NOVEL CATALYSTS AND
PHOTOELECTROCHEMICAL SYSTEM
FOR SOLAR FUEL PRODUCTION

by

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ABSTRACT

Solar fuel production from abundant raw chemicals such as CO$_2$ and water is highly desired as a clean renewable energy solution for the future. Developing photoelectrochemical cells is viewed as a promising approach to realize this energy conversion and storage process. Efficient and robust oxygen evolution catalyst made from non-precious materials remains a major challenge for such a system. This thesis basically consists of three parts of work, including studies on enhancing the photocatalytic oxygen evolution activity of cobalt-based spinel nanoparticles by manganese$^{3+}$ substitution, in situ formation of cobalt oxide nanocubanes as highly active catalyst for photocatalytic oxygen evolution reaction, and development of a photoanode-driven photoelectrochemical cell for CO$_2$ reduction with water.

The first part of this thesis work devotes efforts in the development and study on cobalt and other transition metal oxide based oxygen evolution catalyst. Photocatalytic oxygen evolution is a critical step for solar fuel production from abundant sources. It poses a significant challenge because it requires an efficient catalyst to bridge the one-electron photon capture process with the four-electron oxygen reaction. Among all the metal oxides, Co$_3$O$_4$ spinel exhibits a high activity as an oxygen evolution catalyst. The results of this work demonstrate that the photocatalytic oxygen evolution activity of Co$_3$O$_4$ spinel can be further enhanced by substituting Co with Mn in the spinel structure. Using a facile hydrothermal approach, Co$_3$O$_4$ spinel nanoparticles as well as Mn-substituted and Ni-substituted Co$_3$O$_4$ spinel nanoparticles with a typical particle size of 5-7 nm were successfully synthesized.
The morphology and crystal structures of the as-synthesized nanoparticle catalysts have been carefully examined using various structural characterization techniques, including powder x-ray diffraction (PXRD), transmission electron microscope (TEM), gas adsorption, and x-ray absorption spectroscopy (XAS). The photocatalytic activities of as-made nanoparticles were investigated using a well-studied visible light driven \([\text{Ru(bpy)}_3]^{2+}\)-persulfate system. In both Clark electrode and reactor/gas chromatography (GC) systems, Mn-substituted \(\text{Co}_3\text{O}_4\) nanoparticles exhibited the highest turnover frequency (TOF) among all the three kinds of catalysts. The data presented in this paper suggest that the photocatalytic oxygen evolution activity of \(\text{Co}_3\text{O}_4\) spinel catalyst can be further enhanced by \(\text{Mn}^{3+}\) substitution at the octahedral sites.

The second part of this piece of work was carried out to further investigate cobalt oxide based photocatalytic oxygen evolution catalyst. A new strategy was developed to synthesize nonsupported cobalt oxide nanocubanes through an \textit{in situ} phase transformation mechanism using a layered \(\text{Co(OH)(OCH}_3\) precursor. Under sonication, the precursor was exfoliated and transformed into cobalt oxide nanocubanes in the presence of \(\text{NaHCO}_3\)-\(\text{Na}_2\text{SiF}_6\) buffer solution. The resulting cobalt catalyst with an average particle size less than 2 nm exhibited a turnover frequency of 0.0023 per second per cobalt in photocatalytic oxygen evolution reaction. X-ray absorption results suggested that a unique nanocubane structure, where 13 cobalt atoms fully coordinated with oxygen atoms and hydroxide groups in an octahedral arrangement to form 8 \(\text{Co}_4\text{O}_4\) cubanes, may be responsible for the exceptionally high oxygen evolution catalysis activity.
This thesis work is completed with the development of a photoanode-driven photoelectrochemical cell for CO₂ reduction. A NiOₓ decorated Si photoanode and nanoporous Ag cathode were employed. With an external bias of 2.0 V, a current density at cathode of 10 mA/cm² and Faradaic efficiency of 70% for CO₂ to CO was achieved. Compared to a normal electrochemical cell, the photoelectrochemical cell saves 0.4 V electrical energy by absorbing photo-energy. In addition, post-test photoanodes were carefully characterized by SEM, XAS, and XPS analysis.
Chapter 1

INTRODUCTION

1.1 Sustainable and Clean Energy Solution for the Future

According to the energy consumption distribution statistics reported by the U.S. energy information administration (EIA, Figure 1.1), traditional fossil fuels including coal, petroleum and other liquids made up the majority of total energy consumption for many years. This situation is projected to continue for the following several decades. As is well known, most of the fossil fuels we are mining and burning today were formed back to millions of years ago. Considering the enormous global energy demand, they are limited resources which can only last for a certain time span. Besides, fossil fuels are naturally unevenly distributed around the world. This has been affecting global economics and politics in a non-beneficial way.

In addition, coal-firing and petroleum burning emit various pollution gases and even particles into the air, which causes environmental issues. One example is carbon dioxide, which is a major greenhouse gas. As measured by the NOAA Earth system research laboratory, CO$_2$ has been accumulating in the atmosphere rapidly during the past half century, and the atmospheric CO$_2$ concentration at Mauna Loa Observatory has exceeded 400 ppm in 2013 (Figure 1.2). Though regulations for gas emission have been developed and enforced, the environmental concerns will not be eliminated from the root unless a revolutionary energy solution is developed.
Figure 1.1 Projected energy consumption distribution

Figure 1.2 The carbon dioxide data (red curve) measured as the mole fraction in dry air on Mauna Loa. The black curve represents the seasonally corrected data.
As a result of the advancement in hydraulic fracturing technology, the exploration and production of shale gas has experienced rapid growth over the last decade. This leads to a new abundance of natural gas supply and a significant impact on the energy market and society. However, regardless of the great amount of technically recoverable resources and the expected trend of continuous growth in production, shale gas is still a limited, unevenly distributed resource. CO₂ emission problem also exists at natural gas-fired power plants. In addition, CH₄ leaking during the mining and transportation may also cause environmental concerns since methane is another well-known greenhouse gas. Though shale gas provides additional energy supply to traditional fossil fuels, it is not the solution to powering the world in the long run.

At the meantime, renewable power and fuels are undergoing intensive research and development. Biomass, hydropower, wind power, solar energy, and other renewable energy sources have been estimated to contribute to almost 20% of global final energy consumption share in 2013 (Figure 1.3). The demand and confidence in renewable energy development are also reflected in the continuously increasing global investment (Figure 1.4).
Figure 1.3 Data on estimated renewable energy share of global final energy consumption. Obtained from Renewable Energy Policy Network for the 21 century (http://www.ren21.net/status-of-renewables/global-status-report/).

Figure 1.4 Data on global new investment in renewable energy by technology in developed and developing countries. Adapted from Renewable Energy Policy Network for the 21 century (http://www.ren21.net/status-of-renewables/global-status-report/).
Solar energy is one of the most attractive renewable energy resources since it is abundant, widely-distributed, and basically free. As shown in Figure 1.4, solar power has received the most investment among all renewable energy technologies and the number is still increasing. Solar energy can be harvested using photovoltaics, but the storage of the harvested electrical energy remains a challenging project. Efforts have been devoted to the development of electrical energy storage technologies such as batteries and super conductor. As a result of these new technologies, major change in the current infrastructure would be required. An alternative way of harnessing solar energy is to store the harvested energy in the form of chemical bonds. This solution is referred to as solar fuel production. Using water, carbon dioxide and maybe other abundant chemicals as the starting materials, the solar fuel produced can fit into the current infrastructure with minor alteration.

1.2 Photoelectrochemical (PEC) Cell for Solar Fuel Production

The key point of a photoelectrochemical cell is to harvest solar energy and store it within chemical bonds. Hydrogen and CO\textsubscript{2} reduction products are usually employed for the chemical energy storage. Semiconductor material are the important component of a photoelectrochemical cell since they harvest incident photon energy and generate excited electrons and holes. When the semiconductor is immersed in an aqueous electrolyte, a potential is built up at the interface of the semiconductor and electrolyte. This potential energy would be capable of driving redox chemical reactions. Thus in a photoelectrochemical cell, semiconductor materials are used as photoelectrodes to convert photon energy for redox reactions of fuel production. To make a closed circuit, a metal or metal oxide is connected to the photoelectrodes through an external wire. A scheme illustrating the principle of a basic
photoelectrochemical cell is shown in Figure 1.5. In this scheme, an n-type semiconductor as a photoanode for water splitting is used as an example. During the operation of this photoelectrochemical cell, H$_2$O is oxidized by photon-excited holes to evolve oxygen at the surface of the photoanode. The protons and electrons generated from oxygen evolution are transported to the counter electrode (cathode) and reduced to evolve hydrogen. This is very similar to a water splitting electrolyzer except that the driving force is partially/fully obtained from photon energy. Alternatively, p-type semiconductor materials can be used as a photocathode with a normal anode. In addition, a photocathode and photoanode can be used simultaneously for a photoelectrochemical cell when necessary. Regardless of what kind of photoelectrode is used, the band alignment of the semiconductor materials needs to meet certain requirements to be capable of driving the redox reactions.

![Figure 1.5](image-url) An illustration of operation principle of photoelectrochemical cells based on n-type semiconductors. Adapted by permission from Macmillian Publishers Ltd: Nature 11, copyright 2001.
In terms of solar fuel production from water and carbon dioxide, key redox reactions are oxygen evolution (also referred to as water oxidation), $\text{H}_2$ evolution from water, and $\text{CO}_2$ reduction. (Some details about the reactions will be covered in Section 1.3). In order to be capable of driving the reactions, the photoelectrode needs to provide potential energy that is higher/lower than the thermodynamic equilibrium potential of the oxidation reaction/reduction reaction, respectively. In reality, the redox reactions take place at a decent reaction rate only when some additional potential energy beyond the thermodynamic equilibrium potential, which is overpotential, is provided $^{12,13}$. To accelerate the redox reactions and save energy, a catalyst is usually incorporated to lower the energy barrier introduced by the overpotential. Ideally, the semiconductor material can also serve as catalyst. However, this turns out to be extremely challenging since very few material can perform both functions simultaneously $^{14,15}$. Therefore, for most of the photoelectrodes reported, semiconductors are decorated with electrocatalysts to assist chemical reactions $^{16}$.

Many technical challenges have been encountered during research activities towards efficient, robust and low-cost photoelectrochemical cell for solar fuel production $^{15}$. Enormous efforts have been devoted to developing semiconductor materials with proper band positions and highly efficient electrocatalyst that can be incorporated with photoelectrodes $^{17,18}$. In addition, electron transportation at interface between semiconductor and electrocatalyst as well as device level engineering have also been a primary concern of research $^{15,19}$. 
Recently, some exciting progress has been made on PEC cells for water splitting \(^{20}\). These exciting work combined with the strong motivation for CO\(_2\) utilization have intrigued the enthusiasm for research activities on photoelectrochemical CO\(_2\) reduction worldwide \(^{21}\). This is obviously reflected in the citation report from *Web of Science* presented in Figure 1.7. Different from water splitting, CO\(_2\) reduction in aqueous solution usually requires pH-neutral environment \(^{21-25}\). Thus the semiconductor and electrocatalyst need to be able to operate in such solution. Despite of all the devoted efforts, there is still a long way towards developing
a highly efficient and ready-for-application photoelectrochemical cell that can be used for solar fuel production.

Figure 1.7 Citation report retrieved from Web of Science, searching key words of photoelectrochemical in topic and CO$_2$ reduction in topic, within all databases, updated on 10/28/2015.

1.3 Photocatalytic Oxygen Evolution Reaction (OER)

As mentioned in Section 1.2, oxygen evolution reaction is at the heart of renewable-energy technologies including solar fuel production. Solar fuels are usually directly generated from reduction reactions which require electrons and protons$^{10, 26}$. Oxygen evolution from water has been viewed as the only solution to provide electrons and protons that can fulfill the demand for large scale production of solar fuels$^{15, 27}$. As presented in equation 1.1, oxygen evolution from water involves four-electron transfer and therefore has slow kinetics. This results in a large overpotential when it comes to a decent reaction rate (which is the current, in the context of electrocatalysis). In addition, as an energetic up-hill process, the reverse reaction is very likely to happen during OER. Conductive metal oxides have been widely used as
active catalysts for OER to lower the overpotential. A general mechanism for oxygen evolution reaction on metal oxide in acidic environment is given in Equation 1.2-4.

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad \text{Eqn. 1.1}
\]

\[
\text{*OH} + \text{H}_2\text{O} \rightarrow [\text{HO*OH}] + \text{H}^+ + \text{e}^- \quad \text{Eqn. 1.2}
\]

\[
\text{HO*OH} \rightarrow \text{O*OH} + \text{e}^- + \text{H}^+ \quad \text{Eqn. 1.3}
\]

\[
2\text{O*OH} \rightarrow 2\text{OH} + \text{O}_2 \quad \text{Eqn. 1.4}
\]

Substantial efforts have been devoted to developing efficient OER catalysts. Early works made breakthrough by using electrodes made of RuO$_2$ and IrO$_2$\textsuperscript{28,29}. Despite the high catalytic activity and good stability exhibited by these precious metals, the high cost hinders any large scale applications of them. In the exploration of non-precious catalysts, transition metals including cobalt, nickel, and manganese have received enormous research interests\textsuperscript{30-36}. Challenges also arise from the implementation of OER catalysts into PEC cells for CO$_2$ reduction\textsuperscript{24}. Developing non-precious metal oxide that is stable and efficient in the pH-neutral environment of CO$_2$ reduction, as well as the interfacial conducting issue between the catalyst and semiconductor turn out to be the major technical challenges\textsuperscript{37,38}.

1.4 Electrocatalytic CO$_2$ Reduction Reaction

As mentioned in Section 1.1, CO$_2$, the byproduct from fossil fuel burning and a major greenhouse gas, is accumulating rapidly in the atmosphere. Electrocatalytic reduction of CO$_2$ has been suggested as a promising approach for fixation of CO$_2$ and generation of carbon-neutral fuels and other value-added chemicals\textsuperscript{37,39,40}.

\[
\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{-}, \quad E^0 = -1.90 \text{ V};
\]

\[
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}, \quad E^0 = -0.53 \text{ V};
\]
\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH}, \quad E^0 = -0.61 \text{ V;} \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{HCHO} + \text{H}_2\text{O}, \quad E^0 = -0.48 \text{ V;} \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \quad E^0 = -0.38 \text{ V;} \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \quad E^0 = -0.24 \text{ V}. \\
\end{align*}
\]

As presented in the equations, CO\textsubscript{2} reduction leads to a variety of products. There have been divergent opinions in the field regarding the reaction mechanism. The development of advanced spectroscopy techniques as well as computing ability, has led to more fundamental understandings of the catalytic process. Regardless of whether mechanism is considered, the first step of the reduction reaction is the addition of one electron to a CO\textsubscript{2} molecule. This step sets an energy barrier as high as 1.9 eV resulting from the transformation of the linear molecule to bent radical anion. To reduce this large energy waste, efficient electrocatalysts are highly desired to drive the reaction with lowered energy penalty.

Another important requirement for electrocatalytic CO\textsubscript{2} reduction catalyst is high product selectivity. This is because a wide product distribution generally results in the requirement of costly separation. However, as given in the equations, the energy barriers toward different reduction products are very close, which makes it very challenging to obtain high selectivity of a specific product. The exhibited selectivity has been suggested to relate to the binding energy between the metal catalyst surface and reduction intermediate species.

Early studies on electrocatalytic CO\textsubscript{2} reduction dated back to 1970s. Following a series of studies on CO\textsubscript{2} reduction on various bulk metals surfaces, this

\footnote{1 The thermodynamic data correspond to the following condition: pH 7 in aqueous solutions versus NHE, 25 °C, 1 atmosphere gas pressure, and 1 M for the other solutes. Data are obtained from literature (ref. 41).}
field has received substantial research interests. Some exciting progress has been made by developing nanostructured metal electrocatalysts during the last few years \cite{47,48}. Cu received a lot of attention since it is versatile toward multiple products \cite{49,50}. Besides, Zn and Sn are also viewed as promising candidates since they exhibited good selectivity on CO and formate, respectively \cite{48,51}. Gold and silver are of particular interest due to the extremely good CO selectivity observed on both of them \cite{42,52-54}. For example, Kanan’s research group reported electrocatalytic CO$_2$ reduction on oxide-derived gold nanoparticles at very low overpotential \cite{52}. Using silver which is much cheaper than gold, Jiao and coworkers have successfully developed nanoporous silver which is capable of delivering 18 mA/cm$^2$ with 92% CO selectivity at under overpotential<500 mV \cite{54}. More recently, bimetallic nanostructured materials have been seen as promising to achieve high efficiency and selectivity due to their tunable properties \cite{55}. In addition, device-level development of CO$_2$ reduction electrolyzers as well as photoelectrochemical cells are highly desired for future commercial application and are under active research \cite{37,40}.

1.5 Thesis Scope and Structure

There are five chapters in this thesis. Following the introduction chapter, the next three chapters presenting three major projects. In chapter 2 and chapter 3, two types of novel OER catalysts are developed based on non-precious materials. In chapter 4, a photoelectrochemical cell for CO$_2$ reduction is developed and tested. Finally, conclusions and some recommendations for further research are included in chapter 5.
Chapter 2

STUDY OF THE EFFECT ON DOPING MANGANESE AND NICKEL INTO SPINEL COBALT OXIDE NANOPARTICLES AS AN EFFICIENT OXYGEN EVOLUTION CATALYST

A portion of this work has appeared in a modified form in *Catalysis Today* \(^{35}\). Permission has been obtained for the replication of figures and texts as a part of Chapter 2 of this thesis.

2.1 Introduction

Low-cost and high efficient energy storage holds the key to the future of green and sustainable energy, because renewable and sustainable energy sources (e.g. solar panels, biomass, wind, and wave energy) are intermittent\(^{56-58}\). One ideal medium for energy storage is liquid fuel, since it take the advantage of the current infrastructure\(^ {58}\). In the past decades, many approaches have been proposed to produce fuels from water and carbon dioxide using sunlight as the energy source\(^ {18, 57, 59, 60}\). A range of methods, including solar thermal, photoelectrochemical, and photochemical approaches, have been proposed to produce solar fuel efficiently and economically\(^ {11, 58, 61}\). Regardless of which approach is used, catalytic oxygen evolution from water is the critical reaction, because it provides electrons and protons for solar fuel production through either hydrogen evolution and/or proton-assisted CO\(_2\) reduction to hydrocarbons\(^ {58, 62, 63}\). In order to produce solar fuel on a terawatt scale, photon-assisted water oxidation is the only way to generate a sufficient source of protons and electrons. Compared to the reduction half reaction, visible light assisted oxygen evolution from water has slow
kinetics and requires large overpotential. Therefore, an efficient oxygen evolution catalyst is essential to enhance the reaction rate and/or lower the overpotential for complete solar fuel production. Many efforts toward this goal have recently been made with catalysts made of abundant first-row transition metals. Among all the catalysts, cobalt-based materials exhibited high activities for the water oxidation reaction through photocatalytic approaches. In 2009, Dr. Feng Jiao and his coworkers reported the first example of Co₃O₄ nanoclusters supported in mesoporous silica SBA-15, which exhibited a high activity in visible-light-driven water oxidation reaction. Following that work, a few other nanostructured cobalt-based oxides have been reported to be efficient oxygen evolution catalysts. For example, Dismukes and his co-workers demonstrated that Li₂Co₂O₄ with a spinel structure is a highly efficient water oxidation catalyst. A turnover frequency (TOF) of 1 × 10⁻³ s⁻¹ per cobalt was observed, which is similar to the TOF of Co₃O₄ nanoclusters supported in mesoporous silica. Another report by Wang et al. described a successful synthesis of Co₃O₄ nanoparticles with tunable particle size and showed that Co₃O₄ nanoparticles are much more active than other cobalt catalysts in photochemical and electrochemical water oxidation. Although these works suggest that cobalt oxide with a spinel structure shows a unique property in photocatalytic water oxidation, the origin of the high oxygen evolution activity in the Co₃O₄ spinel remains unknown. A better understanding of the spinel oxygen evolution catalyst is crucial for us in order to rationally design more efficient water oxidation catalysts.
2.2 Experimental Section

2.2.1 Synthesis Procedure of Spinel Nanoparticle Catalysts

The Co$_3$O$_4$, Mn-Co$_3$O$_4$, and Ni-Co$_3$O$_4$ nanoparticles were synthesized using a straightforward hydrothermal method adapted from literature$^{73}$. In a typical synthesis procedure, a precursor slurry was obtained by mixing 2 mmol Co(CH$_3$COO)$_2$·4H$_2$O with solvent (2 mL DI water and 23 mL ethanol) in a 40 mL Teflon liner. Then 2.5 mL ammonia aqueous solution (25 wt%) was added to the slurry under stirring. After continuously stirring for about 10 min a dark-colored suspension formed. The liner was then sealed in an autoclave and held at 150 °C for 3 h. After the autoclave is cooled to room temperature the nanoparticles was washed and collected by centrifugation-redispersion method with DI water. In the case of doped cobalt nanoparticles, one thirds (molar basis) of cobalt precursor salt was substituted with manganese or nickel precursor salt (M(CH$_3$COO)$_2$·4H$_2$O) to synthesis M-Co$_3$O$_4$ nanoparticles.

2.2.2 Structural Characterization of Nanoparticle

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was carried out in the Soil Lab at the University of Delaware. Powder X-Ray Diffraction (PXRD) analysis was performed with a PANalytical X’Pert X-ray diffractometer using Cu K-radiation. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2010F field-emission transmission electron microscope, using an accelerating voltage of 200 kV. Surface area measurements were performed using an isothermal nitrogen adsorption/desorption instrument at 77 K. FT-IR analysis was done by an Alpha-T spectrometer and the OPUS spectroscopic software. X-ray absorption experiments were carried out through the user program at beamline X10c at
the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL). And the XAS data were analyzed using the free software IFEFFIT pack-age (version 1.2.11, released on August 11, 2008), including Athena and Artemis.

2.2.3 Test and Evaluation of Catalytic Activity of Nanoparticles in Photocatalytic Oxygen Evolution Reaction

Photocatalytic oxygen evolution activities were measured at room temperature using reactor–gas chromatography (GC) and Clark electrode systems. The Clark electrode system was able to access the activity at shorter time scales (1 min) while the reactor-GC set-up was able to measure activity at much longer time scales (30 min). A well-studied \([\text{Ru}(\text{bpy})_3]^{2+}\)-persulfate system was used to drive the thermodynamically uphill reaction. In both the Clark electrode and reactor-GC experiments, an aqueous Na$_2$SiF$_6$–NaHCO$_3$ buffer with a pH value of 5.8 was used to control the pH of the system. In the Clark electrode system, 1.0 mg of catalyst, 2.5 mg of \(\text{Ru(bpy)}_3\text{Cl}_2\cdot\text{H}_2\text{O}\), 7.1 mg of Na$_2$S$_2$O$_8$, and 21.5 mg of Na$_2$SO$_4$ were mixed in 2.2 mL of buffer. The mixture was then purged with nitrogen gas until virtually no oxygen was present according to the Clark electrode signal. Oxygen concentration was then measured for several minutes to establish a base-line level of oxygen. The reaction solution was then exposed to a 300 W Xe research lamp (UV fused silica, 1.3 in collimated, F/1, 1.5 in.) with a 400 nm cut-off filter. During exposure to light, the oxygen concentration was monitored for at least 1 min. In the reactor GC system, scaled-up amounts of sensitizer, buffer, electrolyte, and electron acceptor were used. This corresponds to 40 mL of aqueous Na$_2$SiF$_6$–NaHCO$_3$ buffer, 390 mg Na$_2$SO$_4$, 130 mg Na$_2$S$_2$O$_8$, and 45 mg \([\text{Ru}(\text{bpy})_3]\text{Cl}_2\cdot\text{H}_2\text{O}\). 5 mg of catalyst were used, instead of a scaled up 18 mg, after it was determined that large amounts of catalysts affect the ability of the
sensitizer to absorb photons. Several optimization and control experiments were also performed to prove that cobalt catalysts are responsible for the observed oxygen evolution activity. After loading the reactor with proper amounts of reactants, the system was then purged with helium for 10-20 min. Similar to the Clark electrode system, the reactor was then irradiated with a 300 W Xe research lamp with a 400 nm cut-off filter. GC measurements of the headspace after 15 and 30 min of illumination were measured by a Shimadzu GC system (Shimadzu 2014). In order to properly calculate the oxygen produced in the reactor-GC system, oxygen dissolved in the liquid phase of reactor must be accounted for (40 mL of 127 mL reactor). We assume that the concentration of oxygen in the liquid phase is 4 mg/L (i.e. half of the oxygen concentration in water at room temperature).

2.3 Result and Discussion

2.3.1 Structural Characterization

We first confirmed the compositions of Co$_3$O$_4$, Mn-Co$_3$O$_4$, and Ni-Co$_3$O$_4$ nanoparticles using chemical analysis using ICP-OES, and the ratios of Mn/Ni to Co are shown in Table 2.1. Although the initial ratios of metal precursors are the same (M/Co = 0.5), the amounts of Co that are substituted by Mn/Ni are very different. This difference in atomic ratios might be due to the hydrothermal synthetic conditions. N$_2$ adsorption–desorption measurements were also performed to obtain the surface areas of as-prepared nanoparticles, and their surface areas were estimated using the Brunauer, Emmett and Teller (BET) method (Table 2.1). It is evident that all three nanoparticle catalysts have an almost identical surface area, which allows us to decouple the surface area effect in studying water oxidation activities of as-made
catalysts. The morphology of as-made nanoparticles was examined using transmission electron microscopy (TEM). Typical low magnification TEM images are shown in Figure 2.1 a-c and near-monodispersed spherical particles were clearly observed in all three samples. By examining many particles, an average particle size for each nanoparticle sample was estimated (Table 2.1). Particle size distributions for all the three samples can be found in Figure 2.2 a-c. Turning to the atomic structure, three nanoparticle materials were examined by high resolution TEM (HRTEM) first. The HRTEM images (Fig. 2.1 d–f) show clearly lattice fringes in all the as-made catalysts, indicating their highly crystalline nature. The distances between fringes measured from the HRTEM images are consistent with the d-spacings of [1 1 1] and [2 2 0] of a typical Co$_3$O$_4$ spinel structure, suggesting that the three as-made nanoparticle samples have a spinel-type crystal structure.

Table 2.1 Structural characterization results of three types of cobalt oxide-based nanoparticles

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal/Co ratio</th>
<th>Size$^1$ (nm)</th>
<th>Size$^2$ (nm)</th>
<th>TEM surface$^3$ Area (m$^2$/g)</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Co$_3$O$_4$</td>
<td>0.12</td>
<td>6.4</td>
<td>6.66 ± 0.28</td>
<td>142-155</td>
<td>134</td>
</tr>
<tr>
<td>Mn-Co$_3$O$_4$</td>
<td>0.77</td>
<td>5.3</td>
<td>7.00 ± 0.22</td>
<td>137-146</td>
<td>135</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>N/A</td>
<td>7.4</td>
<td>7.14 ± 0.18</td>
<td>135-142</td>
<td>132</td>
</tr>
</tbody>
</table>
Figure 2.1 TEM and HRTEM images for as-synthesized (a, d) Co$_3$O$_4$, (b, e) MnCo$_2$O$_4$, and (c, f) NiCo$_2$O$_4$ nanoparticles.

Figure 2.2 Particles size distributions for (a) Co$_3$O$_4$, (b) Ni-Co$_3$O$_4$, (c) Mn-Co$_3$O$_4$ estimated from TEM images.

The crystal structures of Co$_3$O$_4$, Mn–Co$_3$O$_4$, and Ni–Co$_3$O$_4$ nanoparticles were further confirmed by wide-angle PXRD results (Figure 2.3). Several broad diffractions peaks have been clearly observed for all the as-made cobalt based nanoparticle
samples, confirming that the catalysts are highly crystallized. All the diffraction peaks can be assigned to the standard Co$_3$O$_4$ spinel crystal structure and no additional peak was observed, and therefore, we can conclude that all the samples have a highly pure spinel crystal structure. Note that although all the three samples share a similar spinel crystal structure, the powder X-ray diffraction peaks for Ni-Co$_3$O$_4$ show a small shift toward high degrees, indicating that the unit cell of Ni–Co$_3$O$_4$ is slightly smaller than that for pure Co$_3$O$_4$. The broadness of diffraction peaks suggests the nanocrystalline nature of the samples, which is in good agreement with the HRTEM results (Figure 2.1 d-f). We calculated the particle sizes using the Scherrer equation, which are also consistent with the values estimated from TEM analysis (Table 2.1).

![Figure 2.3 PXRD patterns for Co$_3$O$_4$ (black), Mn-Co$_3$O$_4$ (red), and Ni-Co$_3$O$_4$ (blue) nanoparticles. A standard pattern for Co$_3$O$_4$ spinel (green) is also shown for comparison.](image-url)
Although HRTEM and PXRD analysis confirmed the successful synthesis of Co$_3$O$_4$, Mn-Co$_3$O$_4$, and Ni-Co$_3$O$_4$ nanoparticles with an identical spinel crystal structure, it is important to know the exact oxidation state and coordination of Mn/Ni in the spinel structure, which may enable us to elucidate the structure-property relationship in the cobalt based spinel water oxidation catalysts. In our previous studies, we have successfully utilized XAS techniques to explore the detailed atomic structures of mesoporous metal-doped Co$_3$O$_4$ catalysts, and therefore the same techniques were applied here to the cobalt-based nanoparticle systems.$^{34, 74}$ In a typical Co$_3$O$_4$ spinel structure, tetrahedral coordinated cobalt cations are in the 2+ oxidation state and octahedral coordinated cations are in the 3+ oxidation state, resulting in an average oxidation state of +2.67. The oxidation states of cobalt, manganese, and nickel can provide important insights into the atomic level structure, and therefore, we first examined the oxidation states of Co, Mn, and Ni using XANES technique. Co K-edge XANES data are shown in Fig. 2.4a. In the case of pure Co$_3$O$_4$ nanoparticle, a small shift ($\sim$0.9 eV) to the higher binding energy compared to standard Co$_3$O$_4$ spinel was observed, indicating a higher average oxidation state of Co in the Co$_3$O$_4$ nanoparticle. We suspect that due to the hydrothermal reaction conditions, the surface of Co$_3$O$_4$ nanoparticle is occupied partially by OH groups (where Co is 3+) or the surface of particle is Co$^{3+}$ terminated. In both cases, a slightly higher Co oxidation state (approximately +2.8) could be achieved. Regarding Mn-Co$_3$O$_4$ and Ni-Co$_3$O$_4$ nanoparticles, the Co K-edges are shifted to lower energies, suggesting that their Co oxidation states are slightly lower than +2.67. This may be due to a preferential occupation of Mn/Ni at octahedral sites in the spinel structure, leading to a reduced average oxidation state of Co. Such a preferential occupation at octahedral sites has
been demonstrated in the mesoporous Mn and Ni doped Co$_3$O$_4$ materials. To investigate the possibility of surface OH groups, FTIR experiments were carried out and the spectra are shown in Figure 2.5. It should be noted here that all the samples were carefully dried in an oven before the measurements to minimize the moisture influence. In Figure 2.5, all the spectra, including the one for bulk Co$_3$O$_4$ standard have bands at 500-700 cm$^{-1}$, which can be assigned to the metal-O vibrations. A small shift ($\sim$13 cm$^{-1}$) to low wavenumbers for both Mn-Co$_3$O$_4$ and Ni-Co$_3$O$_4$ nanoparticles was observed, which is likely due to the metal substitution effect. At high wavenumber region, spectra for nanoparticulate samples show a broad peak at around 3385 cm$^{-1}$, which can be ascribed to the stretching of OH group$^{75}$. The formation of OH groups is likely due to the nature of hydrothermal reaction environments. In contrast, no peak at the same wavenumber was observed for the bulk Co$_3$O$_4$ standard.

We also performed EXAFS analysis on the Co K-edge to examine the coordination environments of cobalt in all three spinel nanoparticles (Fig. 2.4b). Data for a standard Co$_3$O$_4$ spinel sample is also shown for comparison. The Co K-edge EXAFS spectrum for bulk Co$_3$O$_4$ (Fig. 2.4b) shows three major peaks below 4 Å (apparent distance). The apparent distance can be converted into a real distance by adding a typical value of 0.3-0.4 Å. In this paper, we simplify our discussion by using apparent distances. In Fig. 2.4b, the first large peak at $\sim$1.5 Å corresponds to the distance of Co-O, while the peak at approximately 2.5 Å and 3.2 Å correspond to Co$^{\text{octa}}$-Co$^{\text{octa}}$ and Co$^{\text{tetra}}$-Co$^{\text{octa}}$ distances, respectively. All three nanoparticle catalysts show similar Co K-edge EXAFS patterns as the standard Co$_3$O$_4$ spinel (Fig. 2.4b), indicating that the samples share a similar spinel structure. One observation is that the relative intensities for all the three nanoparticle catalysts are lower than that of standard Co$_3$O$_4$. It is likely due
to a significant portion of atoms sitting on the surface of nanoparticles, resulting in a decrease of the number of atoms at long distances.

Figure 2.4 Co K-edge (a) XANES and (b) EXAFS data for Co$_3$O$_4$ (black), Mn-Co$_3$O$_4$ (red), and Ni-Co$_3$O$_4$ (blue) nanoparticles. Patterns for standard Co$_3$O$_4$ spinel (green) are also shown for comparison.

Figure 2.5 FTIR spectra for all the cobalt-based spinel nanoparticles. A spectrum for standard Co$_3$O$_4$ is also shown.
2.3.2 Catalytic Activity Evaluation

Photocatalytic water oxidation experiments were carried out using two different configurations, a Clark electrode system and a reactor/GC system. In both systems, \([\text{Ru(bpy)}_3]^{2+}\) was used as the sensitizer and sodium persulfate was used as the sacrificial electron acceptor. The pH of the system was set to 5.8 using a \(\text{Na}_2\text{SiF}_6–\text{NaHCO}_3\) buffer. With the Clark electrode, we can measure oxygen concentration in the liquid phase. The reaction time was set to 1 min, beyond which oxygen concentration in the solution may reach its saturation point. The oxygen yields of all three nanoparticle catalysts are shown in Fig. 2.6a. The TOFs for \(\text{Co}_3\text{O}_4\), Mn-\(\text{Co}_3\text{O}_4\), and Ni-\(\text{Co}_3\text{O}_4\) nanoparticles estimated from the Clark electrode experiments are \(1.3 \times 10^{-3}\), \(1.8 \times 10^{-3}\), and \(8.3 \times 10^{-4}\) s\(^{-1}\) per transition metal, respectively. Because all the nanoparticles have a similar surface area, a similar particle size, and similar surface properties (Table 2.1 and Figure 2.5), it allows us to directly compare their oxygen evolution activities and elucidate the doping effect. Clearly, Mn-\(\text{Co}_3\text{O}_4\) nanoparticles exhibited a better oxygen evolution activity than that of pure \(\text{Co}_3\text{O}_4\) and Ni-\(\text{Co}_3\text{O}_4\) nanoparticles. The oxygen evolution activities of the three nanoparticle catalysts have the following trend: Mn-\(\text{Co}_3\text{O}_4\) > \(\text{Co}_3\text{O}_4\) > Ni-\(\text{Co}_3\text{O}_4\). Turning to the reactor/GC system, a similar trend was observed after a total photocatalytic reaction time of 30 min (Figure 2.6b). The TOFs calculated from Figure 2.6b are \(5.8 \times 10^{-4}\), \(8.7 \times 10^{-4}\), and \(4.5 \times 10^{-4}\) s\(^{-1}\) per transition metal for \(\text{Co}_3\text{O}_4\), Mn-\(\text{Co}_3\text{O}_4\), and Ni-\(\text{Co}_3\text{O}_4\) nanoparticles, respectively. It is evident that the trend of oxygen evolution activities for all the three nanoparticle catalysts remains the same, while the TOFs observed at 30 min are significantly lower than those with much shorter reaction time. This phenomenon is consistent with the results obtained in our previous studies of mesoporous cobalt based oxygen evolution catalysts \(^{34}\).
Figure 2.6 Photocatalytic oxygen evolution results obtained from (A) a Clark electrode system, and (B) a reactor/GC system using [Ru(bpy)$_3$]$^{2+}$ as the sensitizer and sodium persulfate as the sacrificial electron acceptor. TM, transition metal. The solubility of oxygen in water is ~8 mg/L so that the oxygen yield in the first minute (A) is less than half of oxygen saturation point.
It should be noted that in our previous study mesoporous Co$_3$O$_4$ exhibited a higher TOF than Mn-Co$_3$O$_4$ and Ni-Co$_3$O$_4$ counterparts. The origin of the low TOF for metal substituted Co$_3$O$_4$ was found to be the high oxidation states of Mn and Ni (Mn$^{3.7+}$ and Ni$^{3.3+}$) in the doped Co$_3$O$_4$ catalysts, which are unfavorable for oxygen evolution and resulted in a significant decrease of TOF. However, the data shown in the current study (Figure 2.6) clearly demonstrated that Mn-Co$_3$O$_4$ nanoparticles can be more active than Co$_3$O$_4$ nanoparticles in visible light driven water oxidation reaction. Our speculation is that the high TOF of Mn-Co$_3$O$_4$ nanoparticles is due to the optimal binding energy between Mn surface sites and surface intermediate. Since the binding energy is closely related to the oxidation state, we performed XAS measurements on the Mn K-edge and the data are shown in Figure 2.7. It can be seen that the Mn K-edge of Mn-Co$_3$O$_4$ nanoparticles is only slight shifted to right (Figure 2.7a), suggesting that the average oxidation state of Mn in Mn-Co$_3$O$_4$ is slightly higher than +3. The EXAFS data (Figure 2.7b) show a weak peak corresponding to the Mn$^{\text{tetra}}$-Me$^{\text{octa}}$ distance, confirming the Mn cations are preferentially occupied the octahedral sites in the Co$_3$O$_4$ spinel. In our previous study of mesoporous silica supported manganese oxides, we have already shown that the Mn oxidation state has a near-linear relationship with the binding energy. Using the same strategy, we can roughly estimate that Mn cations in the Mn-Co$_3$O$_4$ sample have an average oxidation of +3.1 ± 0.1 (the resolution of oxidation state is approximately 0.1 unit). Such an oxidation state of Mn is significantly lower than that of mesoporous Mn-Co$_3$O$_4$, which is very likely due to the difference in the synthetic conditions: low temperature (150 °C) for hydrothermal reaction and much higher temperature (~400-600 °C) for solid state approach. The Mn K-edge XAS data presented here suggest that the
photocatalytic water oxidation activity of Co$_3$O$_4$ spinel catalyst could be further improved by Mn$^{3.1+}$ substitution at the octahedral sites. We also applied the same XAS techniques to Ni-Co$_3$O$_4$ nanoparticles and found that the average oxidation of Ni in Ni-Co$_3$O$_4$ is approximately +3.3 ± 0.1.

Figure 2.7 Mn K-edge (a) XANES and (b) EXAFS data for Mn–Co$_3$O$_4$ nanoparticles. Data for standard Mn$_2$O$_3$ are also shown for comparison. Me = Co or Mn.

2.4 Conclusion

In a summary, we have successfully synthesized three cobalt-based spinel nanoparticles. Using a simple hydrothermal approach, nickel and manganese have been substituted into the Co$_3$O$_4$ spinel structure. The as-synthesized nanoparticle catalysts have been carefully examined using various structural characterization techniques, including PXRD, TEM, gas adsorption, and XAS. It has been found that Mn-substituted Co$_3$O$_4$ nanoparticles exhibited a higher TOF than pure Co$_3$O$_4$ nanoparticles, while the oxygen evolution activity of Ni-Co$_3$O$_4$ nanoparticles is lower than pure Co$_3$O$_4$. The origin of this enhancement has been explored and it is likely that Mn$^{3.1+}$ at octahedral sites of the Co$_3$O$_4$ spinel have the optimal binding energy to oxygen evolution intermediates.
2.5 Acknowledgements

This work was sponsored by the University of Delaware Startup Fund and Schipper Fellowship in the Chemical and Biomolecular Engineering Department. In addition to my advisor, I would like to thank Jonathon Rosen for initial help on experiment configuration and material synthesis, Dr. Gregory S. Hutchings for XAS data collecting and electron microscopy imaging.
Chapter 3

INVESTIGATION ON IN SITU FORMED COBALT OXIDE NANOCUBANES AS HIGHLY EFFICIENT OXYGEN EVOLUTION CATALYST

A portion of this work has appeared in a modified form in *Journal of American Chemistry Society* \(^{33}\). Permission has been obtained for the replication of figures and texts as a part of Chapter 3 of this thesis.

3.1 Introduction

A sustainable energy future heavily depends on the capability to store energy in a cheap and efficient way, because of the mismatch between energy demand and intermittent power generation from renewable energy sources (e.g., solar panels, biomass, wind, and wave energy). Liquid fuel is an ideal medium for energy storage, because it can easily be stored and used in the current energy infrastructure \(^{60, 76}\). In the past decades, many approaches have been proposed and investigated for fuel production from water and carbon dioxide through artificial photosynthesis \(^{34, 54, 63, 68, 77}\). Regardless of which approach is used, catalytic oxygen evolution from water is the critical half reaction, because it provides electrons and protons for solar fuel production through either hydrogen evolution or proton-assisted CO\(_2\) reduction to hydrocarbons \(^{57, 58, 78}\). For solar fuel production on a terawatt scale, visible-light driven water oxidation is the only way that we can potentially produce sufficient protons and electrons economically. However, photocatalytic oxygen evolution reaction (OER) has slow kinetics and requires large overpotentials, because oxygen evolution from water is a four-electron reaction, while photon capture is a single electron/hole process \(^{77}\).
Therefore, a multi-electron catalyst is essential for efficient visible-light driven water oxidation.

Cobalt-based OER catalysts, especially Co$_3$O$_4$ spinel, have been intensively studied in photocatalytic systems because of their superior properties, good stability, and high abundance$^{34, 63, 68, 72, 79-81}$. There are two distinct cobalt sites in Co$_3$O$_4$ spinel: four-oxygen coordinated tetrahedral sites and six-oxygen coordinated octahedral sites. The octahedral cobalt atoms and neighboring oxygen atoms are in a Co$_4$O$_4$ cubane arrangement, which has been suggested to be crucial for OER$^{31}$. In our previous work, we have synthesized a series of metal-doped Co$_3$O$_4$ nanoparticles and mesopores and investigated their OER activity under visible light at near-neutral pH conditions$^{35, 71}$. The results agree well with the speculation that the OER active site in spinel is the octahedral Co$^{3+}$. Therefore, in an ideal OER catalyst, cobalt atoms have an average oxidation state of 3+ and form Co$_4$O$_4$ cubanes. An extremely small particle size is desired to ensure that most of cobalt atoms sitting on the particle surface act as catalytic centers for oxygen evolution, but at the same time the particles must remain stable (ideally under near-neutral pH conditions). It is also important for the catalyst to be freestanding without any inert support so that it can be directly attached to semiconductors. However, there are only very few catalysts that meet all the requirements.

In a traditional solution synthesis, nanoparticles aggregate easily during drying and redispersing processes, especially those surfactant-free or support-free particles. Here, we report a new strategy to synthesize freestanding, and highly active cobalt oxide nanocubanes with an average cobalt oxidation state close to 3+ through an in $situ$ phase transformation mechanism. The new approach enables us to prepare
freestanding nanoparticles directly inside the reaction solution without the presence of any surfactant or inert support. A new layered cobalt compound, Co(OH)(OCH₃), was first synthesized as the precursor of the cobalt oxide nanocubane catalyst using a solvothermal method. The precursor, upon sonication, was exfoliated and transformed into cobalt oxide clusters in the reaction buffer. X-ray absorption spectra for the postreaction catalyst show that the cobalt catalyst under reaction conditions contains multiple Co₄O₄ cubanes with an average cobalt oxidation state of ≈2.8+. An exceptional turnover frequency (TOF) of 0.023 per second per cobalt atom was observed for the cobalt oxide nanocubanes, which represents the highest TOF reported to date for nonprecious metal based OER catalysts driven by visible light.

3.2 Experimental Section

3.2.1 Material Synthesis

The synthetic procedure of Co(OH)(OCH₃) was modified from a previous report of Mg(OH)(OCH₃)⁸². In a typical synthesis, 0.01 mol of cobalt acetate tetrahydrate was dissolved in 100 mL of anhydrous methanol. The solution was then transferred into a hydrothermal bomb (200 mL) and placed in an oven at 180 °C for 24 h. After the solvothermal treatment, the bomb was cooled down to room temperature. The sample was recovered by filtering, washed with dry methanol, and dried in air. The synthesis of 6 nm Co₃O₆ spinel nanoparticles was reported in our previous study of metal-doped Co₃O₆ spinel nanoparticles⁸². In a typical procedure, 0.50 g of Co(CH₃COO)₂·4H₂O (2 mmol) was mixed with 2 mL water and 23 mL ethanol in a 40 mL Teflon liner. Then, a 2.5 mL of aqueous ammonia solution (wt. 25%) was added under stirring. After stirring for 10 min, a brownish-gray slurry was formed and the liner containing the
suspension was carefully sealed in an autoclave, which was heated at 150 °C for 3 h. After the autoclave was cooled down to room temperature in air, the product was collected by washing with deionized water, following by a drying process at 60 °C.

3.2.2 Structural Characterizations

Powder X-ray diffraction (PXRD) measurements were performed using a PANalytical X’Pert X-ray diffractometer using Cu Kα radiation. FTIR spectrum was collected using a Nicolet Nexus 470 FTIR instrument equipped with an MCT-A detector. Scanning electron microscopy (SEM) images were collected using a Zeiss Auriga-60. Transmission and scanning transmission electron microscopy (TEM and STEM) imaging were conducted on a JEOL JEM-2010F equipped with a high angle annular dark field (HAADF) detector and operated at 200 kV.

Crystal Structure simulation. To determine the unit cell the peak positions were manually fit using the CMPR program\textsuperscript{83} by starting from the unit cell and space group ($R\overline{3}m$) for presumably isostructural compounds reported by Le Bihan et al. and Yu et al.\textsuperscript{84} After choosing the unit cell parameters we confirmed our cell thru a Le Bail fit of an analogous structure with a similar space group (LiCoO$_2$) using EXPGUI and GSAS.\textsuperscript{85}

3.2.3 Photocatalytic Activity Test

The detailed procedure of photocatalytic oxygen evolution from water has been reported in our previous publication\textsuperscript{82}. In this work, a few modifications have been made. In a typical preparation of cobalt oxide nanocubane catalyst, cobalt precursor was dispersed in aqueous Na$_2$SiF$_6$-NaHCO$_3$ buffer with a pH value of 5.8 by sonication for 20 min prior to photolysis. In a typical experiment, a certain amount of
catalyst and Ru(bpy)$_3$Cl$_2$·6H$_2$O, 7.1 mg of Na$_2$S$_2$O$_8$, and 21.5 mg of Na$_2$SO$_4$ were mixed in 2.2 mL of buffer, followed by purging with helium gas until oxygen concentration reached its minimum (recorded as the baseline). Then, the Clark electrode system was exposed to a 300 W Xe research lamp (UV fused silica, 1.3 in collimated, F/1, 1.5 in.) with a 400 nm cutoff filter. During exposure to light, the oxygen concentration was monitored for at least 1 minute. Additionally, control experiments were also performed to ensure that the photocatalytic water oxidation driven by the cobalt catalysts is the oxygen source. Experiments without either catalyst or Ru(bpy)$_3$Cl$_2$ sensitizer gave no oxygen production.

3.2.4 XAS Measurement and Analysis

The samples were mixed with amorphous SiO$_2$ powder and sealed in polyimide tape for the XAS measurements. We also collected XAS data for bulk CoO and Co$_3$O$_4$ standards under identical conditions for comparison. Co K-edge XAS spectra were recorded on beamline X18A of the National Synchrotron Light Source at Brookhaven National Laboratory. A Si(111) channel cut monochromator was employed to sweep the incident X-ray energy through the measurement range, and a rhodium-coated focusing mirror was used to direct the beam into the measurement hutch. The beamline resolution is approximately $5 \times 10^{-4} \Delta E/E$. Since the post-reaction materials were necessarily prepared with relatively low concentration, data collection was optimized for fluorescence with a PIPS detector. The free Demeter software package was used for all data alignment, reduction, and post-processing (Athena), as well as EXAFS fitting analysis (Artemis). Energy measurements were calibrated to the known edge position of a pure Co foil (7709 eV).

Simulated scattering paths were fit to the data via the EXAFS equation:
\[ \chi(k) = S_0^2 \sum_j N_j e^{-2k^2 \sigma^2} e^{\frac{2R_j}{\lambda(k)} f_j(k)} \sin[2kR_j + \delta_j(k)] \]

where \( k \) is the wavenumber of the photoelectron, \( S_0^2 \) is the amplitude reduction factor, \( N_j \) is the coordination number for a particular path, \( \sigma^2 \) is the mean square displacement factor (disorder), \( R_j \) is the path length, \( \lambda(k) \) is the mean free path of the photoelectron, \( f_j(k) \) is the scattering amplitude function, and \( \delta_j(k) \) is the phase shift.

For the fitting results represented in Figure 3.3.3.1, Figure 3.3.3.2, and Table 3.3.3.1, the following variables were parameterized and optimized: \( N_j \) and \( S_0^2 \) (inverse relationship), \( R_j, \sigma^2 \), and the energy deviation between theory and experiment, \( \Delta E_0 \).

### 3.3 Result and Discussion

#### 3.3.1 Synthesis and Characterization of Cobalt Catalyst

The layered Co(OH)(OCH\(_3\)) was obtained by treating a cobalt(II) acetate tetrahydrate methanol solution in a sealed hydrothermal bomb at 180 °C. A typical scanning electron microscopy (SEM) image of the as-synthesized Co(OH)(OCH\(_3\)) is shown in Figure 3.1a, in which a nanoflake-like morphology is evident. The typical size of each flake is approximately 0.5-2 µm in diameter and 20-50 nm in thickness. A close examination of the as-made flake using high resolution transmission electron microscopy (HRTEM) revealed its polycrystalline nature Figure 3.1b. To identify the crystal structure of Co(OH)(OCH\(_3\)), the as-made cobalt compound was examined using powder X-ray diffraction (PXRD) and a few diffraction peaks were clearly observed Figure 3.1c. However, the PXRD pattern does not match any existing compound in the Inorganic Crystal Structure Database (ICSD), indicating that it may be an unknown crystal structure. Because of its highly polycrystalline nature, it is not
possible to solve the crystal structure of Co(OH)(OCH₃) using single crystal X-ray diffraction. Previous work on Ni(OH)(OCH₃) and NiₓMg₁₋ₓ(OH)(OCH₃) (0 < x < 1) reported a very similar layered structure, which provides us an opportunity to use it as a model structure for the cobalt compound. Here, we used the General Structure Analysis System (GSAS) software to create a model of Co(OH)(OCH₃) based on the crystal structures of NiₓMg₁₋ₓ(OH)(OCH₃) and LiCoO₂ with a space group of \( R\bar{3}m \) (more details in Table 3.1). Interlayer atoms were excluded from the simulation due to their highly disordered nature. As can be seen in Figure 3.1c, the simulated PXRD pattern (red bars in Figure 3.1c) matches that of as-made cobalt precursor very well, indicating that the simulated structure is likely to be the actual crystal structure for the cobalt precursor (a model structure shown in Figure 3.1c, inset). There is one additional peak at \( \sim23° \) which does not directly match the simulated PXRD pattern for Co(OH)(OCH₃). This could be due to the scattering of interlayer atoms or a small amount of unknown impurity. The composition of Co(OH)(OCH₃) was also confirmed by thermogravimetric analysis (Figure 3.2). A 25% weight loss was observed when the sample was heated in air to 600 °C. This observed loss is consistent with the expected value of the conversion of Co(OH)(OCH₃) to Co₃O₄ through thermal decomposition. The structure of Co(OH)(OCH₃) was further examined by Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum is almost identical to that of NiₓMg₁₋ₓ(OH)(OCH₃), indicating that they may share a similar structure (Figure 3.3). In situ transformation of the layered Co(OH)(OCH₃) precursor to the free-standing cobalt oxide nanocubane catalyst was performed using a simple sonication treatment in the presence of NaHCO₃−Na₂SiF₆ buffer (pH = 5.8). It should be noted that Co(OH)(OCH₃) precursor (Figure 3.4a) is not soluble in NaHCO₃−
Na$_2$SiF$_6$ buffer under magnetic stirring, while a transparent pink solution can be formed using ultrasonication (Figure 3.4a). Once it is transparent, the solution was stable for days and no precipitation could be observed. To determine the structure of in situ formed cobalt catalyst, we first examined its morphology using electron microscopy analysis. The SEM image in Figure 3.4b clearly shows that upon sonication nanoflake like morphology disappeared and very small clusters were formed. The large structures in the SEM image correspond to dried components of the buffer solution. To elucidate the formation mechanism of the cobalt oxide nanocubanes, we performed a control experiment, in which layered Co(OH)(OCH$_3$)$_2$ precursor was sonicated in water instead of a NaHCO$_3$-Na$_2$SiF$_6$ buffer solution. No nanocubanes can be observed and the nanoflake morphology of precursor was preserved (Figure 3.5a). Further examination of cobalt catalyst was performed in STEM. Extremely small clusters were clearly observed for the sample sonicated in buffer, visible as bright dots on the dried buffer salts (Figure 3.4c). The particle size distribution (Figure 3.6) clearly confirms that the average size of cobalt oxide nanocubanes is below 2 nm. However, the sample treated in deionized water did not show any significant change in morphology (Figure 3.5b). In another control experiment, we sonicated the precursor in a diluted HCl solution (pH = 5.8), which resulted in a partial transformation of layered cobalt precursor to small clusters with a broad size distribution. Both control experiments suggest that a slightly acidic environment and the buffer itself played some critical roles in the formation of cobalt oxide nanocubanes. The overall in situ transformation process is summarized in Figure 3.4d for the cobalt oxide nanocubane formation. Identification of the atomic structure
of in situ formed cobalt oxide clusters will be discussed later together with X-ray absorption results.

Figure 3.1 (a) A typical SEM image, (b) HRTEM image, and (c) PXRD pattern for as-synthesized layered Co(OH)(OCH₃) compound. The red bars in (c) represent the expected diffraction peaks for the simulated structure. The inset in (c) is the model structure of the layered Co(OH)(OCH₃) compound. Blue ball: Co; red ball: O; green ball: H or CH₃.

Table 3.1 Fitted unit cell parameters of as-made Co(OH)(OCH₃) material

<table>
<thead>
<tr>
<th>Space Group</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(\alpha)</th>
<th>(\beta)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R\bar{3}m)</td>
<td>3.165 Å</td>
<td>3.165 Å</td>
<td>23.5 Å</td>
<td>90</td>
<td>90</td>
<td>120</td>
</tr>
</tbody>
</table>
Figure 3.2 TGA result for as-made Co(OH)(OCH$_3$)$_3$. The end product was found to be Co$_3$O$_4$ and ~25% weight loss was observed during the heat treatment in air to 600°C, which is consistent with the expected weight loss of Co(OH)(OCH$_3$) to Co$_3$O$_4$ conversion.

Figure 3.3 FTIR spectrum for as-made Co(OH)(OCH$_3$)$_3$. The spectrum agrees with previously published spectra for Ni$_x$Mg$_{1-x}$(OH)OCH$_3$.84,89
Figure 3.4 (a) Photographs of the Co(OH)(OCH$_3$) precursor, buffer solution, and \textit{in situ} formed cobalt oxide nanocubanes in buffer, from left to right. (b) SEM and (c) STEM images for layered Co(OH)(OCH$_3$) after sonication in buffer. The large structures in (b) and (c) are precipitates from buffer components. (d) Schematic of the formation of cobalt oxide nanocubanes via sonication of the Co(OH)(OCH$_3$) precursor in the buffer solution.

Figure 3.5 (A) SEM and (B) STEM images for layered Co(OH)(OCH$_3$) after sonication in water
3.3.2 Catalyst Evaluation

Photocatalytic oxygen evolution from water was performed using a well-established \([\text{Ru(bpy)}_3]^{2+} - \text{S}_2\text{O}_8^{2−}\) system in an aqueous NaHCO₃-Na₂SiF₆ buffer (pH = 5.8). The details of the \([\text{Ru(bpy)}_3]^{2+} \text{S}_2\text{O}_8^{2−}\) photocatalytic cycle can be found in our previous publications or other literature ²⁹, ⁶⁶, ⁷¹. In a typical reaction, a mixture containing a certain amount of cobalt catalyst, persulfate, sensitizer, and 2.2 mL of buffer was placed in a Clark electrode reactor. After bubbling with helium gas for 5-10 min, the reactor was exposed to a 300 Xe lamp equipped with a 400 nm cutoff filter and the oxygen concentration in the solution was recorded. To obtain the optimal result, we first varied the cobalt catalyst loading and investigated catalyst loading effects. A maximum TOF of 0.023 s⁻¹Co⁻¹ was observed at a cobalt loading of approximately 0.5 mmol/L (Figure 3.7a). Then, we fixed the cobalt catalyst loading at 0.48 mmol/L and investigated how \([\text{Ru(bpy)}_3]^{2+}\) sensitizer concentration affects the TOF of oxygen evolution from water. On the basis of the
results shown in Figure 3.7b, the activity dependence on sensitizer concentration is weak as long as a minimum amount of sensitizer is present in the system. The optimal sensitizer concentration is around 0.9 mmol/L. To demonstrate the superior catalytic properties of *in situ* formed cobalt oxide nanocubanes, we also synthesized Co₃O₄ nanoparticles with an average particle size of 6 nm using a prior reported hydrothermal route. The 6 nm Co₃O₄ nanoparticles were tested at the identical conditions (cobalt loading of 0.48 mmol/L and sensitizer concentration of 0.9 mmol/L). The results (Figure 3.8) clearly show that the TOF of *in situ* formed cobalt oxide nanocubanes (∼0.023 s⁻¹ Co⁻¹) is more than ten times higher than that of 6 nm Co₃O₄ nanoparticles (∼0.002 s⁻¹ Co⁻¹), one of the state-of-the-art cobalt-based spinel catalysts. For comparison, we have reviewed recent literature of cobalt based OER catalysts driven by visible light (Table 3.2). The TOF of cobalt oxide nanocubane is the highest value reported to date among all the nonprecious metal based water oxidation catalysts driven by visible light. Regarding catalyst stability, the current setup (i.e., Clark electrode and [Ru(bpy)₃]²⁺ sensitizer) is not an ideal system to study photocatalytic activity over a long period of time. Follow up work will be performed in a more robust semiconductor based system.
Figure 3.7 (A) Cobalt oxide nanocubane catalyst loadings vs. TOFs with a [Ru(bpy)$_3$]Cl$_2$ concentration of 0.9 mmol/L. (B) [Ru(bpy)$_3$]Cl$_2$ concentrations vs. TOFs with a cobalt oxide nanocubane catalyst loading of 0.48 mmol/L. The red lines in (B) and (B) indicate the trends of TOF change.

Figure 3.8 Oxygen evolution activities for cobalt oxide nanocubanes (blue curve) and 6 nm Co$_3$O$_4$ nanoparticles (red curve). Experiment without the presence of catalyst showed no oxygen generation (black curve).
Table 3.2 Turnover frequencies (TOFs) for Co-based OER catalysts in photo-driven systems.

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>TOF [a]</th>
<th>Sensitizer</th>
<th>Buffer solution with initial pH</th>
<th>Use a support?</th>
<th>Ref.</th>
</tr>
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<tr>
<td>Cobalt oxide nanocubanes</td>
<td>$2.3 \times 10^{-2}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$-NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>This work</td>
</tr>
<tr>
<td>6 nm Co$_3$O$_4$ nanoparticles</td>
<td>$2.0 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$-NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>This work</td>
</tr>
<tr>
<td>6 nm Co$_3$O$_4$ nanoparticles</td>
<td>$1.3 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$-NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>35</td>
</tr>
<tr>
<td>6 nm Mn doped Co$_3$O$_4$ nanoparticles</td>
<td>$1.8 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$-NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>35</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>$2.7 \times 10^{-3}$</td>
<td><a href="ClO$_4$">Ru(bpy)$_3$</a>$_2$</td>
<td>Phosphate, pH = 7.0</td>
<td>N</td>
<td>70</td>
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<tr>
<td>Cubic Li$_2$Co$_2$O$_4$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>31</td>
</tr>
<tr>
<td>Hollow Co$_3$O$_4$ microsphere</td>
<td>$2.7 \times 10^{-4}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>90</td>
</tr>
<tr>
<td>Mesoporous Co$_3$O$_4$</td>
<td>$2.4 \times 10^{-4}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 5.8</td>
<td>N</td>
<td>34</td>
</tr>
<tr>
<td>CoSBA (single site)</td>
<td>$1.4 \times 10^{-2}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 5.6</td>
<td>Y</td>
<td>91</td>
</tr>
<tr>
<td>Co-APO-5</td>
<td>$2.3 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 5.8</td>
<td>Y</td>
<td>92</td>
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<tr>
<td>β-Co(OH)$_2$ anchored on zeolite Y</td>
<td>$1.9 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 6.0</td>
<td>Y</td>
<td>80</td>
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<tr>
<td>3 nm Co$_3$O$_4$ nanoparticles /SBA-15</td>
<td>$1.9 \times 10^{-3}$</td>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>NaHCO$_3$ + NaSiF$_6$, pH = 5.8</td>
<td>Y</td>
<td>72</td>
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Table 3.2 Continued

<table>
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<tr>
<th>Catalyst</th>
<th>Current Density</th>
<th>Complex</th>
<th>Solution Composition</th>
<th>Activity</th>
<th>selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIT-6/Co₃O₄-HEX</td>
<td>4.0×10⁻⁴</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>NaHCO₃ + NaSiF₆, pH = 5.8</td>
<td>Y</td>
<td>71</td>
</tr>
<tr>
<td>Co₃O₄ nanoparticles (20-50 nm)</td>
<td>4.9×10⁻⁵</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>NaHCO₃ + NaSiF₆, pH = 6</td>
<td>N</td>
<td>93</td>
</tr>
<tr>
<td>Co₄Se₃O₉Cl₂</td>
<td>5.4×10⁻³</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>NaHCO₃ + NaSiF₆, pH = 5.8</td>
<td>N</td>
<td>94</td>
</tr>
<tr>
<td>Fe₂O₃@NiO core-shell nanoparticles</td>
<td>6.0×10⁻⁴</td>
<td><a href="ClO%E2%82%84">Ru(bpy)₃</a>₂</td>
<td>Borate, pH = 8.0</td>
<td>N</td>
<td>95</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>1.9×10⁻³</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>Phosphate, pH = 7.0</td>
<td>N</td>
<td>96</td>
</tr>
<tr>
<td>Co₃V₂O₈</td>
<td>4.3×10⁻³</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>Borate, pH = 8.5</td>
<td>N</td>
<td>97</td>
</tr>
<tr>
<td>Active MnOₓ</td>
<td>4.8×10⁻⁵</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>Phosphate, pH = 7.2</td>
<td>N</td>
<td>98</td>
</tr>
<tr>
<td>[Co₄(H₂O)₃(VW₉O₃₄)₂]₁₀⁻⁺</td>
<td>2.2×10⁻³</td>
<td>[Ru(bpy)₃]Cl₂</td>
<td>Borate, pH = 9.0</td>
<td>N</td>
<td>99</td>
</tr>
</tbody>
</table>

* Calculated based on all the Co atoms in the catalyst. The unit is [per second per cobalt atom].

3.3.3 Atomic Structure of Cobalt Catalyst

To elucidate the origin of the exceptional OER activity for in situ formed cobalt catalyst, it is crucial to identify its atomic structure. We first attempted to separate the catalyst particles from the solution. However, the nanocubanes are too small to be separated via a traditional centrifuge method, making it not possible to perform bulk structural characterizations, such as PXRD and gas absorption. Therefore, we employed X-ray absorption spectroscopy (XAS), a very useful tool to probe the structure of small clusters, to extract structural information on the cobalt.
oxidation state and coordination environment for \textit{in situ} formed catalyst. The X-ray absorption near-edge structure (XANES) data for the Co K-edge in Figure 3.9 show a clear edge shift to high energy for the layered Co(OH)(OCH₃) after 1 min of photolysis, while no further edge shift in the spectrum was observed between the 1 and 10 min postreaction data (Figure 3.9a), indicating that the phase transformation from layered precursor to cobalt oxide nanocubane was finished after sonication in the buffer solution and within 1 min of visible light radiation. On the basis of the edge positions of catalysts and standards (Figure 3.9a), the estimated average oxidation states of cobalt precursor and \textit{in situ} formed catalyst are $+2.2$ and $+2.8$, respectively. The oxidation of Co$^{2+}$ in the precursor to a higher oxidation state is very likely due to the highly oxidizing environment for photocatalytic oxygen evolution. The atomic structure of cobalt oxide nanocubanes was further investigated using extended X-ray absorption fine structure (EXAFS). The as-made layered precursor showed two well-defined peaks in R-space at 1.7 and 2.9 Å (all the distances discussed here are apparent distances without phase correction), corresponding to the cobalt-oxygen and cobalt-cobalt distances in the cobalt oxide layer (Figure 3.9b). Because of the polycrystalline nature of the layered compound, no distinguishable peaks at long distances are observed. To explore the atomic structure of catalyst in working conditions, we run the photocatalytic OER reaction in a large batch type reactor for more than 10 min. The EXAFS data for both 1 and 10 min postreaction catalysts show almost identical characteristics in R-space, with one major peak at 1.4 Å and the other at 2.4 Å, suggesting that the cobalt nanocubanes were formed within the first minute of reaction. The postreaction data also suggest a good stability of the \textit{in situ} formed
nanocubanes. The contraction of Co-O and Co-Co bond distances is also consistent with the observed oxidation state increase that occurs during reaction.

Figure 3.9 (a) K-edge XANES spectra of as-made Co(OH)(OCH3) compound (blue line), the catalyst after 1 min. reaction (black line), the catalyst after 10 min. reaction (red line) and two standards: CoO (magenta line) and Co3O4 (green line). (b) EXAFS spectra for the as-made (green line), post-reaction after 1 min. (black line), and post-reaction after 10 min. (blue line) samples, and (c) result of fitting the first Co-O and Co-Co single-scattering paths (red line). The proposed structure of the cobalt oxide nanocubane material generated in situ is shown in (d). The blue and red spheres represent cobalt and oxygen atoms, respectively.

Spinel-type cobalt oxides have been investigated as potential OER catalysts in both photochemical and electrochemical systems. In a typical Co3O4 spinel structure,
octahedral cobalt atoms and neighbor oxygen atoms form Co₄O₄ cubanes, which are likely the activity sites for oxygen evolution in a manner similar to the Mn₄CaO₅ catalytic site in nature’s photosystem II. Therefore, it is important to check whether in situ formed cobalt catalyst contains Co₄O₄ cubanes in its structure. Curve fitting was performed for the EXAFS spectrum of the 1 min postreaction sample. The results are shown in (Figure 3.9c and Figure 3.10), and the fitting details can be found in Table 3.3. Assuming that Co atoms are fully coordinated by O atoms with an octahedral arrangement, the Co-O coordination number was fixed at 6 during the fitting. All other parameters were allowed to vary within physically meaningful ranges. By considering the first Co-O and Co-Co single scattering paths, we found a Co-Co coordination of 5.8 ± 0.6. On the basis of the fitting, we propose a nanocubane structure consisting of 13 cobalt atoms per cluster with a particle size of ~1.1 nm (Figure 3.8d). Although we did not include any hydrogen atoms in the model, it is possible that some of the outer layer oxygen atoms are actually hydroxide groups. The proposed nanocubane structure has a Co-Co coordination of 5.5, which is in agreement of the fitting result. Expanded analysis of the next two features in R-space indicates that they represent additional Co-O and Co-Co scattering at distances consistent with the cluster of cobalt octahedra. The additional peaks with low intensities may also result from long-range ordering of some large clusters. It should be noted that distinct from previous work on phosphate-derived Co-Pi catalysts and Co₃O₄ spinels, the proposed structure contains a large number of Co₄O₄ cubanes in a small cluster (8 Co₄O₄ with 13 Co atoms). It is very likely that the unique biomimetic Co₄O₄ cubanes are responsible for the exceptional photocatalytic water oxidation activity of cobalt oxide nanocubanes.
Figure 3.10 Real part of the $q$-space representation of the EXAFS fit to the 1 min. post-reaction sample.

Table 3.3 EXAFS fitting parameters corresponding to the fit in Fig. 3.8.

<table>
<thead>
<tr>
<th>Path</th>
<th>$S_0^2$</th>
<th>$R$</th>
<th>$N$</th>
<th>$\sigma^2$</th>
<th>$\Delta E_0$</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>0.78 (0.05)</td>
<td>1.903 (0.008)</td>
<td>6</td>
<td>0.001 (0.0001)</td>
<td>-2.4 (1.1)</td>
<td>2.0%</td>
</tr>
<tr>
<td>Co-Co</td>
<td>2.854 (0.008)</td>
<td>5.8 (0.6)</td>
<td>0.002 (0.0003)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uncertainties in parentheses. Bold values are fixed (only the coordination number of Co-O). Restraints were applied to keep all $\sigma^2$ values in physically meaningful range without arbitrarily fixing these values. The amplitude reduction factor ($S_0^2$) was found to be in close agreement with values used in previous work on small phosphate-derived cobalt oxide nanostructures.$^{67,102}$ The fitting range is $1 \leq k \leq 10, 1 \leq R \leq 4$.

In a recent mechanistic study, water oxidation intermediates have been observed using time-resolved FTIR technique.$^{103}$ Frei and his co-workers studied the behavior of $\text{Co}_3\text{O}_4$-nanoparticles in the visible light driven $[\text{Ru(bpy)}_3]^{2+}\text{S}_2\text{O}_8^{2-}$ system. They proposed two distinct active sites, namely oxo-bridged Co(III)OH binuclear site and single Co(III)OH sites. The time-resolved FTIR results suggested that the presence of adjacent CoOH groups coupled with an oxygen bridge could lead to a fast reactive site with a TOF higher than $3 \text{ s}^{-1}$, while the single cobalt site exhibited a much
slower TOF (∼0.02 s\(^{-1}\) per surface atom). In our cobalt oxide nanocubane catalyst, 12 out of 13 cobalt atoms are on the surface and all the cobalt octahedra are interconnected with edge sharing, which, based on Frei’s mechanism, should result in a much higher turnover than what was observed in our experiments (0.023 s\(^{-1}\) Co\(^{-1}\)). It should be noted that the TOF observed for cobalt oxide nanocubanes is at the same order of magnitude of that observed for single site Co catalyst reported by Tilley and his co-workers (∼0.014 s\(^{-1}\) Co\(^{-1}\))\(^9\). Therefore, we suspect that regardless of the presence of a second Co(III)OH at the adjacent site, the dominant reaction pathway for cobalt oxide catalyst may be the single Co(III)OH site mechanism. There are several potential reasons why a significantly higher TOF has not been observed yet. For instance, hole injection from [Ru(bpy)\(_3\)]\(^{2+}\) sensitizer to the adjacent Co(III)OH site could be difficult considering the large size of [Ru(bpy)\(_3\)]\(^{2+}\) complex (∼11 Å) compared to the Co-O-Co distance (∼2.8 Å). Additionally, charge transfer from the sensitizer to the active site is a random process with no control of directionality, which also reduces the chance for the two neighboring cobalt atoms to be cooperative. A precise control of charge transfer may be required to achieve a higher TOF. Further investigation will be required to fully determine the oxygen evolving reaction mechanism on the surface of cobalt oxide nanocubanes.

3.4 Conclusion

In summary, we have successfully synthesized cobalt oxide nanocubanes with a particle size less than 2 nm through an in situ transformation process under a photocatalytic environment. Each in situ formed nanocubane contains 13 cobalt atoms, fully coordinated with oxygen atoms to form 8 Co\(_4\)O\(_4\) cubanes. The nanocubanes exhibited an order of magnitude higher TOF in photocatalytic water oxidation activity
compared to traditional 6 nm Co$_3$O$_4$ spinel nanoparticles. The performance of the nanocubane catalyst represents the highest TOF that has been reported to date among all nonprecious metal oxide OER catalysts. The *in situ* formed cobalt nanocubanes are freestanding and support-free, which may be implemented in a wide range of photocatalytic systems.

### 3.5 Acknowledgements

This part of work was supported by the University of Delaware Research Foundation Strategic Initiatives (DERF-SI) grant. In addition to my advisor, I would like to thank collaborators in Prof. Kake Zhu’s research group for precursor material synthesis, Dr. Bryan Yonemoto for XRD pattern fitting, and Dr. Gregory S. Hutchings for SEM and TEM imaging as well as EXAFS fitting. I would also like to acknowledge the X18A beamline support staff at Brookhaven National Laboratory.
Chapter 4

DEVELOPING A PHOTOELECTROCHEMICAL CELL FOR CARBON DIOXIDE REDUCTION IN AQUEOUS SOLUTION

4.1 Introduction

Solar energy has been viewed as one of the most promising renewable energy sources for the future world as it is abundant, widely spread and basically free \(^5,^{104}\). Utilizing solar energy to produce fuels and other chemical feedstock has attracted significant interests since it is not only able to deal with the intermittency issue, but also has great compatibility with the current infrastructure \(^{12,22}\). When carbon dioxide is used as the starting chemical for solar fuel production, the process is even more attractive as it can potentially create a carbon-neutral energy cycle \(^{37,105}\). To realize this energy conversion and storage process, photo-driven CO\(_2\) reduction systems is a highly desired approach. There are several types of such systems (so-called artificial photosynthesis system), such as photoelectrochemical cells driven by photoelectrodes, photovoltaic cells coupled with a traditional electrolyzer, and photocatalyst suspensions \(^{10,21,37,106}\). Each type of system provides advantages in certain aspects and there have been discussions regarding this \(^{107}\). Here in this work the attention is focused on the first type, which is photoelectrode-driven photoelectrochemical cells. Basically, the photo-energy absorber in a photoelectrochemical cell could be a photoanode, photocathode, or even a PV cell/multiple PV cells in series incorporated as part of the electrode. Though there have been some progress within the third scenario, a PV cell is obviously much more complicated and expensive compared to a
simple photoelectrode\textsuperscript{108}. As summarized in Table 4.1(1-6), efforts have also been
devoted in the development of photocathode for CO\textsubscript{2} reduction. Semiconductors such
as p-InP, p-ZnTe, Mg-doped CuFeO\textsubscript{2}, and CuInS\textsubscript{2} have been investigated as
photocathode materials for CO\textsubscript{2} reduction\textsuperscript{23, 109-111}. However, due to the complexity of
CO\textsubscript{2} reduction catalysis and strict requirements for band gap alignment of the
semiconductor material, it remains a major challenge to develop efficient and stable
CO\textsubscript{2} reduction photocathodes. Most of current available photocathodes suffer from a
number of issues including high overpotential, low current density, limited stability,
and poor selectivity. In addition, some of the elements (such as Te, In) in the
suggested materials as photocathodes are rarely stored on the Earth, which will
potentially limit the application of the materials in the future.

An alternative way would be employing a photoanode decorated with oxygen
evolution catalyst(s) and a CO\textsubscript{2} reduction cathode. The advantage of employing a
photoanode as the light absorber lies in the intrinsic better stability. To utilize the
potential benefits of constructing a photoanode-driven photoelectrochemical cell for
CO\textsubscript{2} reduction, several demonstration works have been reported (Table 4.1 (7-9)). In a
recent work, PEC cells for CO\textsubscript{2} reduction was developed by incorporating WO\textsubscript{3} as the
photoanode and Cu, Sn/SnO\textsubscript{x} as CO\textsubscript{2} reduction cathode\textsuperscript{24}. Though 2-electrode tests
were suggested and carried out to evaluate the cell performance, the current density
and selectivity are not even close to requirements of real application.
Table 4.1 Selected photoelectrode-driven PEC systems for CO$_2$ reduction reported in literature

<table>
<thead>
<tr>
<th>Current density</th>
<th>Electrolyte</th>
<th>Electro-catalyst</th>
<th>Photoelectrode</th>
<th>Type</th>
<th>Entry</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024 mA/cm$^2$</td>
<td>Purified water</td>
<td>Ruthenium-complex polymer</td>
<td>p-type InP</td>
<td>Photocathode</td>
<td>1</td>
</tr>
<tr>
<td>1 mA/cm$^2$</td>
<td>0.1 M NaHCO$_3$</td>
<td>None</td>
<td>Mg-doped CuFeO$_2$</td>
<td>Photocathode</td>
<td>2</td>
</tr>
<tr>
<td>0.02 mA/cm$^2$</td>
<td>0.1 M tetrabutylammonium hexafluorophosphate in DMF</td>
<td>Rhenium complex</td>
<td>p-type NiO and Zn-porphyrin</td>
<td>Photocathode</td>
<td>3</td>
</tr>
<tr>
<td>0.016 mA/cm$^2$</td>
<td>0.1 M KHCO$_3$</td>
<td>None</td>
<td>Polypyrrole-coated p-ZnTe</td>
<td>Photocathode</td>
<td>4</td>
</tr>
<tr>
<td>Not specified</td>
<td>0.1 M acetate</td>
<td>Pyridinium ion</td>
<td>CuInS$_2$</td>
<td>Photocathode</td>
<td>5</td>
</tr>
<tr>
<td>14 mA/cm$^2$</td>
<td>0.5 M H$_2$SO$_4$ and 0.5 M NaHCO$_3$</td>
<td>Pt-RGO</td>
<td>TiO$_2$</td>
<td>Photocathode</td>
<td>6</td>
</tr>
<tr>
<td>1 mA/cm$^2$</td>
<td>0.5 M KHCO$_3$</td>
<td>Cu, Sn/SnO$_x$</td>
<td>WO$_3$</td>
<td>Photoanode</td>
<td>7</td>
</tr>
<tr>
<td>1 mA</td>
<td>1 M NaOH and 0.1 M KHCO$_3$</td>
<td>Cu</td>
<td>GaN</td>
<td>Photoanode</td>
<td>8</td>
</tr>
<tr>
<td>0.7 mA/cm$^2$</td>
<td>0.1 M KHCO$_3$</td>
<td>Ag</td>
<td>3C-SiC</td>
<td>Photoanode</td>
<td>9</td>
</tr>
</tbody>
</table>
Si has been used to serve as the photoanode for water splitting since it is abundant and is capable of absorbing a large portion of the solar spectrum\textsuperscript{115,116}. One important obstacle for developing such a system rises from the compatibility of the photoanode/OER catalyst with the near-neutral environment required by CO\textsubscript{2} reduction. Recently, solutions have been developed to passivate Si at basic and even near-neutral conditions. When coupled with NiO\textsubscript{x} oxygen evolution catalyst, the silicon photoanode was proven to be a stable efficient photoanode for water splitting at slightly basic (pH = 9.5) condition\textsuperscript{117}. This is especially interesting since the pH value of the testing solution is very close to that in electrocatalytic CO\textsubscript{2} reduction (pH 6-8). In addition, the metal oxide layer is inexpensive and facile to make. Thus, it would be very interesting to employ this Ni-Si photoanode for PEC CO\textsubscript{2} reduction.

<table>
<thead>
<tr>
<th>Potential at the cathode</th>
<th>External bias</th>
<th>Major reduction product and Faradaic efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 V (vs. Ag/AgCl)</td>
<td>-</td>
<td>Formate, 62.3%</td>
<td>23</td>
</tr>
<tr>
<td>0.9 V (vs. SCE)</td>
<td>-</td>
<td>Formate, 10%</td>
<td>109</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>CO, 6.2%</td>
<td>114</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Format, 37.2%, CO, 13.8%</td>
<td>110</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Methanol, 97%</td>
<td>111</td>
</tr>
<tr>
<td>0.54 V (vs. SCE)</td>
<td>-</td>
<td>HCOOH, 40%</td>
<td>113</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>CH\textsubscript{4}, 67%</td>
<td>24</td>
</tr>
<tr>
<td>-</td>
<td>1.95 V</td>
<td>HCOOH, 3.2%</td>
<td>112</td>
</tr>
<tr>
<td>-</td>
<td>None</td>
<td>CO, 30%</td>
<td>38</td>
</tr>
</tbody>
</table>
In a recent work, our group has developed a nanoporous Ag electrocatalyst that is highly efficient and selective for CO₂ to CO catalytic reaction at moderate overpotential \(^{43,54}\). In addition to the superior catalytic properties, silver is an attractive candidate cathode for PEC cell also because it is much cheaper than gold which is commonly used in the PV-electrolyzer systems for CO₂ reduction \(^{118}\).

In this work, a photoanode-driven photoelectrochemical cell based on non-precious material was designed for CO₂ to CO conversion. The implementation of Ni-Si photoanode and nanoporous Ag for photoelectrochemical CO₂ reduction cell has been investigated. Ni-Si photoanode was adapted to operate in a near-neutral solution (pH = 7.5), which allows CO₂ reduction taking place at cathode. This system has been demonstrated to deliver a current density of 10 mA/cm² and Faradaic efficient of 70% for CO₂ to CO conversion with moderate external bias (2.0 V) with good stability. Compared to a normal electrochemical cell, this photoanode-driven photoelectrochemical cell is capable of saving 0.4 V electrical energy by utilizing photo-energy.

4.2 Experimental Section

4.2.1 Synthesis of Cathode for CO₂ Reduction

The nanoporous silver was made following the procedure from a previous work of our group. Aluminum and silver alloy ingot (Al:Ag = 80:20 atom%) was made as the precursor using arc-melting method. The alloy ingot was then cut into thin slices (~300 um). The slices were heated up to 1057 °C and held for 12 hr followed by quenching in ice water. The quenched alloy slices were then collected and polished to form a smooth surface. 5% chloric acid and 1 % chloric acid were used to leach out
the Al in the alloy. The remaining nanoporous sliver was then rinsed with DI water to remove any acid residue and dried in a vacuum oven. A nickel wire was attached to the nanoporous silver piece using silver paste to make it a ready-to-test cathode.

4.2.2 Synthesis of Photoanode with Oxygen Evolution Catalyst

Double-side polished 400 um-thick phosphorus-doped n-Si (110) wafers were ordered from Universitywafer. They were cleaned with acetone, DI water, ethanol and DI water in sequence before use. Metal layers were deposited using a magnetron sputtering chamber at room temperature. The deposition rate was calibrated based on X-ray reflection (XRR) measurement and controlled by the power applied to the gun. A 10 nm Ni layer was deposited (10 W) on the front side of the Si using magnetron deposition. A 20 nm Ti layer was deposited (20 W) on the back side of the Si using magnetron deposition. The sputtering targets (99.999%) were ordered from K.J.L. The wafers were then cut into pieces of 5 mm by 1 mm and nickel wire was attached to the pieces using silver paste. Epoxy (Corning 8490) was used to cover the backside and edges of the anode to prevent contact with the electrolyte. After the epoxy was cured at 75 °C for 2 hr, the photoanodes were stored in an Ar-filled glovebox before anodization and testing. For a normal anode, the synthesis followed the same procedure except that a thick layer of 50 nm Ti was deposited on the front side between Si and Ni and ohmic contact was made between the Ni wire and Ti layer. In this way, the Si wafer only serves as an inert substrate rather than a photon absorber.

4.2.3 Preparation of Anion-conducting Membrane

N115 Nafion and hp Nafion membranes were purchased from Ion Power. The membranes were cleaned in 5% H₂O₂ at 90 °C for 1 hr and then rinsed in DI water
bath at 90 °C for 1 hr. The membranes were soaked in anolyte overnight before applied on a testing cell.

4.2.4 Preparation of Electrolytes

Anolyte was prepared by adding 6.2 g of boric acid, 6.4 g of potassium chloride and 0.8 g of potassium hydroxide to 200 mL DI water. The solution was stirred overnight until the salts were fully dissolved. Catholyte was prepared by purging research-purity carbon dioxide into 0.5 M potassium bicarbonate solution until the solution was saturated by CO₂.

4.2.5 Cell configurations, Photoanode Pretreatment, and Performance Test

A customized one-compartment cell was used for anodization of the photoanode. A made-in-house two-compartment cell was used for system performance test. As shown in Figure 4.1.

Figure 4.1 Digital photographs of (A) one-compartment cell for anodization of the photoanode and (B) two-compartment cell for photoelectrochemical test.
The one-compartment cell has a boric glass body equipped with a quartz window which maximized the light transmission. On the top of the cell there are three necks which accommodate the working electrode (photoanode), reference electrode (Ag/AgCl electrode), and counter electrode (Pt wire), respectively. The two-compartment cell is made of polycarbonate with a quartz window at the front side. An anion-conducting membrane was implemented to separate the cell into two chambers. There are outlets at the top of each chamber for insertion of electrodes. There is one outlet with septum on the side of each chamber for gas sampling. The front-side chamber was filled with anolyte (30 mL solution, 13 mL headspace) and the back-side chamber was filled with catholyte (30 mL solution, 13 mL headspace). Before each test, the catholyte was purged was research-grade CO$_2$ for over 30 min to saturate the catholyte and the headspace. 30 µL gas sample was taken using a gas-tight syringe every 30 min during test course and analyzed using GC (Shimadzu, GC-2014). The GC is equipped with PLOT MolSieve 5A and Q-bond PLOT columns and a PDHID detector.

A 300 W Xe lamp equipped with a 400 nm filter was used as the light source. A potentiostat (Princeton Applied Research VersaSTAT 3 or Metrohm Autolab) test station was used to control the potential at the working electrode, provide external bias and monitor the current profile.

4.2.6 Material Characterization

X-ray diffraction (XRD) measurements were conducted on a Bruker D8 X-ray diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) images were collected using a Zeiss Auriga-60. Scanning transmission electron microscopy
(STEM) imaging was performed on a JEOL JEM-2010F equipped with a high angle annular dark field (HAADF) detector.

X-ray absorption spectroscopy (XAS) data were collected on beamline 5-BM-D of the Advanced Photon Source at Argonne National Laboratory. The samples were placed front-side up horizontally to allow the beam scanning through the thin Ni layer. Fluorescence data was collected. The free Demeter software package was used for data alignment and processing. Energy measurements were calibrated to the knowledge position of a pure Ni foil.

4.3 Result and Discussion

4.3.1 Cathode Characterization

The quenched Al$_{80}$Ag$_{20}$ alloy pieces had a pure FCC phase according to the XRD pattern (Figure 4.2). After Al was leached out in acid, the remaining Ag piece maintained a FCC phase and exhibited a nanoporous morphology (SEM image in Figure 4.2). This is consistent with our previous result $^{54}$. To examine the structural stability of the nanoporous Ag, XRD of post-test cathode was also carried out. After a 3-hour photoelectrochemical test, XRD pattern showed that the nanoporous Ag cathode still had a clean FCC phase with high crystallinity. This indicates that the nanoporous Ag cathode has a good structural stability during the photoelectrochemical test course.
Figure 4.2 XRD patterns for quenched Al$_{80}$Ag$_{20}$ (top), leached nanoporous Ag (middle), and post-test nanoporous Ag (bottom). The insert is a typical SEM of the nanoporous Ag cathode.

4.3.2 Photoanode Pretreatment

The as-deposited Ni thin film is a uniform, continuous layer on top of the Si wafer as shown in the scanning electron microscopy (SEM) image (Figure 4.3 (A)). To measure the thickness of the as-made Ni layer, the sample was cut using focused ion beam (FIB). Scanning transmission electron microscopy (STEM) images taken at the cross-section of the sample shows that the as-made Ni film is a continuous layer with a thickness about 12 nm (Figure 4.4). This thin metallic Ni layer can be transformed into an active oxygen evolution catalyst layer by conducting an anodization process $^{30,117}$. The anodization was carried out by holding the potential at the photoanode at 1.54 V (vs RHE) for 2 hours. The condition was determined to
maximize the photoanode performance in terms of current density and stability during PEC test. After anodization, the continuous film morphology remained as observed in SEM image (Figure 4.3 (A)).

Figure 4.3 Top-view SEM images of Ni-Si photoanode: (A) As-made; (B) After anodization for 2 hr; (C) After test at 1.7 V for 3 hr; (D) After test at 2.1 V for 3 hr. The scale bars in all the four images are 500 nm.
Figure 4.4 A typical cross-section STEM image taken at the surface of a as-made Ni-Si photoanode. The Ga is deposited to protect the Ni layer before FIB cutting.

The current profile at the anode recorded along the anodization course is shown in Figure 4.5. The current density at the photoanode increases quickly from 1 mA/cm$^2$ to 6 mA/cm$^2$ during the first hour and gradually reaches a plateau in the second hour. As the current corresponds to catalytic oxygen evolution reaction rate, this indicates the formation of a highly active oxygen evolution catalyst$^{30}$. The bumps of the profile during the second hour are due to bubbles formed at the photoanode surface$^{117}$. The active NiO$_x$ catalyst layer formed during this process serves as the catalyst for oxygen evolution reaction at the photoanode surface during photoelectrochemical cell test.
Figure 4.5 Anode current density profile during the course of anodization of a Ni-Si photoanode.

4.3.3 Photoelectrochemical Test

To evaluate the performance of the photoelectrochemical cell, a short two-electrode test was performed with 1.9 V external bias. As shown in Figure 4.6, the cell exhibited a clear photo-response to visible light irradiation. This indicates that with the assistance of a small external bias, the photovoltage generated at the photoanode can drive the catalytic oxidation reaction at anode and the catalytic reduction reaction at the cathode simultaneously.
Long term photoelectrochemical tests were performed using two-electrode set-up in the two-chamber cell in a batch reaction fashion. Various external biases were applied between the photoanode and cathode to study the cell performance in terms of current density and faradaic efficiency. The current profile at the cathode was monitored and shown in Figure 4.7. With a gentle external bias of 1.7 V, a total current density of 5 mA/cm² was observed at the nanoporous silver cathode. When a slightly higher external bias was applied, the total current arises accordingly. It only takes an external bias of 2.0 V for the PEC cell to achieve a current density of 10 mA/cm², which is generally viewed as the goal for a solar fuel production system. During the course of testing, gas samples were taken from the cathode chamber and analyzed using a GC every 30 min. CO was detected as the major gas reduction
product as shown in Figure 4.7 (right axis). This is consistent with previous studies on the silver electrode catalyzing CO₂ reduction⁴⁹, ⁵⁴. Among all the possible reduction products from CO₂, CO stores the largest amount of energy on the molecular basis and serves as an important chemical feedstock in industry⁴². The CO faradaic efficiency at the cathode increased with the external bias and reached its peak at 70% at 1.9 V and 2.0 V. The current densities and CO Faradaic efficiencies measured after conducting photoelectrochemical tests for 1 hour are summarized in Figure 4.7f.

Stability is an important parameter when evaluating a system towards commercial application. There was no evident degradation of either current density or CO faradaic efficiency observed during the 3-hour test course with moderate external bias up to 2.0 V (Figure 4.7). This implies that the photoelectrochemical cell is under stable operation during the course of testing. However, when an external bias of 2.1 V is applied to the photoelectrochemical cell, the current density starts to gradually drop after about one hour. From previous work, the nanoporous silver cathode is proven to be stable for an 18-hour test ⁵⁴. The membrane was also examined by reusing it in a fresh batch test, which proved the membrane was stable throughout the test. This implies that most likely the photoanode has gone through some changes during the test. Therefore, scanning electron microscopy, X-ray absorption measurement and X-ray photon spectroscopy analysis were carried out on both as-made and post-test photoanodes. Those results will be discussed later in the section of post-test analysis.
Figure 4.7 Cathode current profile (left axis) and CO faradaic efficiency (right axis) in photoelectrochemical two-electrode tests at various external bias: (A) 1.7 V, (B) 1.8 V, (C) 1.9 V, (D) 2.0 V, and (E) 2.1 V. (F) a summary of those at one hour during the test course.

It is critical to evaluate the amount of photo-energy harvested and converted in this photoelectrochemical cell. Therefore, an electrochemical cell, with the photoanode replaced with a non-photo-responsive normal anode (details can be found
in Section 4.2.2), was tested for comparison. The tests were carried out in a similar fashion as photoelectrochemical tests except that there is no illumination on the anode. The current profile and CO faradaic efficiency were monitored and recorded as shown in Figure 4.8. The current density increases with applied external bias, which is very similar to what is observed in photoelectrochemical tests. When 2.4 V external bias was applied, the CO faradaic efficiency reaches its peak value at about 70%. This is comparable to the performance of the photoelectrochemical cell with 2.0 V external bias. Therefore, from the comparison, the photoelectrochemical cell saves 0.4 V electrical energy by absorbing photo-energy.
Figure 4.8 Cathode current profile (left axis) and CO faradaic efficiency (right axis) in electrochemical two-electrode tests at various external bias: (A) 2.1 V, (B) 2.2 V, (C) 2.3 V, (D) 2.4 V, and (E) 2.5 V. (F) a summary of those at one hour during the test course.

4.3.4 Post-test Analysis of the Ni-Si Photoanode

The stability of the photoelectrochemical cell is of great importance. The nanoporous silver cathode has been proven to be stable after continuously CO₂ reduction test for 18 hours. Thus it is more interesting to examine the stability of the Ni-Si photoanode in this work. A morphology change of the NiO₅ layer after test is
observed in SEM images (Figure 4.3cd). After photoelectrochemical test for 3 hr, there are islands formed on the surface of the photoanode. The diameter of the islands is estimated to be 200-300 nm. Based on the SEM images, it is hard to identify if the catalyst went through any structural transformation accompanying the morphology change. Thus it is necessary to perform structural analysis on the NiO\text{\textsubscript{x}} catalyst layer to further investigate the photoanode before and after test. Since the catalyst is a very thin layer (~12 nm, as shown in Figure 4.4), traditional structural analysis techniques such as x-ray diffraction is not able to pick up any meaningful information. Therefore, x-ray absorption analysis was employed as it is capable of extracting atomic structural information from thin films. To gather a significant signal from the absorption, the photoanode was aligned carefully to allow the X-ray swiping along the very surface layer of the NiO\text{\textsubscript{x}} catalyst. Firstly, the as-made Ni-Si photoanode along with a metallic Ni standard sample was examined and the X-ray near-edge structure (XANES) spectra are shown in Figure 4.9. The Ni K-edge in the XANES data from the as-made Ni-Si photoanode is very close to that from the standard Ni foil, verifying the metallic nature of the as-made Ni layer. The XANES spectrum from NiO\text{\textsubscript{x}} catalyst after pretreatment was also obtained with model compounds NiO and LiNiO\textsubscript{2} possessing formal nickel oxidation states of +2 and +3, respectively (Figure 4.9). The edge position of each compound shifts to higher energies compared to that from metallic Ni with increasing formal oxidation state. The Ni K-edge of the NiO\textsubscript{x} layer after pretreatment is at the same position as NiO, indicating that the mean oxidation state of Ni in the NiO\textsubscript{x} catalyst is +2. To probe any possible structural change in the catalyst layer after test, XANES spectra from catalysts after testing at different external bias for 3 hours were collected as well (Figure 4.10). There is no evident difference observed among the Ni
K-edge spectra of the catalysts after pretreatment and after testing at various conditions. This implies that there is no change in average oxidation state of Ni in the catalyst after test, despite the morphology change as seen in SEM images. This is actually further verified by the XPS spectra collected from the same series of samples shown in Figure 4.12. The XPS results revealed that the surface of the NiOx catalyst thin film remained stable under these photoelectrochemical test conditions. It should be noted the XPS spectra collected from the as-made Ni layer surface consisted of signals from metallic Ni as well as Ni at higher oxidation state. This could be due to the partially oxidation of the Ni layer when exposed to air during transfer and electrode fabrication.

Extended x-ray absorption fine structure analysis (EXAFS) were also performed to further explore the atomic structure of Ni-Si photoanodes. The EXAFS spectra collected from photoanodes after pretreatment and after testing at various external bias are presented in Figure 4.11. The spectra show that the NiOx in the photoanode has the same atomic coordination no matter the photoanode is after testing at a small external bias (1.7 V) or an elevated external bias (2.1 V).

Based on the results from XAS and XPS, it is clear that the NiOx catalyst didn’t go through any atomic structural change during the photoelectrochemical tests. However, the morphology change observed in SEM images implies one possible explanation for the degradation at external bias of 2.1 V, which is conducting issue at the interface between the catalyst layer and Si semiconductor115,119. When the NiOx catalyst layer go through a morphology change of aggregation during the test, the underlying Si surface becomes exposed to the electrolyte and tends to get corroded upon the oxidative condition. Since this corrosion is a very slow process when a small
to moderate external bias is applied, no degradation is observed during a 3-hour test. However, when a higher external bias is applied, the exposed surface of the Si semiconductor experiences a much faster corrosion process. Therefore, after about 2-hour test, the electron transfer between the oxygen evolution catalyst and semiconductor encounters a higher barrier due to the formation of excess SiO$_2$. Elemental mapping of the surface of Si at exposed regions as well as covered regions would be helpful to obtain more insights to better understand this process. As this is beyond the scope of this work, it may be conducted in the following study for further exploration.

![Figure 4.9 Ni K-edge XANES spectra](image)

Figure 4.9 Ni K-edge XANES spectra of as-made Ni-Si photoanode (black), Ni-Si photoanode after 2-hr anodization (red), Ni-Si photoanode after 3-hr test at 1.7 V (blue), and three standards: Ni metal (magenta), NiO (navy), and LiNiO$_2$ (green). The vertical lines were added indicating the edge positions.
Figure 4.10 Ni K-edge XANES spectra of Ni-Si photoanode after test at 1.7 V (black), 1.8 V (red), 1.9 V (blue), 2.0 V (magenta), and 2.1 V (green). The vertical line was added indicating the edge positions.
Figure 4.11 EXAFS spectra of Ni-Si photoanode after test at 1.7 V (black), 1.8 V (red), 1.9 V (blue), 2.0 V (magenta), and 2.1 V (green).
Figure 4.12 XPS spectra of Ni-Si photoanode under conditions of: as made (black), after pretreatment (red), after photoelectrochemical test at 2.0 V for 3 hr (magenta), and after photoelectrochemical test at 2.2 V for 3 hr (olive).

4.4 Conclusion

In a summary, a photoelectrochemical cell for CO₂ reduction was developed by the implementation of a NiOₓ-decorated Si photoanode and nanoporous Ag cathode. With a moderate external bias of 2.0 V, a current density of 10 mA/cm² and Faradaic efficiency of 70% for CO₂ to CO was achieved. This PEC cell can operate stably at moderate conditions for 3 hours. Compared to a normal electrochemical cell, the photoelectrochemical cell saves 0.4 V electrical energy by absorbing photo-energy. Post-test photoanodes were carefully characterized by SEM, XAS, and XPS.
The results indicate that though there is a morphology change in NiO\textsubscript{x} catalyst layer after test, the atomic structure of the NiO\textsubscript{x} catalyst remains after photoelectrochemical test even with elevated external bias. In total, this work provides an example of a photoanode-driven PEC cell for CO\textsubscript{2} reduction with good current density and high CO Faradaic efficiency.

### 4.5 Acknowledgements

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Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

In this thesis, novel catalysts based on non-precious materials were developed for photocatalytic oxygen evolution reaction. Some insights on structure-activity relations and reaction mechanism are also presented in this work. In addition, a device-level study of CO$_2$ reduction photoelectrochemical cell was included.

In chapter 2, nickel-doped, manganese-doped, and pure cobalt oxide spinel nanoparticles were successfully synthesized using a facile hydrothermal method. Structural characterization was performed on as-synthesized and post-test samples using various techniques including PXRD, TEM, gas adsorption, and XAS. The results verified that nickel and manganese have been incorporated into the Co$_3$O$_4$ spinel structure by substituting Co in the crystal lattice. It has been found that Mn-substitution in Co$_3$O$_4$ nanoparticles enhanced the OER catalytic activity, while Ni-substitution exhibited a reverse effect. As the oxidation state of Mn at octahedral sites in the spinel nanoparticles is revealed to be +3.1 by XAS data, it is suggested that Mn$^{3.1+}$ has the optimal binding energy to oxygen evolution intermediates.

In chapter 3, the oxygen evolution catalytic activity of cobalt-based material was further enhanced by the 2 nm cobalt oxide nanocubanes. Successfully synthesized through an in situ transformation process, the nanocubanes were found to consist of 8 Co$_4$O$_4$ cubanes that are made up by 13 cobalt atoms in total. The nanocubanes exhibited an exceptional activity in photocatalytic oxygen evolution with a TOF that is
one order of magnitude higher compared to 6 nm CoO\textsubscript{3}O\textsubscript{4} spinel nanoparticles reported previously. Actually, this represents the highest TOF that has been reported to date among all nonprecious metal oxide OER catalysts. In addition, the freestanding and support-free cobalt nanocubanes may be implemented in a wide range of photocatalytic/electrocatalytic systems.

In chapter 4, a photoanode-driven cell for photoelectrochemical CO\textsubscript{2} reduction with water was successfully developed. A NiO\textsubscript{x}-decorated Si photoanode and nanoporous Ag cathode were incorporated for light absorbing and redox reaction catalysis, respectively. A stable performance of 10 mA/cm\textsuperscript{2} with 70\% CO Faradaic efficiency was achieved at a moderate external bias. This PEC cell was tested at moderate condition for 3 hours with no sign of degradation. Compared to a normal electrochemical cell, the photoelectrochemical cell saves 0.4 V electrical energy by absorbing photo-energy. Post-test characterization analysis on the photoanode was performed with the assistance of SEM, XAS, and XPS. Though it has been shown that though there was a morphology change, the NiO\textsubscript{x} oxygen evolution catalyst has the same atomic structure and average oxidation state after the photoelectrochemical test even with elevated external bias. In total, this work demonstrated that Ni-Si photoanode and nanoporous Ag cathode can be combined to build up a photoelectrochemical cell, which could serve as an example of a photoanode-driven CO\textsubscript{2} reduction PEC cell with good efficiency, selectivity and stability.

5.2 Recommendations for Future Studies

Based on the work presented in this thesis, several possible research directions that may lead to further insights are outlined here.
5.2.1 Enhancing the Photoanode for Photoelectrochemical CO₂ Reduction

In chapter 4, Si photoanode decorated with NiOₓ OER catalyst was employed for photoelectrochemical CO₂ reduction. The NiOₓ catalyst layer was found to go through a morphology change after PEC test, which would potentially result in degradation of catalytic activity and thus cell performance. In chapter 3, cobalt oxide nanocubanes were studied as a highly efficient photo-driven OER catalyst in near-neutral pH solution. Since the nanocubanes are highly active and free standing, it would be interesting to implement them on the photoanode for photoelectrochemical CO₂ reduction. In this way, the overpotential for OER would be further reduced and a higher energy efficiency would be achieved in addition to a very likely enhanced stability of the PEC cell.

Regarding the semiconductor used for the photoanode, Si has a relatively small band gap which intrinsically limits the amount of energy to drive redox reactions. Copper zinc tin sulfide (CZTS) has been emerging as a promising semiconductor material for solar cells 120. With a band gap of ~1.5 eV, CZTS holds the potential to harvest the maximum amount of energy from the solar spectrum and has been proven to reach power conversion efficiency of >10% 121. In addition, this material consists of only earth-abundant elements. Thus it would be very interesting to incorporate this material with OER catalyst as photoanode for PEC CO₂ reduction. By doing this, the external bias to drive the system would be further reduced.

5.2.2 Development of Flow System for Photoelectrochemical CO₂ Reduction

In chapter 4, a batch-type CO₂ reduction photoelectrochemical cell was developed. In that work, 3-hr tests were performed due to the limited amount of CO₂ dissolved in the cell. To conduct prolonged tests, a continuous flow system which
allows the replenishment of fresh CO$_2$ into the solution is required. In addition, continuous flow reactors are preferred for future application at an industrial scale, where capital costs will be of importance $^{122}$. In a recent report, Rajeshwar and his coworkers developed a continuous flow photoelectrochemical reactor for CO$_2$ reduction using a hybrid p-type CuO/Cu$_2$O semiconductor nanorod arrays as the photocathode $^{123}$. A much higher product yield as well as longer-chain alcohol products were obtained compared to the batch-type reactor. Thus, it would be very interesting to upgrade the Ni-Si photoanode-driven photoelectrochemical cell studied in chapter 4 into a continuous flow system.
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2. Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrippsc02.ucsd.edu/).


Appendix A

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