appl. Phys.* 2002, *92*, 7641–7646.
- (15) Green, M. L.; Ho, M. Y.; Busch, B.; Wilk, G. D.; Sorsch, T.; Conard, T.; Brijs, B.; Vandervorst, W.; Räisänen, P. I.; Muller, D.; et al. Nucleation and Growth of Atomic Layer Deposited HfO₂ Gate Dielectric Layers on Chemical Oxide (Si-O-H) and Thermal Oxide (SiO₂ or Si-O-N) Underlayers. J. Appl. Phys. 2002, 92, 7168–7174.
- (16) Puurunen, R. L.; Vandervorst, W. Island Growth as a Growth Mode in Atomic Layer Deposition: A Phenomenological Model. J. Appl. Phys. 2004, 96, 7686–7695.
- (17) Kaigawa, R.; Funahashi, K.; Fujie, R.; Wada, T.; Merdes, S.; Caballero, R.; Klenk, R. Tandem Solar Cells with Cu(In,Ga)S₂ Top Cells on ZnO Coated Substrates. *Sol. Energy Mater. Sol. Cells* **2010**, *94* (11), 1880–1883.
- (18) Kaigawa, R.; Ohyama, a.; Wada, T.; Klenk, R. Electrical Properties of Homogeneous Cu(In,Ga)S₂ Films with Varied Gallium Content. *Thin Solid Films* **2007**, *515*, 6260–6264.
- (19) Zheng, J. Y.; Song, G.; Kim, C. W.; Kang, Y. S. Facile Preparation of P-CuO and P-CuO/n-CuWO4 Junction Thin Films and Their Photoelectrochemical Properties. *Electrochim. Acta* 2012, 69, 340–344.
- (20) Thimsen, E.; Baryshev, S. V; Martinson, A. B. F.; Elam, W.; Veryovkin, I. V; Pellin, M. J. Interfaces and Composition Profiles in Metal-Sulfide Nanolayers Synthesized by Atomic Layer Deposition. *Chem. Mater.* **2013**, *25*, 313-319.
- (21) Ginestra, C. N.; Sreenivasan, R.; Karthikeyan, A.; Ramanathan, S.; Mcintyre, P. C. Atomic Layer Deposition of Y₂O₃/ZrO₂ Nanolaminates A Route to Ultrathin Solid-State Electrolyte Membranes. 2007, 10, 161–165.
- (22) Resasco, J.; Dasgupta, N. P.; Rosell, J. R.; Guo, J.; Yang, P. Uniform Doping of Metal Oxide Nanowires Using Solid State. J. Am. Chem. Soc. **2014**, 136, 10521–10526.
- (23) Liu, R.; Lin, Y.; Chou, L. Y.; Sheehan, S. W.; He, W.; Zhang, F.; Hou, H. J. M.; Wang, D. Water Splitting by Tungsten Oxide Prepared by Atomic Layer Deposition and Decorated with an Oxygen-Evolving Catalyst. *Angew. Chemie Int. Ed.* **2011**, *50*, 499–502.
- (24) Kihlborg, L.; Gebert, E. CuWO₄, a Distorted Wolframite-Type Structure. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1970**, *26*, 1020–1026.
- (25) Pouchard, M.; Krussanova, M. A Photoelectrochemical Study of CuWO₄ Single Crystals. *Phys. Stat. Sol.* **1984**, *82*, 285–294.

- (26) Biloen, P.; Pott, G. T. X-Ray Photoelectron Spectroscopy Study of Supported Tungsten Oxide. J. Catal. **1973**, *30*, 169–174.
- (27) Katrib, A.; Hemming, F.; Wehrer, P.; Hilaire, L.aire, G. Journal of Electron Spectroscopy and Related Phenomena. J. Electron Spectros. Relat. Phenomena **1995**, 76, 195–200.
- (28) Salvatl, L.; Makovsky, L. E.; Stencel, J. M.; Brownls, F. R.; Hercules, D. M. Surface Spectroscopic Study. **1981**, *104* (1977), 3700–3707.
- (29) Diaz-Reyes, J. Optical and Structural Properties of WO₃ as a Function of the Annealing Temperature. *Adv. Sensors, Signals Mater.* **2010**, 99–104.
- (30) Desbat, B.; Lassegues, J. C. Infrared and Raman Study of WO₃ Tungsten Trioxides and WO₃, xH_zO Tungsten Trioxide Tydrates. *J. Solid State Chem.* **1987**, *247*, 235–247.
- (31) Zhang, J.; Zhang, W.; Yang, Z.; Yu, Z.; Zhang, X.; Chang, T. C.; Javey, A. Sensors and Actuators B: Chemical Vertically Aligned Tungsten Oxide Nanorod Film with Enhanced Performance in Photoluminescence Humidity Sensing. *Sensors Actuators B. Chem.* 2014, 202, 708–713.
- (32) Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* 2011, 257 (3), 2717–2730.
- (33) Tahir, D.; Tougaard, S. Electronic and Optical Properties of Cu, CuO and Cu₂O Studied by Electron Spectroscopy. *J. Phys. Condens. Matter* **2012**, *24*, 175002.
- (34) Biesinger, M. C.; Lau, L. W. M.; Gerson, A. R.; St, R.; Smart, C. Applied Surface Science Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides : Sc, Ti, V, Cu and Zn. *Appl. Surf. Sci.* 2010, 257 (3), 887–898.
- (35) Åsbrink, S.; Norrby, L. J. A Refinement of the Crystal Structure of copper(II) Oxide with a Discussion of Some Exceptional E.s.d.'s. Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 1970, 26 (1), 8–15.
- (36) Asbrink, S.; Waskowska, A. CuO: X-Ray Single-Crystal Structure Determination at 196 K and Room Temperature. *J. Phys. Condens. Matter* **1991**, *3*, 8173–8180.
- (37) Langford, J. I.; Louer, D. High-Resolution Powder Diffraction Studies of copper(II) Oxide. *J. Appl. Crystallogr.* **1991**, *24*, 149–155.
- (38) Xu, J. F.; Ji, W.; Shen, Z. X.; Li, W. S.; Tang, S. H.; Ye, X. R.; Jia, D. Z.; Xin, X. Q. Raman Spectra of CuO Nanocrystals. *J. Raman Spectrosc.* **1999**, *30*, 413–415.
- (39) Hagemann, H.; Bill, H.; Sadowski, W.; Walker, E.; François, M. Raman Spectra of Single Crystal CuO. *Solid State Commun.* **1990**, *73* (6), 447–451.

- (40) Goldstein, H. F.; Kim, D. S.; Yu, P. Y.; Bourne, L. C.; Chaminade, J. P.; Nganga, L. Raman Study of CuO Single Crystals. *Phys. Rev. B* **1990**, *41* (10), 7192–7194.
- (41) Dolgushev, N. V.; Malkov, a. a.; Malygin, a. a.; Suvorov, S. a.; Shchukarev, a. V.; Beljaev, a. V.; Bykov, V. a. Synthesis and Characterization of Nanosized Titanium Oxide Films on the (0001) α-Al2O3 Surface. *Thin Solid Films* 1997, 293 (1–2), 91–95.
- (42) Kim, H.; Rossnagel, S. M. Growth Kinetics and Initial Stage Growth during Plasma-Enhanced Ti Atomic Layer Deposition. J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 2002, 20 (2002), 802.
- (43) Yourey, J. E.; Bartlett, B. M. Electrochemical Deposition and Photoelectrochemistry of CuWO4, a Promising Photoanode for Water Oxidation. J. Mater. Chem. 2011, 21, 7651– 7660.
- (44) Bohra, D.; Smith, W. A. Improved Charge Separation via Fe-Doping of Copper Tungstate Photoanodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9857–9866.
- (45) Ruiz-Fuertes, J.; Errandonea, D.; Segura, A.; Manjón, F. J.; Zhu, Z.; Tu, C. Y. Growth, Characterization, and High-Pressure Optical Studies of CuWO₄. *High Press. Res.* **2008**, *28*, 565–570.
- (46) Ruiz-Fuertes, J.; Sanz-Ortiz, M. N.; González, J.; Rodríguez, F.; Segura, A; Errandonea, D. Optical Absorption and Raman Spectroscopy of CuWO₄. J. Phys. Conf. Ser. 2010, 215, 12048.
- (47) Klahr, B. M.; Martinson, A. B. F.; Hamann, T. W. Photoelectrochemical Investigation of Ultrathin Film Iron Oxide Solar Cells Prepared by Atomic Layer Deposition. *Langmuir* 2011, 27, 461–468.
- (48) Gaillard, N.; Chang, Y.; Deangelis, A.; Higgins, S.; Braun, A. A Nanocomposite Photoelectrode Made of 2.2 eV Band Gap Copper Tungstate (CuWO₄) and Multi-Wall Carbon Nanotubes for Solar-Assisted Water Splitting. *Int. J. Hydrogen Energy* 2013, 38, 3166–3176.
- (49) Chang, Y.; Braun, A.; Deangelis, A.; Kaneshiro, J.; Gaillard, N. Effect of Thermal Treatment on the Crystallographic, Surface Energetics, and Photoelectrochemical Properties of Reactively Cosputtered Copper Tungstate for Water Splitting. J. Phys. Chem. C 2011, 115, 25490–25495.
- (50) Lacomba-Perales, R.; Ruiz-Fuertes, J.; Errandonea, D.; Martinez-Garcia, D.; Segura, A. Optical Absorption of Divalent Metal Tungstates: Correlation between the Band-Gap Energy and the Cation Ionic Radius. **2008**, *83*, 37002.
- (51) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Electrochemical

and Photoelectrochemical Investigation of Water Oxidation with Hematite Electrodes. *Energy Environ. Sci.* **2012**, *5*, 7626–7636.

- (52) Nakaoka, K.; Ueyama, J.; Ogura, K. Photoelectrochemical Behavior of Electrodeposited CuO and Cu₂O Thin Films on Conducting Substrates. *J. Electrochem. Soc.* **2004**, *151*, C661.
- (53) Heumann, T.; Stolica, N. The Electrochemical Behaviour of tungsten—I. The Dissolution of Tungsten and Tungsten Oxides in Buffer Solutions. *Electrochim. Acta* **1971**, *16* (5), 643–651.
- (54) Heumann, T.; Stolica, N. The Electrochemical Behaviour of tungsten—II. The Dissolution of Tungsten in NaOH Solutions. *Electrochim. Acta* **1971**, *16* (10), 1635–1646.
- (55) Hill, J. C.; Choi, K. Synthesis and Characterization of High Surface Area CuWO₄ and Bi₂WO₆ Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, 1, 5006–5014.
- (56) Pyper, K. J.; Yourey, J. E.; Bartlett, B. M. Reactivity of CuWO₄ in Photoelectrochemical Water Oxidation Is Dictated by a Midgap Electronic State. J. Phys. Chem. C 2013, 117, 24726–24732.
- (57) Valenti, M.; Dolat, D.; Biskos, G.; Smith, W. A. Enhancement of the Photoelectrochemical Performance of CuWO₄ Thin Films for Solar Water Splitting by Plasmonic Nanoparticle Functionalization. *J. Phys. Chem. C* **2015**, *119*, 2096-2104.
- (58) Yourey, J. E. J.; Pyper, K. K. J.; Kurtz, J. B.; Bartlett, B. M. Chemical Stability of CuWO₄ for Photoelectrochemical Water Oxidation. *J. Phys. Chem. C* **2013**, *117*, 8707–8718.

Chapter 3:QuantifyingHoleCollectionEfficiencyofCuWO4forWaterOxidationCuWO4Collection

Adapted with permission from:

*Quantitative hole collection for photoelectrochemical water oxidation with CuWO*₄, Yuan Gao and Thomas W. Hamann, *Chem. Comm.*, **2017**, *53*, 1285-1288. Copyright 2017 The Royal Chemistry Society.

3.1 Abstract

The hole collection efficiency of water oxidation was evaluated for CuWO₄ electrodes from comparisons of the photocurrent of H_2O_2 and Na_2SO_3 oxidation as well as intensity modulated photocurrent spectroscopy (IMPS) measurements. We found current multiplication using H_2O_2 , however use of Na₂SO₃ and IMPS revealed quantitative water oxidation at 1.23 V vs RHE.

3.2 Introduction

In chapter 1, copper tungstate (CuWO₄) was introduced as a promising photoanode material for water splitting due to its suitably low band gap (2.3 eV), stability in neutral and slightly basic solutions under illumination and its earth abundant composition.^{1–5} Previous studies have indicated that the water oxidation efficiency of CuWO₄ is limited by both charge separation in the bulk of the electrode as well as hole collection via water oxidation at the electrode surface.^{4–7} Efforts to nanostructure the electrode have been made to overcome the inefficient charge separation of this weakly absorbing material.^{8,9} Even if such strategies are successful, however, all photogenerated holes that reach the electrode surface must selectively drive the water oxidation reaction instead of other side or recombination reactions.

The water oxidation kinetics at the CuWO₄/electrolyte interface has been suggested to be sluggish with competing surface recombination reactions resulting in a loss in efficiency.^{3,4,6} Smith's group compared the photocurrent measured in H₂O and in an aqueous electrolyte containing H₂O₂ as a sacrificial hole scavenger and extracted a hole collection efficiency η_{HC} , from the ratio of the photocurrent densities: ⁷

$$\eta_{HC} = J_{H_2O} / J_{scavenger} \tag{3.1}$$

These results indicated that the hole collection efficiency is only 60 % at 1.23 V vs RHE, the thermodynamic water oxidation potential. This is the only report that has attempted to quantify the hole collection efficiency of water oxidation with CuWO₄ electrodes, although others have used H_2O_2 to make semi-quantitative evaluations of water oxidation with CuWO₄ electrodes.^{4,10} This result suggests that surface modification strategies, such as adding a water oxidation co-catalyst to the surface, can potentially greatly improve the water oxidation performance of CuWO₄.

Interestingly, however, only a manganese phosphate catalyst has been reported to somewhat improve the performance.^{11,12}

In this chapter, we will examine the use of various hole scavengers to determine the water oxidation efficiency of bare CuWO₄ electrodes, and compare this to results of intensity modulated photocurrent spectroscopy (IMPS) measurements. These results will allow us to quantify the extent to which surface recombination inhibits water oxidation on the surface of CuWO₄ and elucidate possible causes of the lack of improvement observed from adding known water oxidation catalysts to the surface.

3.3 Experimental

3.3.1 Film Preparation and Characterization

Copper tungstate (CuWO₄) thin films were deposited on fluorine-doped tin oxide (FTO) coated glass (Hartford Glass, $12 \Omega \text{ cm}^{-2}$) and Si wafer (University Wafer) by an atomic layer stack deposition-annealing (SDA) method via atomic layer deposition (ALD) (Savannah 100, Cambridge Nanotech Inc.) using a procedure described in chapter 2.⁵ ~170 ALD cycles of CuO was deposited on 1000 cycles of WO₃ according to calculations described in chapter 2⁵ to match 1:1 ratio between the two metals. After deposition, the stack of binary oxides was annealed at 550 °C in air for 30 min with a ramping rate of 2 °C/min. The slight adjustment of annealing temperature is explained in Appendix.

3.3.2 Characterization

The thickness of as-deposited WO₃ films were measured to be ~65 nm thick on Si by ellipsometry measurements (Horiba Jobin Yvon, Smart-SE). The thickness of the CuWO₄ thin film was calculated to be ~80 nm using the method described in chapter 2,⁵ which agrees with the measured growth rate and previous measurement using AFM and SEM in chapter 2.⁵ The annealed

films were characterized by X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) using the same instruments as described in chapter 2. The characterization results are shown in Appendix.

3.3.3 Photoelectrochemical Measurements

CuWO₄ electrodes were assembled and measured in the same three-electrode system as described in chapter 2, with an active area of 0.28 cm². The CuWO₄ electrodes were examined in contact with aqueous pH 9.0 1 M KB_i buffer with or without 0.5 M Na₂SO₃ or H₂O₂. All potentials measured in aqueous solutions were converted to the reversible hydrogen electrode (RHE) scaled by the equation $V_{RHE} = V_{Ag/AgCl} + 0.197 + pH(0.059)$. Current density-voltage (J-V) curves were measured using a scan rate of 20 mV s⁻¹. The white light condition was the same as described in chapter 2. All photoelectrochemical measurements were performed by shining light on the CuWO₄ electrode through the electrolyte. Photocurrent densities $(\underline{J_{photo}})$ are obtained by subtracting the dark current density (J_{dark}) from the current density under illumination (J_{total}) . Intensity modulated photocurrent spectroscopy (IMPS) was gathered using 10% of the fixed LED driving current as the ac perturbation of the incident light intensity from 10000 to 0.1 Hz. The incident light of IMPS measurements was provided by a 470 nm LED with an LED driver from Metrohm, and the light intensity was calibrated using the current measured with a photodiode from the same manufacturer. The constant light intensity was adjusted to 116 mW cm⁻² so that the J-V curve is close to that under 1 sun illumination. This ensures that the flux of holes reaching the surface is about the same as 1 sun condition, so that the surface dynamics (rate of hole collection and recombination) is comparable.

3.4 Results and Discussion

Current density, J, vs applied voltage, V, curves were measured in the dark and under simulated AM 1.5 (1 sun) illumination for CuWO₄ electrodes in contact with an aqueous electrolyte and the same electrolyte containing two different sacrificial hole scavengers: 0.5 M Na₂SO₃ and 0.5 M H₂O₂. Figure 3-1 shows plots of the *J*-V curves where the photocurrent density, J_{photo} , is determined by subtracting the dark current density, J_{dark} , from the total current density, J_{total}, measured under 1 sun illumination, since CuWO₄ has significant dark current when in contact with the hole scavengers. The corresponding J_{dark} -V and J_{total} -V curves are shown in Figure A3-3. The J_{photo}-V curve measured in contact with H₂O shows an onset potential at ~0.85 V vs RHE and a photocurrent density of 0.15 mA cm⁻² at 1.23 V vs RHE, which is comparable to the results in chapter 2 and many other studies.³⁻⁶ Na₂SO₃ and H₂O₂ have both been widely used as hole scavengers to study the hole collection efficiency of water oxidation using different semiconductor materials assuming that their hole collection is quantitative.^{13–17} The photocurrent onset potential measured with either hole scavenger shows a negative shift of 150 - 200 mV compared to the water oxidation onset potential. This shift can be attributed to the limited η_{HC} of water oxidation at the CuWO₄ surface, due to surface recombination kinetically competing with water oxidation.^{3,4,6,18,19}



Figure 3-1. *J-V* curves of a CuWO₄ electrode immersed in a pH 9.0 KB_i electrolyte in contact with H_2O (black dashed curve), Na_2SO_3 (red solid curve) and H_2O_2 (blue dash dot) under 1 sun illumination. The vertical gray dash represents the thermodynamic potential of water oxidation (1.23 V vs RHE).

Interestingly, the *J-V* curves measured with CuWO₄ electrodes immersed in Na₂SO₃ and H₂O₂ solutions show very different photocurrents. The photocurrent measured in a Na₂SO₃ electrolyte is higher than that measured in H₂O at low potentials, but when the potential passes 1.23 V vs RHE, the photocurrent in both electrolytes are essentially identical. However, the photocurrent measured in a H₂O₂ electrolyte is 1.5 - 2 times of that in Na₂SO₃ or H₂O at all potentials. This is the first report of the *J-V* behavior of CuWO₄ with Na₂SO₃, however. The higher photocurrent measured in H₂O₂ compared to Na₂SO₃ can result from either 1) a less than unity η_{HC} for CuWO₄ in oxidizing Na₂SO₃ or 2) a current multiplication effect due to H₂O₂ oxidation with CuWO₄. In order to test the first possible cause of the discrepancy, we measured the photocurrent of CuWO₄ with different concentrations of Na₂SO₃. Figure 3-2a shows that *J_{photo}*

initially increases with Na₂SO₃ concentration and reaches saturation at 0.05 M, indicating that when the diffusion limitation of Na₂SO₃ is eliminated, the photocurrent is independent of its concentration.²⁰ Current transient measurements were also conducted to evaluate the extent of surface recombination. Figure 3-2b shows that when CuWO₄ is immersed in 0.5 M Na₂SO₃, after turning the light on, the instantaneous current remains constant, and the steady state photocurrents extracted from the current transient measurements are consistent with those from the J-V curve. These results suggest that the hole collection is not limited by the recombination of charge carriers at CuWO₄ surface when in contact with Na₂SO₃ and thus that η_{HC} is quantitative. Control experiments conducted in H₂O are shown in Figure 3-3, where the current transient shows an instantaneous spike when the light is turned on which quickly decays to a lower steady state value. This indicates recombination of photogenerated holes at CuWO₄ surface with conduction band electrons in the case of water oxidation at low potentials. The decrease in the instantaneous current appears less obvious at higher potentials, suggesting less severe surface recombination at these potentials, which coincides with the similar photocurrent of water oxidation and oxidation of hole scavenger Na₂SO₃ after 1.23 V vs RHE.



Figure 3-2. a) Photocurrent densities measured with a CuWO₄ electrode in an aqueous electrolyte containing Na_2SO_3 with various concentrations at 0.88 (red squares), 1.23 (green triangles) and 1.53 (blue circles) V vs RHE under 1 sun illumination. b) Current transients measured under 1 sun illumination in 0.5 M Na_2SO_3 electrolyte at 0.88 (red solid), 1.23 (green dash) and 1.53 (blue dots) V vs RHE.



Figure 3-3. Current transients measured with $CuWO_4$ in an aqueous electrolyte (H₂O) under 1 sun illumination at 0.88 (red solid), 1.23 (green dash) and 1.53 (blue dots) V vs RHE.

We thus speculate that the higher photocurrent in the presence of H_2O_2 may result from a current multiplication effect of H_2O_2 at the CuWO₄ surface. H_2O_2 is well known to give rise to current doubling in the cathodic region on p-type semiconductors under illumination.^{21,22} There has also been one report of current doubling on n-type InP with H_2O_2 in its anodic region under illumination.²³ While it is not common to observe current doubling in the anodic region with H_2O_2 , many other species such as methanol, formic acid, sodium formate, etc. have been reported to show current multiplication effect in the anodic region.^{24–26} One possible mechanism of current doubling with H_2O_2 in the anodic region involves the injection of an electron from the radical intermediate of H_2O_2 oxidation into the conduction band, where the normal 2-hole oxidation process becomes a 1-hole process (see Appendix).²³ Thus, the resulted current multiplication factor would vary from 1 to 2 (i.e. current doubling) since the two oxidation mechanisms compete with each other. Such current multiplication effects can be detected using intensity modulated

photocurrent spectroscopy (IMPS), since IMPS can provide information about quantum efficiency (QE) of charge transfer processes at an interface. Therefore, IMPS measurements were conducted in H_2O , Na_2SO_3 and H_2O_2 to determine the extent of current multiplication.

IMPS was measured over a potential range from 0.73 to 1.73 V vs RHE. The output signal is expressed by:

$$\hat{H} = \hat{I}_{photo} / \hat{I}_{LED}$$
(3.2)

where \hat{I}_{photo} is the photocurrent, \hat{I}_{LED} is the driving current for LED, and \hat{H} represents the transfer function of the output. Therefore, the horizontal and vertical axes of a Nyquist plot represent the real and imaginary parts of this output. The Nyquist plots of water oxidation are shown in Figure 3-4. In the upper quadrant of the Nyquist plot, a semicircle provides information about charge transfer and recombination at the surface. In the low frequency limit, the illumination condition is very close to steady state. Thus, the low frequency intercept on the real axis, H_{LF} , is related to the actual water oxidation photocurrent. When the frequency of the modulated light increases, the recombination at the surface is "frozen out" at the high frequency limit, H_{HF} , so that it reflects the total flux of holes reaching the surface. The semicircle at higher frequency in the lower quadrant is assigned to the RC attenuation of the electrochemical cell, which is beyond the scope of our discussion.



Figure 3-4. Nyquist plots of IMPS measured with CuWO₄ in H₂O under 470 nm monochromatic light with intensity of 116 mW cm⁻². Potential ranges from 0.73 to 1.73 V vs RHE with an interval of 0.1 V corresponding to the red, orange, yellow, dark yellow, green, dark green, dark cyan, blue, navy, purple and wine colored circles.

If first order kinetics with respect to the hole concentration at surface is assumed as in previous reports, ^{27–29} the quantum efficiency, QE, which is equivalent to η_{HC} in the case of water oxidation, can be extracted from IMPS data by:

$$\eta_{HC} = H_{LF} / H_{HF} \tag{3.3}$$

 H_{HF} should be identical in different electrolytes. If current multiplication occurs, two semicircles in the lower quadrant are expected, with the low frequency part representing the charge transfer process and the high frequency part representing RC attenuation, and the QE should be between 1 and 2.^{23,26,27} This behavior is exactly what we observe in the presence of H₂O₂, as shown in Figure 3-5; the Nyquist plots show two semicircles in the lower quadrant with H_{LF} greater than H_{HF} , indicating a QE greater than unity. The calculated current multiplication factor, represented by QE, is shown in Figure 3-6, where the QE is ~1.5 at lower potentials and reaches ~1.9 after 1.1 V vs RHE. The lower quantum efficiency measured at lower potentials agrees with literature reports, where current multiplication has to compete with recombination due to lower degree of band bending.^{23,26} We noticed that the Nyquist plots measured in the presence of Na₂SO₃ look similar as that of water oxidation, except that in the photocurrent onset potential region, the recombination semicircle is smaller, indicating less surface recombination at low potentials.



Figure 3-5. Nyquist plots of IMPS measurements under 116 mW cm⁻² light at 470 nm measured in H_2O (black squares), Na_2SO_3 (red circles), and H_2O_2 (blue triangles) electrolyte at a) 0.93 V and b) 1.23 vs RHE.



Figure 3-6. Current multiplication factor of CuWO₄ in contact with H₂O₂ represented as quantum efficiency (QE) extracted from IMPS data.

It can be seen in Figure 3-7a that η_{HC} extracted from IMPS matches perfectly with that calculated using equation 3.3 when using Na₂SO₃ as a hole scavenger. Water oxidation with CuWO₄ shows a limited η_{HC} around its onset potential region, but is essentially quantitative after 1.23 V vs RHE. However, as shown in Figure 3-7b, " η_{HC} " calculated using H₂O₂ only has a maximum of ~60% which does not agree with the IMPS results, but is in excellent agreement with the report by Smith et al.⁷ This discrepancy is consistent with the current multiplication effect of H₂O₂ with CuWO₄, which would produce an artificially low hole collection efficiency; thus, H₂O₂ cannot be used to determine the hole collection efficiency of CuWO₄ electrodes.



Figure 3-7. Calculated η_{HC} of water oxidation with CuWO₄ electrodes extracted from IMPS data at 116 mW cm⁻² with 470 nm LED (orange triangles) and from comparisons of *J*-*V* curves of water oxidation and oxidation of a) Na₂SO₃ (purple solid) and b) H₂O₂ under 1 sun illumination (green solid).

3.5 Conclusion

In conclusion, while prior reports have suggested that sluggish water oxidation on CuWO₄ limits the hole collection efficiency to $\sim 60\%$ at 1.23 V vs RHE via comparisons with H₂O₂ oxidation, we showed that such use of H_2O_2 can be problematic as it gives rise to current multiplication. The combined PEC and IMPS measurements presented here clearly show that Na_2SO_3 does act as an ideal sacrificial hole scavenger for CuWO₄ and can be used to accurately evaluate the hole collection efficiency of water oxidation with CuWO₄ electrodes. Interestingly, we found that the water oxidation hole collection efficiency is quantitative at 1.23 V vs RHE. Thus, it is not feasible to increase the photocurrent density at this potential through surface modification strategies such as addition of water oxidation co-catalysts. This finding explains the recently reported challenge in identifying effective cocatalysts.¹² Comparison of the J-V curves for Na₂SO₃ vs water oxidation (Figure 3-1) shows that an improvement of the onset potential by up to 200 mV is feasible, however, due to surface recombination.⁶ Interestingly, there has been only one catalyst reported^{12,30} to be integrated with CuWO₄ photoanode that shows moderate improvement on its water oxidation performance, which is also consistent with our findings. Thus, CuWO₄ appears to have excellent surface properties, with only limited further possible improvement in η_{hc} , and thus must primarily be limited by charge separation in the bulk. Finally, we note that the findings reported here may depend somewhat on the preparation route, as we have recently shown for hematite photoelectrodes, which is worth further investigation.³¹

APPENDIX



Figure A3-1. SEM images of a) as-deposited CuO on WO₃, and CuWO₄ annealed at b) 550 $^{\circ}$ C and c) 600 $^{\circ}$ C.



Figure A3-2. Raman spectra of a) CuWO₄ annealed at 550 °C and b) FTO. c) X-ray diffraction pattern of CuWO₄ annealed at 550 °C. Vertical gray dashed lines represent the peak positions of CuWO₄ recorded in literature^{32–34}.

The SEM images in Figure A3-1 show that the as-deposited CuO on WO₃ makes a uniform film. After annealing at 550 °C, the grains are sharpened but the film is still uniform. However, after annealing at 600 °C, although Raman and XRD show a pure composition of CuWO₄⁵, severe aggregation occurs at the surface of the film, while underneath the top aggregated layer there are smaller grains. We adjusted the annealing temperature to 550 °C for the ease of fundamental investigations especially on-going charge carrier collection length studies in our laboratory. Raman and XRD spectra in Figure A3-2 show that the peaks of the resulted film match with CuWO₄ peaks in literature³²⁻³⁴, except for those from the underlying FTO substrate. The XRD pattern of FTO can be found in chapter 2⁵. X-ray photoelectron spectroscopic (XPS) results are also shown in chapter 2 to determine the composition and chemical state of our CuWO₄ film.⁵



Figure A3-3. J_{dark} -V (black dash) and J_{total} -V (red solid) curves of CuWO₄ electrode measured in a) H₂O, b) 0.5 M Na₂SO₃ and c) 0.5 M H₂O₂ electrolytes in the dark and under 1 sun illumination.

Current multiplication mechanism of H_2O_2 in the anodic region proposed by previous studies²³ (the reaction is considered in a basic electrolyte):

$$H_2O_2 + h_{VB}^+ + OH^- \rightarrow HO_2^\bullet + H_2O \tag{A3.1}$$

$$HO_2^{\bullet} + h_{VB}^+ + OH^- \to O_2 + H_2O \tag{A3.2}$$

$$HO_2^{\bullet} + OH^- \rightarrow O_2 + H_2O + e_{CB}^- \tag{A3.3}$$

 H_2O_2 captures a hole from the valence band (VB) of the n-type semiconductor to form a radical intermediate (equation A3.1). The radical either captures another hole from VB, which is the route of normal photoelectrochemical oxidation of H_2O_2 (equation A3.2), or inject an electron to the conduction band (CB) of the semiconductor (equation A3.3). The second pathway contributes to the current doubling effect, since the original two-hole process becomes a one-hole process.

REFERENCES

REFERENCES

- (1) Benko, F. A.; MacLaurin, C. L.; Koffyberg, F. P. CuWO₄ and Cu₃WO₆ as Anodes for the Photoelectrolysis of Water. *Mat. Res. Bull.* **1982**, *17*, 133–136.
- (2) Lalić, M. V.; Popović, Z. S.; Vukajlović, F. R. Electronic Structure and Optical Properties of CuWO₄: An Ab Initio Study. *Comput. Mater. Sci.* **2012**, *63*, 163–167.
- (3) Yourey, J. E.; Bartlett, B. M. Electrochemical Deposition and Photoelectrochemistry of CuWO₄, a Promising Photoanode for Water Oxidation. *J. Mater. Chem.* 2011, 21, 7651– 7660.
- (4) Hill, J. C.; Choi, K. S. Synthesis and Characterization of High Surface Area CuWO₄ and Bi₂WO₆ Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, *1*, 5006–5014.
- (5) Gao, Y.; Zandi, O.; Hamann, T. W. Atomic Layer Stack Deposition-Annealing Synthesis of CuWO₄. *J. Mater. Chem. A* **2016**, *4*, 2826–2830.
- (6) Pyper, K. J.; Yourey, J. E.; Bartlett, B. M. Reactivity of CuWO₄ in Photoelectrochemical Water Oxidation Is Dictated by a Midgap Electronic State. J. Phys. Chem. C 2013, 117, 24726–24732.
- (7) Bohra, D.; Smith, W. A. Improved Charge Separation via Fe-Doping of Copper Tungstate Photoanodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9857–9866.
- (8) Ye, W.; Chen, F.; Zhao, F.; Han, N.; Li, Y. CuWO₄ Nanoflake Array-Based Single-Junction and Heterojunction Photoanodes for Photoelectrochemical Water Oxidation. ACS Appl. Mater. Interfaces 2016, 8, 9211–9217.
- (9) Hu, D.; Diao, P.; Xu, D.; Xia, M.; Gu, Y.; Wu, Q.; Li, C.; Yang, S. Copper (II) Tungstate Nanoflake Array Films: Sacrificial Template Synthesis, Hydrogen Treatment, and Their Application as Photoanodes in Solar Water Splitting. *Nanoscale* 2016, *8*, 5892–5901.
- (10) Gaillard, N.; Chang, Y.; Deangelis, A.; Higgins, S.; Braun, A. A Nanocomposite Photoelectrode Made of 2.2 eV Band Gap Copper Tungstate (CuWO₄) and Multi-Wall Carbon Nanotubes for Solar-Assisted Water Splitting. *Int. J. Hydrogen Energy* **2013**, *38*, 3166–3176.
- (11) Nam, K. M.; Cheon, E. A.; Shin, W. J.; Bard, A. J. Improved Photoelectrochemical Water Oxidation by the WO₃/CuWO₄ Composite with a Manganese Phosphate Electrocatalyst. *Langmuir* 2015, *31* (39), 10897–10903.
- (12) Lhermitte, C. R.; Bartlett, B. M. Advancing the Chemistry of CuWO₄ for

Photoelectrochemical Water Oxidation. Acc. Chem. Res. 2016, 49, 1121–1129.

- (13) Seabold, J. a.; Choi, K. S. Efficient and Stable Photo-Oxidation of Water by a Bismuth Vanadate Photoanode Coupled with an Iron Oxyhydroxide Oxygen Evolution Catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 2186–2192.
- (14) Chang, X.; Wang, T.; Zhang, P.; Zhang, J.; Li, A.; Gong, J. Enhanced Surface Reaction Kinetics and Charge Separation of P-N Heterojunction Co₃O₄/BiVO₄ Photoanodes. *J. Am. Chem. Soc.* **2015**, *137*, 8356–8359.
- (15) Mali, M. G.; Yoon, H.; Kim, M. W.; Swihart, M. T.; Al-Deyab, S. S.; Yoon, S. S. Electrosprayed Heterojunction WO₃/BiVO₄ Films with Nanotextured Pillar Structure for Enhanced Photoelectrochemical Water Splitting. *Appl. Phys. Lett.* **2015**, *106* (15), 151603.
- (16) Duret, A.; Grätzel, M. Visible Light-Induced Water Oxidation on Mesoscopic α-Fe₂O₃
 Films Made by Ultrasonic Spray Pyrolysis. J. Phys. Chem. B 2005, 109, 17184–17191.
- (17) Dotan, H.; Sivula, K.; Gr, M.; Warren, S. C.; Grätzel, M.; Rothschild, A.; Warren, S. C.;
 Gr, M.; Warren, S. C. Probing the Photoelectrochemical Properties of Hematite (α-Fe₂O₃)
 Electrodes Using Hydrogen Peroxide as a Hole Scavenger. *Energy Environ. Sci.* 2011, *4*, 958–964.
- (18) Klahr, B.; Gimenez, S.; Fabregat-santiago, F.; Hamann, T.; Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. J. Am. Chem. Soc. 2012, 134, 4294–4302.
- (19) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Electrochemical and Photoelectrochemical Investigation of Water Oxidation with Hematite Electrodes. *Energy Environ. Sci.* 2012, *5*, 7626–7636.
- (20) Klahr, B. M.; Hamann, T. W. Current and Voltage Limiting Processes in Thin Film Hematite Electrodes. J. Phys. Chem. C 2011, 115, 8393–8399.
- (21) Memming, R. Mechanism of the Electrochemical Reduction of Persulfates and Hydrogen Peroxide. *J. Electrochem. Soc.* **1969**, *116* (6), 785–790.
- (22) Minks, B. P.; Vanmaekelbergb, D.; Kelly, J. J. Current-Doubling, Chemical Etching and the Mechanism of Two-Electron Reduction Reactions at GaAs Part 2. A Unified Model. *J. Electroanal. Chem.* **1989**, *273*, 133–145.
- (23) Theuwis, A.; Vermeir, I. E.; Gomes, W. P. Chemical and Electrochemical Interaction of Acidic H202 Solutions with (100) InP. *J. Electroanal. Chem.* **1996**, *410*, 31–42.
- (24) Hykaway, N.; Sears, W. M.; Morisaki, H.; Morrison, S. R. Current-Doubling Reactions on Titanium Dioxide Photoanodes. J. Phys. Chem. **1986**, 90 (25), 6663–6667.

- (25) Fujishima, A.; Kato, T.; Maekawa, E.; Honda, K. Mechanism of the Current Doubling Effect. I. The ZnO Photoanode in Aqueous Solution of Sodium Formate. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1671–1674.
- (26) Herrasti, P.; Peter, L. Photocurrent Doubling during the Oxidation of Formic Acid at N-CdS : An Investigation by Intensity Modulated Photocurrent Spectroscopy. J. Electroanal. Chem. 1991, 305, 241–258.
- (27) Peter, L. M.; Vanmaekelbergh, D. Time and Frequency Resolved Studies of Photoelectrochemical Kinetics. In *Advances in Electrochemical Science and Engineering*, *Volume 6*; Wiley Online Library, 1999; pp 125–131.
- (28) Peter, L. M.; Ponomarev, E. A.; Fermin, D. J. Intensity-Modulated Photocurrent Spectroscopy : Reconciliation of Phenomenological Analysis with Multistep Electron Transfer Mechanisms. J. Electroanal. Chem. 1997, 427, 79–96.
- (29) Peter, L. M.; Upul, K. G.; Tahir, A. A. Kinetics of Light-Driven Oxygen Evolution at α-Fe₂O₃ Electrodes. *Faraday Discuss.* **2012**, *155*, 309–322.
- (30) Nam, K. M.; Cheon, E. A.; Shin, W. J.; Bard, A. J. Improved Photoelectrochemical Water Oxidation by the WO₃/CuWO₄ Composite with a Manganese Phosphate Electrocatalyst. *Langmuir* 2015, *31* (39), 10897–10903.
- (31) Zandi, O.; Schon, A. R.; Hajibabaei, H.; Hamann, T. W. Enhanced Charge Separation and Collection in High-Performance Electrodeposited Hematite Films. *Chem. Mater.* 2016, 28 (3), 765–771.
- (32) Kihlborg, L.; Gebert, E. CuWO4, a Distorted Wolframite-Type Structure. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1970**, *26*, 1020–1026.
- (33) Ruiz-Fuertes, J.; Errandonea, D.; Segura, A.; Manjón, F. J.; Zhu, Z.; Tu, C. Y. Growth, Characterization, and High-Pressure Optical Studies of CuWO₄. *High Press. Res.* 2008, 28, 565–570.
- Ruiz-Fuertes, J.; Sanz-Ortiz, M. N.; González, J.; Rodríguez, F.; Segura, a; Errandonea,
 D. Optical Absorption and Raman Spectroscopy of CuWO₄. J. Phys. Conf. Ser. 2010, 215, 12048.

Chapter 4:

Elucidation of Role of CuWO₄ Surface States During Photoelectrochemical Water Oxidation

Adapted with permission from:

Elucidation of CuWO₄ Surface States During Photoelectrochemical Water Oxidation, Yuan Gao and Thomas W. Hamann, J. Phys. Chem. Lett. **2017**, 8, 2700-2704. Copyright 2016 American Chemistry Society.

4.1 Abstract

Electrochemical, photoelectrochemical and impedance spectroscopy measurements were performed to investigate the role of CuWO₄ surface states during water oxidation. We found that a capacitive feature related to a surface state is clearly observable under water oxidation conditions. The magnitude of the surface state capacitance is light intensity-dependent, with a peak potential that coincides with the water oxidation onset potential region. The surface state is not observed in the dark nor in contact with non-aqueous solvents. These results strongly support our assignment of this surface state as the build-up of water oxidation intermediate species at the surface of CuWO₄ photoanodes, not a permanent or intrinsic state as previously reported. We suggest this is a general feature that controls the behavior and efficiency of solar water splitting reactions.

4.2 Introduction

In chapter 3, it was determined that the hole collection efficiency of CuWO₄ in water oxidation is actually quantitative at potentials higher than 1.23 V vs. RHE.¹ This finding required use of Na₂SO₃ as a suitable sacrificial hole scavenger, whereas we found that H₂O₂ gives rise to current multiplication with CuWO₄.² Thus, poor hole collection via water oxidation with CuWO₄ only occurs in the low potential region. There is only one report to date that has investigated the nature of the surface states of CuWO₄, where it was concluded to be an intrinsic state.³ This interpretation is different from what we have now established with hematite electrodes, where a surface state develops as a water oxidation intermediate species.^{4–7}

In this chapter, we aim to elucidate the nature of surface states in CuWO₄ and better understand water oxidation on semiconductors in general.

4.3 Experimental

4.3.1 Film Preparation

1) CuWO₄ by Atomic Layer Deposition

CuWO₄ thin films were deposited by an atomic layer stack deposition-annealing (SDA) method using a procedure described in chapter $3.^8$ 1000 ALD cycles of WO₃ was deposited on fluorine-doped tin oxide (FTO) coated glass substrate followed by ~170 ALD cycles of CuO to match 1:1 ratio between the two metals. After deposition, the stack of binary oxides was annealed at 550 °C in air for 30 min with a ramping rate of 2 °C / min. The thickness of the CuWO₄ thin film was calculated to be ~80 nm.

2) CuWO₄ by spray pyrolysis (SP-CuWO₄)

CuWO₄ was also synthesized by spray pyrolysis using a modified procedure from literature.⁹ An aqueous precursor solution containing 0.01 M of Cu (II) and 0.01 M of W (II) was

prepared from CuCl•2H₂O (Sigma-Aldrich, \geq 99.0%,) and (NH₄)₆H₂W₁₂O₄₀ (Alfa Aesar, metal impurity \leq 0.1%). FTO coated glass substrate was kept at 275 °C at a distance of 31 cm from the nozzle. The precursor solution was sprayed onto the substrate for 1 s and the wait time was 5 s. The as-deposited film was then annealed at 550 °C in air for 1 hr with 1 hr ramping time.

4.3.2 Film Characterization

The composition and structure of the film synthesized via spray pyrolysis was characterized using Raman spectroscopy and X-ray diffraction using the same instruments as in chapter 2. The thickness of the resulted film was determined to be $2 \mu m$ by cross-section scanning electron microscopy (SEM) (Carl Zeiss Microscopy).

4.3.3 Electrochemical / Photoelectrochemical Measurements

All electrochemical and photoelectrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. Current density-voltage (J-V) curves were measured using a scan rate of 20 mV s⁻¹. The white light source was a 450 W Xe arc lamp (Horiba Jobin Yvon). An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm⁻² (1 sun). A neutral density filter was used to reduce the light intensity to 33 (0.33 sun) or 10 mW cm⁻² (0.1 sun). All photoelectrochemical measurements in aqueous solutions were performed by shining light on the CuWO₄ electrode through the electrolyte. Photocurrent densities (J_{photo}) were obtained by subtracting the dark current density (J_{dark}) from the total current density under illumination (J_{total}).

Cyclic voltammogram (CV) surface state measurements were performed by applying a positive potential under 1 sun illumination or in the dark for 60 seconds, and then scanning toward the cathodic direction over a potential range in the dark.

EIS data were gathered using a 10 mV amplitude perturbation of between 10000 and 0.04

Hz in the dark or under illumination of 0.1 sun, 0.33 sun or 1 sun. Data were fitted using Zview software (Scribner Associates).

4.3.4 Measurements in Aqueous Electrolytes

CuWO₄ electrodes measured in aqueous electrolytes were in the same three-electrode setup as described in chapter 2, with a photoanode active area of 0.28 cm². The working electrodes were examined in contact with aqueous pH 9.0 1 M KB_i buffer with or without 0.5 M Na₂SO₃. Ag/AgCl was used as the reference electrode and a high surface area Pt mesh was used as the counter electrode. All potentials measured in aqueous solutions were converted to the reversible hydrogen electrode (RHE) scaled by the equation $V_{RHE} = V_{Ag/AgCl} + 0.197 \text{ V} + \text{pH}(0.059) \text{ V}.$

4.3.5 Measurements in Non-aqueous Electrolytes

When in contact with a non-aqueous electrolyte, the active area of the photoanode was defined by the o-ring which is 0.64 cm^2 . A custom-made glass electrochemical cell without a quartz window was used in the case of a non-aqueous electrolyte to avoid dissolution of the glue. 0.01 M AgNO₃ was dissolved in acetonitrile (MeCN) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) to form Ag/AgNO₃ as the reference electrode. The working electrodes were examined in contact with anhydrous MeCN or dichloromethane with 0.2 M TBAPF₆ as the supporting electrolyte. Measurements in anhydrous solutions were conducted in the glove box.

4.4 Results and Discussion

The J_{photo} -V curves of CuWO₄ in contact with H₂O and with a sacrificial hole scavenger, Na₂SO₃, are compared in Figure 4-1. The raw data of J_{total} -V and J_{dark} -V are shown in Figure A4-1. Na₂SO₃ has been shown to be a suitable sacrificial hole scavenger which produces quantitative hole collection with CuWO₄.¹ The photocurrent onset potential of water oxidation is ~0.85 V vs.
RHE. When Na_2SO_3 is in the electrolyte, however, the onset potential is shifted negatively to 0.6 V *vs*. RHE. The discrepancy in the onset potential, as well as the photocurrent in the onset potential region, between water oxidation and oxidation of Na_2SO_3 is due to inefficient hole collection via water oxidation at the CuWO₄ surface.¹



Figure 4-1. J_{photo} -V curves of a CuWO₄ electrode in contact with a pH 9.0 KB_i electrolyte in the absence (black solid curve) and presence (red dashed curve) of 0.5 M Na₂SO₃ under 1 sun illumination. The vertical gray dash represents the thermodynamic potential of water oxidation (1.23 V *vs.* RHE).

EIS measurements were performed on nominally identical CuWO₄ electrodes in contact with H₂O and Na₂SO₃ electrolytes to elucidate the processes that control the *J-V* behavior.⁴ Figure 4-2 displays Bode plots which indicate capacitive elements that appear in the EIS spectra. The Bode phase plots are presented instead of the Nyquist plots since in some cases the two semicircles are merged together, however the corresponding Nyquist plots are shown in Figure A4-2. In the dark, the Bode phase plots show only one peak at all potentials, in contact with either H_2O or Na_2SO_3 electrolyte, which is assigned to the space charge capacitance. This suggests that the surface state capacitance is not observable in the dark. Under 1 sun illumination, in the potential range of 0.68-1.23 V *vs*. RHE, two capacitive peaks are clearly observed in the Bode phase plot for CuWO₄ electrodes immersed in the H₂O electrolyte, however at higher potentials only one peak is seen. On the other hand, only one peak could be observed in the Na₂SO₃ electrolyte at all potentials under illumination.



Figure 4-2. Bode phase plots of CuWO₄ electrode at 0.93 V *vs.* RHE a) in the dark and b) under 1 sun illumination and c) at 1.53 V *vs.* RHE under 1 sun illumination. Data measured in H₂O (black squares) and 0.5 M Na₂SO₃ (red circles) are both shown. Fitting curves are shown as black dash for H₂O and red dots for Na₂SO₃. The resulted parameters from fitting are listed in Table A4-1 to Table A4-5.

The EIS data with two capacitive features were fit to a model shown in Figure 4-3a, which includes the impedance from a surface state, which is adopted from the model established with hematite.^{4,10} All the fitting results are shown in Table A4-1 to Table A4-5. Here R_s represents the series resistance from the bulk of the semiconductor, electrical contacts, and electrolyte, C_{bulk}

describes the bulk capacitance, which in this potential region is dominated by space charge capacitance, R_{trap} is the resistance of trapping of holes in the surface states. C_{ss} is the surface state capacitance, and $R_{ct,ss}$ describes the charge transfer resistance via the surface states. For EIS data in the dark and under illumination with only one capacitive feature, the Randles circuit is used (Fig 4-3b).



Figure 4-3. a) Equivalent circuit for EIS data with two capacitive features. b) Randles circuit.

Values of R_{trap} , $R_{ct,ss}$, C_{bulk} and C_{ss} extracted from fitting EIS data to the equivalent circuits displayed in Figure 4-3 are plotted in Figure 4-4. The only spectra that exhibited two capacitive features, as shown in Figure 4-2, are measured under illumination with an H₂O electrolyte - *i.e.* under PEC water oxidation conditions. The magnitude of the fitted C_{ss} peak in Figure 4-4a decreases when the light intensity is decreased from 1 sun to 0.1 sun. The peak in C_{ss} at ~1.0 V vs. RHE is associated with a dip in $R_{ct,ss}$ (Fig 4-4b), which is close to the water oxidation onset potential. The peak position of C_{ss} also matches the charge stored at the surface determined by integration of photocurrent transient measurements shown in Figure 4-6c. These results strongly support the assignment of this peak to a water oxidation intermediate species as opposed to an intrinsic state.



Figure 4-4. Plots of equivalent circuit parameters obtained from fitting EIS data in the dark (open squares), under 0.1 sun (blue triangles) and 1 sun (red circles) illumination in H₂O electrolyte. a) Surface state capacitance; b) Charge transfer resistance; c) Bulk capacitance; d) Resistance of trapping of holes in surface states.

The fitted C_{bulk} values decrease with applied voltage, but are essentially invariant at a given potential in the dark and under different light intensities (Fig 4-4c). The flat band potential, V_{fb} , and the dopant density, N_D , can be calculated from the following equation:

$$C_{bulk}^{-2} = \frac{2}{q \varepsilon \varepsilon_0 N_D} \left(V - V_{fb} - \frac{kT}{q} \right)$$
(4.1)

where *q* is the elementary charge $(1.6 \times 10^{-19} \text{ C})$, ε is the dielectric constant of CuWO₄ $(83)^{11}$, ε_0 is the vacuum permittivity (8.854 × 10⁻¹² F m⁻¹), *V* is the applied potential, *k* is the Boltzmann constant $(1.38 \times 10^{23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1})$, *T* is the room temperature (300 K). The Mott-Schottky plots displayed in Figure 4-5a measured in the dark, under 0.1 sun and 1 sun conditions overlap with each other. The flat band potential (E_{fb}) of CuWO₄ was calculated to be 0.50 ±0.02 V *vs*. RHE, and the dopant density (N_d) is $6.3 \pm 0.1 \times 10^{19} \text{ cm}^{-3}$ based on the data measured in the dark. The calculated results under different illumination conditions are compared in Table 4-1. This flat band potential is comparable to literature values of ~0.42 V *vs*. RHE.^{12–14} In contrast to a prior report by the Bartlett group³, no indication of Fermi level pinning is observed herein for CuWO₄ in contact with H₂O, nor with the hole scavenger, Na₂SO₃ (Fig 4-5b).



Figure 4-5. Mott-Schottky plots of CuWO₄ immersed in a) aqueous electrolyte (H₂O), measured in the dark (open squares), under 0.1 sun (blue triangles) and 1 sun (red circles) illumination; and in b) 0.5 M Na₂SO₃, measured in the dark (open squares) and under 1 sun (red circles) illumination.

Illumination / sun	V_{fb} / V vs. RHE	N_d / cm ⁻³
0	0.50 ± 0.02	$6.3(\pm 0.1) \times 10^{19}$
0.1	0.47 ± 0.04	$8.0~(\pm 0.3) imes 10^{19}$
1	0.51 ± 0.02	$6.7~(\pm 0.1) \times 10^{19}$

Table 4-1. Flat band potential and dopant density calculated from Mott-Schottky plots in the dark and under illumination.

Current transient measurements were taken on CuWO₄ to study the charge storage behavior of its surface states. Figure 4-6a shows that a spike in current appears upon turning the light on, which decays to a lower steady state current. This indicates that upon illumination, photogenerated holes accumulate at the surface, resulting in the initial transient current. Afterwards, only a portion of these photogenerated holes undergo charge transfer (water oxidation) at the electrode/electrolyte interface, which contributes to the steady state photocurrent. When the light is switched off, as in Figure 4-6b, the accumulated holes at the surface recombine with conduction band (CB) electrons, which causes the cathodic spike, and eventually the current reaches its steady state level (dark current). We note that the scale of the transient current first increases with potential, and after it reaches a maximum level, it decreases with potential. Each cathodic transient current is integrated in order to calculate the charge stored in the surface state. The Gaussian behavior of the charge as a function of potential shown in Figure 4-6c agrees well with the behavior of a chemical capacitance.^{15,16} Interestingly, the peak of accumulated charge appears around 1.0 V vs. RHE, which is at the same potential as C_{ss} peak in EIS measurements. This confirms that the second capacitive feature observed in EIS measurements is related to the charging of the surface state of CuWO₄.



Figure 4-6. Current transients of CuWO₄ in H₂O after turning the 1 sun illumination a) on and b) off. The applied potential varies from 0.68, 0.73, 0.83, 1.03, 1.23 and 1.43 V *vs.* RHE corresponding to red solid, orange dash, yellow dots, green dash dots, blue short dash and purple short dots. c) Charge stored at CuWO₄ surface calculated from current transients after turning off the light (black squares) and Gaussian fitting of the charge (red dash) at 0.68, 0.73, 0.83, 0.93, 1.03, 1.13, 1.23, 1.33 and 1.43 V *vs.* RHE.

Cyclic voltammetry (CV) was also utilized to examine the charging / discharging of the surface state.¹⁷ A pretreatment of holding a positive potential of 2.3 V *vs.* RHE either under

illumination or in the dark for 60 s was performed, followed by a fast potential scan in the negative direction. We note this potential is sufficiently positive to oxidize the surface state even in the dark. As seen in Figure 4-7a and Figure A4-3, a cathodic peak appears around 0.9 V *vs*. RHE, indicating the reduction of the surface state, which is equivalent to recombination of surface-trapped holes with CB electrons. The intensity of the peaks increases with scan rate, which confirms the capacitive nature. The peak position is very close to the C_{ss} peak at 1.0 V *vs*. RHE we observed in EIS measurements, as well as the peak position of the stored charge in current transient measurements, although in CV it is slightly shifted towards the negative potential due to the non-steady state conditions at the fast scan rates. This further suggests that the peak of C_{ss} is associated with charging the surface state, which is related to water oxidation.



Figure 4-7. a) CVs taken after holding potential at 2.3 V *vs*. RHE for 60 s under 1 sun illumination at scan rates from 200, 400, 600, 800, 1000, 1200 and 1500 mV s⁻¹ corresponding to red, orange, dark yellow, green, dark green, blue and purple solid. b) CV after holding potential at ~1.8 V *vs*. V_{fb} for 60 s in the dark, measured in H₂O (black solid) and MeCN (red dash). Scan rate is 1500 mV s⁻¹.

Analogous fast scan CVs were also performed in non-aqueous solvents, to determine if the generated surface state is consistent with a water oxidation intermediate species. These experiments were conducted in a sealed electrochemical cell in the glovebox to minimize the influence of trace amounts of water. The CV curves measured in anhydrous acetonitrile (MeCN) are plotted *vs.* V_{fb} of CuWO₄ measured in the same electrolyte (see Fig A4-4 for Mott-Schottky plots). No corresponding peak was observed even with fast scan rate (1500 mV s⁻¹) as shown in Figure 4-7b. We added 2% of H₂O to the MeCN electrolyte and conducted the same CV measurement. A small peak appeared at 0.4 V *vs.* V_{fb} , which is the same potential where we observed a peak in aqueous electrolytes (Fig A4-5). Similar CV measurements were also performed in a non-coordinating solvent, dichloromethane, to eliminate the influence of any coordination of electrolyte species to the electrode surface. Figure 4-8 shows that no peak is under these conditions either. These results indicate that the surface state is available only in the presence of water, with sufficient applied bias or illumination to oxidize water which confirms our argument that the surface state of CuWO₄ is related to water oxidation.



Figure 4-8. CV after holding potential at ~1.8 V *vs.* V_{fb} for 60 s in the dark, measured in 0.2 M TBAPF₆ in dichloromethane in the glovebox. Scan rates varies from 200, 800, 1500 and 2000 mV / s corresponding to pink, yellow, cyan and purple solid lines. Initial scan is in the cathodic direction.

Electrodes prepared via ALD were utilized since this produces reproducible, uniform and compact films which allows a more straightforward interpretation of EIS data compared to nanostructured, porous films. Since differences in synthetic methods may potentially lead to different surface properties, we also carried out a complete set of control experiments with CuWO₄ synthesized via spray pyrolysis (SP-CuWO₄). As shown in Appendix, the C_{ss} obtained from fitting EIS data increased with increasing illumination intensity corresponding to 0.1, 0.33 and 1 sun, consistent with results discussed above of the ALD films. The Mott-Schottky plots of the SP-CuWO₄ in the dark show no indication of Fermi level pinning. Thus, in all cases, the electrodes prepared by SP behaved in nearly identical fashion as electrodes prepared by ALD. These

combined results indicate that photogenerated surface states we observe for CuWO₄ is general to this material.

In conclusion, a surface state is clearly observed on CuWO₄ via several electrochemical methods. Importantly, we are only able to observe this state under water oxidation conditions, at a potential closely related to the water oxidation onset potential. These results strongly support an assignment of this surface state as a water oxidation intermediate species. This assignment contradicts prior reports who identified an intrinsic Cu-centered surface state.³ Since the results did not depend on the synthetic method of preparing CuWO₄ electrodes, the assignment of the surface state to water oxidation intermediate species appears to be general for CuWO₄ photoanodes. It is also striking how similar CuWO₄ behaves compared to hematite, where it is established that a surface state arises from the first step of water oxidation. Recombination of this intermediate species with conduction band electrons gives rise to the shift in photocurrent onset potential since an additional potential needs to be applied to reduce surface electron concentration and thus recombination. Thus, the results presented here offer the first indication that this behavior of photoinduced surface state recombination is general for water oxidation with metal oxide semiconductors with suggests a fundamental limitation to solar water splitting with bare electrodes. Addition of co-catalysts, such as Co-Pi or NiFeO_x to the electrode surface, however, offers a route to circumvent this recombination path since photogenerated holes at the electrode surface can oxidize the catalyst preferentially to the electrode surface. Work is ongoing to elucidate the detailed charge transfer pathways and kinetics of the complex semiconductor / catalyst interface during water oxidation.

APPENDIX



Figure A4-1. J_{dark} -V (black dash) and J_{total} -V (red solid) curves of CuWO₄ electrode measured in a) H₂O and b) 0.5 M Na₂SO₃ electrolytes in the dark and under 1 sun illumination.



Figure A4-2. Nyquist plots of CuWO₄ electrode at 0.93 V *vs.* RHE a) in the dark and b) under 1 sun illumination and c) at 1.53 V *vs.* RHE under 1 sun illumination. Data measured in H_2O (black squares) and 0.5 M Na₂SO₃ (red circles) are both shown. Fitting curves are shown as black dash for H_2O and red dots for Na₂SO₃.

V / V vs. Ag/AgCl, pH 9	V / V vs. RHE	R_s / Ω	R_{ct} / Ω	C _{bulk} / F
-0.20	0.53	147.9	3.31E+05	1.33E-05
-0.15	0.58	147.5	6.43E+05	8.73E-06
-0.10	0.63	146.7	7.83E+05	6.54E-06
-0.05	0.68	145.5	7.46E+05	5.62E-06
0.00	0.73	146.7	2.27E+05	4.73E-06
0.05	0.78	147.1	2.09E+05	4.21E-06
0.10	0.83	147.2	3.56E+05	3.81E-06
0.15	0.88	147.5	1.25E+06	3.62E-06
0.20	0.93	148.0	1.12E+06	3.38E-06
0.25	0.98	148.1	4.99E+05	3.21E-06
0.30	1.03	148.5	1.61E+05	3.03E-06
0.35	1.08	148.7	57352	2.84E-06
0.40	1.13	148.2	25559	2.64E-06
0.45	1.18	147.6	15293	2.49E-06
0.50	1.23	147.4	11386	2.39E-06
0.55	1.28	147.4	9561	2.33E-06
0.60	1.33	147.4	8276	2.28E-06
0.65	1.38	147.1	6738	2.22E-06
0.70	1.43	146.8	5149	2.15E-06
0.75	1.48	146.7	3810	2.08E-06
0.80	1.53	146.3	2725	2.01E-06
0.85	1.58	146.0	1912	1.96E-06
0.90	1.63	145.4	1321	1.90E-06
0.95	1.68	144.6	902.6	1.85E-06
1.00	1.73	144.0	620.8	1.80E-06

Table A4-1. Parameters extracted from fitting EIS data in 0.5 M Na₂SO₃ electrolyte in the dark.

V / V vs. Ag/AgCl, pH 9	V / V vs. RHE	R_s / Ω	R_{ct} / Ω	C _{bulk} / F
-0.20	0.53	147.8	1.53E+05	1.73E-05
-0.15	0.58	143.8	1.19E+05	1.09E-05
-0.10	0.63	149.6	56657	7.54E-06
-0.05	0.68	150.5	28487	5.92E-06
0.00	0.73	150.7	16358	4.89E-06
0.05	0.78	153.5	11906	4.29E-06
0.10	0.83	155.7	9468	3.98E-06
0.15	0.88	155.7	7792	3.73E-06
0.20	0.93	155.7	7162	3.49E-06
0.25	0.98	155.7	7319	3.27E-06
0.30	1.03	154.8	7645	3.11E-06
0.35	1.08	154.3	7276	2.94E-06
0.40	1.13	154.2	6208	2.79E-06
0.45	1.18	153.1	5126	2.67E-06
0.50	1.23	153.6	4466	2.60E-06
0.55	1.28	153.9	4042	2.55E-06
0.60	1.33	153.3	3635	2.49E-06
0.65	1.38	152.4	3139	2.43E-06
0.70	1.43	152.0	2587	2.37E-06
0.75	1.48	150.4	1992	2.31E-06
0.80	1.53	149.6	1510	2.24E-06
0.85	1.58	149.3	1134	2.19E-06
0.90	1.63	148.7	826.9	2.14E-06
0.95	1.68	147.9	594.4	2.09E-06
1.00	1.73	146.9	431.9	2.05E-06

Table A4-2. Parameters extracted from fitting EIS data in 0.5 M Na2SO3 electrolyte under 1 sun

illumination.

V / V vs. Ag/AgCl, pH 9	V / V vs. RHE	R_s / Ω	R_{ct} / Ω	C _{bulk} / F
-0.20	0.53	188.8	5363	1.39E-05
-0.15	0.58	188.5	25555	8.70E-06
-0.10	0.63	188.3	3.14E+05	5.61E-06
-0.05	0.68	188.2	2.98E+06	4.31E-06
0.00	0.73	188.5	1.04E+07	3.75E-06
0.05	0.78	189.0	1.65E+07	3.37E-06
0.10	0.83	189.3	2.04E+07	3.06E-06
0.15	0.88	189.6	2.23E+07	2.81E-06
0.20	0.93	189.9	2.10E+07	2.62E-06
0.25	0.98	190.0	1.79E+07	2.48E-06
0.30	1.03	190.3	1.58E+07	2.37E-06
0.35	1.08	190.6	1.61E+07	2.27E-06
0.40	1.13	190.7	1.87E+07	2.19E-06
0.45	1.18	191.0	2.26E+07	2.12E-06
0.50	1.23	191.1	2.60E+07	2.06E-06
0.55	1.28	191.2	2.80E+07	2.00E-06
0.60	1.33	191.2	2.73E+07	1.95E-06
0.65	1.38	191.3	2.46E+07	1.90E-06
0.70	1.43	191.3	2.20E+07	1.86E-06
0.75	1.48	191.4	2.27E+07	1.81E-06
0.80	1.53	191.6	2.37E+07	1.77E-06
0.85	1.58	191.7	2.25E+07	1.74E-06
0.90	1.63	191.9	1.92E+07	1.72E-06
0.95	1.68	192.1	9.27E+06	1.70E-06
1.00	1.73	192.3	1.61E+06	1.68E-06

Table A4-3. Parameters extracted from fitting EIS data in aqueous electrolyte (pH9 KB_i buffer)

in the dark.

V / V vs. Ag/AgCl, pH 9	V / V vs. RHE	R_s / Ω	C _{bulk} / F	R_{trap} / Ω	C _{ss} / F	$R_{ct,ss}$ / Ω
-0.20	0.53	239.2	1.70E-05	-	-	4040
-0.15	0.58	236.1	9.95E-06	-	-	19084
-0.10	0.63	233.4	6.25E-06	-	-	2.20E+05
-0.05	0.68	230.4	4.31E-06	26731	8.96E-07	2.09E+06
0.00	0.73	231.0	3.80E-06	25558	7.59E-07	4.78E+06
0.05	0.78	231.5	3.49E-06	34145	8.50E-07	3.01E+06
0.10	0.83	232.4	3.27E-06	49570	1.42E-06	1.00E+06
0.15	0.88	232.6	3.05E-06	37032	2.76E-06	3.02E+05
0.20	0.93	232.4	2.86E-06	28345	5.39E-06	1.16E+05
0.25	0.98	232.6	2.70E-06	28631	9.32E-06	58638
0.30	1.03	232.9	2.58E-06	36213	1.12E-05	41131
0.35	1.08	233.3	2.46E-06	52497	8.74E-06	39867
0.40	1.13	233.5	2.36E-06	69903	4.05E-06	56107
0.45	1.18	231.6	2.16E-06	20136	5.70E-07	1.41E+05
0.50	1.23	231.4	2.06E-06	15222	4.65E-07	1.80E+05
0.55	1.28	231.7	1.99E-06	15319	4.28E-07	2.05E+05
0.60	1.33	231.7	1.94E-06	18017	4.14E-07	2.24E+05
0.65	1.38	234.2	2.07E-06	-	-	2.49E+05
0.70	1.43	234.1	2.02E-06	-	-	2.59E+05
0.75	1.48	234.1	1.98E-06	-	-	2.73E+05
0.80	1.53	234.3	1.95E-06	-	-	2.83E+05
0.85	1.58	234.8	1.92E-06	-	-	2.92E+05
0.90	1.63	235.1	1.90E-06	-	-	2.81E+05
0.95	1.68	234.9	1.88E-06	-	-	1.83E+05
1.00	1.73	235.6	1.84E-06	-	-	62570

Table A4-4. Parameters extracted from fitting EIS data in aqueous electrolyte (pH9 KB_i buffer) under 0.1 sun illumination.

V / V vs. Ag/AgCl, pH 9	V / V vs. RHE	R_s / Ω	C _{bulk} / F	R_{trap} / Ω	C_{ss} / F	$R_{ct,ss}$ / Ω
-0.20	0.53	235.1	1.44E-05	-	-	2176
-0.15	0.58	231.3	8.86E-06	-	-	12966
-0.10	0.63	230.4	5.80E-06	-	-	1.64E+05
-0.05	0.68	230.1	4.33E-06	40293	1.20E-06	1.56E+05
0.00	0.73	230.3	3.85E-06	13033	1.37E-06	77806
0.05	0.78	231.3	3.59E-06	6187	2.43E-06	34892
0.10	0.83	231.8	3.33E-06	3112	4.51E-06	14666
0.15	0.88	231.7	3.07E-06	2044	8.47E-06	6716
0.20	0.93	231.4	2.83E-06	1844	1.36E-05	3662
0.25	0.98	231.1	2.64E-06	2086	1.59E-05	2505
0.30	1.03	230.7	2.49E-06	2761	1.57E-05	2055
0.35	1.08	230.5	2.35E-06	3765	1.14E-05	1985
0.40	1.13	229.6	2.22E-06	4593	5.71E-06	2366
0.45	1.18	229.2	2.12E-06	5202	3.03E-06	3020
0.50	1.23	229.1	2.06E-06	6642	5.21E-06	2753
0.55	1.28	230.0	2.06E-06	-	-	10058
0.60	1.33	229.7	1.97E-06	-	-	11139
0.65	1.38	229.4	1.91E-06	-	-	11739
0.70	1.43	228.5	1.85E-06	-	-	12260
0.75	1.48	228.5	1.81E-06	-	-	12957
0.80	1.53	228.3	1.76E-06	-	-	13218
0.85	1.58	228.4	1.75E-06	-	-	14248
0.90	1.63	228.5	1.71E-06	-	-	13686
0.95	1.68	228.5	1.71E-06	-	-	14931
1.00	1.73	230.4	1.69E-06	-	-	14752

Table A4-5. Parameters extracted from fitting EIS data in aqueous electrolyte (pH9 KB_i buffer) under 1 sun illumination.



Figure A4-3. CV taken after holding potential at 2.3 V *vs.* RHE for 60 s in the dark. Scan rates varies from 200, 400, 600, 800, 1000, 1200 and 1500 mV s⁻¹ corresponding to red, orange, dark yellow, green, dark green, blue and purple solid. The peak intensity after the dark pretreatment is slightly smaller compared to the light pretreatment.



Figure A4-4. Mott-Schottky plots (black scattered points) and linear fit (red dash) of CuWO₄ in a) MeCN electrolyte, b) MeCN electrolyte containing 2% H₂O, and c) dichloromethane electrolyte.



Figure A4-5. CV after holding potential at ~1.8 V *vs.* V_{fb} for 60 s in the dark, measured in H₂O (black solid), MeCN (red dash) and MeCN with 2% H₂O (blue dot). Scan rate is 1500 mV s⁻¹.



Figure A4-6. a) Raman spectrum and b) XRD pattern of CuWO₄ synthesized by spray pyrolysis and annealed at 550 °C for 1 hr (SP-CuWO₄). Experimental data of CuWO₄ are shown as black curves and peak positions from literature are shown as vertical dark yellow dash. The XRD pattern of FTO substrate is shown as blue curve as control experiment, and the diffraction peaks from FTO are labeled as *.

As shown in Figure A4-6, the resulted SP-CuWO₄ films show Raman and XRD peaks corresponding to CuWO₄ peaks in literature^{18–20}, apart from those from the underlying FTO substrate marked as * in XRD pattern. These results confirm the pure CuWO₄ composition of the resulted films.



Figure A4-7. *J-V* curves of SP-CuWO₄ under 1 sun (red solid), 0.33 sun (green dash), 0.1 sun (blue dots) illumination and in the dark (black dash dot) measured in pH 9 aqueous (H_2O) electrolyte.



Figure A4-8. Bode phase plots of SP-CuWO₄ at 0.93V *vs.* RHE in the dark (black squares) and under 1 sun illumination (red circles) measured in pH 9 aqueous (H₂O) electrolyte. Fitting curves are shown as black dash and red dots for dark and 1 sun measurements, respectively.



Figure A4-9. C_{ss} obtained from fitting EIS measured in pH 9 aqueous (H₂O) electrolyte under 0.1 sun (blue triangles), 0.33 sun (green diamonds) and 1 sun (red circles) illumination with SP-CuWO₄.



Figure A4-10. Mott-Schottky plots of SP-CuWO₄ measured in the dark in pH 9 aqueous (H₂O) electrolyte.



Figure A4-11. CVs taken after holding potential at 2.3 V *vs*. RHE for 60 s under 1 sun illumination at scan rates from 200, 400, 600, 800, 1000, 1200 and 1500 mV s⁻¹ corresponding to red, orange, dark yellow, green, dark green, blue and purple. Experiment was conducted in pH 9 aqueous electrolyte.

As shown in Figure A4-7, the J-V curves of SP-CuWO₄ measured under illumination for water oxidation show an onset potential of 0.85 - 0.90 V vs. RHE, depending on the light intensity. The photocurrent at 1.23 V vs. RHE under 1 sun illumination is ~0.13 mA cm⁻², which is similar as reported values.^{3,8,9,12} In Figure A4-8, the EIS data show two capacitive features in the Bode phase plot under 1 sun illumination, while only one is observed in the dark. The surface state capacitance, C_{ss} , increases with increasing light intensity, as shown in Figure A4-9. These facts suggest that the surface state of SP-CuWO₄ is light-induced, rather than intrinsic. The Mott-Schottky plot measured in the dark in Figure A4-10 shows no Fermi level pinning, further confirming that the surface state is not present in the dark. Lastly, the CV surface measurement in Figure A4-11 shows a capacitive peak around 0.9 V vs. RHE, the peak position of which shifts negatively with increasing scan rate, while its peak current increases. This peak position is close to that of C_{ss} in Figure A4-9, and matches with water oxidation onset potential, which is essentially the same observation with CuWO₄ synthesized via ALD. Therefore, we conclude that the role of surface state as water oxidation intermediate is general for CuWO₄, rather than specifically limited to our electrode made by ALD.

REFERENCES

REFERENCES

- (1) Gao, Y.; Hamann, T. W. Quantitative Hole Collection for Photoelectrochemical Water Oxidation with CuWO₄. *Chem. Commun.* **2017**, *53*, 1285–1288.
- (2) Bohra, D.; Smith, W. A. Improved Charge Separation via Fe-Doping of Copper Tungstate Photoanodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9857–9866.
- (3) Pyper, K. J.; Yourey, J. E.; Bartlett, B. M. Reactivity of CuWO₄ in Photoelectrochemical Water Oxidation Is Dictated by a Midgap Electronic State. *J. Phys. Chem. C* **2013**, *117*, 24726–24732.
- Klahr, B.; Gimenez, S.; Fabregat-santiago, F.; Hamann, T.; Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. J. Am. Chem. Soc. 2012, 134, 4294– 4302.
- (5) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Electrochemical and Photoelectrochemical Investigation of Water Oxidation with Hematite Electrodes. *Energy Environ. Sci.* **2012**, *5*, 7626–7636.
- (6) Zandi, O.; Hamann, T. W. Determination of Photoelectrochemical Water Oxidation Intermediates on Haematite Electrode Surfaces Using Operando Infrared Spectroscopy. *Nat. Chem.* 2016, 8, 778–783.
- (7) Klahr, B.; Hamann, T. Water Oxidation on Hematite Photoelectrodes: Insight into the Nature of Surface States through in Situ Spectroelectrochemistry. *J. Phys. Chem. C* 2014, *118*, 10393–10399.
- (8) Gao, Y.; Zandi, O.; Hamann, T. W. Atomic Layer Stack Deposition-Annealing Synthesis of CuWO4. J. Mater. Chem. A **2016**, *4*, 2826–2830.
- (9) Lhermitte, C. R.; Bartlett, B. M. Advancing the Chemistry of CuWO₄ for Photoelectrochemical Water Oxidation. *Acc. Chem. Res.* **2016**, *49*, 1121–1129.
- (10) Bertoluzzi, L.; Bisquert, J. Equivalent Circuit of Electrons and Holes in Thin Semiconductor Films for Photoelectrochemical Water Splitting Applications. J. Phys. Chem. Lett. 2012, 3, 2517–2522.
- (11) Arora, S. K.; Mathew, T. Dielectric Studies of CuWO₄ Crystals. *Phys. Stat. Sol.* **1989**, *116*, 405–413.
- (12) Yourey, J. E.; Bartlett, B. M. Electrochemical Deposition and Photoelectrochemistry of CuWO₄, a Promising Photoanode for Water Oxidation. J. Mater. Chem. 2011, 21, 7651– 7660.

- (13) Yourey, J. E. J.; Pyper, K. K. J.; Kurtz, J. B.; Bartlett, B. M. Chemical Stability of CuWO₄ for Photoelectrochemical Water Oxidation. *J. Phys. Chem. C* **2013**, *117*, 8707–8718.
- (14) Hill, J. C.; Choi, K. Synthesis and Characterization of High Surface Area CuWO₄ and Bi₂WO₆ Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, 1, 5006–5014.
- (15) Bisquert, J. Chemical Capacitance of Nanostructured Semiconductors: Its Origin and Significance for Nanocomposite Solar Cells. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5360–5364.
- (16) Bisquert, J. Physical Electrochemistry of Nanostructured Devices. *Phys. Chem. Chem. Phys.* **2008**, *10*, 49–72.
- (17) Bertoluzzi, L.; Badia-bou, L.; Fabregat-santiago, F.; Gimenez, S.; Bisquert, J. Interpretation of Cyclic Voltammetry Measurements of Thin Semiconductor Films for Solar Fuel Applications. *J. Phys. Chem. Lett.* **2013**, *4*, 1334–1339.
- (18) Kihlborg, L.; Gebert, E. CuWO₄, a Distorted Wolframite-Type Structure. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1970**, *26*, 1020–1026.
- (19) Ruiz-Fuertes, J.; Errandonea, D.; Segura, A.; Manjón, F. J.; Zhu, Z.; Tu, C. Y. Growth, Characterization, and High-Pressure Optical Studies of CuWO₄. *High Press. Res.* 2008, 28, 565–570.
- (20) Ruiz-Fuertes, J.; Sanz-Ortiz, M. N.; González, J.; Rodríguez, F.; Segura, a; Errandonea, D. Optical Absorption and Raman Spectroscopy of CuWO₄. J. Phys. Conf. Ser. 2010, 215, 12048.

Chapter 5:

Investigations of Charge Separation Limitations of CuWO₄

5.1 Abstract

In this chapter, mesoporous CuWO₄ electrodes of ~800 nm thick were synthesized by spray pyrolysis. The pores of CuWO₄ were filled by depositing Al_2O_3 using atomic layer deposition (ALD) followed by removing the excess top Al_2O_3 layer using 1 M KOH solution. By comparing the PEC performance with front and back illumination on the resulted compact film, it was determined that the electrons are the limiting charge carriers of CuWO₄. The wavelength dependent behavior of incident photon-to-current efficiency (IPCE) suggests that the electron collection length of CuWO₄ is shorter than 577 nm.

5.2 Introduction

As discussed in chapter 1, CuWO₄ in theory should produce a maximum photocurrent density of ~9 mA cm⁻², reaching a theoretical maximum solar-to-hydrogen (STH) efficiency of 11% if paired with a suitable photocathode in a tandem cell configuration for photoelectrochemical (PEC) water splitting. However, the actual photocurrent density that has been achieved with CuWO₄ so far has been low, which varies from 0.1 to 0.3 mA cm⁻² at the thermodynamic potential of water oxidation (1.23 V vs RHE). It was discussed in chapter 2 and chapter 3 that water oxidation is limited by surface recombination, i.e., recombination of oxidized water oxidation intermediate species at the surface with conduction band electrons, at low applied bias. However, once it passes the photocurrent onset potential region, the hole collection efficiency is essentially quantitative at potentials higher than 1.23 V vs RHE. Therefore, the huge discrepancy between the actual photocurrent density and the theoretical value indicates that charge separation efficiency (η_{cs}) is not optimized. As was mentioned in chapter 1, due to the weak absorption of this indirect semiconductor, to absorb 95% of the incident light, a thickness of several hundred nm to several µm is required, depending on the wavelength. However, the charge carriers are not necessarily able to travel that far. The fact that thin film CuWO₄ photoelectrode (80 nm to 200 nm thick)^{1,2} produces similar photocurrent as much thicker films (2 to 3 µm thick)^{3,4} suggests that the charge carrier collection length is limiting the performance of CuWO₄. Efforts have been made by many research groups to solve the contradiction between a long light penetration depth and short carrier collection length by doping⁵ and nanostructuring^{6–9}. Bohra et al.⁵ and Gaillard et al.⁸ compared the performance of CuWO₄ by illuminating from different directions and concluded that the electronic transport properties are the major limiting factors based on the better performance by illuminating from the substrate-electrode (back) side. Therefore, Bohra et al. employed Fe-doping for their
CuWO₄ photoanode, which is the only example of doping this material for PEC water oxidation.⁵ As a result, their doped film shows 1.5 times the photocurrent as the bare one, which is 0.25 mA cm⁻² at 1.23 V vs RHE.⁵ Gaillard et al. used a nanocomposite of CuWO₄ and multi-wall carbon nanotubes (MWCNT) to reduce the bulk resistance of CuWO₄ electrode. A photocurrent density of ~0.20 mA cm⁻² was achieved for this photoanode.⁸ Other nanostructured electrodes were also pursued in order to improve η_{cs} , such as CuWO₄ nanoflakes.^{6,7} The improvement, however, has been limited.

Nanostructured electrodes (e.g. nanorods as shown in Figure 5-1b) are typically encouraged to overcome the opposing properties of a long light absorption depth and short minority carrier collection length. As shown in Figure 5-1a, for a thin film electrode deposited on a flat substrate, the direction of charge separation is the same as light absorption. Therefore, if the thickness of the film is made close to the light absorption depth, which is assumed longer than the collection length of the minority charge carrier (which are holes for n-type semiconductors), the holes generated close to the back contact will not be able to reach the semiconductor/electrolyte interface to realize water oxidation. In Figure 5-1b, however, for a nanostructured electrode, the light is absorbed along the direction of the nanorods, while the holes transport in the direction perpendicular to that of light absorption. To optimize light absorption and charge separation at the same time, the length and width of the nanorods can be made the same as light penetration depth and hole collection length, respectively. However, this electrode morphology is helpful only for reducing the distance that holes need to travel. The photogenerated electrons still need to travel through the length of the nanorods to reach the back contact.



Figure 5-1. Scheme of charge separation in a) planar CuWO₄ electrode and b) optimized nanostructured CuWO₄ photoanode.

In practice, the improvement with nanostructuring in reported works has been limited,^{6,7} with photocurrents still close to those observed with our 80 nm thin films. One possible reason is that the length and width of the CuWO₄ nanoflakes are not optimized. The other possible reason is that even if the dimensions of the nanoflakes had been optimized, the electrons might still have a short collection length, therefore limiting the bulk property of the photoanodes, which is suggested by previous works. ^{5,8} This indicates that although doping, nanostructuring, or even tuning the substrate could potentially improve the bulk properties of the semiconductors in some cases, they have to be rationally designed based on the knowledge of the material. Therefore, this motivated us to carry out fundamental investigations with the bulk properties of CuWO₄.

The first question to answer about bulk CuWO₄ is whether the limiting charge carriers are electrons or holes. According to previous literature, the bulk of CuWO₄ is limited by its electronic transport properties.^{5,8} For a semiconductor, the conductivity, σ , is given by:

$$\sigma = q\mu_n n + q\mu_p p \tag{5.1}$$

where μ_n and μ_p are the mobilities of the electrons and holes, respectively; q is the elementary charge; n and p are the concentrations of the electrons and holes, respectively. For a n-type semiconductor, $n \gg p$. Therefore, if electrons are the limiting charge carrier, $\mu_n \ll \mu_p$. This is a rare situation but is possible as for n-type BiVO₄ photoanodes reported in previous literature.^{10,11} However, the CuWO₄ electrodes in previous works are nanostructured or mesoporous,^{5,8} which makes it insufficient to justify the argument that electrons are limiting. Compact films are preferred instead to conduct these fundamental investigations.

Once the limiting charge carrier is understood, the knowledge of its collection length would be helpful to direct design of the nanostructured electrode. Because of a lack of knowledge of this length, all of the nanostructuring work (including nanoflakes and coat MWCNT with CuWO₄) have only achieved moderate improvement. Therefore, it is crucial to quantify the hole collection length of CuWO₄.

5.3 Approaches and Methods

To answer the first question, *whether electrons or holes are the limiting charge carriers*, the PEC performance of CuWO₄ by illuminating from different directions will be evaluated. As illustrated in Figure 5-2, photogenerated charge carriers always have a higher concentration in the thin film closer to the side of illumination (holes are presented but electrons are generated together with holes). When the electrode is illuminated from the electrolyte-electrode (front) side, more charge carriers are generated closer to the electrode/electrolyte interface. Therefore, electrons have to travel for a longer distance to reach the back contact than holes to reach the interface. The situation is the opposite when illuminating the electrode from the substrate-electrode (back) side. Therefore, by comparing the performance with different illumination directions, one should be able to determine whether electrons or holes are the limiting charge carriers.



Figure 5-2. Schematic illustration of hole generation and charge separation in CuWO₄ photoanode illuminated from a) electrolyte-electrode (front) side and b) substrate-electrode (back) side. The red arrows represent hole collection and green arrows represent electron transport.

There are several considerations about this method. Firstly, the electrode should be thick enough to generate significant difference in charge carrier concentration throughout the film. Generation profile of charge carriers can be calculated using the following equation:

$$G = -\frac{dI}{dx} = \alpha I_0 e^{-\alpha x}$$
(5.2)

$$G(\lambda, x) = \alpha(\lambda) I_0(\lambda) e^{-\alpha(\lambda)x}$$
(5.3)

$$G(\lambda, x) / I_0(\lambda) = \alpha(\lambda) e^{-\alpha(\lambda)x}$$
(5.4)

where *G* represents the generation rate of charge carriers; *I* and *I*₀ represent the intensity of the transmitted light at a certain distance (*x*) into the electrode and incident light, respectively; α is the absorption coefficient; λ is the wavelength of the incident light. Based on the α we obtained with CuWO₄ by atomic layer deposition (ALD) as shown in chapter 2, the drop in G through an 80 nm thick film with 405 nm monochromatic light is 18.2 %, and is 11.1 % with 470 nm light. This change in charge carrier concentration throughout the film is too small to observe significant

difference in PEC performance by shining the electrode from different directions. We also did the calculation for a 1 μ m thick CuWO₄ film assuming same α . The drop in G is 94.0 % under 405 nm illumination and 73.1 % under 470 nm illumination. ALD is ideal for depositing ultrathin films with thickness control down to the nm or even Å level, but is inefficient for depositing films of several hundred nm to even μ m. Therefore, we decided to use spray pyrolysis to synthesize our CuWO₄ film for its bulk studies.

Another consideration is the morphology of the film. As mentioned earlier, a nanostructured or mesoporous film could lead to inaccurate results. Therefore, we decided to adopt a method similar as what was used by the Lewis group¹² to fill the pores in CuWO₄ with Al₂O₃ by ALD and then remove the excess Al₂O₃ layer at the top. As illustrated in Figure 5-3, instead of mechanically polishing the top Al₂O₃ layer, we used 1 M KOH to etch the excess Al₂O₃ at the top so that CuWO₄ photoanode is exposed. With this treatment, the direction of hole and electron transport will be along the light absorption direction, which will provide insight into identifying the limiting charge carriers.



Figure 5-3. Scheme of a) a nanostructured CuWO₄ film, b) a nanostructured film with pores filled with excess Al_2O_3 and c) after etching the top Al_2O_3 layer with 1 M KOH to expose CuWO₄ electrode to the electrolyte.

The third consideration is optical control. When using a regular glass PEC cell to perform measurements, we found that the quartz window and the glass wall of the cell would increase the intensity of incident light, while the fluorine doped tin oxide (FTO) coated glass substrate would absorb and reflect some light, resulting in lower incident light on CuWO₄ electrodes. It is difficult to calibrate the actual incident light when illuminating from the front side because of the irregular geometry of the glass cell. Therefore, for this study, we decided to use a CuWO₄ PEC sandwich cell which helps optical control.

Once we have determined that the electrons are the limiting charge carriers, the other question to answer is the *electron collection length*. Analysis of the wavelength dependent behavior of incident photon-to-current efficiency (IPCE) would allow us to extract information about the electron collection length of CuWO₄. According to the scheme shown in Figure 5-4a, when CuWO₄ is illuminated from the front side, if the wavelength of the incident light is so short that it is absorbed outside the electron collection region, there should be minimal photocurrent. As the wavelength increases, a higher portion of absorbed photons will be able to contribute to photocurrent. Therefore, we should expect an increase in IPCE with increasing wavelength. However, once the wavelength is too long for CuWO₄ to absorb all of the photons, IPCE will decrease. Therefore, we should expect to see a peak in IPCE where the light absorption depth is close to the film thickness. Typically, the light penetration depth is defined as the depth at which the intensity of the radiation inside the material drops to 1/e (~37%) of its original value just beneath the surface, which should be $1/\alpha$. However, here we use $3/\alpha$ which represents the depth at which 95% of the photons are absorbed. Figure 5-4b shows the scheme of illuminating $CuWO_4$ from the back side with monochromatic light of different wavelengths. When the light absorption depth is shorter than the electron collection length, L_n , IPCE should essentially remain the same when increasing the wavelength. Once the penetration depth of light is longer than L_n , not all the photogenerated electrons will be able to reach the FTO/CuWO₄ back contact. Therefore, one should expect to see a decrease in IPCE when increasing the wavelength further. Based on these theories, L_n of CuWO₄ could be estimated.



Figure 5-4. Schematic illustration of light absorption in CuWO₄ electrode by a) front and b) back illumination. L_n is the electron collection length. The light red, orange, green, blue and purple arrows represent illumination from relatively long wavelengths to short wavelengths.

5.4 Experimental

5.4.1 Film Preparation

CuWO₄ was deposited on FTO coated glass substrate by spray pyrolysis using the procedure described in chapter 4. After deposition, the film was annealed in air at 550 °C for 1 hr allowing for 1 hr to ramp up and cool down. 1500 cycles of Al_2O_3 (~150 nm) was deposited using ALD (Savannah 200, Cambridge Nanotech Inc.) to fill the pores in CuWO₄ film.

Trimethylaluminum (TMA, Aldrich) was used as the Al source and H_2O was the oxidant. The substrates were kept at 230 °C and the two precursors were kept at room temperature. In each cycle, the Al precursor and H_2O were alternatively pulsed for 0.015 s and kept under exposure mode for 20 s to allow sufficient diffusion of the precursor vapor into the pores. Between each pulse, the chamber was pumped for 10 s to remove excess precursor and by-product. The excess top Al_2O_3 layer was removed by etching the film with 1 M KOH aqueous solution for 40 min.

5.4.2 Film Characterization

The thickness of Al₂O₃ layer is ~150 nm based on ellipsometric measurement (Horiba Jobin Yvon, Smart-SE) with 1500 cycles of Al₂O₃ on Si substrate, assuming it has the same growth rate on CuWO₄. The morphology and thickness of CuWO₄ electrode was examined by top-down and cross-section scanning electron microscopy (SEM) (Carl Zeiss Microscopy). Absorption of electrolytes was measured using a Perkin-Elmer Lambda 35 UV-vis spectrometer. Absorbance measurements of thin films and integrated sandwich cells were performed with the same UV-vis spectrometer with a Labsphere integrating sphere.

5.4.3 Sandwich Cell Preparation

A platinized FTO (Pt-FTO) electrode was used as the counter electrode. Prior to platinization, the FTO substrate was sonicated in soap water, water, 0.1 M hydrochloric acid in ethanol, and isopropanol (IPA) for 15 min, respectively. The Pt-FTO was made by drop-casting 15 μ L of a 5 mM chloroplatinic acid hydrate (≥99.9% trace metals basis, Aldrich) solution in IPA on a 2×2 cm² FTO coated glass substrate followed by spreading out the Pt precursor, drying in a petri dish with holes on its cover for 10 min, and annealing in air at 380 °C for 20 min. The CuWO₄ working electrode and counter electrode were attached by sandwiching a 25 μ m thick Surlyn frame (Solaronix) by applying light pressure at 145 °C to seal the cell. Electrolytes consisting of 1 M

 KB_i buffer (pH 9), 200 mM KI and 5 mM I₂ were introduced by capillary force through the two pre-drilled holes on Pt-FTO counter electrode, which were subsequently sealed with microglass and Surlyn film. The holes were positioned apart from the cell active area to avoid undesired light loss when the light was illuminated from the counter electrode side.

5.4.4 Photoelectrochemistry

All electrochemical and photoelectrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. Current density-voltage (J-V) curves were measured using a scan rate of 20 mV s⁻¹. The white light source was a 450 W Xe arc lamp (Horiba Jobin Yvon). An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm⁻² (1 sun). 1 M KB_i buffer (pH 9) with or without 200 mM KI / 5 mM I₂ or 0.5 M Na₂SO₃ was used as the electrolyte. Photoelectrochemical measurements of thin film electrodes in aqueous solutions were performed by shining light on the CuWO₄ electrode through the substrate. Photocurrent densities (J_{photo}) were obtained by subtracting the dark current density (J_{dark}) from the total current density under illumination (J_{total}). IPCE of CuWO₄ sandwich cell was measured at short circuit (corresponding to 1.03 V vs RHE in the three-electrode configuration) using the same light source coupled with a grating monochromator with a 10 nm step. Monochromatic J-Vresponse was measured under the illumination of a 470 nm LED with an LED driver from Metrohm, and the light intensity was calibrated using the current measured with a photodiode from the same manufacturer.

5.5 Results and Discussion

Absorption of bare CuWO₄ deposited on FTO substrate was measured using UV-vis and the results are shown in Figure 5-5. The absorption coefficient in Figure 5-5a was calculated using the equation described in a previous work.¹² The thickness of the film was determined to be \sim 800

nm by cross-section SEM as shown in Figure 5-10b. The absorption coefficient is nonzero at wavelengths longer than 539 nm due to the side scatter of light in this thick and mesoporous film. An indirect bandgap of ~2.3 eV was obtained according to the Tauc plot in Figure 5-5b if the plateau region < 2.3 eV is corrected as the baseline. This bandgap is close to CuWO₄ synthesized by other methods.^{3,12} It has been suggested in chapter 4 that the composition of our CuWO₄ by spray pyrolysis is pure crystalline CuWO₄.



Figure 5-5. a) Absorption coefficient and b) Tauc plot of $CuWO_4$ indicating its indirect bandgap. The red dashed line represents the fitting result of the linear region in Tauc plot. The blue dash represents the corrected baseline according to the plateau region in Tauc plot.

The absorptance of $CuWO_4$ (A%) on FTO was calculated by using equation

$$A\% = (1 - T\% - R\%) - (1 - T_{sub}\% - R_{sub}\%) = T_{sub}\% + R_{sub}\% - T\% - R\%$$
(5.5)

where T% and R% are the total transmittance and reflectance of CuWO₄ thin film on FTO, and $T_{sub}\%$ and $R_{sub}\%$ are the transmittance and reflectance of FTO substrate. According to its bandgap of 2.3 eV, CuWO₄ should in theory absorb up to 539 nm. However, as shown in Figure 5-6a, A% around 550 nm is still ~20%. This is due to the side scattering of light of the relatively thick and mesoporous film. Therefore, the baseline of A% was corrected by subtracting the apparent A% at 539 nm, which is demonstrated in Figure 5-6b.



Figure 5-6. a) Calculated raw data and b) corrected absorptance of CuWO₄.

In this work, 200 mM KI / 5 mM I₂ (Γ/I_3^-) was used as the hole scavenger to eliminate surface recombination in order to investigate the bulk properties of CuWO₄ instead of Na₂SO₃ since a redox couple was needed in the sandwich cell. As shown in Figure 5-7, bare CuWO₄ generates comparable J_{photo} -V response in oxidizing Γ/I_3^- redox couple as oxidizing Na₂SO₃, which indicates that it works as a suitable hole scavenger for CuWO₄. Another advantage of using Γ/I_3^- instead of Na_2SO_3 is that with I/I_3 ⁻ CuWO₄ shows minimal dark current in our interested potential region (Figure 5-8b) while Na_2SO_3 shows significant dark current (Figure 5-8a) which makes the interpretation of the results less straightforward.



Figure 5-7. *J*_{photo}-*V* response of CuWO₄ in a pH 9 KB_i electrolyte with 0.5 M Na₂SO₃ (blue dash) and 200 mM KI / 5 mM I₂ (red solid) under 1 sun illumination.



Figure 5-8. Dark *J-V* curves of CuWO₄ measured in a) Na₂SO₃ and b) I^{-}/I_{3}^{-} electrolyte.

Charge separation efficiency (η_{CS}) of CuWO₄ under 1 sun illumination was calculated using equation:

$$\eta_{\rm CS} = J_{\rm scavenger} \,/\, J_{\rm abs} \tag{5.5}$$

$$J_{abs} = q \int_{330}^{539} \Phi(\lambda) A \% d\lambda$$
(5.6)

where $J_{scavenger}$ and J_{abs} are the photocurrent with a hole scavenger and the maximum photocurrent if all the photogenerated charge carriers are collected; q is the elementary charge; $\Phi(\lambda)$ is the flux of incident light at a certain wavelength (λ). The calculated result is shown in Figure 5-9. CuWO₄ shows a poor η_{cs} which is 7.5% at 1.23 V vs RHE and < 5% at 1.03 V vs RHE. This further confirms that the major limitation of CuWO₄ is its poor bulk properties.



Figure 5-9. Charge separation efficiency of CuWO₄ electrode.

The top-down morphology of the mesoporous CuWO₄ synthesized by spray pyrolysis is

shown in Figure 5-10a with the pore size up to ~ 150 nm. Therefore, 1500 cycles (~150 nm) of Al_2O_3 was deposited by ALD to fill these pores. After deposition, the Al_2O_3 insulates the contact between CuWO₄ electrode and I^{-}/I_{3}^{-} electrolyte, as the back dashed J-V curve shown in Figure 5-11, which shows no photocurrent. The coated electrode was further etched in 1 M KOH aqueous solution for different lengths of time, and the time dependent J-V curves under 1 sun illumination are shown in Figure 5-11. From 30 min to 38 min, the photocurrent slowly increases, which is associated with gradual removal of Al_2O_3 . However, the photocurrent is low possibly due to only islands of CuWO₄ that are exposed. After 40 min of etching, the photocurrent increases drastically but is still lower than that of bare CuWO₄, indicating full removal of top Al₂O₃ without damaging the Al₂O₃ that are in the pores. After this, the photocurrent increases even higher until it reaches the same photocurrent as the bare electrode after 44 min of etching. This suggests that the Al₂O₃ in the pores are also removed. Therefore, all the electrodes with Al_2O_3 were etched for 40 min for bulk studies. The morphology of these electrodes after Al₂O₃ deposition and KOH etching treatment was examined using SEM. As shown in Figure 5-10c, the pores between grains of CuWO₄ are filled with Al₂O₃, and CuWO₄ is exposed at the surface. In the cross-section SEM image in Figure 5-10d, the thin film is compact with a thickness of ~800 nm.



Figure 5-10. SEM image of a) top-down and b) cross-section view of bare CuWO₄ by spray pyrolysis, c) top-down and d) cross-section view of CuWO₄ deposited with 1500 cycles (\sim 150 nm) of Al₂O₃ and etched in 1 M KOH for 40 min.



Figure 5-11. *J-V* curves of CuWO₄ coated with ~150 nm of Al₂O₃ (black dash) and etched in 1 M KOH for 30 min (red), 32 min (orange), 34 min (yellow), 36 min (green), 38 min (dark cyan), 40 min (blue), 42 min (purple) and 44 min (wine). These *J-V* curves are also compared with that of bare CuWO₄ (pink dots). All measurements are done in pH 9 KB_i electrolyte under 1 sun illumination.

The post-treated CuWO₄ electrodes were then made into sandwich cells. As a consideration for optical control, when light is illuminated through the working electrode (back) side, the light penetrates through the FTO substrate and then CuWO₄ electrode as shown in Figure 5-12. However, when the light is illuminated through the counter electrode side, it goes through Pt-FTO and then electrolyte before it reaches CuWO₄. Therefore, the actual light incident on CuWO₄ as to be calibrated. We firstly examined the absorption of Pt-FTO compared with bare FTO. The absorptance calculated for FTO and Pt-FTO in Figure 5-13 shows that their absorption is close in our interested wavelength region. Therefore, the absorption of Pt is negligible. The absorption of the electrolyte was also analyzed. The major absorbing species in the electrolyte is I₂. Therefore, different concentrations of I₂ was dissolved in pH 9 KB_i buffer with 200 mM KI to examine its extinction coefficient. The absorbance as a function of I₂ concentration at different wavelengths are presented in Figure 5-14. Based on the length of solution of 1 cm, the extinction coefficients were calculated to be 61.3 (\pm 0.2), 12.38 (\pm 0.06), and 1.70 (\pm 0.02) mM⁻¹ cm⁻¹ at 350nm, 405nm, and 470nm. Since the thickness of the electrolyte inside the sandwich cell is 25 µm (thickness of Surlyn film), the absorptance of I₂ in the cell should be 54%, 14% and 2%. Therefore, it is necessary to consider the absorption of the electrolyte, especially at shorter wavelengths.



Figure 5-12. Schematic illustration of CuWO₄ sandwich cell and light illumination.



Figure 5-13. Absorptance of FTO-coated glass (black solid) and platinized FTO-coated glass (blue dash). Both were measured by illuminating from the glass side.



Figure 5-14. Absorbance of different concentrations of I_2 in pH9 KB_i buffer with 200 mM KI at a) 350 nm, b) 405 nm and c) 470nm.

The absorptance of the integrated cell with (red solid) and without (black dash) electrolyte is compared by illuminating from the front side to examine the absorption of the electrolyte. As shown in Figure 5-15a, when the cell is filled with electrolyte, the total absorptance is slightly higher than without electrolyte, indicating the non-negligible absorption of the electrolyte species when shining light from the front side. By substracting the absorptance of the unfilled cell from the filled cell, the absorptance of the electrolyte was calculated and presented in Figure 5-15b. Therefore, for monochromatic PEC measurements, the incident light intensity was corrected by subtracting the absorptance of FTO substrate when illuminating from the back side, and by subtracting the absorptance of FTO substrate and electrolyte when illuminating from the front side.



Figure 5-15. a) Absorptance of the integrated sandwich solar cell with (red solid) and without (black dash) electrolyte by illuminating from the front side. b) Absorptance of the electrolyte inside the sandwich cell.

The *J*-*V* response of the sandwich cell with post-treated CuWO₄ under AM 1.5 1 sun illumination are shown in Figure 5-16. The J_{photo} -*V* curves are shown in Figure 5-16b by subtracting dark current from the total current. As clearly shown in Figure 5-16b, the photocurrent generated by back illumination is higher than front illumination, as was observed in previous literature^{5,8}. However, the intensity of the incident light was not corrected. Therefore, we further analyzed the *J*-*V* behavior of this cell under monochromatic light with optical control.



Figure 5-16. a) *J-V* response of CuWO₄ sandwich by illuminating from front (red dash) and back (blue solid) side under AM 1.5 1 sun illumination and in the dark (black dots). b) J_{photo} -V of CuWO₄ sandwich cell illuminated from front (red dash) and back (blue solid) side.

In order to better quantify the photocurrent by correcting the light incident on CuWO₄ electrode, monochromatic measurements were conducted. The raw data of *J*-*V* response are shown in Figure 5-17a, and the corrected J_{photo} -*V* and quantum efficiency (QE) curves are shown in Figure 5-17b and c. The corrected photocurrent is calculated using these equations:

$$J_{photo}(front, corrected) = J_{photo}(front, raw) / (1 - A_{FTO} \% - A_E \%)$$
(5.7)

$$J_{photo}(back, corrected) = J_{photo}(back, raw) / (1 - A_{FTO}\%)$$
(5.8)

where A_{FTO} % and A_E % are the absorptance of FTO substrate and electrolyte. QE was calculated using equation:

$$QE = J_{photo}(corrected) / J_{flux}$$
(5.9)

where J_{flux} is the maximum possible photocurrent generated by the incident light. It was observed that after optical correction, the photocurrent generated by back illumination appears higher than that by front illumination. This indicates that for our compact CuWO₄ with post treatment, the electrons are the limiting charge carriers.



Figure 5-17. a) *J-V* response, b) J_{photo} -*V* response and c) quantum efficiency of CuWO₄ sandwich cell with front (red dash) and back (blue solid) illumination and in the dark (black dots). Light source was 470 nm LED with 218 mW cm⁻² power density.

IPCE of CuWO₄ sandwich cell was measured at short circuit (V=0 V vs V_s) under monochromatic light in its bandgap range. The un-corrected IPCE data are shown in Figure 5-18a. The IPCE data under 330 nm were eliminated due to the influence of the strong absorption of FTO substrate at shorter wavelengths. The IPCE values were corrected by using equation (5.9), and are shown in Figure 5-18b. Similar as what was observed in the monochromatic *J-V* response at 470 nm, IPCE is higher when the cell is illuminated from the back side. It was also noticed that QE values at short circuit calculated in Figure 5-17c agree with the IPCE values in Figure 5-18b at 470 nm (3% for front illumination and 4% for back illumination) within reasonable experimental error.



Figure 5-18. a) Original data and b) corrected IPCE of CuWO₄ sandwich cell under front (red circles) and back (blue triangles) illumination.

The IPCE results were further analyzed to extract information about the electron collection length of CuWO₄. As shown in Figure 5-18b, IPCE by front illumination shows a small peak at ~390 nm. Using the absorption coefficient that we calculated in Figure 5-5a, this wavelength corresponds to a $3/\alpha$ value of 947 nm, which is somewhat close to the ~800 nm thickness we measured with SEM. IPCE by back illumination shows a monotonous decrease when increasing the wavelength. This indicates that L_n should be shorter than the penetration depth ($3/\alpha$) of 330 nm light, which is 577 nm. However, this is the upper limit of electron collection length in our CuWO₄ electrode. Since a plateau region is never observed in the back illuminated IPCE data before it comes to a decrease, the actual electron collection length could be way smaller than this number. The absorbed photon-to-current efficiency (APCE) can be calculated using equation:

$$APCE = \frac{IPCE}{A\%} \tag{5.10}$$

where *A*% is the absorptance calculated in Figure 5-6b. As shown in Figure 5-19, the low APCE value indicates that the electron collection length is indeed much shorter than 577 nm.



Figure 5-19. Absorbed photon-to-current efficiency of CuWO4 sandwich cell under front (red circles) and back (blue triangles) illumination.

5.6 Conclusions

In this chapter, it was shown that apart from non-optimized hole collection efficiency at low applied bias due to recombination of surface-stored holes with conduction band electrons, the major limitation of CuWO₄ for water oxidation is its low charge separation efficiency. Mesoporous CuWO₄ electrodes with \sim 800 nm thickness were made by spray pyrolysis in order to investigate its fundamental bulk properties. Al_2O_3 was deposited by ALD to fill the pores of CuWO₄ in order to understand its limiting charge carriers and relevant collection length. By comparing the PEC performance with front and back illumination, it was determined that the electrons are the limiting charge carriers of CuWO₄. By analyzing the wavelength dependence of IPCE, the electron collection length of CuWO₄ was semi-quantified, which is shorter than 577 nm. This explains the reason why thicker nanostructured CuWO₄ electrodes (2 to 3 µm) has similar performance as thinner electrodes (80 to 200 nm).^{1,3,4,13} However, further systematic thickness dependent studies should be conducted to extract more accurate electron collection length in order to optimize the film thickness. Meanwhile, analogous measurements should be performed with single crystal CuWO₄ to understand its intrinsic properties such as limiting charge carriers, charge carrier mobility and diffusion length. These investigations will in theory provide some clue of overcoming the opposing properties of weak light absorption and short electron collection length by depositing CuWO₄ thin film of a suitable thickness on a nanostructured transparent conductive oxide (TCO) substrate. Other strategies such as doping or applying an under layer could also potentially improve the charge separation efficiency.

REFERENCES

REFERENCES

- (1) Gao, Y.; Zandi, O.; Hamann, T. W. Atomic Layer Stack Deposition-Annealing Synthesis of CuWO₄. *J. Mater. Chem. A* **2016**, *4*, 2826–2830.
- (2) Pyper, K. J.; Yourey, J. E.; Bartlett, B. M. Reactivity of CuWO₄ in Photoelectrochemical Water Oxidation Is Dictated by a Midgap Electronic State. J. Phys. Chem. C 2013, 117, 24726–24732.
- (3) Yourey, J. E.; Bartlett, B. M. Electrochemical Deposition and Photoelectrochemistry of CuWO₄, a Promising Photoanode for Water Oxidation. *J. Mater. Chem.* 2011, 21, 7651– 7660.
- (4) Hill, J. C.; Choi, K. S. Synthesis and Characterization of High Surface Area CuWO₄ and Bi2WO6 Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, 1, 5006–5014.
- (5) Bohra, D.; Smith, W. A. Improved Charge Separation via Fe-Doping of Copper Tungstate Photoanodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9857–9866.
- (6) Hu, D.; Diao, P.; Xu, D.; Xia, M.; Gu, Y.; Wu, Q.; Li, C.; Yang, S. Copper (II) Tungstate Nanoflake Array Films: Sacrificial Template Synthesis, Hydrogen Treatment, and Their Application as Photoanodes in Solar Water Splitting. *Nanoscale* 2016, *8*, 5892–5901.
- (7) Ye, W.; Chen, F.; Zhao, F.; Han, N.; Li, Y. CuWO₄ Nanoflake Array-Based Single-Junction and Heterojunction Photoanodes for Photoelectrochemical Water Oxidation. ACS Appl. Mater. Interfaces 2016, 8, 9211–9217.
- (8) Gaillard, N.; Chang, Y.; Deangelis, A.; Higgins, S.; Braun, A. A Nanocomposite Photoelectrode Made of 2.2 eV Band Gap Copper Tungstate (CuWO₄) and Multi-Wall Carbon Nanotubes for Solar-Assisted Water Splitting. *Int. J. Hydrogen Energy* 2013, *38*, 3166–3176.
- (9) Zhang, H.; Yilmaz, P.; Ansari, J. O.; Khan, F. F.; Binions, R.; Krause, S.; Dunn, S. Incorporation of Ag Nanowires in CuWO4 for Improved Visible Light-Induced Photoanode Performance. J. Mater. Chem. A 2015, 3, 9638–9644.
- (10) Abdi, F. F.; Van De Krol, R. Nature and Light Dependence of Bulk Recombination in Co-Pi-Catalyzed BiVO₄ Photoanodes. *J. Phys. Chem. C* 2012, *116*, 9398–9404.
- (11) Park, Y.; McDonald, K. J.; Choi, K.-S. Progress in Bismuth Vanadate Photoanodes for Use in Solar Water Oxidation. *Chem. Soc. Rev.* **2013**, *42*, 2321–2337.
- (12) Pala, R. a.; Leenheer, A. J.; Lichterman, M.; Atwater, H. a.; Lewis, N. S. Measurement of

Minority-Carrier Diffusion Lengths Using Wedge-Shaped Semiconductor Photoelectrodes. *Energy Environ. Sci.* **2014**, 7 (10), 3424–3430.

(13) Lhermitte, C. R.; Bartlett, B. M. Advancing the Chemistry of CuWO₄ for Photoelectrochemical Water Oxidation. *Acc. Chem. Res.* **2016**, *49*, 1121–1129.

Chapter 6: Conclusions and Future Directions

6.1 Conclusions

As discussed in chapter 1, as a promising semiconductor photoanode material for photoelectrochemical (PEC) water splitting, CuWO₄ has received moderate attention partially due to its limited water oxidation performance. Only a handful of works have made effort to investigate the limitations of CuWO₄ and relevant water oxidation mechanisms with this material in order to provide strategies to improve its efficiency and to understand general rules of water oxidation with semiconductor materials. Systematic studies were thus performed in this dissertation in order to better understand water oxidation with CuWO₄.

1. A new atomic layer deposition (ALD) based stack deposition-annealing (SDA) method was applied to deposit planar and uniform CuWO₄ thin films with controllable thickness (chapter 1).¹ The resulted thin films show linear growth with increasing deposition cycles, which is essentially one benefit of ALD. Compared with the widely used traditional ALD route to deposit ternary or quaternary metal oxides, this SDA method has various advantages: 1) the ALD temperature windows of the binary oxides do not have to overlap; 2) the problem of surface-inhibited growth of some materials (e.g. WO₃ on CuO) is solved; 3) there is an easier control of stoichiometry if the growth rates of the binary oxides on their relevant substrates are known. The resulted CuWO₄ electrodes show comparable water oxidation performance compared with other synthetic methods reported in previous literature, suggesting the promise of this method.

2. CuWO₄ electrodes were evaluated in contact with H₂O, Na₂SO₃, and H₂O₂ (chapter 2) by photoelectrochemical measurements and intensity modulated photocurrent spectroscopy (IMPS) in order to understand its hole collection efficiency (η_{HC}).² It was shown that Na₂SO₃ is a suitable hole scavenger with quantitative hole collection at CuWO₄

surface to quantify water oxidation η_{HC} with CuWO₄. Meanwhile, H₂O₂, which was used in previous literature as a hole scavenger for CuWO₄,^{3,4} has current doubling effect which makes it problematic for quantifying η_{HC} of water oxidation with CuWO₄. With Na₂SO₃ as the suitable hole scavenger and using IMPS, identical results were obtained within reasonable error for η_{HC} from two different methods. CuWO₄ shows non-optimal η_{HC} at low applied bias due to surface recombination resulted from insufficient band bending. However, at higher potentials, η_{HC} is essentially unity, suggesting quantitative hole collection once it has passed the onset potential region.

3. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) surface measurements and photocurrent transient measurements were employed under different conditions of applied potential, illumination, and electrolytes to understand the role of surface states of CuWO₄ in water oxidation (chapter 3).⁵ It was shown that a surface state capacitance coincides with the turn-on of water oxidation, which is only available under photoelectrochemical water oxidation conditions. This capacitance is correlated to the charging of surface state measured from CV surface measurements, which is only observable in aqueous electrolyte but absent in non-aqueous solvents. It was therefore concluded that the surface state of CuWO₄ is a water oxidation intermediate species.

4. Apart from surface recombination at low applied potentials, the major limitation of CuWO₄ for PEC water oxidation is its low η_{CS} (chapter 5). The PEC performance of a sandwich cell made of a thick and compact CuWO₄ film with pores filled with inert Al₂O₃ was examined by illuminating from different directions. It was concluded that electrons are the limiting charge carriers of CuWO₄. Incident photon-to-current efficiency (IPCE) was further measured to semi-quantify the collection length of electrons in CuWO₄. It was

determined that the electron collection length is smaller than 577 nm for our CuWO₄ film. These results partially explains why thicker nanostructured CuWO₄ electrodes (2 to 3 μ m) show similar performance as thinner electrodes (80 to 200 nm).^{1,6–8}

6.2 Future Directions

The surface state of CuWO₄ has been identified as a water oxidation intermediate species based on our complementary photoelectrochemical and EIS measurements. We hypothesize that charging the surface state of CuWO₄ with holes constitutes of the first oxidative step of water oxidation. However, there is no direct evidence of this intermediate species. In attempts to identify these species, operando ATR-IR measurements will be used in the future with CuWO₄ electrodes in contact with a D₂O electrolyte in response to applied bias and illumination.⁹ Possible intermediates that can potentially be detected are either oxo or peroxo groups such as W=O, W-O-O-D, W-O-O-W, W-O-O-Cu, or Cu-O-O-Cu. We don't expect a Cu oxo species to exist since Cu is beyond the oxo wall. Oxygen isotope labeling will be utilized to distinguish between oxo and peroxo species.⁹ There is a large body of literature that show W=O, W-O-W or W-O₂ IR vibrational peaks which will facilitate our determination of water oxidation intermediates (or defects) with the proposed IR measurements.^{10–14} Isotope labeling (H vs D) will also be used to try and distinguish M–O–O–M from M–O–O–D/H species. We note that it will be difficult to clearly distinguish species such as Cu–O–O–D and W–O–O–D. We plan to address this by preparing samples with W and Cu rich surfaces, which can be controlled by the subsequent ALD of the desired metal oxide on the electrode surface which will help elucidate the small difference in vibration expected. We will also perform complementary *in-situ* UV-vis spectroelectrochemistry measurements, analogous to our prior measurements on hematite, where the absorption spectra can help differentiate whether the hole is trapped as a Cu or W based intermediate.¹⁵

From these measurements, we expect to definitively determine whether the surface state is actually a water oxidation intermediate species as we hypothesize. We will further gain information about the nature of the surface state (acknowledging exact species may be hard to resolve as noted above). This information is important in developing a mechanistic picture of water oxidation on CuWO₄ as well as obtaining a general understanding of performance controlling processes of photo-induced water oxidation on semiconductor electrodes.

It was suggest by our work that the water oxidation performance of CuWO₄ is limited by surface recombination at low applied potentials. Therefore, the photocurrent onset potential in theory can be reduced by applying a water oxidation catalyst. By comparing the onset potential of water oxidation and oxidation of Na₂SO₃, one should expect a reduction in water oxidation onset potential by 200 mV when a suitable catalyst is applied.² However, no catalyst so far can reduce the onset potential significantly.^{8,16} The effect of water oxidation catalyst on CuWO₄ will be investigated by integrating PEC, EIS, IMPS and operando spectroscopic measurements.

In chapter 5, it was suggested that apart from surface recombination at low applied bias, the low η_{CS} is the major limitation of CuWO₄. Since the measurements were taken with polycrystalline CuWO₄, the bulk properties might rely on the synthetic method. It would be interesting if analogous measurements could be taken with single crystal CuWO₄ electrodes in order to get some intrinsic parameters such as charge carrier mobilities, diffusion length, etc. of CuWO₄. Thickness dependent measurement should also be performed to get more accurate value for the electron collection length.

Interesting strategies such as intentional doping and using suitable substrates or underlayer may benefit improving η_{CS} . Crystal orientation-dependent charge transport would also be interesting to investigate in order to optimize its bulk and surface properties. Once the bulk and

surface properties are optimized, CuWO₄ thin film with suitable thickness can be scaled up on nanostructured transparent conductive oxide (TCO) substrates to overcome the opposing properties of weak light absorption and limited electron collection length. Given the suitable properties of bandgap, band positions, stability and earth abundance of CuWO₄, as well as our comprehensive understanding of its limiting factors in PEC water oxidation, CuWO₄ has the promise of enabling cost-effective and durable PEC water splitting in a tandem cell. REFERENCES

REFERENCES

- (1) Gao, Y.; Zandi, O.; Hamann, T. W. Atomic Layer Stack Deposition-Annealing Synthesis of CuWO₄. *J. Mater. Chem. A* **2016**, *4*, 2826–2830.
- (2) Gao, Y.; Hamann, T. W. Quantitative Hole Collection for Photoelectrochemical Water Oxidation with CuWO₄. *Chem. Commun.* **2017**, *53*, 1285–1288.
- (3) Bohra, D.; Smith, W. A. Improved Charge Separation via Fe-Doping of Copper Tungstate Photoanodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9857–9866.
- (4) Hill, J. C.; Choi, K. Synthesis and Characterization of High Surface Area CuWO₄ and Bi₂WO₆ Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, *1*, 5006–5014.
- (5) Gao, Y.; Hamann, T. W. Elucidation of CuWO₄ Surface States During Photoelectrochemical Water Oxidation. *J. Phys. Chem. Lett.* **2017**, *8*, 2700-2704.
- (6) Yourey, J. E.; Bartlett, B. M. Electrochemical Deposition and Photoelectrochemistry of CuWO₄, a Promising Photoanode for Water Oxidation. J. Mater. Chem. 2011, 21, 7651– 7660.
- Hill, J. C.; Choi, K. S. Synthesis and Characterization of High Surface Area CuWO₄ and Bi2WO6 Electrodes for Use as Photoanodes for Solar Water Oxidation. *J. Mater. Chem. A* 2013, *1*, 5006–5014.
- (8) Lhermitte, C. R.; Bartlett, B. M. Advancing the Chemistry of CuWO₄ for Photoelectrochemical Water Oxidation. *Acc. Chem. Res.* **2016**, *49*, 1121–1129.
- (9) Zandi, O.; Hamann, T. W. Determination of Photoelectrochemical Water Oxidation Intermediates on Haematite Electrode Surfaces Using Operando Infrared Spectroscopy. *Nat. Chem.* 2016, *8*, 778–783.
- (10) Rice, C. A.; Kroneck, P. M. H.; Spence, J. T. Tungsten(V)-Oxo and Tungsten(VI)-Dioxo Complexes with Oxygen, Nitrogen, and Sulfur Ligands. Electrochemical, Infrared, and Electron Paramagnetic Resonance Studies. *Inoganic Chem.* **1981**, *20* (7), 1996–2000.
- (11) Sugimoto, H.; Tano, H.; Tajima, R.; Miyake, H.; Tsukube, H.; Ohi, H.; Itoh, S. In Situ Generation of Oxo-sulfidobis(dithiolene)tungsten(VI) Complexes: Active-Site Models for the Aldehyde Ferredoxin Oxidoreductase Family of Tungsten Enzymes. *Inorg. Chem.* 2007, 46 (21), 8460–8462.
- (12) Zaki, M. I.; Mekhemer, G. A. H.; Fouad, N. E.; Rabee, A. I. M. Structure-Acidity Correlation of Supported tungsten(VI)-Oxo-Species: FT-IR and TPD Studies of Adsorbed
Pyridine and Catalytic Decomposition of 2-Propanol. Appl. Surf. Sci. 2014, 308, 380–387.

- (13) Hazarika, P.; Kalita, D.; Sarmah, S.; Islam, N. S. New Oxo-Bridged Peroxotungsten Complexes Containing Biogenic Co-Ligand as Potent Inhibitors of Alkaline Phosphatase Activity. *Mol. Cell. Biochem.* 2006, 284, 39–47.
- (14) Aleeva, G. P.; Kotorlenko, L. A.; V. A. Lunenok-Burmakina. Study of the Structure of Peroxo Compounds of Tungsten and Molybdenum by Infrared Spectroscopy. J. Struct. Chem. 1972, 13 (4), 590–593.
- (15) Klahr, B.; Hamann, T. Water Oxidation on Hematite Photoelectrodes: Insight into the Nature of Surface States through in Situ Spectroelectrochemistry. *J. Phys. Chem. C* 2014, *118*, 10393–10399.
- (16) Nam, K. M.; Cheon, E. A.; Shin, W. J.; Bard, A. J. Improved Photoelectrochemical Water Oxidation by the WO₃/CuWO₄ Composite with a Manganese Phosphate Electrocatalyst. *Langmuir* 2015, *31* (39), 10897–10903.