INVESTIGATING TANTALUM NITRIDE AND HEMATITE-CATALYST INTERFACE FOR PHOTOELECTROCHEMICAL WATER OXIDATION

By

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ABSTRACT

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This dissertation is focused on the synthesis and characterization of semiconductor materials for photoelectrochemical (PEC) water oxidation and it is comprised of two sections. In the first section, synthesis and characterization of Ta₃N₅ thin films for photoelectrochemical water oxidation were investigated. Despite promising properties, the harsh synthesis conditions, involving high-temperature ammonolysis limits the PEC water oxidation efficiency on Ta_3N_5 . From synthetic point of view, this method is highly energy intensive, produces a sizable quantity of chemical wastes, inefficient on chemical utilization, and provides highly reducing conditions, preventing to integrate it in the tandem cell. As the first study, the electrodeposition of tantalum oxide from aqueous solution followed by ammonolysis to synthesize Ta₃N₅ films was investigated. This is a promising approach as it requires fairly simple instrumentation, maximizes the chemical utilization, and allows to realize Ta₃N₅ on any conductive substrate. In order to eliminate the ammonolysis step, the atomic layer deposition (ALD) was utilized to directly deposit tantalum nitride on transparent conductive oxides (TCO) which otherwise require highly reactive (reducing) ammonolysis conditions. It was discovered that the low-temperature ALD (175- 280 °C) only results in amorphous TaO_xN_y films which still need to be crystalized/ nitridized in ammonia but practically at more moderate conditions. This further allowed to integrate Ta₃N₅ with a Ta-doped TiO₂ – a newly developed TCO that is stable in reducing conditions- and to realize the first example of a Ta₃N₅ electrode on TCO. Lastly, a high temperature and fully automated ALD system was designed and built to directly deposit crystalline Ta₃N₅ on FTO.

In the second section of this dissertation, hematite as another promising candidate for PEC water oxidation was investigated. The goal of this project was to understand how catalyst interfaces with underlying semiconductor and how it affects the performance of catalytically modified electrodes. To this end, the $Ni_{1-x}Fe_xO_y$ catalysts with various composition were utilized to coat hematite electrodes. A combination of structural and electrochemical techniques such as steady-state and transient photocurrent measurements, electrochemical impedance spectroscopy (EIS), intensity modulated photocurrent spectroscopy (IMPS), and dual-working electrode (DWE) measurements (in collaboration with Prof. Boettcher) were opted to elucidate the role of catalyst. The findings from these studies are of great importance as they provide a clear picture of the device under operando conditions. It was found that the catalyst layer acts as a hole storage layer where the photogenerated holes from underlying semiconductor are stored in the catalyst layer, causing the potential of catalyst to drop until a sustainable water oxidation is achieved. In addition, it was discovered that the effect of catalyst (improving or suppressing) on the PEC performance of the catalyst-coated electrodes strongly relates to the electronic conductivity of the catalyst and the morphology of the underlying hematite photoelectrode. For example, in case of highly conductive catalyst and porous hematite substrate (in presence of pinholes), the potential of the catalyst layer is pinned to the conductive substrate which subsequently limits the built-in potential in the catalyst layer.

Dedicate to my wife (Maryam), my mom and dad (Mehri & Masoud), my brother (Vahid), and my teachers for helping and guiding me here.

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KEY TO ABBREVIATIONS

IPCC	Intergovernmental Panel on Climate Change
EIA	Energy Information Administration
IEA	International Energy Agency
PV	Photovoltaic
STH	Solar to hydrogen
$E_{ m f}$	Fermi level
$E_{ m FB}$	Flat band energy
L	Diffusion length
D	Diffusion coefficient
τ	Charge carrier life time
μ	Charge carrier mobility
Т	Temperature
kB	Boltzman constant
η_{LH}	Light harvesting efficiency
η_{CS}	Charge Separation Efficency
η_{HC}	Hole collection efficiency
q	Elementary charge
$J_{ m ph}$	Photocurrent density
Φ	Photon flux
DOS	Density of State
α	Absorption coefficient

% A	Percent of absorptance
TRMC	time resolved microwave conductance
TAS	Transient absorption spectroscopy
IPCE	Incident photon-to-current-efficiency
APCE	Absorbed photon-to-current efficiency
P _{mono}	Intensity of monochromatic light
SC	Semiconductor
WOC	Water Oxidation Catalyst
RHE	Reversible hydrogen electrode
MS	Mott Schottky
εo	Permittivity of free space
ε	Dielectric constant of the semiconductor
A	Surface area of the electrode
Cbulk	Capacitance of the space charged region
V _{app}	Applied potential
V_{FB}	Flat band potential
V_{bi}	Built in potential
N_d	Dopant density
W	Thickness of space charged region
ТСО	Transparent conductive oxide
HCE	Hole collection efficiency
FTO	Florin doped tin oxide
ITO	Tin doped indium oxide

AZO	Alumina doped zinc oxide
ТТО	Tantalum doped titanium dioxide
Ta ₃ N ₅	Tantalum nitride
TiO ₂	Titanium dioxide
Ga ₂ O ₃	Gallium oxide
Та	Tantalum
GaN	Gallium nitride
Fe ₂ O ₃	Iron oxide
Ni1-xFexO _y	Nickel iron oxide
FeOOH	Iron oxy-hydroxide
SnO ₂	Tin Oxide
CoPi	Cobalt phosphide
CH_4	Methane
CO_2	Carbon dioxide
H ₂ O	Water
H_2O_2	Hydrogen peroxide
HCl	Hydrogen chloride
KCl	Potassium Chloride
KNO ₃	Potassium nitrate
TaCl ₅	Tantalum pentachloride
TaBr ₅	Tantalum pentabromide
TaF5	Tantalum pentafluoride
PDMAT	Pentakis(dimethylamino)tantalum(V)

Ta(NEt ₂) ₅	Pentakis(diethylamino) tantalum(V)
ММН	Monomethyl hydrazine
(Ga ₂ (NMe ₂) ₆	Tris-(dimethylamido)gallium(III)
NH ₃	Ammonia
NH ₄ PF ₆	Ammonium hexafluorophosphate
Pt	Platinum
Ti	Titanium
$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate(II)
IPA	Isopropanol
DI water	Deionized water
IMPS	Intensity modulated photocurrent spectroscopy
DWE	Dual-working electrode
LF	Low frequency
HF	High frequency
EIS	Electrochemical impedance spectroscopy
CV	Cyclic voltammetry
SE	Spectroscopic ellipsometry
XRD	X-ray Diffraction
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
UPS	Ultraviolet photoelectron spectroscopy
SEM	Scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy

AFM	Atomic force microscopy
NMR	Nuclear magnetic resonance spectroscopy
FT-IR	Fourier-transform infrared spectroscopy
ALD	Atomic layer deposition
CVD	Chemical vapor deposition
ED	Electrodeposition
DC	Direct current
AC	Alternative current
DAC	Digital to analog convertor
ADC	Analog to digital convertor
SSR	Solid state relay

Chapter 1:

Introduction

1.1. Motivation and Approach

The climate of our planet has changed many times throughout its history. Most of these changes are attributed to small variations of earth's orbit affecting the amount of solar energy striking the Earth's surface.¹ The chemical composition of the atmosphere surrounding our planet is another important factor that directly influences its climate. Many chemicals such as carbon dioxide (CO_2) , water (H_2O) , and methane (CH_4) contributes to the greenhouse effect by absorbing the infrared radiation (heat) of the solar spectrum and trapping heat in the atmosphere. By far, carbon dioxide variations have contributed the most to the climate changes due to both natural and artificial (anthropogenic) causes.² CO₂ concentration for centuries have been fluctuating but because of the human activities in recent history (since the beginning of the industrial revolution in the mid-18th century) the atmospheric concentration of carbon dioxide has begun to rise significantly above its historical average. While the concentration of CO_2 in the atmosphere is regulated by natural processes such as photosynthesis that can absorb some of the anthropogenic CO₂, the mid-20th century CO_2 levels has steeply increased (Figure 1–1) with a rate that is far beyond the capacity of such natural processes. As a result, the atmospheric concentration of CO₂ has reached an unprecedented record of ~ 400 ppm in 2017 (~ 40% increase since the 1800s), see Figure $1-1.^3$

The deleterious effect of increased levels of atmospheric CO_2 has already influenced the global climate and biological life on earth. For example, global temperatures have increased about 1.1 °C since the late 19th century,^{4,5} the average oceanic temperatures (top 700 meters) has increased by as much as 0.17 °C since 1969,⁶ and the acidity oceanic waters at the surface has increased by ~ 30% since the industrial revolutions.^{7,8} As a result of global warming, ice sheets are shrinking,

snow-covered lands are diminishing, sea levels are rising, and the Climate change is now affecting everyone around the world, with the consequences that keep getting worse every year.



Analysis Center, accessed July 26, 2017

Figure 1–1. World CO_2 emissions from fossil fuel combustion and global atmospheric concentration adapted from the U.S. Energy Information Administration.³

What is/are the source(s) of anthropogenic CO₂? To answer this question, we take the energy consumption of the United States, i.e. the largest economy in the world, as an example. Figure 1– 2 shows the total energy consumption and resources of the U.S. in 2016. As shown, the U.S. energy consumption in 2017 was 97.4 quadrillion Btu (quadrillion = 10^{15}) or 3.2 TW, which roughly accounts for 18.6% of the global energy consumption. More than 80% of this energy is supplied from nonrenewable and carbon-based energy resources such as petroleum, natural gas, and coal which are ultimately released as anthropogenic CO₂ into the atmosphere. In order to emphasize

the magnitude of the released CO₂, we now consider the U.S. energy consumption by sector (Figure 1–3). As can be seen, $\sim 30\%$ of the energy is used for transportation. The U.S. Energy Information Administration (EIA) estimates that combination of gasoline and diesel fuels accounts for 82% of the U.S. transportation which emitted ~ 1.5 billion metric tons of CO_2 in 2016.⁹ This number alone accounts for ~ 4.2% of the global CO₂ emission in 2016 (Figure 1–1). An Intergovernmental Panel on Climate Change (IPCC) analysis published in 2013² suggests that in order to limit the global warming caused by anthropogenic CO₂ emissions to less than 2 °C (relative to pre-industrial level, ~ 1860s) with an occurrence probability of 33, 50, and 66% it requires to keep the cumulative CO_2 emissions from all anthropogenic sources below 1.57, 1.21, and 1.00 trillion tons, respectively. By 2011, approximately 515 billion tons of CO_2 have been emitted, leaving the carbon budget below 500 billion tons to limit the global warming within 2 °C in most probable case.^{2,10} These numbers and reports are overwhelming, further emphasizing the necessity for comprehensive and immediate actions to decarbonize the global energy diet by improving the efficiencies of existing technologies and inventing alternative and renewable technologies that minimize our reliance on fossil fuels.

Biomass, hydropower, geothermal, wind, and solar energy are the five major renewable energy sources. Among them, solar energy is the largest source of energy, and the only one exceeding the global energy consumption. In order to utilize this great source of energy, three main pathways are generally adopted: (1) solar to thermal energy, (2) solar to electrical energy *via* photovoltaic (PV), and (3) solar water splitting which represents the conversion of solar energy into potential energy of the chemical bonds of hydrogen. The PV technology has gained a lot of attention in the past few years and is considered as one of the primary routes to convert solar energy into

electricity. Thanks to the technological advances made in the manufacturing of crystalline silicon and improvements in the design of efficient module, the global installed capacity of PV at the end



U.S. energy consumption by energy source, 2017

Note: sum of components may not equal 100% because of independent rounding.

Figure 1–2. The U.S. energy consumption in 2016 by energy sources. Graph is reproduced from the U.S. Energy Information Administration.¹¹

of 2016 amounted to 303 GW which has grown by a factor of > 6 since 2010.¹¹ In addition to the solar energy, other renewable energy sources including wind, and hydropower have made a large contribution to the production of sustainable and renewable electricity. Based on the most recent report by International Energy Agency (IEA), the global renewable electricity capacity in 2016¹² was 805 GW and is estimated to reach a record number of 1.15 TW by 2022.

The common issue with the direct conversion of solar energy to electricity, however, is the intermittent, fluctuating output power which also varies with season. Therefore, the energy storage in the form of potential energy of electrons and chemical bonds becomes progressively important, opening up a new series of challenges and opportunities. Solar energy can be directly stored in the





Figure 1–3. The U.S. energy consumption in 2017 by sector. Graph is reproduced from the U.S. Energy Information Administration.¹¹

chemical bonds of hydrogen by splitting water into hydrogen and oxygen. Hydrogen has a large energy density $(142 \text{ MJ/kg} \text{ at } 700 \text{ bar})^{13}$, it is not intermittent (it is available any time of the day and night), and produces a constant energy output. In addition, renewable hydrogen can be coupled with many industrial productions of valuable chemicals - e.g. synthesis of ammonia, hydrochloric acid, reduction of metallic ores – allowing to decarbonize these processes and moving toward

sustainability. The main focus of this thesis is on solar water splitting *via* semiconductor light absorbers and how the electrocatalyst interface with the underlying semiconductor.

1.2. Solar Water Splitting

The water-splitting reaction is an uphill reaction with a change in standard Gibbs free energy of 238 kJ mol⁻¹ or 1.23 eV (equation1-1). The water splitting reaction can be simplified as two half-reactions (water reduction and oxidation reactions) described by equation 1-2 and 1-3:

$$2H_2O_{(1)} \longrightarrow 2H_{2(g)} + O_{2(g)}$$
 $\Delta G^0 = 238 \text{ kJ mol}^{-1} (1.23 \text{ eV})$ 1-1

$$4H_2O_{(1)} + 4e^- \longrightarrow 2H_{2(g)} + 4OH_{(aq)}^- E^0 = 0.00 \text{ V } \text{vs. RHE}$$
 1-2

$$40H_{(aq)}^{-} \longrightarrow O_{2(g)} + 4e^{-} + 2H_2O_{(1)} \qquad E^0 = 1.23 \text{ V vs. RHE}$$
 1-3

In solar water splitting applications, the energy of this endothermic reaction is provided by the energy of photons from sunlight. Semiconductors films are often used as the light absorber and photocatalyst and are therefore the heart of many solar water splitting schemes. The solar water splitting reaction, then, can be driven by either (1) a single semiconducting light absorber to power the reaction according to equation 1-1, or (2) photoelectrochemical (PEC) cell that is comprised of two physically separated semiconductors to divide the overall water splitting reaction into two half-reactions according to equation 1-2 and 1-3. It is important to remember that the standard Gibbs free energy of the reaction is a state function, therefore regardless of the pathway, the overall energy balance of the reaction is ideally constant. Depending on the pathway, however, the overall solar conversion efficiency can be drastically different. In the first scheme, the semiconductor must

have a band gap of $\geq 1.8 \text{ eV}$ – the thermodynamic energy plus activation energy (discussed in next section) - and band edge potentials that straddle both water oxidation and reduction reactions. These requirements greatly limit the selection of materials with the right band gap and band edge positions. In addition, in this scheme, the oxygen and hydrogen gases are generated in the same locale which further limits overall solar conversion efficiency by requiring extra energy to separate and purify hydrogen and by promoting the reverse recombination reaction of hydrogen and oxygen, i.e. hydrogen oxidation and oxygen reduction. Moreover, the recombination reaction of hydrogen and oxygen is extremely exothermic, leading to potentially hazardous conditions. Alternatively, in the second scheme, the water oxidation and reduction reactions are physically separated. This readily relaxes the constraints of a single light absorber. The most efficient PEC cell to drive solar water splitting to date has a tandem cell configuration.^{14,15} The cell was comprised of a p-type semiconductor wirelessly connected to a n-type semiconductor via a transparent conductive layer (Figure 1–4). In this scheme, the n-type semiconductor (photoanode: drives the water oxidation reaction via energetic photogenerated holes) has a wider band gap than the p-type semiconductor (photocathode: drives the water reduction reaction via energetic photogenerated electrons). The light is therefore shone through the photoanode where the subbandgap photons (not absorbed by photoanode) are transmitted to the photocathode. The transparent conductive layer is, therefore, the crucial component of the tandem cell. This type of the cell is additionally advantageous as it allows researchers to independently study and optimize each half-cell. The multi-electron transfer nature of the water oxidation reaction (equation 1-3), makes this half-reaction sluggish, and generally limit the overall efficiency of water splitting reactions. Consequently, the majority of efforts in this area have focused on the water oxidation



Figure 1–4. The schematic representation of PEC water oxidation in a tandem cell comprised of: 1) a p-type semiconductor as the photocathode, 2) a transparent conductive oxide - this is a degenerately doped wide-bandgap (> 3.2 eV) semiconductor - which is optically transparent and electronically conductive to produce an ohmic contact with the top layer, 3) n-type semiconductor as the photoanode.

reaction. This dissertation is therefore focused on investigating photoanode material for PEC water oxidation.

1.3. Photoanode Material

The photoelectrochemical reaction mediated by a semiconductor is a chain process initiated by light absorption and charge carrier generation (i.e. photogenerated electron and holes) followed by charge separation, charge diffusion, and ultimately charge transfer at the surface of the electrode.

Therefore, the photocurrent response of a photoanode for PEC water oxidation reaction is controlled by three efficiencies summarized in equation 1-4:

$$J_{\rm ph}(V) = -q \emptyset \left[\eta_{\rm lh}(V) \times \eta_{\rm cs}(V) \times \eta_{\rm hc}(V) \right]$$
 1-4

In this equation, q is the elementary charge, \emptyset is the photon flux, η_{LH} , η_{CS} , and η_{HC} represent the light harvesting efficiency (LH), charge separation efficiency (CS), and hole collection efficiency (HC), respectively. The latter is basically determined by the catalytic activity of the surface for charge transfer. The first two efficiencies depend on the bulk characteristics of the semiconductor (absorption coefficient, dielectric constant, charge carrier lifetime, charge carrier diffusion length, and charge carrier mobility), and are defined by its composition, structure, and the synthetic conditions used. Throughout this thesis we utilized atomic layer deposition (ALD), electrodeposition or electroplating (ED), and spin coating to prepare thin films of semiconductor on various substrates.

In practice, any given photoelectrode must meet several criteria to be suitable for efficient PEC water oxidation: (1) its valence band (VB) edge position must be positive compared to the electrochemical potential of water oxidation (E^0 (H₂O/O₂) = 1.23 V vs. RHE) – this is the thermodynamic requirement which is required to ensure that the reaction between photogenerated holes in the VB and water is thermodynamically feasible. (2) The band gap of semiconductor should be narrow to allow for maximum overlap with the solar spectrum. (3) In addition to the favorable bulk properties such as absorption coefficient, charge carrier lifetime, charge carrier diffusion length and mobility, it must have a catalytically active surface toward water oxidation to maximize the charge separation on surface and charge transfer to solution. (4) It also needs to be stable under PEC water oxidation conditions, i.e. under illumination in neutral to basic aqueous

solutions. Due to their high stability in neutral and basic solutions - e.g. TiO₂, Fe₂O₃, WO₃, BiVO₄, and CuWO₄ - metal oxide semiconductors are promising candidates for PEC water oxidation reaction. On the other hand, non-oxide semiconductors such as metal nitrides, oxynitrides, and phosphides - such as Ta₃N₅, TaON, GaN, and GaP – suffer from surface corrosion and instability under PEC water oxidation conditions. For example, the photogenerated holes in the VB of Ta₃N₅ are sufficiently energetic to oxidize the surface nitride groups to dinitrogen forming the wide bandgap tantalum oxide on the surface (equation 1-5). The instability of tantalum nitride under PEC water oxidation reaction is thus one of its drawbacks that halts efficient water oxidation and is discussed in section 1.3.1.6.

$$Ta_3N_5 + 15h^+ + 15OH^- \longrightarrow \frac{3}{2}Ta_2O_5 + \frac{5}{2}N_2 + \frac{15}{2}H_2O$$
 1-5

As for any technology, the large-scale production the photoanode requires the use of earthabundant, cheap, and non-toxic elements. Based on these criteria, tantalum nitride (Ta_3N_5) and hematite (Fe₂O₃) stand out as promising candidates for PEC water oxidation. In the following sections the promises and challenges of these materials is discussed.

1.3.1. Tantalum Nitride

1.3.1.1 Crystal Structure

Tantalum (V) nitride (Ta₃N₅) crystalizes in the orthorhombic structure with the space group of Cmcm as shown in Figure 1-5.¹⁶ As shown, the structure is comprised of the corner-shared irregular octahedral N groups with Ta atom at the center. Two types of N sites with four (type 1: shown as N1 and N3) and three (type 2: shown as N2 in Figure 1–5.b) neighboring Ta can be

realized. Tantalum in octahedral coordination is therefore coordinated by two N (type1) and four N (type2) with the Ta-N bond length ranging from 1.96 to 2.24 Å. Based on this crystal structure, a total number of 24 phonon modes with the symmetry of A_g and B_g have been theoretically (DFPT/PBE) predicted for Ta₃N₅.¹⁷ However some of these peaks have not been observed experimentally.^{18,19}



Figure 1–5. a) The crystal structure of Ta_3N_5 along the c-axis, b) the unit cell of tantalum nitride representing different types of nitrogen group and coordination environment around tantalum.

1.3.1.2 Optical Properties of Ta₃N₅

Theoretical methods have been utilized to assess the electronic structure of Ta_3N_5 .^{20–22} For example, Galli and coworkers²⁰ studied the optoelectronic properties of tantalum nitride *via ab initio* calculations and ellipsometry measurements. The calculated density of states (DOS) for Ta_3N_5 at the experimental geometry is shown in Figure 1–6.a. As depicted, the top of the valence



Figure 1–6. a) The calculated density of states (DOS) of Ta_3N_5 at the experimental geometry, b) comparison between calculated and experimental spectra of the absorption coefficient of Ta_3N_5 . These plots are reprinted with permission from ref. 20. Copyright (2014) by the American Physical Society.

band (VB) and the bottom of the conduction band (CB) are primarily comprised of N 2p and Ta 5d orbitals, respectively.^{22,23}

UV-vis measurements on both powder and thin-films of Ta₃N₅ showed an absorption edge of ~ 600 nm corresponding to an optical band gap of ~ 2.1 eV (Figure 1–6.b).^{18,20,24} In addition, the absorption spectrum exhibits two prominent features with absorption edges occurring at ~ 600 and ~ 550 nm (Figure 1–6.b). To assess the origin of these transitions (direct or indirect), Galli and coworkers²⁰ used the Bethe-Salpeter (BSE) equation to calculate the absorption spectra of Ta₃N₅; the importance of this equation is that it does not include the phonon-assisted electronic transition. The experimental and calculated spectra of Ta₃N₅ are compared in Figure 1–6.b. As depicted, the

calculated spectrum is in good agreement with the experimentally measured spectrum. Therefore, these electronic transitions are direct electronic transition originating from the electron transition from N 2p to Ta 5d orbitals (Figure 1–6.a).

In addition to the band gap electronic transitions, a sub-band gap absorption centered around 720 nm has repeatedly been observed.^{25–29} This absorption feature is assigned to two distinctive sites: (1) reduced Ta⁵⁺ sites, i.e. Ta⁴⁺ or Ta^{3+,25,29} and (2) N-vacancies.^{26,28} The main difference between these two sites is that the former is basically a trap state where the charges are localized on the Ta-sites while in the second scheme the charge is delocalized over the conduction band. Moreover, the location of these sites, located on the surface or in the bulk, remains an open question. If this is a property of bulk, a high carrier density and low resistivity is expected. These are the physical properties that can be experimentally measured (see section1.3.1.4). On the other hand, if these sits are dominantly located on the surface, they influence the dynamic of charge at the surface (fermi level pinning) which influence the photocurrent onset potential. Therefore, the origin and location of the sub-band gap absorption features and their effect on the PEC performance of Ta₃N₅ are important questions yet to be addressed.

1.3.1.3 The Band Edge positions in Ta₃N₅

The Mott-Schottky plot and ultraviolet photoelectron spectroscopy (UPS) are among the most versatile techniques to determine the flat band energy (E_{FB}) or the Fermi level (E_f) of a semiconductor. When coupled with optical measurements, the band edge positions of the semiconductor can be evaluated. In photoelectrochemistry the band edge positions are the important characteristics of a semiconductor that essentially determine the feasibility of the

electrochemical reaction at the surface and the magnitude of the photovoltage gained from the photoelectrochemical device. For a n-type semiconductor the photogenerated holes (the minority charge carriers located in the valence band) drive the oxidation reaction at the surface of the photoanode. The valence band position of a semiconductor with respect to the potential of a hole acceptor in solution is therefore the thermodynamic quantity that determines the feasibility of the oxidation reaction. For example, for PEC water oxidation the valence band position of the semiconductor must be more positive than the water oxidation potential. The band edge positions of a series of common photoanodes as well as the oxidation and reduction potential of water are compared in Figure 1–7. As can be seen, the valence band edges of these semiconductors are located at positive potential with respect to the water oxidation potential with decreasing overpotentials from $Ta_2O_5 (\sim 2 V) > Fe_2O_3 (\sim 1.2 V) > TaON (\sim 1 V) > Ta_3N_5 (\sim 500 mV)$. The magnitude of the difference between the water oxidation potential and the valence band edge position is another important factor to be considered. This value defines the overpotential (kinetic energy) available to initiate the electrochemical reaction. The minimum overpotential for water oxidation for most of the metal oxides ranges between 300 to 500 mV.³⁰ Therefore, for efficient photoelectrodes the difference between the valence band edge position and water oxidation potential should ideally lie within the same range. The valence band edge position of Ta_2O_5 and Fe_2O_3 for example, are ~ 2.0 and ~ 1.2 V more positive than the water oxidation potential, respectively. The photogenerated holes in these semiconductors are more energetic than the overpotential required to oxidize water. As a result, the excess energy is lost as heat which further limits the efficiency of the photoelectrode. On the other hand, the valence band edge position of Ta_3N_5 is located ~ 1.6 - 1.7 V vs. RHE which lies within the ideal potential for water oxidation reaction, making it a promising candidate for efficient PEC water oxidation.²⁴



Figure 1–7. The schematic representation of band edge positions of a series of common photoanodes suitable for PEC water oxidation. The numbers on the graph represent the optical band gap. The vertical two-pointed arrows represent the theoretical photovoltage gained from Ta_3N_5 and Fe_2O_3 under water oxidation conditions. The water reduction and oxidation potentials at 0.0 and 1.23 V *vs.* RHE are shown with horizontal dashed lines. The data used for preparation of this scheme were adapted from reference 31 and 24.

The photovoltage gained from a photoanode is the difference between the electrochemical potential of semiconductor, i.e. E_{FB} , and the potential of donor (reductant). For a given solution this potential is constant, and the magnitude of the photovoltage is thus linearly related to E_{FB} . The E_{FB} for a n-type semiconductor is located more positive than the conduction band edge position. This depends on the density of states of the conduction band and the dopant density of the

semiconductor. As depicted in Figure 1–7, the conduction band edge position of Ta-based semiconductors are relatively similar and are located negative of the water reduction potential while the conduction band edge position of hematite is about 500 mV more positive than the water reduction potentials. Under identical conditions, therefore it is theoretically expected that Ta-based semiconductors produce a larger photovoltage than hematite electrodes. Accordingly, a photovoltage greater than 1.23 V can theoretically be gained from Ta₃N₅.

1.3.1.4 Charge Transport Properties of Ta₃N₅

In photoelectrochemical devices the majority of the light absorption occurs deep in the bulk of the semiconductor (depending on the absorption coefficient), while the charge transfer occurs at the surface. Therefore, the photogenerated charges must be transported to the surface. The schematic representation of charge transport in an n-type Ta_3N_5 as a function of distance from the electrolyte is shown in Figure 1–8. As shown, the photogenerated charges are transported *via* (1) diffusion and (2) drift.³² Diffusion refers to the net movement of charge carriers as a result of the gradient in charge carrier concentration in the absence of electrical fields and thus it is the main mechanism of charge transport in the neutral region (bulk) of the semiconductor. The diffusion length and charge carrier life time are two of the fundamental characteristics of a semiconductor that controls its charge separation efficiency.

The diffusion length (L) is the mean distance that a carrier moves between generation and recombination and is mathematically defined as:

$$L = \sqrt{D\tau}$$
 1-6
$D \text{ (cm}^2 \text{ s}^{-1})$ and $\tau \text{ (s)}$ are the diffusion coefficient and the charge carrier life time. The diffusion coefficient relates to mobility of the charge carrier according to Einstein relationship as:

$$D = \mu k_B T / q 1-7$$

In this equation, μ (cm² V⁻¹ s⁻¹) is the charge carrier mobility, k_B (J K⁻¹) Boltzmann constant, T (K) temperature, and q (C) is the elementary charge.³³



Figure 1–8. The energy-level diagram of a n-type semiconductor under illumination representing charge carrier generation and different charge transport mechanisms as a function of distance from the electrolyte.

Consequently to determine the diffusion length, the carrier mobility and lifetime need to be determined. The four-probe (Van der Pauw method) measurement coupled with Hall effect measurements are widely used methods to determine the charge carrier density and mobility.³⁴ It should be bore in mind that these methods are informative when the characteristics of majority charge carriers are concerned. In order to determine the lifetime of the photogenerated charge carrier, various methods such as transient absorption spectroscopy (TAS) and time resolved microwave conductance (TRMC) have been used.³⁴⁻³⁶ The latter measurement (TRMC) is appealing as it can be used to simultaneously determine the charge carrier life time and mobility. Alternatively, the space-charge model is another approach that have been widely used to extract the diffusion length of minority charge carrier through fitting.^{37,38} Recently, Van de Krol and coworkers³⁵ utilized TRMC to extract the mobility and lifetime of the photogenerated charge carriers in Ta₂O₅, TaON, and Ta₃N₅. They showed that Ta₃N₅ exhibits a longlife time of 1.6 ms with a moderate mobility of $0.08 \text{ cm}^2 \text{ V s}^{-1}$ corresponding to an exceptionally large diffusion length of $\sim 18 \,\mu\text{m}$. In a separate study, a combination of TAS and Hall Effect measurements were utilized to assess the lifetime and mobility of the compact thin films of Ta₃N₅ with various thicknesses.³⁹ A mobility of $\sim 4 \text{ cm}^2 \text{ V s}^{-1}$ and an average life time of 5 picosecond were measured. As mentioned earlier, for Ta_3N_5 as an n-type semiconductor, the Hall Effect measurements results in the mobility of the majority carriers, i.e. electrons, therefore the diffusion length of holes cannot be calculated. Clearly, these two independent studies suggest drastically different charge carrier life time and mobility. This further indicates that the bulk properties of Ta_3N_5 are poorly understood and its charge carrier lifetime and diffusion length remain elusive. In addition, it is not clear that the transport of which charge carrier, i.e. electrons or holes, is limiting.

1.3.1.5 Synthesis of Ta₃N₅

Ta₃N₅ (films and powder) is commonly synthesized via ammonolysis – crystallization and nitridization by annealing in ammonia- of Ta₂O₅ (tantalum oxide) at high temperatures (> 850 $^{\circ}$ C) for a prolonged durations (from 8h to 120h).^{40–42} Interestingly, it has been shown that regardless of ammonolysis conditions (temperature or duration), all the samples contained oxygen impurity - even after annealing at 900 °C for 120h.40 Expectedly, they showed that as the annealing temperature and duration (but to less extent) increases more nitrogen is incorporated into the structure and the oxygen contents decreases. However, the rate at which the ratio of N:O increases was less than the theoretical ratio of N/O (0.66, for Ta_3N_5 to Ta_2O_5 that corresponds to two N³⁻ for every three O²⁻ sites) which was found to decrease as the ammonolysis temperature increases. The discrepancy between the experimental and theoretical ratio, therefore, was ascribed to the formation of anion-vacancy where its density increases with ammonolysis temperature. Formation of these vacancies can explain the observed sub-band gap absorption at ~ 720 nm (see section 1.3.1.2). In a separate study, Terao⁴³ utilized electron diffraction to explore the structural and compositional evolution of Ta_3N_5 film by heating in vacuum (10⁻⁵ Torr) at the temperature range of 1100 - 1800 °C. It was discovered that tantalum nitride has a dynamic structure and composition which varies with temperature (equation 1-8). With increasing temperatures, nitrogen is successively pulled out of the structure – which it is accompanied by concomitant reduction of Ta- resulting in different tantalum nitride.

$$Ta_{3}N_{5} \xrightarrow{\sim 1100 \ ^{\circ}\text{C}} Ta_{4}N_{5} \xrightarrow{\sim 1300 \ ^{\circ}\text{C}} Ta_{5}N_{6} \xrightarrow{\sim 1400 \ ^{\circ}\text{C}} TaN \xrightarrow{>1400 \ ^{\circ}\text{C}} Ta_{2}N \qquad 1-8$$

The common synthesis procedure of Ta_3N_5 electrode start with the oxidation of Ta-substrate *via* electrochemical anodization or simply heating in air to oxidize the top Ta layer to a mesoporous/

nanostructure or planner tantalum oxide film, respectively.^{26,27,41,44,45} Subsequently, the oxidized sample is nitridized in a flow of ammonia at elevated temperatures (850 - 1000 °C) for a prolonged period of time (2 - 15 hours). The Ta-substrate serves as the source of Ta, the substrate, and the conductive layer to collect the majority charge carriers necessary to fabricate electrode.



Figure 1–9. Schematic representation of the synthesis procedure of Ta₃N₅ photoelectrode.

Although this method is simple and resulted in the best PEC water oxidation performance of Ta₃N₅,^{41,44} vide infra, from synthetic point of view however, multiple draw backs makes this method unsuitable to realize efficient photoelectrodes as this method: (1) is highly energy intensive, (2) produces a sizable quantity of chemical wastes, (3) is inefficient on chemical utilization, (4) provides highly reducing conditions which limits Ta₃N₅ to be only compatible to Ta-substrate or Nobel metals, e.g. Pt,^{26,45} (5) precludes its application in the tandem cell (see Figure 1–4) as Ta or other metal substrates are not transparent to the sub-bandgap photons, (6) results in the formation of electronic resistive phases at the Ta₃N₅|Ta junction which further limits the electron collection efficiency. In addition, Ta as a substrate becomes very brittle after heating in ammonia which makes the post-annealing electrode processing very challenging. For example, Jaramillo and coworkers²⁷ studied the structure and phase transformation of tantalum oxide to tantalum nitride films on Ta foil and fused silica as a function of ammonolysis temperature (850 -1000 °C). They showed that the synthesized Ta₃N₅ films on fused silica are pure, but the films prepared on the Ta substrate contained impurity phases where the formation of Ta₂N and Ta₅N₆ phases are favored as the ammonolysis temperature increase. A similar behavior was further

observed by Van de Krol and coworkers.^{26,35,45} They explored the effect of ammonolysis duration on the optical and PEC performance of Ta_3N_5 photoanode prepared on Pt conductive substrate *via* a three steps method of: (1) sputtering of Ta on Pt (or fused silica), (2) oxidation of Ta in air, and (3) ammonolysis. Interestingly, they did not detect no N-poor phases. As confirmed by the depth profile GIXS measurements²⁷, these observations indicate that the N-poor resistive phases are specifically formed at $Ta_3N_5|Ta$ junction. In a separate study, Domen and coworkers⁴¹ showed that ammonolysis of anodized Ta-substrate results in the formation of N-poor phases, e.g. Ta_5N_6 , which suppress the electron collection efficiency at the back contact. Interestingly, doping with barium excludes the formation of Ta_5N_6 which it substantially improves the PEC water oxidation performance of the electrode (discussed in the next section).

These examples highlights the complexity of the synthesis of Ta_3N_5 electrodes that requires a precise control over temperature, atmosphere, and duration of ammonolysis. These findings are extremely important as the composition, density, and distribution of vacancies (dopant) ultimately define the dynamic of charge carrier within and on the surface of semiconductor. To rationalize the fundamental characteristics of Ta_3N_5 , therefore, a synthesis method where the density of these vacancies can be controlled is highly desirable. One of the promising approach to circumvent this issue is to directly synthesize Ta_3N_5 from oxygen free precursors by eliminating the ammonolysis step *via* vacuum deposition techniques at moderate deposition temperatures.

1.3.1.6 PEC Performance of Ta₃N₅

One of the best example of efficient water oxidation on Ta_3N_5 was introduced by Domen *et al.*⁴¹ The two step procedure of mask anodization followed by ammonolysis at 1000 °C for 2h was utilized to fabricate a high aspect ratio films of pristine (undoped) and Ba-doped Ta_3N_5 on Ta

substrate. The morphology along with the PEC water oxidation performance of these electrodes (*J-E* curves) are shown in Figure 1–10. As shown, the mask anodization resulted in the well-defined vertically oriented nanorods of Ta_3N_5 with a diameter and length of ~ 60 and 600 nm, respectively. The light *J-V* measurement of undoped Ta_3N_5 produced a current density of ~ 5 mA cm⁻² at the thermodynamic water oxidation potential. Upon doping with barium, remarkably, a substantial improvement in both photocurrent density and photocurrent onset potential were observed. In line with conductivity measurements, this improvement was further ascribed to selective suppression of the formation of resistive interlayer at $Ta_3N_5|Ta$ junction (see section 1.3.1.5).



Figure 1–10. The morphology and PEC performance of Ta_3N_5 . a) cross section of Ba-doped Ta_3N_5 on Ta substrate, b) the *J-V* curves of undoped and Ba-doped Ta_3N_5 coated with CoPi catalyst under 1 sun illumination at pH = 13. Adapted by permission from Springer Nature: Nature Communication (ref. 41), copyright 2013.

The state-of-the-art Ta₃N₅ photoanode was introduced by Li and coworkers⁴⁴ with the photocurrent density approaching its theoretical limit (~ 12.5 mA cm⁻²). They synthesized the porous Ta₃N₅ film

via ammonolysis of NaTaO₃ film formed by anodization and hydrothermal process on Ta substrate. To promote the charge collection efficiency at the surface of electrode several layers including a thin layer of TiO_x as an electron blocking layer to suppress the electron hole recombination, a hole storage layer comprised of FeOOH and Ni(OH)₂ to further facilitate the charge separation efficiency at the surface, and finally a layer of molecular catalyst to promote the kinetic of water oxidation reaction at the surface of electrode were successively deposited on the surface (shown in Figure 1–11.a). Accordingly, the integrated electrode with a combination of molecular water oxidation catalyst at the surface produced 12.5 mA cm⁻² at water oxidation potential with a current onset potential at ~ 0.65 V *vs*. RHE (shown in Figure 1–11.b).



Figure 1–11. a) The schematic representation of Ta_3N_5 electrode comprised of six layers from bottom to top as: (1) Ta (conductive substrate), (2) Ta_3N_5 , (3) TiO_x , (4) FeOOH, (5) $Ni(OH)_2$, (6) a combination of molecular catalyst shown on the right hand side; b) *J-V* curves of the integrated electrode with various combination of molecular catalyst in dark and under 1 sun illumination at pH = 13.6 in 1 M NaOH. These figures were adapted from ref. 44 with permission from The Royal Society of Chemistry.

While these examples highlight the potentials of Ta_3N_5 as a promising candidate for PEC water oxidation, the instability under PEC water oxidation conditions is one of the immense challenges

limiting the efficiency its efficiency. It is generally accepted that surface oxidation - formation of tantalum oxide or TaO_xN_y (equation 1-5) - induced by photocorrosion is the dominant cause of instability. The surface oxide layer lowers the PEC performance by blocking hole transfer to the solution (tantalum oxide is a highly resistive layer with a more positive valence band position with respect to Ta_3N_5 see Figure 1–7), introducing surface trap states that promote surface recombination, and/or by pinning the fermi level that lowers the built-in potential. For example, Wang and coworkers⁴² utilized a combination of electrochemical, TEM, and ambient pressure XPS spectroscopy measurements to investigate the effect of the surface oxidation on the PEC performance of Ta_3N_5 . On the basis of their findings, they proposed that the formation of surface oxide layer is self-limiting, and it causes a severe fermi level pinning that drastically diminishes the photoactivity of Ta₃N₅. Furthermore, to assess the origin of instability they evaluated the PEC in presence of various hole scavengers, e.g. H₂O₂, Fe^{II}(CN)/Fe^{III}(CN)₆. It was shown that Ta₃N₅ exhibits a relatively stable performance in presence of fast hole scavengers. This observation indirectly suggests that Ta₃N₅ has a relatively low catalytic activity toward water oxidation reaction and accumulation of holes on the surface is the main cause of surface oxidation. Thus, the catalytic modification of surface is an effective strategy to suppress the photo-induced surface oxidation. In addition, the surface encapsulation or protection is another viable strategy that has widely been used to protect the surface of photoelectrodes against oxidation.^{41,42,44,46–48} For example, recently Domen and coworkers⁴⁸ explored the PEC performance of Ta₃N₅ modified with 50 nm of GaN (surface protection layer) and a layer of CoPi catalyst. The schematic configuration of the electrode and its stability under PEC water oxidations are summarized in Figure 1–12. As depicted, without the protection layer where the surface is only modified with CoPi catalyst, the performance of electrode is diminished within ~ 1 h of continuous illumination.



Figure 1–12. Comparison between the stability of Ta_3N_5 and Ta_3N_5 coated GaN at pH = 13 under 1 sun illumination at 1.2 V *vs.* RHE. The figure is adapted with permission from ref. 48. Copyright 2017 John Wiley & Sons.

Remarkably, when the surfaces are protected with GaN layer and CoPi catalyst, it exhibited a stable performance for 10 h continuous illuminations which to date it is the most stable Ta_3N_5 photoelectrode under PEC water oxidation conditions.

1.3.2. Hematite

Hematite (α -Fe₂O₃) stands out as another promising photoanode material for PEC water oxidation. Hematite exhibits outstanding stability in a wide pH range from pH 7 to 14, which is favorable for oxygen evolution reactions. In addition, Fe is one of the most abundant elements in Earth's upper continental crust after O, Si and Al.⁴⁹ It also possesses a reasonably small bandgap of ~ 2.1 eV which has a large overlap with the solar spectrum. With the absorption edge extended to 590 nm it can produce a theoretical maximum photocurrent density of 12.5 mA cm⁻² which corresponds to 15% solar-to-hydrogen (STH) efficiency. In addition, the valence band edge position of α -Fe₂O₃ is sufficiently positive, making it suitable for water oxidation (Figure 1–7). The first example of photolysis of water with hematite was introduced in 1976.⁵⁰ Since then, a progressively large number of studies were conducted to identify and improve the bottleneck processes limiting the efficiency of water oxidation on hematite. Despite the remarkable improvements of the PEC performance of hematite made over the past decade, the solar energy conversion efficiency of hematite is still far from its theoretical value. Hematite has a relatively long absorption depth but a short minority carrier collection length.^{51–56} In order to realize a highly efficient hematite photoanode, therefore, both the LHE and charge separation efficiencies need to be simultaneously maximized. Nanostructuring and doping with foreign elements are the two well-studied strategies to optimize LHE and charge separation efficiency.^{57–62} Although these strategies are highly effective to improve the performance of hematite,^{63–65} they are found to have less effect on HCE at the surface of the electrode which is mainly controlled by the surface properties of the semiconductor and it depends on the surface terminal atoms and surface crystal orientations.^{66–69} Hematite surface has a low catalytic activity toward water oxidation, thus hole transfer to the acceptor species in solution (injection) competes with the parallel electron-hole recombination reaction on the surface. To suppress the surface recombination, a large overpotential with respect to the flat band potential is thus necessary to achieve a sustainable water oxidation.⁴¹ To realize a high-performing hematite photoanode, it is important to minimize this overpotential by promoting the kinetics of water oxidation and/or suppressing the unfavorable surface electron-hole recombination. Surface modification with various catalytic and non-catalytic materials have been shown to be effective strategies to improve the performance of hematite.^{31,70–74} Although the true mechanisms that these surface modifications reduce the overpotential are not fully understood, the common observation among these studies indicates a strong correlation between the concentration of long-lived photogenerated holes at the surface, i.e. reduced electron-hole recombination, and the water oxidation overpotential.^{71,75–77} The role of catalyst in PEC systems can be rationalized by two completely distinctive mechanisms: (1) the catalyst behave as an spectator where it improves the PEC performance of the photoelectrode by suppressing the electron-hole recombination at the surface, and (2) the catalyst is as a hole storage layer and behave as an adoptive junction where it improve the performance of electrode by promoting (catalyzing) the water oxidation reaction. Additionally, there are some examples in literature where the surface modification of photoanode with catalyst, surprisingly, have shown to suppress the performance of the electrode.^{77,78} Therefore, it is highly beneficial to uncover the role of catalyst and the mechanism at which it affect the performance of photoelectrode.

1.4. Synthesis of Semiconductor Thin Films

The art of material synthesis holds fundamental importance for both basic science and practical applications. Unlike molecular systems, the physical characteristics of materials are fundamentally linked to the synthetic conditions used to prepare them. In addition, it is important to note that most materials that are commonly used in advanced technologies and even renewable energy applications are directly or indirectly related to industrial processes that deeply rely on fossil fuels. Therefore, it is highly important to design carbon-free and versatile reaction procedures that provide a good tunability and control over the key material characteristics - i.e. crystallinity, crystal orientations, size (dimension), morphology, and the surface terminal groups where the ordered bonding is interrupted - of the final products. Importantly, a deep knowledge of the material synthesis provides a path for studying the structure-function relationship of materials. This further allows to design exotic materials with unusual properties which will be the foundation of new technologies for catalysis, energy conversion and energy storage. Furthermore, many cutting-edge

technologies and autonomous materials are comprised of various components, each with a specific functionality. Thus, integrating these materials while preserving their functionality to operate as a whole is fundamentally challenging and requires a thorough control over the synthesis of each component as well as the techniques to interface them together. For example, the wireless solar water splitting system (see section 1.2) is comprised of a transparent conductive layer, two semiconductor light absorbers, electrocatalyst, and a separation membrane layer. To realize a high-performance device, it is thus important to minimize any energy loss by elaborate and constructive integration of these layers. The optimization of individual layer and integration of them, of course, covers a wide range of science and research efforts. In this dissertation we utilized atomic layer deposition (ALD) and electrodeposition (ED) to synthesize thin films of semiconductors on various substrates. In addition, spin coating was utilized to modify the electrode surface with a thin layer of electrocatalyst. In the following sections the ALD and ED methods are discussed in more details.

1.4.1. Atomic Layer Deposition

Atomic layer deposition is a promising and robust method for the synthesis of thin films both on industrial and academic scales. ALD is characterized by its precise control over the film thickness and the atomic level control over the composition of the film. In addition, in comparison to the conventional methods, ALD provides substantially moderate synthesis conditions and as the ALD process is performed at reduced pressures in inert atmospheres, it is suitable for the synthesis of non-oxide and air-sensitive materials which otherwise require harsh and reactive synthesis conditions. From a synthesis point of view, this is of great interest as it eliminates the necessity for reactive conditions to integrate multiple layers each with specific functionality.⁷⁹

The self-limiting ALD deposition reaction occurs at the interface of the gas and solid phase and it is comprised of 4 elementary steps which include sequential introduction of precursor and co-reactant into the deposition chamber in a timely fashion (Figure 1–13). Initially, the precursor is introduced in the deposition chamber (step 1) where it reacts with the active surface sites by forming chemical bonds (chemisorption) and the excess precursors are physisorbed. Next, the chamber is purged with a chemically inert carrier gas to remove the loosely bonded precursors (step 2). Ideally, this step provides an atomically clean surface ready for the next step. Subsequently, the co-reactant is introduced into the chamber to react with the fist layer (step 3) followed by a purge step to remove the gaseous products and excess co-reactants (step 4).



Figure 1–13. The schematic representation of atomic layer deposition of a binary reaction.

Together, these four steps complete one ALD cycle that corresponds to a film growth of a few angstrom thickness (the thickness depends on the material and deposition conditions/precursors). To grow a given the whole sequence is therefore repeated many times. The time scale of the ALD process depends on material being deposited, thickness of the film, and also the aspect ratio (porosity) of the substrate. For example, the growth rate of hematite is ~ 0.5 Å/cycle and it takes ~ 83 s to complete 1 ALD cycle. To grow 30 nm hematite film on a planner and non-porous substrate, it takes ~ 18 hours.^{57,63,80–82} Slow grow rate and long deposition durations are certainly two inherent limitations of the ALD, limiting its applicability to the films with nm thicknesses.

1.4.2. Electrodeposition

Electrodeposition, or electroplating, is a method that can be used to prepare both thin films and nano (crystalline) materials. By controlling the composition, ionic strength, pH, and temperature of the deposition bath, the physical characteristic of the final product, such as crystallinity, morphology and composition, can be easily and effectively controlled. In addition, electrodeposition is amenable to large-scale production and requires fairly simple instrumentation and is, at least relative to ALD, considerably cheaper overall. Due to these attributes, electrodeposition is one of the promising techniques for the synthesis of thin-film semiconductors. Unlike the ALD method, ED is limited to conductive substrates. In a typical ED experiment, electrons are considered as one of the reactants that can directly, or indirectly, react with precursors in the solution. Therefore, by controlling the electron energy and concentration at the surface of working electrode, one can control the nature and rate of the deposition reaction occurring at the surface of the working electrode. A schematic picture of an undivided electrodeposition cell in a three-electrode configuration is shown in Figure 1–14. As shown the potential of the working

electrode is controlled/ or monitored relative to a reference electrode while the current is collected/ controlled at the counter electrode. The thickness of the film can simply be controlled by varying the deposition time. The electrodeposition reaction can proceed through two distinctive pathways, namely: (1) the direct reaction of electrons with solubilized precursors, followed by their deposition on the surface of the electrode; (2) the reaction of electrons with sacrificial reagents in solution, which subsequently reacts with precursor in the solution, to then lead to the formation of the film at the surface of the electrode.



Figure 1–14. A typical schematic representation of electrodeposition cell in three-electrode configuration.

1.5. Dissertation Overview and Objectives

This dissertation is focused on the synthesis and characterization of semiconductor materials for photoelectrochemical water oxidation, and consists in two sections. In the first section, the synthesis of tantalum nitride thin films for PEC water oxidation were investigated. To circumvent the issues associated with the conventional two-step synthesis procedure of Ta_3N_5 (oxidation followed by ammonolysis), the ED and ALD as bottom-up procedures are investigated. The aim of these projects is to realize/integrate Ta_3N_5 photoelectrodes on a transparent conductive substrates (TCO), one of the crucial requirements for tandem cell designs. In addition, this platform provides a viable system to study the fundamental properties of tantalum nitride, using the illumination direction as another parameter to explore the fundamental characteristics of Ta_3N_5 electrodes.

In the first project, a two-step electrodeposition of tantalum oxide from aqueous solutions followed by ammonolysis was utilized to fabricate nanostructured thin films of Ta₃N₅ on various substrates. To avoid the ammonolysis step, ALD was utilized to directly deposit thin films of tantalum nitride. It was noted that the films deposited at the temperature range of 1 - 280 °C are amorphous TaO_xN_y which are nitridized to crystalline Ta₃N₅ *via* annealing in ammonia at 750 °C for 30 min. Subsequently, TaO_xN_y was integrated with Ta-doped TiO₂ (a newly developed stable TCO under reducing conditions of ammonolysis) *via* ALD to introduce the first demonstration of Ta₃N₅ grown on a TCO. Inspired by this study, we noted that direct deposition of crystalline Ta₃N₅ requires higher deposition temperatures (\geq 500 °C). Therefore, a fully automated high-temperature ALD system was designed. In this project, the direct deposition of crystalline Ta₃N₅ on FTO (a commercially available TCO which is not stable under ammonolysis conditions) was studied, allowing us to study the fundamental properties of Ta_3N_5 independently of the conductivity of the substrate.

In the second section of this dissertation, the PEC performance of catalytically-modified hematite electrodes was studied. As discussed earlier, the PEC water oxidation performance of hematite is limited by its low catalytic activity toward water oxidation. The aim of the second part of this dissertation is to understand how catalysts interface with underlying semiconductor and how it affects the performance of catalytically-modified electrodes. For this purpose, hematite electrodes were prepared by ALD and ED, and Ni_{1-x}Fe_xO_y with various compositions were utilized as the water oxidation catalyst. The catalyst-coated hematite electrodes were subsequently studied with various electrochemical and spectroscopic methods. In addition, in collaboration with the Rothschild group at Technion, a combinations of two Ni_{1-x}Fe_xO_y catalysts, i.e. Ni-rich and Fe-rich catalysts, prepared by UV light-assisted deposition and hematite electrodes with two distinctive orientations, i.e. (100) and (001) were utilized as model electrodes with systematically different composition / or structure of the interface at the semiconductor|catalyst junction. The preliminary data indicate that the PEC water oxidation performance of the catalyst-coated electrodes depends on both the composition of the catalyst and the crystal orientation of the hematite substrate.

Overall, this dissertation highlights the origins of some of the challenges associated with efficient PEC water oxidation on Ta_3N_5 and hematite electrodes. The knowledge gained from this dissertation are the base of some of the exciting projects carried out in our lab.

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Chapter 2:

Selective Electrodeposition of

Tantalum(V) Oxide Electrodes

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2.1. Abstract

Thin films of TaO_xH_y were cathodically electrodeposited from an aqueous solution containing Ta-IPA precursor and KNO₃ as a sacrificial agent. It was shown that the deposition resulted from a precipitation reaction triggered by the local change of pH at the surface of working electrode. Combined structural and compositional analysis revealed that during the electrodeposition, the oxidation state of tantalum remained constant as Ta(V). The as-deposited films are mesoporous amorphous tantalum oxide hydrate films, which can be converted to either pure Ta₂O₅ or Ta₃N₅ by high-temperature annealing in either air (or Ar) or ammonia, respectively. The Ta₃N₅ electrodes exhibited promising PEC activity for water oxidation. These results open the door for the reduced temperature synthesis of Ta₃N₅ electrodes on TCO substrates which would allow for efficient overall solar water splitting.

2.2. Introduction

Tantalum oxide, Ta₂O₅, is a wide band gap semiconductor with a high refractive index and dielectric constant,¹ that has been used in a wide range of applications including capacitors,² electrochromic devices,^{3–5} and catalysis.^{6,7} Tantalum oxide is also the predominant starting material for synthesis of tantalum nitride (Ta₃N₅), which is a nearly ideal n-type semiconductor for solar water splitting.^{1,8–13} For the formation of Ta₃N₅ electrodes, the oxide is first derived from the oxidation or anodization of a Ta substrate, followed by ammonolysis. Despite the simplicity and great performance that has come from this method, there are multiple negative consequences. First, the initial oxidation of tantalum metal is very energy intensive and generally requires hazardous chemicals such as hydrogen fluoride.^{14–17} Second, the Ta substrate is not transparent to sub-band gap light, Ta₃N₅ cannot be employed as a photoanode in a tandem configuration.

Furthermore, the oxidation of Ta can result in the formation of sub-oxide^{18,19} phases which later are converted to nitrogen-poor phases, TaN_x (x < 1.67), at the interface between Ta_3N_5 and Ta substrate.^{15,20} These phases are normally electronically resistive which can suppress the overall performance of the electrodes.

The above drawbacks of Ta oxidation or anodization can be circumvented via the electrodeposition of tantalum(V) oxide(hydrate) films. Electrodeposition is one of the most powerful techniques to obtain uniform films on conductive substrates, which should also allow use of transparent conductive oxide (TCO) substrates instead of the opaque Ta substrates. Generally, electrodeposition can be divided in two main groups: electroreduction/deposition and precipitation/deposition.²¹ The electroreduction/deposition is widely used for plating a large group of metals on conductive substrates where the metal precursor in the solution is reduced and subsequently deposited on the surface of the electrode. Most Ta-precursors, such as TaCl₅, TaF₅, and K₂TaF₇ are highly moisture sensitive and spontaneously react with water. Therefore, the electrodeposition of tantalum has been limited to the nonaqueous media, with previous studies utilizing either molten salts or ionic liquids with a well-controlled atmosphere. Since the electroreduction of a tantalum precursor is the dominant reaction occurring at the cathode, this synthetic route results in the formation of thin films of metallic Ta.²²⁻²⁵ Recently, Domen and co-workers^{6,7} studied the electrodeposition of TaO_x nanoparticles from a non-aqueous solution to make catalysts for the oxygen reduction reaction. Their results showed that the TaO_x deposited in this way were highly dispersed nanoparticles comprised of sub-oxides of tantalum. In a separate study by Moo and coworkers,²⁶ it was shown that the cathodic deposition of tantalum in nonaqueous media resulted in films with the Ta reduced to lower oxidation states, e.g. Ta⁴⁺ and Ta³⁺. These results suggest that the electrochemically induced deposition from non-aqueous solution results in the formation of TaO_x with a range of compositions, including Ta_2O_5 , TaO_2 , and TaO, through the electro-reduction of a tantalum precursor. To the best of our knowledge, there has been no report of the electrodeposition of pure Ta_2O_5 .

In order to exploit the power of electrodeposition tantalum oxide, where the oxidation state of Ta^{5+} is preserved, the cathodic reaction at the surface of working electrode must be controlled to suppress the reduction of Ta_{2}^{5+} . One method to realize the electrodeposition of $Ta_{2}O_{5}$ is through the two-step precipitation/deposition mechanism. In this method, a co-reactant is electrochemically generated at the surface of the electrode followed by its reaction with a metalprecursor in solution where the products precipitate at the electrode surface. It was further shown that this approach can be used for preparation of both thin films and nanocrystalline powders.^{27–33} In 1996, Izaki et al.^{27,28} and Lincot et al.^{31,32} studied the electrodeposition of ZnO films from an aqueous solution via electroreduction of nitrate and dissolved oxygen, respectively. Choi and coworkers^{34,35} further studied the electrodeposition of zinc oxide films by reduction of nitrate ions in a slightly acidic zinc nitrate solution. It was shown that the electroreduction of these nitrate produced hydroxide ions at the surface of working electrode, thereby increasing the local pH which initiates the precipitation of ZnO films.^{28,34} This technique has now been widely utilized to deposit metal oxides such as Fe₂O₃,^{36,37} ZnO,³⁴ KNbO₃,³⁸ and NiO.³⁹ In this work, we employ the precipitation/deposition approach to directly deposit tantalum oxy(hydrate) as thin films from aqueous solution, where the oxidation state of Ta^{5+} is preserved. The resulting film is highly hydrated, and upon annealing in air or ammonia atmosphere it can be converted to phase pure films of Ta₂O₅ or Ta₃N₅, respectively.

2.3. Experimental Section

2.3.1. Electrodeposition of tantalum oxide

All electrodeposition reactions were carried out in an undivided cell using Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. Homemade saturated Ag/AgCl and high surface area platinum mesh electrodes were used as the reference and counter electrode, respectively. The thin films of TaO_xH_y were electrodeposited on different substrates, including Ti (Sigma-Aldrich, 99.7% trace metal), Pt (Sigma-Aldrich, 99.99%), and Ta (Alfa Aesar, 99.95%) metal basis). The substrates were cleaned by sequential sonication in soap (FisherbrandTM Sparkleen[™] 1 Detergent), deionized (DI) water, and isopropyl alcohol (IPA) for 15 minute each. Electrodeposition was performed at ambient temperature in aqueous solutions. The tantalum precursor solution, labeled as Ta-IPA, was separately prepared by dissolving the calculated amount (895 mg) of TaCl₅ (Alfa Aesar 99.8% metal basis), in 5 mL 99.9% isopropyl alcohol (Sigma-Aldrich, used as received without further purifications or drying) to make a 0.5 M solution. This solution was further aged at room temperature for 24 hours and any particulate formed during aging the solution, presumably tantalum oxide due to the reaction of TaCl₅ with the trace amount of water in IPA or air, was subsequently filtered with 0.45 µm syringe filter (Lab Depot, Inc.). For electrodeposition, we tested Ta-IPA solution aged for various durations, as-prepared and aged for 1h to 1 day. The best results in terms of reproducibility of the deposited film were obtained when the Ta-IPA solution was aged at least for 24 hours. An aliquot was transferred to the plating bath to prepare a 50 mM solution of the Ta precursor containing 1 M KCl and 0.5 M KNO₃. The resulting solution was sonicated for 1 hour at room temperature until a milky solution was obtained. The cathodic deposition was carried out at -1 V vs. Ag/AgCl for a fixed time. The asdeposited films were soaked in DI water for at least 2 hours. The samples were frozen by immersing in liquid nitrogen for 15 minutes and immediately transferred to a freeze dryer (lyophilizer labconco freezone 2.5 plus) and dried for 12 hours.

The surface coverage of the film was electrochemically determined by cyclic voltammetry (CV) using an aqueous solution containing 1 mM $K_3Fe(CN)_6$ and 0.5 M KCl as the supporting electrolyte. The potential was cathodically swept from 0.6 to 0 V *vs.* Ag/AgCl with a scan rate of 100 mV s⁻¹.

The as-deposited films were crystallized by annealing in Ar (99.99%, in tube furnace) and air (in muffle furnace) for 1 h at 850 °C. For nitridization to Ta_3N_5 , the deposited films were annealed in a flow of dry ammonia (99.99%) with a flow rate of 500 mL/min, at 850 °C for 1 h with the heating rate of 10 °C/min and then left to naturally cool down to room temperature.

Control samples of TaO_xH_y were prepared *via* precipitation by adjusting the pH of the electrodeposition bath to $pH \ge 4$ by addition of 1 M KOH. The white precipitate was then filtered and washed 3 times with excess amount of DI water and dried under vacuum for 6 hour. The white powder was then annealed in air in a preheated furnace at 850 °C for 1 hour.

2.3.2. Film Characterization

The morphologies of the films were examined by scanning electron microscopy (Carl Zeiss Auriga, Dual Column FIB-SEM). Energy dispersive spectroscopy (EDS) was used to determine the film composition. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin Elmer Phi 5600 ESCA system using a monochromatic Mg k α source to illuminate the sample at a takeoff angle of 45°. Survey scans of 0 - 1100 eV binding energy and detailed scans for C 1s, O 1s, and Ta4f regions were measured for all samples. The binding energies were corrected in reference to

C 1s peak (284.8 eV). The Raman spectra were collected using inVia Raman Microprobe (Renishaw) equipped with a 45W Cobalt DPSS laser (532 nm line) laser and a 100x microscope to focus the laser on the film surface. The spectrometer was calibrated (wavelength position) with internal silicon standard. For comparison, Raman spectra were normalized to the total area. The X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advanced diffractometer using Cu radiation with a K α 1 wavelength of 1.5418 Å.

2.3.3. Photoelectrodeposition of CoPi

Prior to PEC measurements the surface of electrodes were modified with CoPi using a photoelectrodeposition method reported previously.^{36,40} Briefly, the electrodes were immersed in a solution containing 0.5 mM $Co(NO_3)_2$ 6H₂O in 0.1 M phosphate buffer (pH 7). A bias of 1.0 V *vs*. RHE was applied under 1 sun illumination. The thickness of the CoPi film was controlled by the deposition time, with a 300 s deposition used for these electrodes.

2.3.4. Photoelectrochemical Measurements

The PEC measurements were performed in an aqueous solution of 1 M KOH (pH = 13.6). Homemade saturated Ag/AgCl electrode and platinum mesh were used as a reference and counter electrode, respectively. The reference electrode was frequently calibrated to a commercial saturated calomel electrode (Koslow Scientific). The potential *vs*. Ag/AgCl were converted to reversible hydrogen electrode (RHE) by the equation $E_{RHE} = E_{Ag/AgCl} + 0.197 V + (0.059V)$ pH. The chopped light *J-E* curves were measured at a scan rate of 20 mV s⁻¹. The light source was a 450 W Xe arc lamp (Horiba Jobin Yvon). The incident light was chopped using a computercontrolled ThorLabs solenoid shutter. An AM 1.5 solar filter was used to simulate sunlight at 100 mWcm⁻² (1 sun).

2.4. Results and Discussion

TaCl₅ was dissolved in IPA under ambient conditions, then mixed with water, which resulted in a transparent and highly acidic solution (pH < 1). No precipitation was observed upon standing for more than 10 hours (Figure A2-1). Upon raising the pH (> 1.7) or temperature (> 50 °C), however, a white solid precipitated. These observations indicate that the hydrolysis of tantalum is very slow in acidic solutions at room temperature but can be accelerated by increasing the pH and/or the temperature of the solution. In order to characterize the composition of the initial Ta-IPA solution prior to hydrolysis, any excess IPA solvent was evaporated under vacuum for 48 h which resulted a gel-like sample that was characterized *via* FT-IR and ¹HNMR spectroscopy. The detailed analysis of ¹HNMR and IR spectra are discussed following Figure A2-2. Briefly, both ¹HNMR and IR collectively indicate that TaCl₅ reacts with IPA to form tantalum isopropoxide.⁴¹ HCl is formed as a by-product, which accounts for the low pH upon mixing with water.

Cyclic voltammograms (CVs) of solutions containing 1 M KCl and different combinations of additional species in solution are shown in Figure 2–1.a. In all cases, the potential was scanned from 0.0 to -1.5 V *vs.* Ag/AgCl using Ti foil as a working electrode. The CV of the 1 M KCl solution at neutral pH shows negligible current, attributed to the low activity of Ti for the hydrogen evolution reaction.⁴² Upon the addition of KNO₃, a small increase in cathodic current was observed at potentials negative of -1.1 V *vs.* Ag/AgCl. This increase in cathodic current is attributed to the reduction of NO₃⁻ which causes a local pH increase at the interfacial region of electrode and electrolyte.^{43–45} A positive potential shift along with a substantial increase in the cathodic current was observed for the KCl solution containing the Ta-IPA precursor. The increase in cathodic current with the acidic Ta-IPA precursor can be attributed to either reduction of protons or reduction of Ta⁵⁺ to lower oxidation states. In order to identify the reaction responsible for this

shift, the CVs of solutions with pH = 1 (adjusted by addition of HCl) with and without the Ta-IPA precursor are compared in Figure 2–1.b. The CVs of both solutions are similar, thus the cathodic wave is attributed to the reduction of protons, in agreement with a previous report of proton reduction with Ti substrates in acidic solutions.⁴⁶



Figure 2–1. a) The CVs of solutions containing 1 M KCl (red, pH = 7.0), 1 M KCl + 0.5 M KNO₃ (black, pH = 7.0), 1 M KCl + 50 mM Ta-IPA (green, pH = 0.6), and 1 M KCl + 0.5 M KNO₃ + 50 mM Ta-IPA (blue, pH = 0.6); inset is the magnified CVs of first two solutions. b) The CV of 1 M KCl with pH of 1 adjusted by HCl (dotted orange) and 1 M KCl + 50 mM Ta-IPA (green), c) The CV of 1 M KCl + 0.5 M KNO₃ at pH 1 adjusted by HCl (dotted maroon) and 1 M KCl + 0.5 M KNO₃ + 50 mM Ta-IPA (blue).

When KNO₃ was added to the Ta-IPA solution, an even greater increase in cathodic current was observed at more positive potentials, as depicted in Figure 2–1.a. The CV of the KNO₃ + Ta-IPA solution was compared to the CV of an acidic solution ($pH \le 1$) containing only KNO₃, shown in Figure 2–1.c. As shown both solutions produced nearly identical CVs, suggesting that the cathodic

wave of the electrodeposition bath is due to the reduction of NO_3^- in acidic solutions, not direct reduction of Ta^{5+} or protons. Note the different potentials for NO_3^- reduction (black *vs.* blue lines in Figure 2–1.a) are due to the pH dependence of this reaction; CVs of KNO₃ in acidic and neutral solution are compared in Figure A2-3 to support this.⁴⁷

The CVs of the same solutions were also measured utilizing Pt as the working electrode (Figure A2-4). The CVs of the 1 M KCl solution with and without KNO₃ are very similar, which is due to the high activity of Pt toward proton reduction competing with NO₃⁻ reduction.⁴⁸ Unlike the Ti electrode, the CVs of the solutions containing Ta-IPA precursor with and without KNO3 are also almost identical (Figure A2-4.a) with the cathodic wave substantially shifted to more positive potentials. This behavior is consistent with the CVs of 1 M KCl solution with different concentrations of HCl (Figure A2-4.b) which further indicates that on Pt electrode the reduction of protons is the dominant cathodic reaction. The CVs of the solution containing both Ta-IPA and KNO₃, however, showed an anodic peak at -1.3 V vs. Ag/AgCl after the potential was swept to -1.5 V vs. Ag/AgCl. This new feature was neither observed on Ti electrodes nor on Pt electrodes in contact with solutions containing only Ta-IPA. Interestingly, when the potential was swept to -1 V, the oxidation peak was no longer observed (Figure A2-5). Therefore, we hypothesize that at potentials more negative than ~ -1.0 V, the Ta⁵⁺ in the electrodeposited films was reduced to Ta⁴⁺ or Ta^{2+} , 6.26 and upon scanning anodically it was re-oxidized to Ta^{5+} . To test this hypothesis, two films were deposited by holding the potential at -1.0 and -1.5 V vs. Ag/AgCl and subsequently characterized via XPS. The peak positions of Ta $4f_{7/2}$ and Ta $4f_{5/2}$ strongly depend on the oxidation state of Ta and the immediate surrounding atoms, e.g. ~ 26.6 and 28.5 eV for $Ta^{(5+)}$ -O.¹¹ The detailed XPS spectra of C 1s, O 1s, and Ta 4f are shown in Figure A2-6. The binding energies of all the peaks were referenced to C 1s at 284.8 eV. It was noted that regardless of the deposition

potential, the binding energy of oxygen peaks are not affected. However, at more negative deposition potentials the Ta 4f peak was shifted to the lower binding energies and became broader. This observation readily implies that at more negative deposition potentials, the Ta in the electrodeposited film was reduced which results in the formation of Ta suboxides with lower oxidation states of Ta. This is further consistent with the previous study by Stickney and coworkers where they showed that the surface oxide layer on the tantalum foil can be reduced in aqueous solutions at potentials below -1.5 V.⁴⁹ Thus, electrodeposition was performed at -1.0 V *vs*. Ag/AgCl.

We note that at this potential, the electrodeposition reaction triggered by a local pH increase can be induced by reduction of NO_3^- or by local depletion of H⁺ by direct reduction at the surface. In order to test the extent of these possible competing reactions, depositions were performed from the plating bath with and without NO_3^- . The EDS spectra of the electrodeposited films prepared from solutions with and without NO_3^- are shown in Figure A2-7.a. The observed peaks are assigned to Ti (substrate), Ta and O. The sampling depth of the EDS is in the range of micrometers, therefore, in case of thin films the substrate signals are always observed. The Ta signal, located at ~ 1.7 eV, can be seen for both electrodeposited films. This observation readily indicates that the electrodeposition proceeds by the local increase of pH at the surface of the electrode induced by either proton depletion or reduction of NO_3^- . However, the intensity of Ta signal is noticeably lower for the film grown without NO_3^- ions. We note that the atomic percentage found from EDS is a function of film thickness. Thus, to quantify the difference in the film thickness, we calculated the atomic percentage of Ta with respect to Ti (substrate). As depicted in Figure A2-7.b, the percentage of Ta for the film deposited without NO_3^- is considerably lower than the film deposited
in presence of NO_3^- , further implying that the deposition rate without NO_3^- is much slower. Therefore, NO_3^- was used in all following electrodeposition reactions.



Figure 2–2. a) The survey XPS spectra of electrodeposited tantalum oxide films (black) and precipitated powder by addition of 1 M KOH (red), b) the detailed spectra of Ta 4f, C 1s, and O 1s peaks.

The composition of the electrodeposited film, as well as the tantalum oxide powder precipitated *via* addition of KOH to the plating bath, were analyzed by XPS. All the peaks from survey scan (Figure 2–2.a) are assigned to Ta 4f, O 1s, and C 1s. This observation readily indicates that the electrodeposition reaction taking place at the surface of the electrode is the same reaction as the precipitation reaction induced by raising the pH *via* addition of KOH. The detailed XPS spectra of Ta 4f, O 1s, and C 1s are summarized in Figure 2–2.b. It is expected that the oxidization state of Ta remains unchanged in precipitation reaction induced by ex-situ addition of KOH as confirmed by the Ta 4f peak at 26 - 28 eV, consistent with Ta^{5+,11} The XPS spectra from the electrodeposited film show identical shape and position of the Ta 4f peak as the powder sample. This indicates that during the cathodic electrodeposition at -1.0 V *vs*. Ag/AgCl, tantalum was not involved in the

electrochemical reaction and thus its oxidation state was preserved. The atomic ratio of O/Ta of the as-deposited film and the powder were found to be ~ 2:7, which is greater than the theoretical ratio of 2:5 for Ta_2O_5 . The excess oxygen in as-prepared samples are presumably bonded hydroxide or water groups. Therefore, the as-deposited films were marked as TaO_xH_y .

The surface coverage of the substrate with TaO_xH_y electrodeposited films were studied by cyclic voltammetry of aqueous solutions containing K₃[Fe(CN)₆]. Since the associated redox peaks of $[Fe(CN)_6]^{3-/4-}$ are not detectable on Ti electrodes, a Pt electrode was utilized. The reversible redox peak of Fe^{III}/Fe^{II} on a bare Pt electrode (Figure A2-8) is located at ~ 0.3 V *vs.* Ag/AgCl with the peak separation of ~ 60 mV.⁵⁰ After electrodeposition for 120 s, however, the current of the reversible redox peaks of Fe^{III}/Fe^{II} was reduced. The ratio of the cathodic and anodic peak areas or of the current at the Pt electrode after electrodeposition relative to the bare Pt electrode were found to be ~ 0.15. Thus, ~ 85% of the Pt substrate is assumed to be covered by the insulating TaO_xH_y films, where $[Fe(CN)_6]^{3-/4-}$ cannot contact the platinum surface.

The as-deposited films are gel-like and are highly hydrated (Figure A2-9.a). Therefore, the drying process can greatly influence the final morphology of the film. Freeze drying was used to dry the films since this minimizes the effect of capillary forces induced by water evaporation on the morphology of the film. The SEM micrograph of the dried as-deposited film is shown in Figure 2–3.a. The film has a nanostructured morphology and almost full coverage of the Ti substrate, consistent with the CVs of $[Fe(CN)_6]^{3-/4-}$ described above. Upon heating at 850 °C the morphology of the film was preserved (Figure A2-9.b).



Figure 2–3. a) SEM micro-images of as-deposited TaO_xH_y , the inset is the magnified image, b) the XRD patterns of electrodeposited film (top, cyan) and powder control sample precipitated by addition of 1 M KOH (bottom, dark red) after annealing in air at 850 °C for 1 hour. The vertical dotted lines represent the Bragg positions of Ta_2O_5 with PDF # 01-071-0639 and the stars represents the diffraction lines of TiO₂.

The Raman spectrum of the dried as-deposited films and the KOH precipitated powder are compared in Figure A2-10. The Raman spectra of both samples were nominally identical, with two broad peaks centered at ~ 250 and 650 cm⁻¹, which are consistent with amorphous tantalum oxide.^{51,52} In line with the XPS results, the similarity of the Raman spectra also indicates that the products of the electrodeposition and precipitation reaction induced by ex-situ addition of KOH are similar, therefore, it can be concluded that the electrodeposition is triggered by the local pH-increase and proceeds through precipitation/deposition mechanism. In order to crystallize the asprepared samples, they were annealed under a flow of Ar 99.9% (an inert atmosphere) or air at 850 °C. The inert atmosphere for annealing was utilized to prevent oxidation of any lower valent tantalum that formed during electrodeposition. The XRD patterns of powder and electrodeposited



Figure 2–4. a) Top view SEM image of the film after niridization, the inset is the magnified image. b) XRD pattern of the Ta_3N_5 on Ti foil (top, orange), Ti substrate (bottom, dark red). The vertical dotted lines represent the Bragg positions of Ta_3N_5 (orange diamond) with PDF # 01-089-5200.

thin-film tantalum oxide on Ti substrates after annealing in air are shown in Figure 2–3.b. The diffraction patterns for powder and films are unambiguously assigned to the crystalline phase of Ta_2O_5 .⁵¹ The remaining peaks can be assigned to the TiO₂ which formed upon oxidation of the Ti substrate. As shown in Figure A2-11, the diffraction pattern of the film annealed in Ar is also assigned to a single phase of Ta_2O_5 , and no tantalum suboxide phase is observed. In agreement with XRD patterns, the Raman spectra of the film and powder after crystallization (Figure A2-12) are consistent with the formation of crystalline Ta_2O_5 .⁵¹

The TaO_xH_y samples were also annealed under a flow of ammonia at 850 °C for 1 hour to convert the dried as-deposited films into Ta₃N₅. The SEM micrograph of Ta₃N₅ is shown in Figure 2–4.a, which indicates the substrate is covered with the porous film of Ta₃N₅ with a comparable morphology to the as-deposited or Ta₂O₅ films. The XRD patterns of the nitridized film and Ti substrate are compared in Figure 2–4.b. It is worth mentioning that the Ti substrate was treated in



Figure 2–5. Plots of *J-E* curves for PEC water oxidation with Ta_3N_5 prepared from electrodeposited tantalum oxy(hydrate) film followed by ammonolysis (orange) and the control electrode (dark red) coated with CoPi. Inset is a photograph of control and electrodeposited films on a Ta substrate.

the same ammonolysis conditions. The diffraction peaks are in an excellent agreement with the pure phase of Ta_3N_5 which indicates that the as-deposited film was completely transformed into Ta_3N_5 and the remaining peaks are due to the Ti substrate. In addition, no diffraction peak associated to the nitrogen-poor tantalum nitrides were observed, which further indicates that during the cathodic electrodeposition the oxidation state of Ta^{5+} was preserved. Consistent with XRD, the Raman spectra of the film after nitridization (Figure A2-13) confirms the formation of a pure phase Ta_3N_5 .

In order to test the PEC water oxidation activity of Ta_3N_5 , the current density (*J*) vs. applied potential (*E*) measurements were performed on the electrodeposited thin films on Ta substrates under chopped illumination. As a control experiment, a fresh Ta substrate was subjected to the same electrodeposition conditions without the Ta-IPA precursor followed by ammonolysis at 850 °C for 1 hour. The XRD diffraction of these electrodes are shown in Figure A2-14. Although, both electrodes have the signature of Ta₃N₅, the peaks intensity for electrodeposited film is higher than the control sample which further suggest a higher degree of crystallinity and higher thickness for electrodeposited film. In addition, besides the associated peaks of Ta₃N₅, the control electrode shows some diffraction peaks that can be assigned to the nitrogen-poor phases of tantalum nitride. Interestingly, the sub-nitride layers were not observed for the electrodeposited electrode. The *J*-*E* curves of these electrodes are shown in Figure 2–5. Control samples produced little-to-no photocurrent at low applied potentials. On the other hand, the electrodeposited film resulted in a substantial increase of photocurrent at lower potentials with an onset photocurrent potential of ~ 0.6 V vs. RHE and a photocurrent of 0.4 mA cm^{-2} at 1.23 V vs. RHE.

2.5. Conclusion

The work presents the first example of the selective electrodeposition of tantalum(V) oxide thin films. This was achieved by inducing local pH increases at the electrode surface by either proton or NO_3^- reduction, with the latter being a significantly more efficient route. The resultant electrodeposited films were nanostructured and hydrated, and can be converted to pure Ta₂O₅ or Ta₃N₅ by annealing in Air or NH₃, respectively. The Ta₃N₅ electrodes are active toward solar water oxidation. This methodology thus opens up the possibility of producing Ta₃N₅ electrodes on a variety of substrates. This is advantageous since the substrate can be nanostructured and/or transparent to improve light harvesting, charge transport and integration in a tandem configuration, which is not feasible when relying on a Ta metal substrate. For example, electrodeposition of

 TaO_xH_y on nanostructured Ta-doped TiO₂ substrates, followed by ammonolysis, may allow for realization of highly efficient unassisted water splitting with a suitable small bandgap semiconductor bottom junction.¹¹

APPENDIX



Figure A2-1. Photographs of the electrodeposition solution containing Ta-IPA. The top pictures were recorded just after the solutions were prepared, the bottom pictures were taken after 12 hours sitting in ambient condition.



Figure A2-2. a) FT-IR spectra of IPA (black) and Ta-IPA (red), b) ¹H NMR of Ta-IPA.

The FT-IR spectra of IPA and tantalum isopropoxide are compared in Figure A2-2.a. The O–H characteristic vibration is located at 3330 cm⁻¹. As it can be seen, after drying the Ta-IPA solution under vacuum, some residual IPA can still be detected. The characteristic vibration modes of C–C, C–O, and C–H bonds are located in the range of 3000-1000 cm⁻¹, therefore, as expected the

spectrum of both sample in this region are the same. The several peaks between 2975 cm⁻¹ and 2850 cm⁻¹ are due to C—H stretching vibration of alkoxy groups. The peaks between at 1467 and 1300 cm⁻¹ correspond to the C—H bending vibrations and vibration of methylene. Bands at 1200–1000 cm⁻¹ correspond to the C—O vibrations. As it can be seen, in comparison to pure IPA these bands for Ta-IPA are shifted to the lower energies which can be attributed to the formation of Ta—O bonds. In the spectrum of Ta-IPA, the peak at 919 cm⁻¹ is assigned to in-plane rocking vibration of methyl groups. The broad envelopes of bands below 700 cm⁻¹ correspond to the Ta—O stretching modes.^{53,54}

Figure A2-2.b shows the ¹HNMR spectrum of Ta-IPA in CDCl₃ with respect to TMS. The solvent peaks are observed at 7.26 ppm. Consistent with the IR spectrum, yet after drying there are some residual IPA. The associated peaks of the IPA were observed at 1.2 (d) ppm and 4.0 (m) ppm. These peaks are assigned to H atom of the terminal methyl and H in β -position. The two broad peaks centered at 1.5 (m) and 5.0 (m) ppm are assigned to the isopropoxide groups bonded to Ta.⁵⁴



Figure A2-3. a) The CVs of 1 M KCl aqueous solution without (blue) and with KNO₃ (red) in neutral (dotted line) and acidic (solid line) solutions at pH \approx 1.5.



Figure A2-4. a) The CVs of solutions containing 1 M KCl (red), 1 M KCl + 0.5 M KNO₃ (black), 1 M KCl + 50 mM Ta-IPA (green), and 1 M KCl + 0.5 M KNO₃ + 50 mM Ta-IPA (blue). b) CVs of 1 M KCl solution with varying concentration of HCl. Pt was used as working electrode with the scan rate of 100 mV s⁻¹.



Figure A2-5. The CVs of electrodeposition bath containing 1 M KCl (red), 1 M KCl + 0.5 M KNO₃ (black), 1 M KCl + 50 mM Ta-IPA (green), and 1 M KCl + 0.5 M KNO₃ + 50 mM Ta-IPA (blue). Pt was used as working electrode with scan rate of 100 mV s⁻¹ and potential was swept from 0.0 to -1.0 V *vs.* Ag/AgCl.



Figure A2-6. The detailed XPS spectra Ta 4f, C 1s, and O 1s for tantalum oxide deposited films different potential; -1.0 (black) and -1.5 (green) V *vs.* Ag/AgCl.



Figure A2-7. a) The EDS spectra of the electrodeposited film on Ti substrate with (black) and without (green) KNO₃, b) the atomic percentage of Ta found for electrodeposited films with and without KNO₃. Note: the percentage was calculated by only considering the Ta and Ti signals.



Figure A2-8. Cyclic voltammetry of an aqueous solution containing K_3 [Fe(CN)₆] (1 mM) and KCl (0.5 M) at scan rate of 100 m V s⁻¹ on Pt (gray) and TaO_xH_y/Pt (green) electrodes. TaO_xH_y was electrodeposited at -1.0 V *vs*. Ag/AgCl for 120 second.



Figure A2-9. a) The photograph of bare Ti substrate (1), as deposited film at -1.0 V *vs.* Ag/AgCl for 1h (2), and the film after freeze-drying (3), b) SEM micro-images of electrodeposited film after annealing in Ar at 850 °C for 1 hour.



Figure A2-10. The Raman spectra of the as-deposited film (black) and KOH induced precipitation of TaO_xH_y (red) powder.



Figure A2-11. The XRD pattern of the powder (dark red) and electrodeposited thin film of tantalum oxide on Ti substrate after annealing in Ar (dark blue) at 850 °C for 1 hour. The XRD of Ti substrate (gray) after annealing in Ar is also shown as the reference; the vertical lines represent crystalline Ta₂O₅ with the PDF # 01-071-0639. The open triangle represent the crystalline phase of TiO₂ with PDF # 00-034-0180. The black star represents crystalline phases of suboxide phase of titanium with a range of compositions such as: TiO_{0.48} (01-089-3074), TiO_{0.325} (01-073-1581), Ti₆O (01-072-1471), Ti₃O₅ (01-072-0519), Ti_{2.5}O₃ (03-065-6711), Ti_{0.72}O₂ (01-086-1157).



Figure A2-12. The Raman spectra of the powder (dark red) and electrodeposited thin film of tantalum oxide on Ti substrate after annealing in air (cyan) and Ar (dark blue) at 850 °C for 1 hour.



Figure A2-13. The Raman spectrum of the Ta_3N_5 on Ti foil (purple) and powder Ta_3N_5 (orange) Note: the films were nitridized by ammonolysis at 850 °C for 1 hour.



Figure A2-14. The XRD diffraction pattern of Ta_3N_5 on Ta substrate (orange) and Ta substrate (dark red). The vertical dotted lines represent the Bragg positions of Ta_3N_5 with PDF # 01-089-5200. Note: the films were prepared by ammonolysis at 850 °C for 1 hour.

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Chapter 3:

Tantalum Nitride Films Integrated With Transparent Conductive Oxide Substrates *via* Atomic Layer Deposition for Photoelectrochemical Water Splitting

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3.1. Abstract

Tantalum nitride, Ta_3N_5 , is one of the most promising materials for solar energy driven water oxidation. One significant challenge of this material is the high temperature and long duration of ammonolysis previously required to synthesize it, which has so far prevented the use of transparent conductive oxide (TCO) substrates to be used which would allow sub-bandgap light to be transmitted to a photocathode. Here, we overcome this challenge by utilizing atomic layer deposition (ALD) to directly deposit tantalum oxynitride thin films, which can be fully converted to Ta_3N_5via ammonolysis at 750 °C for 30 minutes. This synthesis employs far more moderate conditions than previous reports of efficient Ta_3N_5 photoanodes. Further, we report the first ALD of Ta-doped TiO₂ which we show is a viable TCO material that is stable under the relatively mild ammonolysis conditions employed. As a result, we report the first example of a Ta_3N_5 electrode deposited on a TCO substrate, and the photoelectrochemical behavior. These results open the door to achieve efficient overall water splitting using a Ta_3N_5 photoanode.

3.2. Introduction

Solar-driven photoelectrochemical (PEC) water splitting is a promising route to directly store solar energy in the chemical bonds of hydrogen. Due to the limitation of available materials capable of overall PEC water splitting, a tandem cell is likely required to efficiently convert solar energy into hydrogen.^{1,2} One promising tandem cell configuration is comprised of an n-type semiconductor as a photoanode to drive the oxygen evolution reaction that is electrically connected to a p-type photocathode to drive the hydrogen evolution reaction (Figure 3–1). This type of PEC cell is advantageous as it allows researchers to independently investigate and optimize each half-cell. Although many semiconductor metal oxides have been proposed as a photoanode for solar water

oxidation, the majority of them have band gap that lies in the UV region which covers a negligible portion of the solar spectrum.^{3–6} Metal oxide materials with narrower optical band gap and absorption edges that extend to the visible region, e.g. Fe_2O_3 ,^{7,8} WO₃,^{9,10} and BiVO₄,^{11,12} have therefore attracted a lot of attention. The state-of-the-art electrodes using these materials have produced promising water oxidation photocurrent densities, with the best examples producing approximately 5 mA cm⁻² at 1.23 V *vs.* RHE. For example, Wang and co-workers recently employed a solution processed hematite photoanode in combination with an amorphous Si electrode to achieve overall water splitting at an efficiency of 0.91%. No metal oxide photoanode, however, has produced a photocurrent density that would enable achieving ~ 10% water splitting efficiency.



Figure 3–1. The tandem cell configuration for overall water splitting composed of n-type, and p-type semiconductor connected through a transparent and conductive layer.

Domen has recently introduced a new class of nitride semiconductors, specifically tantalum nitride (Ta₃N₅), as promising alternative candidates to oxides for PEC water oxidation.^{13–19} In one impressive example, they demonstrated 1.5% efficient solar water splitting with Ba-doped Ta₃N₅ nanorods nitridized at 1000 °C for 2 h.²⁰ Tantalum nitride is intrinsically a n-type semiconductor with an optical band gap of 2.1 eV that theoretically corresponds to a maximum photocurrent density of 12.5 mA cm⁻².^{21,22} If it is coupled with an appropriate photocathode in a PEC tandem cell, it could perform unassisted water splitting at a solar-to-hydrogen efficiency of ~ 15%.²³ Strikingly, Li and coworkers recently reported a Ta₃N₅ photoanode on Ta foil prepared by ammonolysis at 950 °C for 6 h that produced a photocurrent density of ~ 12.1 mA cm⁻² at 1.23 V *vs*. RHE with a photocurrent onset potential of ~ 0.7 V *vs*. RHE.²⁴

Implementing a Ta₃N₅ photoanode in a tandem configuration to achieve efficient overall water splitting is hindered by the lack of a synthetic procedure to prepare Ta₃N₅ electrodes under conditions compatible with a transparent conductive oxide (TCO) substrate. Most of the studies on tantalum nitride (Ta₃N₅) share a similar synthetic route, beginning with the oxidation of Ta(0) to Ta(V), followed by ammonolysis at elevated temperatures (> 800 °C) for long periods of time (> 6 h), as noted in the best literature examples provided above. Despite of the simplicity and great performance that comes with this method, there are multiple negative consequences. The initial oxidation of tantalum metal is very energy intensive. Importantly, the subsequent ammonolysis prevents the use of a TCO substrate as noted by others.¹⁸ In our lab, we found that when conventional TCOs such as FTO (F-doped SnO₂), ITO (Sn-doped In₂O₃), and AZO (Al-doped ZnO) are exposed to ammonia at 600 °C or higher, they are reduced to metallic phases and become flaky with weak adhesion to the substrate. Consequently, their important properties of conductivity and transparency are lost. Therefore, Ta₃N₅ is commonly prepared on Ta foil which excludes the

applicability of the Ta_3N_5 as a photoanode in a tandem configuration (Figure 3–1), since the substrate is not transparent to sub-bandgap light. Furthermore, high-temperature ammonolysis makes it difficult to control the morphology, interfaces and the inherent properties of this semiconductor.

In order to overcome these issues, we synthesized Ta-doped TiO₂ (TTO) films *via* atomic layer deposition (ALD) which we found to be a stable TCO in reducing atmospheres. In addition, to circumvent the high-temperature ammonolysis, ALD was also used to directly deposit thin films of Ta₃N₅ on the TTO substrates. While initial as-deposited films are primarily amorphous TaO_xN_y, these films can be nitridized to Ta₃N₅ at far more moderate nitridation conditions, i.e. 750 °C for 30 minutes, compared to previous reports where hours (>6 h) of nitridation at temperatures higher than 800 °C were necessary. The photoelectrochemical properties of the Ta₃N₅ films deposited on TTO were investigated and the PEC water oxidation performance was analyzed. The excellent material control reported here allowed for a detailed material structure-function relationship to be determined and a path to improved performance elucidated.

3.3. Experimental

3.3.1. Film preparation

Thin films of Ta-doped TiO₂ TCO films were prepared on quartz substrates (Advalue Technology) by alternating the deposition of TiO₂ and TaO_x with four different ratios of TaO_x:TiO_x ALD cycles, 1:200, 1:150, 1:100, and 1:50, to modify the dopant concentration. TiO₂ was deposited using a modified literature procedure;²⁵ briefly, titanium isopropoxide (99.9%, Aldrich) was heated to 80 $^{\circ}$ C and pulsed for 2 s. After purging for 10 s, water was pulsed for 15 ms followed by purging for another 10 s. The growth rate of TiO₂ at 250 $^{\circ}$ C was found to be 0.2 Å/cycle. The deposition of

the TaO_x sub-cycles is described below. The as-deposited TTO films were subsequently annealed under an ammonia atmosphere at 750 °C for 30 minutes with a heating rate of 35 °C/ min and cooled down to the room temperature by opening up the top cover of the tube furnace.

TaO_xN_y and TaO_x films were deposited on quartz, silicon (University Wafer, with ~ 16 Å native SiO₂) or the TTO coated quartz substrates described above using ALD (Savannah 200, Cambridge Nanotech Inc). All substrates were sequentially sonicated for 15 minutes in soap (FisherbrandTM Sparkleen[™] 1 Detergent), DI water and isopropyl alcohol, then blown dry under a nitrogen flow and loaded into the ALD chamber. High purity nitrogen was used as a carrier gas, which was further dried and deoxygenated by in-line molecular sieves 3 Å (Sigma Aldrich) and an O₂ scrubber (Restek), respectively. Throughout the deposition, the N₂ flow rate was adjusted at 5 SCCM, providing a constant pressure of ~ 350 mTorr. Pentakis(dimethylamine)tantalum(V), Ta(N(CH₃)₂)₅ (PDMAT), (99.9%, Aldrich) was used as the tantalum precursor. Monomethylhydrazine, CH₃NHNH₂ (MMH), (99.9%, Aldrich) or DI water (Millipore, 18 MΩm) were used as the co-reactants. The tantalum precursor, PDMAT, was kept at 90 °C and consecutively pulsed 5 times for 2 s duration with 10 s purging in between pulses. The MMH and DI water co-reactants were kept at ambient temperature. Nitridation or oxidation was performed by a 15 ms pulse of MMH or water followed by purging for 15 s to complete one ALD cycle. Films were annealed in an ammonia atmosphere at 750 °C for 30 min to complete the nitridation and crystalize the films.

3.3.2. Film Characterization

Films thickness were determined *via* spectroscopic ellipsometry (SE) using Horiba Jobin Yvon, Smart-SE instrument. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin Elmer Phi 5600 ESCA system using a monochromatic Mg k α source to illuminate the sample at a takeoff angle of 45°. Survey scans of 0-1100 eV binding energy and detailed scans for C 1s, O 1s, N 1s and Ta 4f, Ti 2p regions were measured for all samples. The binding energies were corrected in reference to C 1s peak (284.8 eV) and shirley background subtraction was performed for fitting for each sample. Absorbance spectra were collected on PerkinElmer Lambda35 UV-vis spectrometer equipped with Labsphere integrating sphere. 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. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advanced diffractometer using Cu radiation with a K α 1 wavelength of 1.5418 Å. 4-probe electrical measurements were performed using computer controlled Pro4-440N system equipped with Keithley 2400, and Pro4 software. The film thickness was also measured by cross-section SEM (Carl Zeiss Auriga, Dual Column FIBSEM) and was taken at a tilt angle of 90°.

3.3.3. Photoelectrochemical Measurements

All electrodes were coated with the Co-Pi co-catalyst *via* photoelectrodeposition prior to carrying out further PEC measurements. The Co-Pi co-catalyst was deposited from a solution with 0.5 mM Co(NO₃)₂ in a 0.1 M potassium phosphate buffer at pH 7 at a constant potential of 1.06 *vs*. RHE for 180 s under AM 1.5 G simulated sunlight. A Ag/AgCl and high surface area platinum mesh electrodes were used as the reference and counter electrodes, respectively.

Photoelectrochemical measurements were made with Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. The 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 mWcm⁻² (1 sun). All the photoelectrochemical measurements were performed by shining light on the electrodes through

electrolyte. Current-voltage curves were measured using a scan rate of 10 mV s⁻¹. The incident light was chopped using a computer controlled Thor Labs solenoid shutter. Electrodes were masked with a 60 μ m Surlyn film (solaronix) with a 0.28 cm² hole which was adhered to the electrode by heating to 120 °C. The protected electrodes were clamped to a custom made glass electrochemical cell with a quartz window. A homemade saturated Ag/AgCl electrode was used as the reference electrode and was frequently calibrated to a commercial saturated calomel electrode (Koslow Scientific). Potential *vs.* Ag/AgCl were converted to reversible hydrogen electrode (RHE) by the equation $E_{RHE} = E_{Ag/AgCl} + 0.197 V + (0.059V)$ pH. An aqueous solution of 0.5 M K₂HPO₄ was used as the electrolyte. The pH of the electrolyte was adjusted to 13 by adding KOH. A high surface area platinum mesh was used as the counter electrode.

3.4. Results and Discussion

3.4.1. ALD of TTO

ALD was used to deposit Ta-doped TiO₂ (TTO) on quartz substrates. Different Ta concentrations were introduced by varying the relative number of ALD cycles of TiO₂ and TaO_x. Samples with TaO_x:TiO₂ ALD sub-cycle ratios of 1:50, 1:100, 1:150 and 1:200 were prepared to produce a series of decreasing Ta dopant concentrations in TiO₂. In addition, pure TiO₂ films were prepared as control substrates. The total number of cycles were controlled to keep the final film thickness constant at 100 nm. Energy dispersive spectroscopy (EDS) was used to determine the resultant concentration of Ta in TiO₂. Since the Si (K α : 1.739 eV) signal from the quartz coincides with Ta (M: 1.809 keV), TTO films were also deposited on Al (K α : 1.486 eV) substrates which has a well-separated EDS peak (K α (Al): 1.486 eV).²⁶ The EDS spectra of these films with different concentration of Ta are shown in Figure A3-1. The Ta concentration in the 1:200 film was below

the detection limit of the instrument, so it was not included in this plot, however, all the observed signals for the other three films are readily assigned to Ta, Ti, O, and Al (substrate). As shown in Figure A3-1, the atomic percent of Ta was found to increase linearly with the ALD sub-cycle ratio of TaO_x:TiO₂. The atomic percentages of Ta in the films, then, were calculated from a linear fit of these data and used to assign the following percent of Ta contained in the films: $5.0 (\pm 0.32)$, $2.5 (\pm 0.16)$, $1.67 (\pm 0.11)$ and $1.25 (\pm 0.08)$. We note that the actual concentration of Ta contained in the TTO films does not correspond simply to the pulse ratios of Ta and Ti precursors. The difference can largely be accounted for by the different growth rates; ~ $0.25 \text{ Å/cycle for TiO}_2$ compared to ~ 0.79 Å/cycles for TaOx, *vide infra*.

The resistivity of as-deposited Ta-doped TiO₂ films on quartz were on the order of M Ω -cm. In addition, consistent with a previous study, we observed that when the Ta-doped TiO₂ films were annealed in air or oxygen, they became more insulating.²⁷ Prior examples of Ta-doped TiO₂ were prepared at low oxygen pressure, e.g. 10⁻⁵ Torr, or the films were annealed in vacuum.^{27–29} Since our ultimate goal is to realize TCO films coated with Ta₃N₅, which may have to be annealed under ammonia, *vide infra*, all TCO films were annealed under a reducing ammonia atmosphere at 750 °C for 30 minutes.

XPS measurements were performed on samples deposited on quartz both before and after annealing in ammonia. The surface concentration of Ta for as-deposited films are higher compared to the results from EDS measurements (see Figure A3-2). Since XPS is a surface sensitive technique, this higher apparent concentration of Ta may be attributed to the fact that the deposition of TaO_x was the last ALD cycle of these films. After annealing in ammonia, however, the atomic ratio of Ta/Ti determined by XPS was within error of the ratio determined by EDS on the asdeposited samples. Thus, annealing allows Ta to diffuse and be homogeneously distributed throughout the film. We therefore take the surface compositional analysis done by XPS after annealing as a good approximation of bulk composition. Details of the XPS analysis of asdeposited and annealed TTO films with different concentrations of Ta are discussed following Figure A3-3 in the supporting information. The atomic percentages of oxygen and nitrogen as a function of Ta concentration after annealing in ammonia are shown in Figure 3–2.a. After annealing in ammonia the atomic percentage of O decreased and a new N signal emerged which indicates oxygen is substituted by nitrogen in the films. Thus, the annealing step results in TiO₂ co-doped with Ta and N. Interestingly, at high concentration of Ta, i.e. ~ 5%, another N signal is detectable which can be assigned to a Ta-N bond. Further, the Ta signal from the same film shows two types of Ta present in the films. Therefore, we attribute this to the formation of TaN_x as a separate phase at high Ta concentrations. This observation is supported by XRD results of the films and the resistivity of the films discussed below.

The XRD diffraction patterns of all annealed samples were unambiguously assigned to anatase TiO_2 . Detailed analysis of the XRD patterns of the N- and Ta- co-doped TiO_2 films with different Ta concentrations are discussed in the supporting information following Figure A3-4. Depending on dopant concentration, however, the peak positions of anatase are shifted to the lower angles which indicates an increase in cell volume as expected from doping Ta into TiO_2 .³⁰

The resistivity of the TTO films as a function of concentration of Ta are shown in Figure 3–2.a. The resistivity decreases sharply with introduction of Ta, reaching a minimum for the film with 1.6% Ta. This is ~ 3 times smaller than the optimum Ta concentration reported in the literature.^{28,31} The main difference between the Ta-doped TiO₂ synthesized in this study to those reported in literature is the annealing atmosphere. As noted above, use of ammonia as the reducing atmosphere results in TiO₂ films co-doped with Ta and N. As depicted in Figure 3–2.a, the resistivity of the
films has a strong correlation to the atomic concentration of oxygen and nitrogen. The film without Ta exhibits a surprisingly low resistivity which results from the formation of nitrogen-doped TiO_2 or segregation of metallic TiN phases. The lowest resistivity occurs for the film with 1.6% Ta, which has the highest concentration of nitrogen and the lowest concentration of oxygen, i.e. highest concentration of oxygen vacancies. Based on the formal charge of oxygen and nitrogen, it can be inferred that substitution of oxygen with nitrogen induces an increase in the concentration of oxygen vacancies. On the other hand, substitution of Ti^{4+} with Ta^{5+} may reduce the number of oxygen vacancies. Therefore, co-doping of N and Ta into TiO_2 may have an opposing influence on carrier concentration and conductivity, which explains the difference between the optimal doping concentration found here compared to prior reports.²⁷



Figure 3–2. a) Resistivity (brown) and atomic % of O (blue) and N (red) of Ta-doped TiO₂ as a function of Ta%. b) Optical transmittance of Ta-doped TiO₂ films, un-doped TiO₂ (orange), 5.0% Ta (pink), 2.5% Ta (Cyan), 1.67% Ta (red) and 1.25% Ta (black). c) Photograph of the TTO films after annealing in ammonia at 750 °C for 30 min.

The optical transmittance of un-doped and Ta-doped TiO₂ thin films after annealing in ammonia are shown in Figure 3–2.b. Note that these transmittances were not corrected for reflectance, which accounts for ~ 25% loss of incident photons (Figure A3-5). The transmittance of the TiO₂ without Ta was below 50% in the visible region, which is in line with numerous reports of N-doped TiO₂.^{32,33} Substitution of oxygen with nitrogen introduces new states in the band gap which results in absorption edge tailing to the visible region. Upon Ta-doping, however, the average transmittances in the visible region are increased with a maximum transmittance of ~ 70% for 1.6% Ta-doped in TiO₂.

3.4.2. ALD of Ta₃N₅

TaO_x films were deposited from 50 – 500 ALD cycles at 250 °C. The resultant film thickness increases linearly with the number of ALD cycles (Figure A3-6). The growth rate found to be 0.79 Å/cycle, which is in good agreement with the previous report of the ALD deposition of TaO_x (0.85 Å/cycle).³⁴ The ALD of tantalum nitride using PDMAT and MMH has previously been studied, where an ALD deposition temperature window between 200 - 300 °C was found with a growth rate of ~ 0.3 Å/cycle.³⁵ It has been previously reported that PDMA suffers from thermal decomposition at temperatures above 300 °C, therefore, to avoid the decomposition of the precursor and ensure an ALD process, 280 °C was used as the maximum deposition temperature.^{34,35} Interestingly, while we confirmed an ALD temperature window over 175 to 280 °C, we found a growth rate approximately three times larger with a small temperature dependence. Plots of thickness *vs.* number of ALD cycles are provided in Figure A3-7. From the slope of these plots, growth rates were found to reproducibly vary from 0.86 Å/cycle at 175 °C to 1.04 Å/cycle at 280 °C, as shown in Figure 3–3.^{35,36} These growth rates were confirmed by cross-section SEM



Figure 3–3. Growth rate of TaO_xN_y (green) and TaO_x (pink) as a function of deposition temperature. Also shown are the ratios of atomic concentrations of O/N (purple) as a function of the deposition temperature found from EDS analysis.

measurements of films grown with 1000 ALD cycles at 175 and 280 °C, shown in Figure A3-8. The images indicate a ~ 28 nm difference in film thicknesses which is consistent with the different growth rates displayed in Figure 3–3.

In addition to the growth rate, the temperature affected the composition of the deposited films. The bulk composition of the as-deposited films was analyzed by EDS (Figure A3-9). Silicon with ~ 16 Å SiO₂ was used as the substrate. The Ta and Si signals overlap which prevents accurate determinations of these individual elements. The atomic percentages of nitrogen and oxygen were calculated based on the signal of these two elements and shown in Figure 3–3. Oxygen was detected in all films. We note that only a minimal amount of oxygen can be attributed to the ~ 16 Å SiO₂ substrate since the film thicknesses are ~ 100 nm. Thus, despite the lack of oxygen in either

ALD precursors, and use of high purity nitrogen as a carrier gas, all deposited films are actually TaO_xN_y . Thus, there must be some source of oxygen which we were not able to fully eliminate despite significant efforts to control the ALD atmosphere. Further, as the deposition temperature increases from 200 to 250 °C there is a change in the relative percentage of oxygen and nitrogen; the relative amount of O compared to N decreases from ~ 65 to ~ 25%.



Figure 3–4. a) XPS signals of O 1s, N 1s, and Ta 4f, b) calculated atomic percentages of Ta-N (red) and Ta-O (purple) as a function of deposition temperature.

The surface composition of the as-deposited films was also analyzed by XPS. Fitted spectra are shown in Figure 3–4.a. As the deposition temperature increases, the N1s signal grows and it can only be fitted to a single Ta-N peak. The oxygen signal was fitted to 3 peaks. Two peaks with binding energies > 531 eV were assigned to carbon species, i.e. C-OH and C=O groups. The peak at 529 - 530.5 eV was assigned to the Ta-O group which was correlated to the Ta 4f peak. The

peak positions of Ta 4f_{7/2} and Ta 4f_{5/2} strongly depend on the immediate surrounding atoms, e.g. ~ 26.6 and 28.5 eV for Ta-O and 25.0 eV and 26.9 eV for Ta-N, respectively.³⁷ Therefore to avoid complexity arising from carbon species, the surface atomic percentages of Ta-O and Ta-N were estimated from the Ta 4f peaks (Figure 3–4.b). As it can be seen, at lower temperatures the film is mostly composed of Ta-O groups. On the other hand, at higher deposition temperatures, the Ta-N becomes the dominant composition. This result is in line with EDS analysis discussed earlier. These combined results are also in agreement with the previous study by Ritala *et al.* who studied the deposition of thin films of Ta₃N₅ at temperatures from 200 to 500 °C *via* ALD using TaCl₅ and NH₃ as the reactants.³⁸ Their results showed that the composition of the films were strongly correlated to the deposition temperature and the concentration of oxygen was decreased from 25 to ~ 5% as the deposition temperature increased from 200 to 500 °C.

The composition and growth rates of the films deposited at 280 and 250 °C are similar; since we found 280 °C to be the edge of the ALD temperature window, all the subsequent depositions of TaO_xN_y were performed at 250 °C unless otherwise mentioned. A lack of diffraction peaks in XRD and phonon modes in Raman spectrum of as-deposited films indicate that these films are in fact amorphous TaO_xN_y (Figure A3-10). Therefore, to improve the crystallinity and to modify the composition, they were annealed ammonia. There are three parameters which control the results of annealing; temperature, time and flow rate of ammonia. It was found that the optimum conditions (details discussed surrounding Figure A3-11 to Figure A3-13) to form pure crystalline Ta₃N₅ films from as-deposited films is ammonolysis at 750 °C for 30 min with ammonia flow rate of ≥ 200 mL/min. It is worth noting that both ALD deposited thin films of TaO_x and TaO_xN_y were nitridized to Ta₃N₅ (Figure A3-14) at far more moderate conditions compared to previous reports.^{20,39,40}



Figure 3–5. Plots of absorbance of thin films of Ta_3N_5 on quartz with different thicknesses: 50 nm (blue), 70 nm (orange), 99 nm (red), and 122 nm (green). Inset is the absorbance at 350 nm *vs.* the thickness of the films.

Four TaO_xN_y films of different thicknesses were deposited on quartz followed by ammonolysis at 750 °C for 2 hours. Based on the XRD patterns of the films (Figure A3-15), they can all be unambiguously matched to Ta₃N₅. The thicknesses of Ta₃N₅ films were evaluated *via* both crosssection SEM and SE (Figure A3-16). As shown in Figure A3-16.d, the growth rate found by both methods are in good agreement. However, the growth rate of pure Ta₃N₅, i.e. ALD deposition followed by ammonolysis, was ~ 0.77 Å/cycle while the growth rate of as-deposited films is ~ 1.0 Å/cycle. This discrepancy in the growth rates is due to the fact that the as-deposited films are amorphous TaO_xN_y, whereas ammonolysis transforms the films to crystalline Ta₃N₅ which has 22% smaller molar volume per Ta atom than Ta₂O₅. ^{41,42}

The absorbance of Ta₃N₅ as a function of the thickness is plotted in Figure 3–5 (absorptance, transmittance and reflectance are shown in Figure A3-17). The absorbance was corrected for the substrate using a previously developed model.⁴³ The absorbance scales linearly with the film thickness confirming a linear growth of tantalum nitride by ALD/ammonolysis. The absorption coefficient, α (λ) (cm⁻¹), was calculated from absorbance using the average film thicknesses from SEM and SE (Figure A3-18.a). Ta₃N₅ has two optical transitions, located at ~ 2.10 eV and ~ 2.50 eV. A recent study on optoelectronic properties of Ta₃N₅ suggest that both electronic transitions of Ta₃N₅ are direct.⁴⁴ The corresponding Tauc plots for direct transitions is shown in Figure A3-18b.

To study the PEC performance, ~ 75 nm (1000 cycles) of TaO_xN_y was deposited on 100 nm TTO films with different Ta concentrations, followed by ammonolysis at 750 °C for 30 minutes. Attempts to increase the ammonolysis time to 2 hours resulted in transformation of the anatase-TiO₂ to rutile-TiO₂ in the TTO, based on the XRD patterns of the films, which resulted in an electrode with negligible photocurrent (Figure A3-19). Our initial results produce a photocurrent density of ~ 0.77 mA cm⁻² at 1.23 V *vs*. RHE with an onset photocurrent potential of ~ 0.8 V *vs*. RHE. The PEC performance of these electrodes are strongly correlated to the conductivity of TTO substrates. The photocurrent response of electrodes at 1.23 V *vs*. RHE as a function of Ta concentration are shown in Figure A3-21 (the XRD pattern of the films are shown in Figure A3-20). Interestingly, the observed photocurrents are in good agreement with the conductivity of TTO shown in Figure 3–2.a - i.e. the least resistive TTO substrate, produces the highest photocurrent - suggesting that the performance of these electrodes are controlled by the conductivity of the TTO substrate. This performance falls short of the recent report by Li and coworkers,²⁴ who reported a photocurrent density of ~ 12.1 mA cm⁻² at 1.23 V *vs*. RHE with a

photocurrent onset potential of ~ 0.7 V *vs.* RHE for the electrode prepared on Ta foil which was nitridized under ammonia at 950 °C for 6 hrs. Van de Krol *et al* also recently studied the formation of Ta₃N₅ as a function ammonolysis conditions on Pt foil.¹⁴ The maximum photocurrent density of ~ 1.1 mA cm⁻² at 1.23 V *vs.* RHE with an onset photocurrent potential of ~ 0.9 V *vs.* RHE was found for the Ta₃N₅ film prepared at 800 °C 10 hrs after IrO₂ treatment. To the best of our knowledge, however, this is the first report of PEC water oxidation of Ta₃N₅ on any TCO (Figure 3–6).



Figure 3–6. PEC performance of CoPi modified Ta_3N_5 (~ 75 nm) on TTO with 1.6% Ta concentration under 1 sun illumination. The inset is the photograph of the working electrode.

Finally, since we have not yet eliminated the ammonolysis step in the synthesis, we compared the behavior of the TaO_xN_y deposited films to TaO_x . 40 nm of TaO_x was deposited on the best TTO (1.6% Ta) followed by ammonolysis at 750 °C for 30 minutes. The transmittance/reflectance

spectrum of the corresponding films are compared to that of TaO_xN_y -derived film in Figure A3-22. The TaO_x -derived film is colorless with a take-off transmittance at ~ 450 nm. On the other hand, TaO_xN_y -derived film is orange with a take-off transmittance at ~ 590 nm which corresponds to the known band gap of Ta_3N_5 , i.e. 2.1 eV, discussed above. The PEC performance of these electrodes are compared in Figure A3-23. The TaO_x derived film shows negligible photocurrent superimposed on a large dark current. Therefore, it can be concluded that the TaO_x -derived films require harsher nitridization conditions (higher temperature and longer duration) where the TTO is not chemically stable.

3.5. Conclusions

The realization of photoactive Ta₃N₅ films on a TCO electrode was demonstrated for the first time. This required two breakthroughs. First, we established the ALD of TTO and found that it is structurally and chemically stable (unlike conventional TCO materials including FTO, ITO and AZO) under the reducing atmosphere employed (ammonolysis at 750 °C for 30 min), and can therefore be used as a conductive transparent layer for tantalum nitride electrodes. The TTO films were not able to withstand the harsher nitridation conditions which must be employed for Ta₃N₅ films produced from TaO_x, however, which is the synthetic route of all prior examples of Ta₃N₅ photoelectrodes. Therefore, the second necessary breakthrough consisted of the direct deposition of TaO_xN_y films *via* ALD which can be crystallized and completely converted to Ta₃N₅ under sufficiently milder ammonolysis conditions to maintain the TCO properties of TTO. The resultant Ta₃N₅ films on TTO produced promising solar water oxidation performance, especially considering the films are quite thin and not yet optimized. We found that the performance of the photoelectrodes correlated to the conductivity of the TCO. Thus, it would beneficial to utilize stateof-the-art TCOs such as FTO. Since these are not stable under even the mildest ammonolysis procedures utilized here, it would clearly be advantageous to directly deposit crystalline Ta_3N_5 films under sufficiently mild conditions on a TCO, which do not require a subsequent annealing (thus ammonolysis) step. While we are actively working on such an ideal synthetic method, the results reported herein represent a significant step towards realizing a high-efficiency solar water oxidation electrode which can be employed in a tandem configuration.

APPENDIX



Figure A3-1. EDS spectrum of Ta-doped TiO₂ as a function of ratio of cycles of TaO_x to TiO₂, a) 1:150, b) 1:100, and c) 1:50. d) Atomic percentage of Ta as a function of ratio of cycles of TaO_x:TiO₂.



Figure A3-2. Comparison of atomic percentage of Ta as a function of ratio of cycles of TaO_x/TiO_2 found by EDS and XPS.



Figure A3-3. XPS spectra of Ta-doped TiO₂ as a function of Ta% doping, a) as deposited, b) after annealing in ammonia at 750 °C for 30 min.

The as-deposited films are only comprised of Ti, O and, Ta. After annealing in ammonia, nitrogen signal is also observed. The main features of XPS spectra for the Ta-doped TiO₂ would be better captured by analyzing each individual elements before and after annealing in ammonia.

Ti: The Ti main peak before and after annealing in ammonia were located at the same position. Upon annealing in ammonia, however, two new peaks associated to Ti-O-N (blue) and Ti-N (green peak) groups were appeared which confirms that besides Ta, N is also doped into TiO₂.^{45–47}

O: As expected, oxygen peak (metal-oxygen bond) at 29 - 30 eV was not affected by annealing in ammonia, however, the atomic percentage of oxygen was changed by both annealing in ammonia and the atomic percentage of Ta. The other oxygen peaks at higher binding energies were assigned to C=O and C-OH groups.

N: As it can be seen, the as-deposited films did not have any nitrogen, however, after annealing in ammonia the nitrogen signal was emerged. At high concentration of Ta, there is a small shoulder (orange peak), which further indicates the formation of a different type metal-N bonding.

Ta: Before annealing in ammonia, there was only one type of Ta present which can be associated to Ta-O groups. Upon annealing in ammonia, however, Ta signals became broadened which is an indication of doping of Ta into the structure with a range of atomic interaction with its neighbors. The Ta signal for the film with high concentration of Ta, i.e. 5% Ta, could not be fitted to one peak, and it was fitted to two peaks. Therefore, there are two types of Ta groups. This observation is in line with the extra N peak for the film with high concentration of Ta. Then it was hypothesized that at high Ta% doping, TaN_x would segregate off from TiO₂ and form a separate phase.

The atomic percentages of Ta, Ti, O and N were calculated using the following equation:

% X = 100 ×
$$(\frac{S_X}{S_{Ta} + S_{Ti} + S_O + S_N})$$
 A3-1

The S_x is the normalized peak area associated to each element. For normalization, the raw peak area was divided to the sensitivity factor. The sensitivity factor of Ti, Ta, N, and O are 52.013, 75.608, 12.231, and 18.643, respectively.



Figure A3-4. a) XRD and b) calculated cell volume of TiO₂ as a function of Ta% doping. Undoped TiO₂ (orange). 5.0% Ta \pm 0.32 (pink), 2.25% Ta \pm 0.016 (cyan), 1.67% Ta \pm 0.11 (red), and 1.25% Ta \pm 0.08 (black).

The diffraction patterns were unambiguously matched to anatase TiO_2 . Since the ionic radii of Ta^{5+} is slightly larger than $Ti^{4+}(0.64 \text{ vs. } 0.60)$,⁴⁸ therefore, upon doping TiO_2 with Ta the unit cell would slightly expand. The films with low and high Ta% doping as well as un-doped samples have almost the same peak positions. This observation suggests that these two films have the lowest Ta incorporation. The slight peak shift of lightly doped film, 1.25% Ta doping, can be ascribed to the low concentration of Ta to make a detectable alteration in anatase structure. On the other hand, the heavily doped film, 5% Ta doping, has a high concentration of Ta which makes it energetically more favorable to form a separate phase of tantalum (oxy)nitride. This is consistent with the extra N and Ta peaks observed in XPS (Figure A3-3). On the other hand, for the films with Ta% doping in between, however, the diffraction peaks are shifted to the lower angels. GSAS^{49,50} was used to

calculate the cell parameters. The calculated volumes *vs*. Ta% doping level are shown in Figure A3-4.



Figure A3-5. a) reflectance and corrected transmittance of TTO as a function of Ta concentration. Films were annealed in ammonia at 750 °C for 30 min. 200/1 (pink), 150/1 (cyan), 100/1 (red), 50/1 (black), and un-doped TiO₂ (orange).



Figure A3-6. Thickness of TaO_x *vs.* the number of cycles deposited at 250 °C.



Figure A3-7. Thickness of TaO_xN_y vs. number of cycles deposited at a) 175, b) 200, c) 250, and d) 280 °C.



Figure A3-8. Cross-section SEM of 1000 cycles of TaO_xN_y deposited at a) 280 and b) 175 °C.



Figure A3-9. EDS spectrum of as-deposited TaO_xN_y as a function of deposition temperature. Silicon wafer with 16 Å native SiO₂ was used as the substrate. Ta main peak is buried under large Si signal.



Figure A3-10. a) XRD and b) Raman scattering of 100 nm TaO_xN_y deposited on FTO at 250 °C. The red curve represent the reference spectrum of crystalline Ta_3N_5 .



Figure A3-11. The XRD of TaO_xN_y after annealing in ammonia at different temperature for 10 hours. The vertical dashed lines represent the Bragg positions of Ta_3N_5 with PDF number of 01-089-5200.

To eliminate the effect of flow rate, high throughput ammonia (~ 500 SCCM) was used and the annealing temperature and duration were optimized. Based on the XRD, the minimum temperature required to form pure phase Ta_3N_5 was found to be 750 °C.



Figure A3-12. a) The XRD pattern of TaO_xN_y deposited film after annealing at 750 °C for different durations. The vertical dashed lines represent Bragg positions of Ta_3N_5 with PDF number of 01-089-5200.

Optimization of annealing duration was done by soaking temperature at 750 °C for different durations from 10 hours to 30 minutes. Evidently, the formation of pure Ta_3N_5 is completed after 30 minutes ammonolysis. However, increasing the annealing duration, results in a more well-defined and sharper peaks (more crystalline films). All the following films were annealed for 2 hours unless otherwise mentioned.

4



Figure A3-13. XRD of TaO_xN_y deposited film after ammonolysis at 750 °C for 2 hours as a function of ammonia flow rate. The vertical dotted lines represent the Bragg positions of Ta_3N_5 with PDF number of 01-089-5200.

The effect of the ammonia flow rate on crystallinity and phase purity of the films were studied by annealing at 750 °C for 2 hours with different flow rate of ammonia. From Figure A3-13, films annealed at low flow rate of ammonia, e.g. 50 and 100 mL min⁻¹, had poor crystallinity and were comprised of impure phases (possibly TaON). On the other hand, for the flow rate more than 200 mL min⁻¹, the observed peaks were sharper (more crystalline) and Ta₃N₅ was the only detectable phase. This observation is consistent with previous study, where thin films of TaO_x and Ta₃N₅ were prepared on Ta foil. It was found that at lower flow rates of ammonia the formation of TaON is more favorable where at higher flow rates only Ta₃N₅ films are observed.³⁷ Here we found that the optimum ammonolysis conditions to form pure and crystalline Ta₃N₅, is annealing at 750 °C for 2 hours with flow rate of ammonia of ≥ 200 mL min⁻¹.



Figure A3-14. XRD of 50 nm ALD deposited TaO_xN_y (green) and TaO_x (gray) films after ammonolysis at 750 °C for 30 minutes as a function. The vertical dotted lines represent the Bragg positions of Ta_3N_5 with PDF number of 01-089-5200.

The XRD of the ALD deposited TaO_x and TaO_xN_y are compared in Figure A3-14. As it can be seen the ALD deposited TaO_x were completely nitridized to Ta_3N_5 after ammonolysis at the same conditions of 750 °C for 30 minutes.



Figure A3-15. XRD of Ta_3N_5 with different thickness after ammonolysis. The film thicknesses are: 50 nm (blue), 70 nm (orange), 99 nm (maroon), and 122 nm (green). The vertical dashed lines represent Bragg positions for Ta_3N_5 with PDF number of 01-089-5200.



Figure A3-16. a) Cross-section SEM image of Ta_3N_5 different number of cycles with the scale bar of 100 nm, b) growth rate of pure Ta_3N_5 found by SE and cross-section SEM.



Figure A3-17. a) absorptance, b) % transmittance, and c) % reflectance of thin films of Ta_3N_5 as a function of thickness, 50 nm (blue), 70 nm (orange), 99 nm (red), and 122 nm (green).



Figure A3-18. a) absorption coefficient of Ta_3N_5 as a function of wavelength and b) Tauc plots for direct transitions.



Figure A3-19. XRD of the films as a function of ammonolysis duration at 750 °C, 2 hours (red), and 30 minutes. The dashed line are the Bragg positions of Ta_3N_5 (green), anatase TiO_2 (blue), rutile TiO_2 (pink).



Figure A3-20. a) XRD of 40 nm of Ta_3N_5 on TTO with different Ta concentration after annealing in ammonia at 750 °C for 30 min. The vertical dashed lines represent the Bragg positions of Ta_3N_5 with PDF number of 01-086-1155.



Figure A3-21. The photocurrent of 70 nm Ta_3N_5 on TTO at 1.23 V vs. RHE as a function of Ta percentage in TTO.



Figure A3-22. Transmittance and reflectance spectrum of electrodes with 5% Ta-doped $TiO_2 \sim 40$ nm either TaO_xN_y ALD-deposited (Orange) or TaO_x ALD-deposited (gray) after ammonolysis at 750 °C for 30 minutes. The solid black line represents the transmittance of quartz.



Figure A3-23. PEC performance of TaN_x (orange) or TaO_x (gray) on 5% Ta-doped TiO₂ (100nm)/quartz after annealing in ammonia at 750 °C for 30 min level under 1 sun illumination and 0.5 M K₂HPO₄ phosphate solution with pH = 13. Note: prior to PEC water oxidation measurements, for all the electrodes, CoPi was photo-electrodeposited at 1.06 V *vs.* RHE for 60s.

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Chapter 4:

Direct Deposition of Ta₃N₅ via High-

Temperature ALD

4.1. Abstract

In this project the direct deposition of crystalline Ta₃N₅ on FTO substrate *via* a custom-built ALD system is studied. A combination of TaCl₅ (Ta-precursor) and with ammonia (N-source) were sequentially pulsed into the reactor with the substrate heated to 550 °C to deposit compact and thin films of Ta₃N₅ with controllable thicknesses on FTO substrates. Importantly, it is shown that the FTO is chemically and structurally stable under the reducing conditions of ammonia at 550 °C. This is a significant progress as it allows to study the fundamental characteristics of Ta₃N₅ independently of the conductivity of the substrate. These electrodes produced a photocurrent onset potential of ~ 0.3 V *vs*. RHE and a maximum photocurrent of ~ 2.4 mA cm⁻². In addition, the PEC characterizations as a function of film thickness and illumination direction (through the electrolyte and substrate) reveal that the PEC performance of Ta₃N₅ is controlled by the limited hole diffusion length (<100 nm).

4.2. Introduction

Tantalum nitride (Ta₃N₅) is one of the promising semiconducting materials for photoelectrochemical (PEC) water oxidations and has attracted a lot of attention in the past few year. State of the art Ta₃N₅ photoanodes for PEC water oxidation were introduced by Li *et al.*¹ with a photocurrent density approaching the theoretical limit of ~ 12.5 mA cm⁻². The synthesis of Ta₃N₅ electrodes commonly start with the oxidation of Ta-substrate *via* electrochemical anodization or simply by heating in air to oxidize the top Ta layer to nanostructured or planar tantalum oxide films, respectively.^{1–5} Subsequently, the oxidized sample is nitridized in a flow of ammonia at elevated temperatures (850 - 1000 °C) for a prolonged period of time (2 - 15 hours). The Ta-substrate serves as the source of Ta, the conductive layer to collect the majority charge

carriers necessary to fabricate electrode, and the substrate. Although this method is simple and resulted in the best performing Ta₃N₅ photoanodes,^{1,2} from a synthetic point of view however, multiple drawbacks make this method unsuitable to realize efficient photoelectrodes; specifically, this method: (1) is highly energy intensive, (2) produces a sizable quantity of chemical waste, (3) provides highly reducing conditions which limit Ta₃N₅ to be only compatible with Ta-substrate or Nobel metals like Pt.^{4,5} (4) precludes its application in the tandem cell configuration as Ta or other metal substrates are not transparent to the sub-bandgap photons, (5) results in the formation of electronically resistive phases at the Ta_3N_5/Ta junction which further limits the electron collection efficiency. In addition, Ta as a substrate becomes very brittle after heating in ammonia which makes the post-annealing electrode processing very challenging. For example, Jaramillo et al.³ studied the structure and phase transformation of tantalum oxide to tantalum nitride films on various substrates including Ta foil and fused silica. They showed that the films on fused silica were single phase Ta₃N₅, but that the films prepared on Ta substrates were comprised of impurity phases and upon rising the ammonolysis temperature, the formation of Ta₂N and Ta₅N₆ phases were favored.³ These observations, along with the depth profiling GIXS analysis, confirmed that N-poor phases are exclusively formed at the $Ta_3N_5|Ta$ junction.^{3–6} Domen *et al.*² showed that the ammonolysis of anodized Ta-substrate results in the formation of N-poor phases, e.g. Ta₅N₆, which limits the electron collection efficiency at the back contact. Interestingly, doping with barium suppressed the formation of interfacial Ta₅N₆ resistive layer, which substantially improved the PEC water oxidation performance of the electrode. Importantly, these examples highlights the complexity of the synthesis of pure Ta₃N₅ which requires a precise control over ammonolysis temperature, atmosphere, and reaction duration.^{7,8} For example, Henderson and Hector⁷ studied the structural and compositional evolution of Ta_3N_5 from amorphous tantalum oxide as a function of ammonolysis temperature (from 680 to 900 °C) and duration (from 8h to 120h). Their results are quite remarkable, showing that regardless of ammonolysis conditions (temperature or duration), all samples contained oxygen impurities - even after annealing at 900 °C for 120 h. In addition, Terao⁸ showed that at elevated temperatures (>1000 °C) Ta₃N₅ has a dynamic structure and composition where nitrogen is successively pulled out of the structure upon increasing temperature in vacuum – this is accompanied by the concomitant reduction of $Ta^{(V)}$ – which subsequently results in the formation of various phases of tantalum nitride. Therefore, it is highly beneficial to directly synthesize crystalline Ta₃N₅ films at lower temperatures from an oxygen-free precursors and atmosphere by eliminating the ammonolysis step. This approach is additionally beneficial as it allows to integrate Ta_3N_5 with different materials, e.g. Ta_3N_5 on various TCO, and to study its structure-function relationship. The vacuum deposition techniques such as atomic layer deposition (ALD) or chemical vapor deposition (CVD) provide an oxygen-free atmosphere suitable to synthesize none-oxide materials with a controllable thickness and composition. A series of previous studies for the deposition of tantalum nitride using ALD or CVD are listed in Table 4-1. Briefly, these studies indicates that (1) tantalum halides, e.g. TaCl₅ and TaBr₅, coupled with ammonia are commonly used as the tantalum and nitrogen sources to directly deposit crystalline Ta_3N_5 thin films. (2) The near atmospheric pressure CVD synthesis of Ta_3N_5 from these sources require a high deposition temperature of \geq 900 °C, while the low-pressure CVD or ALD deposition can be done at considerably lower temperatures in the range of 400 - 500 °C.

Inspired by these reports, we studied the direct deposition of crystalline Ta_3N_5 on FTO substrates *via* a custom-built and fully automated ALD system capable of operating at elevated temperatures with a maximum temperature of 640 °C. Furthermore, we showed that this technique provides a suitable method to integrate Ta_3N_5 on a rather chemically unstable substrate like FTO in reducing

atmospheres of ammonia. Subsequently, the photoelectrochemical performance of $Ta_3N_5|FTO$ electrodes with various thicknesses as a function of illumination direction were explored, showing that the PEC performance of Ta_3N_5 is controlled by the limited diffusion length of holes (10s of nm).

Ta- Source	N- Source	Method	Temp. (°C)	Substrate	Characterization	Crystalline or Amorphous	Growth Rate	Ref.
TaCl ₅	$N_2^{(plasma)}$	PECVD	715	Si(100)	TEM/ SAED	Microcrystalline	NA	[9]
TaCl ₅	NH ₃	CVD (400 Torr)	900-1300	Fused silica	Electron Diffraction, Conductivity	Crystalline (Ta ₃ N ₅)	30 nm/min	[10]
PDMAT	NH ₃	CVD	200	Silicon, Glass	XPS, XRD, TEM, RBS	Amorphous	200 nm/min	[11]
PDMAT	NH ₃	CVD	200-400	Various	RBS: (N/Ta) = 1.7	Amorphous	NA	[12]
TaBr ₅	NH ₃	CVD 0.96 Torr	500	Si, SiO ₂	RBS, AFM, XRD, AES, XPS	Crystalline (Ta ₃ N ₅)	3-7.5 nm/min	[13]
Ta(NEt ₂) ₅	NA	LPCVD	>500	Si(100)	XRD	NA	NA	[14]
TaBr ₅	NH ₃	ALD	500	Soda lime	NA	NA	NA	[15]
TaF5	H ₂ /NH ₃	ALD	200	NA	Amorphous	NA	0.05 nm/cycle	[16]
TaCl ₅	NH ₃	ALD	400-500	Soda lime glass, ITO	XRD, Conductivity	Crystalline (Ta ₃ N ₅)	0.025 nm/cycle	[17]
TaCl ₅	NH ₃	ALD	500	Soda glass	XRD	Crystalline (Ta ₃ N ₅)	~ 0.02 nm/cycle	[18]
PDMAT	MMH	ALD	175-280	SiO ₂ , Al, FTO	XRD, Raman, XPS, EDS	Amorphous	0.07-0.1 nm/cycle	[19]
PDMAT	MMH/NH ₃	ALD	200-375	Si(100)	RBS, Conductivity	NA	0.02-0.1 nm/cycle	[20]

Table 4-1. The summary of the experimental conditions and techniques utilized for deposition of thin film of tantalum nitride.

1) NA: Not Assigned; 2) CVD: Chemical vapor deposition; PECVD: Plasma enhanced chemical vapor deposition; LPCVD: Low pressure chemical vapor Deposition; ALD: Atomic Layer Deposition; PDMAT: Pentakis(dimethylamino)tantalum(V); TEM: Transmission electron microscopy; SAED: Selected area electron diffraction; RBS: Rutherford backscattering spectrometry; MMH: Monomethyl Hydrazine. 3) We note that in these studies a generic term of tantalum nitride as oppose to the exact composition of material is used. In addition, only a few of them fully characterized the material and some of just gust the composition/crystalline phase based on the color of the films.

4.3. Experimental

4.3.1. Instrumentation

4.3.1.1 Atomic Layer Deposition

Figure 4–1 shows the building blocks of a typical ALD instrument. As shown, it is comprised of three main blocks of: software, electronic box, and the ALD reactor. In following, these components and their functionality will be briefly discussed.



Figure 4–1. The building blocks of an atomic layer deposition system.

4.3.1.2 Software

The ALD is comprised of several different components such as heaters, valves, gas flow controller, and vacuum stage which all require a continuous monitoring and controlling. In addition, the ALD procedure is a well-timed process that is comprised of sequential pulse of precursors into the reactor in a timely fashion (see Figure 1–13). In some cases it may require a complex sequence of pulses of precursors. Moreover, depending on the deposition rate and the desired thickness, the ALD deposition can be a long process. These requirements, thus, emphasize the importance of a sophisticated program that not only provides a remote access to each component of the instrument but also it produces reproducible pulses and steps in each ALD cycle. For this purpose, Labview programming software was used. The screenshot of the program in action is shown in Figure A4-1. This program allows to control the sequence and the duration of the precursor pulses (with tens of

ms resolution) and flow rate of the carrier gas (with a resolution of \pm 5 SCCM¹). This program provides a remote access and controls over 5 ALD valves, 1 vacuum valve, 11 heaters, 1 mass flow controller, and 1 pressure sensor.

4.3.1.3 Electronic Box

The electronic box is the heart of the ALD instrument. As shown in Figure 4–1, the electronic box bridges the physical part of the ALD reactor to the computer and the program that controls it. Basically, it reads the physical status of each components of the ALD in terms of voltage (analog) and convert them into digital signals which can then be processed by the software. Subsequently, it converts the digital commands from the computer into the analog output signals (voltage) to set the instrument at the specified condition. The electronic box is comprised of various components (Figure A4-2), each with specific functionality. The wiring diagram of these components as well as the function of each component are summarized following Figure A4-3.

4.3.1.4 Carrier Gas Purification

One of the advantage of ALD is that it can be utilized to synthesize non-oxide and air-sensitive materials. In addition, most of the precursors used in ALD are organometallic complexes with extreme sensitivity to water and/or oxygen. It is thus important to remove any trace of oxygen impurity from the nitrogen as the carrier gas. Here, we used three scrubbers in series to remove any oxygen in forms of water and molecular oxygen. The first scrubber was a glass tube $(1/4" \times 8")$ which was filled with quartz wool and P₂O₅ (which vigorously react with water) and the second

¹ Standard cubic centimeter per minutes

scrubber was made out Pyrex $(1.5" \times 6")$ was filled with activated molecular sieve (3 Å pellets 1.6 mm, Sigma Aldrich). These two scrubbers were used to remove water from. The last scrubber $(1.5" \times 6")$ was made out Pyrex and was filled with metallic copper powder mixed with quartz wool (Figure A4-4). This scrubber was heated to 300 - 400 °C with a band heater (from outside). At elevated temperature, the metallic copper reacts with the residual oxygen and forms copper oxide which consequently removes oxygen from the flowing gas. As shown in Figure A4-4, over time the color of metallic copper was turned to black which indicates that the residual oxygen in the nitrogen line is successfully removed by reacting with copper.

4.3.1.5 Inlet of the Reactor: ALD Valves and Configuration

The schematic representation of the inlet of the ALD reactor is shown in Figure 4–2. All the connection are VCR-type fitting which offers a leak-tight metal to metal seal. To seal the VCR assembly, the 316L stainless steel VCR face seal fitting (Silver Plated Gasket, SS-4-VCR-2) is used. The tubes, fittings, connectors, body of the valves, and the body of the mass flow controller (MFC) are all constructed from stainless steel 316. The tubes and fitting are ¹/₄" in diameter except the inlet and outlet of the reactor that are ¹/₂" and 1", respectively. As depicted in Figure 4–2, two MFCs (Omega, FMA5510A) are used for nitrogen (carrier gas) and ammonia (co-reactant). The MFC for nitrogen has a flow range of 10 - 200 SCCM. The inlet of the MFC for ammonia is directly connected to the ammonia cylinder with a pressure set to 40 PSI¹. A ¹/₄" stainless tube was fashioned in the shape of a spring and it is installed between the MFC and ALD valve (this part

¹ Pounds per square inch

act as a reservoir for ammonia to provide a constant dose of ammonia throughout the ALD process). Experimentally, it was observed that even for a short pulse (0.1 s) of ammonia and long



Figure 4–2. The schematic representation of the Inlet of the ALD reactor.

-purge time (70 s), ammonia diffuses into the carrier gas and find its way into the Ta-precursor cylinder and react with tantalum inside the tantalum cylinder. In order to circumvent this issue, the ammonia line was isolated from the carrier gas and tantalum precursor line *via* a 2-way valve (labeled as the N₂ valve in Figure 4–2). The tantalum precursor was kept in a 50 mL stainless steel 316 cylinder and the cylinder was heated with a flexible heating jacket equipped with a J-type

thermocouple. The tube line from the Ta-precursor to the inlet of the reactor (except for the ammonia line) is wrapped with a flexible band heater and it is thermally insulated from the surroundings. The temperature of this line is set to 170 °C which is monitored by a K-type thermocouple installed on the N₂ valve. For pulsing the reactant, 2-way valves (Swagelok, stainless steel bellows sealed valve, SS-4BK-V51-1C) equipped with solenoid valves (24 V DC, MAC Valve, INC., 34C-ABA-GDFC-1KT) were utilized.

4.3.1.6 Outlet of the Reactor: Vacuum Line and Valves

The Alcatel 2005I (purchased from IdealVac) charged with perfluoropolyether (PFPE, Fomblin 25/6) is used as the vacuum pump. This pump provides a base pressure of ~ 2×10^{-3} Torr. To monitor the pressure of the reactor a vacuum gauge (Edwards Linear Convection Vacuum Gauge, APGX-H-NW16) is installed at the outlet of the reactor. A poppet valve (Genesis Stainless Steel, Model # 051207-20) equipped with a solenoid valve (120 V AC, MAC Valve, INC., 34B-AAA-GAAA-1KC) is used to pump/vent the ALD reactor. Since ammonia is highly reactive and corrosive which cause shortening the lifetime of the vacuum pump, a Metal Wool Foreline Trap made of stainless steel (Kurt J. Lesker, TAR4CS100QF) was installed just before the inlet of the vacuum pump. This trap was charged with copper wool (react with ammonia) to remove ammonia from the effluent gas stream.

4.3.1.7 The ALD Reactor

The ALD reactor is where the chemical reaction takes place. In terms of chemistry, this is the most important part of the ALD system which defines the purity and the quality of the final product. In addition to the reactor configuration, the material used in its construction is also an important aspects of the reactor. The latter becomes highly important when the ALD deposition conditions

are reactive. In this study, we designed, build, and examined three different ALD reactors. The schematic cross-section pictures of these reactors are shown in Figure 4–3 and each one of them are briefly introduced below.



Figure 4–3. The schematic representation of different generation of ALD reactors: a) 1^{st} , b) 2^{nd} , and c) 3^{rd} generation. The body of all generations is constructed from stainless steel 316.

One of the advantage of the commercially available ALD reactor is that loading and unloading of the sample is fairly easy and quick. It is an important aspect of ALD as it minimizes the time required to transfer the substrate which further minimized the possibility of surface contamination. On the other hand, one of the limitation of these types of reactors is the necessity of the specially designed and robust O-rings for high-temperature applications. These O-rings have a limited temperature range and are not stable at temperatures beyond 300 °C. To get around this problem for high-temperature ALD reactor, the heated area must be separated from the loading section.

The 1st Generation ALD reactor is shown in Figure 4–3.a. This generation is a vertically aligned cylindrical reactor with a branch pointing away at the midway. The inlet is located at the top and the outlet of the reactor connected to vacuum pump is located at the bottom. The inlet of the reactor is equipped with a custom-designed shower head to ensure a uniform flow of carrier gas and precursors over the substrate. This is a hot-wall reactor and is constructed from stainless steel 316. The main body of the reactor is heated with flexible band heaters and its temperature is probed by a K-type thermocouple installed on the outer wall. To maintain the temperature, the heated area is thermally isolated with fiberglass insulation sheets. The rectangular branch is designed to separate the heated area from the loading area (this is the place where the O-ring is installed). This area is not thermally insulated and is cooled in air. We note that when the temperature of the reactor is set at 650 °C, the measured temperature in vicinity of the O-ring reaches ~ 200 °C (this measurement was done after ~ 5 hours of temperature stabilization). The pressure of the reactor remained constant during continuous heating for 5 hours which further indicates that the O-ring is stable under this extreme operating condition. For this reactor we used three different sample holders constructed from stainless steel 316, Al (with a maximum temperature of 550 °C), and quartz. The first two holders were fabricated with a screen (~ 1 cm⁻² holes) welded to the bottom of a ring shape holder where the FTO substrates (1.0 cm \times 1.0 cm) were placed on the screen. In this configuration the flow of gas is perpendicular to the substrate. For the quartz sample holder, two parallel racks with a distance of 2.5 cm were welded to the bottom of a quartz ring and the FTO substrates (cut into small slides with the dimensions of $1.0 - 5.0 \text{ cm} \times 1.2 \text{ cm}$ (length \times height)) were mounted on the racks (with 0.3 cm space between the substrates). For this sample holder, the

FTO substrates are oriented parallel to the gas flow (see Figure 4–3.a). Figure 4–4.a shows the EDS spectrum of the film deposited with this reactor. As shown in addition to Ta, FTO (SnO₂), glass (SiO₂) signals, and a well-resolved peak attributed to iron is clearly detectable. The photograph of the film shows that the as-deposited film has an orange/green color which upon annealing in air at 750 °C it turns into a bright orange and the Raman spectrum of the as-deposited film matches to the crystalline hematite (α -Fe₂O₃).

$$3 \operatorname{TaCl}_{5(g)} + 5 \operatorname{NH}_{3(g)} \rightarrow \operatorname{Ta}_{3} \operatorname{N}_{5(s)} + 15 \operatorname{HCl}_{(g)}$$
 4-1

These observations are better understood by considering the chemical reaction between tantalum chloride and ammonia. As shown in eq. 4-1, the byproduct of this reaction is HCl. As the result, at elevated deposition temperature iron is etched from the reactor wall and is deposited on the substrate. In order to circumvent this issue the 2^{nd} generation reactor was designed.



Figure 4–4. The EDS spectra showing the composition of the films deposited on FTO substrate at 500 °C with different generations of the ALD reactor; a) 1^{st} , b) 2^{nd} , and c) 3^{rd} generation. The inset

in the figure (a) shows the photograph of the as-deposited film along with the film annealed in air at 750 °C for 1 minutes; also shown is the comparison of the Raman spectra of the as-deposited film to the hematite (α -Fe₂O₃) film.²¹ The inset in the Figure (c) shows the photograph of the film deposited from 3rd generation reactor on the custom-built substrate heater.

The second generation ALD reactor is a modified version of the 1st generation where its interior composition is changed to quartz which has a neutral composition (Figure 4–3.b). The main body of the reactor is constructed from stainless steel 316, but to change the interior composition a quartz tube is installed inside. Unlike the 1st generation, this reactor is a horizontal tube reactor. Similar to the 1st generation, this reactor is heated with high-temperature flexible band heaters from outside and the heated area is separated from the area where the O-ring is installed (at the outlet of the reactor). The outlet (vacuum) of the reactor is designed so it can be easily and quickly attached/removed and thus it additionally serves as loading section. The sample holder is constructed from pyrex (with the softening point of ~ 820 °C) and it is bend to maximize the effective contact of the flowing gas with the FTO substrate. After several trials and investigating various deposition conditions, no sign of color change was detected. However, it was reproducibly observed that a white powder (more like dust with no adhesion to the substrate which can be easily washed off with water) was deposited on the back side of the FTO substrate. We speculate that this powder is ammonium chloride which is the side product of the ALD. The EDS spectrum of the substrate after deposition with this reactor is shown in Figure 4–4.b. This spectrum is similar to that of the bare FTO substrate which further indicates that nothing is deposited.

The 3rd generation of ALD reactor has a similar configuration as the first generation and it is constructed from stainless steel 316 (Figure 4–3.c). Unlike the first two generations, however, this

generation is a hot-substrate and cold-wall reactor where only substrate is heated and the reactor wall is left uninsulated letting the heat to skip the system. As a result, the reactor wall is cooler than the substrate. Accordingly, the sample holder was modified to accommodate a hightemperature substrate heater (Chromalox, Chrome Steel Sheath) to specifically heat the substrate (see inset of Figure 4–4.c). In this configuration, thereby, the gas flow is perpendicular to the substrate. The EDS spectrum along with the photograph of the film deposited on FTO substrate from this reactor is shown Figure 4–4c. As depicted, all the signals are assigned to the FTO substrate and tantalum nitride deposited film. Importantly, no signature of iron or any other components of the stainless steel is not detected. This reactor configuration was then used to study the deposition of crystalline Ta_3N_5 .

4.3.2. Deposition of Ta₃N₅ Film

The deposition of Ta₃N₅ was carried out in a custom built ALD system described in previous section. The films were deposited on FTO (F-doped tin oxide) coated glass substrates (Tech 15, Hartford Glass Co) with the softening point of ~ 600 °C. The FTO-glass substrates were cut into hexagonal pieces with the diameter of ~ 5.2 cm. Prior to deposition, substrates were cleaned twice by sequential sonication in soap (FisherbrandTM SparkleenTM 1 Detergent), water, and isopropyl alcohol for 15 minutes each (with the total time of 90 minutes). Prior to loading into the instrument, the FTO substrate was dried in a gentle flow of nitrogen. The Ta₃N₅ films were deposited *via* sequential pulses of TaCl₅ (Alfa Aesar, 99.9%) as the source of tantalum and anhydrous ammonia (Airgas) as the co-reactant. The purified N₂ (99.9%) with the flow rate of 20 SCCM was used as the carrier gas. The TaCl₅ cylinder was kept at 120 °C and it was pulsed for 2 s which was followed by 15 s waiting/purging under the flow of nitrogen. Prior to pulsing ammonia the nitrogen line is

closed. This step is required to avoid contamination of carrier gas or even TaCl₅ precursor. After 5 s wait time, ammonia was pulsed for 0.1 s. This step is followed by a 10 s waiting time while the nitrogen line is closed and an additional 15 s purging time while the nitrogen line is in open position. The schematic representation of this recipe is shown in Figure A4-5. A range of substrate temperature from 450 to 550 °C were investigated. The temperature of the substrate heater was externally calibrated with a secondary thermocouple (digital meter model 6802II equipped with a K-type thermocouple) and the calibration points can be found in Table A4-1. The measured temperature by both thermocouple are within \pm 10 °C and throughout this chapter we referred to the set point temperature. To study the stability of FTO under the deposition conditions of tantalum nitride we annealed the FTO|glass substrate at 550 °C under a continuous flow of ammonia with a flow rate of ~ 100 SCCM for 5 hours in a tube furnace equipped with quartz tube (2.5" ×18"). We note that this annealing condition is far more extreme than the deposition conditions (as ammonia is contentiously flowing and is not diluted with N₂) thus it represent the upper limits for the stability FTO.

4.3.3. Film Characterization

The morphology and thickness of the deposited films were examined using scanning electron microscopy (SEM, Carl Zeiss Auriga, Dual Column FIB-SEM). For the cross-section analysis the films were coated with 5-10 nm tungsten conductive layer *via* sputtering (Denton Vacuum Desk II sputter coater). Image J was utilized to analyze the thickness of the films from cross-section SEM. The composition of the deposited films were evaluated *via* energy dispersive spectroscopy (CARL ZEISS EVO LS 25) equipped with Ametek-EDAX Apollo X detector and TEAD EDS software. For simplicity of comparison, the spectrum for each sample was normalized to its total

area. The Raman spectrum were collected *via* inVia Raman Microscope (Renishaw) equipped with 45 W cobalt DPSS laser (532 nm line) and a 100× microscope. Prior to Raman measurements, the instrument was quickly calibrated against internal silicon standard. For simplicity of comparison the Raman spectra were further normalized to the total area. The crystallinity and phase purity of the films were evaluated *via* X-ray diffraction (XRD) using Bruker D8 advanced diffractometer using Cu radiation at 1.5118 Å. It is important to note that during the XRD measurement the sample was spanned to eliminate the artifact arising from the 2D structure of film by contributing all the plane and crystallites.

The optical properties of the Ta₃N₅|FTO films were determined utilizing PerkinElmer Lambda 35 UV-vis spectrometer equipped with Labsphere integrating sphere. The % absorptance (% A) was corrected for the substrate using a model previously developed in our lab.²² The Beer-Lambert law in combination with the absorption coefficient of Ta₃N₅ at 450 nm (188,000 cm⁻¹)²³ was utilized to calculate the film thickness. Atomic force microscopy (AFM, Cypher Atomic Force Microscope/Scanning Probe Microscope (AFM/SPM)) in the tapping mode equipped with silicon AFM probe (Budget Sensor) with 300 kHz resonant frequency and 40 N/m force constant was utilized to measure the film roughness and topology.

4.3.4. Photoelectrochemical Measurements

The electrochemical measurements were carried out with a Autolab potentiostat (PGSTAT128N) equipped with Nova electrochemical software. The photoelectrochemical performance of the electrodes were carried out in contact with an aqueous solution containing 0.1 M K₄[Fe(CN)₆] as the hole scavenger with the pH of 6.8. It is worth mentioning that different concentrations of the K₄[Fe(CN)₆] (50 mM to ~ 400 mM) were tested and it was noted that at concentrations beyond

100 mM, the PEC response is constant. Throughout this chapter the current density (J) vs. potential (E) J-E curves were measured at the scan rate of 20 mV/s. Additionally, the photo-response of the electrodes were measured as a function of illumination direction, the back illumination refering to illumination through the substrate and the front illumination describing the illumination through the solution. A 4500 W Xe lamp (Horiba Jobin Yvon) and AM 1.5 solar filter was used to simulate sunlight at the power of 100 mW cm⁻² (1 sun). The light intensity at the position of the electrode was calibrated with a certified reference cell (Oriel Reference Solar Cell & Meter). A homemade Ag/AgCl which was calibrated against commercial calomel electrode (Koslow Scientific) and a platinum mesh electrodes were utilized as the reference and counter electrode, respectively. The electrochemical impedance measurements were carried out at 10 mV amplitude perturbation in the 0.01 to 10,000 Hz frequency range. Under dark conditions, only one semicircle was observed in the Nyquist plot. The data were fit to the Randle circuit model using Zview software. The incident photon-to-current-efficiency (IPCE) measurements were carried out in the three-electrode setup under monochromatic light in the 400 to 700 nm range with the 10 nm intervals. The white light was monochromatized using a Horiba Jobin Yvon MicroHR monochromotor. The entrance and the exit of the monochromator whereas set at 0.75 mm which correspond to 8 nm linewidth. The light intensity at the electrode position under monochromatic light was measured with Nova II Ophir. The IPCE and absorbed photon-to-current efficiency (APCE) values were calculated according to equations 4-2 and 4-3, respectively.

$$IPCE(\%) = 100 \times \frac{J_{ph}(mA \text{ cm}^{-2}) \times 1239.8 \text{ (V nm)}}{P_{mono}(mW \text{ cm}^{-2}) \times \lambda \text{ (nm)}}$$
4-2

$$APCE(\%) = 100 \times \frac{\% \text{ IPCE}}{\% \text{ A}}$$
 4-3

4.4. Results and Discussion

In this study a combination of TaCl₅ (Ta-source) and NH₃ (N-source) were utilized to deposit crystalline films of Ta₃N₅ on FTO using a home-built ALD. A range of deposition temperatures from 450 to 550 °C were investigated. On the basis of the XRD measurements, it was found that 550 °C is the minimum temperature required to deposit crystalline Ta₃N₅. As discussed in previous chapter, at temperature beyond 550 °C the FTO substrate is not stable under ammonia/ vacuum conditions (a highly reducing atmosphere) as it becomes flaky and loses its inherent property as a TCO. We note that this temperature is higher by 50 - 150 °C in comparison to the previous studies on ALD deposition of Ta₃N₅ (summarized in Table 4-1).^{17,18} The higher temperature required to deposit crystalline films found here can be ascribed to the difference in the configuration of the ALD system, and substrate used.



Figure 4–5. The EDS spectra of the bare FTO (black) and the deposited films as a function of number of cycles; 500 (red), 300 (green), and 150 cycles (blue). The highlighted graph on the right-hand side represents the peak located at 1.7 kV in a reverse order showing a progressive growth of Ta peak as the number of cycles increases. The inset represent the configuration of the film and the origin of signals.

Energy dispersive spectroscopy (EDS) was utilized to assess the composition of the deposited films. The EDS spectra for the bare FTO and the as-deposited films as a function of the number of cycles are compared in Figure 4–5. Due to the large sampling depth of this techniques, in addition to the deposited film (top layer) the FTO substrate (SnO₂) is also detected. The observed peaks are then assigned to Ta, Sn, O, and N (the lists of characteristic X-ray for these elements are summarized in Table A4-2). We also note that for all thicknesses no signature of chloride as an impurity was observed which further suggests that the reaction between ammonia and tantalum chloride runs to completion. The broad peaks located at 0.69 and 3.4 keV are attributed to tin (Sn) from the FTO substrate. For a similar beam energy (15 kV), this peak has the highest intensity for the bare FTO substrate but its intensity progressively declines as the number of deposition cycles

increases. Concurrently, the intensity of Ta peaks (at ~ 1.7 and 7 > keV) grows with the number of cycles used. This is an important observation as it readily indicates that the deposited material forms a layer on top of the FTO substrate and that its thickness grows with the number of cycles. While these spectra confirms the presence of nitrogen (peaks at 0.4 and 0.825 keV, respectively), due to the low sensitivity of this technique to the light elements the ratio of Ta to N cannot be determined.



Figure 4–6. The XRD patterns of the FTO (SnO_2) substrates before (black) and after (orange) annealing in ammonia and tantalum nitride films with various thicknesses on FTO substrate. Films with 150 cycles, 300, and 500 cycles are shown in blue, green, and red colors, respectively. The vertical black dashed lines represents the Bragg positions for the standard crystalline Ta₃N₅ powder with random crystal orientations (PDF # 01-079-1533). The numbers represent the Miller indices of the corresponding diffraction peaks of Ta₃N₅. The yellow diamonds represent the Bragg positions of the standard SnO₂ (PFD # 00-046-1088).

The XRD diffraction patterns of the bare FTO substrates before and after annealing in ammonia with a flow rate of 100 SCCM at 550 °C for 2 h are compared to the deposited films with various number of cycles in Figure 4-6. The diffraction patterns for the bare FTO substrates before and after ammonolysis (control samples) are identical and are assigned to SnO₂. The measured diffraction patterns for the deposited films (for all thicknesses) are unambiguously assigned to Ta_3N_5 and SnO_2 . In addition, the peak positions of SnO_2 for the deposited films are identical to that of the control samples. These observations collectively indicate that FTO is chemically and structurally stable under the deposition conditions of the crystalline Ta₃N₅. Interestingly, we note that under identical XRD measurement conditions, the ratio of the diffraction intensities of SnO_2 to Ta₃N₅ progressively decrease with increasing Ta₃N₅ thicknesses. In agreement with the EDS data (Figure 4-5), this observation indicates that the deposited films form a layer over the FTO substrates. A closer inspection of the XRD pattern as a function of film thickness reveals a strong correlation between the pattern of diffraction (relative peak intensities) and the number of deposition cycles. In comparison to the diffraction pattern of the randomly oriented reference Ta_3N_5 (vertical dashed lines), it can be realized that the diffraction peak located at 24.6° (Miller indices of (110)) - which is one of the intense diffractions for the reference - is missing for all of the films. For this to occur, the (110) plane must be perpendicular to the substrate, implying that the deposited films exhibit a preferential orientation. A detailed analysis of the crystal orientation of the films are discussed following Figure A4-6. In addition, as it can be seen, the relative intensity of (130) plane to (113) plane strongly depends on the number of deposition cycles; it approaches the relative ratio observed for the randomly oriented reference pattern as the number of cycles increases. It can therefore be hypothesized that the different lattice structure of Ta_3N_5 compared to SnO_2 , generated a lattice mismatch, such that the initial growth mode of Ta_3N_5 is different and

proceeds through the formation of a buffer layer on the FTO substrate. Following the formation of the buffer layer, as the number of cycle increases the effect of the lattice mismatch is minimized and Ta₃N₅ grows more randomly. It is therefore expected that the growth rate and morphology of the crystalline Ta₃N₅ by this method is likely strongly substrate-dependent, which is beyond the scope of this study. The Raman spectrum of films of different thicknesses are compared in Figure A4-7. In line with the XRD measurements, the observed phonon modes are consistent with crystalline Ta₃N₅. The SEM images of the bare FTO substrates before and after annealing in ammonia are shown in Figure A4-8. As depicted, while after annealing in ammonia some surface aggregations are observed the film thicknesses are constant ~ 240 nm. In line with the XRD patterns of the FTO, this observation further indicates that SnO₂ phase is stable under reducing atmosphere of ammonia. The top view and cross-section SEM as well as the AFM images of Ta₃N₅ films with various thicknesses are compared to the bare FTO substrate in Figure 4-7. The crosssection SEM images clearly show that the films are comprised of two distinct layers of Ta₃N₅ (top layer) and FTO (bottom layer). The Ta₃N₅ films are compact, and their thicknesses increases with the number of cycles, whereas the thickness of the FTO layer remains constant. Due to the lack of a visually sharp interface between these two layers, the thickness of the Ta₃N₅ film was calculated by subtracting the original thickness of the FTO layer (240 nm) from the total thickness.



Figure 4–7. The SEM and AFM images showing the cross-section, morphology, and topology of the bare FTO and Ta_3N_5 films with different thickness. The scale bars for the SEM images are 200 nm with ~ 200,000X magnification. The 3D AFM images are shown in Figure A4-9.

The thickness of the films with 150, 300, and 500 cycles were found to be 70, 103, and 230 nm, respectively. Based on the top view SEM and AFM topography images, the morphology of the films are strongly correlated to the number of cycles (film thickness). The film with 70 nm thickness has a similar spherical morphology as the FTO substrate but with the bigger features and a porous morphology. Interestingly, the morphology of the film with 103 nm thickness begins to deviates from the FTO substrate exhibiting new oval-shape features where the film with 230 nm thickness only exhibit a randomly distributed oval-shape features perpendicular to surface. Remarkably, the morphology transformation as a function of the film thickness described here follows the same trend as the evolution of the XRD pattern which similarly can be ascribed to the difference in the crystal structure of Ta_3N_5 and FTO as described above. AFM was used to analyze the roughness of the films with various thicknesses. It was found that while the mean roughness

of the films with different thicknesses are similar but it is increased by ~ 3 nm with respect to the bare FTO substrate (Table A4-3).

The optical properties of bare FTO substrates before and after annealing in ammonia are shown in Figure A4-10. As it can be seen, while the reflectance of the FTO substrate is not affected by the annealing in ammonia, however, its transmittance is reduced by $\sim 10\%$. This reduction can be ascribed to the surface agglomeration observed in the SEM image (Figure A4-8). The absorptance spectra for various thicknesses of Ta₃N₅ on FTO substrate are shown in Figure 4–8.a. As shown, the absorptance edge for these films occurs at 575 - 600 nm which is in well agreement with the known bandgap of Ta₃N₅.^{19,24,25} Clearly, the absorptance beyond the bandgap edge does not reach zero, it is specifically more pronounced for the thicker films. The non-zero sub-bandgap absorptance have previously been attributed to the formation of the reduced Ta-sites.³ In addition, a well-resolved sub-bandgap absorption peak centered at ~ 700 nm is uniquely observed for the film with 500 cycles. The origin of this absorption feature have been assigned to two completely distinctive sites: (1) the reduced Ta^{5+} sites, i.e. Ta^{4+} or Ta^{3+} , 26,27 and (2) the N-vacancy as a deep donor accompanied by free electron in the conduction band to compensate the positive charge of the anion vacancy.^{5,28} The main difference between these two sites is that the first one is basically a trap state where the charges are localized on the Ta-sites while in the second one the charge is delocalized over the conduction band.



Figure 4–8. a) Plots of the absorptance of Ta_3N_5 films on FTO substrate with various thicknesses. The corresponding transmittances and reflectances are shown in Figure A4-11. The data shown here are corrected for the pristine FTO substrate using the previously reported procedure.²² b) The thickness of deposited films as a function of number of cycles grown at 550 °C on FTO substrate. The thickness of the films were determined *via* two independent methods of cross-section SEM analysis (black square) and the optical absorbance at 450 nm (red circle) in combination with beerlambert law using the known absorption coefficient reported previously for compact film of Ta_3N_5 .²³

Figure 4–8.a also shows that the absorptance of the film does not scale with the number of cycles and the film with 300 cycles has a slightly higher absorptance than the film with 150 cycles. The plot of thickness *vs.* number of cycles acquired by the cross-section SEM and absorbances are shown in Figure 4–8.b. We note that the film thicknesses found by these methods are different by as much as ~ 50 nm for the thickest film which can be ascribed to the uncertainty in the absorption coefficient and/or the calculated absorbance or change in the density of the films with various thicknesses. The trend in the film thickness as a function of number of cycles between two methods

are remarkably similar, however. As shown, within the window of the number of cycles studied here, the growth of tantalum nitride on FTO substrate is not linear. This phenomena can be better understood by considering the growth of the crystalline tantalum nitride on films FTO. As shown in the SEM images the film with 150 cycle is porous – this is further manifested in the high dark current shown in Figure 4–9 – whereupon growing more materials, they fill the empty spaces. Consistent with the XRD and SEM images, the trend of the film growth indicates that the deposition of the tantalum nitride initiates by seeding and formation of a buffer layer for the first 150 cycles. Based on these thicknesses, the apparent growth rate of the Ta₃N₅ films on FTO is ~ 0.46 nm per cycle. We note that this growth rate is substantially higher than the previously reported values for the ALD deposition of crystalline tantalum nitride by a factor of ~ 18 (see Table 4-1). For example, Ritala et al.¹⁷ utilized TaCl₅ and NH₃ to deposit Ta₃N₅ on soda lime glass and ITO glass substrates. Under ALD growth conditions, i.e. self-terminating surface reaction, they reported an average growth rate of 0.025 nm per cycles at the temperature range of 400 to 500 °C. It is also worth noting that a growth rate of 0.46 nm per cycle is larger than the average bond length of Ta-N (0.21 nm) in Ta₃N₅ by a factor of ~ 2.2.²⁹ These observations collectively indicate that the deposition of Ta₃N₅ here is not under self-limiting ALD deposition conditions. However the higher growth rate of the film with a controlled thickness found here is advantageous as it minimize the processing time to prepare tantalum nitride films.



Figure 4–9. a) The chopped light *J-E* curves of Ta_3N_5 on FTO substrate as a function of film thickness in contact with an aqueous solution containing 0.1 M K₄[Fe(CN)₆] as the hole scavenger with the pH of 6.8. The potential was scanned at 20 mV s⁻¹ and the electrodes were illuminated through the electrolyte with 1 sun intensity. b) The photograph of the electrode with various thicknesses of Ta_3N_5 on FTO substrate. As shown all the edges of the rectangular shape electrode were coated with Ag epoxy and the electrode was clamped to a costume made cell with an O-ring with diameter of 0.19 cm⁻² (the mark of the O-ring is partially visible on the 500 cycles electrode).

The deposited tantalum nitride films on FTO substrate are strongly adhered to the substrate, thus, sandpaper was used to expose the FTO conductive substrate. The *J-E* curves in presence of the 1-electron fast hole scavenger along with the photograph of the electrodes with various thicknesses are shown in Figure 4–9. Previous example of Ta_3N_5 on FTO substrate was reported by Higashi *et al.*³⁰. They used electrophoretic deposition to prepare mesoporous films from nanoparticles Ta_3N_5 .

The best performance was achieved by treating the as-prepared films with TaCl₅ followed by ammonolysis at 500 °C. The other example of Ta₃N₅ photoanode on a transparent conductive substrate was reported by our group via ALD stack deposition of tantalum oxynitrides on Ta-doped TiO₂ followed by ammonolysis (described in previous chapter).¹⁹ To the best of our knowledge this is the first example of directly deposited crystalline Ta₃N₅ photoanode on the FTO substrate. The J-E curves reported here produce a photocurrent onset potential of ~ 0.3 V vs. RHE. This potential is comparable to the onset potential reported by Jaramillo et al. for the tandem core-shell Si-Ta₃N₅ photoanode and also the high performing nanostructured Ta₃N₅ photoanodes introduced by Wang and coworkers.^{31–33} The early photocurrent onset potential readily implies that (1) Ta₃N₅ makes an ohmic contact with the FTO substrate and (2) FTO is sufficiently conductive that the energy lost for electron collection and transport is minimized. This observation is further supported by the conductivity measurement of the FTO substrate before and after annealing in ammonia. As shown in the slope of the J-E curves for both electrodes are nearly identical confirming that FTO is stable and remains conductive under the reducing conditions of ammonia at 550 °C. Another feature of the chopped light J-E curves shown in Figure 4-9 is the saturation of photocurrent density for the film with 103 nm thickness. The current saturation readily indicates that the transport of the holes (minority charge carrier) is limiting while electrons are efficiently collected at 230 nm thickness. The latter can be ascribed to the high dopant density found for Ta₃N₅ (discussed below). The chopped light J-E curves for Ta₃N₅ films with various thicknesses as the function of illumination direction (front vs. back) are compared in Figure A4-13. We note that while the photocurrent onset potential is independent to the illumination direction, the photocurrent density, however, strongly correlates to the illumination direction. The 70 nm film produces a relatively constant photocurrent regardless of the illumination direction. However, as the film

thickness grows the front and back illumination start to diverge with the front illumination constantly producing higher photocurrent and plateauing beyond 103 nm film thickness with a maximum photocurrent density of ~ 2.4 mA cm⁻² at 1.23 V *vs*. RHE. We note that almost all the previous examples of Ta₃N₅ photoanodes that exhibited high photocurrent densities were nanostructured electrodes with high aspect ratios (nanorod, nanotube, or porous cubic morphologies).^{1,2,32,34} Jaramillo and coworkers have also shown that the photocurrent density of Ta₃N₅ predominantly depends on its effective surface area.³⁵ Here we note that for the planar Ta₃N₅ films, the maximum current density reaches ~ 20% of the theoretical limit (12.5 mA cm⁻²). These observations collectively indicate that PEC performance of tantalum nitride is dominantly controlled by its finite diffusion of holes (at best between 70 and 103 nm film thicknesses).

Figure 4–10.a shows the wavelength dependence of incident photon to current efficiency (IPCE%) for various thicknesses of Ta_3N_5 as a function of illumination direction. As depicted, the onset of IPCEs for all the thicknesses of these electrodes is located around 575 nm which is in good agreement with the known band gap value for $Ta_3N_5^{19,24}$, indicating that the observed photoresponse is due to tantalum nitride. The sharp decline in the IPCE% values which is uniquely observed in the front illumination (through electrolyte) at the wavelengths below 450 nm can be ascribed to the absorption of the ferri/ferrocyanide solution.³⁶ In agreement with Figure A4-13, the front IPCE% is larger than the back IPCE%, which further indicates that the transport of holes is kinetically limiting. Consistent with the *J-E* curves, the front IPCE% responses saturates for the films with 103 nm thickness.



Figure 4–10. Wavelength dependence of the a) IPCE% and b) APCE% values at 1.0 V *vs.* RHE for the Ta_3N_5 films with different thicknesses as a function of illumination direction in contact an aqueous solution containing 0.1 M K₄[Fe(CN)₆] as the hole scavenger with the pH of 6.8. The solid and open shapes represent the values under front (through the solution) and back (through) illumination, respectively. Ta₃N₅ films with 230, 103, and 70 nm thicknesses are shown in red diamond, green circle, and blue triangle, respectively.

The back IPCE% response initially increases as the film thickness grows but it steeply declines for the 230 nm thick film. In addition, the back IPCE% values for the films with 70 and 103 nm thicknesses are plateaued with average values of approximately 10 and 15%, respectively. Conversely, the back IPCE% for the 230 nm Ta₃N₅ electrode produced a peak at 525 nm and declined to zero for the lower wavelengths. These observations can be better understood by considering the absorption penetration depth of tantalum nitride and the profile of photo generation of charge carriers as a function of illumination direction (Figure 4–11). The penetration depth of light for Ta₃N₅ for the photons with the wavelength of 525 and 450 nm are 120 and 52 nm, respectively.^{19,23} As a result, for the back illumination photons with larger penetration depths (red

photons) produce charge carrier within the diffusion length of hole (in vicinity of the surface) while the short wavelength lights (blue photons) with short absorption length predominately generate holes close to the FTO substrate. As the result, for the film with 230 nm thickness the back IPEC% produces a peak rather than a constant value. The APCE% values of these films as a function of illumination direction for various thicknesses are shown in Figure 4–10.b. As shown, the maximum APCE% is observed for the film with 103 nm thickness. For Ta_3N_5 with 230 nm thickness, even though the absorptance is quantitative (Figure 4–8.a) but the APCE% decreases. In agreement with IPCE%, this observation indicates that for this films the charge carries are produced outside of the holes diffusion length and thus do not contributed to the photocurrent. The APCE% for 70 nm is lower than the 103 nm film which can be ascribed to its lower IPCE%.



Figure 4–11. The schematic representation of the profile of charge generation as a function of illumination direction; a) back illumination (through the FTO), b) front illumination (through the solutions).
We used dark EIS to assess the electrical properties of Ta_3N_5 on FTO substrate. The EIS responses were fitted to the Rundle model circuit to extract the capacitance of the space charged region (*C*_{bulk}). The Mott-Schottky (MS) plot of Ta_3N_5 with 230 nm thickness in dark is shown in Figure A4-14. The dopant density (N_d) was calculated by linear fitting of the slop to the MS equation 4-4.³⁷ We note that in the literature there is no agreement on the dielectric constant of Ta_3N_5 and different values ranging from 7 to 110 have been reported.^{2,23,24,38,39} The calculated dopant density based on these dielectric constants are summarized in Table A4-4. As shown, the calculated dopant densities span 1 order of magnitude in range with an average value of 8.0×10^{20} cm⁻³ in agreement with previous reports.^{2,23} The flat band potential (V_{FB}) of Ta₃N₅ was calculated from the intercept of the linear fit according to equation 4-4.

$$\left(\frac{A}{C_{\text{bulk}}}\right)^2 = \left(\frac{2}{q\epsilon\epsilon_0 N_{\text{d}}}\right) \left(V_{\text{app}} + V_{\text{FB}} - \frac{k_{\text{B}}T}{q}\right)$$

$$4-4$$

In this equation, A, k_B, T, q, ε_{0} , ε_{0} , and V_{app} are the geometrical surface area, Boltzmann's constant, absolute temperature, elementary charge, dielectric constant of the semiconductor, permittivity of free space, and applied potential, respectively. From the intercept of the linear fit the flat band potential was calculated as 0.21 V *vs*. RHE. With the solution potential of 0.68 V (measured in two-electrode system), therefore the built-in voltage (V_{bi}) is ≈ 0.47 V.

$$w = \sqrt{\frac{2\varepsilon\varepsilon_0 V_{bi}}{qN_d}}$$
 4-5

The depletion width (w) was calculated according to equation 4-5 and the results for various dielectric constants are summarized in Table A4-4. The average depletion widths is only 4 nm.

The narrow depletion width can be ascribed to the high dopant density. Due to the narrow depletion width and the large absorption depth of Ta_3N_5 , a significantly small number of charge carriers are generated in the depletion region which cannot account for the observed photocurrent densities. Since the depletion width is narrow in comparison to the thinnest film here (70 nm) thus the PEC performance of Ta_3N_5 is controlled by the diffusion of photogenerated holes.

4.5. Conclusions

In this chapter, the experimental procedures to build a fully automated ALD instrument is described. In this study, a combination of TaCl₅ and ammonia were used to deposit crystalline Ta₃N₅. It was shown that the quality and the composition of the film strongly depends on the configuration and the composition of the reactor. Specifically, it was discovered that for the deposition of crystalline Ta₃N₅, the cold-wall reactor equipped with substrate heater is advantageous over the hot-wall reactor as it minimizes the deleterious side reaction induced by the highly reactive nature of the deposition conditions of crystalline Ta_3N_5 – temperature > 500 °C and the presence of highly reactive reactants (NH₃) and by product (HCl). Subsequently, crystalline Ta₃N₅ with various thicknesses were deposited on FTO substrate at 550 °C. We note that the crystallinity, morphology and topography, growth rate, and optical density of the deposited films on FTO strongly depend on the number of ALD cycles. These correlations were attributed to the crystal mismatch between SnO₂, i.e. the FTO substrate, and Ta₃N₅. Therefore, for the first ~ 150 cycles a buffer layer with relatively similar morphology to the substrate is formed on the surface of FTO where after this point Ta₃N₅ is randomly deposited. Furthermore, it was shown that FTO is chemically and mechanically stable under reducing conditions of ammonia at 550 °C and remains transparent and conductive which further allowed to realize the 1st example of directly

deposited Ta₃N₅ photoanode on FTO. The Mott Schottky analysis from EIS measurements revealed that Ta₃N₅ is heavily doped (N_d = 8.0×10^{20} cm⁻³) which results in a rather narrow depletion with (< 10 nm). This readily indicates that the charge transport in Ta_3N_5 is under diffusion control. Furthermore, the PEC performance of these electrodes in presence of the fast hole scavenger as a function of illumination direction with various thicknesses have shown that the PEC performance of Ta₃N₅ is controlled by the limited diffusion length of holes with the diffusion length of 70 - 100 nm. This observation contradicts with the previous study by Van de Krol *et al.*⁶ where they predicted that the diffusion length of charge carriers for Ta₃N₅ is in the order of ~ 18,000 nm. However, we note that this observation is consistent with the fact that the best examples of Ta_3N_5 in literature have a nanostructured morphology with feature size of ~ 100 nm.^{1,2,32,33} In conclusion, here we showed that ALD provides a viable and robust technique to integrate crystalline Ta₃N₅ with a transparent conductive substrate like FTO. As a result, it allowed us to study the physical properties of pristine Ta₃N₅ independent of the conductivity of the substrate. Furthermore, the ALD deposited Ta₃N₅ electrodes can further be *in situ* protected against photocorrosion with an over layer of GaN or TiO₂ prior to exposure to the ambient atmosphere.^{40–} 42

APPENDIX



Figure A4-1. The screenshot of the program in use.



Figure A4-2. The photograph of the electronic box.



Figure A4-3. The wiring diagram of the electronic box to the LabJack T7-Pro.

The individual components of the electronic box are briefly described below:

1) Power Supply: two types of power supplies are used here: (i) a 120V alternating current (AC) power supply is used for the heaters and the vacuum valve, and (ii) a 24 V direct current (DC) power supply is used to power the ALD valves.

2) Solid State Relays (SSR): solid state relays are basically electronic switching devices without a moving part. They turn on/off an external circuit (loads) by applying a small external voltage across the control terminal. Sine here we used two different power supplies, i.e. AC and DC, two different types of SSR, DCDC-SSR and DCAC-SSR were accordingly utilized to control the AC and DC loads. It is important to note that the control signal is a 5 V DC voltage supplied by the LabJack (*vide infra*).

3) Digital to Analog Converter (DAC) and Analog to Digital Converter (ADC): The heart of the electronic box is the DAC/ADC. The real world signals, i.e. temperature, position of the solenoid valve, are analog signals in terms of voltage. The ADC converts these signals into digital signals that can be processed by the computer. Conversely, the DAC converts the command from computer into analog signal to be executed on the system. For this electronic box, the LabJack T7-Pro with 14 analog inputs and 24-bit low-speed ADC with resolution of 1 μ V was used. Further information about the specifics of configuration of the converter can be find from the Labjack website [43].



Figure A4-4. The photograph of the metallic copper powder filled scrubber equipped with a band heater and thermocouple. The photograph was taken ~ 4 months after continuous flow of N_2 with an average flow of 20 SCCM. The black area at the inlet represent the formation of the copper oxide and the red copper color at the outlet represent the unreacted copper powder.



Figure A4-5. The schematic representation of the procedure developed to deposit Ta_3N_5 via a custom-built ALD system.



Figure A4-6. The crystal structure of Ta_3N_5 along and its 3 major planes with the Miller indices of: (110) shown in blue, (130) shown in orange, and (113) shown in yellow. The unit cells shown in (a) and (b) are the same but they are represented along different axes: a) along the c axis and b) along the b axis that is rotated by 21° counterclockwise. Since the diffractions from all the planes except (110) are observed, the visual inspection of the relative orientations of the major atomic planes of Ta_3N_5 indicates that Ta_3N_5 is preferentially deposited along the b-axis rotated ~ 21° counterclockwise where the c-axis is parallel to the surface.²⁹



Figure A4-7. Raman spectra of Ta_3N_5 films with different thicknesses on FTO substrate. Films grown with 150 cycles, 300, and 500 cycles are shown in blue, green, and red color, respectively. These phonon modes are in agreement with the previously reported Raman spectrum of Ta_3N_5 .⁴⁴



Figure A4-8. The cross-section and top view SEM images of the as received and bare FTO substrate a-b) before and c-d) after annealing in ammonia with a flow rate of ~ 100 SCCM at 550 °C for 2 hours. The scale bars for the SEM images are 100 nm with ~ 200,000 X magnification.



Figure A4-9. The AFM images of the bare and Ta_3N_5 with different thicknesses on FTO.



Figure A4-10. The transmittance (solid lines) and reflectance (dashed lines) of the bare FTO substrate before (black) and after (orange) annealing in ammonia with a flow rate of ~ 100 SCCM at 550 $^{\circ}$ C for 2h. As it can be seen, while the reflectance of the FTO substrate is not affected by the annealing in ammonia, however, the transmittance of the FTO substrate is reduced by ~ 10% after annealing in ammonia.



Figure A4-11. The optical properties of Ta₃N₅ on FTO substrate as a function of film thickness; a) transmittance and b) reflectance.



Figure A4-12. The electrical properties of FTO before and after annealing in ammonia with a flow rate of 200 SCCM for 2 hours at 550 °C. The *J-E* curves were measured from the electrodes with the same geometry and dimensions (details are shown in the inset).



Figure A4-13. The front *vs.* back illumination *J-E* curves of Ta_3N_5 on FTO substrate with various thicknesses in contact with an aqueous solution containing 0.1 M K₄[Fe(CN)₆] as the hole scavenger with the pH of 6.8; a) 150 cycles (70 nm), b) 300 cycles (103 nm), c) 500 cycles (230 nm). The back illumination (through the FTO substrate) is shown in black and the front illuminations are shown in color.



Figure A4-14. a) the C_{bulk} and b) the calculated Mott Schottky plot of Ta₃N₅ with 230 nm thickness on FTO substrate in dark. The electrode was in contact with an aqueous solution containing 0.1 M K₄[Fe(CN)₆] as the hole scavenger with the pH of 6.8. The inset represents the equivalent circuit used to fit the EIS data.

Set Temperature (°C)	Measured Temperature (°C)
450	444
505	500
550	540

 Table A4-1. The calibration data for the substrate temperature.

Element	Peak position (keV)
Та	1.709 (<i>M</i>), 8.145 (<i>L</i> _α)
Sn	3.443 (<i>L</i> _α), 0.691 (<i>M</i>)
Si	1.739 (<i>K</i> _α)
Cl	2.621 (<i>K</i> _α)
0	0.523 (<i>K</i> _a)
Ν	0.392 (<i>K</i> _α)

Table A4-2. The characteristic X-ray of Ta, Sn, Cl, Si, O, and N.⁴⁵

Sample	Mean Roughness/nm
Bare FTO	8.053
150 cycles	10.50
300 cycles	10.64
500 cycles	11.53

Table A4-3. The measured mean roughness of the FTO substrate and deposited films with different thickness.

ε ^a	$N_d \times 10^{20} \ (cm^{\text{-}3})^{\text{b}}$	W (nm) ^b	Ref.
110	1.68	6	[2]
65	2.84	3.5	[²⁴]
43	4.29	2.5	[³⁸]
17	10.9	1	[²³]
9	20.5	0.5	[³⁹]

^(a) These values were taken from the literature. ^(b) These values are the calculated parameters using the literature dielectric constants.

Table A4-4. The physical properties of Ta₃N₅.

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Chapter 5:

Interface	Control	of
Photoelectroc	hemical	Water
Oxidation	Performance	with
Ni _{1-x} Fe _x O _y	Modified	Hematite
Photoanodes		

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Interface Control of Photoelectrochemical Water Oxidation Performance with $Ni_{1-x}Fe_xO_y$ Modified Hematite Photoanodes, Hamed Hajibabaei, Abraham R. Schon, and Thomas W. Hamann, *Chem. Mater.*, **2017**, 29 (16), 6674–6683. Copyright (2017). American Chemical Society.

5.1. Abstract

In this work, $Ni_{1-x}Fe_xO_y$ -coated hematite electrodes are investigated as a model system of different semiconductor/catalyst interfaces. We found that the PEC performance of the electrodes strongly depends on both the way the hematite electrode is prepared and the composition of the catalyst. Two extreme behaviors are observed for electrodeposited hematite electrodes coated with slightly different compositions of catalyst. In case of Fe-rich catalyst ($Ni_{0.25}Fe_{0.75}O_y$) the performance is substantially enhanced compared to the bare electrode, however the Ni-rich $(Ni_{0.75}Fe_{0.25}O_y)$ catalyst inhibits the PEC performance. A combination of photoelectrochemical, IMPS, and EIS measurements collectively reveal the critical role that the interface states of the semiconductor and catalyst plays in controlling the key interfacial charge transfer and recombination reactions. The photogenerated holes are efficiently collected and stored into the catalyst layer for the $Ni_{0.25}Fe_{0.75}O_{y}$ coated hematite electrodes. An unusually large improvement in performance is attributed to this hole collection circumventing recombination at the hematite surface. For the Ni_{0.75}Fe_{0.25}O_y coated hematite electrodes, however, there is a presence of interface trap states that act as recombination centers and pin the catalyst potential. These combined results provide important new understanding of the role of the interfaces at semiconductor/electrocatalyst junctions.

5.2. Introduction

Hematite continues to attract a lot of interest as an electrode material for photoelectrochemical (PEC) water oxidation. Hematite has an optical band gap of ~ 2.1 eV, is composed of very earthabundant elements, is easily prepared and is chemically stable in basic electrolytes.^{1–3} Due to these attributes, there has been a lot of effort aimed at improving the performance of this material.

Previous studies suggest that one of the key steps preventing efficient PEC water oxidation at hematite electrode is the high overpotential necessary to initiate water oxidation.^{3,4} The large overpotential is generally attributed to the slow kinetics of water oxidation at the surface of the hematite. Experiments by us and others, showed that after deposition of water oxidation catalysts (WOCs), e.g. CoPi or Ni(OH)₂, the photoelectrode characteristics (e.g. photocurrent onset potential, photocurrent, and fill-factor) substantially improve.^{2,5–11} The cause for these improvements, however, are not yet fully understood. The enhancement of PEC performance of electrocatalyst coated photoanodes has been attributed to reducing surface state recombination,^{12,13} increasing band bending,^{14,15} or facilitating charge separation.^{10,16} Recently, Boettcher and coworkers developed a dual working electrode experiment to simultaneously measure the current and potential of the semiconductor (SC) and catalyst.^{17,18} Their results suggest that the SC/WOC interface is strongly affected by the physical structure of the catalyst, specifically whether it is dense or ion permeable. To the best of our knowledge, all catalysts reported in conjunction with hematite are ion-permeable, including the most often reported Co-Pi.⁹ For such ion-permeable WOCs, hole transfer from the semiconductor oxidizes the WOC, and the accumulated holes are charge compensated by ions in the electrolyte. Thus, the catalyst potential drops until it can sustain water oxidation at a rate matching the flux of holes reaching the SC/WOC interface. This type of junction is termed an adaptive junction.

The adaptive junction model assumes an ideal SC/WOC interface and the measurements reported by Boettcher utilized an ideal single crystal TiO₂ semiconductor which did not appear to significantly suffer from surface state recombination.¹⁷ We have shown, however, that surface states on hematite largely control the water oxidation behavior and cannot necessarily be neglected in considering the addition of WOCs to the hematite surface.^{19,20} For example, it was shown that surface modification of hematite that eliminates the surface defects resulted in a substantial improvement of PEC performance of hematite electrodes modified with WOCs.²¹ In addition, it has been reported that many other photoanode materials such as BiVO₄ suffer from surface state recombination as well.^{22,23} The presence of a high density of surface states can result in substantial surface state recombination and Fermi level pinning.^{9,24} Their influence on the interface that forms upon addition of a WOC is unknown, however. Furthermore, the addition of materials to the hematite (and other metal oxide) surfaces can result in new/more interface states that can inhibit the performance. It is also not clear why some hematite/WOC junctions produce exceptional results compared to most other junctions which result in modest improvements.^{21,25,26} Therefore, in this study we aim to expand the understanding of SC/WOC interfaces, including non-ideal junctions, which can be further generalized for a larger groups of photoelectrode/WOCs combinations.

In this work we employ hematite thin films prepared by atomic layer deposition (ALD) and electrodeposition (ED) methods as photoanodes. Recently we have shown that the preparation method of hematite has a great impact on the performance of the photoanode.² The ED hematite electrodes outperformed the ALD-made films which was attributed to enhanced hole transport and collection efficiencies. Therefore, it is expected that the density of defects at the surface may also be altered as a result of different preparation methods. The hematite films were coated with Ni₁. $_{x}Fe_{x}O_{y}$ WOCs. Consistent with prior reports, we found that tuning the composition of the Ni₁. $_{x}Fe_{x}O_{y}$ catalysts results in the formation of one or two separate phases, including FeOOH and Fedoped NiOOH.²⁷⁻³⁰ Thus, a combination of hematite electrodes prepared by different methods and Ni_{1-x}Fe_xO_y WOCs provides a good system for studying the role of the interface formed at the SC/WOC junction. The Ni_{1-x}Fe_xO_y-coated hematite electrodes were studied using electrochemical

impedance spectroscopy (EIS) and intensity modulated photocurrent spectroscopy (IMPS) as a function of catalyst composition to determine the factors controlling the performance of the modified electrodes. These combined results provide new insights on the SC/WOC junction and allow for the development of more efficient solar water splitting systems.

5.3. Experimental

5.3.1. Electrode preparation

Thin films of hematite electrodes were prepared on F:SnO₂ (FTO)-coated aluminoborosilicate glass substrates (Solaronix, 10 Ω /sq) via electrodeposition (ED) and atomic layer deposition (ALD) methods reported previously.^{2,31} Prior to deposition, the FTO glass was cleaned by ~ 15 minutes sequential sonication in soap (FisherbrandTM SparkleenTM 1 Detergent), water, and isopropyl alcohol and dried in a gentle stream of nitrogen. The ED of planar thin films were performed in 0.1 M FeCl₂·4H₂O (pH \approx 4.2) at 60 °C by applying 1.2 V vs. Ag/AgCl reference electrode under gentle stirring for 30 minutes. Subsequently, the amorphous electrodeposited FeOOH films were converted to crystalline hematite by annealing at 800 °C in a pre-heated furnace for 10 minutes followed by quenching to the room temperature by taking it out of the furnace. Analogous thicknesses of hematite were deposited via ALD on a ~ 2 nm Ga₂O₃ underlayer. The Ga₂O₃ was deposited using tris-(dimethylamido)gallium(III) (Ga₂(NMe₂)₆) (Strem Chemicals Inc.) as the Ga precursor and H₂O as the oxidant using a modified version of a previously reported procedure.³² The Ga cylinder was heated to 150 °C and pulsed for 0.2 s under exposure mode for 8 s, followed by 12 s purge. Then, a 0.015 s pulse of H₂O was introduced under the same exposurepurge time to oxidize the Ga precursor. A growth rate of ~ 1.1 Å Ga_2O_3 /cycle was measured by spectroscopic ellipsometry (Horiba Jobin Yvon, Smart-SE) on control Si wafers. The Ga₂O₃ coated FTO substrates were subsequently coated with the ~ 30 nm of Fe₂O₃ by alternating pulses of ferrocene as iron precursor and a combination of water and ozone as the oxidant. The ferrocene cylinder, heated to 70 °C, was pulsed for 20 s which was followed by an oxidation cycle that included 10 subcycles of a 0.015 s H₂O pulse followed by a 2 s ozone pulse, where each subcycle was separated by a 5 s purge. In agreement with our previous report, the growth rate of Fe₂O₃ is 0.55 Å /cycles.⁴ After deposition, the ALD Fe₂O₃ films were annealed at 500 °C for 2 hours with heating/cooling rate of 17 °C/min. Finally, the electrodes were annealed in a preheated furnace at 800 °C for 4 minutes.

5.3.2. Deposition of Catalyst

Thin films of Ni_{1-x}Fe_xO_y were deposited by spin coating on 1 cm² FTO and hematite substrates using a modified version of previously reported procedures.^{21,33} Prior to the deposition of the catalyst on FTO, the substrates were sequentially cleaned by soap (FisherbrandTM SparkleenTM 1 Detergent), DI water, and IPA for 15 min. In order to coat the hematite electrodes with catalyst, the freshly prepared hematite electrodes were only rinsed with DI water followed by drying in a stream of N₂. Precursor solutions were prepared from iron (III) 2-ethylhexanoate (50% w/w in mineral spirits, Strem Chemicals), and nickel (II) 2-ethylhexanoate (78% w/w in 2-ethylhexanoic acid, Strem Chemicals) by dissolving the appropriate amount of metal precursor in hexanes (Table A5-1) to give a total concentration of 15% w/w metal complex. These solutions were further diluted with hexane to prepare a solution with a total metal concentration of 50 mM. Approximately 0.25 mL of the solution was added to the substrate, followed by spinning at 5000 rpm for 60 s. Subsequently, the films were irradiated with UV light (254 nm, 4 W) for 1 hour followed by annealing in a preheated furnace in air at 100 °C for 1 hour. We used Raman Spectroscopy to ensure that the decomposition of organic precursor was completed (Figure A5-1). In order to change the thickness of the catalyst, the deposition procedure was performed 1, 2 or 3 times sequentially to produce three thicknesses of catalysts on the ED hematite electrodes. Note that each deposition cycle involved 1 hr UV light treatment followed by 1 hr annealing at 100 °C. Atomic Force Microscopy (AFM) and Spectroscopic Ellipsometry (ES) were utilized to determine the thickness of the catalyst deposited on silicon substrates using comparable procedures. A wavelength region of 800–1000 nm was used for ES measurements since the oxides are transparent which allows for more accurate determination of thickness.³⁴

5.3.3. Film Characterization

X-ray photoelectron spectroscopy (XPS) was utilized to determine the composition of the thin films of Ni_{1-x}Fe_xO_y catalyst on FTO. The XPS data were collected utilizing Perkin Elmer Phi 5600 ESCA system equipped with a monochromatic Mg k α source to illuminate the sample at a takeoff angle of 45°. Survey scans of 0-1000 eV binding energy and detailed scans for C 1s, O 1s, Ni 2p and Fe 2p, regions were measured for all samples. The binding energies were corrected in reference to C 1s peak (284.8 eV) and Shirley background subtraction was performed for fitting for each sample. For fitting the Ni and Fe 2p regions, the p 1/2 and p 3/2 peaks were bonded together with the relative area of 1 to 2. Raman spectra were collected *via* Raman Microprobe (Renishaw) equipped with a 45W Cobalt DPSS laser (532 nm line) laser and a 100 × magnefication objective to focus the laser on the film surface. The surface morphology of the prepared films were examined by scanning electron microscopy, SEM (Carl Zeiss Auriga, Dual Column FIB-SEM).

5.3.4. (Photo)electrochemical Measurements

Electrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. The electrochemical characterization of Ni_{1-x}Fe_xO_y on FTO was carried out by cycling the potential linearly between 1.0 to 2.0 V *vs.* RHE at a scan rate of 100 mV s⁻¹. The electrodes were examined in contact with 1 M KOH solution (pH = 13.6) as was determined with Fisher Scientific Accument pH meter. Each electrode was activated by cycling the potential between 1 - 2 V *vs.* RHE (40 CVs). All the presented CVs are measured after activation. The potential was corrected for IR drop, using R values determined by impedance measurements. A homemade saturated Ag/AgCl and a platinum mesh electrodes were used as the reference and counter electrodes, respectively. The reference electrode was frequently calibrated against commercial saturated calomel electrode (Koslow Scientific). All the potentials were converted to reversible hydrogen electrode, RHE, by equation $E_{RHE} = E_{Ag/AgCl} + 0.197 V +$ (0.059 V) × pH.

The electrochemical impedance spectroscopic and photoelectrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. Impedance data were gathered using a 10 mV amplitude perturbation of between 10,000 and 0.01 Hz. Data were fit using Zview software (Scribner Associates). For each thickness of catalyst with different compositions two electrodes were prepared and the fitted parameters were averaged and the standard deviations were reported on the graphs. The current density *vs.* applied potential (*J*-*E*) response of bare and modified hematite electrodes were examined by cycling the potential between -0.5 and 0.7 V *vs.* Ag/AgCl at the scan rate of 20 mV s⁻¹ in contact with 1 M KOH. The 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). Unless otherwise stated, all photoelectrochemical tests were carried out by shining light on the electrodes through the electrolyte.

The performance of each electrode was initially tested by measuring the *J*-*E* in light and dark. Subsequently, each electrode was conditioned by cycling between 0.5 - 1.7 V vs. RHE under illumination, followed by another *J*-*E* measurement. Each electrode was then subjected to EIS (~ 2 h under illumination) and IMPS (~ 1 h under illumination) measurements, with additional *J*-*E* measurements after EIS and IMPS measurements to determine any change in behavior. Negligible changes were observed between initial (after conditioning / before EIS) and final *J*-*E* curves for a given electrode. The *J*-*E* data shown are from the final measurements.

IMPS measurements were made with an Eco Chemie Autolab potentiostat equipped with metrohm LED driver accessory which was controlled by Nova electrochemical software. The measurements were performed in 1 M KOH utilizing a three-electrode configuration. A 470 nm LED light was utilized as the light source for all the experiment. The power of the LED was chosen in a way that it provides the same number of photocurrent as was measured under 1 sun illumination. The modulation intensity was set at 10% of the power of the LED to ensure a linear respond and the frequency was swept from 15 kHz to 0.1 Hz with 10 frequency per decade increments. The IMPS data were collected over the potential range of 0.5 to 1.5 V *vs.* RHE with 0.1 V interval.

5.4. Results and Discussion

XPS measurements were performed on five catalysts prepared with variable composition of the $Ni_{1-x}Fe_xO_y$ solution (x = 0, 0.25, 0.5, 0.75, and 1) on FTO substrates. The compositions of the films determined by XPS, summarized in Table A5-2, are in good agreement with the composition of the solutions used for spin coating. The detailed XPS spectra as a function of the composition of

the films are shown in Figure A5-2, followed by interpretation of the spectral features. Depending on the ratio of Ni to Fe, Ni_{1-x}Fe_xO_y may consist of one or more separate phases. For iron concentration up to 25% only one phase, presumably Fe-doped Ni(OH)₂, is discernable. At higher iron content, however, two phases appear to be present, which are assigned to FeOOH and Fedoped Ni(OH)₂, in accord with recent studies on the electrocatalytic activity of Ni_{1-x}Fe_xO_y on different substrates.³⁵ This observation suggests that by tuning the composition of the catalyst, the interface of the electrocatalyst and underlying substrate may be modified by contact with the different catalyst phases.

The cyclic voltammograms (CV) of the Ni_{1-x}Fe_xO_y catalysts on FTO in contact with 1 M KOH are shown in Figure 5–1.a. The CV of Ni(OH)₂ exhibits two characteristic features: a redox wave which is attributed to the transition between Ni(OH)₂ and NiOOH, and an anodic wave at more positive potentials corresponding to water oxidation.^{29,36,37} The CV of FeOOH, on the other hand, only shows an anodic wave associated with water oxidation.²⁹ Similar to the Ni(OH)₂ catalyst, the CV of the Ni_{1-x}Fe_xO_y catalysts shows two features: one redox wave for the transition from Ni(OH)₂ to NiOOH and an anodic wave due to water oxidation. Consistent with previous studies, the position and the area of the redox peaks are strongly correlated to the composition of the film.^{27,37} As the Fe content increases the redox peak shifts to more positive potentials; at iron concentrations beyond 25% the redox peak was merged into the water oxidation wave and is no longer observable.^{29,3635} In order to compare the electrocatalytic activity of the Ni_{1-x}Fe_xO_y catalysts, the current density at 300 mV overpotential and the overpotential required to produce 10 mA cm⁻² were determined. A plot of these two parameters as a function of Ni (content determined by the XPS) are shown in Figure 5–1.b. The maximum current density at 300 mV overpotential and the minimum overpotential required to achieve 10 mA cm⁻², i.e. the highest activity for oxygen evolution reaction (OER), were observed for the film with 75 - 50% nickel content. We note that the composition of the most active catalyst is comparable to previous reports where thin films of Ni-Fe catalysts were prepared by different methods on different substrates.^{29,35,38}

The composition of the catalysts after electrochemical conditioning were studied *via* XPS (Table A5-3). With the exception of the NiO_y catalyst, we did not observe a change in the composition of the catalysts after electrochemical conditioning. Iron was electrochemically intercalated into the NiO_y films, however, in agreement with prior studies.^{29,37} Raman spectroscopy was used to investigate a possible phase change of the catalysts during conditioning, however the catalysts prepared by this method are thin and amorphous and show no distinguishable peaks in agreements with other reports.^{33,39,40}



Figure 5–1. a) IR-corrected CVs of $Ni_{1-x}Fe_xO_y$ catalysts on FTO substrates; FeO_y (cyan), $Ni_{0.25}Fe_{0.75}Oy$ (orange), $Ni_{0.5}Fe_{0.5}O_y$ (pink), $Ni_{0.75}Fe_{0.25}O_y$ (green), and NiO_y (blue). b) plots of current density at 300 mV overpotential (blue diamonds) and overpotential at 10 mA cm⁻² (red triangle) as a function of the % Ni in contact with 1 M KOH; the compositions, activities, and the
error bars are the average and standard deviations acquired from 3 independently prepared samples.

The influence of the electrocatalyst composition on the performance when integrated with hematite electrodes was further investigated. The hematite electrodes were prepared *via* ED and ALD. As shown by Raman and SEM the morphology and crystallinity of the films remained unaffected after modification with catalyst (Figure A5-3 and Figure A5-4). These observations indicate that the catalyst coating with this method is solely a surface modification with no alteration of the bulk characteristic of hematite.

The current density (*J*) *vs.* applied potential (*E*) responses in the dark and under illumination of bare ED and ALD hematite electrodes, as well as ED and ALD electrodes modified with the five compositions of the Ni_{1-x}Fe_xO_y catalysts are shown in Figure A5-5. Though no obvious change in the PEC water oxidation performance of the FeO_y coated electrodes were observed, the performance of both ED and ALD electrodes modified with NiO_y were substantially diminished. In addition, it was noted that for the ALD electrodes all three catalysts, i.e. Ni25, Ni50, and Ni75, resulted in ~ 200 mV cathodic shift of the photocurrent onset potentials and thus improved performance. For the ED electrodes, on the other hand, only Ni25 improved the performance while Ni50 and Ni75, similar to the NiO_y, diminished the photocurrent response of the ED hematite electrode. To determine the underlying cause the different category behavior, two representative catalyst compositions we selected for more in-depth investigations described below: Ni_{0.25}Fe_{0.75}O_y (Ni25) as the Fe-rich catalyst, and Ni_{0.75}F_{0.25}O_y (Ni75) as the Ni-rich catalyst. To ensure the reproducibility of the behavior of the modified electrodes described below, *J-E* measurements for several additional batches of electrodes prepared independently by different people on different days were performed. The *J*-*E* curves for catalyst coated hematite electrodes are shown in Figure A5-6 and Figure A5-7. The PEC behavior of the bare ALD electrodes is very consistent, however there is some variability of the behavior of the bare ED electrodes. This is not too surprising given the different preparation methods. In both cases, however, the trend of performance and the effect of the different catalyst compositions is reproducible.

The dark J-E curves Ni25 and Ni75 catalysts, are compared in Figure A5-8. The dark current behavior follows the same trends in activity as these catalysts on FTO, with increasing activity in the order Ni75 > Ni25 > bare. This result suggests that for the thin film of catalysts the electrocatalytic activates are nominally independent of the hematite substrate. Representative J-E curves under illumination for the bare and modified electrodes are shown in Figure 5–2. Consistent with our prior report, the bare ED electrode somewhat outperformed the bare ALD electrode.² The effect of the different catalysts on the performance of the ED and ALD hematite electrodes is dramatically different, however. For the ALD hematite electrodes (Figure 5–2.a), both catalyst compositions improved the performance. This result agrees with our prior studies that showed surface modification of ALD hematite electrodes by coating with Co-Pi or NiO_y enhanced the overall performance of the electrode by increasing charge separation from hematite to the catalyst at the surface, thereby suppressing surface recombination rates.^{9,41} This behavior is generally consistent with the formation of an adaptive junction at SC/WOC interface.^{9,17} In the case of Ni75 coated ALD electrode a capacitive peak prior to the water oxidation wave is clearly observable. This peak is generally observed for Ni(OH)₂ coated semiconductor electrodes, i.e. Fe₂O₃ or TiO₂, under PEC water oxidation conditions and it is attributed to the Ni³⁺/Ni²⁺ redox reaction.^{6,17}

For the ED hematite electrodes shown in Figure 5–2.b, on the other hand, the *J*-*E* responses are strongly dependent on the composition of the catalyst. For the Ni25 coated ED electrodes, a \sim 300

mV negative shift of the photocurrent onset potential is produced. In addition, the photocurrent density and fill factors are significantly improved compared to the bare electrode. Conversely, for the Ni75 coated ED electrodes, the performance is suppressed. This behavior contrasts the electrocatalytic activity, where Ni75 outperforms Ni25. In addition to the diminished performance, the *J*-*E* curve with Ni75 exhibits two well-separated capacitive features; a redox peak located at ~ 0.7 V *vs*. RHE, similar to the ALD electrodes, and a second peak at ~ 1.35 V *vs*. RHE. The first capacitive wave at ~ 0.7 V *vs*. RHE is assigned to charging of the catalyst film, which is generally seen for Ni-rich Ni_{1-x}Fe_xO_y catalysts and is attributed to oxidation of Ni²⁺ to Ni^{3+,6} Figure A5-9 shows an increase in the magnitude of this wave in response to increasing incident light intensities from 0.1 sun to 3.5 suns, which further supports this assignment.



Figure 5–2. *J-E* curves measured at 20 mV s⁻¹ under 1 sun illumination for bare and modified a) ALD and b) ED hematite electrodes in contact with 1 M KOH solution; bare ALD (red), bare ED (blue), Ni75 coated hematite (green), Ni25 coated hematite (orange). The dark current are not included for the sake of clarity and are shown in Figure A5-8.

Because the dark J-E curve of Ni75 on the ED electrodes (Figure A5-8) and the light J-E curve of the bare ED electrodes both show very good activity, whereas the combination suppresses the performance, we hypothesize that deleterious interface states develop between the ED hematite and Ni75 catalyst films. Interestingly, since the ALD hematite electrode modified with the Ni75 catalyst exhibits good performance, the proposed development of Ni75/hematite interface states is not general, but appears to be a function of the particular hematite surface that is modified with the Ni75 catalyst. An additional control system was fabricated using a NiO_v catalyst, without the intentional incorporation of Fe, deposited on an ED electrode. The *J*-*E* curve of this system showed a redox wave with similar magnitude and potential as the ED/Ni75, displayed in Figure A5-10. The light *J*-*E* behavior is suppressed to a similar extent as the ED/Ni75 system. From these results, we deduce that the deleterious interface is due to Ni bonding with the ED hematite surface. We further deduce that the peak observed at ~ 1.35 V vs. RHE in Figure 5–2.b for the ED/Ni75 system is due to the ED/NiO_v interface states. We therefore focus our attention below on the ED systems. EIS measurements were performed for bare ED as well as electrodes modified with Ni25 and Ni75 catalysts. Examples of Nyquist plots for ED electrodes measured under illumination at 1, 1.2 and 1.4 V vs. RHE can be seen in Figure A5-11. At this potential range two semicircles are clearly visible. The equivalent circuits used to fit the EIS data have been established previously and are shown in Figure A5-12.⁹

Plots of C_{bulk} , as well as Mott-Schottky (MS) plots prepared from C_{bulk} , are shown in Figure A5-13 and Figure 5–3.a, respectively. The C_{bulk} behavior was found to be invariant with respect to catalyst under illumination. Dopant densities of 2.40 (± 0.14) × 10²⁰ cm⁻³, 2.75 (± 0.10) × 10²⁰ cm⁻³, and 2.76 (± 0.12) × 10²⁰ cm⁻³ were determined for ED/Ni75, ED/Ni25, and bare ED electrodes from fitting the capacitance data to the MS equation⁴² using a dielectric constant of 32 for hematite and

the geometric surface area of the electrodes.⁴³ This large dopant density is in good agreement with our previous report of electrodeposited hematite electrodes.² The small deviation in dopant density cannot account for the observed behavior for the catalyst coated electrodes. We note that this high dopant density precludes accurate determination of the flat band potential,^{44,45} however the similar behavior of all electrodes indicates that the catalyst does not shift the band positions or affect band bending by pinning the hematite electron Fermi level. This conclusion is further supported by IMPS results discussed below.



Figure 5–3. a) MS plots for bare and catalyst modified ED electrodes, b) *J-E* curve and C_{ss} values for bare ED electrode under 1 sun illumination in contact with 1 M KOH; bare electrode (blue diamond), Ni75 modified ED electrode (green triangle), and Ni25 coated ED electrode (orange pentagon). The dotted lines are the linear fitting used to extract the dopant density.

The low-frequency capacitance is assigned to surface states (C_{ss}) for the bare and the catalyst layers (C_{cat}) for the modified electrodes. The C_{ss} , displayed in Figure 5–3.b, has two peaks. One peak is coincident with the water oxidation onset potential at ~ 0.8 which we assign to the water oxidation

intermediate species building up on the electrode surface, and a second peak located at more positive potential, ~ 1.3 V *vs*. RHE, which we tentatively assign to a surface defect state.^{19,46} As shown in Figure 5–3.b, there is an apparent inflection of the *J-E* curve at this potential which suggests that recombination at this state mitigates the water oxidation efficiency until sufficient potential is applied to deplete the trap of electrons. We note that the presence of two surface states following high-temperature annealing procedure is a key difference between the ED and ALD electrodes.^{19,20} We therefore hypothesize that this second state is responsible for the dramatically different behavior of catalysts on the ED *vs*. ALD hematite electrodes.

In order to confirm our assignment and understand the effect of the catalysts, the thickness was varied by repeating the deposition procedure one or two additional times to make the series denoted 1, 2, and 3 cycles of catalyst. Atomic Force Microscopy (AFM) and Spectroscopic Ellipsometry (ES) were utilized to determine the thickness of the catalyst deposited on silicon substrates using comparable procedures. The thickness of the catalyst on hematite electrodes were estimated by integration of the cathodic peaks of the dark J-E (Table A5-4). For Ni75 catalyst an approximately linear growth as a function of the number of cycles was measured. Consistent with the experimental values the calculated thickness of the catalyst on hematite was also found to linearly increase with the number of cycles. In addition, the estimated thicknesses via charge integration of modified hematite electrodes were fairly close to the experimentally determined thicknesses of catalyst on silicon substrates by AFM/ES. Any discrepancy in results can be attributed to either the substrate dependence of the growth of the Ni75 catalyst or the possibility that not all the Ni sites are redox active. For Ni25 catalyst, however, the growth mode of the catalyst was found to be non-linear and the measured thicknesses were generally lower than Ni75 (Table A5-5). The light and dark J-E curves of the catalyst coated ED electrodes with varying thickness of catalyst

are shown in Figure A5-14. We note at a given potential the photocurrent was diminished by increasing the thickness of the catalyst. This can be understood by considering the illumination direction; the PEC measurements were all performed by illumination from the electrolyte side, thus a portion of the light is lost by competitive light absorption with the catalyst layer. This observation is important since it supports the increasing thickness of catalyst. The parameters derived from fitting the impedance spectra as a function of the catalyst thickness are shown in Figure A5-15 to Figure A5-18.

The C_{cat} as a function of potential for ED hematite electrodes coated with different thicknesses of Ni25 is compared in Figure 5–4.a. Also shown is the C_{cat} vs. potential of Ni25 measured on FTO. Boettcher and coworkers previously studied the electrocatalytic activity of Ni_{1-x}Fe_xO_y as a function of the catalyst loading.⁴⁷ It was shown that at the potential range where the catalyst is fully oxidized the C_{cat} was increased with the catalyst loading. As it can be seen from Figure 5–4.a, the C_{cat} increases with increasing the thickness of catalyst which further indicates that at this condition Ni25 is fully oxidized. The peak in C_{cat} is shifted negatively by 0.8 V compared to Ni25 on FTO substrate, indicating 0.8 V of photovoltage is produced by the hematite. Interestingly, this is the exact same photovoltage determined by Wang and coworkers for hematite coated with a NiFeO_x catalyst *via* open circuit potential measurements.⁴⁸ Once the potential of the catalyst drops to more positive potentials via oxidation by photogenerated holes in the hematite, represented by the capacitance, the photocurrent density is controlled by the flux of holes reaching the interface. This behavior is generally consistent with the adaptive junction model, and is further supported by IMPS results described below. We note that the magnitude of the C_{cat} for 1 cycle Ni25 on FTO is about 4 times larger than 1 cycle Ni25 on ED electrode, suggesting that the catalyst on FTO is thicker. As the thickness of the catalyst increase, however, the $C_{cat}(ED)$ increases and becomes

almost equal to the C_{cat} (FTO), which indicates that the growth of the catalyst is substrate dependent, and that the catalyst is fully oxidized.

Figure 5–4.b shows C_{cat} for different nominal thickness of Ni75 on hematite as well as Ni75 on FTO. We note that the peak of C_{cat} for Ni75 on FTO is about three times larger than Ni25 on FTO, which is attributed to the expected three times larger charge density, which is on the Ni atoms, for a given thickness. The plots of C_{cat} vs. potential for Ni75 exhibits three features: (1) similar to the Ni25, there is an onset of C_{cat} at approximately 0.6 V vs. RHE, however instead of reaching a peak, the C_{cat} plateaus over an additional 0.6 V applied potential, (2) where it increases to values consistent with Ni75 on FTO, and (3) the C_{cat} was found to be independent to the thickness of the catalyst at the potential range of 0.7 - 1.4 V vs. RHE.



Figure 5–4. a) C_{Ni25} and b) C_{Ni75} obtained from fitting EIS for catalyst coated FTO (1cycle, shown with star symbols) and ED electrodes with varying thickness: 1 cycle (pentagon), 2 cycles (circle), and 3 cycles (triangle).

This behavior is consistent with the potential of the catalyst being pinned. Since the bulk capacitance, and thus band bending, band positions and hole flux from hematite, is constant for all ED electrodes measured, the catalyst potential must be controlled by recombination to interface (or catalyst) states. Once these states are emptied, for example by controlling the electron Fermi level (applied potential), the photogenerated holes should further oxidize the catalyst, resulting in an abrupt increase in C_{cat} and current. Above we assigned the peak observed at ~ 1.35 V vs. RHE in the *J-E* curves for the ED/Ni75 system to the interface states, which is coincident with the sudden increase in C_{cat} . This is also approximately the same potential as the second surface state observed for the bare ED electrode displayed in Figure 5–2.b. Thus, we propose that the interface state results from bonding interactions between the ED surface state and Ni hydroxide species.

Further understanding of the effect of catalyst can be gleaned by comparing the trap (recombination) resistance to surface states for the bare, R_{trap} , or catalyst layer for modified electrodes, R_{cat} , and the charge transfer resistance at the respective electrochemical interface, R_{ct} , (Figure A5-17 and Figure A5-18). Bisquert and coworkers⁴⁹ showed that the R_{trap}/R_{ct} for bare electrodes, which corresponds to R_{cat}/R_{ct} for catalyst coated electrodes, is proportional to the ratio of charge transfer and recombination rate constants. Figure 5–5 shows the ratio of the R_{trap}/R_{ct} and R_{cat}/R_{ct} for bare and catalyst modified ED electrodes, respectively. There is a strong correlation between the ratios of resistances to the *J*-*E* curves displayed in Figure 5–2.b. For the Ni25 coated electrode, improvement in photocurrent and onset potential can be ascribed to an acceleration of charge transfer at the hematite surface compared to the bare electrode. In other words, oxidation of the Ni25 catalyst outcompetes interface recombination to a greater extent than water oxidation competes with surface state recombination at a bare hematite electrode. This result is consistent with our prior report on CoO_x coated hematite electrodes.⁵⁰ For Ni75 coated electrodes, on the

other hand, the R_{cat}/R_{ct} ratio is low and essentially constant, which indicates that fast recombination at the SC/WOC interface inhibits the photocurrent-voltage behavior.



Figure 5–5. R_{trap}/R_{ct} for bare and R_{cat}/R_{ct} for catalyst modified ED electrodes; bare electrode (blue diamond), Ni75 modified ED electrode (green triangle), and Ni25 coated ED electrode (orange pentagon).

IMPS measurements were also performed to interrogate the relevant charge dynamics at the surface of the electrode which give rise to the large difference in effects of the Ni25 and Ni75 catalysts. A set of normalized Nyquist plots for bare and modified ED electrodes at 1.3 V *vs*. RHE are shown in Figure S19. Ideally the low-frequency intercept (LF) with the real axis is equal to the steady-state photocurrent, which is equal to the rate at which the holes are transferred to the catalysts and from catalyst to solution. At sufficiently high frequencies (HF) the surface recombination is proposed to be frozen out and the HF intercept with real axis thus provides a measure of hole flux toward the SC/electrolyte (or SC/WOC) junction.^{51,52} Plots of the LF

photocurrent for bare and catalyst coated ED electrodes are compared in Figure 5–6.a. The LF plots mimic the behavior of the *J*-*E* plots, consistent with the assignment of the LF as the steady-state photocurrent.

The HF photocurrent is shown in Figure 5–6.b. For the Ni25 modified electrodes, the HF response is nominally identical to that of the bare electrode at all potentials. This indicates that after surface modification with Ni25, the flux of holes to the surface are constant. This is consistent with the Mott-Schottky plots which show that the energetics at the surface (band edges and band bending) that control the hole flux reaching the interface remains essentially constant. For the Ni75 coated electrode, similar HF responses are observed at potentials ≤ 1.0 V vs. RHE. At higher potentials, however, the HF response plateaus. This means that either the surface hole flux is constant over a relatively large range of applied potentials, from 1.0 to 1.5 V vs. RHE, or the assignment of the HF is wrong. The validity of the assumption that surface recombination is frozen out at high frequencies obviously depends on the rate of recombination. Just like the bare and Ni25 modified electrodes, the Mott-Schottky plots suggest an increasing hole flux due to increasing band bending over this potential range. The R_{cat}/R_{ct} ratio derived from EIS measurements for the Ni75 electrodes described above suggest fast interfacial recombination, which likewise can explain the HF results. Thus, we assign the plateau region of the HF of the IMPS results to an essentially constant, fast rate of interfacial recombination process, which isn't frozen out.



Figure 5–6. a) variation of low frequency (LF), and b) high frequency (HF) limits of the IMPS response for bare and catalyst coated ED electrodes under monochromatic illumination (470 nm) in contact with 1 M KOH solution; bare electrode (blue diamond), Ni75 modified ED electrode (green triangle), and Ni25 coated ED electrode (orange pentagon).

5.5. Conclusion

The electrocatalytic activity of $Ni_{1-x}Fe_xO_y$ catalysts on FTO substrates and on hematite electrodes in the dark is primarily controlled by the composition of the catalyst, where the nickel-rich Ni75 catalyst is the most active for electrochemical water oxidation. Under illumination, however, the PEC performance of modified hematite photoanodes (prepared by ALD and ED) were found to be dependent both on the substrate as well as the composition of the catalyst. Several unique and interesting specific differences were clearly observed. The PEC performance of the modified ALD electrodes improved upon modification with all catalyst compositions, indicated by the ~ 200 mV cathodic shift in photocurrent onset potential. The modified ED electrodes behaved very differently from the modified ALD electrodes for a given catalyst composition. Regardless of the hematite electrode preparation, however, the iron-rich Ni25 catalyst produces superior performance compared to Ni75, despite the inferior electrocatalytic activity. These results suggest the overall PEC performance is strongly influenced by the interface that can develop upon contacting semiconductors with electrocatalysts.

The most remarkable systems were the modified ED hematite electrodes, where the Ni25 catalyst produced a very large improvement in PEC water oxidation whereas the Ni75 catalyst produced diminished performance. The large improvement of the Ni25 modified ED electrode can be understood by the presence of a surface state defect which influences the *J*-*E* behavior of the bare electrode. The addition of the Ni25 catalyst apparently either passivates this state or just opens a more favorable path of hole transfer to the catalyst which circumvents it. This is supported by the catalyst capacitance which reaches a maximum coincident with the water oxidation onset potential. The capacitance increases with increasing catalyst thickness and illumination intensity, showing it originates from oxidation of the catalyst throughout the entire thickness from photogenerated holes in the hematite. The ratios of R_{cat}/R_{ct} from EIS measurements and HF/LF from IMPS further suggest the improvement in performance derives from an increase in charge separation and reduction in recombination at the hematite surface. These results are generally consistent with modified ALD electrodes,^{6,9} and other reported hematite electrode catalyst combinations^{48,53} which can be generally interpreted *via* the adaptive junction model.¹⁸

The most striking system is Ni75 modified ED hematite electrodes. Independently, they are the best WOC and photoanode examined, however the combination results in the worst PEC behavior of all systems investigated. The decreased performance coincides with the appearance of an additional capacitive wave. This capacitance is initially ascribed to an ED hematite-NiO_y interface state that acts as a recombination center. This is supported by the ratio of R_{cat}/R_{ct} from EIS measurements which indicates fast recombination, and the unusual leveling off of the HF intercept

of IMPS measurements. The capacitance of the catalyst also remains relatively low and constant over a large potential region – from the nominal $Ni^{3+/2+}$ potential to the interface state potential – indicating the catalyst potential is pinned by the interface state. Thus, even a soft interface that is expected from the deposition of an amorphous metal oxide WOC on hematite under mild conditions can produce states which control the behavior of the junction.

Finally, it is interesting to note that there are prior reports that the PEC water oxidation is influenced by surface or interface states, which can be perhaps better understood following the insight provided here.^{19,20} Wang and coworkers²¹, showed that the surface modification of hematite through a re-growth procedure followed by NiFeO_x catalyst coating resulted in a substantial improvement of the photoanode performance. This result is analogous to what we observe with the ED/Ni25 junction. Li and co-workers studied Ni(OH)₂ coated Fe₂O₃ nanowires.⁵⁴ They observed that coating the hematite electrode with Ni(OH)₂, resulted in an initial cathodic shift of the photocurrent density; however, the photocurrent decayed by $\sim 90\%$ – to values lower than the bare hematite – within 30 s. This behavior was attributed to the fast oxidation of Ni²⁺ to Ni³⁺, followed by a rate-limiting step of further oxidation to a Ni⁴⁺ species, thus, resulting in the NiOOH film storing charge but not producing a sustained enhancement of water oxidation. This result can be understood by the NiOOH catalyst being pinned, thus not achieving a potential sufficient to sustain water oxidation, consistent with what we observe with the ED/Ni75 (and NiO_y) system. In another system, Choi and coworkers⁵⁵ showed that the PEC characteristic of BiVO₄ is substantially improved when the interface between the semiconductor and NiOOH, was modified with FeOOH. This result is consistent with our findings that the Ni25, which consists of separate FeOOH and Fe-doped NiOOH phases, passivates the ED hematite interface. This examples emphasize the importance of the SC/WOC interface, where the contact of a Ni-rich phase with otherwise

promising photoanode materials may produce a large density of deleterious states which act as recombination centers, whereas contact with Fe-rich phases may produce a . Clearly more research is needed to understand such phenomena in more detail to develop more general models of this important interface.

In follow-up study in collaboration with Boettcher's group (University of Oregon), the PEC characteristics of the bare and catalyst coated ED-hematite electrode were studied. A combination of electrochemical and spectroscopic characterization including cross-section TEM and dual working measurement were utilized to further assess the relationship between the PEC performance and the composition of the catalyst.⁵⁶ The two key observations of this study are: (1) Ni75 is electrically more conductive than Ni25 by 5 order of magnitudes and (2) the electrodeposited hematite electrodes are porous with presence of pin-holes. On the bases of these observations, it is concluded that the performance of the Ni75 coated ED-hematite is suppressed by the fast recombination of the stored holes in catalyst with the free electrons from the conductive substrate (FTO). In another word the potential of the catalyst is pinned to the conductive substrate.

APPENDIX

Composition	Fe (mg)	Ni (mg)	Hexane (mg)
NiOy	0	20	90
Ni _{0.75} Fe _{0.25} O _y	103	141	920
$Ni_{0.50}Fe_{0.50}O_y$	44	20	212
Ni _{0.25} Fe _{0.75} O _y	411	63	1440
FeOy	50	0	142

Table A5-1. The weight of metal precursor used to prepare the catalyst solutions.

Composition	Theoretical		Fou	Found	
	% Ni	% Fe	% Ni	% Fe	
NiOy	100	0	100	0	
Ni _{0.75} Fe _{0.25} O _y	75	25	73 ± 6	27 ± 6	
$Ni_{0.50}Fe_{0.50}O_y$	50	50	55 ± 4	45 ± 4	
Ni _{0.25} Fe _{0.75} O _y	25	75	28 ± 5	72 ± 5	
FeOy	0	100	0	100	

Table A5-2. Composition of as-prepared $Ni_{1-x}Fe_xO_y$ catalysts found by XPS, the compositions and error bars are the average and standard deviations acquired from 3 independently prepared samples.

	Before			After		
Composition	Theor	etical	Fo	und		
	% Ni	% Fe	% Ni	% Fe	% Ni	% Fe
NiOy	100	0	100	0	80	20
Ni _{0.75} Fe _{0.25} O _y	75	25	71	29	70	30
$Ni_{0.50}Fe_{0.50}O_y$	50	50	52	48	49	51
Ni _{0.25} Fe _{0.75} O _y	25	75	28	72	29	71
FeO _y	0	100	0	100	0	100

Table A5-3. Comparison between catalyst composition before and after electrochemical conditioning on the same electrode. Note: samples were conditioned by cycling the potential at 1.0 -2.0 V vs. RHE for 40 cycles as well as electrochemical characterization by impedance at potential range of 1.3 - 1.8 V vs. RHE with 100 mV interval. Afterward the electrodes were rinsed with extensive amount of DI water.



Figure A5-1. Raman spectra of thin films of $Ni_{1-x}Fe_xO_y$ with different composition before and after irradiation with UV-light for 1h. The loss of the bands after UV-irradiation indicates that ligands are decomposed.



Figure A5-2. The detailed XPS spectra of the $Ni_{1-x}Fe_xO_y$ catalyst on FTO. Note: The C 1s peaks are presented to show that the shift caused by charging the sample during the measurement are correctly accounted for.

For FeO_y film, two peaks in O1s region (530 and 531.7 eV) and one group of peaks in Fe2p region (711 and 724 eV) were observed. This is in agreement with the formation of FeOOH phase.³⁵ For NiO_y, on the other hand, only one O 1s peak (531.7 eV) and one group of Ni 2p peaks (850 and 860 eV) were observed which is consistent with formation of Ni(OH)₂ phase.³⁵ Interestingly, upon

doping Ni(OH)₂ with iron, at the maximum concentration of 25%, the peak position of the Fe 2p and Ni 2p were shifted to the lower binding energies and only one O1s peak (~ 531.7 eV) was observed. However, at concentrations beyond 25%, a new O 1s peak emerged which is consistent with the formation of FeOOH. Consistent with the oxygen peak, in Fe 2p region, up to 25% of the iron, there is only one group of Fe 2p peak. At higher concentration of iron, however, a new group of Fe 2p peaks emerged which were located at the same position as the Fe 2p peaks for FeOOH. In addition, in the Ni 2p region a new group of Ni 2p peaks emerged which was independent to the composition of the films. Therefore, the presence of one O 1s peak and one group of Fe 2p peak for the iron content up to 25% indicates that iron is in fact doped into the nickel phase which formed a single phase of Ni_{1-x}Fe_xO_y. On the other hand, at the higher concentration of iron two distinctive phases of FeOOH and Ni_{1-x}Fe_xO_y were formed. This finding is consistent with previous reports on the electrocatalytic activity of Ni_{1-x}Fe_xO_y on different substrates.^{35,37}



Figure A5-3. The SEM images of bare and catalyst coated ALD (a-c), ED (d-e) electrodes. The first column represents the bare electrodes, the 2^{nd} and 3^{rd} columns represent the electrodes coated with Ni_{0.25}Fe_{0.75}O_y and Ni_{0.75}Fe_{0.25}O_y, respectively. The scale bar is 500 nm with a magnification of 50K.



Figure A5-4. The Raman spectrum of a) bare hematite, b) bare and catalyst modified ALD, c) bare and catalyst modified ED hematite electrodes.

The Raman spectrum of the bare and catalyzed hematite electrodes are shown in Figure A5-4. All the observed peaks are readily assigned to α -Fe₂O₃. Clearly, the Raman spectra of hematite films, i.e. ALD and ED, are almost identical which further indicates that regardless of the preparation method the degree of crystallinity and crystal orientations for both type of hematite films are similar. In addition, after coating hematite electrodes with catalysts, the Raman spectrum of the bare and catalyzed hematite films, in terms of peak position, shape, and patterns, are identical.



Figure A5-5. *J-E* curves measured in light (a and c) dark (b and d) for bare and catalyst coated ALD (top), and ED (below) hematite electrodes in contact with 1 M KOH solution. The plots correspond to bare ALD (red), bare ED (blue), NiO_y coated hematite (violet), Ni75 coated hematite (green), Ni50 coated hematite (pink), Ni25 coated hematite (orange), and FeO_y coated hematite (cyan).



Figure A5-6. *J-E* curves measured in light (left plots, solid lines) and dark (right plots, dotted lines) for three different batch of ALD hematite electrodes coated with catalyst in contact with 1 M KOH solution; bare ALD (red), Ni75 coated hematite (green), Ni25 coated hematite (orange). Note: these electrodes are different from the one shown in the main text.



Figure A5-7. *J-E* curves measured in light (left plots, solid lines) and dark (right plots, dotted lines) for three different batch of ED hematite electrodes coated with catalyst in contact with 1 M KOH solution; bare ED (blue), Ni75 coated hematite (green), Ni25 coated hematite (orange). Note: these electrodes are different from the one shown in the main text.



Figure A5-8. *J-E* curve measured in dark for bare and catalyst coated a) ALD, and b) ED hematite electrodes in contact with 1 M KOH solution.



Figure A5-9. *J-E* curves measured at 20 mV s⁻¹ for ED coated electrodes with Ni75 in contact with 1 M KOH solution as a function of illumination intensity.



Figure A5-10. *J-E* curves measured at 20 mV s⁻¹ under 1 sun illumination for NiO_y and Ni75 coated ED electrodes in contact with 1 M KOH solution.



Figure A5-11. Nyquist plots for bare and catalyst coated ED electrodes measured under illumination at a) 1.0, b) 1.2, and c) 1.4 V *vs.* RHE.



Figure A5-12. a) Equivalent circuit used for interpretation of bare and catalyst coated ED electrodes, b) Randle circuit, when two and one semicircle was observed, respectively.⁹



Figure A5-13. *C*_{bulk} values from EIS measurements for bare and catalyst coated ED electrodes under 1sun illumination in contact with 1 M KOH.

	Integrated	Calculated thickness	Measured	Measured
Number of cycle	charge from	from integrated	thickness with	thickness with
	$CV (mC cm^{-2})$	charge (nm) ^a	AFM (nm)	SE (nm)
1	0.8	15.4	17.8	15
2	1.58	30.5	37.4	29
3	2.2	42.4	48.9	42

Table A5-4. The measured and calculated thickness of the Ni75 on silicon and hematite. ^a For calculation of the thickness the measured composition found by XPS was used and assumed that only Ni atoms are involved in the redox reaction. The cell volume of 0.2108 nm³ (ICSD 159700) for Ni-Fe layered double hydroxide and the geometrical surface area were used to calculate the thickness of the film.^{57–59} For these calculation it was assumed that there is only one Ni per unit cell. Obviously if the number of Ni ion per unit cell is more, the calculated thickness would be smaller. However it does not violate the conclusion that the thickness grows with the number of cycles.

Number of cycle	Measured thickness with AFM (nm)	Measured thickness with SE (nm)
1	13.0	10.0
2	14.0	15.5
3	20.5	23.0

 Table A5-5. The measured thicknesses of the Ni25 on silicon.



Figure A5-14. *J-E* curves measured for bare (blue) and Ni25 (a-b) and Ni75 (c-d) coated ED electrodes; a) Ni25 (light), b) Ni25 (dark), c) Ni75 (light), and d) Ni75 (dark) in contact with 1 M KOH solution.



Figure A5-15. a) C_{bulk}, and b) Mott-Schottky values from EIS data for bare and Ni25 coated ED electrodes with 1cycle (pentagon), 2 cycles (circle), and 3 cycles (triangle pointing down). Also included are the value measured for the bare electrode (blue diamond).



Figure A5-16. a) C_{bulk} , and b) Mott-Schottky values from EIS data for bare and Ni75 coated ED electrodes with 1cycle (pentagon), 2 cycles (circle), and 3 cycles (triangle pointing down). Also included are the value measured for the bare electrode (blue diamond).



Figure A5-17. a) $R_{cat,Ni25}$ and b) $R_{ct,Ni25}$ values from impedance response of ED hematite electrodes with 1cycle (pentagon), 2 cycles (circle), and 3 cycles (triangle pointing down). Bare ED hematite fitting $R_{trap,bare}$ and $R_{ct,bare}$ (blue diamond) are shown for comparison.



Figure A5-18. a) $R_{cat,Ni75}$ and b) $R_{ct,Ni75}$ values fit from impedance response of ED hematite electrodes with 1cycle (pentagon), 2 cycles (circle), and 3 cycles (triangle pointing down). Bare ED hematite fitting $R_{trap,bare}$ and $R_{ct,bare}$ (blue diamond) are shown for comparison.


Figure A5-19. Complex plots of normalized IMPS data for bare and catalyst coated ED electrodes at 1.3 V *vs.* RHE; bare electrode (blue triangle), Ni75 modified ED electrode (green diamond), and Ni25 coated ED electrode (orange circle)

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Chapter 6:

The Role of Catalyst Composition on

the PEC Water Oxidation Performance of Hematite with

Different Crystal Orientations

6.1. Abstract

In this chapter, the PEC water oxidation performance of catalytically modified hematite electrodes with different crystal orientations, i.e. (100) and (001), coated with two compositions of Ni_{1-x}Fe_xO_y catalysts, i.e. Ni75 and Ni25 catalysts, was investigated. A series of photoelectrochemical methods including EIS and IMPS were utilized to assess the dynamics of charge transfer on the catalytically modified electrodes. It was shown that under identical PEC water oxidation conditions, (100)-oriented hematite electrode outperforms the bare electrode with (001) orientation. Interestingly, for the catalyst-coated hematite electrodes, the Ni25 coated-electrodes produced almost identical PEC characteristics for both orientations, whereas the PEC performance of Ni75-coated electrodes exhibited strongly dependent on the crystal-orientation. For example, Ni75 coated (100) and (001) hematite electrodes produced a hole-collection efficiency of ~ 60% and 10%, respectively, at 1.1 V *vs*. RHE, which manifested itself in higher photocurrent densities at this potential. Based on the IMPS and EIS measurements, it was shown that the improved charge-separation efficiency at the surface of the electrode is responsible for the enhancement in PEC efficiency.

6.2. Introduction

A deep knowledge of the dynamics of photogenerated charges at the semiconductor and catalyst junction is highly beneficial as it allows to engineer the photoelectrode surface to enhance its charge collection efficiency. It has been shown that the catalytic modification substantially improves the PEC performance of the semiconductor and for some cases the improvement in is only achieved when prior to deposition of catalyst the semiconductor surface is modified with a non-catalytic layer.^{1–3} These observations clearly underline the role of the interface at the catalyst and semiconductor junction. As mentioned in chapter 5, in presence of pin-holes and conductive

catalyst the PEC performance of catalytically modified hematite electrodes is dominated by shunting to the conductive substrate. Therefore, pin-hole-free electrodes with various crystal orientations are ultimately the ideal model electrodes to investigate the role of semiconductor|catalyst junction. Recently, Rothschild et al.4 studied the effect of the crystal orientation on the bulk and the surface properties of heteroepitaxially-grown Sn-doped hematite by PLD/MBE. They observed that under identical conditions for PEC water oxidation, the photocurrent onset potentials for (110)- and (100)-oriented hematite were located ~ 170 mV more negative than the (001)-oriented hematite electrode. In the presence of a fast hole scavenger such as H₂O₂, however, the photocurrent onset potential and the photocurrent density at any given potential were found to be independent of the crystal orientation. Subsequent analysis via EIS measurements revealed relatively similar bulk properties (dopant density and flat-band potentials) for these series of hematite electrodes. On the basis of these observations, it was concluded that the crystal orientation primarily influences the kinetics of charge transfer at the surface of the electrode.⁴ The heteroepitaxially-grown hematite electrodes by this method are promising candidates for fundamental investigation of the effect of surface orientation on the catalyticallymodified electrodes. In this chapter, the combinations of two compositions of Ni_{1-x}Fe_xO_y catalysts, i.e. Ni-rich and Fe-rich catalysts, prepared by UV light-assisted deposition and hematite electrodes with two distinctive orientations, i.e. (100) and (001), supplied by the Rothschild's group at Technion, were utilized as model electrodes with systematically different interfacial composition/and structure at the semiconductor catalyst junction. The crystal structure of hematite at the surface for these two orientations are shown in Figure 6-1. As it can be seen, the (100) orientation is comprised of two types of terminal hydroxyl groups at the surface whereas the (001) orientation contains only one type of bridging oxygen groups. In addition, the number of iron sites



Figure 6–1. The surface configuration of hematite as a function of crystal orientations, a) (100) and b) (001) orientations. The iron centers and the lattice oxygens are shown in orange (large circle) and red (small circle), respectively. The singly and doubly coordinated oxygen sites at the surface are shown in yellow and cyan, respectively. Throughout this chapter the (100) and (001) orientations are labeled as M and C, respectively.

per unit area is higher for the (001) orientations (18 sites *vs.* 12 sites). As the result, the nature and density of states at the surface of hematite electrodes with different crystal orientations are different. The combination of different surfaces with catalyst therefore creates new states which can modulate the charge transfer from semiconductor to the catalyst. Herein we aim to understand how the PEC water oxidation performance of the catalytically modified hematite electrodes varies as a function of composition and structure of the interface.

6.3. Experimental

6.3.1. Electrode Preparation

The hematite electrodes with various orientations were heteroepitaxially grown by PLD. These electrodes were supplied by the Rothschild's group and used as received. The detailed information about the preparation method and their properties can be found in literature.⁴ Thin films of Ni_{0.75}Fe_{0.25}O_y (Ni75) and Ni_{0.25}Fe_{0.75}O_y (Ni25) catalysts were deposited by spin-coating on the hematite substrates using a modified version of previously reported procedures.^{2,5} Prior to deposition of catalysts, the hematite electrode was sequentially cleaned by spin-coating with DI water and hexane for 30 s at 5000 rpm. Precursor solutions were prepared from iron (III) 2ethylhexanoate (50% w/w in mineral spirits, Strem Chemicals), and nickel (II) 2-ethylhexanoate (78% w/w in 2-ethylhexanoic acid, Strem Chemicals) by dissolving the appropriate amount of metal precursor in hexanes to give a total concentration of metals of 0.05 M with the ratio of 15% w/w metal complex to hexane (see Table A5-1). Subsequently, $250 \,\mu$ L of the catalyst solution was spun coated at 5000 rpm for 60 s. The as-prepared films were irradiated with UV light (254 nm, 5.8W) for 1 h followed by annealing in a preheated furnace in air at 100 °C for 1 h. The ohmic electrical contact was made by gently scratching Ga-In eutectic (99.99% Sigma Aldrich) to the back contact and then attaching a copper wire with silver epoxy on to it. The electrode was then placed on a preheated hot plate at 100 °C to dry out and harden it.

6.3.2. Photoelectrochemical Measurements

The photoelectrochemical and electrochemical impedance spectroscopic measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software.

Unless otherwise stated, all photoelectrochemical tests were carried out by shining light on the electrodes through the electrolyte. Prior to PEC characterization each electrode was aged (conditioned) by 40 cyclic voltammetry in the potential range of 0.5 to 1.8 V vs. RHE with the scan rate of the 100 mV s⁻¹ in 1 M KOH. The current density vs. applied potential (J-E) for the bare and modified hematite electrodes were examined by cycling the potential between 0.5 and 1.5 V vs. RHE at the scan rate of 20 mV s⁻¹ in contact with 1 M KOH with pH = 13.6 as determined with Fisher Scientific Accument pH meter. A 1 M KOH solution containing 0.5 M H₂O₂ was used as a hole scavenger. Subsequently the ratio of $J_{photo}(H_2O)$ to $J_{photo}(H_2O_2)$ was used to calculate the hole collection efficiency. The light source was a 450 W Xe arc lamp (Horiba Jobin Yvon) and the AM 1.5 solar filter was used to simulate sunlight at 100 mW cm⁻² (1 sun). A homemade saturated Ag/AgCl and a platinum mesh electrode were used as the reference and counter electrode, respectively. The reference electrode was frequently calibrated against commercial saturated calomel electrode (Koslow Scientific). All the potentials were converted to reversible hydrogen electrode (RHE) using $E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + (0.059 \text{ V}) \times \text{pH}$. Electrochemical impedance spectroscopic data was measured at the potential range of 0.8 and 1.5 V vs. RHE with 100 mV intervals using a 10 mV amplitude perturbation between 10,000 and 0.01 Hz. Data were fit to the appropriate equivalent circuit using Zview software (Scribner Associates). The IMPS measurements were performed using Eco Chemie Autolab potentiostat equipped with metrohm LED driver accessory. A 470 nm LED light was utilized as the light source. The power of the LED was chosen to produce the same photocurrent as it was measured under 1 sun illumination. The modulation intensity was set at 10% of the power of the LED to ensure a linear respond and the frequency was swept from 15 kHz to 0.1 Hz with 10 frequency per decade increments. The IMPS data were collected over the potential range of 0.8 to 1.5 V vs. RHE with 100 mV intervals.

The data shown here were collected for a total number of 8 electrodes (4 sets \times 2 orientations, see Table A6-1). Due to the limited number of the electrodes, the reproducibility of the results were only examined for Ni25 coated electrodes (set2 and set 4). The *J*-*E* curves, high frequency (HF), and low frequency (LF) IMPS responses for these electrodes are compared to the corresponding bare electrodes (Set1) in Figure A6-1. For Ni25 coated C-hematite electrodes, while the HF responses are highly reproducible but the photocurrent onset potential are different by 100 mV (evident from both *J*-*E* and LF). For the Ni25 coated M-hematite electrodes, the photocurrent onset potentials are relatively similar (evident from both *J*-*E* and LF) but the photocurrent density at the higher potentials and the HF responses are different by ~ 25%. While, the reproducibility of the performances are highly desirable and more experiments are required to statistically evaluate any interface-performance relationship, for the following discussion the results for the best performing electrodes are utilized.

6.4. Results and Discussion

The dark *J*-*E* curves of the bare and catalyst coated electrodes exhibit a highly rectifying behavior and produce a negligible dark (leakage) current only at high positive potentials (shown in Figure A6-2). This is an important observation as it ensures that the behavior of the catalytically-modified electrodes are not influenced by shunting. The light *J*-*E* curves of the catalyst-coated hematite electrodes with various compositions of catalyst are compared to the corresponding bare electrodes in Figure 6–2.a. Under PEC water oxidation conditions the bare M orientation outperforms the bare C orientation hematite electrode. In presence of a fast hole scavenger, however, they produce an indistinguishable *J*-*E* curves (Figure A6-3). These results are consistent with the original report,⁴ the superior performance of M orientation being due to its higher catalytic activity. As shown in Figure 6–2.a, the surface modification with Ni25 and Ni75 results in a cathodic shift in the photocurrent onset potentials. In comparison to the bare electrode, these *J*-*E* curves exhibit a wide hysteresis between the forward (anodic sweep) and reverse scan (cathodic sweep) - especially for Ni75 coated electrodes. To estimate the photocurrent onset potentials, thus, we used chronoamperometry to determine the photocurrent at various applied potentials under steady-state conditions (Figure A6-4). Interestingly, regardless of the crystal orientation of the hematite electrodes, the photocurrent onset potential for both Ni75- and Ni25-coated hematite electrodes are located at relatively similar potentials.



Figure 6–2. Comparison of PEC performance of catalytically modified hematite electrodes with various crystal orientations and different composition of catalysts. a) *J-E* curves of bare, Ni25-(orange) and Ni75-(green) coated hematite electrodes with different orientations, b) hole collection efficiency for bare, Ni25-(orange) and Ni75-(green) coated hematite electrodes. The (100) (labeled as M), and (001) (labeled as C) orientations are shown in broken line with empty shapes and solid lines with solid shapes, respectively. Note: for clarity, the dark currents are omitted and are shown

in Figure A6-2. The ratio of the low frequency (LF) to high frequency (HF) of IMPS responses were used to calculate the $\eta_{\rm hc} \%$.^{6,7}

The *J*-*E* curves of the Ni75-coated electrodes exhibit two additional features: (1) Ni75 improves the turn-on potential, but the current densities at higher potentials are lower than that of the bare or Ni25-coated electrodes. This behavior can be ascribed to the absorption of light by the catalyst (electrode was illuminated through the solution) as confirmed by the spectroelectrochemistry analysis of the Ni75- and Ni25-coated FTO electrodes (results are discussed following Figure A6-5). (2) A unique set of cathodic peaks appeared during the reverse scan, which are not observed for the bare electrodes. This suggests that the photogenerated holes are stored into the catalyst layer. Ideally, the electrochemical properties of the catalyst should be independent of the substrate, thus the redox characteristics, i.e. peak position and area, of the Ni75 catalyst with the same thickness should remain the same. As can be seen the position in Figure 6–2.a, shape and the area of the peaks depend on the substrate and on the crystal orientation of the hematite substrate. A sharp reduction peak can be seen in Figure 6-2.a for Ni75-coated C-hematite electrode, while the Ni75-coated M-hematite produces a rather broad peak. This can be better understood by considering the surface configuration of hematite grown in different crystal orientations (Figure 6-1). The surface of C-hematite ((001) orientation) is uniquely comprised of only doubly coordinated oxygen groups while the surface of M-hematite ((100) orientations) possesses both singly and doubly coordinated oxygen groups with the ratio of 2:1.8 Therefore, it can be postulated that the combination of C-hematite with Ni75 forms a narrow density of interface states, as a result the reduction peak is sharper.

The hole collection efficiency for the bare and catalyst coated hematite electrode with varying crystal orientation and different catalyst composition as a function of potential are shown in Figure 6–2.b. Consistent with the conclusion made in the original work, the better performance of the bare M-hematite in comparison to the C-hematite is due to its superior hole collection efficiency. Figure 6–2.b shows that for the catalyst coated electrodes the hole collection efficiencies (HCE) at the potentials beyond ~ 1.2 V *vs*. RHE is unity. At 1.1 V *vs*. RHE however, the HCE is decreased in the order of M(Ni75) > M(Ni25) \approx C(N25) > C(Ni75) where the Ni75 coated M- and C-hematite produced ~ 60% and 10% hole collection efficiency, respectively. The superior hole collection efficiency is further manifested in the slightly higher current density at 1.1 V *vs*. RHE for Ni75 coated M-hematite (evident from the steady state *J-E* curves shown in Figure A6-4). The reproducibility of these results needs to be evaluated by conducting more experiments.

The light EIS measurement was utilized to further study the effect of crystal orientation on the PEC performance of the bare, Ni75-, and Ni25-coated hematite electrodes. The EIS responses were fitted to the equivalent circuit shown in Figure A5-12. For the potentials with only one semicircle/peak in the Nyquist/Bode plot the Randles circuit and for the potentials with two semicircle/peaks the previously reported equivalent circuit for CoPi coated hematite electrodes⁹ were used to extract the capacitances and charge transfer resistances. Since catalyst coating is solely a surface modification, it is expected that the dopant density and the flat band potential (bulk property) of semiconductor to remain constant. Plots of C_{bulk} and Mott Schottky (MS) for the bare and catalyst coated electrodes with different orientations and catalyst compositions are compared in Figure A6-6. A nearly identical slope and intercept can be calculated for all electrodes. By fitting the linear slope to the MS equation¹⁰ and using a dielectric constant of 32 for hematite¹¹ and the geometric surface area of the electrodes, a dopant density of 8 - 11×10^{19} cm⁻³ was calculated.



Figure 6–3. The calculated a) R_{trap} , R_{cat} and b) R_{ct} for the bare and catalyst coated hematite electrodes with different crystal orientation of hematite and varying composition of catalyst as a function of applied potential. The C- and M-orientation are shown in solid and empty shapes, respectively. The Ni75 and Ni25 catalyst coated electrodes are shown in green and orange, respectively.

Due to the highly doped nature of these electrodes, the MS equation cannot be used to determine the true flat band potential of these electrodes. The high frequency (HF) response from the IMPS measurements - corresponding to the flux of the holes toward the surface of the electrode^{6,7} - was used to assess how band bending changes upon catalyst modification. The value of HF as a function of applied potential for the bare and catalyst coated hematite electrodes with various orientations are shown in Figure A6-7. As it can be seen, across different electrodes the HF values are relatively constant and are independent to the composition of the catalyst or crystal orientation of the hematite electrodes (see Figure A6-3) which further indicates that the catalyst coating is solely a surface modification.

The calculated charge transfer resistance from hematite electrode to the surface state (R_{trap}) and catalyst (R_{cat}) are shown in Figure 6–3.a. As shown, R_{trap} and R_{cat} values are relatively constant for all the electrodes with different orientations and catalyst composition. This further implies that the

charge transfer from semiconductor to the catalyst (or to the surface state) is independent from the crystal orientation of hematite electrode and the composition of the catalyst. The value of the R_{ct} shown in Figure 6–3.b, however is reduced by 1-2 orders of magnitude after catalytic modification. Interestingly, the lowest R_{ct} value was observed for the Ni75 coated M-hematite. This agrees with the slightly better current density and hole collection efficiency observed in Figure 6–3. In addition, at 1.1 V *vs.* RHE (the potential close to the photocurrent onset potential) the calculated R_{ct} value for Ni75 coated C-hematite is about 2-5 times higher than that of other catalyst coated electrodes. This observation is consistent with slightly lower current density for the C(Ni75) electrode.

The calculated surface state capacitance (C_{ss}) and capacitance of the catalyst (C_{cat}) for the bare and catalyst coated hematite with different compositions are shown in Figure A6-8. In line with previous reports,^{4,12} the C_{ss} exhibits a peak that coincides with the photocurrent onset potential (Figure A6-4). Consistent with the original work⁴ the surface state capacitance of C orientation was found to be higher than for the M orientations. As can be seen, the C_{cat} across all the catalytically modified electrodes are larger than the C_{ss} . This observation indicates that the photogenerated holes are stored in the catalyst. Depending on the catalyst composition and orientation of hematite, C_{cat} vs. applied potential exhibit multiple features: (1) For Ni25-coated electrodes, while the peak position is independent to the crystal orientation to M-orientation. (2) For the Ni75-coated electrodes both the value of C_{Ni75} and its position depends on the crystal orientation of the hematite substrate. For the Ni75 coated C-hematite, the capacitance of the catalyst peaks around 200 mV after the photocurrent onset potential, while for the Ni75-coated M-hematite, the analog peak occurs near the photocurrent onset potential. In addition, the magnitude

of C_{cat} for C(Ni75) is ~ 2 times higher than M(Ni75). (3) Due to the higher density of acceptor states in Ni75, i.e. Ni²⁺, it is expected that C_{Ni75} to be larger than C_{Ni25} (by a factor ~ 3), however, this behavior was not observed for these electrodes. The discrepancy in latter can be ascribed to the variation in the catalyst thickness. As discussed in chapter 5, the growth rate of catalyst depends on its composition and varies on different substrates.

At this stage, it is premature to draw conclusion on the effect of crystal orientation of hematite and catalyst composition on these catalytically modified electrodes as more experiments are required to confirm the reproducibility of these observations. In summary, the PEC performance of a series of the catalyst coated hematite electrodes with different crystal orientations were studied. We note that while the photocurrent onset potential of the bare electrode strongly depend on the crystal orientation of hematite, the catalyst coated electrodes (with Ni75 and Ni25) produced a nearly identical photocurrent onset potentials ($1.0 - 1.1 \vee vs$. RHE). The EIS and IMPS measurements have collectively shown that the improved hole collection efficiency/reduced charge transfer resistance at the surface of the electrode is the origin of the enhancement in PEC.

APPENDIX

Sample	C (001)	M (100)
Set1 (Bare)	\checkmark	\checkmark
Set2 (coated with Ni25)	\checkmark	\checkmark
Set3 (coated with Ni75)	\checkmark	\checkmark
Set4 (coated with Ni25)	\checkmark	\checkmark

 Table A6-1. The list of the samples studied in this study.



Figure A6-1. The reproducibility of the PEC performances of the Ni25 coated hematite electrodes with various orientations. The *J*-*E* curve of a) C-(001) and b) M-(100) oriented hematite electrodes; the high frequency (HF, filled shapes) and low frequency (LF, empty shapes) responses of different batches of Ni25 coated hematite electrodes with c) (001) and d) (100) orientations. The bare electrodes are shown with solid lines. The Dark *J*-*E* curves of corresponding electrodes are shown in Figure A6-2.



Figure A6-2. The dark current *J-E* curves of bare and catalytically modified hematite electrodes with various orientations and different catalyst composition. The bottom plot is the zoomed plot indicating residual current at high potentials (>1.6 V *vs.* RHE).



Figure A6-3. A) *J-E* curves of the bare hematite electrodes with various orientations in light (solid lines) and dark (dashed line) in contact with 1 M KOH solution containing 0.5 M H₂O₂ as the hole scavenger. b) Calculated hole collection efficiency using: $J_{photo}(KOH)/J_{photo}(H_2O_2)$; $J_{photo}(KOH)$ or $J_{photo}(H_2O_2)$ was calculated using: $J_{photo}(V) = J_{light}(V) - J_{dark}(V)$.



Figure A6-4. The steady-state light *J-E* curves of the bare and catalytically modified hematite electrode with varying crystal orientation and composition of catalyst. The current was measured in the range of 0.5 - 1.8 V *vs.* RHE with 100 mV intervals. At each applied potential the photocurrent was recorded until a stable current was achieved (~ 120s) and reported as the steady state current density.



Figure A6-5. The transmittance of a) bare, b) Ni25, and c) Ni75 coated FTO electrode as a function of the applied potential in contact with 1 M KOH. For FTO and Ni25| FTO electrodes the potential was scanned from 1.4 to 2.0 V *vs.* RHE with 100 mV intervals. For Ni75| FTO electrode, the potential was scanned in the same range but with 25 mV intervals. The background for each electrode was measured at open circuit potential at the beginning of the experiment. Prior to transmittance measurement at each potential the current was let to stabilize for 60-120 s. As it can be seen, Ni25 electrode produce a very similar % transmittances profile as the bare FTO electrode where the transmittance gradually decrease upon an increase in applied potential with a maximum reduction of ~ 20% at 2.0 V *vs.* RHE (Ni25 catalyst is completely oxidized at this potential, see Figure 5–4a). On the other hand, the transmittance of Ni75 sharply decreases by 50% upon increasing potential by 25 mV from 1.425 to 1.500 V *vs.* RHE (this switching potential is similar to the onset of oxidation potential of Ni75, shown in Figure 5–4a).



Figure A6-6. The fitted parameters of EIS measurements using equivalent circuits shown in Figure A5-15 for the bare and catalyst coated hematite electrodes with various orientations and different composition of the catalyst. a) C_{bulk} and b) Mott Schottky plots calculated from the C_{bulk} . The C and M orientations are shown with the solid and empty shapes, respectively.



Figure A6-7. The HF response of the bare and catalyst coated hematite electrodes with different orientations in contact with 1 M KOH. The C- and M-orientation is shown in solid and empty shapes, respectively. The Ni75 and Ni25 catalyst coated electrodes are shown in green and orange, respectively.



Figure A6-8. The surface state capacitance (C_{ss}) of the bare hematite electrodes and the capacitance of catalyst (C_{cat}) for the catalyst coated electrodes with different crystal orientation and composition of catalyst. The M- and C-orientations are shown with open and closed shapes, respectively. The Ni75 and Ni25 are shown in the green and orange colors, respectively.

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Chapter 7:

Conclusion and Future Directions

7.1. Summary and Conclusions

As outlined in the first chapter, due to its favorable properties Ta_3N_5 stands out as a promising candidate for the PEC water oxidation reaction. Experimentally it has been shown that its performance can reach its theoretical limits. The best examples of PEC water oxidation with Ta_3N_5 have shown promising performance only on tantalum substrate as the electron collector back contact.^{1,2} Ta-substrate is not transparent to the sub-band gap photons. In addition, the oxidation of Ta-substrate followed by ammonolysis (the common synthesis procedure) provides a highly reactive environment which preclude to realize Ta_3N_5 on transparent conductive substrates. To circumvent these issues we utilized electrodeposition and atomic layer deposition as the bottomup approaches to deposit tantalum oxides and nitride. These methods are promising as they provide a viable approach to fabricate tantalum oxide and nitrides on different substrates.

In the first project, the electrodeposition of tantalum(V) oxide from aqueous solution was developed. Electrodeposition of tantalum oxide is challenging because Ta^{5+} is highly susceptible to reduction which often results in the deposition of the metallic Ta or TaO_x sub-oxides. Moreover, most of the Ta precursors vigorously react with water which precipitate as tantalum oxide. To circumvent these issues a highly acidic solution of tantalum precursor was used where the hydrolysis rate of tantalum oxide can be controlled *via* regulating pH at the electrode surface. KNO₃ was further utilized as the sacrificial electroactive reagent which upon electroreduction increases the solution pH near the electrode surface triggering precipitation of tantalum oxide. The as-deposited films were amorphous nanostructured tantalum oxide which further were nitridized to Ta_3N_5 *via* annealing in ammonia. The resultant Ta_3N_5 film showed a promising PEC performance with an early turn on potential of 0.5 V *vs*. RHE.

Although electrodeposition is promising but it is beneficial to eliminate ammonolysis step. In the second project, tantalum nitride was integrate with Ta-doped TiO₂ (TTO), i.e. transparent conductive substrate (TCO), via ALD. It was shown that the low-temperature ALD results in an amorphous film of tantalum oxynitrides where the composition of the films strongly depend on the deposition temperature (more nitrogen is incorporated as the deposition temperature increases). These films were crystalize into Ta₃N₅ by a quick annealing in ammonia at 750 °C for 30 minutes. Subsequently, Ta-doped TiO₂ was developed as a stable TCO under reducing conditions of ammonolysis via ALD. Finally, these two layers were integrated to synthesize the first example of tantalum nitride on a transparent conductive substrate. Furthermore, it was shown that the PEC water oxidation performance of tantalum nitride is strongly correlated to the conductivity of the TTO substrate. Thus, it is highly advantageous to directly deposit crystalline phase of Ta₃N₅ on the state-of-the-art TCO such as FTO. In the subsequent project, a high temperature ($T_{max} = 650$ °C) and fully automated ALD system was designed and built. TaCl₅ coupled with ammonia were utilized to directly deposit crystalline tantalum nitride. It was found that 550 °C is the minimum temperature required to deposit crystalline Ta₃N₅ on FTO substrate. Due to the crystal mismatch between FTO substrate, and Ta_3N_5 the crystallinity, morphology and topography, growth rate, and optical density of the films were correlated on the number of ALD cycles. Therefore, in the first ~ 150 cycles a buffer layer with relatively similar morphology to the substrate is initially formed where after, Ta₃N₅ is randomly deposited. Furthermore, it was shown that FTO remained stable under reducing conditions of ammonia at 550 °C and remains transparent and conductive which further allowed to realize the 1st example of directly deposited Ta₃N₅ photoanode on FTO. The PEC measurements as a function of illumination direction coupled with EIS measurements revealed that the PEC performance of Ta_3N_5 is controlled by the diffusion of hole.

In the next section of this dissertation, the effect of the catalyst on the PEC performance of hematite was studied. The Ni_{1-x}Fe_xO_y coated planner hematite electrodes prepared by ALD and ED were utilized as the model electrodes to investigate how the catalyst interface with the underlying semiconductor. Depending on the catalyst composition and the hematite electrode, two distinctive behaviors were observed. In case of iron-rich catalyst (Ni25), the PEC water oxidation performance of both ALD and ED hematite electrodes were significantly improved. The electrochemical analysis via EIS and IMPS measurement have collectively shown that the Ni25 behave as a charge storage layer which improves PEC performance of the electrode by promoting the charge separation efficiency and reducing the recombination at the surface of electrode. On the other hand, the PEC water oxidation performance of the Ni-rich (Ni75) coated hematite electrodes strongly depends on the preparation method of hematite electrodes. In case of pin-hole free hematite electrodes prepared by ALD, Ni75 improves the performance of the hematite electrode similar to that realized for Ni25 coated hematite electrode. This was further confirmed via dual working electrode and potential-sensing AFM measurements in collaborative studies with Boettcher's group from University of Oregon.^{3–5} However, Ni75 substantially diminished the PEC water oxidation performance of ED-hematite. A combination of electrochemical and spectroscopic methods, e.g. TEM and DWE, have revealed that the electrodeposited hematite electrodes are porous.⁶ Subsequently, upon deposition of relatively thick catalyst (relative to the pore size) the catalyst is shunted to the conductive substrate. As the result, under illumination the catalyst is charged (oxidized) by the photogenerated holes from hematite and immediately discharged (recombination) by the electrons from the conductive substrate. This recombination process is induced by shunting which prevents the catalyst potential to sufficiently be dropped to achieve sustainable water oxidation.
7.2. Future Directions

Electrodeposition is a promising approach to directly deposit tantalum nitride (Ta₃N₅) on a conductive substrate. In chapter 2, the electrodeposition of tantalum oxide from aqueous solution was described. It was shown that the electro-generation of hydroxide ions at the surface of working electrode triggers the hydrolysis of tantalum precursor. Alternatively for electrodeposition of tantalum nitride, ammonia is electrochemically generated *via* electrochemical reduction of ammonium (NH₄⁺),⁷ where it immediately reacts with the tantalum precursor in solution and precipitate at the surface of working electrode. For successful electrodeposition of crystalline tantalum nitride without ammonolysis step, several criteria must be met: (1) the electro generation of ammonia must be more feasible than the reduction of Ta(V), (2) the reaction between electrogenerated ammonia and Ta-precursor in solution must be spontaneous, (3) the product of the reaction must be insoluble, and (4) in case of amorphous products it can should be nitridized to crystalline Ta₃N₅ by annealing in an inert atmosphere (N₂ or Ar).

Our preliminary observations consistent with previous studies^{8–11} indicate that TaCl₅ (Taprecursor) in solution or in the solid phase spontaneously reacts with ammonia gas in the room temperature which is accompanied by a color change from opaque white to a bright yellow precipitates according to equation 7-1 (as shown in Figure 7–1.a). This reaction is very clean and only ammonium chloride is formed as the byproduct which can be easily removed by sublimation under reduced pressure at > 170 °C.⁸ The yellow intermediate is insoluble in most of the commonly used solvents (such as DCM, DMSO, DMF, and acetonitrile but reacts with alcohols such as methanol and ethanol) and irreversibly reacts with atmospheric moisture and produce a white powder (presumably tantalum oxide). Elemental analysis by EDS indicated that the yellow powder is comprised of O, N, Ta, and Cl. The presence of oxygen atom (~ 10 atomic percent) precludes the determination of molecular formula of the yellow intermediate.

$$TaCl_{5}(s) + (5+x-y)NH_{3}(g) \xrightarrow{\sim 25 \circ C} [Ta(NH_{2})_{x}Cl_{y}](s) + (5-y)NH_{4}Cl(s)$$
 7-1

Upon annealing the yellow intermediate in an inert atmosphere of Ar at 800 °C, interestingly, it was converted to a bright orange/red color that is similar to the bandgap of Ta₃N₅, (Figure 7–1.a). The XRD pattern of the orange/red-powder is shown in Figure 7–1.b. The observed pattern is unambiguously assigned to crystalline Ta_3N_5 and Ta_2O_5 . The presence of Ta_2O_5 can be attributed to the residual oxygen in Ar and/or to the formation of oxides during handling and storage of the yellow intermediate sample. Nonetheless, these experiments indicates that the ammonolysis step can effectively be eliminated and the crystalline phase of Ta₃N₅ can be synthesized by annealing the yellow intermediate in an inert atmosphere. This is an important observation as it confirms that this method provide a non-reactive atmosphere that allows to integrate Ta_3N_5 with various substrates including FTO, and ITO that are otherwise unstable under ammonolysis conditions. The cyclic voltammogram of the electrodeposition bath containing various components of electrodeposition bath prepared in an ionic liquid are shown in Figure 7-1.c. As it can be seen, Ta(V) is highly susceptible to electroreduction and its reduction potential is ~ 200 mV more positive than the reduction potential of ammonium. One strategy to circumvent this issue is to use alternative Ta-precursors or complexes with more negative reduction potentials. Alternatively, electrochemical generation of ammonia from other sources other than electroreduction of ammonium is another strategy that can be followed.



Figure 7–1. a) Schematic representation and photographs of the reaction products of TaCl₅ with ammonia and subsequent exposure to air and annealing in Ar, b) the XRD pattern of the powder after annealing in argon; the vertical blue dashed lines and red dashed-doted lines represent Bragg position of Ta₂O₅ (PDF# 00-019-1299 of and Ta₃N₅ (PDF# 00-019-1291), respectively, c) cyclic voltammograms of the electrodeposition bath containing various components; blank is solvent only (1-butyl-3-methylimidazolium tetrafluoroborate) (black), 30 mM TaCl₅ (red), and 60 mM NH₄PF₆ (blue). The Ionic liquid of 1-butyl-3-methylimidazolium tetrafluoroborate was synthesized using previously reported procedure.¹² The water impurity was removed by heating at 100 °C under reduced pressure for 48 hours using Schlenk line and subsequently it was stored in the glove box with the concentration of water and oxygen at ~ 1.2 and 3 ppm, respectively. The scan rate is 100 mV s⁻¹ and the Pt disc electrode was used as the working electrode.

As discussed in chapter 1, one of the issue halting efficient water oxidation with Ta_3N_5 is the surface oxidation as a result of photocorrosion under PEC water oxidation condition. In chapter 4 we showed that ALD provides a viable and robust technique to integrate crystalline Ta_3N_5 with a transparent conductive substrate like FTO. Furthermore, prior to exposure to the ambient atmosphere the ALD deposited Ta_3N_5 electrodes can be *in situ* protected against photocorrosion with an over layer of GaN or TiO₂.

As discussed in chapter 4, the PEC performance of tantalum nitride is controlled by the diffusion of photogenerated holes (the minority charge carrier). Galli and coworkers¹³ have recently shown that the main mechanism for electron and hole transports in tantalum nitride is bandlike which is strongly affected by the effective mass of charge carriers. Moreover, theoretical studies have shown that the charge transport in Ta_3N_5 suffers from the large electron and hole effective masses.¹⁴ DFT calculations were subsequently utilized to study the effect of substitutional impurities and strain on the charge transport characteristics of tantalum nitride.¹³ It was predicted that substitutional impurities - such as Nb and V replacing Ta atoms and P replacing N atoms – significantly reduces the effective mass of both electron (by 19%) and holes (by 39%). Therefore, substitutional doping and introducing strain are two plausible strategies to improve the diffusion length of holes and electrons in Ta_3N_5 and thus its PEC performance.

As discussed in chapter 1, the band edge positions of tantalum nitride straddle both the water oxidation and water reduction reactions. However, most of the research in this area are focused on the water oxidation reaction with few reports only on the *photocatalytic* hydrogen production. For example, Domen and coworkers¹⁵ have shown that in presence of methanol as a hole scavenger Pt-loaded Ta₃N₅ nanoparticles evolve hydrogen under visible light irradiations. In a separate study Seo *et al.*¹⁶ have studied the PEC water oxidation and photocatalytic H₂ evolution (in presence of methanol) performances of Mg- and Zr-doped Ta₃N₅ under visible light irradiation. They have shown that upon co-doping with Mg and Zr (25 at.%), the H₂ evolution rate has increased by a factor of 15 in comparison to the pure sample. The improvement in photocatalytic activity was attributed to the negative shift of band edge positions which provides a higher driving force for hydrogen evolution reaction. While these examples indicate that Ta₃N₅ can photocatalytically generate hydrogen, the applicability of Ta₃N₅ as a *photocathode* for PEC hydrogen evolution is

yet to be demonstrated, however. The challenge in this area is to find a dopant to synthesis a ptype Ta_3N_5 films. The two steps procedure involving spin coating of precursor solution on Tasubstrate followed by ammonolysis (developed in our lab) is a promising and fast method to screen various dopant with variable concertation to explore their effect(s) on the semiconducting, photophysics, and photochemistry characteristics of Ta_3N_5 . REFERENCES

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