

ELECTROCATALYTIC WATER SPLITTING TO PRODUCE FUEL HYDROGEN

By

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ABSTRACT

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Solar energy is regarded as a promising source for clean and sustainable energy. However, it is not a continuous energy source, thus certain strategies have to be developed to effectively convert and store it. Solar-driven electrocatalytic water splitting, which converts solar energy into chemical energy for storage as fuel hydrogen, can effectively mitigate the intermittence of solar radiation. Water splitting consists of two half reactions: water oxidation and hydrogen evolution. Both reactions rely on highly effective electrocatalysts. This dissertation is an account of four detailed studies on developing highly effective low-cost electrocatalysts for both reactions, and includes a preliminary attempt at system integration to build a functional photoanode for solar-driven water oxidation.

For the water oxidation reaction, we have developed an electrochemical method to immobilize a cobalt-based (Co-OXO) water oxidation catalyst on a conductive surface to promote recyclability and reusability without affecting functionality. We have also developed a method to synthesize a manganese-based (MnO_x) catalytic film *in situ*, generating a nanoscale fibrous morphology that provides steady and excellent water oxidation performance. The new method involves two series of cyclic voltammetry (CV) over different potential ranges, followed by calcination to increase crystallinity. The research has the potential to open avenues for synthesizing and optimizing other manganese-based water oxidation catalysts.

For the hydrogen evolution reaction, we have developed a new electrodeposition method to synthesize Ni/Ni(OH)₂ catalysts in situ on conductive surfaces. The new method involves only two cycles of CV over a single potential range. The resulting catalytic film has a morphology of packed walnut-shaped particles. It has superior catalytic activity and good stability over long periods.

We have investigated the feasibility of incorporating manganese-based water oxidation catalysts into TiO₂ to build a composite photoanode. Results show that the composite photoanode has good activity under ultraviolet (UV) illumination, and that its catalytic performance can be significantly improved by enabling light collection over a wider range of wavelengths.

We have also proposed a scheme for a solar-driven water splitting device that integrates both electrocatalysts with solar energy collection and intensification, and is capable of minimizing mass transfer resistance. The dissertation concludes with suggested future work to further explore the MnO_x and Ni/Ni(OH)₂ electrocatalysts.

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To my parents, and all of my teachers and professors who have been outstanding mentors
throughout my entire academic career.

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KEY TO ABBREVIATIONS

AP	artificial photosynthesis
CV	cyclic voltammetry
DSSC	dye sensitized solar cell
EDS	dispersive x-ray spectroscopy
EIS	electrochemical impedance spectroscopy
EXAFS	extended x-ray absorption fine structure
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
FTO	fluorine-doped tin oxide
HER	hydrogen evolution reaction
HERC	hydrogen evolution reaction catalyst
ITO	indium tin oxide
NADPH	nicotinamide adenine dinucleotide phosphate
NHE	normal hydrogen electrode
OEC	oxygen evolution complex
PBS	phosphate buffer solution
PV	photovoltaic
SEM	scanning electron microscope
TEM	transmission electron microscope
UV	ultraviolet
WOC	water oxidation catalyst

XANES	x-ray absorption near edge structure
XAS	x-ray absorption spectroscopy
XRD	x-ray powder diffraction

CHAPTER 1. INTRODUCTION

1.1 Overview and significance of the problem

Society relies on sufficient energy supplies to meet a variety of needs¹. Currently, more than 70% of the global energy supply comes from fossil fuels, including crude oil, natural gas and coal (Figure 1.1). However, the rate of consumption of fossil fuels is much higher than the carbon fixation rate of natural photosynthesis². Also, due to its uneven distribution among countries, decreasing availability, and green-house gas emission issues, fossil fuels are no longer an ideal energy source. This has created a critical global challenge for sustainable energy production. The most effective way to do this is to produce energy from renewable and/or earth-abundant materials.

Solar energy is the only renewable energy source that is capable of powering the entire planet. It has a net output of 125,000 TJ/s, which is magnitudes higher than our current global energy needs^{3,4}. However, there are two major drawbacks that prevent solar energy from practical utilization on a larger scale. The first drawback is that, except in very few situations, it cannot be used directly⁵. It always needs to be converted into other forms such as heat⁶, electrical⁷⁻⁹ or chemical energy¹⁰⁻¹³. Another drawback is that solar radiation is not a continuous energy source. Sunlight is generally available during the day but not at night¹⁴. Thus, strategies have to be developed to store the energy collected during the periods of sunshine. Traditionally, this intermittency has been mitigated by photovoltaic (PV) technology, which stores solar energy in batteries, or solar-thermal technologies which store solar energy in the form of heat. Artificial photosynthesis (AP), a process that mimics natural photosynthesis, has been gaining attention

recently as a promising strategy to convert and store solar energy in the form of chemical energy¹⁵. Typically, there are three artificial photosynthesis schemes: direct hydrogen fuel production through water splitting, direct carbon-based fuel production, and indirect carbon-based fuel production. Figure 1.2a portrays the direct hydrogen production via water splitting, while Figures 1.2b and 1.2c are schemes for direct and indirect carbon-based fuels production that also require carbon dioxide (CO₂) sequestration. In each of the three schemes, the only remnants following consumption of the produced fuels are the water (H₂O) and carbon dioxide (CO₂) used to produce them. Thus, all three schemes are self-sustainable and carbon-neutral.

This dissertation focuses on our group's research on direct hydrogen fuel production via catalytic solar-driven water splitting (Figure 1a).

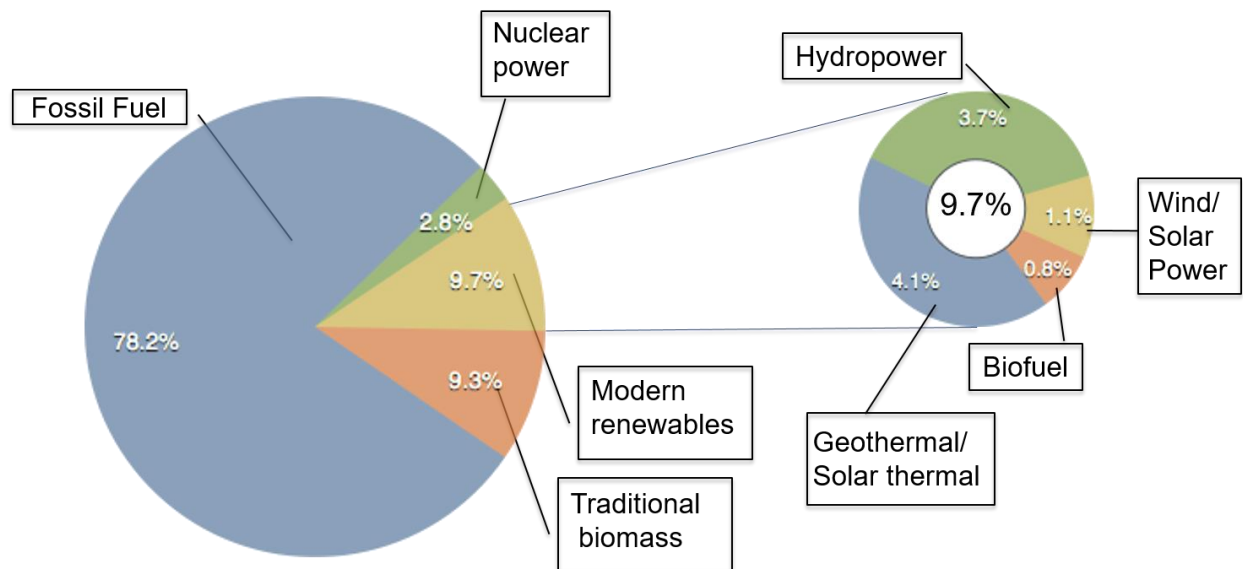


Figure 1.1. Diagram showing our current energy demand. Currently, we utilize 17.3TW of energy, with more than 70% provided by fossil fuels. Solar energy only contributes ~10%.

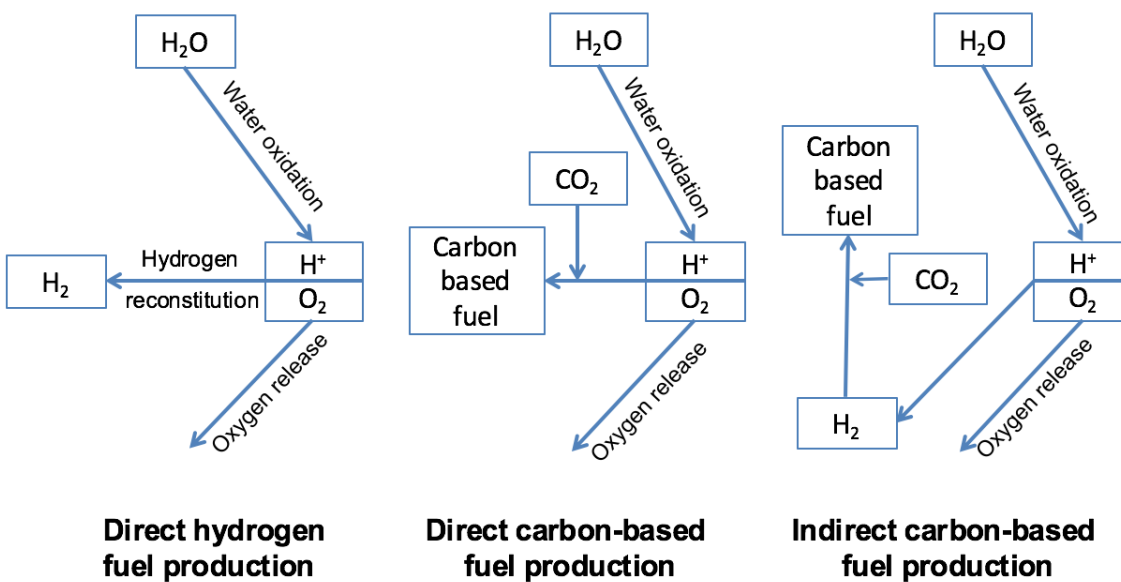
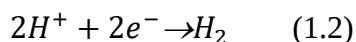
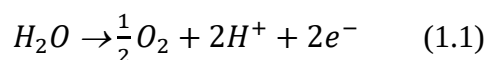


Figure 1.2. Three schemes of typical artificial photosynthesis processes: a) direct hydrogen fuel production through solar-driven water splitting; b) direct carbon-based fuel production using hydrogen ions that react directly with captured CO_2 ; c) indirect carbon-based fuel production with captured CO_2 reacting with reconstituted hydrogen gas.

1.2 Natural photosynthesis and artificial photosynthesis (AP) schemes

There are two main catalytic reactions in the natural photosynthesis process^{16,17}: the light-dependent reaction (light reaction); and the light-independent reaction (dark reaction). In the light reaction, pigments in chlorophyll capture sunlight and use the converted solar energy to oxidize water, producing oxygen gas and protons (in the form of NADPH)^{18,19}. In the following dark reaction, the protons (NADPH) are used to produce organic molecules with CO₂ through the Calvin cycle²⁰. A biomembrane separates the two processes, and provides a means to selectively transfer protons (NADPH).

Similar to natural photosynthesis, the solar-driven electrocatalytic water splitting process involves two half reactions²¹: the water oxidation reaction generates oxygen gas and hydrogen ions (Equation 1.1), and the hydrogen evolution reaction reconstitutes the hydrogen ions into hydrogen gas (Equation 1.2).



As a result, a typical water splitting device has two major components: a solar-powered photoanode and a catalytic hydrogen evolution cathode. Shown in Figure 1.3, the photoanode usually consists of a robust substrate, a layer or layers of semiconducting material for solar energy capture, and a highly-effective water oxidation catalyst. The cathode side consists of a conductive substrate and a hydrogen evolution catalyst.

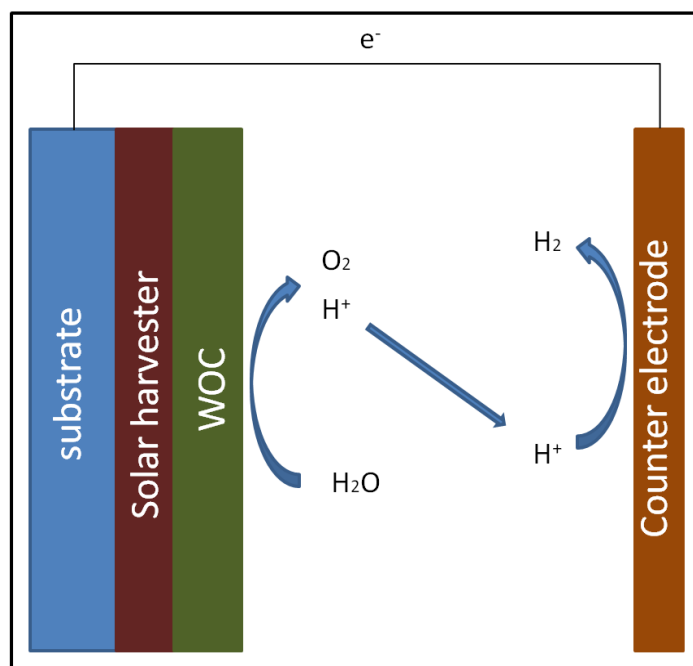


Figure 1.3. Typical solar-driven electrocatalytic water splitting device to produce hydrogen fuel. It usually consists of a composite photoanode and a counter electrode. The composite photoanode should have a robust conductive substrate, a solar harvester which can convert solar energy into the potential required to power the water splitting reaction, and a highly effective water oxidation catalyst to lower the overpotential of the water oxidation reaction. The counter electrode should also have a conductive substrate as well as a hydrogen evolution catalyst for hydrogen reconstitution.

1.3 Outline of this dissertation

The goal of this dissertation is to present the details of our work on developing electrocatalysts for both the water oxidation and hydrogen evolution reactions. We will also present a scheme for system integration to make functional photoanodes for solar-driven water oxidation.

Chapter 2 will focus on our research on the synthesis, immobilization and assessment of a cobalt-based (Co-OXO) water oxidation catalyst (WOC). We developed an electrodeposition method to successfully immobilize the Co-OXO WOC synthesized *ex situ* onto conductive surfaces. The resulting film enabled enhanced recyclability and reusability, while maintaining catalyst functionality in solution.

Chapter 3 describes our research on developing a dual-series CV electrodeposition method to synthesize a MnO_x WOC *in situ* on conductive surfaces. The resulting film provides excellent catalytic performance over long periods of time.

Chapter 4 presents our work on a preliminary system integration of TiO_2 and a Mn WOC to build a functional water oxidation photoanode for solar-driven water oxidation. Assessment of the photoanode showed that it is very effective towards water oxidation under UV illumination.

In Chapter 5, we describe our work on developing a Ni/Ni(OH)_2 electrocatalyst for the hydrogen evolution reaction. The new electrodeposition method involves only two cycles of CV in a single potential range, and produces a film with excellent catalytic properties.

Chapter 6 presents some suggestions for future research. We propose a device capable of minimizing mass transfer resistance, and also suggest future research activities on enhancing the performance of MnO_x and Ni/Ni(OH)₂ electrocatalysts.

Chapter 7 presents the conclusions of the dissertation.

CHAPTER 2. CHARACTERIZATION AND FUNCTIONAL ASSESSMENT OF A COBALT(III)-OXO CUBANE CLUSTER WATER OXIDATION CATALYST IMMOBILIZED ON A CONDUCTIVE SURFACE

2.1 Abstract

We have developed an electrodeposition method that successfully immobilizes a cobalt(III)-OXO (Co-OXO) water oxidation catalyst (WOC) synthesized *ex situ* onto conductive surfaces. This Co-OXO WOC has a cubane-like catalytic core surrounded by stabilizing ligands, which is a structural mimic of the natural oxygen evolving complex (OEC). This method promotes recyclability and reusability of the Co-OXO catalyst. We took Fourier transform-infrared (FTIR) and surface FTIR spectra before and after deposition, respectively, to assess the presence of organic ligands around the core. We used scanning electron microscopy (SEM) to characterize the surface morphology of the immobilized catalyst, and energy dispersive x-ray spectroscopy (EDS) to determine the elemental composition. Finally, we assessed its functionality, stability, and reusability using cyclic voltammetry (CV). The results show that this catalyst can be successfully immobilized on conductive surfaces, achieving a functionality comparable to that of the same catalyst dissolved in aqueous solutions. We believe the separation of the synthesis and immobilization processes has great potential for optimizing catalytic performance.

2.2 Introduction

As discussed in Chapter 1, a complete water splitting process consists of two half reactions^{22,23}: water oxidation and hydrogen evolution. In this study, we focused mainly on the water oxidation half reaction. The water oxidation reaction is important in the natural process of photosynthesis, and the oxygen evolving complex (OEC) in photosynthetic organisms is the only known natural system capable of catalyzing that reaction. It has been shown that the natural OEC has a structure

consisting of an “oxo-bridged heteronuclear cubane cluster of manganese and calcium”²⁴. Much progress has been made in the past two decades towards synthesizing efficient WOCs that are structural mimics of the natural OEC. Since 2000, various catalysts with similar cubane structures have been synthesized and assessed. Successful examples include those developed by Kanady et al.²⁵, Mukherjee et al.²⁶, and Brimblecombe et al.²⁷.

Dismukes and co-workers are generally recognized as the first group to successfully synthesize a WOC that structurally simulates the natural OEC²⁸. Their catalyst had a manganese cubane (Mn_4O_4) core surrounded by stabilizing ligands. A significant problem with this catalyst is that it is insoluble in water and common organic solvents²⁹. As a result, they used porous membranes such as Nafion to immobilize it for assessment and utilization. Other manganese-based compounds such as Mn_3Ca and Mn_3CaO_4 have also been developed recently for the same purpose. In 2007, Das and co-workers introduced a cobalt(III)-based WOC $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CMe})_4(\text{py})_4]$, which is a complex with a $[\text{Co}_4\text{O}_4]$ cubane-like catalytic core surrounded by pyridine and acetate anion stabilizing ligands³⁰. This complex is soluble in water. Thus, its electrochemical and catalytic properties can be easily assessed by a standard electrochemical system, with dissolved catalyst as electrolyte. In this chapter, we refer to this as the “pseudo-homogeneous” system because, even though the catalyst is dissolved in water, the reaction takes place at the electrode-electrolyte interface. While the pseudo-homogeneous system works well on a laboratory scale and enables highly effective catalyst performance, it does not enable catalyst recovery and reuse on a larger scale. As a result, strategies have to be developed to immobilize the catalysts onto substrates to promote recyclability and reusability. The successful immobilization of these WOCs has scientific, technological and environmental merit.

In this study, we focused mainly on designs that promote catalyst recyclability and reusability. We have achieved this by developing a new electrodeposition protocol which can immobilize the catalyst onto conductive surfaces. This method can transform the pseudo-homogeneous reaction system to a heterogeneous system. We chose a Co-OXO WOC as the candidate catalyst, with the goal of determining whether the OEC-mimicking catalytic core (with or without stabilizing ligands) can maintain catalytic function after being anchored onto conductive surfaces. We took Fourier transform-infrared (FTIR) and surface FTIR spectra before and after deposition, respectively, to investigate the presence of organic ligands around the core. We used scanning electron microscopy (SEM) to characterize the surface morphology of the immobilized catalyst, and energy dispersive x-ray spectroscopy (EDS) to determine the elemental composition. Finally, we assessed catalyst functionality, stability and reusability using cyclic voltammetry (CV). The results show that this catalyst can be successfully immobilized on conductive surfaces, with a functionality comparable to the same catalyst dissolved in aqueous solutions. Although some WOCs can be synthesized *in situ*, we still believe that the separation of catalyst synthesis and immobilization processes can enable better control of the catalyst and provide an objective route to optimization of the resulting complex.

2.3 Materials and methods.

2.3.1 Materials

Cobalt nitrate hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$), pyridine ($\text{C}_5\text{H}_5\text{N}$) and hydrogen peroxide (H_2O_2) were all purchased from the Sigma-Aldrich Company, LLC (St. Louis, MO). All chemicals were used without further purification.

Polyethylene terephthalate (PET) films coated with indium tin oxide (ITO) were also purchased from Sigma-Aldrich. Prior to using, ITO substrates were cut into 2cm by 1cm rectangular chips.

2.3.2 Methods

2.3.2.1 *Ex situ* Synthesis of the Co-OXO cubane cluster

We used the protocol reported by Chakrabarty et al. (2007) to synthesize the $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CMe})_4(\text{py})_4]$ catalyst. In the *ex situ* synthesis, 20 mmol (4.76 g) of CoCl_2 was dissolved in 70ml methanol. The solution was kept at 70°C in a water bath with constant reflux. Forty (40) mmol (5.44 g) sodium acetate was added to the stirred solution, followed by addition of 16ml (10mmol) of pyridine (py). Ten (10) ml H_2O_2 (30% v/v) was then added very slowly. A very vigorous oxidation process could be observed, with the color of the mixture changing from purple to black. The mixture was maintained at 80°C for 4 hours. After three days of aging, a dark green powder was observed.

2.3.2.2 Electrodeposition of Co-OXO catalyst synthesized *ex situ*

The electrochemical deposition was carried out on a CHI 660D electrochemical workstation (CH Instruments Inc., Austin, Texas), using the traditional three-electrode setup. ITO chips were used as both the working and counter electrodes, with Ag/AgCl as the reference electrode. We dissolved 0.02 g of dry $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CMe})_4(\text{py})_4]$ powder in an electrolyte containing 0.1 M neutral phosphate buffer solution ($\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer solution at pH 7.0). A potential of +1.2 V was applied to the system for seven (7) hours. For comparison, an identical experiment was run for three (3) hours, except without the catalyst in the solution.

2.3.2.3 Catalytic functionality and stability assessments

The electrodeposition process was tracked by CV, using a typical three-electrode setup on the CHI 660D electrochemical workstation. We did a baseline test using a blank ITO chip as the working electrode. We used two types of electrodes in the catalyst functionality tests: a Co-OXO-coated ITO electrode and a Co-OXO-coated gold electrode. A platinum wire was used as the counter electrode in all tests, with a Ag/AgCl electrode as reference, and the neutral 0.1M phosphate buffer solution (pH 7.0) as the electrolyte. The scan rate was set at 10 mV/s.

The functionality tests were also done using CV in an identical setup as described above. We tested the Co-OXO WOC coated on ITO and on gold substrates. Finally, we tested the bare ITO and pseudo-homogeneous systems for comparison. Following these assessments, we tested the stability and functionality of the catalyst. We obtained 14 CV scans on one sample of Co-OXO immobilized on ITO. In this test, the Co-OXO-coated ITO was used as the working electrode, and was left in the electrolyte solution for 14 consecutive CV scans. To test the recyclability of

the catalyst, we also took eight CV scans on one Co-OXO on ITO sample. Unlike the previous tests, the working electrode was removed from solution after each CV scan, rinsed in DI water, dried in air, and reinserted for the next scan.

2.3.2.4 Characterization of catalysts by FTIR and SEM

We used FTIR to evaluate the structure and morphology of the catalyst in powder form, and following immobilization on ITO. The data for the immobilized catalyst were acquired on a Nicolet 6700 surface FTIR (Thermo Scientific, Inc., West Palm Beach, FL). The data for the catalyst in powder form were acquired on a Galaxy Series 3000 spectrophotometer (Mattson Technology, Inc., Fremont, CA). SEM images were obtained at different magnifications using a JSM 6610-LV electron microscope (JEOL Ltd, Tokyo, Japan). Finally, energy dispersive x-ray spectroscopy (EDS) (Oxford Instruments, High Wycomb, Bucks, England) was used to evaluate the elemental composition of the immobilized catalysts.

2.4 Results and Discussion

2.4.1 Electrodeposition of Co-OXO

A dark film could be clearly observed after the electrodeposition process. We believe this provides direct evidence of the successful coating of the catalytic film on the conductive surface. A control experiment was also performed under identical conditions without dissolved Co-OXO in the electrolyte. The control sample did not produce any color changes on the surface. We recorded the current density profile during the seven-hour electrodeposition process. The red curve in Figure 2.1 shows that the current density of the catalyst sample increased steadily before reaching a steady state value. The blue curve in Figure 2.1 shows the current density profile of

the control sample, which decreased gradually, then reached and maintained a steady state at a current density level magnitudes lower than the electrodeposition sample. We should notice that there is an initial decrease of current density during the first few minutes of deposition. Although we do not have a clear explanation why this occurs, we speculate that it is due to mass transfer resistances³¹.

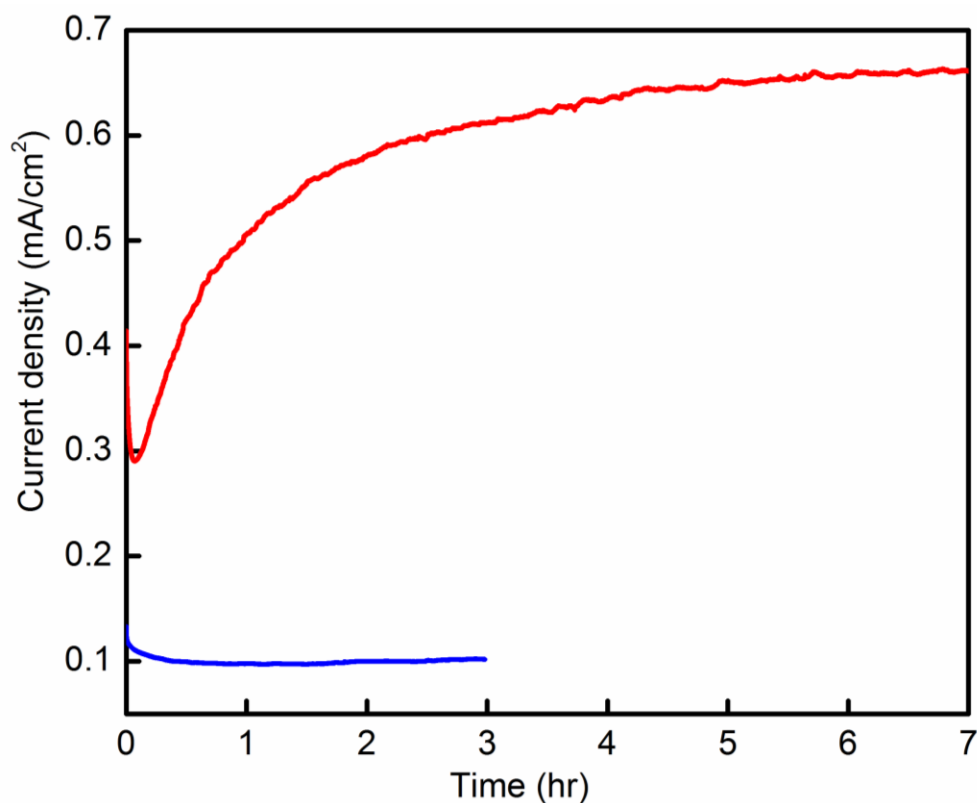


Figure 2.1. Current density profile (red) of the Co-OXO WOC during electrodeposition on ITO. The current density increased gradually to a maximum of 0.67 mA/cm², which is considerably higher than for the case where the electrode was placed in solution without the catalyst (blue curve). Similar results were obtained on gold electrodes. The initial drop in current density is likely due to mass transport effects.

2.4.2 FTIR and surface FTIR characterization of the Co-OXO catalyst

The FTIR spectrum of the catalyst powder sample synthesized *ex situ* has strong peaks at frequencies of 1556, 1407 and 669 cm^{-1} (Figure 2.2), which were assigned to the pyridine ring group, the acetate hydroxyl group, and the carbon backbone -CH- group, respectively. These peaks confirmed the existence of the ligands used to stabilize the catalytic complex during the *ex situ* synthesis process. However, those feature peaks disappeared on the surface FTIR spectrum of the immobilized catalyst samples, which indicates the loss of all organic ligands during electrodeposition, leaving only the catalytic cubane core on the surface.

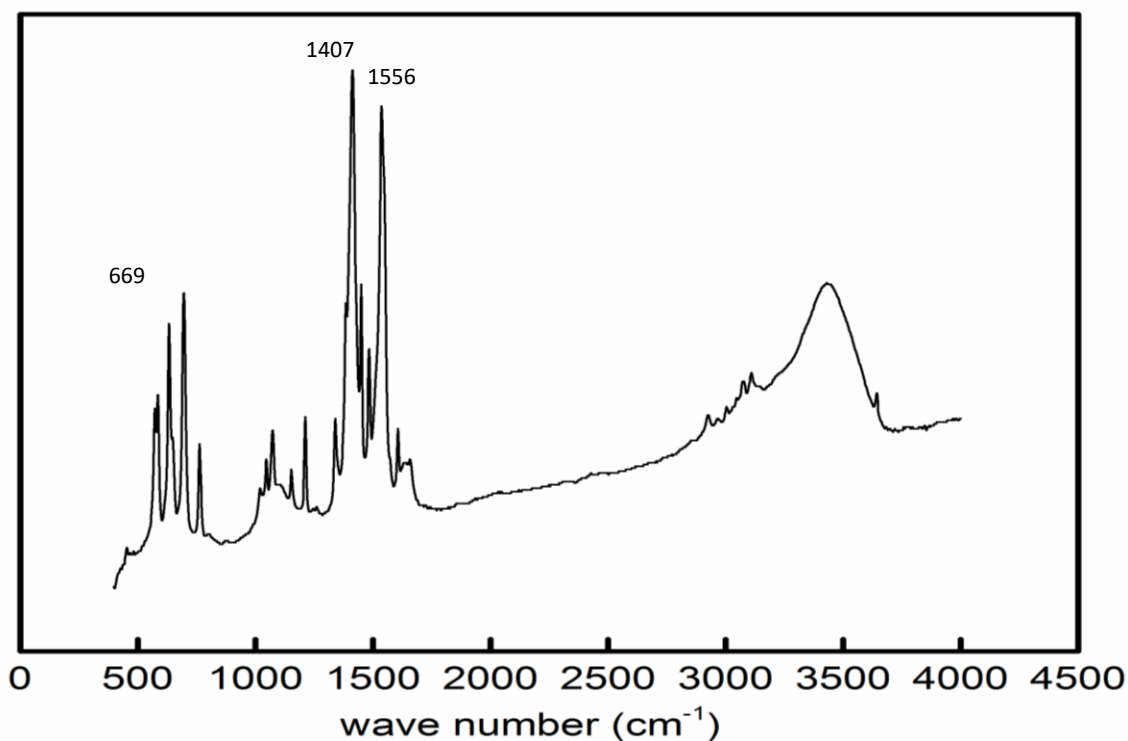


Figure 2.2. FTIR spectra of the catalyst powder prior to immobilization on conductive surfaces. The stretching frequencies at 1556, 1407, and 669 cm^{-1} represent the pyridine ring group, the acetate hydroxyl group, and the carbon backbone -CH- groups, respectively. These frequencies confirm the existence of the stabilizing ligands used in synthesizing the catalyst complex. These feature peaks are not present in the surface FTIR, indicating the loss of all organic ligands during electrodeposition process.

2.4.3 Surface morphology and structure characterizations of immobilized catalyst

As reported earlier, the FTIR results showed that the stabilizing ligands were lost during the deposition process. To determine if the Co-OXO WOC was successfully immobilized, we acquired SEM images at different magnifications, and EDS spectra of the Co-OXO-coated ITO samples. Figure 2.3 shows that the surface morphology of Co-OXO coated on ITO is uniform, although there is some degree of agglomeration. By contrast, the SEM image of bare ITO (Figure 2.3) at the same magnification shows a featureless surface. Figure 2.3c shows the EDS spectrum of the Co-OXO-coated ITO sample, which confirmed the existence of Co by the strong Co peaks. When the data provided by the SEM images and EDS spectra are taken together, we can confirm that the Co-OXO catalytic core was successfully immobilized on the ITO surface.

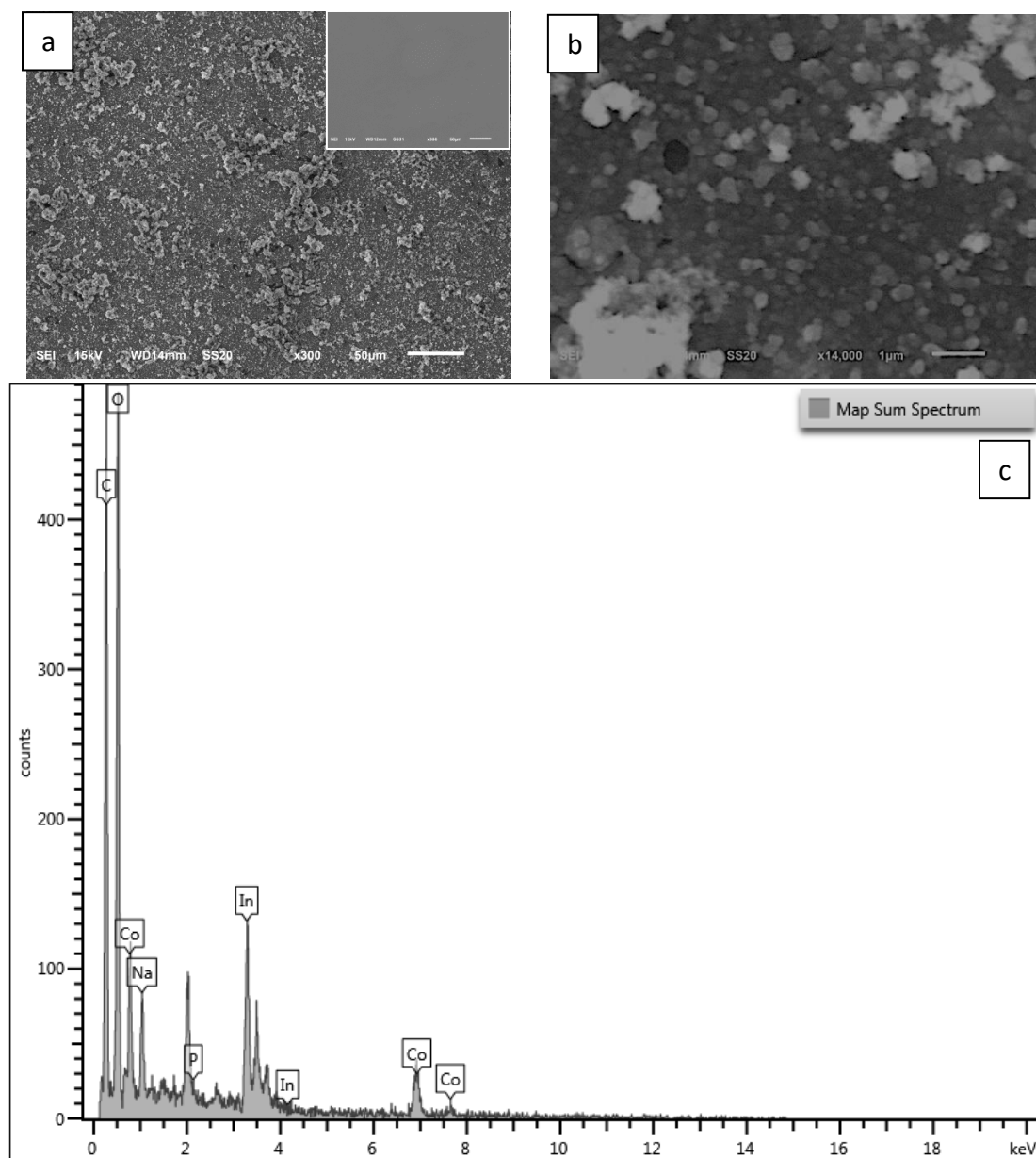


Figure 2.3. a) SEM image of the ITO surface following catalyst immobilization. It gives clear evidence of attachment of the catalyst to the surface. By contrast, the SEM image of ITO prior to catalyst deposition (Figure 2.3a inset) at an equivalent magnification has a featureless surface. b) SEM image of a selected area at a higher magnification. c) EDS diagram of Co-Oxo-coated ITO sample, confirming that the catalyst core remained on the ITO substrate during the electrodeposition process.

2.4.4 Catalytic functionality, stability and recyclability assessments

Although we have confirmed that the catalytic core of Co-OXO WOC can be successfully immobilized via the electrodeposition method we developed, it was still necessary to determine whether the catalytic function of the catalyst has been affected by the loss of the stabilizing ligands. We did this by assessing and comparing the catalytic performance of both the heterogeneous and pseudo-homogeneous systems under identical conditions using cyclic voltammetry. As shown in Figure 2.4, we took CV scans of four systems: the catalyst coated on the ITO electrode (green), catalyst coated on gold (red), Co-OXO in a pseudo-homogeneous system (purple), and a bare ITO electrode (blue) to serve as baseline and control. The Co-OXO-coated ITO, Co-OXO-coated gold and pseudo-homogeneous systems have about the same onset water oxidation potentials, approximately 1.0 V vs. Ag/AgCl. We did a more careful examination of the data (Figure 2.4 inset), to get more accurate estimates of onset potentials 0.93, 0.95 and 1.0 V, respectively, for pseudo-homogeneous, catalyst-coated ITO, and catalyst coated gold. As expected, bare ITO has a flat profile with no significant water oxidation functionality. Based on the analysis above, we can conclude that although Co-OXO WOC lost its stabilizing ligands during the electrodeposition process, its catalytic function remained intact.

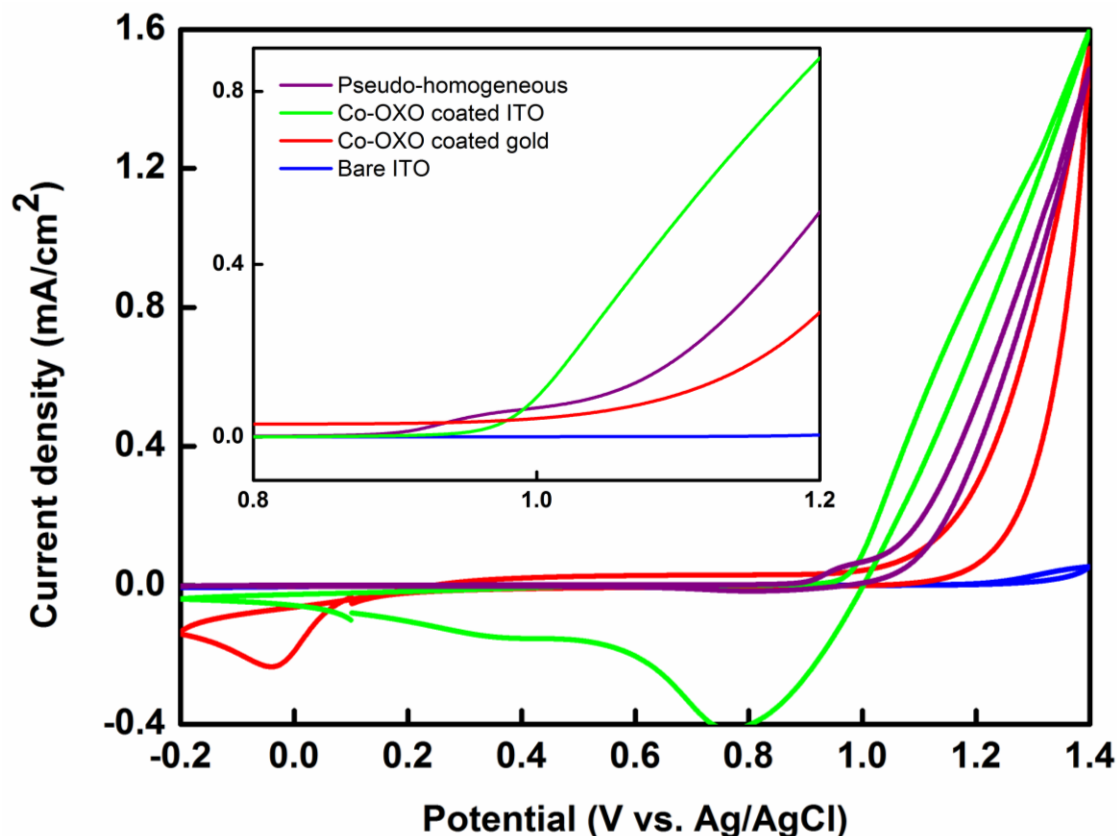


Figure 2.4. Cyclic voltammograms acquired at a scan rate of 10 mV/s on bare ITO (blue curve), Co-OXO immobilized on gold (red), and Co-OXO immobilized on ITO (green) in 0.1M neutral phosphate buffer solution at pH 7.0. This diagram shows that water oxidation occurs at approximately 1 V for Co-OXO on both gold and ITO. For comparison, we have also included the CV of the catalyst in a pseudo-homogeneous system (purple). The profiles of the three scans are essentially identical, providing strong evidence that Co-OXO maintains its catalytic function whether in solution, or immobilized on gold or ITO.

To test for catalytic stability, we acquired 14 consecutive CV scans on one catalyst sample (Figure 2.5). The peak current densities of all 14 CV scans fall in a narrow range (1.54 ± 0.04 mA/cm²). The profiles are also nearly identical for all scans. The total duration of the 14 consecutive scans was 74 min. These facts provide strong evidence that the immobilized catalyst is stable and has reproducible performance over a relatively long period of time.

To test the reusability and recyclability of the catalyst, we obtained 8 CV scans using a single immobilized catalyst sample. As opposed to the stability experiment we described above, this sample was pulled out of the testing solution after each scan, cleaned with DI water and dried in air before being returned to the solution for the next test. The results are shown in Figure 2.6. The profiles lie in a narrow range (1.47 ± 0.05 mA/cm²), providing strong evidence that the immobilized catalyst has stable and reproducible performance upon recycle and reuse.

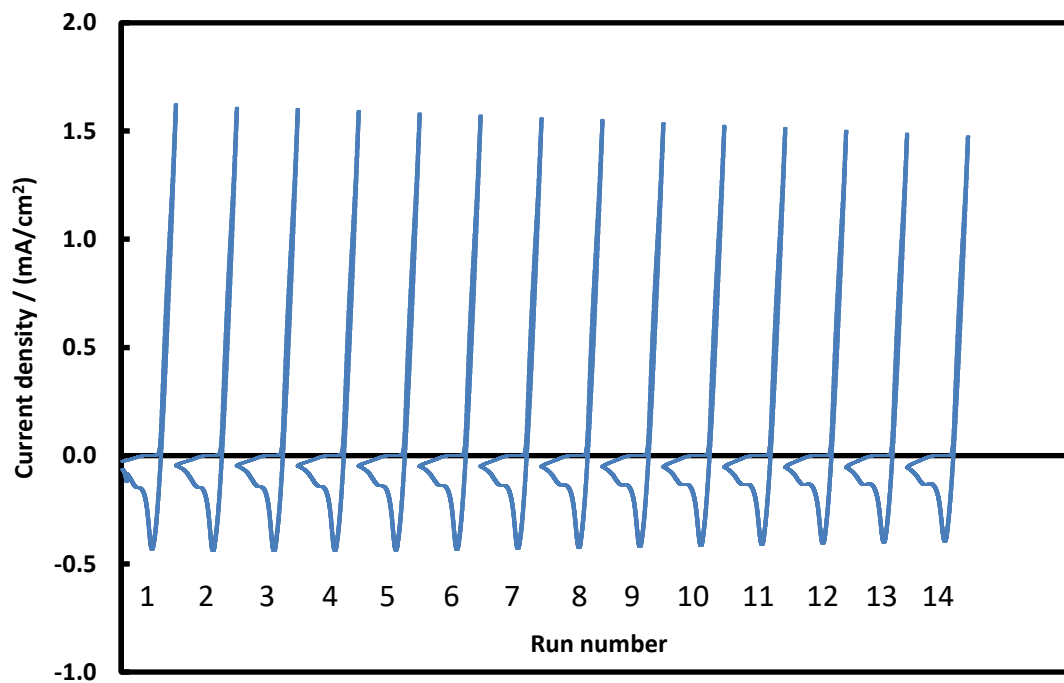


Figure 2.5. Voltammograms acquired at a scan rate of 10 mV/s over 14 cycles of catalyst reuse. To acquire these data, the same catalyst was left in place for 14 consecutive scans. The data show negligible variation in both current density and peak currents, providing strong evidence that the immobilized catalyst is very stable, with a reproducible performance.

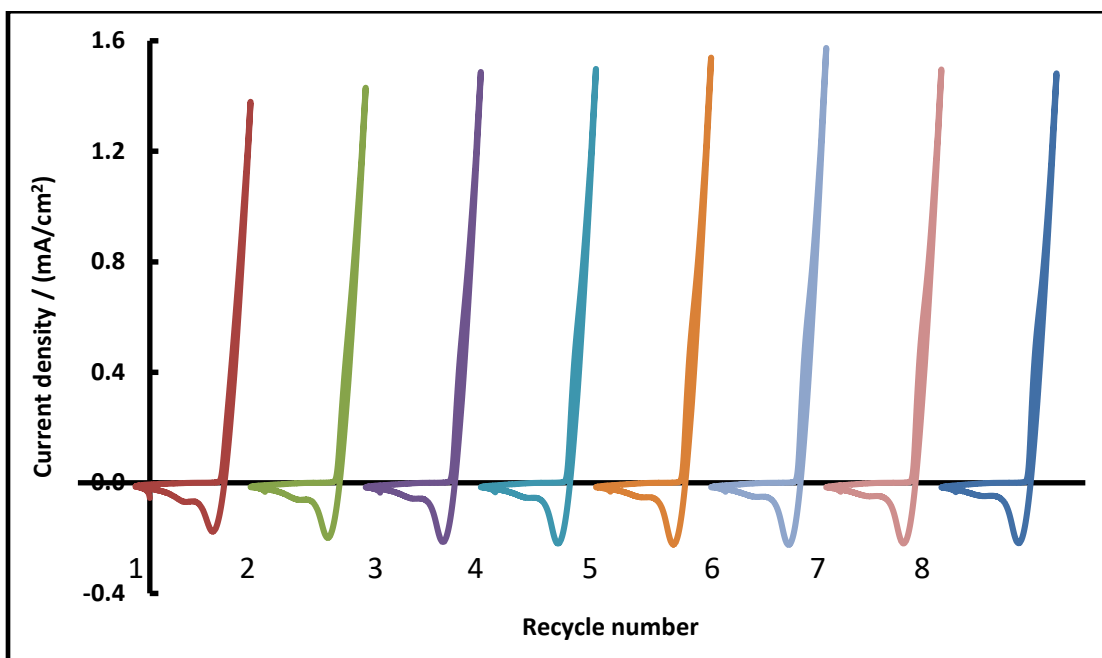


Figure 2.6. Assessment of catalyst recyclability and reusability. In this test, we acquired eight CV scans on a single sample of Co-OXO catalyst coated on ITO. After each scan, the sample was taken out of the solution, rinsed with DI water, dried in air and reinserted into the solution for the next scan. As the data show, all the voltammograms are distributed over a small range of values, confirming a high degree of catalyst reusability, as well as reproducibility in performance.

2.5 Conclusions

In this study, we developed an electrodeposition approach that can successfully immobilize an OEC mimic Co-OXO WOC onto conductive surfaces to promote catalyst recovery and reusability. The results show that, although all the stabilizing ligands of the catalytic complex were lost during the electrodeposition process, the functionality of the catalyst remained intact. This study also shows that the immobilized catalyst has the same performance as one dissolved in solution. We believe that the separation of catalyst synthesis and immobilization into separate processes has the potential of enabling systematic design and optimization of catalysts. The Co-OXO used in this study is only one example of a category of cubane-like WOCs which can be synthesized *ex situ* and immobilized on different conductive surfaces via electrodeposition. This study has provided a reliable pathway for effective recycling of this category of catalysts.

CHAPTER 3. SYNTHESIS OF A MnO_x CATALYTIC FILM ON FTO BY DUAL-SERIES CYCLIC VOLTAMMETRY

3.1 Abstract

We have developed a new method to synthesize a manganese-based water oxidation catalyst in situ in aqueous media. This new method involved multiple cyclic voltammetry (CV) series, followed by programmed calcination to increase crystallinity. The method provides powerful tunability of the electrodeposition parameters, potentially enabling independent control of the surface morphology and the oxidation state of the catalytic film. Our results show that the first CV series produces a film with a nanoscale surface morphology, while the following CV series improves catalytic performance by elevating the oxidation state of the film while largely maintaining the existing surface morphology. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphology of the MnO_x film, cyclic voltammetry (CV) to assess catalyst functionality, and long term amperometry to assess the stability.

3.2 Introduction

As we described in the previous chapters, the water oxidation reaction is the rate-limiting step in the artificial photosynthesis (AP) process, and the major source of overpotential^{1,32,33}. Thus, an effective AP process requires highly effective water oxidation catalysts (WOCs)³⁴. In the past decade, various catalytic complexes capable of water oxidation have been synthesized. Most of these complexes were based on Ru ³⁵⁻³⁷, Pd ³⁸ or Ir ³⁹⁻⁴¹, all of which are earth-rare. These heavy transition metal-based complexes are expensive and usually toxic, which greatly limits their use on a large scale. As a result, using light first row transition metals to replace them has become a

research focus. The potential choices of transition metals are cobalt (Co) and manganese (Mn). Many Co-based WOCs have been successfully developed and tested in the past decade, the most successful example being the ‘Co-Pi’ catalyst developed by Nocera and coworkers⁴². Other examples include the Co-OXO catalytic complexes we described in Chapter 2⁴³. In the last five years, manganese has gained popularity as a new base metal for WOCs because it can form more than 30 minerals, with most of them having water oxidation properties⁴⁴⁻⁴⁶. Also, manganese-based materials are usually very flexible and can be synthesized *in situ*^{26,28,47,48} or *ex situ*⁴⁹⁻⁵¹. More importantly, manganese is the key element in the reaction center of the natural oxygen evolution center (OEC) in plants.

Various methods have been reported for synthesizing manganese-based WOCs, both *in situ* and *ex situ*. *In situ* synthesis, especially by electrodeposition, usually benefits from a simple and easily-controllable setup. Also, the resulting catalysts usually enable much better recyclability. Typically, electrodeposition is carried out by using chronoamperometry^{52,53} or a single-range of potentials^{48,54}.

In this study, we have developed a new method to synthesize a manganese-based water oxidation catalyst *in situ* in aqueous media. This new method involves two series of cyclic voltammetry (CV), followed by calcination to increase crystallinity. This method provides great tunability of the electrodeposition parameters, enabling independent control of the surface morphology and the oxidation state of the catalytic film. The goal of the study was to achieve an enhanced oxidation state and a nanoscale surface morphology⁵⁵.

3.3 Materials and methods

3.3.1 Materials

Manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was purchased from Sigma-Aldrich LLC (St. Louis, MO). Sodium phosphate monobasic (NaH_2PO_4) and sodium phosphate dibasic (Na_2HPO_4) were purchased from J.T. Baker (Phillipsburg, NJ). All chemicals were used without further modification. Fluorine-doped tin oxide (FTO)-coated glass (surface resistance $\sim 7 \, \Omega/\text{cm}^2$) was purchased from the Sigma-Aldrich Company LLC (St. Louis, MO). Prior to use, the FTO glass was cut into $2\text{cm} \times 1\text{cm}$ rectangular chips, cleaned with acetone, and rinsed in DI water.

3.3.2 Electrodeposition of MnO_x on FTO

The electrodeposition process was performed using a typical three-electrode experimental setup on a CHI 660D electrochemical workstation (CH instruments Inc., Austin, Texas). During the deposition process, a blank FTO chip was used as the working electrode, indium tin oxide (ITO) as a counter electrode, and a Ag/AgCl as a reference electrode. The electrolyte was 25 mL of a 50 mM manganese acetate solution. The deposition process was done by conducting two consecutive CV series over different potential ranges. The first series was ten cycles of potential ramps ranging from 0 to 0.6 V, at a scan rate of 10 mV/s. The second CV series was five cycles ranging from 0.6 to 2.0 V at an identical scan rate. During the first CV series, a light yellowish film could be observed forming on the FTO surface. The film turned dark brown during the second CV series. After deposition, the chip was rinsed in DI water and dried in air. It was then calcined at 450°C for five hours following a temperature ramp at a rate of $10^\circ\text{C}/\text{min}$ in a

Lindberg/Blue M tube furnace (Thermo Fisher Science Inc., Waltham, MA), and then cooled to 25°C.

3.3.3 Surface morphology characterization

The surface morphology of the samples was characterized on a JSM 6610 LV SEM (JEOL Ltd, Tokyo, Japan) as well as a JSM 2500FM SEM from the same manufacturer. Tunneling electron microscopy (TEM) images were taken on a JEM 2200FS TEM (JEOL Ltd, Tokyo, Japan). X-ray diffraction (XRD) spectra were acquired on a Bruker Davinci D8 Advanced X-ray diffractometer (Bruker Corporation, Madison, WI).

3.3.4 Catalyst functionality assessments and comparisons

The functionalities of the synthesized catalytic films were assessed by cyclic voltammetry on the CHI 660D electrochemical workstation. In each test, the catalytic film was used as a working electrode, a platinum mesh as counter electrode and a Ag/AgCl electrode as reference. The electrolyte used for all the tests was 25 ml of a 0.1M neutral phosphate buffer solution (pH 7.0) to simulate natural water. Potential ranges for all the CV tests were between -0.2V to 1.4V, at a scan rate of 10 mV/s. In a control experiment, a bare FTO chip was also tested under identical conditions.

3.3.5 Catalyst stability assessment

The stability of the catalytic film was assessed by amperometry at a constant potential of 1.2 V for a period of six hours under identical conditions as described in the functionality test. A control experiment was carried out on a bare FTO chip.

Another stability test was carried out by performing 18 consecutive CV scans on a single catalytic film. The testing and CV conditions were identical to those used for the functionality tests described above.

3.4 Results and discussions

3.4.1 Surface morphology characterizations

Figure 3.1 shows the SEM images of the surface morphology of: a) bare FTO, b) MnO_x film synthesized by dual series CV (S0), c) MnO_x film synthesized by single series CV 0-0.6V (S1), and d) MnO_x film synthesized by single series CV 0-2.0V (S2), respectively. The bare FTO has a featureless but rough surface morphology. We believe that the surface roughness plays an important role in the formation of the MnO_x films, as discussed in the latter part of this chapter. Figure 3.1 b and the inset show that the morphology of the MnO_x film synthesized by dual series CV has a network of long intermingled nanofibers. The diameter of the fibers was estimated to be 10~20 nm. Figure 3.1 c shows the morphology of samples S1 and S2, respectively. S1 has a nanofibrous morphology, which is quite similar to sample S0. This similarity provides important evidence that the morphology of the catalytic film synthesized by the dual-series method was primarily developed during the first CV series, but remained largely intact during the second CV

series. On the contrary, the S2 catalytic film developed into a morphology of micron-scale clusters, which is not optimal for mass transfer. Our analysis provides preliminary but important evidence that the surface morphology could be controlled by tuning the electrodeposition parameters. Since the dual- or multi-series deposition protocol provides more controllable parameters than the traditional single-series protocol, it could become an invaluable tool to enable predictable tuning of surface morphologies that promote catalytic performance.

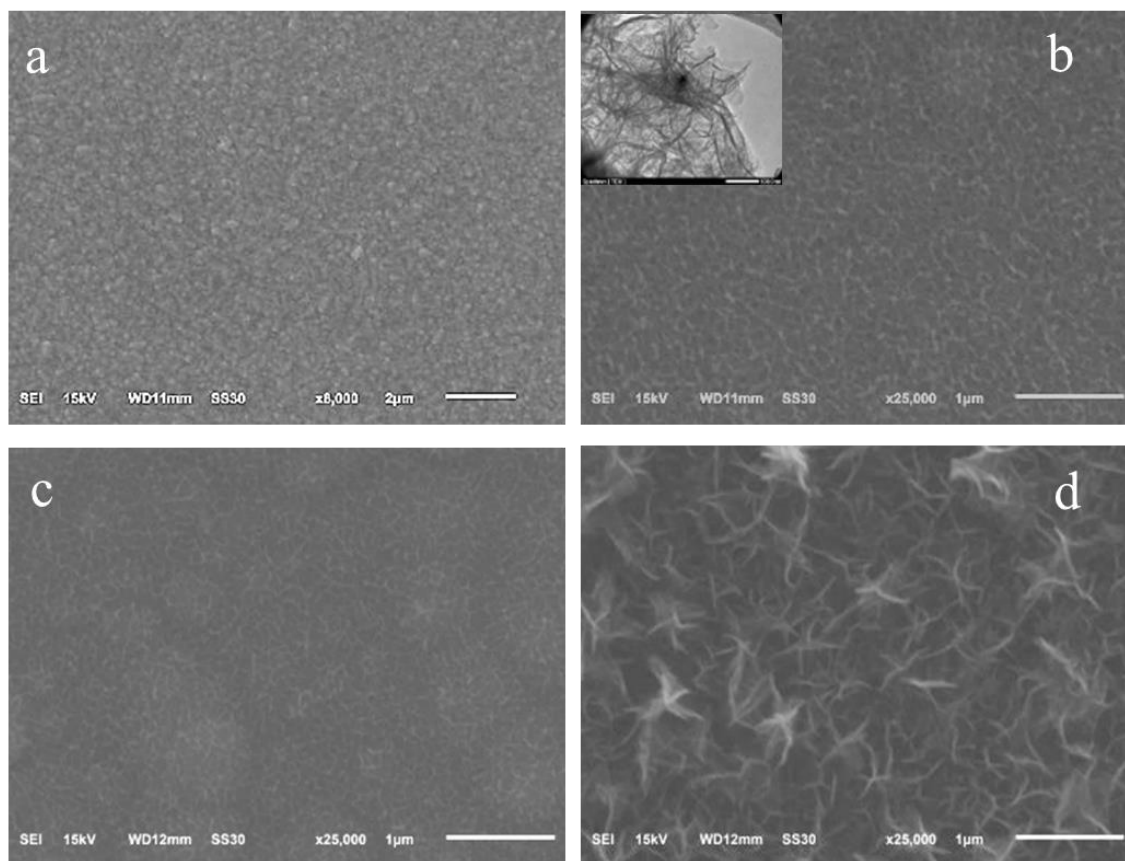


Figure 3.1. SEM images of the surface morphologies of the FTO substrate, and of MnO_x after different in-situ synthesis methods. Image a: Bare FTO, showing a significant degree of surface roughness. Image b: MnO_x after two series of electrodeposition by CV, followed by calcination; the surface is a network of interconnected fibers in both the SEM and TEM (inset) images. Images c and d: MnO_x after electrodeposition by single CV series (0-0.6 V and 0-2.0 V, respectively); image c has a similar morphology to image b, although a few small spherical clusters are visible; image d shows a network of larger micron-sized fibers with random orientations.

3.4.2 Catalytic functionality assessments

As described above, the catalytic functionalities of the three samples were assessed by CV in a 0.1 M neutral phosphate buffer solution (pH 7.0). The S0 sample has an onset potential for water oxidation of approximately 1.2 V vs. SHE (Figure 3.2). We should note that the current density of S0 exceeds 1 mA/cm^2 at 1.45 V vs. SHE, which is the typical standard required to rank a WOC as highly active⁵⁴. For comparison, both the S1 and S2 samples were assessed under identical conditions. The S1 sample, which was synthesized by the single-series (0-0.6 V) method, produced the desired nanoscale surface morphology similar to the dual-series sample. However, the catalytic performance was much lower. We believe this was due to inadequate elevation of oxidation states, as discussed in the next section. The S2 sample has a better catalytic performance than S1, which we believe is due to the more enhanced oxidation state. However, the surface morphology of S2 consists of much larger micrometer-scale fibers that likely retarded electron transfer, leading to a poorer catalytic performance.

To further assess if the dual-series method produces a catalyst that is superior to the catalytic films synthesized by single-series protocols, we evaluated and compared three additional samples synthesized by single-series over different potential ranges: 0-0.4 V, 0-0.8 V, and 0-1.5 V (Figure 3.3). All samples were assessed under the same conditions described above. As shown in Figure 3.3, all the single-series samples have similar catalytic performances except the 0-0.4 V sample, which is essentially non-catalytic. We believe the inadequate development of oxidation state led to the poor performance of the 0-0.4 V sample. The catalytic performance of the dual-series sample is clearly superior in comparison to all the single-series samples. As expected, the FTO chip had no measureable water oxidation effects in the potential range tested.

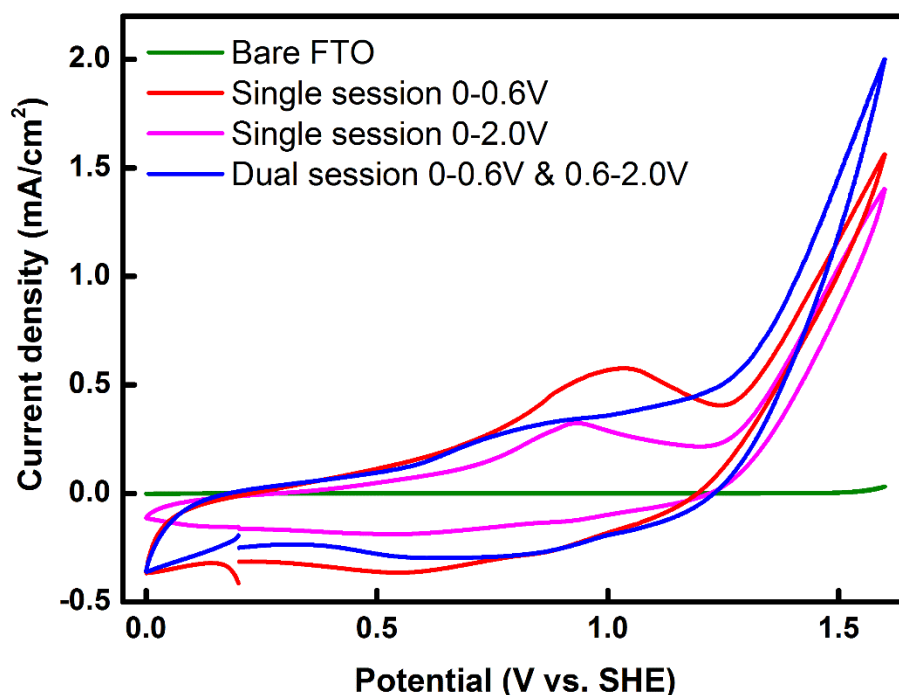


Figure 3.2. Catalytic functionality of the three MnO_x films on FTO. The blue curve is the cyclic voltammogram of the MnO_x film synthesized by the dual-series CV method; the purple and red profiles are the single-series synthesis from 0-0.6 V and 0-2.0 V, respectively; and the green curve is for bare FTO under identical assessment conditions. The MnO_x catalyst synthesized by dual-series CV is clearly superior to the single series species, because it benefits from the nanostructure developed in the first series, and the elevated oxidation state acquired during the second series. The importance of nanostructure is further reflected by the fact that the 0-0.6 V catalyst performs slightly better than the 0-2.0 V sample, even though the latter is at a higher oxidation state.

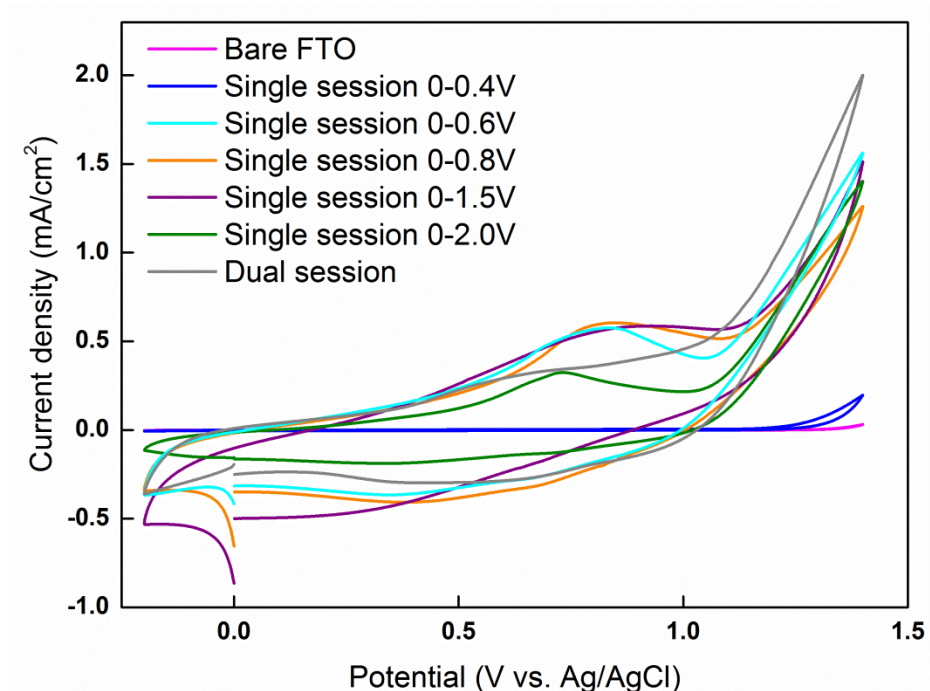


Figure 3.3. Comparison of the catalytic performances of dual series and single session samples by cyclic voltammetry in 0.1M phosphate buffer (pH 7.0). All the single series samples were synthesized under identical conditions as described in the experimental session, with the only difference being the ranges of potential ramps. Bare FTO was used again as a control. All single-series samples had similar performances, except the 0-0.4V sample which has a much lower activity. The dual-series sample has a much better performance than all single-series samples, which we believe to be the result of both an elevated oxidation state and nanoscale surface morphology.

3.4.3 Proposed formation mechanism

As we discussed before, the catalytic film synthesized by the dual-series method benefits from both nanoscale surface morphology and enhanced oxidation state. The data suggest that the surface morphology of the catalytic film was mainly formed during the first CV series, and the oxidation state of the film was elevated during the second CV series.

Currently, we do not know the exact mechanism for the formation of this unique surface morphology, and can only propose a possible hypothesis. We speculate that the protrusions on the rough FTO surface serve as nucleation sites for the nanofibers. During the first CV series, the Mn^{2+} ions would first be oxidized to Mn(III) hydrolysis species which form small nuclei on the protrusions⁵⁶. The small nuclei then grow and extend across the whole surface. During the second CV series, the existing hydrolysis species would be partly oxidized to higher Mn(IV) species while the surface morphology remains largely intact. A schematic of the proposed mechanism is shown in Figure 3.4.

To evaluate this possible mechanism, we took photographs and SEM images after selected stages of deposition. We observed a yellowish film forming on the FTO surface during the first CV series (Figure 3.5). The film then turned to dark brown during the second CV series. Figure 3.6 shows a series of SEM images at different magnifications of the samples shown in the previous figure. Figure 3.6 a shows the sample after two cycles of the first series. Small clusters are clearly observable on the protrusions on the FTO surface. The small clusters gradually developed into a complete film across the conductive surface (Figure 3.6 b-d). During the second CV series, the surface morphology of the catalytic film did not change much (Figure 3.6 e).

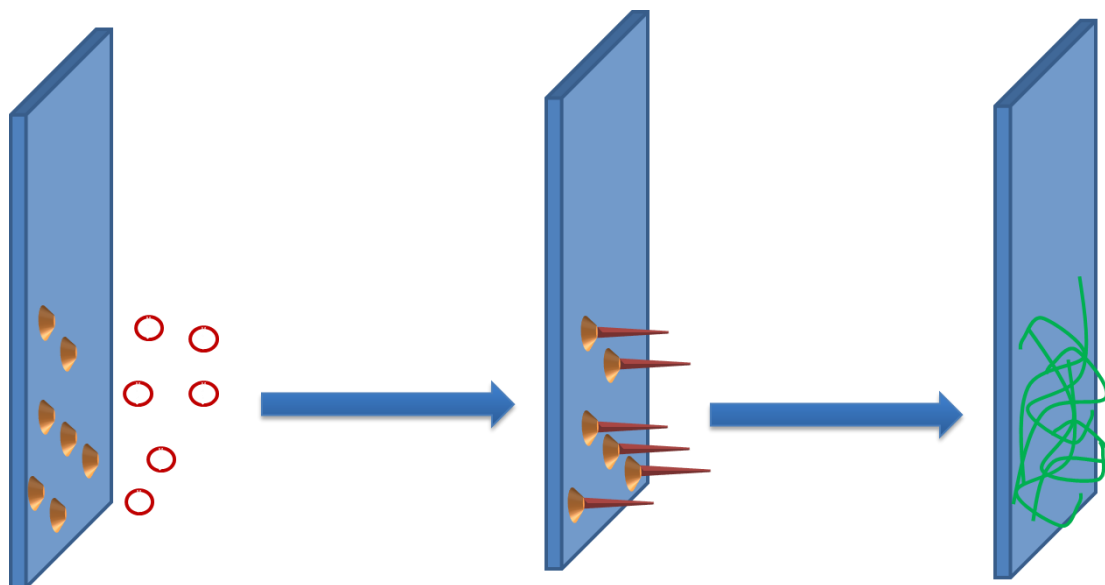


Figure 3.4. Cartoon illustration of the proposed formation mechanism. We propose that Mn^{2+} ions are first oxidized on the protrusions of the FTO surface during the first CV series, forming fibrous MnO(OH) species. During the second CV series, the oxidation state of the catalytic film is further elevated while the surface morphology remains largely intact.

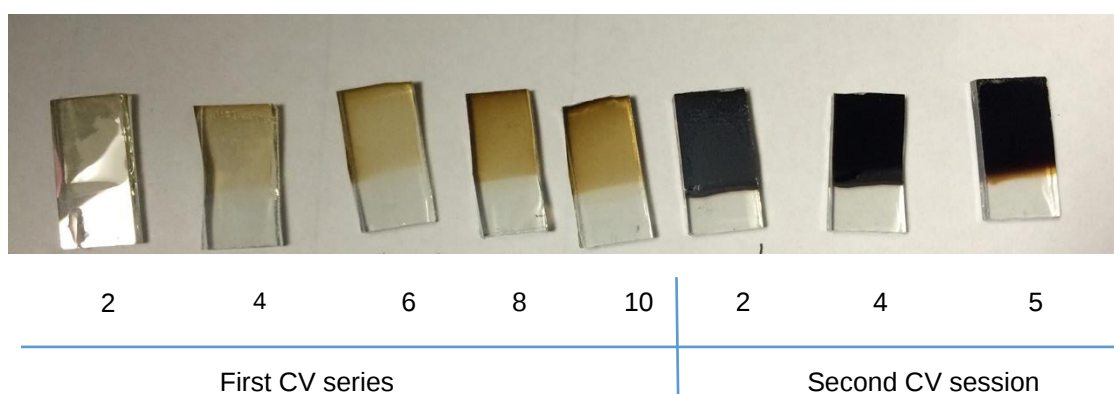


Figure 3.5. Time-lapse photographs of MnO_x samples at selected stages of deposition. During the first CV series, a light yellowish film could be observed on the FTO surface. The film turned to dark brown during the second CV series.

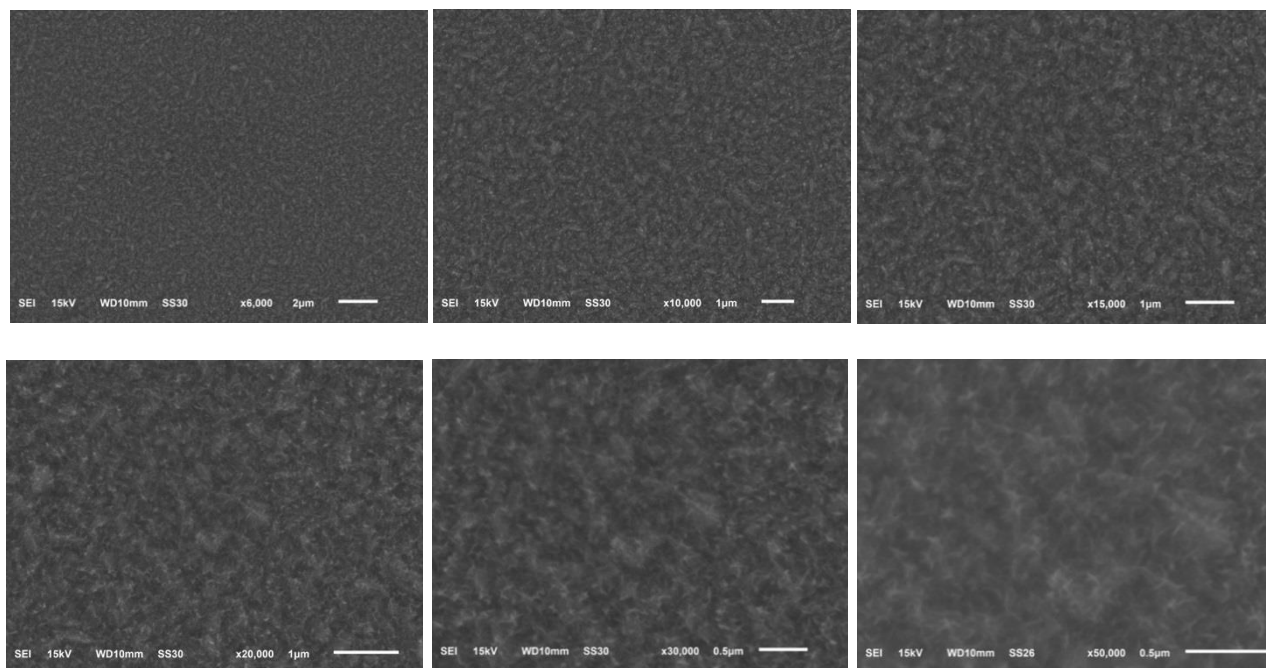


Figure 3.6 a. SEM images at various magnifications of the sample after two (2) cycles in the first CV series. Small clusters can be observed on the protrusions on the FTO surface.

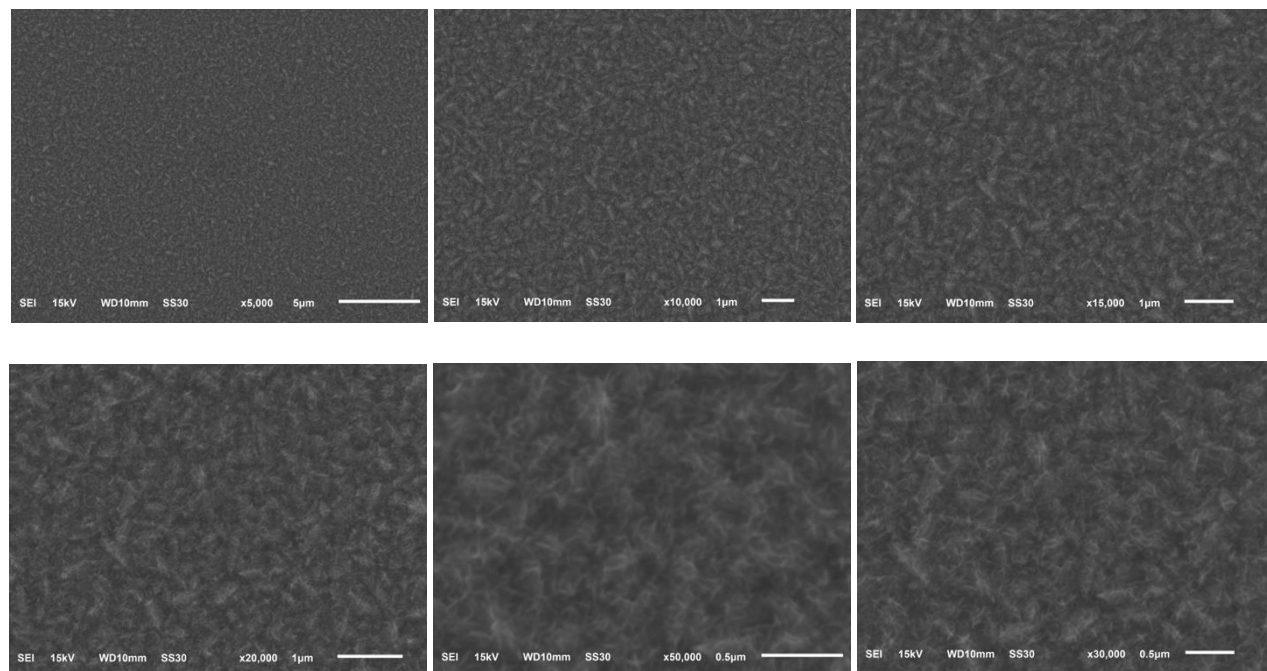


Figure 3.6 b. SEM images at various magnifications of the sample after four (4) cycles of the first CV series. The small clusters in Figure 3.6a have developed into larger clusters.

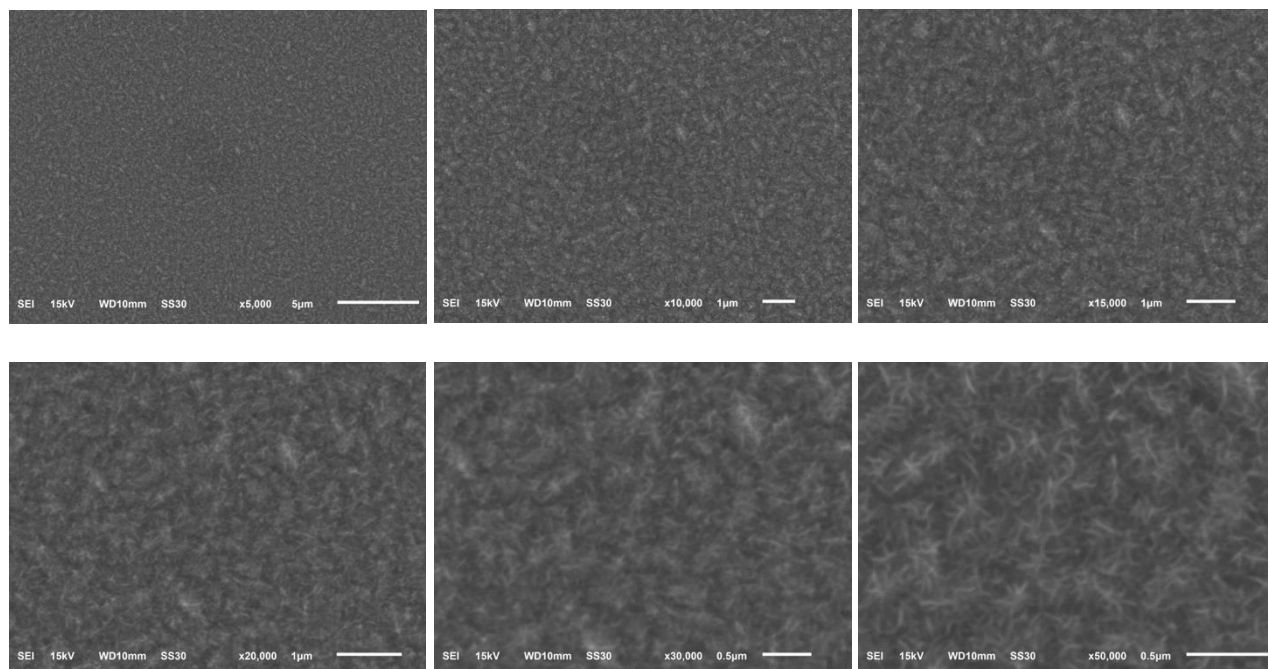


Figure 3.6 c. SEM images at various magnifications of the sample after six (6) cycles of the first CV series. The clusters in Figure 3.6 b continue to grow as the catalytic film is forming.

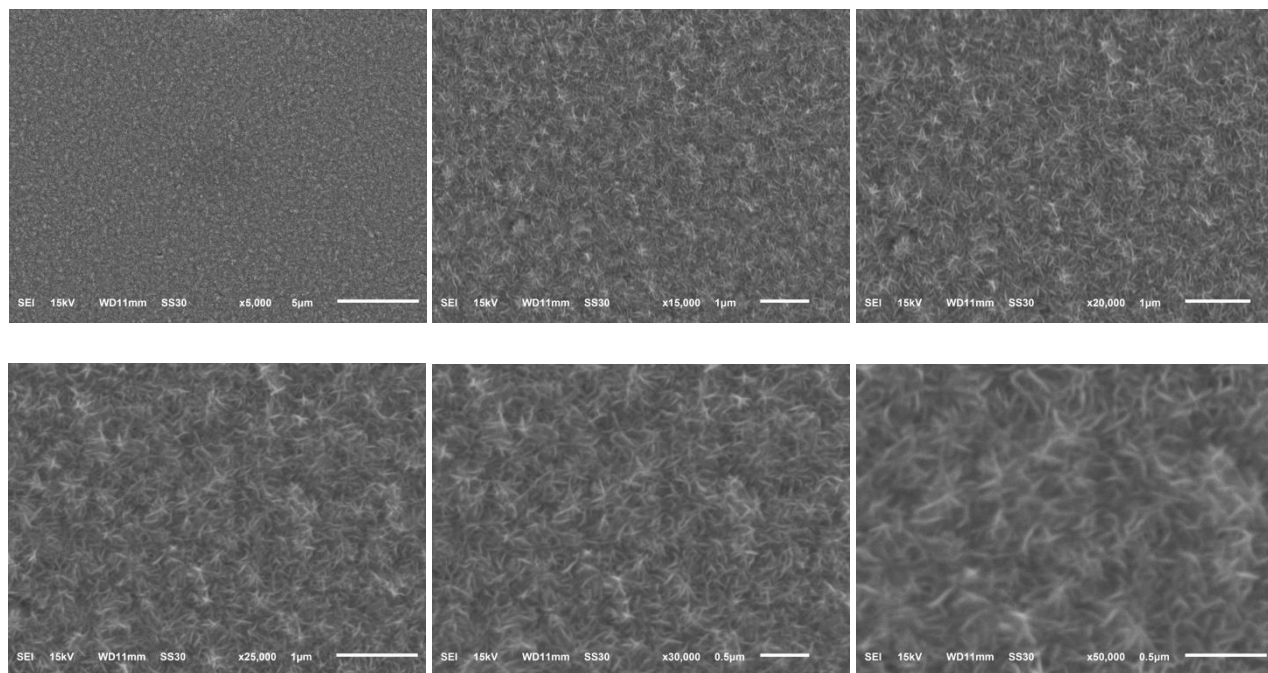


Figure 3.6 d. SEM images at various magnifications of the sample after eight (8) cycles in the first CV series. The catalytic film in Figure 3.6 c has now covered the whole surface.

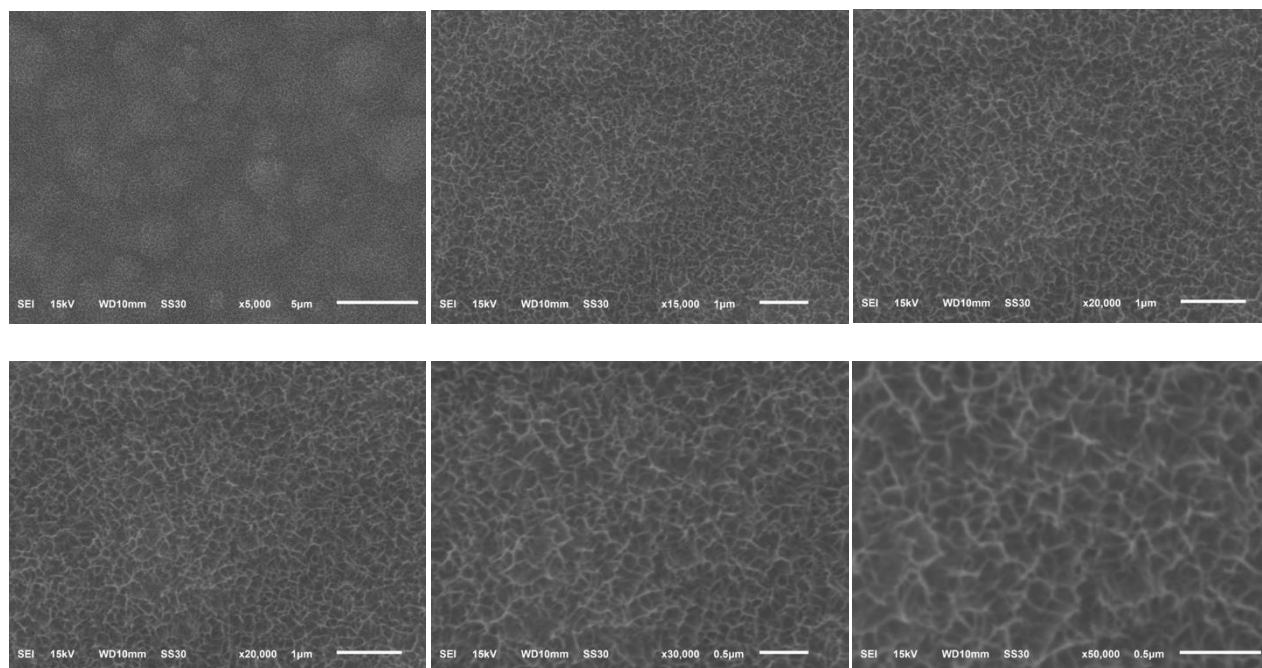


Figure 3.6 e. SEM images at various magnifications of the sample after four (4) cycles in the second CV series. The surface morphology of the catalytic film did not change much during the second CV series.

We also did functionality tests after selected stages of deposition. As shown in Figure 3.7, there is a gradual increase in peak current density during the first CV series. However, the current density increased dramatically during the second CV series, which we believe is due to the increase in the oxidation state of the MnO_x film. It is particularly worth noting the slope of the functionality curve during the second session. There is clearly the possibility of a much further enhanced oxidation state with additional scans over this potential range, or with the use of a third series of electrodeposition over a different potential range.

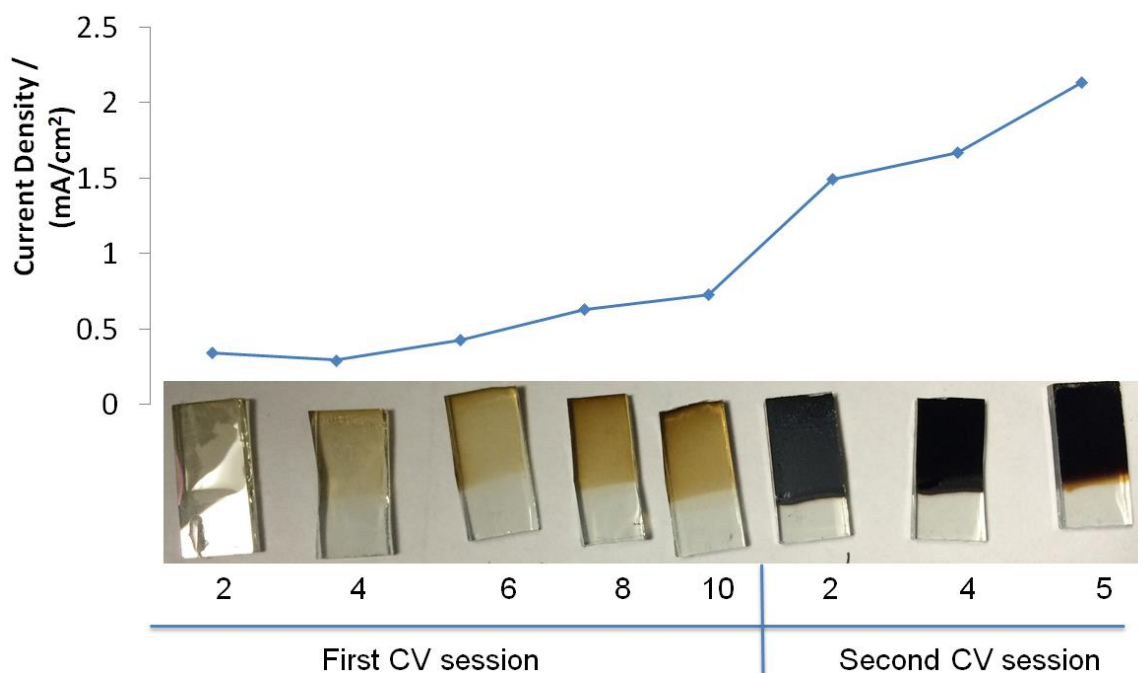


Figure 3.7. Functionality assessment after selected stages of electrodeposition. There is a gradual increase in peak current density during the first CV series. However, the peak current density increases dramatically during the second CV series, which we speculate to be the result of continued enhancement of the oxidation state of the catalyst. It is particularly worth noting that the slope of the functionality curve during the second session is strongly positive, and nowhere near an asymptote. Thus, there is clearly a possibility of much further enhanced oxidation state with additional scans over this potential range (0.6 to 2.0 V) or a third series of CV electrodeposition over a different potential range, with the potential that this method can be used to optimize catalyst function.

3.4.4 XRD characterizations

Our XRD results provide important evidence for this proposition. The black, green and red traces in Figure 3.8 show the XRD patterns for samples S0, S1 and S2, respectively. The major components for the dual-series sample were Mn_2O_3 and MnO_2 , which is similar to sample S2. Sample S1, on the contrary, only has feature peaks for Mn_2O_3 . We speculate that the major transformation in the first CV series (0-0.6V) was the conversion of Mn(II) to Mn(III), with the conversion of Mn(III) to Mn(IV) taking place during the second CV series (0.6-2.0V). Since there was only a very small number of cycles (5 cycles) during the second series, some Mn(III) species remained intact. We should also note that the XRD profile of sample S2 has the same oxidation state as the dual-series catalyst, so its poorer performance could be attributed entirely to transport resistances due to the larger microscale morphology.

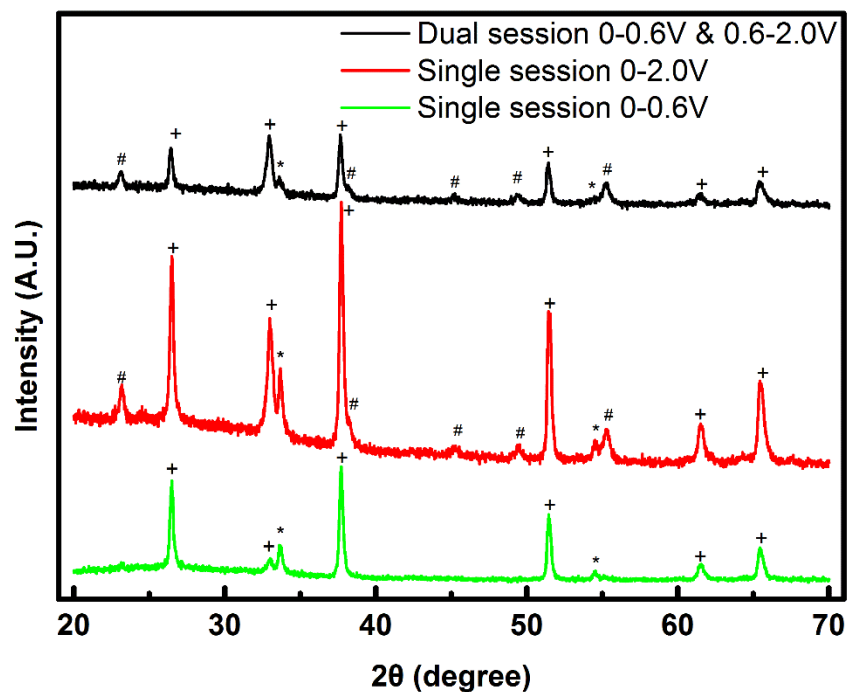


Figure 3.8. X-ray diffraction spectra of the three catalysts: a) MnO_x after two consecutive series of CV electrodeposition (scans over 0-0.6 V and 0.6-2.0 V) followed by calcination; it has the peaks of both Mn_2O_3 and MnO_2 , which indicates that the $\text{MnO}(\text{OH})$ formed in the first CV series has been further oxidized. b) MnO_x after one series of CV (0-2.0 V) and calcination, showing a similar pattern to trace a); this is an indication that the single 0-2.0 V series produces a MnO_x catalyst with a similar oxidation state as the one synthesized by the dual-series. c) MnO_x after one CV series (0-0.6 V) and calcination; the scan shows that the major phase of MnO_x is Mn_2O_3 , meaning that the MnO_x before calcination is $\text{MnO}(\text{OH})$ as proposed. The symbols +, *, and # in this figure designate the feature peaks of the FTO substrate, Mn_2O_3 and MnO_2 , respectively.

3.4.5 Stability tests

Long and stable catalytic performance is also a very important aspect of functional WOCs⁵⁷. The catalytic film synthesized by dual-series methods has very stable catalytic performance during consecutive CV tests and chronoamperometry tests over prolonged periods of time. All the tests were performed using the identical setup and conditions described in the functionality assessments session. Figure 3.9 shows the current densities when 1.2 V (vs. SHE) of potential was applied to the system. After about 1.5 h of decrease in signal (which is typical⁵⁸), the current density was steady for the next 4.5 hours of the six-hour assessment period. As expected, FTO has a flat profile throughout the assessment period, confirming that it is not catalytic.

We performed the same test on samples S1 and S2. The results of these tests show that they are equally stable but at lower current densities than the dual-series sample (Figure 3.10). We also did stability tests with 18 consecutive CV cycles on one S0 sample. Figure 3.11 shows that all the resulting curves were of similar shape, with the peak current densities falling within a narrow range (1.96 ± 0.11 mA/cm²).

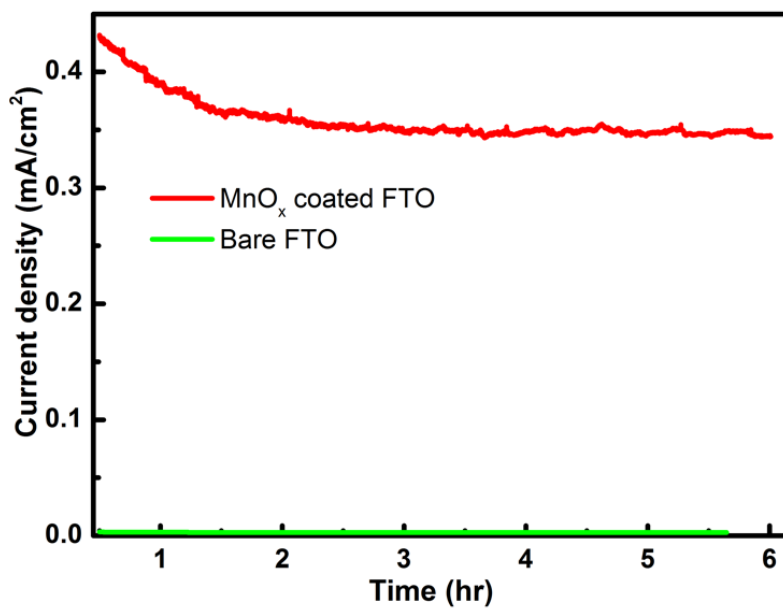


Figure 3.9. Current density profile of the MnO_x catalyst synthesized by the dual-series method during long term catalytic assessment at 1.2 V (vs. SHE) in a 0.1 M phosphate buffer solution (pH 7.0). The steady profile over a long period of time gives an indication of a stable MnO_x film.

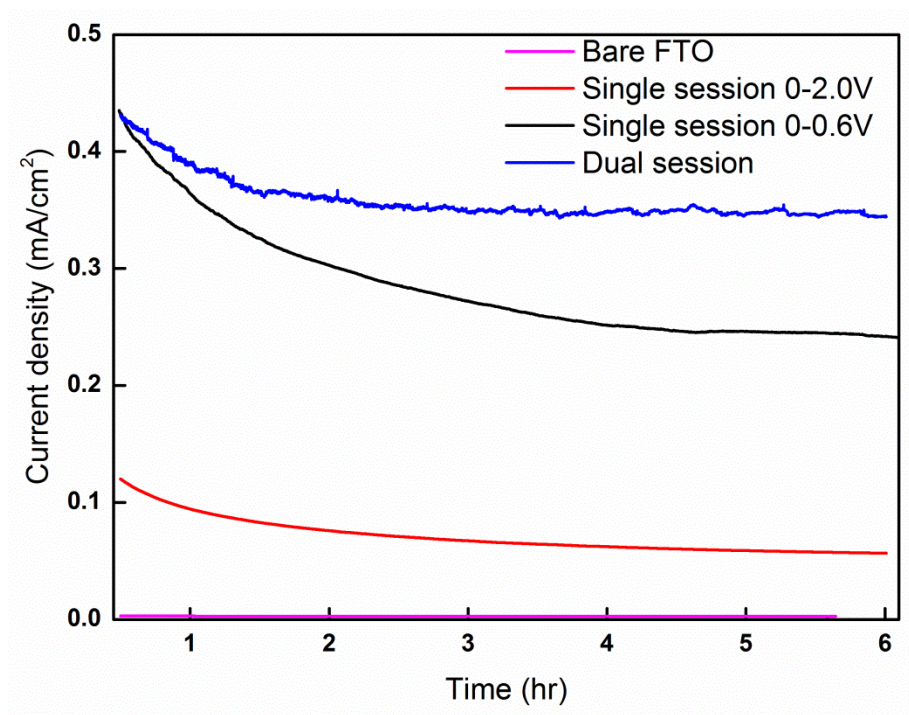


Figure 3.10. Current density profiles showing the stability of the catalytic films: bare FTO (purple curve), single session 0-0.6V sample (black), single session 0-2.0V sample (red), and dual session sample (blue). All tests were carried out in a 0.1M phosphate buffer solution (pH 7.0) at 1.2V (vs. SHE) for six hours. All single session and dual session samples had good stability during the six hours of assessment. However, the dual session sample had a higher stable current density compared to the single session samples, providing further evidence that the dual series method is better than the traditional single session methods.

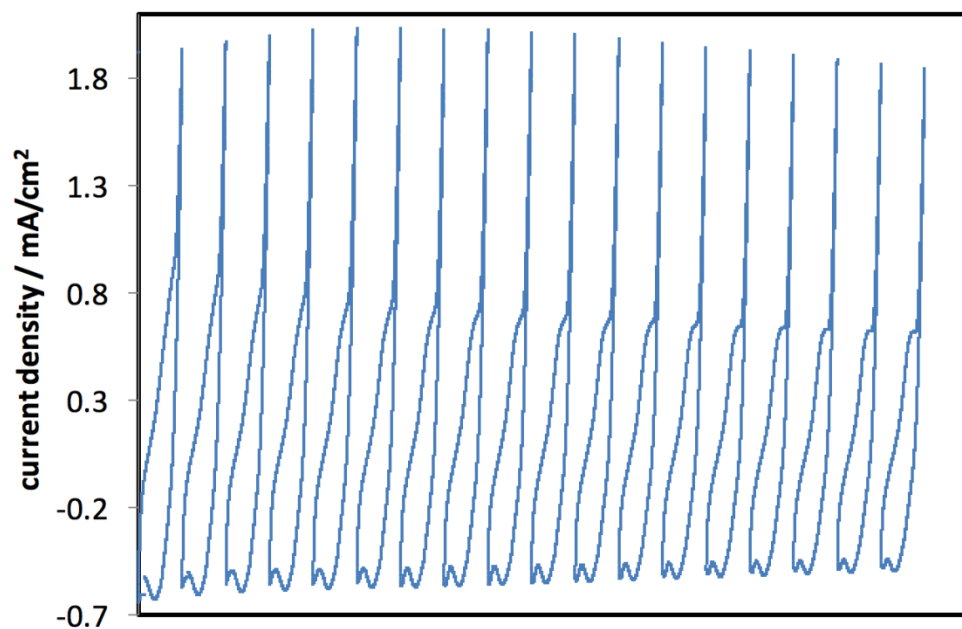


Figure 3.11. Consecutive CV scans on one catalyst sample to assess stability. All 18 scans have similar profiles, with the peak current density falling within a narrow range of values (1.96 ± 0.11 mA/cm²)

3.5 Conclusions

We have developed and assessed a new electrodeposition method for synthesizing stable and highly efficient manganese-based WOCs *in situ* on conductive surfaces. This new method involves multiple consecutive series of CV scans over different potential ranges, followed by calcination. The resulting MnO_x films have well-dispersed porous surface morphologies consisting of nanoscale fibers that promote catalytic performance. Our characterization results support a hypothesis that the first CV series produces a fibrous nanoscale film, while the second series elevates the oxidation state of the catalyst without significantly changing the surface morphology acquired during the first series. The potential to enable independent control of surface morphology and catalyst oxidation state(s) makes this a powerful tunable method for rational catalyst synthesis and optimization.

CHAPTER 4. FUNCTIONAL BIOMIMETIC COMPOSITE Mn/TiO₂ PHOTOANODE FOR WATER SPLITTING

4.1 Abstract

We have designed, fabricated and assessed a composite photoanode for solar-driven water splitting, using an easy approach and inexpensive materials. The photoanode consists of a solar-harvesting layer and a catalytic layer. Scanning electron microscopy (SEM) and x-ray powder diffraction (XRD) were used to characterize the surface morphology and structure, and cyclic voltammetry (CV) was used to assess functionality with and without ultraviolet (UV) illumination. The resulting photoanode provides stable and effective water oxidation under UV illumination. Another potential benefit of this work is that, since TiO₂ is used as the solar-harvesting layer, various dyes can be integrated into the device to broaden its absorption spectrum.

4.2 Introduction

In the previous chapters, we discussed work on developing cost-effective, highly active water oxidation catalysts. In this chapter, we focus on designing, fabricating and assessing a composite photoanode for solar-driven water splitting, using a simple approach and inexpensive materials.

As we described in Chapter 1, a functional artificial photosynthesis device requires an effective solar-driven water oxidation photoanode. A functional photoanode should incorporate the following features: i) a robust and conductive substrate upon which components like a solar harvester and a WOC can both be mounted; ii) a solar harvester that can effectively capture, intensify and convert sunlight from a target range of the solar spectrum; iii) an effective WOC

that is able to effectively catalyze the water oxidation reaction. A double-layer structure is the best configuration for the photoanode, because it has the potential to enable independent design and optimization of the individual components, which could enhance the overall performance of the integrated system.

We had initially planned to integrate a dye-sensitized solar cell (DSSC) with a manganese-based WOC to build the photoanode system. DSSC is a flexible solar converter system that has tunable absorption spectra when different types of dyes are incorporated ⁵⁹⁻⁶¹. A DSSC usually has a TiO₂ support as a substrate incorporated with dyes ⁶²⁻⁶⁵. TiO₂ by itself has a large bandgap (~3eV), which is sufficient for the water oxidation reaction ⁶⁶⁻⁶⁸. In fact, Fujishima and Honda used TiO₂ under intense ultraviolet (UV) light illumination in their pioneering work on using photoelectrochemistry to split water ⁶⁹. However, as shown by Equation 4.1, this bandgap limits its absorption spectrum to no more than 413 nm, which falls in the ultra-violet region.

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s} \times 3 \times 10^8 \text{ m/s}}{3 \times 1.60 \times 10^{-19} \text{ J}} = 4.14 \times 10^{-7} \text{ m} = 414 \text{ nm} \quad (\text{Eq 4.1})$$

On the other hand, TiO₂ has a low and negative conductive band, which is unlike many other semiconducting materials, and can thus enable water splitting without an external electrical bias

^{70,71}. TiO₂ also provides excellent mechanical, thermal and chemical stability under the harsh conditions typically encountered in water oxidation. Finally, TiO₂ can be easily engineered into various morphologies and coated onto different surfaces via a variety of methods. All these benefits make TiO₂ an ideal substrate for the solar harvesting system. To overcome the limitation of the limited absorption spectrum, various dyes can be integrated with TiO₂ to tune and broaden the spectrum and boost the efficiency of the solar harvesting system.

Our goal was to demonstrate the feasibility of building a photoanode using a manganese-based WOC and TiO₂ as a solar harvesting material. If the composite photoanode is capable of solar-driven water splitting, then we can simply add various dyes to improve the absorption spectrum and thus the performance.

We took advantage of the desirable properties of both TiO₂ and manganese-based WOC to develop the photoanode. We then performed electrochemical measurements to assess the functionality of the photoanode, and used SEM and XRD to characterize the structure and surface morphology.

4.3 Materials and methods

4.3.1 Materials

Manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂ • 4H₂O) and P25 titanium dioxide nanoparticles (TiO₂ with an anatase to rutile ratio of 4:1) were purchased from the Sigma-Aldrich Company, LLC (St. Louis, MO) and used without further modification. Fluorine-doped

tin oxide (FTO with a surface resistance of $\sim 7 \Omega/\text{cm}^2$) was also purchased from Sigma-Aldrich. Prior to use, the FTO glass was cut into 2cm by 1cm rectangular substrates, and cleaned in acetone and DI water.

4.3.2 Methods

4.2.2.1 Spin coating of the TiO_2 film

We added 0.15g of P25 TiO_2 nanoparticles to 10 ml of methanol. The mixture was then sonicated for 10 minutes to make a P25 colloid. The colloid was then spincoated onto FTO glass for 20 minutes. The TiO_2 -coated FTO glass was then dried in air.

4.3.2.2 *In situ* synthesis of the Mn WOC catalyst

The Mn WOC was synthesized by the electrodeposition protocol reported by Zaharieva and coworkers (2012)⁵⁴. The electrodeposition was performed using a typical three-electrode setup on a CHI 660D electrochemical workstation (CH Instruments, Inc., Austin, TX). During the deposition, TiO_2 -coated FTO was used as the working electrode, an indium tin oxide-coated polyethylene (ITO) chip as the counter electrode, and a Ag/AgCl electrode as the reference electrode. Twenty five milliliters (25 ml) of a 0.1 M $\text{Mn}(\text{CH}_3\text{COO})_2$ aqueous solution was used as electrolyte. For electrodeposition, 25 cycles of potential ramps ranging from -0.75 V to +2.15 V were applied at a scan rate of 0.1 V/s. A light brown film could be observed forming on the electrode surface, with the film becoming darker during the deposition. After deposition, the photoanode sample was rinsed with D.I. water and dried in air. For comparison, we also

synthesized a Mn WOC on a bare FTO electrode without the TiO₂ coating, using the identical approach described above.

4.3.2.3 Structural characterization by XRD and SEM

We took XRD spectra after each deposition step to track the color changes on the surface. The XRD spectra were acquired on a Bruker Davinci D8 advanced x-ray diffractometer (Bruker Corporation, Madison, WI). We also used a JSM 6610-LV scanning electron microscope (JEOL Ltd, Peabody, MA) to observe the surface morphology, and EDS (Oxford Instruments, High Wycomb, Bucks, England) to determine the surface elemental composition.

4.3.2.4 Functionality assessment by CV and EIS

We did CV and EIS characterizations using a typical three-electrode electrochemical setup. In all the assessments, a platinum wire was used as a counter electrode, a Ag/AgCl electrode as reference electrode and 25ml of 0.1 M neutral phosphate solution (pH 7.0) as electrolyte. We applied a potential range of -0.2 V to 1.4 V at a scan rate of 10 mV/s.

We first tested the Mn WOC that was synthesized directly on clean FTO without TiO₂ coatings, to make sure that the electrodeposition process we described above can produce an active catalyst. As comparison, we used a piece of clean FTO glass as control. We then tested the composite photoanode samples in the dark and under UV illumination. The UV source was a 4 W UVGL-15 compact UV lamp (UVP LLC, Cambridge, UK). For the EIS tests, we collected the

impedance spectrum on a photoanode sample under UV illumination at 0.8 V, using a 10 mV perturbation between 0.1 Hz and 10 kHz.

4.4 Results and discussion

4.4.1 Structural and morphological characterization of the composite photoanode

To track changes on the FTO surface during the photoanode fabrication process, we took XRD spectra after each step. Shown in Figure 4.1 are the XRD patterns for a) pure P25 TiO₂ powder, b) pure FTO substrate, c) FTO substrate coated with TiO₂, and d) the composite photoanode with TiO₂ coating and Mn WOC. Trace ‘a’ is a typical pattern of TiO₂⁷², and trace ‘b’ a typical pattern of the FTO substrate. When we compare traces ‘a’, ‘b’, and ‘c,’ we can conclude that TiO₂ was successfully immobilized on FTO glass using the method described above. We expected to see the feature peaks for manganese in trace ‘d’ to differentiate it from trace ‘c.’ However, there were no significant differences between the two profiles. There are two plausible explanations for this result: i) it is difficult for XRD to detect the manganese-based catalyst on the surface; and ii) the *in situ* synthesis did not deposit the manganese catalyst as had been expected.

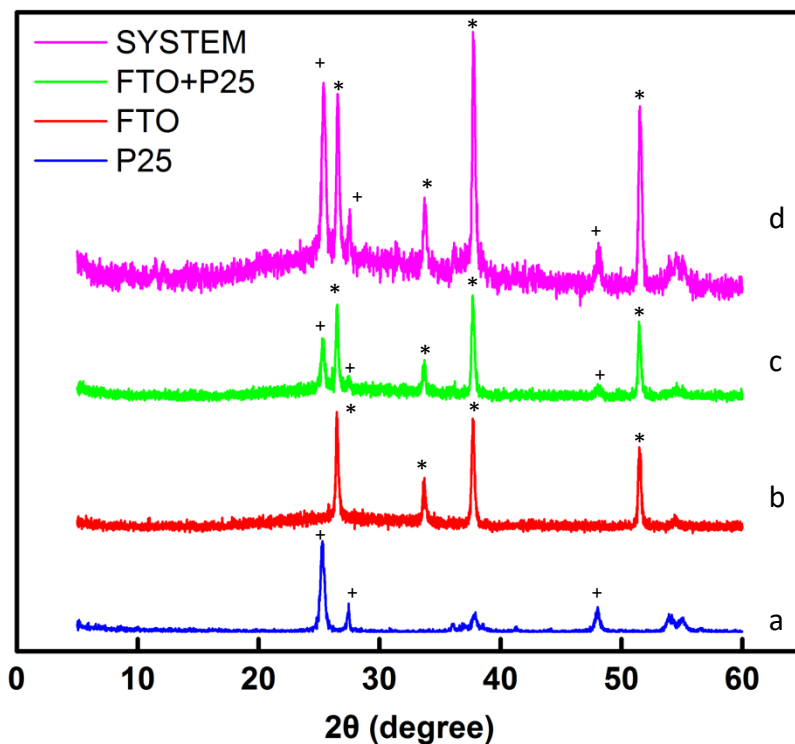


Figure 4.1. XRD spectra of a) pure P25 TiO_2 powder, b) pure FTO glass, c) FTO glass coated with TiO_2 , and d) the composite photoanode. In this figure, + designates the feature peaks of TiO_2 , and * denotes those of FTO. Traces “a” and “b” show the typical patterns for TiO_2 and FTO, respectively. Trace “c” shows all the peaks associated with both TiO_2 and FTO, confirming that the composite photoanode contains all the required elements. However, trace “d” is not significantly different from trace “c,” which could mean that the method described above did not produce the expected composite catalyst, or that XRD is not an appropriate technique for detection of manganese in the complex.

To resolve this issue, we took EDS images of the photoanode to check the structure of the surface. Figure 4.2 shows SEM images of: a) clean FTO surface, b) FTO coated with TiO_2 at low (x200) magnification, c) FTO coated with TiO_2 at a higher (x800) magnification, d) the composite photoanode at low (x160) magnification, and e) the composite photoanode at a higher (x3300) magnification. Compared with bare FTO, which has a flat featureless surface, image b shows the surface has been covered by a film of TiO_2 . However, instead of a uniformly smooth coated layer, we observed many cracks. We speculate that these cracks were formed during the evaporation of the solvent, likely similar to the mechanism for the formation of cracks on the surface of the ground during a long drought. This morphology can be seen more clearly in image c. Image d shows the surface morphology after electrodeposition of the WOC. The morphology appears to be similar to the previous samples with only TiO_2 coatings. However, at a higher magnification (3e), we observed a different coating layer of distinct morphology beneath the TiO_2 substrate. We believe this layer beneath the TiO_2 coating is the manganese WOC film. Since this film was covered by the TiO_2 coating layer, it could not be effectively detected by XRD, which is primarily a surface characterization technique. To further investigate this, we took EDS elemental mapping of a selected area where both layers could be clearly observed.

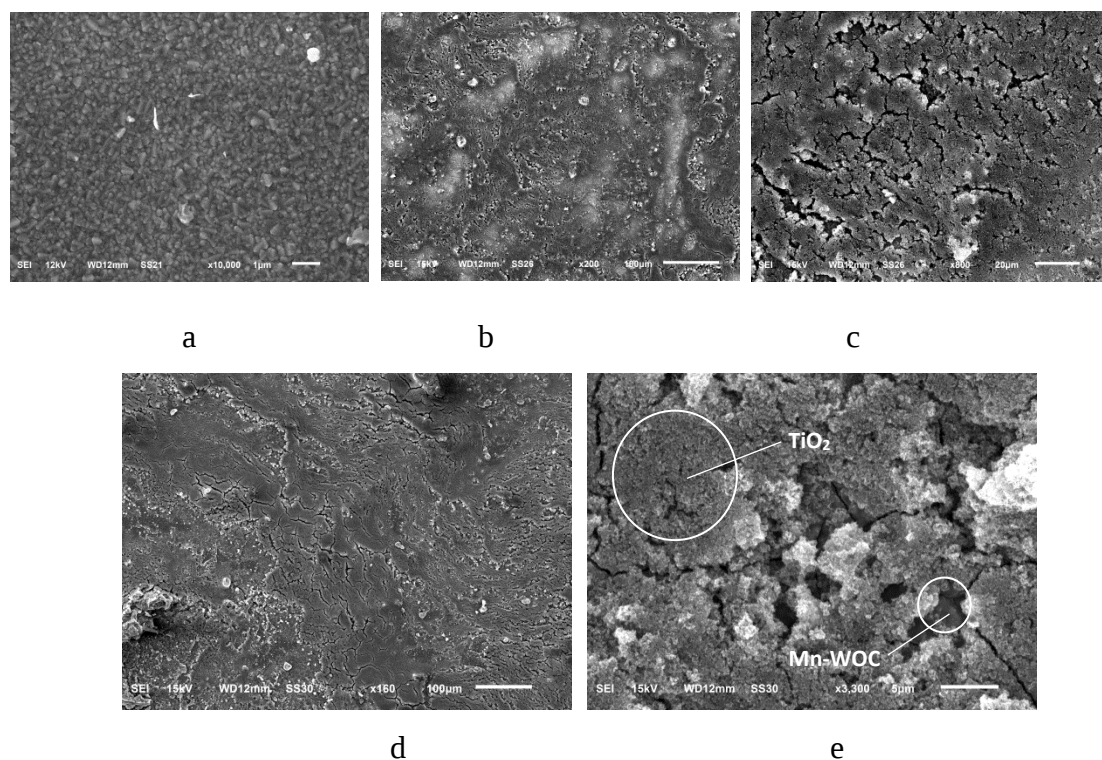


Figure 4.2. SEM images of a) clean FTO substrate; b) FTO surface after coating with TiO₂ (at x200 magnification); c) FTO coated with TiO₂ (at x800 magnification); d) composite photoanode (at x160 magnification); e) composite photoanode (at x3,300 magnification). Images b and c show the morphology of the TiO₂ coating to be essentially a uniform layer, with a porous structure that contains cracks. Images d and e show the morphology of the composite photoanode. Following Mn WOC deposition, the morphology of the surface does not change substantially; however, a new layer could be observed underneath the porous TiO₂ film.

Figure 4.3 is the SEM image of the area we selected for EDS examination. The triangular area in this image is the top TiO_2 coating layer, while the rest of the area is the ‘crack’ in the TiO_2 layer that shows the film underneath. The elemental distribution of titanium and manganese are shown in Figure 4.3 b and c, respectively. Figure 4.3 b shows a high concentration of titanium in the triangular area, with very little manganese detectable. On the other hand, the white dots in Figure 4.3 c clearly portray the presence of manganese in the area that is not covered by TiO_2 . This is an interesting observation because, since TiO_2 was coated prior to the electrodeposition of the Mn WOC, we should expect the Mn WOC to be deposited above the TiO_2 layer instead of below. We believe this anomaly occurred because the Mn(II) ions migrated through the porous TiO_2 layer to reach the electrode surface during electrodeposition, thus forming the catalytic layer underneath the layer of TiO_2 coating.

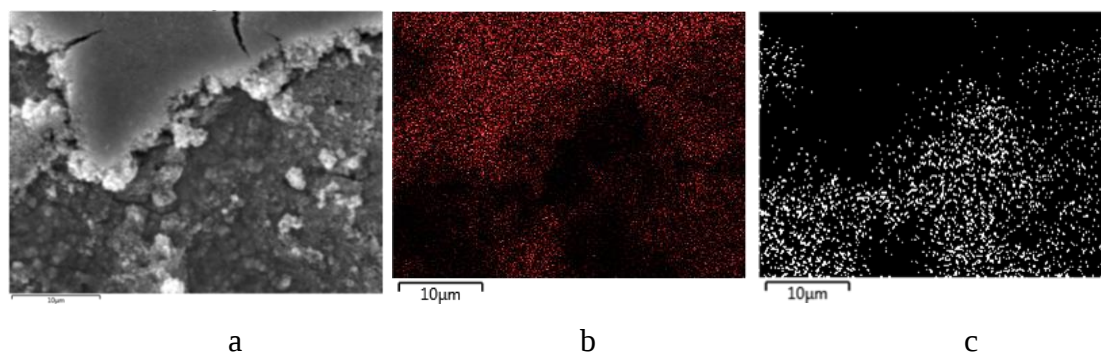


Figure 4.3. EDS mapping of selected area. a) The SEM image provides evidence of both TiO_2 and manganese on the surface. The triangular area at the top is presumed to be the TiO_2 layer, while the rest of the area is covered by the manganese catalyst. b) The distribution of titanium within the selected area. As postulated, the highest accumulation of titanium is in the triangular area. c) Distribution of manganese in the selected area, with the heaviest concentration outside the triangular area.

4.4.2 Electrochemical characterization of the Mn WOC

According to a previous report,⁵⁴ the catalyst comes in active and inactive forms. To determine which form is generated by the method described above, we acquired CV data on pure FTO, and FTO samples coated with Mn WOC. The blue curve in Figure 4.4 represents the CV for the Mn WOC, and the red curve the bare FTO substrate. These data lead to the conclusion that the Mn WOC synthesized using this protocol is active, with an onset potential for water oxidation of approximately 1.1 V vs. Ag/AgCl. We have tested the Mn WOC sample both with and without UV illumination. Similar results were obtained under both conditions, confirming that the Mn WOC is not light-sensitive.

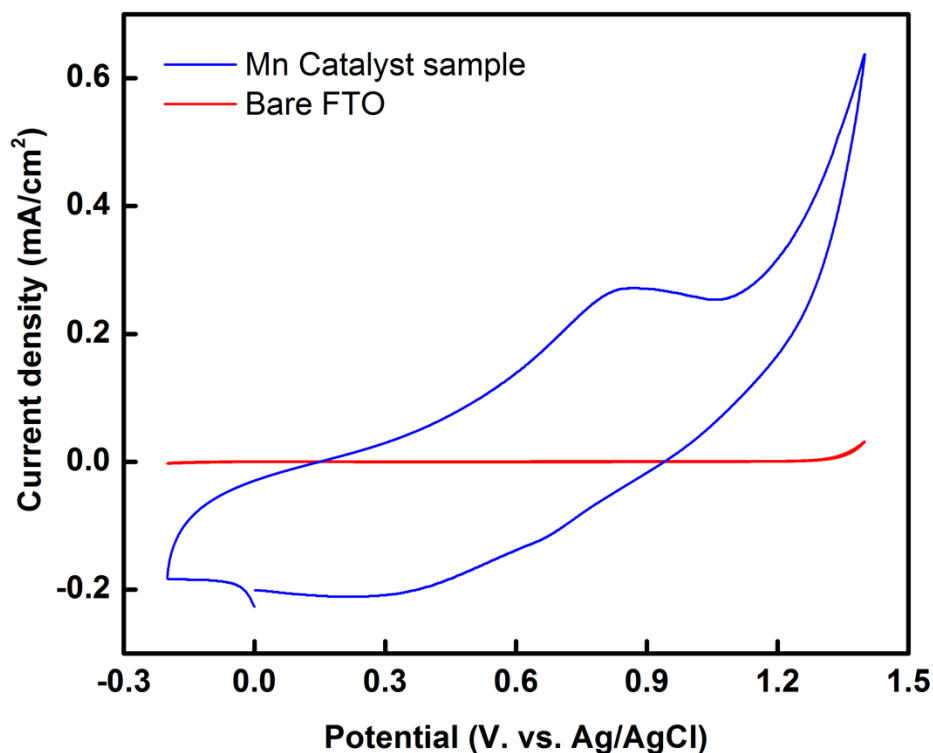


Figure 4.4. Typical cyclic voltammograms during assessment of the manganese catalyst. The red trace represents data for clean FTO glass. The blue trace represents data acquired on the manganese catalyst deposited on FTO, and provides confirmation that the catalyst synthesized by electrochemical deposition is active.

4.4.3 Electrochemical characterization of the composite photoanode.

As described above, TiO_2 has a band gap of ~ 3 eV which corresponds to an absorption spectrum in the UV range⁷³. Therefore, we characterized the photoanode with and without UV illumination. To help identify the inflection point in the curve, we took the first derivative of the current density with respect to the applied potential (Figure 4.5). The point where the first derivative goes to zero can be used as a reliable estimate of the onset potential for the water oxidation reaction. Figure 4.5 a shows the profile of the photoanode sample under UV illumination, while Figure 4.5 b shows the sample without UV illumination. Without UV illumination, the onset potential was estimated at approximately 1.1 V vs. Ag/AgCl, demonstrating that the functionality of the photoanode is similar to that of the pure Mn WOC. However, under UV illumination, the onset potential is reduced by 0.3 V to about 0.8 V vs. Ag/AgCl. This decrease of onset potential represents enhancement of the catalytic functionality under radiation. We also tested the sample with only the TiO_2 coating under identical conditions but, as expected, we observed no measurable catalytic activity. As mentioned before, the Mn WOC by itself is not light-sensitive, thus the decrease of the onset potential should only be the result of the TiO_2 layer.

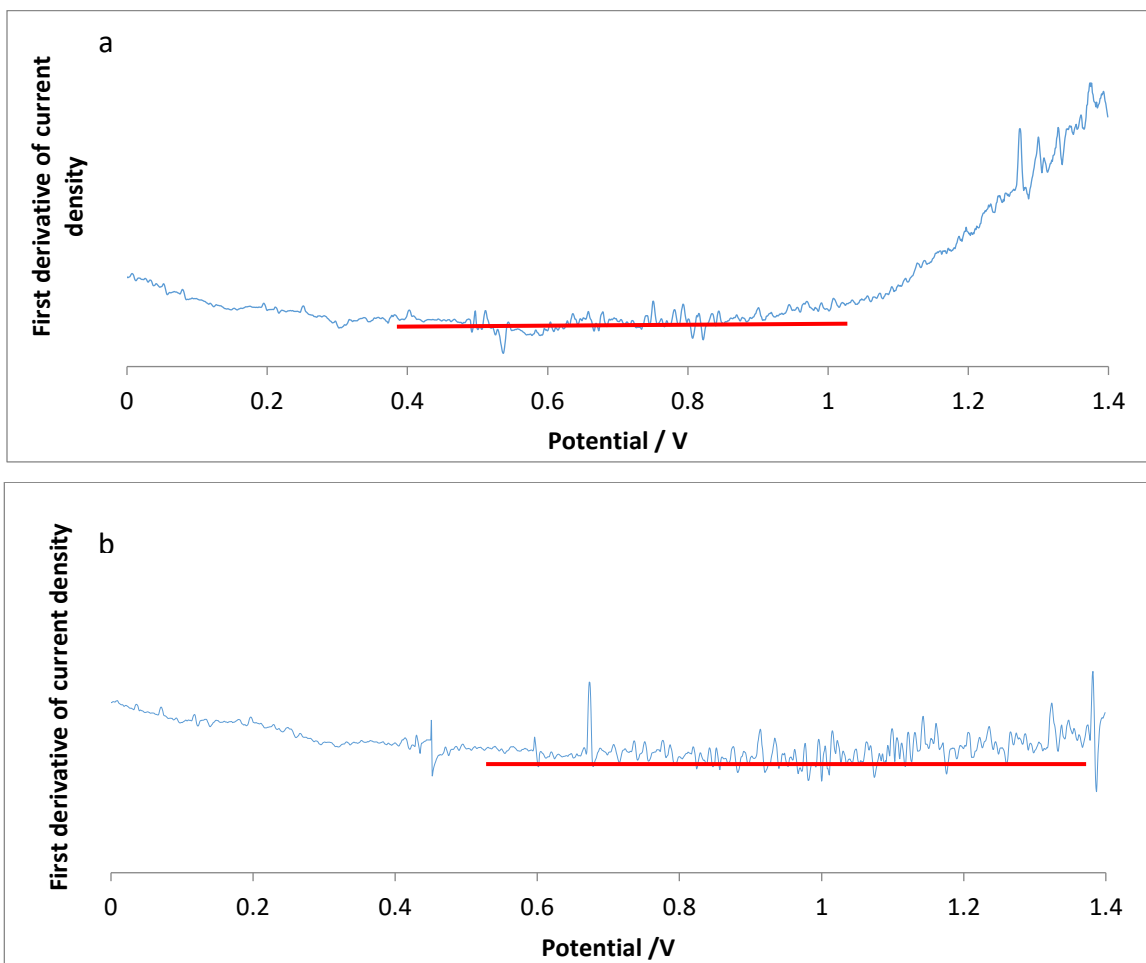


Figure 4.5. First derivative of the current density profile with respect to applied potential, used here as a reliable aid to determining the oxidation voltage. a) Data acquired under UV illumination, showing an oxidation voltage of approximately 0.8 V vs. Ag/AgCl. b) The oxidation voltage for the same sample evaluated without UV illumination was of approximately 1.1 V vs. Ag/AgCl.

As described above, the photoanode should have a “diffusion-reaction” mechanism, where the reactants diffuse through the porous TiO_2 layer to the surface of the catalytic film where they react, and the products diffuse in the opposite direction. To investigate this scheme, we acquired EIS data at 0.8V vs. Ag/AgCl under UV illumination. The resulting Nyquist plot is shown in Figure 4.6. The plot of the photoanode under this condition has a semicircle in the high frequency range, followed by a 45 degree straight line in the low frequency range. A simple Randles Circuit (Figure 4.5 inset) can be used to regenerate the Nyquist plot. The equivalent circuit contains a surface resistance R_s , a double-layer capacitance C_{dl} , a charge transfer resistance R_{ct} , and a Warburg element Z_w which represents the diffusion process. A Randles circuit is a typical model for an electrochemical reaction when it is governed by a semi-infinite diffusion process on a flat electrode. This result further confirms our hypothesis that, during the deposition of the Mn WOC, Mn^{2+} ions diffused through the TiO_2 layer, and formed the WOC catalytic film underneath. Thus, although the catalytic layer is covered by TiO_2 , water molecules can still reach the catalytic surface to enable the reaction.

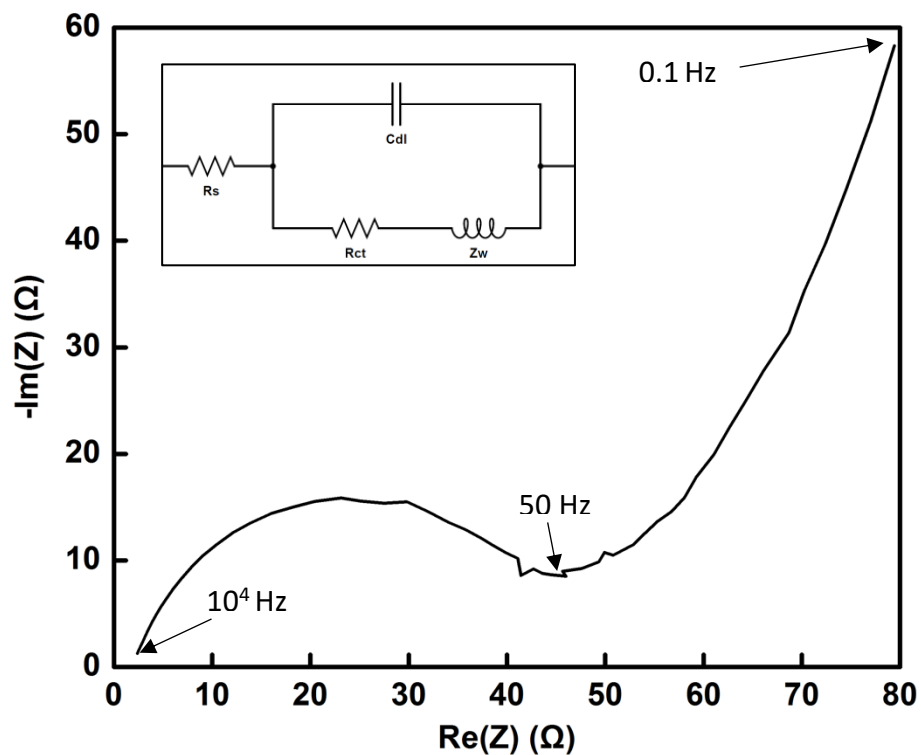


Figure 4.6. Nyquist plot of EIS data acquired at 0.8 V for the composite photoanode under UV illumination. The semicircle at high frequency denotes reaction, while the straight line at low frequency denotes diffusion. Along with the Randles circuit (inset) used to simulate the data, this result provides confirmation that the Mn WOC is covered by a porous layer of TiO_2 .

4.5 Conclusions

We have successfully developed a composite photoanode using a Mn WOC and TiO_2 as a conductive substrate. This work has demonstrated an important and practical approach to using earth-abundant, non-toxic, easy to handle catalysts to fabricate a composite photoanode. Another potential application of this work that is that this catalytic complex can be integrated with CO_2 sequestration to achieve the two carbon-based-fuel production schemes we introduced in Chapter 1. The current photoanode is only functional under UV illumination. However, there are methods to dope various types of substrates with selected dyes to build a DSSC-type solar harvester to broaden the absorption spectrum of the photoanode to obtain a much more efficient system.

CHAPTER 5. ELECTRODEPOSITION OF Ni/Ni(OH)₂ CATALYTIC FILMS BY CYCLIC VOLTAMMETRY FOR THE HYDROGEN EVOLUTION REACTION

5.1 Abstract

We have developed a novel electrodeposition method that synthesizes Ni/Ni(OH)₂ catalytic films *in situ* on conductive surfaces. The new method involves only two cycles of cyclic voltammetry, and the resulting film has a surface morphology consisting of a monolayer of firmly packed walnut-shaped particles. The film has superior catalytic activity towards the hydrogen evolution reaction compared to traditional hydrogen evolution reaction catalysts (HERCs) produced by electrodeposition under constant current or constant potential. The method is a simpler and more cost-effective way to produce highly-effective electrocatalysts for the hydrogen evolution reaction (HER). It creates large numbers of Ni(OH)₂/Ni interfaces that significantly promote catalyst performance towards that of platinum mesh.

5.2 Introduction

As we described in Chapter 1, active and low-cost electrocatalysts for both the water oxidation and hydrogen evolution reactions are crucial for an effective AP process to produce hydrogen by water splitting^{33,74-76}. For a long time, the water oxidation half-reaction attracted most of the attention because it is the major source of overpotential in the water splitting process⁷⁷. Our group has also worked extensively on the water oxidation reaction, as discussed in the previous chapters. For the hydrogen evolution half reaction, platinum and its alloys are considered the “state of art” catalysts, and are widely used at the laboratory scale⁷⁸⁻⁸⁰. However, the high cost and extremely low availability of platinum and its alloys render them impractical for use on a

large scale^{81,82}. To make affordable artificial photosynthesis devices at scale, highly effective, robust catalysts based on earth-abundant metals have to be developed. Over the last decade, HER catalysts based on earth-abundant transition metals, especially nickel, have been extensively studied and assessed⁸³⁻⁹³. Most of these Ni-based HERCs are synthesized *ex situ* through benchtop wet chemistry methods. As previously discussed, electrodeposition has the benefit of significantly simplified experimental setup as well as easily-controllable synthesis conditions. It can also promote catalyst recovery and recyclability, which are usually significant problems for traditional catalysts synthesized by benchtop methods.

In this chapter, we discuss the development of an electrodeposition method to produce Ni/Ni(OH)₂ catalytic films *in situ* for hydrogen evolution on conductive surfaces. The new method involves only two cycles of cyclic voltammetry over a voltage range of 0 V to -1.2 V vs. Ag/AgCl (immersed in 3M NaCl). We believe the method provides a simpler and more inexpensive way to fabricate highly-effective hydrogen evolution electrocatalysts.

5.3 Experimental session

5.3.1 Materials

Nickle acetate tetrahydrate ($\text{Ni}(\text{COOCH}_3)_2 \cdot 4\text{H}_2\text{O}$) was purchased from the Sigma Aldrich Company, LLC (St. Louis, MO). Sodium phosphate monobasic (NaH_2PO_4) and sodium phosphate dibasic (Na_2HPO_4) were purchased from J.T. Baker (Phillipsburg, NJ). All chemicals were used without further modification. Fluorine-doped tin oxide (FTO)-coated glass (surface resistance $\sim 7 \Omega/\text{sq}$) was also purchased from the Sigma-Aldrich Company, LLC (St. Louis,

MO). Prior to use, the FTO electrode was cut into $2\text{ cm} \times 1\text{ cm}$ rectangular chips, cleaned in methanol and acetone, and rinsed in D.I. water.

5.3.2 Synthesis by electrodeposition

The electrodeposition process was performed using a typical three-electrode setup on a CHI 660D Electrochemical Workstation (CH Instruments Inc., Austin, Texas). A blank FTO chip was used as the working electrode, with an indium tin oxide (ITO) chip as a counter electrode, and a Ag/AgCl electrode as reference. The electrolyte used for electrodeposition was 25 ml of a 150 mM $\text{Ni}(\text{OCOCH}_3)_2$ solution. Two cycles of cyclic voltammetry (CV) scans were conducted between 0.0 V and -1.2 V vs. Ag/AgCl at a scan rate of 0.01 V/s. The cumulative charge was ~ 1.0 C. During the electrodeposition process, a light grayish film could be observed on the FTO working electrode. After deposition, the chip was rinsed in DI water and dried in air.

For comparison, we also synthesized a Ni-based HER catalyst using the traditional electrodeposition method of constant current density of 8 mA/cm^2 for 125 seconds^{94,95}. A shiny silvery film could be observed after the deposition. We also compared the performance of the Ni/Ni(OH)₂ catalytic film to that of platinum mesh. For brevity, we will designate the Ni/Ni(OH)₂ catalyst as cv-Ni, and the traditional catalyst as cc-Ni.

5.3.3 Materials characterization

The surface morphologies of both samples were characterized by a JSM 6610-LV and a JSM 7500F scanning electron microscope (SEM) (JEOL Ltd, Tokyo, Japan). The detailed

morphology was evaluated by a JEM 2200FS transmission electron microscope (JEOL Ltd, Tokyo, Japan). X-ray diffraction spectra were acquired on a Bruker Davinci D8 Advance X-ray diffractometer (Bruker Corporation, Madison, WI).

5.3.4 Electrochemical assessment of functionality

The functionality of the samples was assessed by cyclic voltammetry on a CHI660D electrochemical workstation. FTO glass coated with cc- or cv-Ni was used as a working electrode, a platinum wire as counter electrode, and a Ag/AgCl electrode as reference, with 25 ml of 1 M KOH solution as electrolyte. Potential scans were conducted between -0.4 V and -0.8 V vs. Ag/AgCl at a scan rate of 0.01 V/s. A Tafel plot was also obtained at a scan rate of 0.01 V/s. The catalytic functionalities of all samples were assessed in neutral media with 25 mL 0.1 M phosphate buffer (pH 7.0) as electrolyte. For comparison, a Ni foil and a platinum mesh were also assessed.

The catalyst stability test was also performed using the setup described above. The potential was maintained at -1.0 V for 10 hours and the corresponding current density was recorded as a function of time. We also did 201 cycles of CV scans on one cv-Ni sample, with the same setup used for the functionality tests in neutral media.

5.4 Results and discussions

5.4.1 Structural characterization

Figure 5.1 shows the surface morphology of the FTO substrate and the two samples obtained by FESEM. The bare FTO again has a rough but otherwise featureless surface (Figure 5.1 a). The cc-Ni sample also has a featureless surface (Figure 5.1 b). On the contrary, the cv-Ni sample has a surface morphology consisting of a monolayer of evenly distributed, firmly packed spherical walnut-shaped particles (Figure 5.1 c). The inset in Figure 5.1c shows the surface morphology of the cv-Ni sample at a higher magnification. From this image, we can estimate the diameter of the spherical particles at approximately 0.1~0.2 μm (100-200 nm). We believe the uniform surface morphology promotes mass transfer and enhances the catalytic performance of the cv-Ni catalyst. Based on recent reports, we believe the edges on the particles are most likely nano-walled $\text{Ni}(\text{OH})_2$ ^{96,97}.

To determine the elemental composition of both cc- and cv-Ni samples, energy dispersive x-ray spectra (EDS) were obtained on the two catalytic films. To eliminate the influence of oxygen from the underlying tin oxide substrate, we scratched off the catalytic films before EDS measurements. The EDS spectrum of cc-Ni only shows the signal for Ni (Figure 5.1 d). This indicates that the cc-Ni catalyst is a purely metallic nickel film. On the other hand, the cv-Ni sample (Figure 5.1 e) has signals for both Ni and O, which provides evidence that the spherical particles have a composite structure with both Ni and $\text{Ni}(\text{OH})_2$ present. Figure 5.2 shows the cross-section SEM image of cv-Ni sample. The thickness of the catalyst layer was estimated at $\sim 0.3\mu\text{m}$. It also confirms that the surface morphology of the cv-Ni sample is a monolayer of spherical particles.

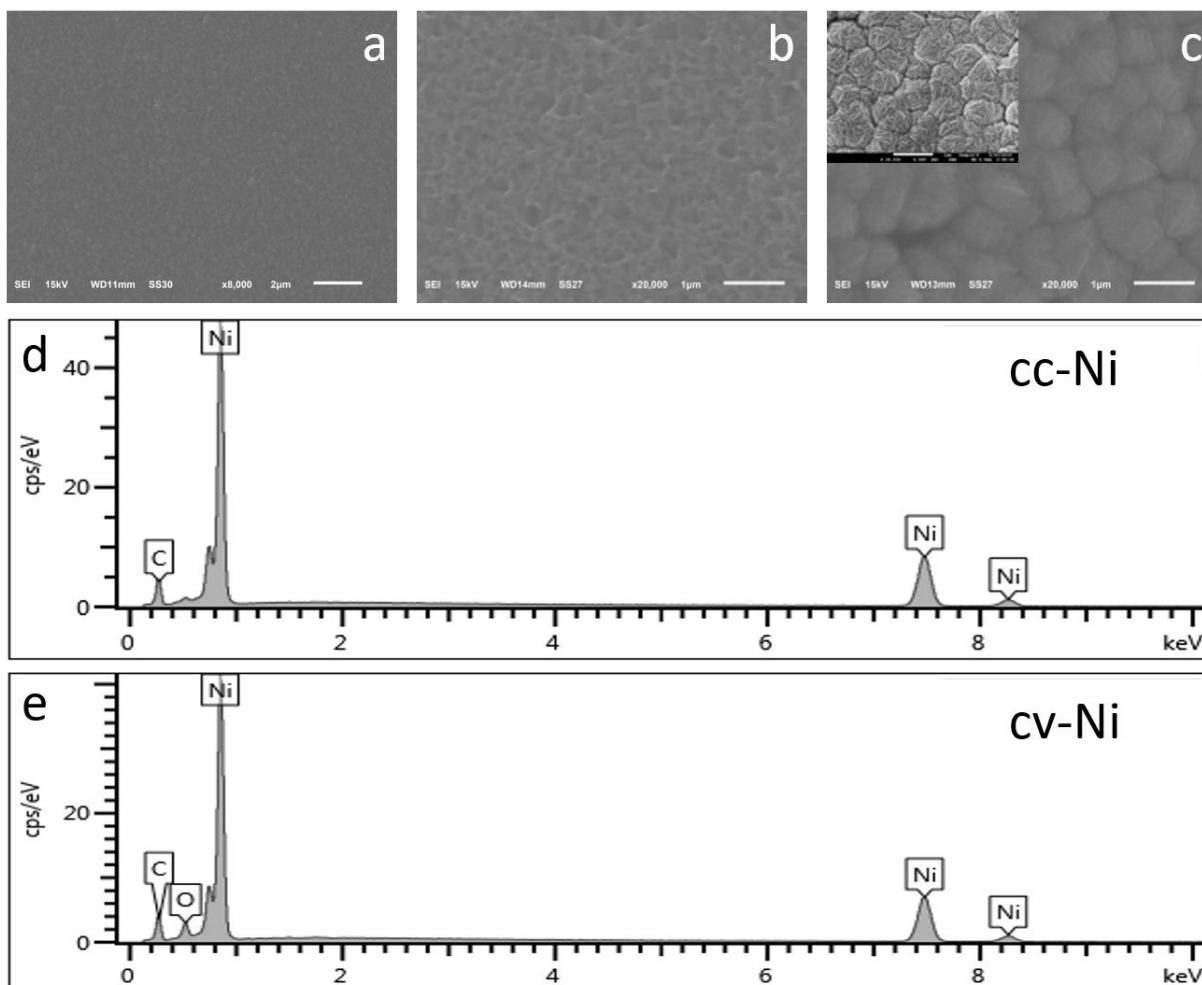


Figure 5.1. SEM images and EDS characterization of cc-Ni and cv-Ni. a) SEM image of a bare FTO substrate, showing a featureless but rough surface. b) SEM image of the cc-Ni sample, showing a featureless metallic surface. c) cv-Ni at an identical magnification, showing a film consisting of a monolayer of evenly-distributed walnut-shaped particles with diameters of 0.1~0.2 μm . The inset is the surface of the cv-Ni sample at a higher magnification, showing a detailed morphology of spherical particles with patterns on the surface. d) EDS characterization of cc-Ni, showing only the signal for Ni, which is an indication that it consists mainly of a Ni film. e) EDS characterization result for cv-Ni showing both Ni and O, an indication that cv-Ni contains both Ni and $\text{Ni}(\text{OH})_2$. The carbon signals in both EDS spectra are from supporting SEM slabs and patches.

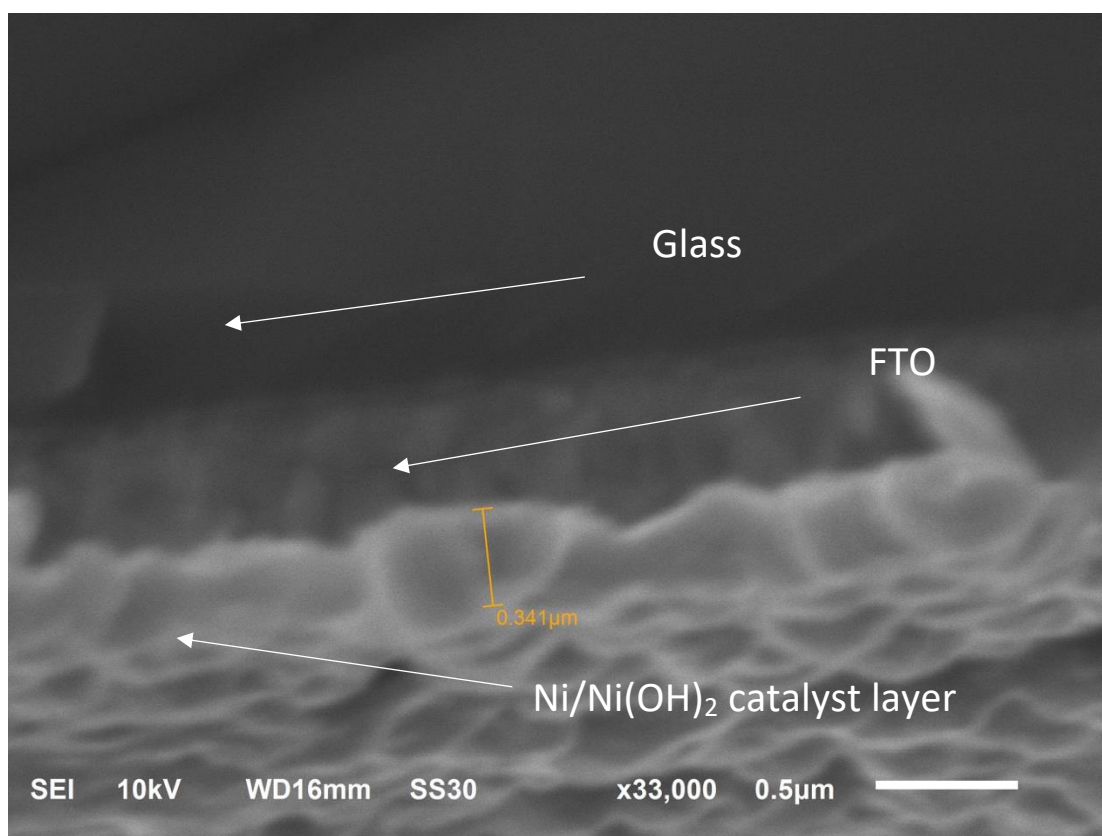


Figure 5.2. Cross-sectional SEM image of the cv-Ni sample. The thickness of the Ni/Ni(OH)₂ catalytic film was estimated at ~0.3 μm. This also confirms that the surface morphology of the catalyst layer is a monolayer of firmly packed spherical particles.

Figure 5.3 shows the XRD spectra of bare FTO and both Ni-based catalyst samples. In all spectra, + designates the feature peaks for the conductive substrate FTO, * the peaks for Ni, and # the peaks for Ni(OH)_2 . As expected, both the cc- and cv- Ni samples clearly show the feature peaks for Ni. However, the cv-Ni sample also shows additional small peaks at 34, 38 and 44 degrees, which are indicators of the existence of Ni(OH)_2 ⁹⁸⁻¹⁰⁰. Due to the relatively small amount of Ni(OH)_2 compared to much larger quantities of FTO and Ni, those peaks are not very prominent.

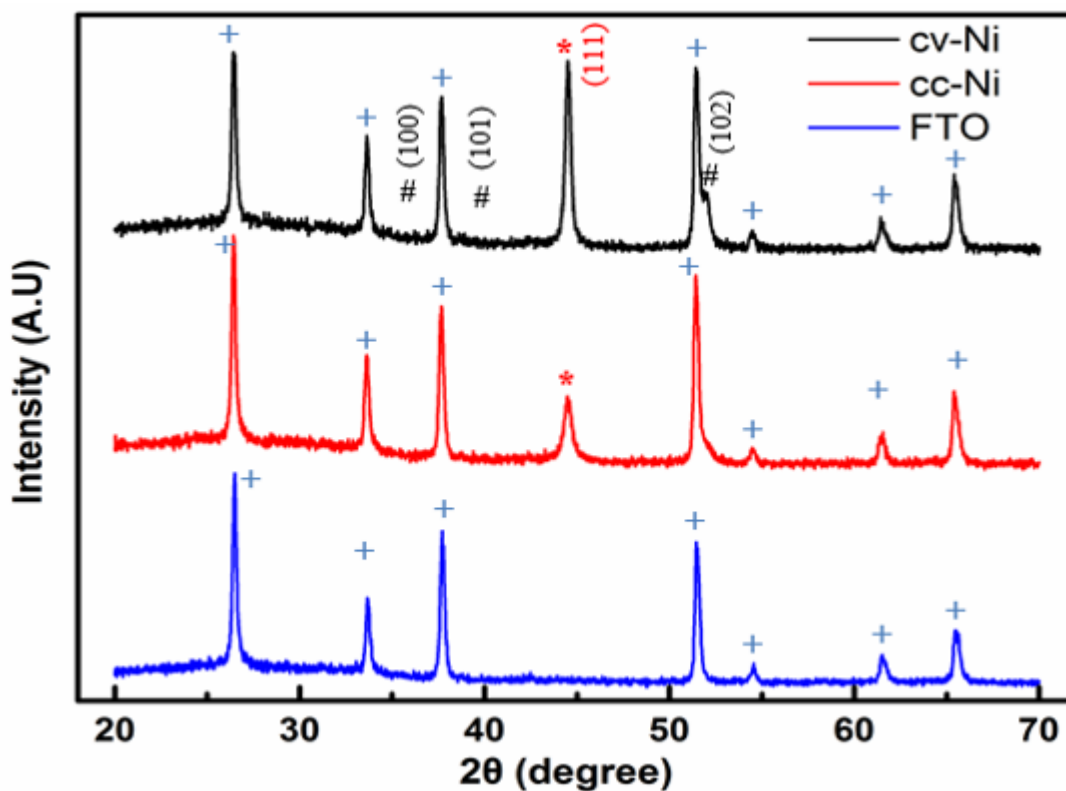


Figure 5.3. XRD spectra of a) cv-Ni, b) cc-Ni and FTO films. The symbol + designates feature peaks of FTO, * of Ni, and # of Ni(OH)_2 . The cc-Ni film has peaks of FTO and Ni, while the cv-Ni spectrum has peaks of FTO, Ni and Ni(OH)_2 . Due to the small amount of Ni(OH)_2 in the cv-Ni samples compared with FTO and Ni, the Ni(OH)_2 peaks are not prominent.

5.4.2 Functionality assessments

Cyclic voltammetry was used to assess and compare the functionalities of the cc- and cv-Ni samples, and Pt mesh in neutral and alkaline media. Figure 5.4 shows the CV spectra acquired in 0.1M neutral phosphate buffer. The black curve shows the current density of cc-Ni in response to applied potential. The red and green curves are for cv-Ni and platinum mesh, respectively.

Although both the cc- and cv-Ni samples have higher onset potentials compared with Pt mesh, cv-Ni is much closer to platinum than cc-Ni. This result indicates that cv-Ni has a better catalytic performance than cc-Ni. The peak current density of cv-Ni (0.806 mA/cm^2) is much larger than for cc-Ni (0.211 mA/cm^2), based on geometric surface area at -0.3 V vs. NHE. We also assessed the samples in 1 M KOH alkaline media (Figure 5.5). Again, the peak current density of cv-Ni is about twice that of cc-Ni, which demonstrates much better catalytic performance.

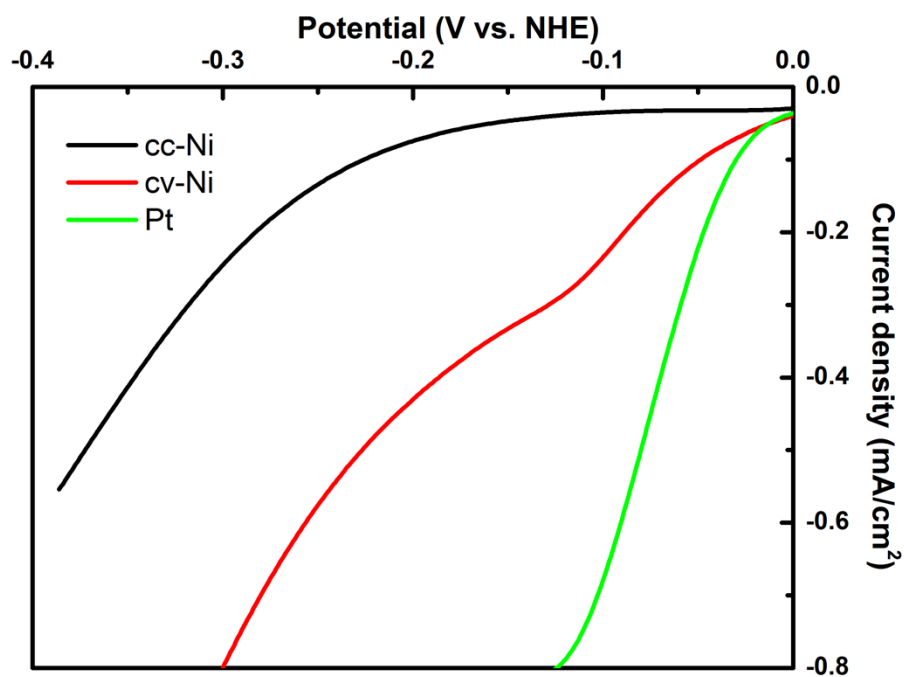


Figure 5.4. Comparison of the functionality of cv-Ni, cc-Ni, and platinum mesh by cyclic voltammetry in neutral media. The black, red, and green curves are for cc-Ni, cv-Ni, and Pt mesh, respectively. Both cc- and cv- Ni have higher onset potentials than Pt, but the cv-Ni catalyst has a lower onset potential than cc-Ni.

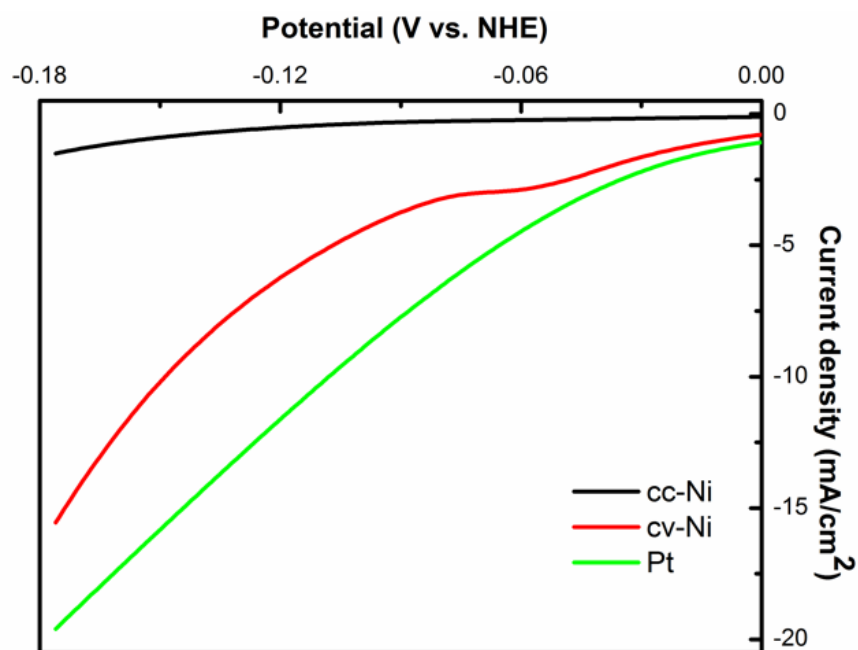


Figure 5.5. Comparison of the functionality of cv-Ni, cc-Ni, and platinum mesh by cyclic voltammetry in alkaline media. The black, red, and green curves are for cc-Ni, cv-Ni, and Pt mesh, respectively. Both cc- and cv- Ni have higher onset potentials compared to Pt, but the cv-Ni catalyst has a lower onset potential than cc-Ni.

We compared the Tafel slopes and exchange current densities of the cc- and cv-Ni catalysts in 0.1 M neutral phosphate buffer. The cc-Ni has a slope of 0.34 V/dec, while cv-Ni has a much lower slope of 0.25 V/dec (Table 5.1). As comparison, the Ni foil has a slope of 0.35 V/dec, which is very close to the value for cc-Ni. We believe this offers further evidence that cc-Ni is a simple metallic Ni film, while cv-Ni has a Ni/Ni(OH)₂ composite structure. The cv-Ni also has a higher exchange current density compared with cc-Ni, which is an indication of much better catalytic performance.

Table 5.1. Comparison of Tafel slopes and exchange current densities of cc-Ni, cv-Ni, and Ni foil catalysts assessed in neutral media. The lower slope and higher exchange current density of cv-Ni are indicators of much better catalytic performance.

Sample	Slope (mV/dec)	Log (i_{ex})
cv-Ni	0.25	-3.13
cc-Ni	0.34	-3.97
Commercial Ni foil	0.32	-3.72

5.4.3 Stability assessments

Stability tests were carried out by applying a constant potential (-1.0 V vs. Ag/AgCl) for a prolonged period of time on both the cc- and cv-Ni samples. As shown in Figure 5.6, the current density was very stable during the ten-hour testing period, demonstrating excellent stability. We also did a stability test involving 201 consecutive CV cycles with one cv-Ni catalyst sample. As shown in the inset of Figure 5.6, the first and 201st cycles are identical in shape as well as peak current densities, a result that also demonstrates excellent stability over a long period of time.

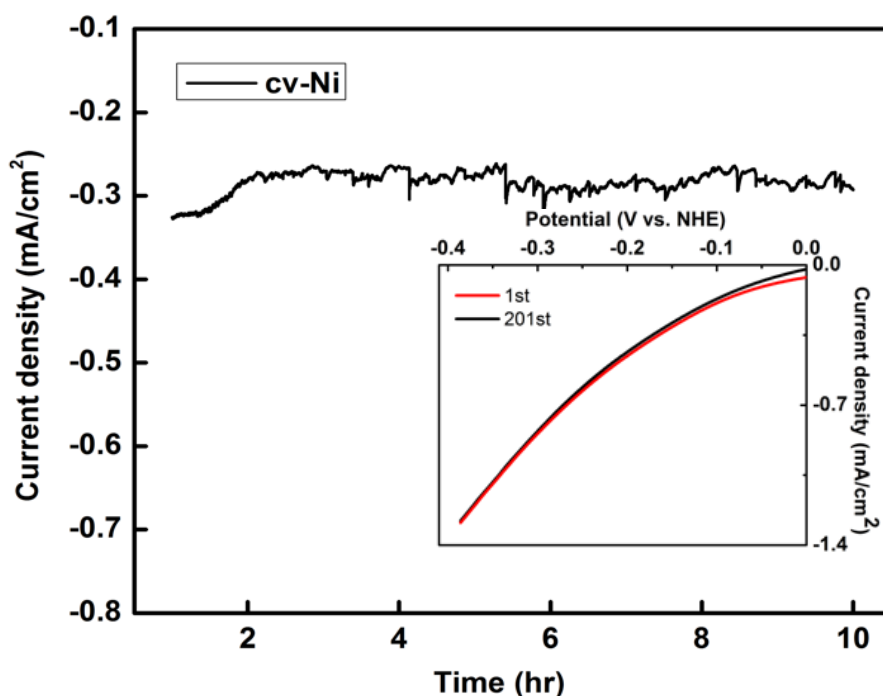


Figure 5.6. Current density profile of cv-Ni in a 0.1 M neutral phosphate buffer under an applied potential of -1.0V vs. Ag/AgCl. After the first two hours, the current density was steady over the remaining eight-hour testing period, demonstrating stable catalytic performance. The inset shows the cyclic voltammograms of the first and 201st cycles of a functionality test on a single cv-Ni catalytic sample. The similarity in the two profiles as well as peak current densities is an indication of very stable catalytic performance.

5.4.4 Effects of electrolyte concentration on electrodeposition

We synthesized catalysts using different concentrations of electrolyte. The number of CV cycles was tuned to ensure an identical accumulated charge of 1 C during each deposition. All samples had a similar onset potential of -0.1V vs. NHE for the hydrogen evolution reaction, but the catalytic performance varied with electrolyte concentration. Table 5.2 is a summary of the corresponding current densities at -1.2 V vs. Ag/AgCl. The results portray a typical volcano behavior, with the sample synthesized in 200 mM solution giving the best performance. In general, this profile suggests that electrolyte concentration offers another possible parameter for optimization.

Table 5.2. Peak current density at -0.5 V vs. NHE for samples synthesized in different concentrations of electrolyte.

Electrolyte Concentration / mM	Peak current density / (mA/cm ²)
25	0.77±0.01
50	1.22±0.16
100	1.49±0.08
200	1.83±0.04
250	1.45±0.10

5.4.5 Hypothesis of the formation mechanism

Although we do not yet understand the exact mechanism for the formation of the structured film, we propose a plausible hypothesis. In the traditional constant current deposition process, Ni^{2+} ions are continuously dragged to the electrode surface at a constant rate, and reduced to metallic Ni. In the CV deposition case, the applied potentials are constantly changing, therefore Ni^{2+} ions are dragged to the surface at various rates, then reduced. Also, over certain ranges of potential, the Ni^{2+} ions are not reduced, resulting in the formation of only $\text{Ni}(\text{OH})_2$ hydrolysis species. Under this scenario, it is possible for the walnut-shaped ‘core-shell’ type of structures to form with metallic Ni accumulating in the center of the particles, surrounded by the nanowall-shaped $\text{Ni}(\text{OH})_2$ hydrolysis species on the outer shell. Under such conditions, we would expect a higher Ni to $\text{Ni}(\text{OH})_2$ ratio in the central area of the particles than on the edge. Our preliminary EDS and ID analysis data support this hypothesis, showing that the ratio of Ni to $\text{Ni}(\text{OH})_2$ in the center is 6.74 to 1, which is about twice the ratio on the edge.

Some studies have reported that $\text{Ni}(\text{OH})_2/\text{metal}$ interfaces play an important role in the hydrogen evolution reaction, with the $\text{Ni}(\text{OH})_2/\text{Ni}$ interface being the most effective^{101,102}. Usually, such interfaces are created by complicated wet chemistry procedures. However, we have shown in this work that such interfaces can also be created using simple CV electrodeposition methods. This simpler more controllable synthesis method has successfully enabled a core-shell structure that contains large numbers of $\text{Ni}(\text{OH})_2/\text{Ni}$ interfaces, leading to excellent catalytic performance towards the hydrogen evolution reaction.

5.5 Conclusions

We have developed a new method of synthesizing Ni/Ni(OH)₂ HER catalysts *in situ* onto conductive surfaces via a simple electrodeposition method using cyclic voltammetry. This simple and inexpensive approach involves a single CV session of two potential ramps ranging from 0 to -1.2V. The resulting catalytic film has a uniform surface morphology consisting of an evenly distributed monolayer of spherical particles that promotes overall catalytic performance. The resulting film has stable and much better catalytic performance than traditional cc-Ni HER catalysts or Ni foil, with an effectiveness that shifts significantly towards that of platinum. We believe this work provides an easier inexpensive way of synthesizing this HER catalyst, and demonstrates the potential for using CV as a deposition method. This work also has the potential to serve as a new way of creating large quantities of Ni(OH)₂/metal interfaces to promote the performance of HER catalysts, and provide options for catalyst synthesis and optimization through electrochemistry.

CHAPTER 6. SUGGESTIONS FOR FUTURE RESEARCH

6.1 Introduction

In Chapters 3 and 5, we discussed our research activities on developing electrocatalysts for both the water oxidation and hydrogen evolution reactions. Although both the MnO_x WOC and $\text{Ni}/\text{Ni}(\text{OH})_2$ HERC have excellent and stable catalytic functionalities, there are still some parameters that can be further explored to enhance performance. Also, some characterization devices used in this work are not ideal for the current system. Thus, more advanced instrumentation could be used in the future to better characterize both catalytic films. Finally, it would serve a valuable function to integrate more precise measurements and computational work to guide future electrocatalyst synthesis.

For system integration, our eventual goal was to build an affordable but highly effective solar-driven water splitting device. As discussed in Chapters 1 and 4, traditional AP devices have been based on the schemes in Figure 6.1. Our solar-driven photoanode for water splitting is also based on the two-chip face-to-face scheme. Although performances of such devices could be enhanced by adopting highly effective solar harvesting systems and electrocatalysts, its overall performance is still limited by mass transfer resistance. Another big issue is that the density of solar radiation is quite low, with the result that large quantities of semiconducting materials and catalysts would be required to achieve effective hydrogen production.

In this chapter, we suggest some future work for both electrocatalyst synthesis and system integration to build solar-driven water splitting devices.

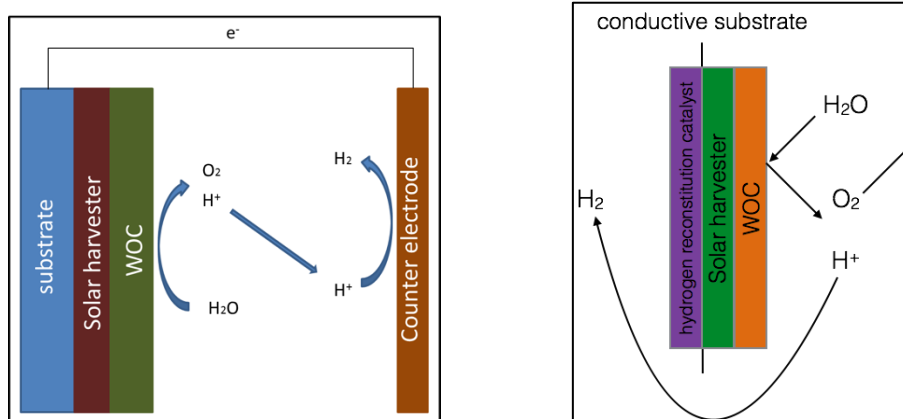


Figure 6.1. Schematics of two water splitting devices. Each scheme has a photoanode complex containing a solar harvester and a WOC, and a counter electrode for hydrogen ion reconstitution to produce fuel. a. Two-chip protocol (face-to-face scheme), where the counter electrode does not share the conductive support with the photoanode; b. One-chip protocol, where the counter electrode and photoanode share one conductive support.

6.2 Further research on improving the MnO_x WOC

The dual series CV electrodeposition protocol described in Chapter 3 is a novel and excellent method for synthesizing WOCs, in comparison to other methods. Multi-series CV has tunable parameters such as number of series, potential ranges of each series, number of cycles in each series, ionic strength of the electrolyte, and the concentration of doping elements. Each parameter may have a specific effect on the resulting catalyst. It would be of scientific value to assess the effects of these parameters on the resulting catalytic films. This could also lead to a comprehensive understanding to enable rational design of catalysts.

In our current research, we used XRD to measure the oxidation state of the MnO_x catalyst. However, XRD is not a very accurate technique for measuring the oxidation state of manganese compounds. We recommend advanced x-ray absorption techniques such as x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) to measure the oxidation states and the bonding patterns for MnO_x WOCs. Also, since manganese is notoriously hard for traditional transmission detectors, we would recommend the use of off-angle fluorescence detectors. This would be valuable for developing a comprehensive understanding of the mechanism for the formation of the catalytic films.

6.3 Further research on improving the Ni/Ni(OH)₂ HER catalyst

The single series CV procedure described in Chapter 5 is a new method for synthesizing Ni/Ni(OH)₂ HER catalysts *in situ*. There are still other parameters that should be explored. Some, such as doping elements, may have high possibilities to promote catalytic performance or catalyst stability. We again suggest using x-ray absorption (XAS) techniques to study the details

of changes in oxidation states, and bonding patterns during electrodeposition and functional assessments. We also suggest the use of environmental SEM to characterize changes in surface morphology during the deposition. Combining these two characterization results listed above, one can get a detailed knowledge of both surface morphology and changes in oxidation states and develop a theory to guide the future development of electrocatalysts.

6.4 Further research on system integration

To address the problems in our current water splitting system, we recommend a new scheme featuring multiple photoanode modules for further investigation (Figure 6.2). Each photoanode module contains: a) a device that can collect solar energy over a large area (front surface) and concentrate it in a much smaller area along the edge; b) one or more layers of semiconducting material to convert the solar energy to the electrical potential required to power the water splitting reaction; c) a layer of conductive material such as ITO to be used as the substrate for the electrodeposition of the MnO_x WOC (to enhance the electron-hole separation, a thin hole-attraction layer could also be coated); and d) a layer of MnO_x WOC synthesized using the method described above. To minimize mass transfer resistance, we propose using the photoanode modules to form microfluidic water channels that reduce the distance for ion migration. Hydrogen evolution catalysts would be deposited on the bottom of the water channels via electrodeposition.

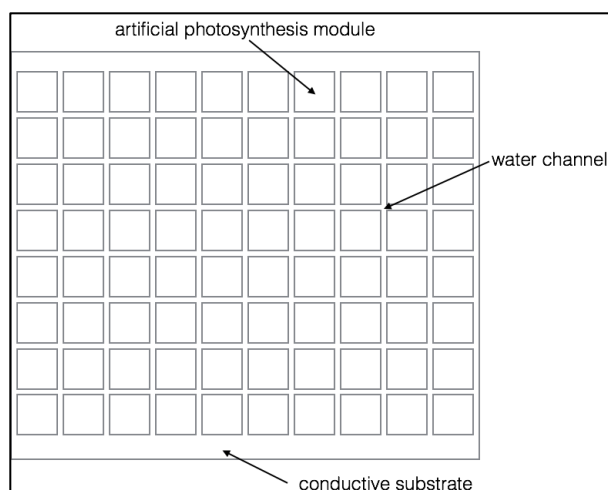


Figure 6.2. Overview of the proposed scheme. All the components of the proposed solar-driven water splitting device are supported by a robust conductive substrate. The squares are the AP modules which can be engineered into various shapes and sizes. Water channels are formed by the edges of the AP modules. The water oxidation catalyst is coated on the edges of the AP modules, and the hydrogen evolution catalyst is coated on the bottom of the water channel to greatly reduce the distance for ion migration, resulting in a much lower resistance to mass transfer. The detailed structure of the AP module is shown in the figure below.

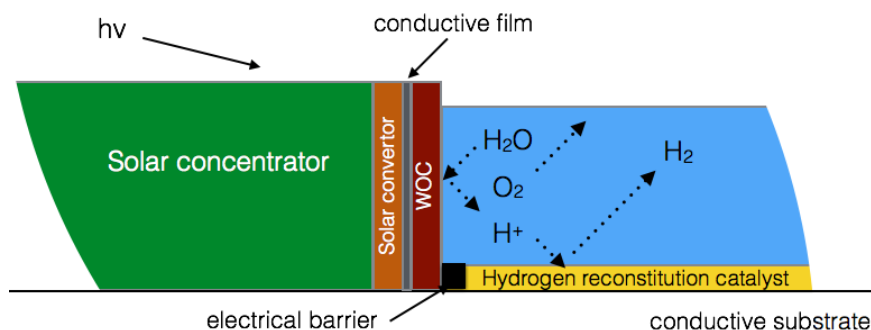


Figure 6.3. Cross-sectional view of the AP module in a microfluidic channel. Each AP module features a) a solar concentrator to collect solar energy on the larger surface and transmit it to the edge; b) a converter to transform the concentrated solar energy into the potential required for the water splitting reaction; c) a conductive layer for the electrodeposition of WOC; d) an optional p+ layer to promote electron-hole separation; and e) a WOC layer directly in contact with water.

Since the solar concentrator is a flexible material, the resulting photoanode modules can be fabricated in various sizes and shapes. As a result, the size and shape of the final device could be tuned by changing the number and pattern of the photoanode modules. Also, the final device could be attached to any surfaces if the substrate is not rigid. Successful development of a device based on this new scheme would be of great scientific and technological value.

As also described in Chapter 4, Mn-based WOCs have the capability for integration with semiconducting materials like TiO_2 . The major problem with TiO_2 is that its absorption spectrum is quite limited to the far UV range. Thus, if future researchers could find suitable dyes to broaden the absorption spectrum of the solar harvester, the efficiency of the photoanode modules could be greatly improved.

CHAPTER 7. CONCLUSIONS

This dissertation is a detailed account of our group's research activities in developing highly effective yet inexpensive electrocatalysts for the water splitting reaction. In Chapter 2, we demonstrated that a Co-OXO water oxidation catalyst that is synthesized *ex situ* can be effectively immobilized onto conductive surfaces to enhance the recyclability and reusability of the resulting catalytic film without losing functionality.

Chapter 3 covered our research on developing a dual-series cyclic voltammetry (CV) electrodeposition method to synthesize a MnO_x *in situ* on conductive surfaces. The new method involves two consecutive series of CV scans over different potential ranges, followed by calcination. Our results showed that the MnO_x WOC has stable and excellent catalytic performance over long periods of time. We also proposed a nucleation-growth formation theory that agrees with the experimental observations.

In Chapter 4, we report on our study to integrate Mn-based WOC synthesized *in situ* with the semiconducting material TiO_2 to build a functional photoanode. The photoanode has a double-layer structure that promotes water splitting under ultraviolet (UV) illumination. Although the current system is only functional under UV light, the addition of various dyes could broaden its absorption spectrum and lead to a more effective system.

Chapter 5 covered our study on developing effective electrocatalysts for the hydrogen evolution reaction (HER). We used only one series of CV to synthesize the Ni/Ni(OH)_2 HER catalyst in

situ onto conductive surfaces. Our results show that the catalytic film has a surface morphology of firmly packed monolayer of walnut-shaped spherical particles, with stable and excellent performance. We believe this work has provided an inexpensive way to create large numbers of Ni(OH)₂/metal interfaces to promote the performance of HER catalysts.

We believe the results of the four studies listed in this dissertation are valuable in opening new ways of synthesizing highly effective yet low cost electrocatalysts *in situ* on conductive surfaces. These studies have the potential to help guide the development of highly effective solar-driven water splitting devices in the future.

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