PHOTOCATALYTIC WATER SPLITTING: MATERIALS DESIGN AND HIGH-THROUGHPUT SCREENING OF MOLECULAR COMPOSITIONS

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ABSTRACT

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Due to the expected increases on energy demand in the near future, the development of new catalytic molecular compositions and materials capable of directly converting water, with the aid of solar photons, into hydrogen becomes obviated. Hydrogen is a combustible fuel and precious high-energy feedstock chemical. However, for the water-splitting reaction to proceed efficiently and economically enough for large-scale application, efficient light-absorbing sensitizers and water splitting catalysts are required. To study the kinetics of the water reduction reaction, we have used titania (TiO$_2$) nanoparticles as a robust scaffold to photochemically grow platinum (Pt) nanoparticles from a unique surface-anchored molecular precursor Pt(dcbpy)Cl$_2$ [dcbpy = 4,4’-dicarboxylic acid-2,2’-bipyridine]. The hybrid Pt/TiO$_2$ nanomaterials obtained were shown to be a superior water reduction catalyst (WRC) in aqueous suspensions when compared with the benchmark platinized TiO$_2$. In addition, cobalt phosphate (CoPi) water oxidation catalyst (WOC) was photochemically assembled on the surface of TiO$_2$, and its structure and mechanism of activity showed resemblance to the established electrochemically grown CoPi material. Both WRC and WOC described above possessed near unity Faradaic efficiency for hydrogen and oxygen production respectively, and were fully characterized by electron microscopy, x-ray absorption spectroscopy, electrochemistry and photochemistry. While there are established materials and molecules that are able to drive water splitting catalysis, some of these efficient semiconductors, including titanium dioxide (TiO$_2$) and tungsten trioxide (WO$_3$), are only able to absorb high-energy (ultraviolet or blue) photons. This high-energy light represents merely a fraction of the solar spectrum that strikes the earth and the energy content of those remaining photons is simply wasted. A strategy to mitigate this problem has been
developed over the years in our laboratory. Briefly, photons of low energy are converted into higher energy light using a process termed photon upconversion. Using this technique, low energy photons supplied by the sun can be converted into light of appropriate energy to trigger electronic transitions in high energy absorbing photoactive materials without any chemical modification of the latter. We have shown, that this technology is capable of upconverting visible sunlight to sensitize wide-bandgap semiconductors such as WO$_3$, subsequently extending the photoaction of these materials to cover a larger portion of the solar spectrum. Besides the engineering of different compositions that serve as either sensitizers or catalysts in these solar energy conversion schemes, we have designed an apparatus for parallel high-throughput screening of these photocatalytic compositions. This combinatorial approach to solar fuels photocatalysis has already led to unprecedented fundamental understanding of the generation of hydrogen gas from pure water. The activity of a series of new Ru(II) sensitizers along with Co(II) molecular WRCs were optimized under visible light excitation utilizing different experimental conditions. The multi-step mechanism of activity of selected compositions was further elucidated by pump-probe transient absorption spectroscopy.
To my parents (Samir and Wafaa)

To my brothers (Bassam, Gebran and Samir Jr.)

To the soul of my grandfather (Georges)

To Nina, all my family members and friends who believed in me

Without your constant support I couldn’t have made it

Thank you for your sacrifices

Thank you for your love
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CHAPTER I

INTRODUCTION

1.1 GLOBAL ENERGY DEMAND AND CO₂ EMISSION RATES

The number of individuals populating the earth is expected to increase dramatically over the following century approaching 10.4 B persons in 2100, Figure 1.1. These projected values are also paralleled with an anticipated increase of 30 TW in yearly energy demand, Figure 1.1. Carbon dioxide (CO₂), a greenhouse gas correlated with global warming, is a common by-product of oil, coal and natural gas combustion. As a result, if we keep burning fossil fuels to supply energy in the future, the CO₂ emission rates are going to reach unprecedented historical values close to 13.3 GtC/yr by the end of the century which can undoubtedly alter our terrestrial environment, Figure 1.1. \(^1\) \(^3\)

![Figure 1.1. Current and expected population of earth (blue, billion), CO₂ emission rates (red, gigaton per year) and energy consumption (green, terawatt).](image)
Compounding this problem, our global reserves to production ratio (R/P) of oil is ~ 54.2, which means that if we keep extracting oil at the same annual rate, we have less than a century before oil is exhausted from the currently discovered reserves.⁴ Due to market fluctuations, the oil price varies with time (Figure 1.2 left) and most of its production is located in politically unstable geographical areas.⁴⁻⁶ Nuclear power has been supplying a considerable amount (~ 4-5 %) of our energy in the last decade (Figure 1.2 right), but uranium and other radioactive elements are not very earth-abundant.¹⁴ It was estimated that conventional nuclear fission reactors can still provide only a total of 100 TW of power from the uranium available.¹ In addition, nuclear power plant pollution and radioactive hazards have been of a large concern especially in the case of natural disasters. These facts leave us with a rational solution of harvesting more of the renewable energy like wind, geothermal, solar and biomass.¹⁵⁶ Nowadays, renewable energy provides < 2% of the global energy consumption because of the current high cost of energy production from renewable sources, Figure 1.2 right.¹⁴⁷

![Figure 1.2. Average crude oil price as a function of calendar year (left). Global energy consumption in percent produced from different sources (right).](image-url)
1.2 STORAGE OF SOLAR ENERGY BY WATER SPLITTING

As a matter of fact, the sun provides energy to the earth per hour \(4.3 \times 10^{20}\) J equivalent to our global consumption in a year.\(^{1,5}\) However, sunlight is diffuse and intermittent that obviates the necessity to develop systems to store this energy.\(^{1,8}\) Batteries are still expensive for such applications given their small lifespan and low discharge depth.\(^1\) Mechanical storage of energy by pumping water uphill is impractical because the sun is diurnal which implies a charging and discharging cycles of ~ 12 hrs.\(^1\) Given the drawbacks of the already established energy storage methods like batteries and mechanical storage, researchers have focused their efforts to develop new energy storage techniques.\(^9\) Of a particular interest, water splitting is a thermodynamically uphill process requiring 1.23 V/e\(^-\) (Eqs. 1-3).\(^{10-16}\)

\[
\begin{align*}
O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O & E_{\text{anodic}} = 1.23 - 0.059(pH) \quad [1] \\
4H^+ + 4e^- &\rightarrow 2H_2 & E_{\text{cathodic}} = 0 - 0.059(pH) \quad [2] \\
\hline
2H_2O &\rightarrow 2H_2 + O_2 & E_{\text{reaction}} = -1.23 \text{ V} \quad [3]
\end{align*}
\]

The overall voltage stored in the two electron proton reduction into hydrogen (H\(_2\)) is 2.46 V. H\(_2\) has a very high energy storage capacity ~ 119,000 J/g which is three times higher than the capacity of oil.\(^{17}\) Contrary to common perception, hydrogen doesn’t represent a tremendous safety concern because its explosive limit ~ 4\% in air which is two times higher than butane.\(^{17}\) The energy input to drive the water splitting reaction can be considered a form of solar energy storage in chemical bonds, Figure 1.3 left.\(^{13}\) When needed this energy can be readily harvested by running the reverse of water splitting in a fuel cell to generate water and electricity as the desired products, Figure 1.3 right.\(^{18}\)
Figure 1.3. Wireless water splitting device composed of a solar harvesting (photovoltaic “PV” or photoelectrochemical “PEC”) assembly that absorbs sunlight to create electron/hole pairs along with a water oxidation catalyst that evolve oxygen using the holes and water reduction catalyst that evolve hydrogen using the electrons (left). Fuel cell assembly that oxidizes hydrogen at the anode and reduces oxygen at the cathode to provide water and electricity as products (right). The combination of both devices provides a comprehensive solar energy storage system.

The carbon-free cycle in Figure 1.3 is very attractive especially that it has the potential to provide energy security for future generations. To deploy hydrogen as a commercial fuel is challenging from a scientific and practical point of view especially that all processes involved in the scheme have to be collectively cost-effective.\(^7\) This includes production, storage, delivery and fuel cells.\(^7\) In the Castellano laboratory, we are working on the solar fuels production side of the problem. Theoretically, photons with \(\lambda < 1008\) nm are energetically poised to split water into hydrogen and oxygen.\(^9,17\) Practically, water doesn’t absorb in the UV-Vis part of the spectrum, it only absorbs the IR (low energy photons) and deep-UV light (very high energy photons).\(^9,17\) IR radiation is usually converted into heat, and very deep-UV energy is not provided by the sun
since it is filtered by atmospheric gases (AM 1.5G spectrum). For these reasons, the development of molecular systems and materials capable of efficient solar light harvesting and conversion of the $e^-/h^+$ equivalents to split water is required.$^9,17$

1.3 PHOTOCATALYTIC WATER SPLITTING ON THE SURFACE OF SEMICONDUCTORS

Besides the challenges to find systems that can energetically split water (equation 1-3), the two redox reactions have to be kinetically balanced in order to make the products at significant rates. For this purpose, efficient and earth-abundant water oxidation catalysts (WOCs) and water reductions catalysts (WRCs) have to be developed and engineered to work in tandem with the other components of the fuel producing system.$^{19,20}$ Figure 1.4 represents a simple architecture of a system comprised of a semiconductor decorated with co-catalysts that theoretically is capable of water splitting.$^{21}$ Upon photoexcitation, the conduction band electrons should be energetic enough to induce hydrogen evolution from a WRC and the valence band oxidizing enough to relay holes to a WOC. Titania for example represents an earth abundant and stable semiconductor that has good energetics in water. Chapter 2 will address the practical advantages of growing nanoscopic platinum based WRCs on the surface of titania (TiO$_2$) from a novel Pt(II) surface anchored precursor. In the work presented in Chapter 2, methanol was used to scavenge holes at a fast rate in order to better understand the kinetics of water reduction occurring on the surface of TiO$_2$. 
Figure 1.4. Direct solar to hydrogen energy conversion from semiconductor nanoparticles (black) suspended in water and decorated with water oxidation catalyst (grey) and water reduction catalyst (orange).

1.4 PHOTOELECTROCHEMICAL WATER SPLITTING

Despite the ease of using a suspension of heterogeneous photocatalysts to split water (Figure 1.4), challenging problems arise like charge recombination and gaseous product separation.21 Another system can be applied based on the concept of separating the two half reactions (Eqs. 1-2) to occur in two different compartments, Figure 1.5.9,22 The photoanode part of the photoelectrochemical device is typically composed of an n-type semiconductor responsible for oxygen evolution with the aid of a WOC.23 The cathode part can operate in the dark when utilizing a Pt counter-electrode for example, or it can be composed of a p-type semiconductor24 having absorbance complimentary to the photoanode (Figure 1.5).22 The
photocathode is commonly responsible for hydrogen evolution with the aid of WRC on the surface. Energetically, the valence band holes of the photoanode should oxidize water and the conduction band electrons of the photocathode (if utilized) should reduce water.\textsuperscript{22} Chapter 3 of this dissertation will focus on the photochemical growth and characterization of cobalt based WOCs on the surface of TiO\textsubscript{2} photoanode.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cell_diagram.png}
\caption{General scheme of a photot electrochemical cell composed of an n-type semiconductor photoanode and a p-type photocathode in direct contact with water.}
\end{figure}

\section*{1.5 PHOTON UPCONVERSION TO ENHANCE THE PHOTOACTION OF SEMICONDUCTORS}

The major drawback of using TiO\textsubscript{2} is its wide bandgap ~ 3.0-3.2 eV which restricts its photoaction spectrum to the UV region (< 5\% of the solar spectrum).\textsuperscript{22} Other wide bandgap
semiconductors like WO$_3$ (~ 2.7 eV) also possess high efficiency when utilized as photoanodes.\textsuperscript{22} Several strategies have been developed to mitigate the problem of light absorption in such materials, most of which impose a chemical modification of the semiconductor like dye sensitization.\textsuperscript{12} An interesting approach to this problem was presented by our group termed upconversion (UC) where light of low energy can be converted to higher energy through a regenerative photochemical process.\textsuperscript{25} Scheme 1 represents the generalized Jablonski diagram of the UC process. This scheme can readily furnish appropriate photon energy to sensitize semiconductors below their respective bandgaps. The process is initiated when the photosensitizer (PS) chromophore absorbs low energy photons and internally converts (intersystem crossing, ISC) to the long-lived lowest energy triplet excited state ($^3$PS*). The initial formation of triplet sensitizer can occur in certain type of chromophores with quantum efficiency close to unity (\(\Phi_{\text{ISC}} \sim 1\)). Then, Dexter-type triplet-triplet energy transfer (TTET) occurs to an acceptor molecule to produce the excited triplet acceptor ($^3$A*). When the concentration of $^3$A* is sufficient, triplet-triplet annihilation (TTA) occurs and the desired high energy fluorescence from the singlet acceptor ($^1$A*) is produced.\textsuperscript{25} Transition metal-based photosensitizers with high spin-orbit coupling are commonly used in conjunction with a variety of strongly emitting organic-based acceptors/annihilators in solution or in polymer films. In Chapter 4, we provide a proof-of-concept that UC can sensitize semiconductors below their bandgap energies. Different strategies aimed at achieving considerable efficiency under solar irradiance are also presented.
Scheme 1.1. Generalized Jablonski diagram of the sensitized photon upconversion process. Straight lines indicate radiative events whereas dashed and wavy lines indicate non-radiative processes.

1.6 Z-SCHEME OF PLANTS

Besides materials, researchers have been interested in the development of molecular systems capable of water splitting. Learning from examples in nature, precisely from photosynthesis in plants, different homogeneous approaches have been developed to mimic the complex molecular water splitting reaction. In plants, NADP$^+$ (nicotinamide adenine dinucleotide phosphate) cofactor is reduced to NADPH by electrons supplied from Photosystem I and water is oxidized by a CaMn$_4$O$_4$ catalyst utilizing holes supplied from Photosystem II, Figure 1.6. The overall processed is referred to as the Z-scheme where electron transfer is regulated by a series of redox mediators like plastoquinone, cytochrome f and plastocyanine, Figure 1.6. To the best of our knowledge, there is no efficient photocatalytic artificial water splitting molecular systems that can simultaneously reduce and oxidize water to date.
1.7 HOMOGENEOUS WATER SPLITTING

Figure 1.7 represents a schematic diagram of the mechanism of photocatalytic hydrogen evolution from a mixture of photosensitizer (PS) electron donor (D) and a molecular cobalt water reduction catalyst (Co).\textsuperscript{11,17} The electron donor, in the ideal case, is a WOC or an electron relay that can transfer the holes equivalents to a WOC. Practically water oxidation is a very slow process and sacrificial electron donors like tertiary amines and ascorbate are commonly used as surrogates for water oxidation having faster electron transfer.

Two mechanisms for the initial electron transfer leading to photocatalytic hydrogen production are plausible, the reductive and oxidative quenching pathway, Figure 1.7.\textsuperscript{9,11,17} In the reductive quenching mechanism, an electron is delivered from an electron donor (D) into the excited PS (PS\textsuperscript{*}), producing the reduced ground state PS (PS\textsuperscript{-}) and oxidized donor (D\textsuperscript{+}). Then,
the PS\(^{-}\) delivers an electron in the dark to the catalyst or to an electron relay (R) which ultimately reduces the WRC. Ascorbic acid (H\(_2\)A)/ascorbate (HA\(^{-}\)) oxidation to dehydroascorbate (A) which is proton coupled (H\(_2\)A \(\rightarrow\) A + 2e\(^{-}\) + 2H\(^{+}\)) along with hydrogen production is an interesting process because it represents a total energy storage of \(\sim 0.41\) V at pH 4, Eqs. 4-7.\(^{26,27}\) Dehydroascorbate is usually hydrated and subsequently converted irreversibly to other species.

\[
\begin{align*}
H_2A & \rightarrow HA^- + H^+ \quad [4] \\
2PS + 2 HA^- & \rightarrow 2 PS^- + 2 HA^\cdot \quad [5] \\
2 HA^\cdot & \rightarrow H^+ + HA^- + A \quad [6] \\
\hline
H_2A + 2PS & \rightarrow 2 PS^- + 2H^+ + A \quad [7]
\end{align*}
\]

Alternatively, in the oxidative quenching mechanism, an electron is directly transferred from the PS\(^{\ast}\) to the relay or to the WRC. Then, the oxidized ground state sensitizer (PS\(^{\ast}\)) can be reduced by D in the dark. The electron equivalents generated by either mechanism are commonly transferred to a WRC-molecular cobalt catalyst for example, Figure 1.7. The Co(II) catalyst was shown to evolve hydrogen either homolytically or heterolytically as depicted by Figure 1.7.\(^{11,19,28,29}\) In the homolytic mechanism, one electron and one proton equivalents are transferred to a cobalt center and hydrogen is typically evolved by the bimolecular reaction of two cobalt hydride complexes. In the heterolytic mechanism, two electrons and two protons are delivered to the same cobalt center and hydrogen is produced from a typical dihydrogen-cobalt \(\sigma\) complex.\(^{11}\) In both the homolytic and the heterolytic mechanism, sequential electron and proton transfer occurs at the cobalt center, and the order followed is strongly dependant on the catalyst and the conditions used.
Figure 1.7. Photocatalytic mechanisms of hydrogen production from molecular photosensitizer (PS) and cobalt water reduction catalyst (Co). The electrons are initially transferred to the PS by the oxidative or reductive quenching mechanism then electrons and protons are relayed to the cobalt center that can undergo the homolytic or heterolytic pathway to evolve hydrogen.

The difference between the reductive quenching and oxidative quenching pathways in transition-metal sensitized hydrogen production is energetically important and often not well explained in the literature. If we take the prototypical tris(bipyridine) ruthenium(II) ([Ru(bpy)_3]^{2+}) PS, the absorption in the visible region is attributed to a typical charge transfer from a t_{2g} metal orbital to a \(\pi^*\) orbital of the bipyridine ligand (t_{2g} \rightarrow t_{2g} \pi^*). The charge transfer excited state (PS*) has redox potentials different than the ground state PS. These potentials are estimated by the Rehm-Weller equation (Eqs. 8-9):
\[ E[\text{LL}^0/-(\text{Ru}^{3+})] = E[\text{Ru}^{3+/2+}(\text{LL})] - E_{00} \quad [8] \]
\[ E[\text{Ru}^{3+/2+}(\text{LL})] = E[\text{LL}^0/-(\text{Ru}^{2+})] + E_{00} \quad [9] \]

\( E_{00} \sim 2.1 \text{ V} \) is the energy difference between the lowest lying charge transfer excited state and the ground state, \( E[\text{LL}^0/-(\text{Ru}^{3+})] \) is the excited state oxidation potential (removal of electron from the lowest singly occupied ligand orbital in the excited state, -0.84 V vs NHE in H\(_2\)O), \( E[\text{Ru}^{3+/2+}(\text{LL})] \) is the ground state oxidation potential (removal of an electron from the metal orbital in the ground state, + 1.26 V vs NHE in H\(_2\)O), \( E[\text{Ru}^{3+/2+}(\text{LL}^-)] \) is the excited state reduction potential (addition of electron to the lowest singly occupied metal orbital in the excited state, + 0.84 V vs NHE in H\(_2\)O) and \( E[\text{LL}^0/-(\text{Ru}^{2+})] \) is the ground state reduction potential (addition of an electron to the ligand orbital in the ground state, -1.26 V in H\(_2\)O), Figure 1.8.\(^{32,35}\)

As a result, the initial electron transfer in both the oxidative and reductive quenching mechanism has to be initiated from \(^*\)[Ru(bpy)\(_3\)]\(^{2+}\) because the excited state is relatively easier to reduce and oxidize than the ground state by 2.1 V, Figure 1.8 left. In [Ru(bpy)\(_3\)]\(^{2+}\) and related Ru(II) molecules, reductive quenching yields a PS\(^-\) species which is \(\sim 0.4-0.5 \text{ V} \) more reducing than PS\(^*\). Also, upon oxidative quenching PS\(^+\) species is generated which is \(\sim 0.4-0.5 \text{ V} \) more oxidizing than PS\(^*\), Figure 1.8 right.\(^34\) Chapter 5 is dedicated to investigations of different molecular compositions for photocatalytic hydrogen production utilizing a high-throughput screening method intended to glean insight into the experimental factors related to proton reduction in these compositions.
Figure 1.8. Free energy diagram of [Ru(bpy)$_3$]$^{2+}$ electron transfer deactivation from the excited state to the ground state (left). Relative redox potentials and corresponding energies of the electrons (e$^-$) and holes (h$^+$) in the ground and excited state (right).

1.8 REFERENCES


CHAPTER II

DEPOSITION AND PHOTOCATALYTIC ACTIVITY OF TITANIA-SUPPORTED PLATINUM NANOCLUSTERS DERIVED FROM SURFACE-ANCHORED MOLECULAR PRECURSORS


2.1 ABSTRACT

Degussa P-25 TiO$_2$ bearing surface-anchored Pt(dcbpy)Cl$_2$ [dcbpy = 4,4’-dicarboxylic acid-2,2’-bipyridine] prepared with systematically varied surface coverage produced Pt$^0$ nanoparticles under bandgap illumination in the presence of methanol hole scavengers. Energy dispersive X-ray spectroscopy confirmed the presence of elemental platinum in the newly formed nanoparticles during scanning transmission electron microscopy (STEM) experiments. According to the statistical analysis of numerous STEM images, the Pt$^0$ nanoclusters were distributed in a segregated manner throughout the titania surface, ranging in size from 1 to 3 nanometers in diameter. The final achieved nanoparticle size and net hydrogen production were determined as a function of the Pt(dcbpy)Cl$_2$ surface coverage as well as other systematically varied experimental parameters. The hybrid Pt/TiO$_2$ nanomaterials obtained upon complete
decomposition of the Pt(dcbpy)Cl₂ precursor displayed higher photocatalytic activity (300 µmol/hr) for hydrogen evolution in aqueous suspensions when compared with platinized TiO₂ derived from H₂PtCl₆ precursors (130 µmol/hr), as ascertained through gas chromatographic analysis of the photoreactor headspace under identical experimental conditions. The conclusion that H₂ was evolved from Pt⁰ sites rather than from molecular Pt(dcbpy)Cl₂ entities was independently supported by Hg and CO poisoning experiments. The formation of small Pt nanoparticles (1.5 nm in diameter) prevail at low surface coverage of Pt(dcbpy)Cl₂ on TiO₂ (0.5-2% by mass) that exhibit enhanced turnover frequencies with respect to all other materials investigated, including those produced from the in-situ photochemical reduction of H₂PtCl₆. Pt¹¹ precursor absorption in the ultraviolet region appeared to be partly responsible for attenuation of the H₂ evolution rate at higher Pt(dcbpy)Cl₂ surface coverage. The nanoparticle size and hydrogen evolution characteristics of the surface-anchored materials generated through photodeposition were directly compared to those derived from chemical reduction using NaBH₄. Finally, Degussa P-25 thin films deposited on FTO substrates enabled electrochemically-induced (-1.0 V vs. Ag/AgCl, pH = 7.0, phosphate buffer) electron trapping (TiO₂(e⁻)) throughout the titania. After removal of the applied bias and the anaerobic introduction of Pt(dcbpy)Cl₂, the accumulated electrons reduce this molecular species to Pt⁰ nanoparticles on the titania electrode surface, as confirmed by TEM measurements, with the concomitant production of H₂ gas. The combined experiments illustrate that TiO₂(e⁻), generated with bandgap excitation or via electrochemical bias affords the reduction of Pt(dcbpy)Cl₂ to Pt⁰ nanoparticles that in turn are responsible for heterogeneous hydrogen gas evolution.
2.2 INTRODUCTION

The utilization of solar photons for the generation of energy-rich chemical fuels from abundant energy-deficient molecules requires the development of new catalytic systems and redox assemblies.\textsuperscript{1-5} Of particular interest is the utilization of sunlight to produce H\textsubscript{2} by the reduction of water, thereby providing an environmentally sensible fuel from naturally-abundant precursors.\textsuperscript{1-9} The challenge in designing catalysts to promote these reactions lies in the fact that single photon driven electron transfer must somehow be coupled to a multi-electron fuel-forming step. In other words, the reduction of protons to H\textsubscript{2} requires the coupling of two protons and two electrons to produce one molecule of the desired combustible fuel. The catalyst serves to bring all reacting species together, permits H\textsubscript{2} evolution, and must ultimately be regenerated to repeat the sequence. Surprisingly, efficient photo-initiated multi-electron-transfer chemistry remains largely unrealized in photocatalysis despite decades of research on the subject. The use of metal complexes as molecular photocatalysts for hydrogen evolution in homogeneous systems has gained widespread popularity due to both fundamental mechanistic questions and its possible transformative potential.\textsuperscript{10-15} Originally, we were inspired by the notion that molecular catalysts could be readily linked to heterogeneous nanoparticles to yield materials that both absorb light and drive the 2-electron reduction of protons to hydrogen gas. During the course of this work, evidence began accumulating that molecular Pt- and Pd-containing complexes were susceptible to photolytic reduction, forming their corresponding metallic nanoparticles, which were ultimately responsible for the majority of H\textsubscript{2} evolution observed in these systems.\textsuperscript{16,17} This was not too surprising given the fact that Finke and coworkers previously also noted that the molecular Pt\textsuperscript{II} species Pt(1,5-COD)Cl\textsubscript{2} and Pt(1,5-COD)(CH\textsubscript{3})\textsubscript{2} (COD is 1,5-cyclooctadiene) both form Pt\textsuperscript{0} nanoclusters in situ, the latter being ultimately responsible for substrate
hydrogenation catalysis.\textsuperscript{18,19} During the course of these studies, we linked Pt(dcbpy)Cl\textsubscript{2} (dcbpy is 4,4'-dicarboxy-2,2-bipyridine), originally believed to be a viable molecular hydrogen evolution catalyst,\textsuperscript{10-15} to the surface of Degussa P-25 TiO\textsubscript{2}, which serve as electron storage reservoirs in the presence of bandgap excitation and appropriate hole scavengers such as methanol.\textsuperscript{20} While these composites were indeed superior hydrogen-evolving photocatalysts when directly compared to more conventional materials, they did not function via molecular chemistry at the surface-anchored Pt\textsuperscript{II} complexes.\textsuperscript{20} Rather, the Pt\textsuperscript{II} complexes served as molecular precursors that yielded highly segregated nanoscopic Pt\textsuperscript{0} particles decorating the TiO\textsubscript{2} surface and formed from bandgap illumination. Notably, this system has been used for aerobic water detoxification under visible-light illumination where the Pt\textsuperscript{II} complex acted as a dye sensitizer that injected electrons into titania initiating a cascade of mineralizing decomposition chemistry of the prototypical 4-chlorophenol.\textsuperscript{21}

The work related to nanoparticle-based photodeposition served as a caveat to researchers employing noble metal-containing complexes as H\textsubscript{2} generating catalysts that photodecomposition of these complexes could in fact occur and that the identity of the true catalysis needs to be rigorously addressed. The present study revealed that surface-bound molecular Pt(dcbpy)Cl\textsubscript{2} complexes were photochemical precursors to segregated Pt\textsuperscript{0} nanomaterials that displayed enhanced hydrogen evolution from TiO\textsubscript{2} surfaces under bandgap illumination. We view this latter result as significant since the electrocatalytic activity of platinum clusters toward the four-electron reduction of oxygen to water has recently been demonstrated to exhibit drastic size-dependent behavior; smaller nanoparticles (1-1.2 nm in diameter) promote enhanced catalytic activity.\textsuperscript{22} Variation in Pt\textsuperscript{0} particle size may indeed be the reason for the wide variation of H\textsubscript{2} evolution rates we observed as a function of Pt(dcbpy)Cl\textsubscript{2}
surface coverage on TiO$_2$ in the original study,\textsuperscript{20} and the current effort develops this concept further through photochemical, chemical, and electrochemical reduction processes to prepare nanoscopic Pt$^0$ clusters on the surface of titania. We chose these three distinct reduction methods based on previous work by Pichat and coworkers who extensively studied the nanoscopic deposition of Pt on TiO$_2$ prepared from a variety of co-dissolved precursors.\textsuperscript{23-25} It should also be noted that the ligands present in the Pt(dcbpy)Cl$_2$ precursor likely help stabilize the resultant Pt$^0$ nanoparticles distributed on the titania surface. The nature of the titania support renders any surface study of the Pt$^0$ sites experimentally tedious, therefore, research on the aqueous suspended nanoparticles is underway to better understand the nature of the analogous materials produced on titania.\textsuperscript{18,26-29} We clearly demonstrate from heterogeneous poisoning experiments\textsuperscript{30,31} that hydrogen-evolving catalytic activity in these hybrid materials emanate from the nanoparticulate catalysts rather than molecular compounds. The combined data revealed that the H$_2$ evolution yields monitored as a function of Pt(dcbpy)Cl$_2$ surface coverage could be rationalized in terms of three distinct variables: (1) the mass of Pt$^0$ deposited, (2) the Pt$^0$ nanoparticle size, and (3) undecomposed Pt$^{II}$ precursors in competition for the absorption of TiO$_2$ bandgap photons.\textsuperscript{32,33}

2.3 EXPERIMENTAL SECTION

2.3.1 General. $^1$H NMR spectra were recorded on a Bruker Avance 300 (300 MHz) or Bruker Avance III 500 (500 MHz) spectrometer. All chemical shifts were referenced to the residual solvent signals and splitting patterns were designated as s (singlet) or d (doublet). UV-Vis absorption spectra were measured on a Cary 50 Bio spectrophotometer. A VWR 75HT sonicator
was used to sonicate the colloidal suspensions. Raman spectra were acquired on a Renishaw inVia Raman Microscope using 442 nm He-Cd Laser excitation, and IR spectra were measured using a FT-IR spectrometer (JASCO FT/IR-4100) equipped with an ATR accessory. All electrochemical measurements were performed using a BAS Epsilon electrochemistry workstation using a traditional three electrode arrangement.

2.3.2 Materials. P-25 TiO$_2$ (ca. 80% anatase, 20% rutile; BET area, ca. 50 m$^2$g$^{-1}$) was obtained from Degussa and used as received. Potassium tetrachloroplatinate, hexachloroplatinic acid hexahydrate, 4,4’-dimethyl-2,2’-bipyridine, and sodium borohydride (NaBH$_4$) were purchased from Aldrich and used without further purification. Fluorine doped tin oxide (FTO) conducting glass substrates (TEC 15) were purchased from Hartford Glass. Water was deionized using a Barnstead nanopure system. All reagent grade solvents and reactants were used as received. cis-Pt(DMSO)$_2$Cl$_2$ was synthesized in 90% yield according to the established literature procedure.

2.3.3 TiO$_2$ Film formation. FTO conducting glass substrates were cleaned by sonication using a solution of HCl in isopropanol, a solution of soap in water, then finally acetone. The FTO glass was then dried in an oven. A mixture of 3:1 by volume H$_2$O:CH$_3$COOH (glacial acetic acid) was mixed slowly with TiO$_2$ (Degussa P-25) (12 wt.%) and hydroxypropylcellulose (6 wt.%). This mixture was sonicated and stirred vigorously overnight. The resultant paste was doctor bladed on FTO glass between 3 Scotch tape layers resulting in a material with ~20 µm thickness and a TiO$_2$ electrode area of 1 cm$^2$. The electrode was sintered at 500°C for 30 minutes at a heating rate of 5°C per min and finally cooled to room temperature.
2.3.4 Synthesis and materials production.

2.3.4a Pt(dcbpy)Cl₂. This complex was synthesized according to a slightly modified literature procedure. 4,4’-Dicarboxy-2,2’-bipyridine (dcbpy) was prepared as described in the literature from 4,4’-dimethyl-2,2’-bipyridine. A suspension of 98 mg dcbpy and 212 mg of cis-Pt(DMSO)₂Cl₂ were mixed with 40 mL of methanol and refluxed for 8 hours in an oil bath at 80°C. The yellow solid was filtered, washed with methanol, hot ethanol, and then dried under vacuum (77% yield). Anal. calcd for C₁₂H₈Cl₂N₂O₄Pt: C, 28.25; H, 1.58; N, 5.49; Found: C, 28.53; H, 1.81; N, 5.09. ¹H NMR (300 MHz, (CD₃)₂SO, ppm), δ: 9.72 (d, J = 6 Hz, 2H), 9.04 (s, 2H), 8.24 (d, J = 5.7 Hz, 2H). ¹H NMR (500 MHz, D₂O-NaOD, ppm), δ: 8.50 (d, J = 6 Hz, 2H), 8.09 (s, 2H), 7.60 (d, J = 5.8 Hz, 2H). FT-IR (ATR, ν (cm⁻¹)): 1730, 1619, 1553, 1440, 1412, 1320, and 1233. Raman spectroscopy (neat powder, λₑₓ = 442 nm): ν = 1730, 1619, 1553, 1440, 1412, 1320, and 1233. 

2.3.4b Pt(dcbpy)Cl₂/TiO₂ Compositions. Pt(dcbpy)Cl₂/TiO₂, 1% by mass, was synthesized according to the following procedure: 1 mg of Pt(dcbpy)Cl₂ was dissolved in 15 mL of water with 50 µL of 0.1 M KOH in a round-bottom flask equipped with a stir bar. 100 mg of TiO₂ (Degussa P-25) was added slowly to the solution, sonicated for 1 minute, then stirred for 24 hours at room temperature. The mixture was centrifuged (10 minutes, 10,000 RPM), to separate the solid and liquid phases. Afterwards, the solution was filtered through a 0.2 µm filter several times to remove the suspended particles, and the absorption spectrum of the filtrate was analyzed to calculate the amount of Pt(dcbpy)Cl₂ (λ = 377 nm, ε = 2770 M⁻¹cm⁻¹) that was adsorbed on the surface of TiO₂. The final obtained solid was then dried under vacuum.
To prepare other Pt(dcbpy)Cl$_2$/TiO$_2$ surface coverage, the amount of Pt(dcbpy)Cl$_2$ and 0.1 M KOH added were systematically varied. In routine practice, the minimum amount of base (0.1 M KOH) required to completely dissolve Pt(dcbpy)Cl$_2$ was utilized as excess base facilitates desorption of the surface-anchored species. The following percentages by mass were achieved and further characterized: 0.5%, 1%, 2%, 4.27% and 7.05%. All surface coverage loadings cited in this chapter are by mass equivalents on TiO$_2$ unless otherwise stated.

2.3.5 Photocatalytic Hydrogen Production

2.3.5a Pt(dcbpy)Cl$_2$/TiO$_2$ photodeposition (PD).\textsuperscript{20} Photocatalytic reactions were performed in a 50 mL Pyrex round-bottom flask equipped with a stir bar. All mixtures were sonicated for 1 minute before photodeposition, and stirred at the same speed during the measurements. A suspension of 25 mg of the Pt(dcbpy)Cl$_2$/TiO$_2$ catalyst at a specific % loading by mass and 25 mL methanol:water (1:6 by volume) was degassed using the freeze pump thaw technique and maintained under argon atmosphere in a gas tight Schlenk line directly linked to a gas chromatograph (GC, Shimadzu GC-8A, argon carrier gas, 5 Å molecular sieve column (Restek), thermal conductivity detector, 0.5 mL gas sample injection, calibrated against known H$_2$/argon gas mixtures). Under our experimental conditions, the retention time of H$_2$ was 1.5 minutes, well separated from N$_2$ and O$_2$. Detection of CO$_2$ from the reaction headspace was accomplished using a different custom-made column for gas separation (Supelco). The excitation light source was the broadband output of a 300 W Xe arc lamp (Oriel). The broadband incident power on the reactor was approximately 1 W/cm$^2$. The suspension was subjected to continuous band gap irradiation for 5 hours and hydrogen evolution was analyzed throughout the photolysis. The temperature of the suspension after photocatalysis was consistently \( \geq 50 \) °C. The solid was then
collected by centrifugation (10 minutes, 10,000 RPM). The TiO₂ powder isolated after catalysis had a grey color at 1% and 2% loading and yellowish grey (yellow due to remnant undecomposed Pt(dcbpy)Cl₂) at higher % loading (see Supporting Information for photographs). The solid was examined by STEM to measure the Pt nanoparticle size. The remaining molecular Pt\textsuperscript{II} complexes on the surface of TiO₂ was quantitatively desorbed by treatment with 0.1 M KOH and the resultant absorption spectra were used to quantify the amount of undecomposed Pt\textsuperscript{II} precursors and the associated absorbance/transmittance in the UV region. Pt\textsuperscript{II} precursors desorbed from TiO₂ appear to speciate in the presence of 0.1 M KOH, a behavior well established for similar Pt\textsuperscript{II} complexes.\textsuperscript{37-41} Explicit details regarding the quantification of desorbed Pt\textsuperscript{II} molecules are presented in the Supporting Information. The following percentages of Pt(dcbpy)Cl₂ decomposed on TiO₂ (by mass) after 5 hours of photoreaction/catalysis were determined: 0.4% at 0.5% loading; 0.77% at 1% loading, 1.1% at 2% loading, 1.1% at 4.27% loading and 0.7% at 7.05% loading, see Figure 2.3b. Complete decomposition of the Pt(dcbpy)Cl₂ precursor was only observed in samples with ≤ 2% loading under prolonged photolysis (> 7 hrs), verified by negligible absorbance of desorbed Pt species in the near-visible region. For the Hg poisoning test, which selectively suppresses the hydrogen evolution from heterogeneous noble metal surfaces, the identical experimental setup was used but with the addition of 3 mL of liquid Hg to the reaction mixture.

2.3.5b Benchmark Platinized TiO₂ (Benchmark Photodeposition).\textsuperscript{25,42} Benchmark photodeposited Pt/TiO₂ materials derived from a traditional non-surface-anchored precursor, H₂PtCl₆·6H₂O, were prepared according to a slightly modified literature procedure. In a 50 mL Pyrex round-bottom flask, 100 mg of P-25 TiO₂ was suspended by sonication in a mixture of methanol:water (1:6 by volume). One mg of hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) was dissolved
in the same solvent mixture, added to the TiO$_2$, and stirred for 15 minutes in the dark. The combined suspension was degassed using the freeze-pump thaw technique then argon gas was introduced above the solution. The mixture was irradiated for 5 hours using a 300 W Xe arc lamp (Oriel). The resulting grayish solid was collected by centrifugation washed with water and methanol then dried under vacuum. 12 mg of the resultant solid was used to measure hydrogen evolution and compared with 12 mg Pt(dcbpy)Cl$_2$/TiO$_2$ 1% isolated after complete photodeposition, using the same procedure described above, and STEM of the powders were taken. The full decomposition of H$_2$PtCl$_6$ was indicated by the negligible absorption of the supernatant after 5 hours of continuous photolysis. Since Pt(dcbpy)Cl$_2$ and H$_2$PtCl$_6$6H$_2$O have comparable molecular weights, the weight percent of Pt metal is approximately the same in both cases (~0.4 wt% Pt in 1% by mass sample).

2.3.5c Pt(dcbpy)Cl$_2$/TiO$_2$ Chemical Deposition (CD). 50 mg of Pt(dcbpy)Cl$_2$/TiO$_2$, 1% by mass, was suspended in 25 mL of pure methanol containing a large excess of NaBH$_4$ (2 mg). The chemical reduction of Pt(dcbpy)Cl$_2$ into Pt nanoparticles was vigorous; the resulting grayish solid was collected by centrifugation after 5 hours, washed with methanol, dried under vacuum, and STEM of the powder was taken. 12 mg of the resultant solid was used to measure hydrogen evolution and compared with 12 mg Pt(dcbpy)Cl$_2$/TiO$_2$ 1% isolated after complete photodeposition, using the same procedure described above.

2.3.5d CO Poisoning. Since CO is a highly toxic gas, the CO poisoning test was performed in a well vented fume hood. 10 mg of 1% by mass Pt(dcbpy)Cl$_2$/TiO$_2$ isolated after 5 hours photodeposition in 10 mL of methanol:water (1:6 by volume) was degassed for 30 minutes with argon bubbling in an airtight vial. Another vial containing the same composition was bubbled
with CO for 30 minutes and maintained under 1 atm of CO. Both vials were stirred at the same spin rate and irradiated with a 300 W Xe arc lamp (Oriel) whose output was sent through bifurcated optical fibers (Oriel) to simultaneously yield 200 mW/cm² incident power density on each reactor. The hydrogen was detected from the headspace; samples of gas were taken at different time intervals using a 100 µL gastight syringe (Hamilton) and analyzed using the GC system described above.

2.4 MATERIALS CHARACTERIZATION

Scanning transmission electron microscopy (STEM) data for the Pt nanoparticles were obtained with a JEOL 2010F operating in darkfield STEM mode at 200 keV. Dried Pt/TiO₂ samples were resuspended in ~200 µL of DI H₂O and ~20 µL of this solution was drop-casted onto holey carbon TEM grids and then dried under ambient laboratory conditions. High-resolution images were acquired with a JEOL model 2200-FS electron microscope operated at 200 keV. EDS scans were acquired with a 50 mm² Oxford INCA detector on the 2200FS. High-resolution transmission electron microscopy (HR-TEM) measurements were carried out using a JEOL 3011UHR or 2010 transmission electron microscopes, operated at 300 and 200 kV, respectively. Data were collected by the Murphy group at UIUC.

2.5 RESULTS AND DISCUSSION

Pt(dcbpy)Cl₂ was designed to surface anchor on TiO₂ nanoparticles owing to the carboxylic acid groups present on 4,4’-dicarboxylic acid-2,2’-bipyridine (dcbpy) ligand. This
yellow complex exhibits a modest extinction coefficient at its absorption peak in the near-visible (λ = 377 nm, ε = 2770 M⁻¹ cm⁻¹) which overlaps the titania band edge. This creates a situation where Pt(dcbpy)Cl₂-induced absorbance of bandgap excitation can have a pronounced effect on the resultant material. Minute amounts of aqueous base deprotonates the acids forming carboxylates, promoting the solubility of this complex in water. After stirring mixtures containing Pt(dcbpy)Cl₂ in water and TiO₂, Pt(dcbpy)Cl₂ adsorbed onto TiO₂ was readily obtained, whose loading by mass was easily determined by adsorption isotherms derived from UV-Vis spectra of the supernatant solutions. When required, 0.1 M KOH was used to desorb surface-anchored PtⅡ species (see Supporting Information for more details). The various Pt(dcbpy)Cl₂/TiO₂ materials were tested for hydrogen production upon TiO₂ bandgap excitation (3.0-3.2 eV) in the presence of hole scavengers, which resulted in the photodeposition of Pt⁰ nanoparticles in all instances. Alcohols such as methanol and ethanol have been widely used as hole scavengers due to the thermodynamic and kinetic favorability of alcohol oxidation by TiO₂ valence band holes.¹⁷,⁴³-⁴⁶ In the current work, we used aqueous media composed of 1:6 MeOH:H₂O by volume for all the photocatalytic hydrogen-evolving experiments. These experimental conditions ensured efficient hole scavenging during bandgap illumination that positioned the composition to accumulate electrons at titania, termed TiO₂(e⁻) throughout this chapter. In some instances, Pt⁰ nanoparticles were formed via chemical deposition using direct NaBH₄ reduction of select Pt(dcbpy)Cl₂/TiO₂ compositions, which were compared to the corresponding photodeposited materials.

Atomic resolution STEM images of the 1% Pt(dcbpy)Cl₂/TiO₂ sample after 5 hours of bandgap illumination indicated the presence of Pt nanoparticles (distinguishable as bright areas in Figure 2.1a), with characteristic lattice fringes indexed to the fcc (111) crystal phase. The
high-resolution image in Figure 2.1a confirms that the lattice spacing is 2.2 Å, whereas the expected value for Pt(111) is $a/\sqrt{3}$ (2.26 Å), where $a$ (3.92 Å) is the lattice constant of bulk Pt.\textsuperscript{47} Statistical analysis of multiple STEM images revealed that the formed nanoparticles at 1% loading were approximately 1.5 nm in diameter, with a size dispersion of ± 0.2 nm. Energy dispersive X-ray spectroscopy (EDX) measurements confirmed the presence of elemental platinum in these particles, Figure 2.1b. Most of the remaining signals emanated from the holey carbon substrate and the TiO\textsubscript{2} support.

![Figure 2.1](image)

**Figure 2.1.** (a) Atomic resolution STEM of 1% Pt(dcbpy)Cl\textsubscript{2}/TiO\textsubscript{2} after 5 hours of bandgap illumination, showing nanoscopic platinum particles with high crystallinity indexed to the fcc (111) crystal face, with lattice spacing of 2.2 Å. (b) EDX measurement of the same sample indicating the presence of platinum. Data were collected by the Murphy group at UIUC.

Figure 2 presents the hydrogen evolved versus irradiation time measured as a function of Pt(dcbpy)Cl\textsubscript{2} catalyst precursor (mass percent) originally loaded onto the TiO\textsubscript{2} surface. These samples contained 25 mg of each Pt(dcbpy)Cl\textsubscript{2}/TiO\textsubscript{2} composition suspended in 25 mL of MeOH:H\textsubscript{2}O (1:6), ultimately subjected to 300 W broadband Xe lamp illumination. It is important to note that the precursor loading in these samples does not represent the final Pt nanoparticle catalyst loading; the latter is quantified from surface desorption of remnant Pt\textsuperscript{II}
molecular species subsequent to 5 hours of continuous photocatalysis. The hydrogen evolution yield increases with decreasing surface coverage, exhibiting optimal performance with the 1-2% Pt(dcbpy)Cl₂/TiO₂ composition, Figure 2.2. The first hour of hydrogen evolution in the in-situ photodeposited materials was characterized by a slightly lower rate than the later time periods, behavior attributed to an induction period necessary to form the catalytically active Pt nanoparticles, Figure 2.2. For this reason, the turnover frequency calculation (TOF = [mol H₂ produced] × [mol decomposed Ptⁿ⁺ precursors]⁻¹ × s⁻¹) is reported over the time range between 1 and 5 hours for these in-situ photodeposited materials, Table 2.1. The 0.5% loading was characterized by a lower hydrogen evolution rate (240 µmol/hr) relative to the 1-2% loading (800 µmol/hr). This observation can be rationalized by the lower surface coverage of the Pt catalyst on TiO₂ at loadings below 1%. Related previous optimized systems require the use of ~0.5-1 wt% Pt on TiO₂ to achieve optimal catalysis, and when translated into the current composition mandates 1-2% by mass Pt(dcbpy)Cl₂ on TiO₂.²⁰,²¹,²⁵,⁴³

![Graph](image_url)

**Figure 2.2.** Photochemical hydrogen evolution from 25 mg of Pt(dcbpy)Cl₂/TiO₂ at varied initial surface coverage in 25 mL of MeOH:H₂O (1:6).
An important factor contributing to optimal hydrogen production at 1-2% Pt loading and the decrease of catalytic activity at higher precursor loadings potentially emanates from the absorbance of leftover molecular Pt$^{II}$ species resident on the titania surface. As mentioned earlier, Pt(dcbpy)Cl$_2$ is a yellow complex possessing a broad charge transfer absorption band centered at 377 nm with a modest extinction coefficient ($\varepsilon = 2770 \text{ M}^{-1}\text{cm}^{-1}$) which can serve to attenuate photon flux in the vicinity of the bandgap. We postulated that the observed decrease in hydrogen evolution rates as a function of increased surface coverage might simply be reflecting a systematic attenuation in light absorbed by the TiO$_2$. To test this possibility, 0.1 M KOH was used to quantitatively desorb any surface bound Pt$^{II}$ complexes remaining after 5 hours of photocatalytic reaction, specifically, 25 mg of the Pt/TiO$_2$ sample (after catalysis) was treated with 25 mL of 0.1 M KOH. The corresponding solutions were centrifuged (10 minutes, 10,000 RPM) and filtered using a 0.2 µm pore size filter. The photoinitiated hydrogen evolution of the collected solid catalyst was then monitored by GC. This base treatment did not increase the catalytic activity at ≤ 2% loading. However, the complete removal of the remaining molecular surface-anchored Pt$^{II}$ precursors markedly enhanced the hydrogen evolving activity from 180 to 240 µmol/hr of the deposited Pt at 7.05% initial loading, Figure 2.3a. The same data also implies that the presence of molecular Pt$^{II}$ species on the surface of titania is responsible for a significant amount of light absorption in the vicinity of the bandgap. In fact, the calculated amounts of Pt$^{II}$ precursors remaining on the surface of TiO$_2$ after 5 hours of catalysis suggest that only ~ 10% of the originally present Pt(dcbpy)Cl$_2$ at high surface coverage (7.05% loading) actually decomposed, whereas ~ 75% of this same molecule decomposed at low surface coverage (1% loading), Figure 2.3b. Ultimately at low surface coverage (≤ 2% by mass of Pt(dcbpy)Cl$_2$) the decomposition was complete after prolonged photolysis (> 7 hrs). The combined results suggest
that molecular Pt(dcbpy)Cl\textsubscript{2} is more efficiently decomposed to Pt\textsuperscript{0} at low surface coverage and exerts a rather substantial UV bandgap absorbance at higher surface coverage.

**Figure 2.3.** (a) Hydrogen evolution increases after removal of the remaining molecular Pt\textsuperscript{II} complexes from the surface of TiO\textsubscript{2} at higher surface coverage, illustrating the absorbance of undecomposed Pt\textsuperscript{II} precursors in the UV region of this sample. (b) Normalized percent transmittance at 377 nm (black line and data points) of 5 different solutions and the calculated mass of Pt\textsuperscript{II} precursors remaining on the TiO\textsubscript{2} surface (red line and data points), where the unreacted Pt\textsuperscript{II} precursors are systematically desorbed at each percentage loading from the surface of titania after 5 hours of photocatalysis.

The data shown in Figure 2.4 is representative of catalytic hydrogen-evolving samples formed from complete decomposition of the molecular precursors present. In these instances, 1\% molecular precursor loading (either Pt(dcbpy)Cl\textsubscript{2} or H\textsubscript{2}PtCl\textsubscript{6}) followed by 5 hours of broadband irradiation resulted in quantitative Pt\textsuperscript{0} deposition as ascertained by negligible detection of any molecular precursors desorbed from the titania surface. Subsequent to washing, these materials were resuspended in 1:6 MeOH:H\textsubscript{2}O and tested for their hydrogen photocatalytic activity. Notably, the material isolated after complete photodeposition of Pt(dcbpy)Cl\textsubscript{2} (300 µmol/hr) significantly outperformed that photodeposited from H\textsubscript{2}PtCl\textsubscript{6} (130 µmol/hr), Figure 2.4. The hydrogen evolution rate is lower in these particular samples as a result of the catalyst being
present in smaller quantities (12 mg as opposed to 25 mg used to obtain the data in Figure 2.4) and from post-photolysis processing (washing, drying, etc.). The combined data associated with catalytic samples formed from quantitative decomposition of the Pt-based molecular precursors (1% by mass on titania) are collected in Table 2.2.

![Graph](image)

**Figure 2.4.** Photochemical hydrogen evolution from 12 mg of Pt/TiO$_2$ (1% by mass prepared from complete photodeposition (PD) of Pt(dcbpy)Cl$_2$ on TiO$_2$, red line and data points) versus the benchmark Pt/TiO$_2$ (1% by mass prepared by 5 hours PD of H$_2$PtCl$_6$ on TiO$_2$, black line and data points) both suspended in 25 mL of MeOH:H$_2$O (1:6).

In another set of experiments, chemically deposited platinum nanoparticle performance (produced from NaBH$_4$ reduction) was directly compared to those generated from photodeposition, Figure 2.5. These measurements were acquired with 12 mg of each sample suspended in 25 mL 1:6 MeOH:H$_2$O. Prior to photocatalysis experiments, each solid was isolated immediately after platinum nanoparticle deposition, after washing and vacuum drying. The sample generated from chemical deposition clearly operates at a lower catalytic activity with respect to the one produced via photodeposition (200 and 300 µmol/hr respectively). Since the
surface coverage was the same, the TOF follows the same trend (0.24 and 0.36 s\(^{-1}\) respectively), Figure 2.5 and Table 2.2.

**Figure 2.5.** Comparison of hydrogen evolution from 12 mg of Pt(dcbpy)Cl\(_2\)/TiO\(_2\) using photodeposition (PD) (red line and data points) and chemical deposition (CD), (black line and data points), respectively. Both samples were isolated after complete deposition.

Another possible explanation was experimentally tested to rationalize the observation that the 1-2% loaded samples outperformed all others in hydrogen production activity, Figure 2.2, namely, smaller nanoparticles with enhanced catalytic activity\(^{22}\) were formed at lower surface coverage. Dark field STEM images of Pt particles at varied surface coverage were quantitatively analyzed. At low loading of Pt(dcbpy)Cl\(_2\) (0.5-2%), the resulting particles were 1.5 ± 0.2 nm in diameter whereas at higher coverage (4.27% and 7.05%) they were measurably larger: 1.9 ± 0.3 nm and 2.5 ± 0.4 nm, respectively. Both the Pt(II) precursor and deposition method does influences the Pt particle size. The 1% sample resulting from chemical deposition yields Pt(0) nanoparticles that were 2 ± 0.5 nm in diameter, whereas the 1% H\(_2\)PtCl\(_6\) photodeposited sample results in the generation of 3 ± 0.6 nm particles, Figure 2.6. Therefore, a clear variation in the efficiency of hydrogen production with the ultimate size of resultant nanoparticles was observed.
In theory, small nanoparticle clusters have more exposed platinum surface area potentially leading to higher catalytic efficiencies.\textsuperscript{27} This notion is consistent with the current experimental data, and quantified further in Tables 1 and 2. In summary, the higher photocatalytic efficiency of the photodeposited Pt\textsuperscript{0} catalysts from Pt(dcbpy)Cl\textsubscript{2} precursors at lower loadings was shown to be correlated to the formation of smaller particles and the absence of possible contaminants when Pt\textsuperscript{0} is formed photochemically in-situ, Figures 2-6.

**Figure 2.6.** (a) Variation of particle size as a function of Pt(dcbpy)Cl\textsubscript{2} initial surface coverage on TiO\textsubscript{2}. (b) Comparison of particle size from 1\% Pt(dcbpy)Cl\textsubscript{2} photodeposited (PD), chemically deposited (CD), and the 1\% H\textsubscript{2}PtCl\textsubscript{6} PD benchmark.

Due to the complexity of heterogeneous photocatalytic materials, the activity in terms of \(\mu\text{mol/hr}\) under defined experimental conditions was used as a metric for the relative performance of different samples throughout the literature as summarized in the cited review article.\textsuperscript{9} We also calculated turnover frequencies and surface turnover frequencies for comparative purposes in this study, and these data are summarized in Tables 1 and 2. Assuming spherical Pt(0)\textsubscript{x} nanoparticles, one can estimate the average number of Pt atoms (x) present in the nanoparticles in each sample. Full shell nanoparticles are thermodynamically stable and possess lower
reactivity for surface growth, so it is expected that transition metal nanoparticles are centered around “magic number” clusters: Pt(0)\textsubscript{13}, Pt(0)\textsubscript{55}, Pt(0)\textsubscript{147}, Pt(0)\textsubscript{309}, Pt(0)\textsubscript{561}, Pt(0)\textsubscript{923}, etc.\textsuperscript{48} Then using the “magic number” formula for the number of surface atoms \((10n^2 + 2)\), where \(n\) is the number of shells), we can estimate the percentage of surface atoms (assumed to be catalytically active) in each sample and subsequently calculate a surface turnover frequency, Surface TOF \((s^{-1}) = [\text{TOF (s}^{-1})] \times \text{(fraction of surface atoms)}^{-1}\), whose values are collected in Table 2.1.\textsuperscript{27,48-50} All the values reported were calculated subsequent to the observed induction period for nanoparticle formation present for the in-situ photodeposited samples, Figure 2.2 and Table 2.1. In addition, the number \((N)\) of Pt(0)\textsubscript{x} nanoparticles per mass of TiO\textsubscript{2} (mg) were calculated using Eq. 1, and collected in Tables 1 and 2:

\[
N_{\text{Pt(0)x}} = n \times N_a \times x^{-1} \times (\text{mass of TiO}_2)^{-1} \quad (1)
\]

Here, \(n\) is the number of moles of decomposed Pt precursor, \(N_a\) is Avogadro’s number, and \(x\) is the number of Pt atoms per Pt(0)\textsubscript{x} cluster.

The trends found for the photocatalytic activities in terms of both TOF and surface TOF clearly reflects changes in catalytic behavior in different samples resulting from two main factors discussed throughout this report. The first relates to the absorbance in the UV due to undecomposed Pt\textsuperscript{II} precursors at high surface coverage ultimately resulting in diminished catalytic activity. To further elucidate this concept, surface TOF values can be useful because these values are corrected for the fraction of exposed Pt atoms. For comparative purposes, refer to the surface TOF of the in-situ photodeposited samples at different surface coverage, Table 2.1. The surface TOF is clearly higher at low catalytic loadings (\(\leq 2\%\)). Secondly, the larger number of surface atoms produced in smaller nanoparticles exhibit higher catalytic activity and improved
TOFs, consistent with the materials produced from photodecomposition of Pt(dcbpy)Cl₂ resident on titania at 1-2% by mass. The inadequate surface coverage of Pt on TiO₂ at 0.5% loading is deemed responsible for the lower catalytic activity (240 µmol/hr) since the TOF, which corrects for the amount of Pt decomposed on TiO₂ is 0.35 s⁻¹, greater than the TOF obtained in the 4.27 and 7.05% samples, 0.2 s⁻¹ and 0.14 s⁻¹ respectively. This trend would be anticipated given that the samples at higher loading suffer from Pt II precursor-induced competitive absorbance of bandgap photons and the subsequent formation of larger Pt⁰ nanoparticles.

Table 2.1. Summary of relevant materials parameters and photocatalytic activity of 25 mg Pt(dcbpy)Cl₂/TiO₂ at different initial surface coverage.

<table>
<thead>
<tr>
<th>Surface coverage (%)</th>
<th>Activity (µmol H₂/hr)ᵃ</th>
<th>Precursor Decomposed (mg)ᵇ</th>
<th>Precursor decomposed (µmol)ᶜ</th>
<th>TOF (s⁻¹)ᵈ</th>
<th>Pt(0), per mg “N”mol</th>
<th>Particle Size (nm)ᵉ</th>
<th>Shell number “n”ᶠ</th>
<th>Surface Pt “10n²+2”ᵍ</th>
<th>Pt atoms “x”ʰ</th>
<th>Surface atoms (%)ᵱ</th>
<th>Surface TOF (s⁻¹)ᵱ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>250</td>
<td>0.1</td>
<td>0.2</td>
<td>0.35</td>
<td>3.2×10¹³</td>
<td>~1.5</td>
<td>3</td>
<td>92</td>
<td>~150</td>
<td>~60%</td>
<td>0.6</td>
</tr>
<tr>
<td>1%</td>
<td>810</td>
<td>0.2</td>
<td>0.4</td>
<td>0.56</td>
<td>6.4×10¹³</td>
<td>~1.5</td>
<td>3</td>
<td>92</td>
<td>~150</td>
<td>~60%</td>
<td>0.9</td>
</tr>
<tr>
<td>2%</td>
<td>790</td>
<td>0.28</td>
<td>0.55</td>
<td>0.4</td>
<td>8.8×10¹³</td>
<td>~1.5</td>
<td>3</td>
<td>92</td>
<td>~150</td>
<td>~60%</td>
<td>0.7</td>
</tr>
<tr>
<td>4.27%</td>
<td>390</td>
<td>0.28</td>
<td>0.55</td>
<td>0.2</td>
<td>4.3×10¹³</td>
<td>~2</td>
<td>4</td>
<td>162</td>
<td>~310</td>
<td>~50%</td>
<td>0.4</td>
</tr>
<tr>
<td>7.05%</td>
<td>180</td>
<td>0.18</td>
<td>0.35</td>
<td>0.14</td>
<td>1.5×10¹³</td>
<td>~2.5</td>
<td>5</td>
<td>252</td>
<td>~560</td>
<td>~45%</td>
<td>0.3</td>
</tr>
</tbody>
</table>

ᵃPhotocatalytic activity (µmol H₂/hr) was measured by GC headspace analysis;ᵇamount of decomposed Pt precursor (mg and µmol respectively) was deduced from the quantitative desorption of Pt²⁺ precursors;ᶜturnover frequencies TOF = [mol H₂ produced] × [mol decomposed Pt⁺ precursors]⁻¹ × s⁻¹;ᵈthe number “N” of Pt(0), crystallites per mg of TiO₂ was calculated from obtained data;ᵉaverage nanoparticle size (nm) was measured by STEM;ᶠPt nanoparticles shell number “n” and the magic number of surface atoms “10n²+2” were calculated based on nanoparticles diameter;ᵍtotal number of atoms per nanoparticle was calculated from size distribution data;ʰ% of surface atoms which was assumed to be catalytically active;ᵱsurface TOF (s⁻¹) was calculated from TOF and % of surface atoms.
Table 2.2. Summary of relevant materials parameters and photocatalytic activity of 12 mg Pt⁰/titania 1% composites formed from different precursors (Pt(dcbpy)Cl₂ or H₂PtCl₆) via photodeposition (PD) or chemical deposition (CD).

<table>
<thead>
<tr>
<th>Pt⁰ deposition method</th>
<th>Activity (µmol H₂/hr)ᵃ</th>
<th>Precursor Decomposed (mg)ᵇ</th>
<th>Precursor decomposed (µmol)ᶜ</th>
<th>TOF (s⁻¹)ᵈ</th>
<th>Pt(0), per mg “N”ᵉᶠ</th>
<th>Particle Size (nm)ᵍ</th>
<th>Shell number “n”ᶠ</th>
<th>Surface Pt “10n²+2”ᶠ</th>
<th>Pt atoms “x”ᵍ</th>
<th>Surface atoms (%)ʰ</th>
<th>Surface TOF (s⁻¹)ᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD from Pt(dcbpy)Cl₂</td>
<td>300</td>
<td>0.12</td>
<td>0.23</td>
<td>0.36</td>
<td>7.7×10¹³</td>
<td>~ 1.5</td>
<td>3</td>
<td>92</td>
<td>~ 150</td>
<td>~ 60%</td>
<td>0.6</td>
</tr>
<tr>
<td>CD from Pt(dcbpy)Cl₂</td>
<td>200</td>
<td>0.12</td>
<td>0.23</td>
<td>0.24</td>
<td>3.7×10¹³</td>
<td>~ 2</td>
<td>4</td>
<td>162</td>
<td>~ 310</td>
<td>~ 50%</td>
<td>0.5</td>
</tr>
<tr>
<td>PD from H₂PtCl₆</td>
<td>130</td>
<td>0.12</td>
<td>0.23</td>
<td>0.16</td>
<td>1.3×10¹³</td>
<td>~ 3</td>
<td>6</td>
<td>362</td>
<td>~ 920</td>
<td>~ 40%</td>
<td>0.4</td>
</tr>
</tbody>
</table>

ᵃPhotocatalytic activity (µmol H₂/hr) was measured by GC headspace analysis;ᵇamount of decomposed Pt precursor (mg and µmol respectively) based on complete decomposition of Ptⁿ⁺ precursors;ᶜturnover frequencies TOF = [mol H₂ produced] × [mol decomposed Ptⁿ⁺ precursors]⁻¹ × s⁻¹;ᵈthe number “N” of Pt(0)ₙ crystallites per mg of TiO₂ was calculated from obtained data;ᵉaverage nanoparticle size (nm) was measured by STEM;ᶠPt nanoparticles shell number “n” and the magic number of surface atoms “10n²+2” were calculated based on nanoparticles diameter;ᵍtotal number of atoms per nanoparticle was calculated from size distribution data;ʰ% of surface atoms which was assumed to be catalytically active;ᵢsurface TOF (s⁻¹) was calculated from TOF and % of surface atoms.

In two different experiments under distinct conditions, liquid Hg and gaseous CO (at 1 atm) were introduced into the photoreaction mixture and the hydrogen evolution was found to be significantly attenuated, Figure 2.7. Hydrogen evolution catalysis at Pt⁰ is known to be poisoned by mercury, due to the formation of a Hg/Pt amalgamate. In the present compositions, the Hg strongly interacted with these samples to the point that most of the suspended material accumulated and bound to the mercury at the bottom of the photoreactor. Platinum is also known to have high surface adsorption capacity for CO which easily passivates the surface upon binding. At 1 atm pressure (gas bubbled through the aqueous suspension), the CO substantially inactivates the photocatalytic evolution of H₂ gas from the samples. The two combined heterogeneous poisoning tests strongly suggest that the catalysis responsible for H₂ generation is indeed heterogeneous in nature and results from the Pt nanoscopic particles embedded on the
titania surface rather than from any remnant molecular Pt\textsuperscript{II} species. Similar data were obtained after aqueous base was utilized to remove all molecular Pt\textsuperscript{II} complexes from the titania surface after several hours of photoreaction.

**Figure 2.7.** (a) Mercury poisoning test performed on samples produced via photolysis of 1\% Pt(dcbpy)Cl\textsubscript{2} by mass adsorbed on titania with Pt(0) formed in-situ. (b) CO (1 atm) inhibition experiment performed on photodeposited catalytic samples subsequent to Pt(0) photodeposition. Hydrogen evolution decreases dramatically in the presence of Hg and CO in 1\% Pt(dcbpy)Cl\textsubscript{2}/TiO\textsubscript{2} suggesting that the catalyst is indeed heterogeneous and has its origin in the formed Pt nanoparticles.

DFT and TD-DFT calculations have suggested that Pt(dcbpy)Cl\textsubscript{2} is stable upon one electron reduction. However, photoexcitation of this reduced compound with visible light is expected to result in Pt\textsuperscript{0} agglomerates when these molecules are in solution.\textsuperscript{51} Such a mechanism is qualitatively consistent with the photodeposition of Pt nanoparticles seen in all of the materials presented herein.\textsuperscript{51} While this mechanism justifies the photodecomposition of Pt\textsuperscript{II} molecular complexes under light illumination, Pt nanoparticle formation has also been observed from Pt\textsuperscript{n+} salt precursors, starting with the reduction of Pt\textsuperscript{n+} into Pt\textsuperscript{0} by the conduction band electrons of
TiO\textsubscript{2} upon bandgap excitation, where Pt\textsuperscript{0} adsorbed on the titania surface ultimately agglomerates into small crystallites.\textsuperscript{25} Under equilibrium conditions, the flatband potential of TiO\textsubscript{2} at the TiO\textsubscript{2}/electrolyte interface is defined by $V_{fb} = -0.2 - 0.059 \text{ pH} = -0.613 \text{ V at pH 7.}$\textsuperscript{52,53} In a qualitative experiment, electrons on titania (TiO\textsubscript{2}(\textit{e}^-)s) were produced electrochemically in an argon-saturated H-cell by biasing a TiO\textsubscript{2} film on a fluorine doped tin oxide (FTO) electrode at -1000 mV vs. Ag/AgCl in 0.1 M sodium phosphate buffer at pH 7, in conjunction with a Pt wire counter electrode in a standard 3-electrode arrangement. At this potential, which roughly supplies 390 mV overpotential for hydrogen evolution at pH = 7.0, electrons become trapped rapidly in the conduction band of TiO\textsubscript{2}, and since TiO\textsubscript{2} is not a good electrocatalyst for hydrogen evolution itself, the resultant film turns from white to blue indicating the presence of TiO\textsubscript{2}(\textit{e}^-), Figure 2.8.\textsuperscript{54} The electrochemical bias was removed after 5 minutes, then Pt(dcbpy)Cl\textsubscript{2} in slightly basic water was injected in the working side of the electrochemical cell under an argon atmosphere in the dark, turning the TiO\textsubscript{2} film into a gray cast signaling the formation of metallic platinum. Hydrogen could be readily detected from the headspace by GC after the injection of this molecular precursor and the subsequent formation of platinum nanoparticles, ultimately confirmed using TEM. This experiment verifies that TiO\textsubscript{2}(\textit{e}^-)s are likely responsible for the reduction of the surface-anchored Pt\textsuperscript{II} complex into Pt\textsuperscript{0} which ultimately leads to heterogeneous hydrogen production as a dark reaction. However, this does not necessarily imply that the one-electron reduced Pt(dcbpy)Cl\textsubscript{2} complex is unstable, as multiple electrons can be simultaneously delivered to the molecules under these experimental conditions since the 2 electron reduction potential of Pt(dcbpy)Cl\textsubscript{2} anchored on titania is likely below the conduction band of TiO\textsubscript{2}.

Meyer and coworkers have reported a similar observation on Ru(dcbq)(bpy)\textsubscript{2}/TiO\textsubscript{2} and hemin/TiO\textsubscript{2} systems where TiO\textsubscript{2}(\textit{e}^-) afforded the reduction of these surface-anchored
In a separate experiment, Pt(dcbpy)Cl\textsubscript{2}/TiO\textsubscript{2} (1\%) in pure water was irradiated using broadband white light illumination from a Xe lamp, and the solid isolated after irradiation possessed a gray cast suggesting the formation of Pt nanoparticles. This experiment confirmed that TiO\textsubscript{2}(e\textsuperscript{−}) derived from a photochemical experiment can reduce Pt(dcbpy)Cl\textsubscript{2} into Pt\textsuperscript{0} nanoparticles in the absence of hole scavengers. Similar results have been described in the photoassisted Pt deposition on TiO\textsubscript{2} from various Pt complexes in aqueous media.\textsuperscript{25,52} It is important to note that in the current photocatalytic H\textsubscript{2} production experiments over titania, CO\textsubscript{2} was also qualitatively detected in the reactor headspace by GC, verifying the oxidation of MeOH by hole migration to the surface of TiO\textsubscript{2}, for more details about methanol decomposition products generated (HCHO, CO\textsubscript{2}, etc.) and the associated plausible mechanisms please refer to the cited article.\textsuperscript{43}

**Figure 2.8.** (a) Qualitative electron trapping experiment showing the color change of the white TiO\textsubscript{2} film into blue due to trapped electrons resulting from -1000 mV vs. Ag/AgCl applied bias in 0.1 M sodium phosphate buffer at pH 7.0. Ultimately, this material turns grey after the addition of Pt(dcbpy)Cl\textsubscript{2} to the solution and removal of the bias. (b) TEM image of the scraped film after the experiment indicates the presence of Pt nanoparticles (black) on the TiO\textsubscript{2} support (lighter), 5 nm scale bar.
2.6 CONCLUSIONS

Bandgap excitation of TiO$_2$ containing surface-anchored Pt(dcbpy)Cl$_2$ molecules in 1:6 methanol:water results in their reduction to Pt$^0$ nanoparticles, subsequently photocatalyzing the reduction of protons into hydrogen. Some of the lowest Pt(dcbpy)Cl$_2$ surface coverage (1-2% loading by mass) produced materials exhibiting the highest photocatalytic performance, which significantly outperformed all other surface coverage and the benchmarks. The chemical deposition of this catalyst via NaBH$_4$ reduction on TiO$_2$ gave rise to slightly inferior catalytic materials, suggesting that in-situ photodeposition of surface-anchored precursors represents a superior method for growing hydrogen-evolving Pt$^0$ clusters. At low surface coverage, smaller nanoparticles prevail affording higher surface areas for catalysis. A rather substantial absorbance emanating from unreacted Pt$^{II}$ precursors was observed, which dramatically decreased hydrogen evolution at higher surface coverage. The complete decomposition of the precursor was only achieved only at low percentage loading (< 2% by mass of Pt(dcbpy)Cl$_2$ on TiO$_2$) upon extended photolysis. The combined data suggest that 1-2% Pt(dcbpy)Cl$_2$ on TiO$_2$ represents the minimum surface coverage necessary to produce highly efficient catalytic activity owing to the small nanoparticle diameters generated (1.5 nm), possibly stabilized by both dcbpy and chloride ligands, and the reduced interfering UV absorbance associated with unreacted Pt$^{II}$ precursor molecules. This study promotes the economic usage of noble metals in the area of hydrogen production catalysis as demonstrated by using modest amounts of the surface-anchored molecular precursor Pt(dcbpy)Cl$_2$ for the generation of high activity and monodisperse Pt$^0$. 
2.7 SUPPORTING INFORMATION

**Figure 2.S1.** Histogram for Pt(0) particle size of all the samples analyzed in this chapter. PD stands for photodeposition and CD for chemical deposition.
Figure 2.S2. Representative STEM images of all the samples analyzed in the article from Pt(dcbpy)Cl₂ (first 6 pictures) and H₂PtCl₆ precursor (last picture). All scale bars are 10 nm in size, PD stands for photodeposition and CD for chemical deposition. Data were collected by the Murphy group at UIUC
**Figure 2.S3.** Photograph of Pt(dcbpy)Cl₂/TiO₂ at various percentage (1-7% by mass) loading before (up) and after (down) 5 hours of photocatalysis. The yellow-grey coloration of the sample at 4.27% and 7.05% loading is due to the remaining undecomposed Pt II species on TiO₂ surface after 5 hours of photodeposition. The removal of undecomposed Pt II complexes from TiO₂ using 0.1 M KOH resulted in grayish material similar to the ones at low % loading.

**Figure 2.S4.** Photograph of Pt(dcbpy)Cl₂/TiO₂ at 0.5% loading before (left) and after (right) 5 hours of photocatalysis, as well as Pure TiO₂ p25 (white) and Pt(dcbpy)Cl₂ (yellow) precursors.
Figure 2.5. Pt(dcbpy)Cl$_2$ $^1$H NMR (300MHz, (CD$_3$)$_2$SO, ppm) $\delta$ 9.72 (d, $J = 6$ Hz, 2H), 9.04 (s, 2H), 8.24 (d, $J = 5.7$ Hz, 2H). The signal is low due to the poor solubility of this compound in (CD$_3$)$_2$SO. The peak at 2.5 ppm is coming from (CH$_3$)$_2$SO residuals and the one at 3.33 ppm is coming from H$_2$O.
Figure 2.S6. Pt(dcbpy)Cl$_2$ $^1$H NMR (500MHz, D$_2$O/NaOD, ppm) $\delta$ 8.5 (d, $J$ = 6Hz, 2H), 8.09 (s, 2H), 7.60 (d, $J$ = 5.8 Hz, 2H). In principle, minimum amount of base (NaOD) was used to solubilize this complex in D$_2$O.
Figure 2.S7. dcbpy $^1$H NMR (500MHz,D$_2$O/NaOD, ppm) $\delta$ 8.66 (d, $J = 5$Hz, 2H), 8.28 (s, 2H), 7.75 (d, $J = 5$ Hz, 2H).
2.7.1 Desorbed Pt species characterization. All absorbance spectra reported in this chapter were taken within few minutes of sample preparation. In order to gain insight into the amount of desorbed Pt chemical species after photocatalysis, and subsequently quantify the decomposed mass of Pt, we adsorbed known masses of Pt(dcbpy)Cl₂ on TiO₂ using the procedure listed in
Section 2.3.4b, then we desorbed this amount using 0.1 M KOH solution. The absorbance of the desorbed species was measured, and an equivalent of 0.25 mg Pt(dcbpy)Cl$_2$ desorbed from 25 mg of Pt(dcbpy)Cl$_2$/TiO$_2$ in 25 mL KOH was averaged in Figure 2.S10. We clearly see the formation of a shoulder centered at 477 nm when the complex is desorbed from TiO$_2$ using base. We attributed this absorption shoulder to the speciation of Pt(dcbpy)Cl$_2$ upon desorption, especially that Pt$^{II}$ complexes were shown to be labile in basic aqueous media. Since our goal was to quantify the mass of Pt$^{II}$ precursors desorbed after catalysis (to know the mass of decomposed Pt(dcbpy)Cl$_2$), a calibration based on known masses of desorbed Pt$^{II}$ species was sufficient to make the appropriate calculations.

![Figure 2.S10.](image-url)

**Figure 2.S10.** Average absorbance of 0.25 mg of desorbed Pt species. The Pt species were desorbed in the dark using 0.1 M KOH (25 mg of Pt(dcbpy)Cl$_2$/TiO$_2$ in 25 mL KOH).
Figure 2.S11. Absorption spectra of Pt(dcbpy)Cl$_2$, in water at different concentrations, and the corresponding extinction coefficient at 377 nm was calculated based on Lambert-Beer’s law. The stock solution containing Pt(dcbpy)Cl$_2$ in basic water was freshly prepared, aliquots were added to pure water, and the absorption spectra were measured.

Figure 2.S12. Absorption spectra of systematically desorbed Pt species after 5 hours of photocatalysis (25 mg of Pt(dcbpy)Cl$_2$/TiO$_2$ per 25 mL of 0.1 M KOH) of samples at different initial Pt(dcbpy)Cl$_2$ loading.
2.7.2 Quantification of Pt\textsuperscript{II} decomposed. Using the calibration from known masses of desorbed Pt\textsuperscript{II} species in Figure 2.S10 we calculated the mass of undecomposed Pt. Then the mass of decomposed Pt\textsuperscript{II} precursor was calculated using the following formula: 

\[ m_{\text{decomposed}} = m_{\text{initially adsorbed}} - m_{\text{desorbed/undecomposed}}. \]

We can clearly see that the absorption spectra of the desorbed Pt\textsuperscript{II} species after photocatalysis closely track the one resulting from the desorbed Pt\textsuperscript{II} species in the dark. This observation indicates that the shoulder at 477 nm is mainly due to speciation of Pt(dcbpy)Cl\textsubscript{2} in basic water rather than the formation of photoproducts after catalysis.

2.8 REFERENCES


CHAPTER III

PHOTOCHEMICAL DEPOSITION OF “COBALT PHOSPHATE” OXYGEN EVOLVING CATALYST ON THE SURFACE OF TITANIA


3.1 ABSTRACT

The cobalt phosphate “CoPi” oxygen evolving catalyst (OEC) was photochemically grown on the surface of TiO$_2$ photoanodes short-circuited to a Pt wire under bandgap illumination in the presence of Co(NO$_3$)$_2$ and sodium phosphate (NaPi) buffer. Extended photodeposition (15 hrs) using a handheld UV lamp readily permitted quantitative structural and electrochemical characterization of the photochemically deposited CoPi OEC on titania. The formed catalytic material was characterized by SEM/EDX experiments, illustrating the production of easily visualized micron scale clusters throughout the titania surface containing both cobalt and phosphate. XAFS and XANES studies indicated that the newly formed material was structurally consistent with the production of molecular cobaltate clusters composed of a cobalt oxide core that is most likely terminated by phosphate ions. The oxidation state, structure, and the oxygen evolution activity of this CoPi catalyst photochemically grown on titania were quantitatively similar to the analogous electrodeposited materials on titania as well as those produced on other electroactive substrates. From pH-dependent electrochemical measurements, proton-coupled electron transfer was shown to be an important step in the oxygen evolution
mechanism from the photodeposited OEC clusters on TiO$_2$ in agreement with previous reports on other materials. Similarly, the substitution of NaClO$_4$ as electrolyte during the controlled potential electrolysis experiments failed to maintain an appreciable current density, indicating that the catalyst was rendered inactive with respect to the one immersed in NaPi. The requirement of having phosphate present for long-term catalytic activity implied that the same “repair” mechanism might be invoked for the hybrid materials investigated here. The OEC catalyst operated at Faradaic efficiencies close to 100 % in controlled potential electrolysis experiments, indicating that the holes relayed to the photodeposited CoPi are indeed selective for promoting water oxidation on titania.

3.2 INTRODUCTION

Generating chemical fuels from the energy of photons supplied by the sun is a challenging problem requiring the development of complex catalytic systems desirably from earth abundant materials.$^{1-5}$ The earth’s population is expected to markedly increase over the following century and is forecast to lead to historically unprecedented energy consumption.$^{6,7}$ If the human race continues burning fossil fuels to meet these increasing energy demands, the unparalleled CO$_2$ release into the atmosphere represents a serious threat that may forever modify the terrestrial climate.$^{6,8}$ Fortunately, the energy supplied by the sun far exceeds that of future consumption demands and harvesting only a fraction of this energy could significantly decrease our reliance on fossil fuels.$^{9,10}$ As the sun is diurnal, systems capable of storing solar energy for later use are required. Rechargeable batteries have been used in this regard in tandem with photovoltaic (PV) solar panels but suffer from high cost, low discharge capacity, and short operational lifetimes when compared to the conjoined PV materials. Alternatively, light energy
stored in the form of chemical bonds represents a viable strategy for combining PVs with appropriate reactions to generate desirable high-energy products. One such reaction is water splitting, which is a thermodynamically uphill process (Eqs. 1-3), and light energy would be stored via photo-driven electrolysis in hydrogen and oxygen bonds, desirable feedstock chemicals for fuel cells. Additionally, the exothermic combustion of H\textsubscript{2} (the reverse of Eq. 3) provides a potential carbon-free energy source that yields water as product.

\[
\begin{align*}
O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O & E_{\text{anodic}} = 0.82 & [1] \\
4H^+ + 4e^- &\rightarrow 2H_2 & E_{\text{cathodic}} = 0.41 & [2] \\
----------------------------------------------- & & [V \text{ vs NHE, at pH 7}] \\
2H_2O &\rightarrow 2H_2 + O_2 & E_{\text{reaction}} = -1.23 \text{ V} & [3]
\end{align*}
\]

Modern advances in electrocatalysis appear promising towards the development of earth abundant materials that can effectively promote each necessary half-reaction (Eqs. 1 and 2) ultimately resulting in water splitting. Arguably, oxidation is the more difficult step in the water splitting reaction that requires a merging of four hole equivalents and two oxygen atoms, Eq. 1. More than 30 years ago, Shafirovich and coworkers originally used cobalt ions in the presence of buffered aqueous solutions resulting in the production of oxygen catalytically from water. However the material produced was ill characterized and the mechanism for water oxidation was not rationalized. Recently, Nocera and coworkers have developed and extensively characterized a water oxidation electrocatalyst composed of cobalt and inorganic phosphate, termed CoPi, which operates in neutral water at low overpotentials (\(\eta < 400 \text{ mV}\)) and features a regenerative self-healing mechanism following catalyst dissolution. The oxygen production mechanism of this electrochemically grown catalyst was suggested to be very similar to the S-state pumping of photosystem II in plants also known as the Kok cycle where the manganese metal centers undergo a series of oxidation/reduction reactions concomitant with
proton and electron transfer processes.\textsuperscript{11,17,25-29} The structure, valency, and oxygen evolution mechanism of the electrochemically active cobalt species have been assigned to a Co oxo/hydroxo species whose oxidation numbers vary between 2, 3, and 4 in a series of proton and electron transfer reactions prior to the oxygen evolution step.\textsuperscript{26,28-34} As the photogenerated holes of many semiconductors can provide potentials adequate to drive CoPi catalyst formation, Choi and coworkers recently demonstrated such a photochemical route successfully applied to a variety of \textit{n}-type semiconductors.\textsuperscript{35-37} In such hybrid materials, upon Co(II) oxidation to Co(III) using a photogenerated hole at the surface, an oxide is produced and immediately precipitates on the surface of the semiconductor owing to its the low solubility in buffered aqueous solutions.\textsuperscript{37} To date, this catalyst has been grown using three different methodologies namely, electrochemical, photochemical, and photo-assisted electrochemical on the surfaces of various electrodes\textsuperscript{27} as well as different semiconductors including ZnO,\textsuperscript{37} Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{36,38-41} WO\textsubscript{3},\textsuperscript{42} BiVO\textsubscript{4},\textsuperscript{43-45} TaON,\textsuperscript{46} and Si\textsuperscript{12,47,48}. The advantage of photodepositing CoPi on semiconductors is that the density of the catalyst formed would presumably be large where the holes are highly accessible to operating the desired water oxidation chemistry.\textsuperscript{37,47} In order to photochemically deposit CoPi, two different routes can potentially be applied, short-circuit and open circuit deposition. In short-circuit photodeposition, the semiconductor is submerged in phosphate buffer containing the Co(II) precursor and the photogenerated holes in the valence band are used to oxidize cobalt ions. The Co(III) species can then deposit as an oxide on the surface of the photoactive material. While this method can lead to the photodeposition of cobalt oxide, unfortunately, the reduction of Co(III) to Co(II) by electrons trapped in the conduction band is also thermodynamically favorable. In order to decrease the likelihood of the catalyst reverting back to the starting Co(II) material, electrons are simply short-circuited to a platinum electrode placed remotely from the
titania in order to prevent this undesirable chemistry. For example, the short-circuit method has yielded superior CoPi water oxidation catalysts in comparison to those produced using the analogous open-circuit procedure (conduction band electrons are trapped in the same vicinity as the oxidized Co(III) species) in Fe₂O₃. These results were mainly attributed to the increase of the catalyst’s nucleation density and a corresponding increase in the “average” oxidation number of the resting CoPi catalyst.

To the best of our knowledge, no structural characterization of the photodeposited CoPi OEC on metal oxide semiconductors has been provided in the literature. In the present study, we were interested in determining the structure and activity of this photogenerated catalyst deposited on the surface of titania electrodes, which is essential for the development of stand-alone systems capable of growing the catalyst and sustaining long-term water oxidation chemistry at a biased electrode. Titania or TiO₂, is characterized by high stability in aqueous solutions under a wide pH range and possesses a very positive valence band potential poised > 1 eV overpotential to facilitate both CoPi deposition and water oxidation. We therefore selected the TiO₂ support in order to characterize the CoPi catalyst formed on the surface without complications associated with semiconductor corrosion processes. Despite its wide bandgap of 3.0-3.2 eV, rendering absorption only in the UV portion of the spectrum, TiO₂ was used by Fujishima and Honda in the first photoelectrochemical water splitting device reported using solar illumination. In these early studies, TiO₂ was operated under extreme pH values and was not interfaced with any catalyst. However, the presence of appropriate catalysts on the surface can increase the quantum yield of water splitting by avoiding unwanted oxidation reactions thereby rendering this facile photochemistry feasible under benign conditions by decreasing the barrier for water oxidation. For example, a simple cobalt treatment markedly enhanced the visible light photoelectrochemical
properties of N-modified TiO$_2$ nanowires in basic solution through passivation of surface states, subsequently facilitating water oxidation chemistry.\textsuperscript{53} Similar observations were previously described on $\alpha$-Fe$_2$O$_3$ films treated with Co(II) ions.\textsuperscript{54} In this study we report the photochemical growth of the CoPi catalyst on the surface of electroactive TiO$_2$ films prepared by the sol-gel method on conducting fluorine-doped tin oxide (FTO) glass substrates. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy characterized the bulk properties of the photogenerated catalyst with ultimate structural determination by X-ray absorption fine structure (XAFS) spectroscopy taken in a quasi in-situ state. The electrochemical and photoelectrochemical properties of the new material were quantitatively compared to the previously reported electrochemically deposited CoPi catalyst.

3.3 EXPERIMENTAL

3.3.1 General. Cobalt nitrate hexahydrate, titanium isopropoxide, hydroxypropyl cellulose ($M_n = 10$ 000, $M_w = 80$ 000), cobalt oxide (CoO), and glacial acetic acid were purchased from Aldrich. Cobaltic oxide (Co$_2$O$_3$) was obtained as a black powder from J.T. Baker. Sodium hydrogen phosphate heptahydrate and sodium dihydrogen phosphate dihydrate were purchased from Alfa Aesar and used as received. Fluorine-doped tin oxide (FTO) conducting glass substrates (TEC 15) were purchased from Hartford Glass. Water was deionized using a Barnstead nanopure system. All reagent grade solvents and reactants were used as received. Thickness of the TiO$_2$ films was measured by a KLA-Tencor Alpha-Step IQ Surface Profiler. Electrochemical measurements were performed using a Bioanalytical Systems Epsilon electrochemical workstation in a three-electrode arrangement. The SEM images were acquired on a Hitachi S-
2700 equipped with an EDX genesis energy dispersive x-ray spectroscopy detector at 10-20 keV acceleration voltage. The photodeposition of CoPi was achieved by using a 4 W compact UV handheld lamp at $\lambda_{ex} = 365$ nm. The light source in the photoelectrochemical experiments was a 300 W xenon arc lamp (Oriel) whose output was passed through a water filter. The 200 mW/cm$^2$ broadband illumination was realized by coupling a bifurcated fiber bundle to the experiment. The oxygen produced was measured using a gas chromatograph (Shimadzu GC-8A, argon carrier gas) equipped with a 5 Å molecular sieve column (Restek) and thermal conductivity detector.

### 3.3.2 Colloidal TiO$_2$ Synthesis

The TiO$_2$ paste was prepared according to a literature procedure.$^{55,56}$ Briefly, a solution containing titanium(IV) isopropoxide (37 mL) and isopropanol (10 mL) was added dropwise to a mixture of glacial acetic acid (80 mL) and water (250 mL) at $\sim$ 0°C as measured by a thermometer immersed in the solution. This temperature can be maintained by submersing the flask in an acetone bath and occasionally adding dry ice into the acetone bath. The resulting solution changes from colorless to white when heated to 80°C, maintained for 8 h with stirring. After cooling to room temperature, 80 mL of the resultant solution was sonicated for 5 min using a high energy sonicator (Branson Sonifier 250), and finally maintained at 230°C over 8 h while stirring in a titanium autoclave (Parr Instrument Company). The final TiO$_2$ colloidal solution at room temperature was sonicated for 5 min and concentrated to 12 wt % (TiO$_2$) using a rotary evaporator (30°C, 30 Torr). Hydroxypropyl cellulose (6 wt %) previously dissolved in water was added slowly to the final mixture and the paste produced was maintained under constant stirring until used to prepare the titania electrodes.

### 3.3.3 TiO$_2$ Film Formation on Conductive Glass

FTO conducting glass substrates were cleaned using conventional sonication, first with a solution of HCl in isopropanol, then a solution
of soap in water, then finally acetone. The FTO glass was then dried in an oven. TiO$_2$ (12 wt %) and hydroxypropylcellulose (6 wt %) in water:glacial acetic acid (3:1 by volume) was sonicated and stirred vigorously overnight. The resultant paste was doctor bladed on FTO glass between 3 Scotch tape layers resulting in a TiO$_2$ electrode area of $\sim$ 1 cm$^2$ and $\sim$ 8 µm thickness. The electrode was sintered at 500°C for 30 minutes at a heating rate of 5°C per min and finally cooled to room temperature.

3.3.4 O$_2$ Evolution Measurements. Oxygen evolution during electrochemical and photoelectrochemical measurements was detected from the headspace of an airtight H-cell of known headspace volume. The H-cell contained two compartments separated by a frit of medium porosity, the working compartment contained the working electrode and the reference electrode (Ag/AgCl), and the auxiliary compartment contained the counter electrode (Pt wire). The solution and headspace were deaerated by continuous argon bubbling for 1 hour prior to the experiment. At all times the solutions were stirred at constant rate using a stir bar when the electrochemical and photoelectrochemical controlled potential electrolysis were acquired. Gas samples were withdrawn from the working compartment using a 100 µL gastight syringe (Hamilton), whose contents were injected and analyzed in a gas chromatograph (Shimadzu GC-8A, argon carrier gas) equipped with a 5 Å molecular sieve column (Restek) and thermal conductivity detector. O$_2$ produced was calculated by extrapolation from a calibration curve. The GC yielded a constant ratio for O$_2$:N$_2$ area in all samples of ambient air. Therefore, the O$_2$ contribution from residual air was simply subtracted from the measured O$_2$ area to obtain the actual O$_2$ evolved from the analyzed reaction. Oxygen evolved was corrected using Henry’s law to account for the amount of dissolved oxygen in the electrolyte solutions.
3.3.5 Photodeposition, Electrodeposition, and Photoelectrochemistry. In all the photodeposition, electrochemical, and photoelectrochemical experiments presented herein, the ohmic contact to the TiO\(_2\) electrode was achieved by using copper tape between the FTO support and a thick Ag wire that was attached to external alligator clips. The connections were then wrapped with Kapton non-conductive tape to provide mechanical support and electrical insulation. In a fused silica photoelectrochemical cell equipped with home built Teflon cap that snugly fits all the electrodes, the photodeposition of CoPi was achieved by front-side bandgap illumination of the TiO\(_2\) films immersed in a solution of 0.5 mM Co(NO\(_3\))\(_2\) in 0.1 M of sodium phosphate (NaPi) buffer at pH 7, using a handheld UV lamp (\(\lambda_{ex} = 365\) nm) over the course of 15 hours. During the photodeposition, the films were short-circuited to a platinum wire using an external copper conducting wire equipped with alligator clips.\(^{36}\) In control experiments, Co\(^{2+}\) ions were simply adsorbed onto the TiO\(_2\) electrodes under the same conditions with the excitation light off. The electrodeposited catalyst studied by EXAFS was grown by applying a 1.1 V (vs. Ag/AgCl) bias to the TiO\(_2\) electrode immersed in a solution of 0.5 mM Co(NO\(_3\))\(_2\) in 0.1 M of NaPi buffer at pH 7. The electrodeposition was allowed to proceed for two hours under a current density of \(~ 0.5\) mA/cm\(^2\). The electrochemical and photoelectrochemical characterization of the resultant films were performed using a three electrode arrangement where the CoPi/TiO\(_2\) material was used as a working electrode, Ag/AgCl as a reference electrode, and a Pt wire as auxiliary electrode in an airtight H-cell equipped with stir bars. The 200 mW/cm\(^2\) fiber optic output of the xenon lamp was used for backside illumination (through the FTO support) to measure the resultant photocurrents. All electrochemical and photoelectrochemical measurements were accomplished without iR compensation except for the Tafel plots presented.
in Figure 3.7. In all electrochemical experiments presented, potentials were measured against Ag/AgCl, where $V_{\text{NHE}} = V_{\text{Ag/AgCl}} + 0.197$ V.

3.3.6 XAFS and XANES Measurements of CoPi on Titania. These experiments were performed and analyzed by M. W. Marra and L. X. Chen at Argonne National Laboratory. The cobalt K-edge X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (XAFS) spectra were collected at beamline 12BM at the Advanced Photon Source of Argonne National Laboratory. Si(111) double crystals were used in the monochromator. The X-ray absorption spectra at the cobalt K-edge of the CoPi/TiO$_2$ films (electrochemically and photochemically deposited CoPi on TiO$_2$, along with the control sample where Co(II) salt solution was simply adsorbed onto the TiO$_2$ electrode) were collected by the fluorescence detection mode, using a Canberra 13-element germanium solid-state detector array, with the fluorescence photon energy window set for the cobalt Kα emission. Upon completion of the deposition, all samples were dried quickly using laboratory tissue (Kimwipe) and then immediately frozen in liquid nitrogen. Samples were then quickly transferred into a cryostat and held at 16 K to prevent any damage to the films over the duration of the experiment. A cobalt foil was placed in between two ionization chambers after the sample and used for the in situ energy calibration. XANES measurements of CoO and Co$_2$O$_3$ powders were taken and used as references for the oxidation state of cobalt in the deposited CoPi catalyst. The CoO and Co$_2$O$_3$ reference samples were powders diluted in boron nitride by grinding the mixtures. The transmission detection mode was used for the XANES spectra of the references. XAFS data analysis was performed with the Athena and Artemis packages based on IFEFFIT and FEFF programs. Theoretical models were constructed in Hyperchem (Hypercube Inc.); the
theoretical XAFS spectra were constructed using the FEFF package and were fit to the experimental data using Artemis.\textsuperscript{57,58}

3.4 RESULTS

3.4.1 Structural Characterization of CoPi on TiO\textsubscript{2}

3.4.1a SEM/EDX. SEM and EDX experiments were performed on the deposited catalyst following 15 hours of photodeposition on the mesoscopic titania electrode films. The SEM images after CoPi photodeposition feature both micrometer and sub-micrometer size particles of different shapes distributed throughout the semiconductor surface (Figure 3.1a and b, bright areas), along with a layer of catalyst distributed across the TiO\textsubscript{2} surface as suggested by EDX mapping of both cobalt and phosphate (Figures S2 and S3). The SEM of the layered catalyst was blurry with some bright spots containing cobalt and phosphate depicted in Figure 3.1b. The EDX elemental analysis indicated the presence of cobalt and phosphate consistent with previously reported CoPi catalysts.\textsuperscript{27,36,37} The ratio of Co:P lies between a 1:1 to 2:1 ratio and a strong background from the titania support (Ti) was clearly detected in the EDX profile.

![Figure 3.1](image)

**Figure 3.1.** (a) and (b) SEM images of the CoPi catalyst after 15 hours photodeposition on TiO\textsubscript{2}. (c) EDX spectrum. The elemental analysis shows the presence of cobalt and phosphate.
3.4.1b XANES and XAFS spectra. The XANES spectrum contains information on the structural and electronic characteristics of the X-ray absorbing atom. Figure 3.2 presents the Co K-edge (7.709 keV) XANES spectra of the CoO and Co$_2$O$_3$ model compounds along with the electrodeposited and photodeposited CoPi films on titania. The edge energy of the metal center is defined as the peak of the first derivative of the energy-space spectrum and is related to the oxidation state of the metal center; an increase in net cobalt oxidation state leads to an increase in cobalt edge energy because higher energy X-ray photons are required to eject the 1s electron to the continuum in a metal center with higher positive charges. The cobalt K-edge energy of both CoPi films closely matches that of the Co$_2$O$_3$, which indicates that the oxidation state of cobalt in the CoPi films is primarily +3. In addition, all XAFS data presented here were collected on freshly prepared samples in a quasi in-situ state at 16 K. These conditions were important to prevent the catalyst from slowly converting to Co(II) induced by residual water oxidation when subjected to moisture for prolonged time periods under open circuit conditions.$^{26}$ In samples where the CoPi OEC were deposited long in advance of the XAFS studies (several days) the primary oxidation state of the cobalt in those samples was +2, consistent with the resting state of the inactivated catalyst.$^{29,33}$
Figure 3.2. XAFS spectra of the photodeposited and electrodeposited CoPi films on TiO$_2$, CoO, and Co$_2$O$_3$. Black: Co$_2$O$_3$; Red: CoO; Blue: photodeposited CoPi; Green: electrodeposited CoPi. (a) XANES spectra of each cobalt sample showing the edge in each instance. (b) First derivative of the energy-space spectra illustrating the energy shift of the CoPi samples relative to CoO. Data were collected and analyzed by the Chen group at ANL.

The extended X-ray absorption fine structure (EXAFS or XAFS) spectrum contains information on the local structure surrounding the X-ray absorbing metal center, e.g. cobalt. The post-edge oscillations in the XAFS spectrum are caused by the interference between the outgoing photoelectron wave originated from the metal center, such as cobalt and the back scattered photoelectron waves from the surrounding atoms.$^{59-61}$ The Fourier transform of this interference pattern yields a pseudo radial distribution function centered at the Co atoms, where the peaks correspond to specific atom-atom distances. By fitting a theoretical model to the experimental data, the structural parameters corresponding to the structure of the film can be extracted from the following Eq. 4.$^{59-61}$

$$\chi(k) = \sum_i F_i(k)S_0^2(k)N_i/(kR_i^2)\exp(-2\sigma^2k^2)\sin[2kR_i + \phi_i(k)] \quad [4]$$

in which $F(k)$ is the magnitude of the backscattering, $S_0$ the amplitude reduction factor, $N$ the coordination number, $R$ the average distance, $\sigma^2$ the mean-squared displacement, and $\phi$ the
phase shift; the subscript indicates the \(i\)th atom, \(k\) the electron wavevector. Figure 3.3 presents the Fourier-transform of the XAFS of the CoPi films on titania, using a k-range of 3-13 Å\(^{-1}\) and a k-weight of 3. Structural models shown in Figure 3.4 were constructed from Hyperchem (Hypercube Inc.) and used as the reference structures in the FEFF calculations to produce reference scattering intensities and pathways. The first model (Figure 3.4a) with a complete and incomplete CoO cubane structure, and the second model (Figure 3.4b) with CoO\(_6\) edge-sharing octahedron structure were proposed in previous XAFS experiments and analyses.\(^{32,33,62-64}\) The structural parameters extracted from the fits for the films from both the electrochemical and photochemical depositions are listed in Tables 1 and 2, respectively. The structures of the films seem to be independent of the deposition technique and consist of 6 \(\mu\)-oxo oxygen atoms as the nearest neighbors for the cobalt center with a Co-O bond length of \(\sim 1.90\) Å. The next coordination shell contains on average 3.5 and 3.8 Co atoms at an average distance of \(\sim 2.81-2.82\) Å.
Figure 3.3. Magnitude and imaginary part of the Fourier transform of electrodeposited and photodeposited CoPi films on titania. Experimental data (black) was fit over an $R$ range of 1.0 – 2.8 Å (red). Figures (a) and (b) correspond to the magnitude and imaginary portions for the electrodeposited films respectively, while (c) and (d) correspond to the magnitude and imaginary portions for the photodeposited films respectively. Fourier transforms were performed over $k$-range of 3-13 Å$^{-1}$ using a $k$-weight of 3. Data were collected and analyzed by the Chen group at ANL.
Figure 3.4. Proposed structures for the CoPi film on titania. (a) Corner-sharing Co-oxo cubane model. (b) Edge-sharing molecular cobaltate cluster (MCC); models were constructed in Hyperchem and the geometry was optimized using a PM3 semi-empirical calculation. The atoms are color coded as cobalt (blue) and oxygen (red). Data were collected and analyzed by the Chen group at ANL.

Table 3.1. XAFS parameters for electrodeposited CoPi films on titania. $S_0^2$: passive reductive factor; $\Delta E$: energy shift; N: coordination number; R: atom-atom distance; $\sigma^2$: Debye-Waller factor. (The errors for the distances R are about 0.02Å, and that for the coordination number N is about 0.5). Data were collected and analyzed by the Chen group at ANL.

<table>
<thead>
<tr>
<th>Distance</th>
<th>$S_0^2$</th>
<th>$\Delta E$</th>
<th>N</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>0.70</td>
<td>0.50</td>
<td>6.0</td>
<td>1.90</td>
<td>0.0020</td>
</tr>
<tr>
<td>Co-Co</td>
<td>0.70</td>
<td>0.50</td>
<td>3.5</td>
<td>2.81</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

Table 3.2. XAFS parameters for photodeposition of CoPi films on titania. All parameters are identical to those in Table 1. Data were collected and analyzed by the Chen group at ANL.

<table>
<thead>
<tr>
<th>Distance</th>
<th>$S_0^2$</th>
<th>$\Delta E$</th>
<th>N</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>0.70</td>
<td>0.33</td>
<td>6.0</td>
<td>1.91</td>
<td>0.0028</td>
</tr>
<tr>
<td>Co-Co</td>
<td>0.70</td>
<td>0.33</td>
<td>3.8</td>
<td>2.83</td>
<td>0.0058</td>
</tr>
</tbody>
</table>
3.4.2 Electrochemical and Photoelectrochemical Measurements

3.4.2a TiO\textsubscript{2} Films with Adsorbed Co\textsuperscript{2+}. All electrochemical measurements as well as oxygen production are done in Co(II)-free solutions of 0.1 M NaPi at pH 7. TiO\textsubscript{2} films were soaked for 15 hours in 0.1 M sodium phosphate buffer at pH 7 containing 0.5 mM Co(NO\textsubscript{3})\textsubscript{2}. CV were recorded at 50 mV/s and revealed a dark quasi-reversible oxidation wave for Co\textsuperscript{3+/2+} at 0.93 V vs. Ag/AgCl corresponding to the oxidation of cobalt with hydroxo ligands, immediately followed by a catalytic water oxidation wave (Figure 3.5a, black).\textsuperscript{27,30} The cyclic voltammogram under bandgap illumination shows a slight cathodic shift for the onset of the catalytic wave that now overlaps the cobalt oxidation wave. The slight increase of current densities of few µA/cm\textsuperscript{2} at low potentials (< 0.93 V) with respect to the significant increase in catalytic behaviour at > 0.93 V lead us to run the controlled potential electrolysis at 1.1 V. Since we were primarily interested in the characterization of the photodeposited catalyst in terms of structure and activity, the deposition time was optimized for the XAFS experiments and electrochemical data, not for photocurrent generation. The dark current (Figure 3.5b, black) shows a current density of 0.22 mA/cm\textsuperscript{2} whereas the photocurrent density (Figure 3.5b, red) was approximately 0.35 mA/cm\textsuperscript{2}. Control experiments performed on bare FTO electrodes showed no appreciable current whether the light was on or off at V\textsubscript{applied} < 1.2 V vs. Ag/AgCl (Figure 3.5c). The dark current for blank TiO\textsubscript{2} films was almost negligible, and the photocurrent at 1.1 V was only ~ 0.04 mA/cm\textsuperscript{2} (Figures 5c and 5d).
Figure 3.5. (a) Cyclic voltammograms of TiO₂ film electrodes containing Co²⁺ ions adsorbed on the surface recorded at 50 mV/s under broadband illumination (red) and in the dark (black). (b) Controlled potential electrolysis of TiO₂ film electrodes containing Co²⁺ ions adsorbed on the surface at 1.1 V bias under broadband illumination (red) and in the dark (black). (c) Cyclic voltammograms performed on FTO glass when the light is off (black line) and on (red line), and TiO₂ films when the broadband light source is off (blue line) and on (green line). The light source was the 200 mW/cm² output from a Xe arc lamp passed through a water filter. (d) Controlled potential electrolysis of TiO₂ at 1.1 V bias under broadband illumination (red) and in the dark (black). The electrolyte in all experiments was Co(II)-free solution composed of 0.1 M NaPi buffer at pH 7.

3.4.2b Short-circuit Photodeposited CoPi on TiO₂. TiO₂ films decorated with photodeposited CoPi were evaluated for their ability to electrocatalyze water oxidation. The cyclic voltammogram of a typical sample reveals the presence of a sharp catalytic wave when recorded
in the dark (Figure 3.6a, black). The photocurrent at low applied potentials (< 0.93 V) was < 50 µA/cm² (Figure 3.6a, red), and the onset of the catalytic wave overlapped the cobalt oxidation (Co²⁺/Co³⁺) peak. The electrolysis performed at 1.1 V generated a dark current density stabilizing at ~0.5 mA/cm² after 5 hours of continuous electrocatalysis and a current density of 0.8 mA/cm² was produced under broadband illumination at ~200 mW/cm² (Figure 3.6b).

**Figure 3.6.** (a) Cyclic voltammograms of CoPi/TiO₂ subsequent to photodeposition, recorded at 50 mV/s in the presence (red) and absence of broadband illumination (black). (b) Controlled potential electrolysis of CoPi/TiO₂ after photodeposition, measured at 1.1 V bias in the presence (red) and absence (black) of broadband illumination. The electrolyte in all experiments was Co(II)-free solution composed of 0.1 M NaPi buffer at pH 7.

In Figure 3.7a, the current density in 0.1 M NaPi at pH 7 was recorded as a function of the overpotential for water oxidation, which was calculated based on Eq. 4.

\[
\eta (V) = V_{\text{appl}} - 0.62 - iR \quad [4]
\]

In Eq. 4, \(V_{\text{appl}}\) is the applied potential referenced against Ag/AgCl, where \(E_{\text{anodic}} = 0.62\) V, the equilibrium potential for water oxidation, \(i\) is the current density, and \(R\) is the solution resistance.
as measured by the potentiostat at 0.0 V. In all instances, the current density representative of each data point was permitted to stabilize prior to being recorded. The Tafel plot was measured in the dark using a fresh CoPi/TiO$_2$ electrode and yielded a slope of 63 mV/decade (Figure 3.7a). In Figure 3.7b, the current density was measured in 0.1 M NaPi at constant applied potential (1.1 V vs Ag/AgCl) but at varied pH. We assumed Nernstian behavior and corrected for the iR drop of the solution in order to calculate the overpotential in Eq. 5:

$$\eta (V) = [V_{\text{appl}} + 0.059 \times \Delta pH - iR] - 0.62 \quad [5]$$

where most parameters are identical to those in Eq. 4 and $\Delta pH = pH_{\text{solution}} - 7.0$, and $R$ is the solution resistance as measured by the potentiostat at 0.0 V at each pH value. The slope obtained from this modified Tafel plot was 56 mV/decade over pH 5-7, and then deviates when the phosphate buffer loses its buffering capacity at pH values higher than its second pKa (7.2). Operating the electrode under high current densities at pH > pKa$_2$ can result in a pH variation across the surface of the electrode as compared to the bulk pH of the solution, which results in a marked decrease of the expected current densities, thereby generating a deviation from the Tafel slope observed between pH 5 to 7 (Figure 3.7b).
Figure 3.7. (a) Tafel plot obtained after stepwise increase of the overpotential that was recorded after iR correction versus log of the current density. (b) Tafel plot obtained after stepwise increase of pH at 1.1 V vs Ag/AgCl, which was recorded after iR correction as overpotential versus log of the current density obtained. In both measurements a fresh CoPi/TiO$_2$ after 15 hrs photodeposition was used in 0.1 M NaPi buffer at pH 7 containing no Co(II).

The current density of the photodeposited CoPi film on titania at a 1.1 V applied bias was also measured in a weak proton acceptor electrolyte containing 0.1 M NaClO$_4$ where the current density dropped to $\sim$20 $\mu$A/cm$^2$ in comparison to the NaPi buffer where a 0.5 mA/cm$^2$ current density was sustained over the long term, Figure 3.8.

Figure 3.8. Comparison between the controlled potential electrolysis of CoPi photodeposited on a titania electrode at 1.1 V applied bias in strong proton acceptor 0.1 M NaPi Co(II)-free buffer (black line) and poor proton acceptor 0.1 M NaClO$_4$ Co(II)-free aqueous electrolyte (red line).
The oxygen yield was measured by headspace analysis using gas chromatography for the CoPi/TiO₂ film in a Co(II)-free NaPi buffer at pH 7 operating in controlled potential electrolysis mode at 1.1 V applied potential, resulting in the sustained generation of oxygen whether the light is off (Figure 3.9a) or on (Figure 3.9b). Assuming 100 % Faradaic efficiency, the theoretical oxygen yield was calculated by dividing the charge Q (C) passed through the circuit by Faraday’s constant, which was subsequently divided by 4 since it takes four hole equivalents to produce one molecule of oxygen. The amount of oxygen measured was corrected for the injection volume and Henry’s law. Therefore, the overall Faradaic efficiency is simply the amount of oxygen measured by GC divided by the theoretical yield extracted from the electrochemical charge passed. The product formation analysis presented in Figure 3.9a indicates that the rate of hydrogen production starts lower than the theoretical one; after 4 hours of electrocatalysis the rate become > 95 % matching the theoretical rate calculated by taking the first derivative of the theoretical number of moles of oxygen versus time (Figure 3.9a, light off). The initial slow rate of oxygen production detected in the headspace can be attributed to oxygen bubble formation on the electrode surface which does not release in the headspace of the photoelectrochemical cell despite stirring and the excess holes used to maintain the high oxidation state of the catalyst (≥ Co(III)). It is worth noting that prolonged photoelectrolysis as well as dark electrolysis performed on the CoPi/TiO₂ material produced ~100 ± 5 % Faradaic efficiency as ascertained by GC headspace analysis after > 10 hours of continuous catalysis, during which the amount of oxygen not released in the headspace becomes negligible versus the large amount of oxygen produced. The rate of oxygen production is ~ 4.5 µmol/hr when the light is off, and ~ 7 µmol/hr when the light is on. For illustration purposes, only data from the photoelectrolytic oxygen production measurements are presented in Figure 3.9b, where the
measured amount of oxygen produced and the theoretical yield were plotted when the CoPi/TiO$_2$ electrode was subjected for 17 hours to 1.1 V under constant 200 mW/cm$^2$ irradiation.

![Graph](image)

**Figure 3.9.** (a) Theoretical rate of O$_2$ produced in the dark calculated from the current/time plot produced under controlled potential electrolysis of a photodeposited CoPi film on a mesoscopic titania electrode under 1.1 V applied bias (black) and the corresponding rate of O$_2$ evolved as measured by GC headspace analysis produced in the identical sample (red). (b) Oxygen evolution as measured by GC headspace analysis compared with the theoretical yield after 17 hours photoelectrolysis of the same sample at 1.1 V applied bias under 200 mW/cm$^2$ backside illumination. The electrolyte in all experiments was Co(II)-free solution composed of 0.1 M NaPi buffer at pH 7.

3.5 DISCUSSION

In previous reports, CoPi has been grown with different macroscopic shapes depending on the length and method of deposition.$^{27,36,37,39,41,42,44}$ The ratio of cobalt to phosphate in the catalyst film doesn’t seem to affect the activity of the cobalt-oxo core, especially when one considers that the phosphate ions are most likely terminating the cluster.$^{33,37}$ The blurred image in SEM (Figures 1a and 1b) suggests that the catalyst likely renders the surface of titania more insulating and subsequently prone to charging effects from the electron beam.$^{39}$ In this study, we were
interested in the characterization of the as-deposited catalytic material. Hence, the deposition time was more elongated than previously reported materials,\textsuperscript{36-39} where the magnitude of deposition was assessed based on photocurrent optimization. In this regard, it is important to note that the dark brown CoPi catalyst deposited on TiO\textsubscript{2} (Figure 3.S1) will eventually have large competitive absorption for bandgap photons. In order to alleviate this effect, the photodeposition was performed using front-side illumination of the films and the photocurrent measurements were accomplished using backside illumination of these films.

The first model structure (Figure 3.4a) used in the EXAFS fitting of the electrochemically and photochemically-deposited films was a simple CoO cubane structure, similar to that previously proposed.\textsuperscript{32} Both the Co-O and Co-Co bond distances (1.89 Å and 2.81 Å, respectively) fit those in the model. The average Co-Co distance of 2.81 Å is consistent with two Co atoms connected by a μ-oxo bridge.\textsuperscript{32} The average first and second shell coordination numbers from this model are 6.0 and 2.4 respectively. While the coordination number for the cobalt with the first shell oxygen atoms agrees with the experimental value, the coordination number for the second coordination shell (Co – Co) from the fitting the experimental data were 3.5 and 3.8 for the electrochemically and photochemically deposited films respectively. According to the structure in Figure 3.4a, one central Co atom has a coordination number of 4 for the second coordination shell Co – Co distances, while each of the four peripheral Co atoms has a coordination number of 2 corresponding to the same Co – Co coordinating shell. Hence the average coordination number for the Co – Co shell in this cluster model should be \((4+4\times2)/5=2.4\), which is much lower than the values of 3.5 or 3.8 from the fitting. Using the model structure in Figure 3.4b, the Co – Co coordination numbers for the central Co atom is 6 and for each of the six peripheral Co
atoms is 3. The average coordination number for the Co – Co shell in the structure shown in Figure 3.4b is therefore \((6+6\times3)/7 = 3.43\), which is much closer to the experimental values listed in Tables 1 and 2. Hence, the XAFS results for the catalysts prepared electrochemically and photochemically on titania prefer an edge-sharing molecular cobaltate cluster (MCC) similar to the structural model suggested by Nocera and co-workers, Figure 3.4b.\(^{33}\) In addition, X-ray pair distribution function (PDF) analysis and high-energy X-ray scattering experiments performed at room temperature in the atmosphere on the electrodeposited “CoPi” catalyst suggested multiple edge-sharing CoO\(_6\) octahedra consisting of total 13-14 cobalt atoms with possible distorted geometries at the domain edges.\(^{66}\) However, their conditions for sample measurements (i.e., at room temperature in the atmosphere) differ from ours (i.e., cooled immediately in liquid nitrogen after being prepared and then measured at 16 K in vacuum). It is important to note from our results that the electrochemically-deposited film and the photochemically-deposited film on titania are indistinguishable within the resolution of the XAFS experiment, indicating that equivalent films are likely generated regardless of deposition technique. Originally, the MCC model was proposed based on a prepared “bulk” CoPi analyzed in-situ, since this type of structure can support Co-Co coordination numbers > 4.\(^{33}\) Our EXAFS results are also in favor of the edge-sharing CoO\(_6\) octahedra for both the electrodeposited and photodeposited CoPi on mesoscopic titania, confirming the in-situ EXAFS data and other electrochemical experiments performed on similar materials.\(^{30,33,64}\)

The presence of photodeposited CoPi enhanced the photocurrents at high potentials (> 0.93 V) as compared with the “naked” TiO\(_2\) or TiO\(_2\) bearing adsorbed Co(II) which indicates the formation of additional catalytic sites for water oxidation in the former, and a possible decrease
of charge recombination sites, which are primary prerequisites for photocurrent enhancement.\textsuperscript{37,53} The dark current density arising from this photodeposited catalyst were promising given the low coverage of cobalt on TiO\textsubscript{2} as compared with electrodeposited films of several micrometer thickness on conductive glass which gave \( \sim 1 \text{ mA/cm}^2 \) at 1.1 V vs Ag/AgCl.\textsuperscript{27} In addition, the photochemically grown catalyst was shown to be electrochemically active towards water oxidation. These results complement previous reports which demonstrated that electrochemically formed CoPi on BiVO\textsubscript{4} acted as an efficient photocatalyst for oxygen production.\textsuperscript{43}

The increase of one pH unit in the window of operating pH was equivalent to increasing the overpotential by \( \sim 59 \text{ mV} \), Figure 3.7. The Tafel slope of 59 mV/decade, which is equivalent to \( 2.3 \times RT/F \) (Figure 3.7) and the strong proton acceptor electrolyte requirement (Figure 3.8) suggest a proton-coupled electron transfer (PCET) process prior to the rate limiting oxygen evolution step.\textsuperscript{12,28,30,65,67,68} The drastic drop of current density in NaClO\textsubscript{4} electrolyte versus the sustainably of catalysis in NaPi buffer (Figure 3.8) demonstrates the necessity of phosphate to act as proton acceptor in the oxygen evolution cycle. In fact, proton transfer is considered a very important step in the oxygen production mechanism of CoPi, and NaClO\textsubscript{4} is a weak proton acceptor, rendering oxygen evolution inoperable. A rapid one-electron coupled to one-proton equilibrium between Co\textsuperscript{III}-OH and Co\textsuperscript{IV}-O most likely occurs before the oxygen production step, with the involvement of bridging oxygen atoms, analogous to the electrodeposited CoPi catalyst.\textsuperscript{11,29,30} This PCET was suggested to be a core step of the mechanism of oxygen evolution, and the subsequent self-healing property upon re-application of potential following catalyst dissolution; the latter could be induced by simply subjecting the electrodeposited CoPi to
open-circuit conditions.\textsuperscript{26,29,31} During prolonged controlled potential photoelectrolysis measurements performed for 17 hours at 1.1 V applied bias, the CoPi/TiO\textsubscript{2} system yielded \(\sim 100\pm 5\%\) current to oxygen conversion efficiencies (Figure 3.9b). This efficiency was the same whether the light is on or off, indicating that the holes supplied to the catalyst via electrochemical and photochemical methods are equivalent in terms of oxygen product formation once the CoPi catalyst is formed on the surface of TiO\textsubscript{2}. All these combined results confirm that the photochemically grown catalyst is similar in terms of activity to the electrochemically formed films, with both operating with near unity Faradaic efficiencies for oxygen production.

### 3.6 CONCLUSIONS

The CoPi OEC was photodeposited on mesoscopic TiO\textsubscript{2} films whose structure and electrocatalytic activity was characterized using a variety of techniques and illustrated remarkable consistency with the analogous established electrodeposited materials, already shown to be superior catalysts enabling water oxidation at neutral pH. The structure of the photodeposited CoPi material on titania is most likely composed of molecular cobaltate clusters featuring edge-sharing CoO\textsubscript{6} octahedra wherein water oxidation occurs through a series of redox processes involving proton coupled electron transfer prior to the ultimate oxygen evolving event. The OEC catalyst operated at near unity Faradaic efficiencies in controlled potential electrolysis experiments, indicating that the holes relayed to the photodeposited CoPi are indeed selective for promoting water oxidation on mesoscopic titania electrodes. The quantitative similarity in structure and operational mechanism of the water oxidation process strongly suggests that materials formed as a result of in-situ photodeposition on wide bandgap metal oxides represent a
viable strategy for the synthesis of next generation catalysts using earth abundant elements.

3.7 SUPPORTING INFORMATION

Figure 3.S1. Photograph of plain TiO$_2$ films (white, left) deposited on FTO glass and CoPi/TiO$_2$ films (dark brown, right) after 15 hrs photodeposition.
Figure 3.S2. EDX mapping of cobalt (CoK, blue dots) on TiO$_2$ after 15 hours of CoPi photodeposition, showing the distribution of cobalt on TiO$_2$. 
3.7.1 Co(II) adsorption to TiO$_2$ films. Co(II) ions can be adsorbed to TiO$_2$ films. As a control, TiO$_2$ films were soaked in 0.1 M NaPi containing 0.5 mM Co(NO$_3$)$_2$ for 15 hours in the absence of UV light or applied potential. The film was then dried with Kimwipe and the XANES spectrum of these films was measured at the Co K-edge. The results can be found in Figure 3.S4. The edge of the TiO$_2$ control is evident of the presence of cobalt primarily in the +2 oxidation state. The XANES of the CoPi films and of CoO are shown for comparison. The TiO$_2$ control and CoPi films were both held at 16 K during measurement, while the CoO was at room temperature. Figure 3.S5 shows the EDX spectrum of the TiO$_2$ along with cobalt and phosphate adsorbed on the surface in a ratio of $\sim$ 1:2:30 (Co:P:Ti).
Figure 3.S4. XANES spectra of TiO<sub>2</sub> control films previously soaked in 0.1 M NaPi containing 0.5 mM Co(NO<sub>3</sub>)<sub>2</sub>, CoPi films formed via photodeposition and electrodeposition, and CoO. TiO<sub>2</sub> control films show presence of Co(II), indicating that the Co(II) ions adsorb to the TiO<sub>2</sub>. The cobalt K-edge energy in the TiO<sub>2</sub> control is consistent with that in CoO, indicating primarily +2 oxidation state. Data were collected and analyzed by the Chen group at ANL.

Figure 3.S5. EDX spectrum of TiO<sub>2</sub> control films previously soaked in 0.1 M NaPi containing 0.5 mM Co(NO<sub>3</sub>)<sub>2</sub>. 
3.7.2 XAFS Spectra of CoO and Co$_2$O$_3$. The XAFS spectra of CoO and Co$_2$O$_3$ were measured and used as reference samples to elucidate the oxidation state and structure of the CoPi films. The k-space spectra of CoO and Co$_2$O$_3$ are shown in Figure 3.S7 and plotted with the photodeposited film (Figure 3.S7a) and the electrodeposited film (Figure 3.S7b). The low-frequency oscillations of the Co$_2$O$_3$ are quite similar to those seen in the photodeposited films, which indicate that the structures of the CoPi films are quite similar to that of Co$_2$O$_3$. The Fourier transform of these spectra was performed with a k-weight of 3 over a range of 3 – 13 Å$^{-1}$ and is displayed in Figure 3.S7C; only the electrodeposited film is shown for clarity. The first two peaks for the CoPi film, which represent the Co-O and Co-Co scattering paths, are identical with those of Co$_2$O$_3$, with the exception being the magnitude of the peaks. This indicates that the CoPi film has Co-O and Co-Co distances like those of Co$_2$O$_3$, with the difference being in the coordination numbers associated with these paths.
Figure 3.S7. XAFS spectra of CoO (red) and Co$_2$O$_3$ (blue) plotted in k-space with the photodeposited (a) and electrodeposited (b) CoPi films, and plotted in R-space with the photodeposited film (c). The similarity in the k-space oscillations and the peaks in the Fourier transform indicate that both the electrodeposited and photodeposited CoPi films exhibit Co-O and Co-Co distances similar to those of Co$_2$O$_3$; however, the coordination numbers associated with those paths differ from those in Co$_2$O$_3$, as evidenced by the differences in relative amplitudes of the first two peaks in the Fourier transform. Data were collected and analyzed by the Chen group at ANL.
3.8 REFERENCES


CHAPTER IV

INCREASING THE EFFICIENCY OF PHOTOELECTROCHEMICAL CELLS USING NON-COHERENT PUMPED UPCONVERSION PHOTOCHEMISTRY


4.1 ABSTRACT

Regenerative upconversion photochemistry occurring between palladium(II) octaethylporphyrin (PdOEP) and 9,10-diphenylanthracene (DPA) in toluene successfully sensitized nanostructured WO$_3$ photoanodes ($E_g = 2.7$ eV) to sub-bandgap non-coherent green photons. This effect was afforded by placing a vacuum degassed optical cell containing the upconverting composition in close proximity to a forward biased WO$_3$ electrode (+0.9 V vs Ag/AgCl in a 3-electrode arrangement) immersed in 1.0 M H$_2$SO$_4$ while exciting the sample with long pass filtered light, $\lambda_{ex} > 500$ nm ($< 2.5$ eV). Modulated (light on/light off) photocurrent response was demonstrated under these sub-bandgap excitation conditions and upon aeration of the cell, the upconversion process is quenched along with the loss of generated photocurrent. The incident photon-to-current efficiency (IPCE) response clearly demonstrates that WO$_3$-sensitized photoaction is derived exclusively from the porphyrin-based Q-bands (500 – 570 nm absorption).
In addition, we showed that the photochemical upconversion based on sensitized triplet-triplet annihilation can exhibit anti-Stokes emissions whose intensities with respect to the excitation power can vary between quadratic and linear using a Xe lamp non-coherent light source. The linear power dependence was achieved using solar light flux, which is a necessary prerequisite towards realizing the highest possible annihilation-limited upconversion quantum efficiencies, essential for device integration. The combined results represented the first experimental observations of sub-bandgap sensitization of a semiconductor using non-coherent pumped upconversion photochemistry.

4.2 INTRODUCTION

One of the main barriers to the performance of single-junction solar cells exceeding the Shockley-Queisser limit is their inability to harvest the complete solar spectrum, particularly at lower energies with respect to the bandgap. A potentially useful strategy towards realizing sub-bandgap photon capture and conversion in these devices lies in the phenomenon of regenerative photochemical upconversion based on sensitized triplet-triplet annihilation (TTA), a process resulting in the frequency upconversion of light, Scheme 1.1. In general terms, photon upconversion is facilitated by selective excitation of strongly absorbing sensitizer chromophores that internally convert to the long-lived lowest energy triplet excited state with high quantum efficiency. Dexter-type triplet-triplet energy transfer then occurs to molecular acceptor species energetically poised for TTA and thus, the desired annihilation-producing fluorescence. In the majority of recent cases, late transition metal-based sensitizers are used in tandem with a variety of organic-based triplet acceptors/annihilators in fluid solution, and the upconverted photons
are easily visualized by the naked eye. As the quantum efficiency of these processes have already been demonstrated to be substantial,\textsuperscript{2,5,18,23} approaching an annihilation limit of more than 40\%,\textsuperscript{10} widespread device integration appears inevitable. While there has been remarkable progress towards generalizing the phenomenon of regenerative photochemical upconversion and integrating this photonics into polymeric hosts, this light-producing photochemistry has not been used to generate any photocurrent responses to date. Interested in driving sensitized triplet fusion processes at their highest possible efficiency using solar photons, we experimentally demonstrate for the first time incident light power dependence ranging between quadratic and linear in photochemical upconversion from the prototypical PdOEP/DPA composition in toluene solutions using appropriately filtered lamp excitation. Importantly, the high quantum efficiency linear regime is achieved with non-coherent pumping of the Pd sensitizer at incident light power levels provided by the sun (AM 1.5G) integrated across the low energy Q-bands of the sensitizer.

4.3 EXPERIMENTAL

4.3.1 Materials. Tungsten(VI) oxide (WO\textsubscript{3}) nanopowder (<100 nm particle size (TEM)), hydroxypropylcellulose, hexachloroplatinic acid hexahydrate, anhydrous isopropanol and glacial acetic acid were purchased from Aldrich and used without further purification. Concentrated sulfuric acid was purchased from EMD. Water was deionized using a Barnstead nanopure system. Fluorine doped tin oxide (FTO) conductive glass substrates (TEC 15) were purchased from Hartford Glass. Pd(II) octaethylporphyrin (PdOEP) was purchased from Frontier Scientific and used without further purification. 9, 10-Diphenylanthracene (DPA) was purchased from Alfa Aesar and used as received. Spectroscopic grade toluene was purchased from Aldrich.
4.3.2 WO₃ film formation. FTO conducting glass substrates were cleaned by sonication using a solution of HCl in isopropanol, a solution of laboratory soap in water, then finally acetone. The FTO glass was then dried in an oven. A mixture of 3:1 by volume H₂O:CH₃COOH (glacial acetic acid) was mixed slowly with the WO₃ solid (12 wt.%) and hydroxypropylcellulose (6 wt.%). This mixture was sonicated and stirred rigorously overnight. The resultant paste was doctor bladed on FTO glass between 3 Scotch tape layers and the final WO₃ electrode area was adjusted to 1 cm² after the electrode was sintered at 500 °C for 30 minutes at a heating rate of 5 °C per min. The sintering resulted in a material with 10 µm average thickness as measured using a KLA-Tencor Alpha-Step IQ surface profiler.

4.3.3 Photoelectrochemical (PEC) characterization. Electrochemical measurements were performed using a BAS Epsilon electrochemistry workstation using a standard three-electrode arrangement and corrected for the dark current which was allowed to stabilize for several minutes before initiating the measurements. The PEC cell consisted of fused optically flat silica possessing a cubic shape equipped with a Teflon cap where all the electrodes were inserted. All solutions were degassed for 30 minutes before each experiment and maintained under an Ar atmosphere blanket. Current/time measurements were performed using controlled potential electrolysis (CPE) at a positive overpotential to assist water oxidation. The potential for CPE was chosen in order to achieve a stable current after few minutes of electrolysis while simultaneously producing detectable photocurrents. PEC linear sweep voltammetry (LSV) experiments were also performed to obtain photocurrent response as a function of applied potential. LSV was performed at a scan rate of 1 mV/s and 0.033 Hz light chopping frequency. The electrolyte in all these experiments was 1.0 M H₂SO₄ solution owing to the stability of WO₃ in acidic media. The light source in these experiments was a 300 W Xe lamp equipped with a water filter to remove
IR irradiation (heat) and two 500 nm long pass filters. The output of this apparatus was passed through a bifurcated fiber optic bundle to give 25 mW/cm$^2$ flux at the two outputs. The upconversion cuvette was placed as close as possible to the WO$_3$ photoanode affording backside illumination of the electrode. The irradiation of the upconversion mixture was achieved by simultaneously exciting two sides of the optical cell using the bifurcated fiber optic, as photographed in Figure 4.2.

4.3.4 Upconversion Photoaction Spectra. The IPCE curve presented in Figure 4.4 was calculated from the measured photocurrent (BAS Epsilon instrument) at different wavelengths using the identical PEC setup as described immediately above. Photocurrents were allowed to stabilize for 2-3 minutes and were corrected for dark current background. The light source in this experiment was a 450 W xenon arc lamp coupled to a monochromator installed in an Edinburgh Instruments fluorimeter (FS920) in tandem with a 455 nm long pass filter. The light power at different wavelengths was measured using a Nova II/PD300-UV power meter/detector head from Ophir. The following formula was used to calculate the IPCE as a function of excitation wavelength:

$$\text{IPCE} (\lambda) = \frac{h \times c \times \lambda^{-1} \times \text{Photocurrent} \times \text{Incident Optical Power}^{-1}}{1}$$

where, $h$ = Planck’s constant = $6.626 \times 10^{-34}$ (J × s$^{-1}$), $c$ = speed of light = $299,792,458$ (m × s$^{-1}$), $\lambda$ = wavelength in meters (m), photocurrent was measured in amps (A), and incident optical power was measured in watts (W).
4.4 RESULTS AND DISCUSSION

The current experimental effort explores the concept of utilizing molecular upconversion phenomena to achieve photoaction from sub-bandgap photons to sensitize oxidation chemistry in photoelectrochemical cells. In essence, we questioned whether select portions of the solar spectrum could be frequency shifted through upconversion to spectrally align with optical transitions within wide bandgap semiconductors, thereby achieving long wavelength light harvesting without chemical modification of the functional material. This is conceptually identical to employing upconversion phenomena to drive sub-bandgap responses from operational photovoltaics, with the advantage of detection sensitivity. Figure 4.1 presents our initial strategy for integrating frequency upconversion into operational water splitting photoelectrochemical cells where water is oxidized at a WO$_3$ semiconductor photoanode ($E_g = 2.7$ eV)$^{33}$ only in the presence of appropriate catalyst and hydrogen is produced at a dark Pt cathode in a standard 3-electrode arrangement.$^{33-38}$ The anode is photoactivated through the benchmark upconverting composition (PdOEP (1) and DPA (2) in toluene)$^{9,13,16,29}$ contained inside a vacuum degassed optical cell that is placed proximate to the working electrode. The optical output of a 300 W Xe lamp is passed through a water filter and two 500 nm long pass filters prior to entering a bifurcated fiber optic bundle, ultimately delivering long wavelength excitation photons ($\lambda_{ex} > 500$ nm) to the upconversion cell (from two sides) at a broadband power of 25 mW. In the present instance, upconverted photons are being stochastically collected at the WO$_3$ photoanode and no attempts were made to improve optical coupling.
Figure 4.1. Chemical structures of PdOEP (1) and DPA (2) along with a schematic representation of an upconversion-powered photoelectrochemical cell relying on stochastic collection of photons.

Nanoscopic WO$_3$ colloidal photoanodes of 10 µm thickness were deposited on FTO glass (1 cm$^2$ active area) and used as the working electrode (1.0 M H$_2$SO$_4$ electrolyte) in the experiment depicted in the digital photograph in Figure 4.2. The electrode was biased to +0.9 V vs Ag/AgCl, conditions enabling detection of stable and reproducible photocurrents arising from PdOEP/DPA upconversion pumping resulting from broadband non-coherent lamp excitation above 500 nm. It is important to note that most of the 25 mW optical power contained in this long-passed excitation is not absorbed by PdOEP so the present experiment is truly conservative with respect to what can be achieved with higher incident optical powers.

Figure 4.2. Digital photograph of the operational upconversion-driven photoelectrochemical cell.
Figure 4.3a and 4.3b present the current/time plots and linear sweep voltammograms, respectively, obtained under modulated (on/off) long wavelength excitation directed at the upconversion optical cell after passing through the electrolyte solution (see Figure 4.2). The isolated toluene solution contained in the optical cell is either degassed (red line) or aerated (black line), conditions enabling or nearly quantitatively quenching the upconversion process, respectively. Since the upconversion photochemistry relies exclusively on the efficient generation of the triplet excited states of both sensitizer and acceptor/annihilator, dissolved O\textsubscript{2} strongly competes for these formed triplets. Clearly, the blue photons ($\lambda_{\text{max}} = 430$ nm) generated from the upconversion process, presented as singlet DPA fluorescence, become randomly absorbed by the WO\textsubscript{3} anode resulting in measurable photocurrents under quite modest non-coherent excitation conditions. The measured photoresponses are justifiably small (Figure 4.3) given the fact that these proof-of-concept experiments rely exclusively on the stochastic collection of photons at the WO\textsubscript{3} photoanode, which can be greatly improved in terms of geometric format, light delivery, and photon collection. Please note that removal of either chromophore from the composition completely ceased all sub-bandgap sensitization of the WO\textsubscript{3} electrode. Control experiments were performed with FTO electrodes, containing no WO\textsubscript{3} on the surface. These samples were tested to eliminate the possibility that the FTO support is contributing to the photocurrent observed. Indeed, no photocurrent was observed when WO\textsubscript{3} wasn’t present because FTO is optically transparent in the visible spectrum.
Figure 4.3. Shuttered current/time response of a WO$_3$ photoanode biased to +0.9 V vs Ag/AgCl (a) and linear sweep voltammetry of WO$_3$ (b) in 1.0 M H$_2$SO$_4$ resulting from long wavelength excitation ($\lambda_{ex} > 500$ nm, broadband power of 25 mW) of a proximate optical cell containing a mixture of PdOEP (16 µM) and DPA (0.5 mM) in toluene. The red current response is obtained when the upconversion solution is deoxygenated and the black current (control) response occurs when upconversion is almost completely quenched by aerating the toluene. In all instances, the WO$_3$ anode collects the upconverted photons stochastically and the measurements are adjusted to zero baseline for clarity.

To further substantiate that the upconversion process is solely responsible for all generated photocurrent, sub-bandgap photoaction spectra were measured for the operational vacuum degassed composition from Figure 4.3. In order to calculate the relative incident photon-to-current efficiency (IPCE) as a function of excitation wavelength, the photocurrent was measured in the same three electrode arrangement as described above, however, the excitation source was changed to a 450 W Xe lamp coupled to a monochromator, also equipped with appropriate long pass filters. Figure 4.4 presents the normalized IPCE response from the WO$_3$ anode measured as a function of excitation wavelength (± 5 nm) between 500 and 570 nm. Clearly, the relative photocurrent response closely tracks the absorption profile of the PdOEP Q-band.
absorptions, illustrating that the sub-bandgap response is indeed resulting from the sensitization afforded by the PdOEP/DPA upconversion composition.

Figure 4.4. Sub-bandgap normalized photoaction response of a WO$_3$ photoanode measured as a function of wavelength in 1.0 M H$_2$SO$_4$ at +0.9 V vs Ag/AgCl forward bias. The photoaction ($\lambda_{ex} = 500$-570 nm, 5 nm steps) is generated from selective excitation of an upconversion composition (16 µM PdOEP and 0.5 mM DPA) that is either degassed (red line) or aerated (black line), respectively facilitating or quenching the photochemical upconversion process. The blue data points represent normalized absorption values at select wavelengths.

Finally, the question remained as to whether photochemical upconversion could achieve completely linear incident light power dependence when pumped by non-coherent photons. We decided to increase the sensitizer concentration to provide an optical density of 1.9 in the Q-band maximum at 545 nm and measure the resultant upconverted DPA emission (420 ± 4 nm) in front-face geometry in the spectrofluorimeter. The results of these experiments are presented in Figure 4.5, plotted as a double logarithm response, with the inset plotted as linear plot. From below 100 µW cm$^{-2}$ to approximately 1 mW cm$^{-2}$ incident power density using 545 ± 10 nm Xe lamp excitation, the power law exhibited by the composition was clearly quadratic. Deviations away from this “square” behaviour occurred at ~ 2 mW cm$^{-2}$ and continued to flatten towards a
pure linear response, which was finally achieved at 10 mW cm\(^{-2}\). Unfortunately, the maximum light fluence that we could obtain in our fluorimeter was only slightly larger, thereby limiting a more thorough examination of the linear regime under these experimental conditions. Importantly, non-coherent photon absorption does indeed achieve sensitized upconverted emission obeying a linear power law in this benchmark composition. The irradiance supplied by the sun (AM 1.5G spectrum) integrated over the entire Q-band absorption profile of PdOEP (475 - 575 nm) gives \(~13\) mW cm\(^{-2}\) with a corresponding photon flux of \(~3.5\times10^{16}\) photons s\(^{-1}\) cm\(^{-2}\), indicated by the green vertical line in Figure 4.5. This flux is positioned above the threshold necessary for achieving linear power dependence for sensitized triplet fusion in this composition under the experimental conditions of Figure 4.5. Consequently, AM 1.5G sunlight illumination is clearly poised for achieving the highest possible upconversion quantum yield in concentrated vacuum degassed solutions of these two chromophores. To estimate the maximum absorbed photon-to-current conversion efficiency (APCE) that can be achieved at 515 nm using PdOEP/DPA and a wide bandgap semiconductor electrode, the quantum yield of upconversion (\(\Phi_{UC}\)) based on two absorbed photons was measured to be \(\Phi_{UC} = 0.36 \pm 0.01\) under 350 mW/cm\(^2\) Ar\(^+\) laser excitation at 514.5 nm, when \(A_{515nm} = 0.09\). Please note that \(\Phi_{UC}\) was measured in the strong annihilation regime where the largest possible upconversion yields will be produced. Presumably, if all upconverted photons are absorbed and converted into photocurrent with 50% efficiency (IPCE at bandgap) across the DPA emission profile, then \(APCE_{515\ nm} = \frac{1}{2} \times \Phi_{UC} \times IPCE_{bandgap} = 9\%\), representing modest sub-bandgap photoaction at this wavelength. This value can be readily translated across the entire width of the porphyrin Q-band region (~60 nm), producing net sensitized photocurrent over its absorption profile.
Figure 4.5. Upconversion emission signal at $420 \pm 4$ nm measured as a function of $545 \pm 10$ nm incident non-coherent photons (photons s$^{-1}$ cm$^{-2}$ upper scale and mW cm$^{-2}$ lower scale) in a mixture of PdOEP (38 µM, O.D. @ 545 nm = 1.9) and DPA (0.78 mM) in vacuum-degassed toluene. The solid lines are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively. The green vertical line indicates the solar irradiance (AM 1.5G) integrated across the Q-band absorption profile of PdOEP (475 - 575 nm). Inset: linear plot of the same data, the blue data points fitted the quadratic power regime, the red fitted the linear regime whereas the black ones were intermediates.

4.5 CONCLUSIONS

In summary, sub-bandgap photoaction from a prototypical wide bandgap semiconductor in an operational photoelectrochemical cell has been demonstrated for the first time using the concept of regenerative photon upconversion. Specifically, nanostructured WO$_3$ photoanodes ($E_g = 2.7$ eV) in aqueous solution were sensitized to non-coherent green light using the tandem benchmark composition of PdOEP and DPA dissolved in vacuum degassed toluene self-contained in a proximate optical cell. Shuttered light on/light off sub-bandgap photoresponses recorded when the optical cell was either degassed or aerated resulted in the observation of modulated photocurrent or dark current, respectively, demonstrating that upconversion photochemistry
was indeed responsible for the generated photocurrent. The normalized IPCE response recorded for the operational composition illustrated that the long wavelength photoaction of the \( \text{WO}_3 \) is intimately tied to the PdOEP Q-band absorptions above 500 nm. Although the current experiments simply intended to demonstrate proof-of-principle, we note that the quantum efficiency of the photocurrent response is strongly dependent on the spatial arrangement of the upconverting composition relative to the electrical device and significant optimization in the near future is envisioned. This will potentially lead to new classes of photoelectrochemical cells poised to contribute in the solar fuels photochemistry arena. Fortunately, the power dependence linear regime was experimentally realized using non-coherent photons at solar power densities. Consequently, slightly concentrated terrestrial sunlight can potentially achieve annihilation-limited upconversion with high efficiencies, an important prerequisite for device integration. With improved optical coupling between elements, regenerative photon upconversion appears well positioned to assist with long wavelength light harvesting in next generation solar cell materials including dye-sensitized solar cells and organic bulk heterojunctions.

4.6 SUPPORTING INFORMATION

4.6.1 Relative actinometry, quantum yield (QY) measurements. \( \Phi, A, I \) and \( \eta \) represents the quantum yield, absorbance at \( \lambda = 515 \) nm (Figure 4.S1, \( A_{515} \sim 0.09 \)), integrated photoluminescence intensity and refractive index respectively of the upconversion sample (UC) and the standard (std). UV-Vis absorption spectra were measured on a Cary 50 Bio spectrophotometer. Steady-state photoluminescence spectra were recorded using QM-4/2006SE fluorescence spectrometer obtained from Photon Technologies Incorporated coupled with an argon ion laser (Co-
herent Innova 300) excitation source, whose 515.5 nm line was isolated using a series of diffraction grating, band-pass filter, 500 nm long-pass filter and neutral density filters to obtain 350 mW/cm$^2$ beam power measured by a Molectron Power Max 5200 power meter. The QY standard was Ru(bpy)$_3$Cl$_2$ in aerated water whose $\Phi_{\text{std}} = 0.04 \pm 0.002$. The refractive index of the solvents used were $\eta_{\text{water}} = 1.340$ and $\eta_{\text{toluene}} = 1.496$ as obtained from Sigma-Aldrich solvent physical properties. The following formulas was used to calculate the quantum yield of upconversion:

$$\Phi_{\text{UC}} = 2 \Phi_{\text{std}} \left(\frac{\Delta \eta}{\Delta \Phi_{\text{UC}}}\right) \left(\frac{I_{\text{UC}}}{I_{\text{std}}}\right) \left(\frac{\eta_{\text{toluene}}}{\eta_{\text{water}}}\right)^2 \tag{1}$$

$$\Phi_{\text{UC}} = \Phi_q \times \Phi_{\text{TTA}} \times \Phi_f \tag{2}$$

Where $\Phi_{\text{UC}}$ is the upconversion QY, $\Phi_q$ is the quenching QY, $\Phi_{\text{TTA}}$ is the triplet-triplet annihilation QY and $\Phi_f$ is the emitter’s QY (DPA in this case).

The upconversion mixture in toluene contained $[\text{PdOEP}] = 5 \mu\text{M}$ and $[\text{DPA}] = 0.1 \text{ mM}$; a condition allowing the $\Phi_q$ close to unity. The factor 2 comes from the fact that for each upconverted photon, two triplet excited states should be consumed in the TTA process. The emission spectra of DPA in the upconversion mixture suffers from re-absorption coming from the Soret band of PdOEP at $\lambda < 430 \text{ nm}$. To mitigate this problem, a simulated DPA emission spectra based on $\lambda_{\text{em}} = 432 \text{ nm}$ was used to calculate the QY. The emission of the Ru(bpy)$_3$Cl$_2$ was integrated over 550–850 nm and the simulated upconversion emission was integrated over 375-550 nm (Figure 4.S2). The value of the upconversion QY was: $\Phi_{\text{UC}} = 0.36 \pm 0.01$. Since $\Phi_f = 0.95$ for DPA, the $\Phi_{\text{TTA}} = 0.38$. 
Figure 4.S1. Absorption spectra of the upconversion sample (UC) in vacuum degassed toluene and Ru(bpy)$_3$Cl$_2$ (std) in aerated water.

Figure 4.S2. Simulated photoluminescence spectra of the upconversion sample (UC) in vacuum degassed toluene and Ru(bpy)$_3$Cl$_2$ (std) in aerated water under the same excitation conditions.
4.7 REFERENCES


5.1 ABSTRACT

A newly conceived series of cobalt polypyridine water reduction catalysts have been investigated photocatalytically in aqueous ascorbic acid (H$_2$A)/ascorbate (HA$^-$), where HA$^-$ served as the sacrificial reductant and potential proton source during photocatalysis. These Co catalysts were coordinated to redox active ligands, allowing catalysis to operate under lower overpotential with respect to the ones coordinated to redox innocent ligands. Owing to the stability of this catalyst framework, we identified the decomposition product derived from the [Ru(bpy)$_3$]$^{2+}$ photosensitizer (PS) as an adduct consistent with the stoichiometry of [Ru(bpy)$_2$HA]$^+$ that was found to be inefficient for photocatalysis. The Co(II)-2-(bis(2-pyridyl)(methyl)methyl-6-pyridylpyridine (termed Co(bpyPY2Me)) catalyst achieved a turnover number (TON) of $\sim$ 4200 (H$_2$/Co) with a corresponding turnover frequency (TOF) of $\sim$ 3160 (H$_2$/Co/hr) under simulated sunlight (AM 1.5G, 100 mW/cm$^2$) in aqueous H$_2$A/HA$^-$ at 1 µM Co concentration. The reductive quenching mechanism leading to hydrogen production and all related rate parameters were examined by pump-probe transient absorption spectroscopy and dynamic photoluminescence. Photocatalytic experiments performed in D$_2$O/(H$_2$A/HA$^-$) solutions showed > 90% deuterium incorporation in the gaseous hydrogen products (H$_2$, HD, and D$_2$), verifying the ability of this cobalt catalyst to reduce aqueous protons into hydrogen gas. In this chapter, a newly investigated Ru(II) molecular PS demonstrated considerable photostability with respect to [Ru(bpy)$_3$]$^{2+}$ per-
mitting enhanced hydrogen-evolving photocatalysis to be observed in conjunction with the Co(bpyPY2Me) catalyst under visible light illumination using similar experimental conditions as in the [Ru(bpy)_3]^{2+} case.

5.2 INTRODUCTION

Hydrogen is a desirable high energy feedstock chemical whose oxidation leads to the formation of water and energy as products.\textsuperscript{1-4} Hydrogen gas is currently being produced on industrial scales by steam reforming of natural gas or from coal.\textsuperscript{5} However, this reforming process yields CO and CO\textsubscript{2} as by-products, and the cost of energy produced in this manner is still several times higher than energy produced by burning fossil fuels.\textsuperscript{5} Therefore, alternative methods to produce hydrogen should be engineered in order to provide a sustainable clean source of energy to meet the growing global demand for energy and fuel. Learning from examples in nature, efforts have been focused for decades to develop biomimetic artificial photosynthetic schemes\textsuperscript{6-11} capable of storing solar energy in the form of electricity or chemical bonds. The development of photocatalytic systems for hydrogen evolution reactions in water has been a challenging problem for more than few decades.\textsuperscript{1-4,12-15} Very few light-triggered systems based on earth abundant catalytic materials are capable of achieving proton reduction from water with no organic co-solvent.\textsuperscript{9,16-21} Interestingly, some efficient catalysts for hydrogen generation are composed of Co,\textsuperscript{16,18,22-29} Ni\textsuperscript{30-33}, Mo\textsuperscript{34-36} or Fe\textsuperscript{37,38} centers, which constitute a large advancement in the field of solar fuels. Most of these systems were recently reviewed.\textsuperscript{39-42} The molecular compositions that were reported to work in pure water mostly required high-energy ultraviolet light irradiation, and they are commonly plagued with low catalytic activity under visible illumination.\textsuperscript{16,18,19} In this work, we developed a multi-component composition capable of producing copious amounts of hydrogen
from aqueous solutions under visible illumination while maintaining large turnover parameters (TON and TOF vs catalyst). More importantly, the catalysts in these systems were cobalt complexes bearing different polypyridine ligand frameworks, allowing plausible application of these molecules for solar energy storage. The main PS utilized in these compositions was the benchmark metal-to-ligand charge transfer (MLCT) chromophore ruthenium(II) tris-(2,2’-bipyridine) ([Ru(bpy)₃]²⁺) which possesses a long-lived excited state with concomitant visible electronic transitions providing desirable solar-photons harvesting ability.⁴³-⁴⁵ A high-throughput photochemical hydrogen production apparatus has been designed, allowing rapid screening of chemical species for their ability to perform proton reduction catalysis. This strategy has been successful to characterize photochemical reactions under a variety of conditions in a combinatorial manner. Then, the optimized compositions were also evaluated under simulated sunlight (AM 1.5G, 100 mW/cm²). In this chapter, we have investigated in depth the mechanism of the individual electron transfer steps leading to hydrogen production and identified the decomposition pathways that occur. The MLCT PS [Ru(bpy)₃]²⁺ in H₂A/HA⁻ media formed the corresponding [Ru(bpy)₂HA]⁺ after prolonged photolysis. While ligand loss and photoannation in ruthenium polypyridyl complexes have been investigated heavily in the 1980’s,⁴⁶-⁴⁹ we characterized the decomposition product of the [Ru(bpy)₃]²⁺ PS by analytical HPLC, MS and UV-Vis spectroscopy. This by-product was found to be an inefficient PS for hydrogen production and, in fact, leads to a decrease of hydrogen evolution rates as [Ru(bpy)₃]²⁺ is depleted during the course of the photoreaction. The Co(bpyPY2Me) catalyst, separated by HPLC after photocatalysis, was found to be largely intact and therefore more stable than the PS when both were present at low initial concentrations (< 10⁻⁴ M). The turnover numbers and frequencies versus catalyst increased drastically with decreasing catalyst concentration, a TON of ~ 4200 (H₂/Co) and a TOF of ~
3160 (H₂/Co/hr) was achieved under simulated sunlight (AM 1.5G, 100 mW/cm²) at room temperature. The mechanism of hydrogen production was thoroughly investigated by transient absorption spectroscopy following 452 nm pulsed laser excitation. The photoexcited Ru(II) PS undergone reductive quenching by the H₂A/HA⁻ at pH = 4. In the absence of catalyst, recombination occurred between the reduced PS and the oxidized HA⁻ (termed HA'). However, in the presence of catalyst, the resulting ruthenium bound ligand radical anion transferred an electron to Co(II) which subsequently entered the hydrogen evolution cycle. MS analysis of the headspace suggested that hydrogen was the major gaseous product, and experiments performed in D₂O showed > 90% deuterium incorporation into the gaseous hydrogen-based products (H₂, HD, D₂) strongly suggesting that water was providing the primary source of protons ultimately reduced by the catalyst. The redox-active tetradentate bpyPY2Me and pentadentate bpy2PYMe ligands have been investigated here and their corresponding Co(II) transition metal complexes were tested for photocatalytic water reduction. Related Co complexes with redox-inert ligands catalyzed proton reduction at higher overpotential and lower rates than these complexes, which indicated the importance of redox active ligands for catalyzing hydrogen evolution with transition metal centers. Throughout the search for molecular compositions for hydrogen production in water, researchers have commonly used the prototypical [Ru(bpy)₃]²⁺ and its derivatives as PS. [Ru(bpy)₃]²⁺ has been extensively studied since the discovery of its luminescence in 1959 because of its attractive photophysical and electrochemical properties. This PS is widely available, and possesses appropriate energetics for both water oxidation and water reduction. However, [Ru(bpy)₃]²⁺ was found to be unstable due to ligand loss and photoannation chemistry. This photochemistry was shown to be thermally activated, since the dissociative metal centered triplet state (³*MC) is ~ 3600 cm⁻¹ above the lowest ³*MLCT excited state.
Despite the intrinsic instability of this PS in solution, especially in the presence of high concentration of potential ligands including H$_2$O and ascorbate, it is still widely utilized in photocatalysis.\textsuperscript{16,24,65} In the midst of the new advances in designing highly stable electrocatalytic water reduction catalysts composed of earth abundant materials,\textsuperscript{21,26,33,35,36} the search for new PS that can be coupled to these catalysts becomes necessary. Ir(III)\textsuperscript{22,66-68} and Re(I)\textsuperscript{9,19,69} molecules have demonstrated superior stability compared to [Ru(bpy)$_3$]$^{2+}$ but they generally have small extinction coefficients in the visible region or simply do not absorb visible light at all. In addition, Pt(II)\textsuperscript{25,28} and organic chromophores\textsuperscript{70-72} have been utilized in photocatalysis but they commonly photobleach rapidly during catalysis. Here we describe a Ru(II) PS that displays superior stability relative to [Ru(bpy)$_3$]$^{2+}$ during photocatalysis. The newly investigated PS, Ru(II)-tris(bathophenanthroline-disulfonate) tetrasodium salt Na$_4$[Ru(BPS)$_3$],\textsuperscript{73,74} was based on the concept of producing a hydrophobic rigid core with projecting hydrophilic sulfonate groups. This ligand framework furnished a Ru(II) complex with an overall 4$^-$ charge which can potentially enhance the interaction (ion pairing) with Co(II) catalysts possessing 2$^+$ charge. In addition, the hydrophobic core was also found to increase the stability of the respective Ru(II) molecule. We also believe that the rigidity of the phenanthroline ligands plays an important role to reduce ligand loss photochemistry.\textsuperscript{75} In side-by-side comparisons, [Ru(BPS)$_3$]$^{4-}$ significantly outperformed [Ru(bpy)$_3$]$^{2+}$ in terms of turnover numbers. The stability of the complexes was assessed by UV-Vis before and after catalysis when placed in 1 M H$_2$A/HA$^-$ solutions at pH 4. Also, the reductive quenching mechanism along with other rate constants and electron transfer cage escape yields were investigated by flash photolysis. These findings provide insights into the development of molecular compositions capable of hydrogen evolution in aqueous media without the need of organic co-solvents.
5.3 EXPERIMENTAL SECTION

5.3.1 Materials. Tris(2,2’-bipyridyl)dichlororuthenium(II) hexahydrate ([Ru(bpy)$_3$]Cl$_2$.6H$_2$O), Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride (Ru(phen)$_3$Cl$_2$), L-ascorbic acid and bathophenanthroline disulfonic acid disodium salt trihydrate (BPS) were purchased from Aldrich and used without further purification. The synthesis of Na$_4$[Ru(BPS)$_3$] was carried out using a reported literature procedure.$^{73}$ NMR characterization was performed and the meta substituted complex was exclusively obtained (Figure S37-S38). All Co(II) catalysts were synthesized and characterized at the University of California, Berkeley (Long and Chang groups).

5.3.2 Photocatalysis Experiments. Hydrogen production measurements were performed on a home-built 16 well combinatorial apparatus (see picture below). Typically, 10 mL of total catalytic solution volume prepared in a 40 mL air-tight EPA vial (VWR Scientific) was irradiated from the bottom using a royal-blue LED (Philips, Luxeon Rebel series) mounted on a starboard (LXMS-PR01-0425-CT) whose output was passed through a Fraen narrow beam lens (12° beam angle, FLP-N4-RE-HRF). The current passing through the LED was controlled by a home-built circuit board and could be adjusted between 450 and 800 mA. The optical power output at $\lambda_{\text{max}} = 452 \pm 10$ nm was monitored using a power meter and this output (typically 540 mW @ 700 mA) was easily fine-tuned before each run. All experiments were performed at a constant rotation speed of 150 rpm controlled by an IKA orbital shaker. All reaction vials and LEDs were temperature controlled by aluminum blocks cooled using a circulating chiller. The temperature was set to $\sim 20 ^\circ$C in most reactions, unless otherwise stated. Solutions containing H$_2$A/HA$^-$ (prepared by titration of ascorbic acid with NaOH) and the PS were thoroughly deaerated using a number of
vacuum/argon pressurization cycles. The molecular cobalt catalysts were introduced under inert atmosphere and degassing was continued; finally terminated by equilibration to atmospheric pressure. Ar was also used in our system as an internal standard to get the percent of H\textsubscript{2} produced by MS. The vials are each connected to pressure transducers (SSI technologies, P51 pressure sensors) through a Teflon spacer by stainless steel fittings and to a universal gas analyzer (Stanford Research Systems, UGA-hydrogen) by capillary tubes. During the course of a given reaction, head space pressure is monitored in real-time using a multifunction data acquisition box (National Instruments, NI-USB-6210) and data were logged using LabVIEW SignalExpress software. After the end of each photocatalytic reaction, headspace sampling (100 µL) was performed using a Hamilton syringe followed by injection into a GC-8A (Shimadzu) equipped with a 5Å molecular sieves column and TCD operated with Ar carrier gas. In addition, the headspace, which was pressurized by H\textsubscript{2} buildup during the course of photocatalysis, was equilibrated to atmospheric pressure and the percent of H\textsubscript{2} relative to Ar was analyzed by MS. GC and MS data were calibrated against a certified Ar/H\textsubscript{2} standard (Praxair). Quantitative results of hydrogen were typically averaged and the processed pressure data were normalized to the final amounts of hydrogen measured. For the deuteration experiments, water was replaced by deuterium oxide, and the kinetics of hydrogen production was measured as well as gas mixture analysis was performed using MS. The calibration of the MS for D\textsubscript{2} and HD was done against standards produced following the reaction of Li metal with D\textsubscript{2}O and H\textsubscript{2}O:D\textsubscript{2}O mixtures respectively and the calculations were based on the pressure buildup during the course of the reaction. Our method for D\textsubscript{2} and HD calibration was verified by obtaining identical sensitivity factors for H\textsubscript{2} when using the certified standards (Praxair) or following the reaction of Li with H\textsubscript{2}O.
The measurements under 1 sun illumination were performed in a pyrex 50 mL round-bottom flask. 25 mL of aqueous solution containing the electron donor, PS and catalyst was deaerated by freeze-pump-thaw technique and left under reduced Ar pressure (~ 100 torr). The mixture was irradiated using a 300 W xenon arc lamp equipped with a water filter and an AM 1.5G filter (Oriel) mounted in series with appropriate neutral density filters in order to obtain ~ 100 mW/cm$^2$ broadband optical output. The reaction was stirred at constant rate and the headspace was analyzed by injection into a GC at regular intervals (see picture below).
5.3.3 Transient Absorption Spectroscopy. The optical density of the samples was ~ 0.35 at 452 nm excitation wavelength. All samples were placed in 1 cm pathlength cuvettes and deoxygenated by ~ 1 h Ar bubbling and then kept under positive pressure of Ar during the course of the experiments. Transient absorption data were collected with an Edinburgh Instruments laser flash photolysis system (LP920) equipped with LP900 software. The excitation source was a Vibrant LD 355 II Nd:YAG/OPO system (OPOTEK), (~ 5 mJ/pulse, 1 Hz). Transient absorption spectra were collected with an iStar ICCD camera (Andor Technology) whereas kinetic traces at a specific wavelength were acquired using a PMT (R928 Hamamatsu).

5.3.4 Spectroelectrochemistry. Experiments were performed in a N₂ filled glovebox (MBraun) using a 1 mm pathlength spectroelectrochemical cell (BASi). Pt mesh was used as working, Ag/AgNO₃ as reference, and Pt wire as counter electrode. Solutions were prepared in acetonitrile containing 0.1 M Tetrabutylammonium hexafluorophosphate (TBAPF₆) supporting electrolyte. Controlled-potential electrolysis was performed at potentials ~50-100 mV more negative than the first reduction peak using a BASi Epsilon potentiostat. While reducing the molecules by 1 e⁻ each, absorbance spectra were collected with a SI440 CCD spectrometer every 30-60 seconds. \[ A_f = \Delta A + A_i \], where \( A_f \) is the absorbance of the reduced species, \( \Delta A \) the difference spectra collected after the end of electrolysis, and \( A_i \) is the initial absorbance of the compound before reduction. Extinction coefficients of the reduced species were then calculated using the Beer-Lambert law considering ~ 100 % reduction of the initial compound after the end of bulk electrolysis.

5.3.5 Static Photophysical Experiments. Absorption spectra were acquired using a Cary 50 spectrophotometer and static luminescence was measured using a FL/FS920 Edinburgh Instru-
ments single photon counting fluorimeter. Solutions were thoroughly deaerated by Ar bubbling for at least 1 h before each measurement.

5.4. RESULTS AND DISCUSSION

5.4.1 [Ru(bpy)$_3$]$^{2+}$ photosensitizer and Co(bpyPY2Me) catalyst.

The design of water-soluble catalysts for proton reduction represents an on-going challenge in the search for viable systems for H$_2$ production, and a relatively small percentage of cobalt-catalysts for this purpose display water compatibility.$^{41}$ Interestingly, the Chang group reported the synthesis of a cobalt 2-bis(2-pyridyl)(methoxy)methyl-6-pyridylpyridine catalyst that, while aqueous-compatible, was not soluble in pure water at mM concentrations,$^{23}$ and a similar version of this catalyst containing an OH group instead of the methoxy substituent was utilized at low concentrations by the Alberto group to produce hydrogen photocatalytically from water.$^{19}$ Postulating that the ether moiety resulted in water-insolubility at high concentrations, we sought the use of a cobalt complex with 2-(bis(2-pyridyl)(methyl)methyl-6-pyridylpyridine (bpyPY2Me) as a ligand. Figure 5.1 illustrates the chemical structure of all the catalysts and PS utilized in this chapter.
Figure 5.1. Chemical structures of all Ru(II) PS and Co(II) water reduction catalysts investigated in this chapter. \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Ru(phen)}_3]^{2+}\) contain 2 Cl\(^-\) counter-ions, \([\text{Ru(BPS)}_3]^{4-}\) contains 4 Na\(^+\), and all Co(II) complexes had acetonitrile or water solvent coordinated and triflate (CF\(_3\)SO\(_3\)) counterions. In some cases the triflate was directly bound to the Co(II) complexes as shown for the crystal structure for complex 3. The crystal structures were performed at UC Berkeley by the Chang and Long groups. Purple, blue, grey, red, orange, and green spheres represent Co, N, C, O, S, and F atoms, respectively; hydrogen atoms have been omitted for clarity.
The newly conceived catalysts 1 and 2 were investigated electro- and photocatalytically for their hydrogen evolution activities. In order to understand the relative performance of these catalysts in aqueous solution, we decided to conduct cyclic voltammetry (CV) in 0.3 M H₂A/HA⁻ buffer at pH 4. This buffer was chosen based on optimized photocatalytic data collected during the course of high-throughput screening of different molecular compositions, Figure 5.S1-5.S3. Since H₂A/HA⁻ (pKₐ ~ 4.2) acts as sacrificial electron donor to the excited state of [Ru(bpy)₃]²⁺,¹⁸,¹⁹,⁷⁶ we postulated that its corresponding buffer (both acid and base forms coexist at pH 4) would be an appropriate media to study the potentials at which the cobalt reduction occurs and subsequently understand the energetics of the photocatalytic systems. Molecule 1 exhibited a significant electrocatalytic activity for hydrogen production in 0.3 M H₂A/HA⁻ at pH 4 at onset potential of ~ -0.9 V vs NHE, Figure 5.2a. Since electrocatalytic hydrogen production was commonly preceded by Co(II) to Co(I) reduction waves as observed for 2, the onset of the catalytic current which likely overlapped with Co(II)/Co(I) wave in 1 was estimated to be the reduction potential of Co(II) in the latter case, Figure 5.2a. Importantly, the electrochemical data suggested that the incorporation of CF₃ groups in 2 decreased the catalytic current density with respect to 1, Figure 5.2a. Thus photochemical hydrogen production was expected to be faster for 1 relative to 2 given the significant reducing power of the ground state reduced ruthenium PS (-1.26 V vs NHE for [Ru(bpy)₃]²⁺/[Ru(bpy)₃]¹⁺). Indeed, the incorporation of CF₃ electron withdrawing groups into the ligand structure had negative effects on the rate of photocatalytic hydrogen production, Figure 5.2b. This observation was attributed to the possible stabilization of the Co(I) in 2 with respect to 1 which rendered the former intermediate less basic to react with protons in the hydrogen evolution cycle. The effect of attaching CF₃ groups into redox active ligand is discussed further in Section 5.3.2. Also, it was observed that the presence of methyl instead of
the previously reported OH\textsuperscript{19} and OMe\textsuperscript{23} groups in bpyPY2 greatly enhanced the activity of the corresponding Co catalyst, Figure 5.2b. Please note that more rigorous electrochemistry experiments are currently being performed at UC Berkeley to understand the structure/activity relationship of all the catalyst series presented here.

**Figure 5.2.** Cyclic voltammograms at 100 mV/s of 3 \times 10^{-4} M Co(bpyPY2Me)/1 and Co(bpyPYCF\textsubscript{3}2Me)/2 in aqueous solution containing 0.3 M H\textsubscript{2}A/HA\textsuperscript{-} at pH 4 (a). Photocatalytic hydrogen production under 452 ± 10 nm (540 mW) of a solution containing 2 \times 10^{-5} M 1 (blue, pH 4), 2 (magenta, pH 4.5), Co(bpyPY2OMe) (red, pH 4.5), Co(bpyPY2OH) (black, pH 4) or CoCl\textsubscript{2} control (green, pH 4), 3.3 \times 10^{-4} M [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} and 0.3 M H\textsubscript{2}A/HA\textsuperscript{-} (b). Electrochemical experiments were performed by A. King and M. Nippe at UC Berkeley.

Figure 5.3 summarizes all the redox properties of the ground and excited states (Eqs. 8-9 in Chapter I) of the PS utilized in this chapter along with the redox potential of 1, proton reduction and H\textsubscript{2}A/HA\textsuperscript{-} oxidation at pH 4 as a reference. The values of \(E_{\text{ox}}^0\) and \(E_{\text{red}}^0\) for [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} and [Ru(phen)\textsubscript{3}]\textsuperscript{2+} were converted to NHE values in water by Sutin and coworkers from the potentials measured in ACN vs SCE by subtracting 30 mV\textsuperscript{43,77}. The redox potentials of [Ru(BPS)\textsubscript{3}]\textsuperscript{1+} were measured by Zanarini et al\textsuperscript{73} and the following conversion was applied: \(E^0\) (V vs SCE) = \(E^0\) (V vs Fc/Fc\textsuperscript{+}) + 0.4 V. The values obtained were converted vs NHE in water by the same methodology reported by Sutin\textsuperscript{77}, using \(E_{0-0} = 2.15\) eV for [Ru(BPS)\textsubscript{3}]\textsuperscript{1+} in water. Please
note that the values reported in Figure 5.3 are just a rough estimate of the actual values for Ru(II) with error of at least 100 mV. Our collaborators at UC Berkeley are currently attempting to measure the redox properties of the PS in water.

Figure 5.3. Energy diagram of the ground state and excited state potentials of [Ru(BPS)$_3$]$^{4+}$, [Ru(bpy)$_3$]$^{2+}$ and [Ru(phen)$_3$]$^{2+}$; the reduction potential of Co(bpyPY2Me)/I measured in H$_2$A/HA$^-$ buffer, the oxidation of ascorbic acid (H$_2$A) to dehydroascorbate (A) and the thermodynamic potential of hydrogen evolution (red values are at pH 4).

Photostability of the compositions was investigated by UV-Vis spectroscopy and HPLC coupled to an LC-MS in order to understand the limiting factors leading to system degradation. HPLC of the reaction mixture before and after catalysis indicated that the cobalt catalyst is more stable with respect to the PS, Figure 5.S4. The [Ru(bpy)$_3$]$^{2+}$ was found to be the limiting factor when present at $< 10^{-4}$ M concentrations, and the by-product of decomposition was identified to be mainly [Ru(bpy)$_2$HA]$^+$, Figure 5.S5. Based on our data, we favored the [Ru(bpy)$_2$HA]$^+$ pho-
toproduct, however we cannot rule out the possibility of other side products that can result from
the ligand substitution.

Whereas ligand loss is not uncommon in the well studied \([\text{Ru(bpy)}_3]^{2+}\), it is widely ac-
cepted that the mechanism of dechelation is the population of dissociative \(^3\text{MC}\) (metal centered,
ligand field, or d-d) states which are thermally accessible after photoexcitation to the MLCT
state.\(^{47,61,62,64}\) A schematic representation of the decomposition process and the identification of
the photoproduct are illustrated in Scheme 5.1. Besides being unable to sensitize hydrogen pro-
duction, \([\text{Ru(bpy)}_2\text{HA}]^+\) acts as an inner light-filtering agent. With an estimated extinction coef-
ficient of 6000 M\(^{-1}\) cm\(^{-1}\) at 452 nm excitation, this undesirable by-product inhibited the complete
regeneration of catalysis following the addition of fresh PS at high concentrations (> 10\(^{-4}\) M),
due to the competitive absorbance of incident photons. At equimolar concentration of 1 and
\([\text{Ru(bpy)}_3]^{2+}\) (2 x 10\(^{-5}\) M), the catalysis could be readily regenerated by the addition of an equiv-
alent of PS, whereas the addition of any other component of the system failed to regenerate ca-
talysis (Figure 5.S7).

**Scheme 5.1.** Mechanism of ligand loss in \([\text{Ru(bpy)}_3]^{2+}\) upon photoexcitation.

To verify the mechanism of decomposition previously proposed, we performed tempera-
ture dependence study on hydrogen produced. Surprisingly, we found that the overall amount of
hydrogen formed, hence stability, increased with the decrease of temperature paralleled with slower initial rates of hydrogen production, Figure 5.4. These results provide evidence that the decomposition can be thermally activated, and the decrease in the rate of hydrogen production at low temperatures was attributed to a slower kinetics of dark reactions involved in the hydrogen production cycle. Our findings elucidate the importance of temperature control in the photocatalytic hydrogen production measurements utilizing [Ru(bpy)$_3$]$^{2+}$ PS. Most of the photocatalytic experiments reported here are performed at ~ 20°C unless otherwise stated.

**Figure 5.4.** Kinetic analysis of hydrogen production performed at different temperatures. Conditions: 2 x $10^{-5}$ M I, 3.3 x $10^{-4}$ M [Ru(bpy)$_3$]$^{2+}$ and 0.3 M H$_2$A/HA$^-$ at pH 4.

To verify the homogeneity of the photocatalytic system, several independent experiments were performed. The Hg (0.1 mL) poisoning test$^{78,79}$ showed no significant changes of photocatalytic rate of hydrogen produced in presence or absence of Hg (Figure 5.S8). DLS studies before and after catalysis showed no significant formation of nanoparticles (Figure 5.S9). In addition, a linear dependence of the number of moles of hydrogen produced on the concentration of each component was observed (Figure 5.S10). Under these conditions investigated in Figure
5.S10 (0.1 M H₂A/HA⁻ at pH 4 and 10⁻⁵-10⁻⁴ M concentrations of catalyst/PS), the rate of hydrogen production was largely independent of the concentration of PS or catalyst, and catalytic rates were mainly limited by light absorption and subsequent electron transfer (Figure 5.S10). However, the stability and subsequently the overall hydrogen produced increased as we incremented 1 and [Ru(bpy)₃]²⁺. All these combined results provide significant evidence towards the molecular nature of the photocatalytic cycles leading to hydrogen production.

After verifying the homogeneity of the system, turnover numbers (TON) versus cobalt were assessed at different concentrations of 1, in the presence of 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ in 0.3 M H₂A/HA⁻ at pH 4. We found that the TON increased drastically with lowering cobalt concentration, to reach values > 10,000 (H₂/Co) at sub-micromolar concentrations, Figure 5.5. As we expected, the amount of hydrogen produced decreased as we lowered the concentration of catalyst, and the volume of hydrogen generated at < 10⁻⁶ M Co are insignificant for any practical application. Here we outline the importance of achieving good photocatalytic metrics of a given catalyst while producing significant amount of hydrogen. We also emphasize on the large variation of turnover metrics at different experimental conditions (concentrations, temperature, light source and media). Since solar energy storage is the desired goal of producing hydrogen, we tested 1 under solar illumination (AM 1.5G, 100 mW/cm²). A solution of 10⁻⁶ M 1 and 2.7 x 10⁻⁴ M [Ru(bpy)₃]²⁺ in 0.3 M H₂A/HA⁻ at pH 4 gave a TON of ~ 4200 (H₂/Co) and TOF of ~ 3160 (H₂/Co/hr) while producing ~ 0.08 L H₂/L solution/hr at room temperature, Figure 5.S11.
Figure 5.5. Hydrogen production as a function of time at different concentration (a) and TON (H\textsubscript{2}/Co) versus concentration of 1 (b) in the presence of 3.3 x 10\textsuperscript{-4} M [Ru(bpy)]\textsuperscript{2+} in 0.3 M H\textsubscript{2}A/HA\textsuperscript{-}, pH 4.

The quantum yield of hydrogen production was 7.5 ± 0.8 % based on two photons absorbed under conditions relevant to our photocatalytic experiments, Figure 5.S12. The mechanism of activity of hydrogen production was further investigated by nanosecond pump-probe transient absorption (TA) spectroscopy. The [Ru(bpy)]\textsuperscript{3+} subsequent to light absorption, forms quantitatively the *3[Ru(bpy)]\textsuperscript{2+}, which possesses a 0.6 µs lifetime, Figure 5.S13.\textsuperscript{43-45} The excited state was reductively quenched at pH 4 with a bimolecular rate constant k\textsubscript{q} = 2.6 x 10\textsuperscript{7} M\textsuperscript{-1}s\textsuperscript{-1} measured using dynamic Stern-Volmer lifetime quenching, Figure 5.S14. At optimized conditions (0.3 M H\textsubscript{2}A/HA\textsuperscript{-}, pH 4) and in the absence of any cobalt catalyst, the [Ru(bpy)]\textsuperscript{3+} radical anion (ε\textsubscript{505nm} = 1.2 x 10\textsuperscript{4} M\textsuperscript{-1}cm\textsuperscript{-1}, measured in ACN by spectroelectrochemistry (Figure 5.S15)) recombined with HA\textsuperscript{-} in a diffusion controlled fashion, Figure 5.S16.\textsuperscript{80} The cage escape\textsuperscript{81,82} for the [[Ru(bpy)]\textsuperscript{3+}, HA\textsuperscript{-}] was found to be 0.55 ± 0.05, consistent with previously reported values\textsuperscript{18}, Figure 5.S16. Upon the addition of 1, the lifetime of the reduced ruthenium PS became shorter due to the electron transfer reaction forming Co\textsuperscript{1}(bpyPY2Me), Figure 5.6.
Figure 5.6. Transient absorption spectra recorded after a certain time delay (µs) following laser excitation (452 nm). *[Ru(bpy)$_3$]$_{2+}$ represents the excited state absorption features, [Ru(bpy)$_3$]$_{2+}$ the ground-state bleach, [Ru(bpy)$_3$]$_{3+}$ the radical anion formed following electron transfer from HA$^-$ to [Ru(bpy)$_3$]$_{2+}$, and the formed Co$^1$(bpyPY2Me) has a broadband absorption in the visible. Conditions: 2.9 x 10$^{-4}$ M, 2.5 x 10$^{-5}$ M [Ru(bpy)$_3$]$_{2+}$ in 0.3 M H$_2$A/HA$^-$ at pH 4.

The resulting Co(I) species is then thought to undergo a protonation reaction forming the Co(III)-H which accepts another electron from a second [Ru(bpy)$_3$]$_{3+}$ to form the Co(II)-H. The relay of an electron to Co(I) before the protonation step is also possible, forming the Co(I) radical anion species which then gets protonated. The resulting Co(II)-H (or Co(III)-H depending on the system) is then believed to be the species responsible for hydrogen evolution upon a heterolytic reaction with a proton forming the initial Co(II) (or Co(III) depending on the system) species and molecular hydrogen.$^{26,41,42,83}$ Ultimately, the sequential or coupled transfer of 2 e$^-$ and 2 H$^+$ has to occur in order to form one H$_2$, Figure 1.7 in Chapter I. Even though we favored the heterolytic reaction path, we couldn’t rule out, based on our data, the homolytic reaction between two Co-H and other possible routes. The heterolytic mechanism of hydrogen production is expected to occur in our photocatalytic system given the low concentration of reduced cobalt species present at a given time in the reaction mixture.$^{42}$
The pseudo-first order rate constant $k_{\text{Co(bpyPY2Me)}}$ of the reaction between the reduced PS and the cobalt catalyst was also calculated, Figure 5.7. The slope of the inverse lifetime of $[\text{Ru(bpy)}_3]^+$ [K (s$^{-1}$)] versus concentration of cobalt gave rise to $k_{\text{Co(bpyPY2Me)}} \sim 2 \times 10^9$ M$^{-1}$ s$^{-1}$, Figure 5.7b. The biexponential nature of the decay at 505 nm arises from the overlap of the absorption of $[\text{Ru(bpy)}_3]^+$ and Co(I), which happened to absorb at the same wavelength as depicted by spectroelectrochemistry measurements in ACN (Figure 5.S17, $\varepsilon_{505 \text{ nm}} \sim 5500$ M$^{-1}$ cm$^{-1}$). Interestingly, based on the data in Figure 5.7a, we estimated a cage escape yield for $[[\text{Ru(bpy)}_3]^+, \text{Co(I)}]$ to be $\sim 0.85 \pm 0.10$. Co(I) absorbed across the entire range of the visible spectrum as evidenced by the TA spectrum obtained after $>5$ µs delay of the laser pulse, at which time cobalt is the only species possessing a difference spectrum since $[\text{Ru(bpy)}_3]^{2+}$ went back to the ground state and H$_2$A/HA$^-$ or any of its by-products didn’t possess absorption features in the visible region of the spectrum, Figure 5.6. The biexponential nature of the decay at 505 nm was verified by probing at 650 nm where the reduced cobalt species exclusively absorbs, and the long lived component at 505 nm matched the lifetime of that Co(I) species, Figure 5.S18. It is worth noting that no significant decomposition of $[\text{Ru(bpy)}_3]^{2+}$ was seen during the course of TA experiments confirmed by identical UV-Vis absorption spectra before and after flash photolysis. The decomposition was observed only after few hours of photolysis under high light flux.
Figure 5.7. Transient absorption versus time monitored at 505 nm where both [Ru(bpy)$_3$]$^+$ and Co$^I$(bpyPY2Me) absorb (a). Rate of the reaction between [Ru(bpy)$_3$]$^+$ and Co$^{II}$(bpy2PYMe) versus the concentration of the catalyst (b). Conditions: $2.5 \times 10^{-5}$ [Ru(bpy)$_3$]$^{2+}$ in 0.3 M H$_2$A/HA$^-$ at pH 4.

In order to explore the source of protons in the hydrogen product, we performed deuteriation experiments. H$_2$O was replaced by D$_2$O in 0.1 M H$_2$A and titrated with NaOD until the measured pH was 4 (which correspond to pD $\sim$ 4.4) and the resulting gas in the headspace after photocatalysis was analyzed by MS, Figure 5.8. Importantly, we measured $>90\%$ deuterium incorporation (1% H$_2$, 15% HD, 84% D$_2$) in the product with D$_2$ being the major product, Figure 5.8a. Please note that the MS was calibrated for each gas separately, especially that the sensitivity factors are dependent on the mass. The small H incorporation predominantly as HD was due to the proton exchange between the initial H$_2$A/HA$^-$ along with their decomposition products with D$_2$O. In addition, D$_2$O itself had traces amounts of H$_2$O. The small hydrogen gas background measured from the headspace of solution without the PS/catalyst mixture resulted from MS outgassing Figure 5.8a. The H$_2$A/HA$^-$ acts as an electron and a H$^+$ donor, so the pH of the solutions before and after irradiation are typically within 0.2 pH unit despite the production of massive volume of H$_2$ since H$_2$A/HA$^-$ oxidation is proton coupled, yielding 2e$^-$ and 2H$^+$ per
two photons absorbed, Chapter 1 Eqs. 4-7. Figure 5.8b shows clearly the hydrogen gas exclusively formed in the headspace of the reactor containing our catalytic composition in water. Ar was used as inert gas for deaeration and as internal standard for MS calibration purposes. Our combined data clearly demonstrate that hydrogen produced originates from water and not as a by-product of H₂A/HA⁻ dehydrogenation.

5.4.2 [Ru(bpy)₃]²⁺ photosensitizer and Co(bpy2PYMe) catalyst.

Photocatalytic experiments (λₑₓ = 452 ± 10 nm, 540 mW) were performed using various cobalt catalysts at fixed concentration (2.0 x 10⁻⁵ M) with [Ru(bpy)₃]²⁺ PS at 3.3 x 10⁻⁴ M in the presence of H₂A/HA⁻ sacrificial reductant at optimized pH values, Figure 5.9a. Figures 5.S19, 5.S23, and 5.S24 illustrate the combinatorial searches that ultimately led to the optimized photocatalysis conditions presented in Figure 5.9a. In this apparatus, real-time H₂ evolution was monitored using pressure transducers and the molecular composition of the headspace confirmed
independently using GC\textsuperscript{37} and mass spectrometry. Under optimized conditions, the composition with catalyst 3 produced copious amounts of $\text{H}_2$ with an estimated initial TOF with respect to catalyst of 660/h, Figure 5.9a. Catalyst 4 displayed somewhat lower $\text{H}_2$ evolution activity with an initial TOF of 500/h. However, both of these bpy2PYMe-based molecules clearly outperform the previously reported Co(PY5Me\textsubscript{2}) and Co(CF\textsubscript{3}-PY5Me\textsubscript{2}) catalysts in optimized side-by-side comparisons, Figure 5.9a. Control experiments using CoCl\textsubscript{2} as catalyst (Figure 5.9a, green line), the removal of light activation, or deletion of any single molecular constituent resulted in little to no $\text{H}_2$ production. Furthermore, no considerable change in activity was observed if the photocatalytic experiments were performed in the presence of Hg (0.1 mL), consistent with the homogeneous nature of the reactions (Figure 5.S20).\textsuperscript{37,38} Similarly, the linear increase of hydrogen production scaling directly with both catalyst and PS concentration (Figures 5.S21, 5.S22) strongly suggests that the reactions are indeed homogeneous in nature. The $\text{H}_2$ evolution ceases to function after approximately 13 h of continuous irradiation and catalysts 3 and 4 achieved total TONs of 1630 and 1390, respectively. A crucial observation relates to the noteworthy stability of 3 and 4 as decreases in the rate of hydrogen production at pH 4 in the presence of lower concentrations of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} (1.1 x 10\textsuperscript{-4} M) was found to be largely induced by the decomposition of the PS, Figure 5.9b. Addition of one equivalent of fresh [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} to the respective catalytic mixtures after 3 hours of irradiation largely restored the $\text{H}_2$ evolution activity (Figure 5.9b), whereas reconstitution of each catalyst in parallel experiments did not.
Figure 5.9. (a) Comparison of H₂ evolution during 452 ± 10 nm photocatalysis in water using 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ and 2.0 x 10⁻⁵ M solutions of 3 (blue, pH 4), 4 (red, pH 4.5), Co(CF₃-PY₅Me₂) (magenta, pH 6), Co(PY₅Me₂) (black, pH 6) and CoCl₂ (green, pH 4) in the presence of 0.3 M H₂/A/H₂⁻. (b) Regeneration of catalytic activity resulting from the addition of one equivalent of [Ru(bpy)₃]²⁺ in compositions containing 2.0 x 10⁻⁵ M of 3 (blue, pH 4) and 4 (red, pH 4) after 3 hours of continuous illumination in the presence of 1.1 x 10⁻⁴ M [Ru(bpy)₃]²⁺.

Combined computational and electrochemical methods were utilized by our collaborators at University of California, Berkeley to understand the structure/activity relationship of these catalysts. In short, it was found that under catalytically relevant conditions (weak acid regime; no protonation of Co(I)), two subsequent one electron reductions yielding a transient Co(I)-bpy⁻ radical species were necessary to enter the catalytic cycle. The extent of π backbonding from Co(I) to the π* orbitals of the bpy moieties was significantly affected by substitution of the pyridine moieties. This π type interaction was reduced in the case of 4 in which the electron-withdrawing CF₃ group rendered the pyridine a weak σ donor and stabilized the Co(I) species too strongly as compared to 3. This diminished communication between Co(I) and the redox active ligand reduced the rate of electro- and photocatalytic hydrogen evolution in 4 versus 3.

5.4.3 [Ru(BPS)₃]⁺ photosensitizer and Co(bpyPY₂Me) catalyst.

Since [Ru(bpy)₃]²⁺ was found to be labile for photocatalysis, we decided to test other Ru(II)
compounds for their ability to sensitize hydrogen production. The total hydrogen produced after
the end of photocatalysis at equal concentration of Ru(II) (6.7 x 10^{-5} M) showed that
[Ru(BPS)_3]^{4-} > [Ru(bpy)_3]^{2+} > [Ru(phen)_3]^{2+}, Figure 5.10. The UV-Vis before and after catalysis
demonstrated that [Ru(bpy)_3]^{2+} completely decomposed into the already characterized
[Ru(bpy)_2HA]^{+} by-product and [Ru(BPS)_3]^{4+} absorbance also changed after prolonged photolysis,
signalling the decomposition (at least partially in the case of [Ru(BPS)_3]^{4+}) of these mole-
cules, Figure 5.S25. We observed a slower hydrogen production kinetics when we used
[Ru(BPS)_3]^{4+} with an overall increase of sustainability of catalysis versus [Ru(bpy)_3]^{2+}. In Figure
5.10, [Ru(BPS)_3]^{4+} achieved a TON of ~ 550 (H_2/Ru) with a TOF of ~ 260 (H_2/Ru/hr) whereas
[Ru(bpy)_3]^{2+} reached a TON of ~ 350 with a TOF of ~ 450. The [Ru(phen)_3]^{2+} failed to produce
hydrogen even though it is energetically poised for photocatalysis,84 Figure 5.3. Turnover num-
bers were strongly dependant on the concentrations used, and under optimum conditions
[Ru(BPS)_3]^{4+} achieved a TON of ~ 3,000 (H_2/Ru) at a concentration of 1.5 x 10^{-6} M whereas 1
achieved a TON of ~ 10,000 (H_2/Co) at a concentration of 3.1 x 10^{-7} M, Figure 5.S26-5.S28.

**Figure 5.10.** Hydrogen production as a function of time under 452 nm LED excitation (540
mW). Conditions: 6.7 x 10^{-5} M Ru(II), 2 x 10^{-5} M Co(bpyPY2Me) and 1 M H_2A/HA\(^{-}\) at pH 4.

<table>
<thead>
<tr>
<th>PS</th>
<th>λ_{max} absorbance (nm)</th>
<th>ε (M^{-1}cm^{-1})</th>
<th>λ_{max} emission (nm)</th>
<th>τ (µs)</th>
<th>k_q (λ) (M^{-1}s^{-1})</th>
</tr>
</thead>
<tbody>
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<td>[Ru(bpy)_3]^{2+}</td>
<td>452</td>
<td>14,500</td>
<td>625</td>
<td>0.6</td>
<td>2.6x10^7</td>
</tr>
<tr>
<td>[Ru(phen)_3]^{2+}</td>
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<td>19,000/77</td>
<td>605/77</td>
<td>1.1</td>
<td>1.4x10^8</td>
</tr>
<tr>
<td>[Ru(BPS)_3]^{4-}</td>
<td>462</td>
<td>27,000/23</td>
<td>615</td>
<td>3.8</td>
<td>5.4x10^7</td>
</tr>
</tbody>
</table>

Table 5.1 summarizes the important photophysical properties of the Ru(II) PS used. In order to understand the trends shown in Figure 5.10, time resolved spectroscopy was utilized to extract rate parameters. Surprisingly, the quantum yield for the electron transfer product formation (or cage escape yield) between the [Ru(phen)_3]^{2+} and HA· termed [[Ru(phen)_3]^+, HA·] was Φ_{cage} < 2%, Figure 5.S29-5.S32. These results suggested that the rationale behind the inactivity of [Ru(phen)_3]^{2+} PS was its inability to produce its respective radical anion after being quenched by HA·. The reasons for this behaviour might be the alteration of the quenching mechanism from electron transfer as depicted for [Ru(bpy)_3]^{2+} to other mechanisms for [Ru(phen)_3]^{2+} or simply a near complete recombination of charges in the charge transfer cage in the latter case.\(^{18}\) Figure 5.11a represents the transient absorption spectra recorded after laser excitation (452 nm, ~ 5 mJ/pulse) of a solution of 2.9 x 10^{-4} M Co(bpyPY2Me), 1.3 x 10^{-5} M [Ru(BPS)_3]^{4-} and 0.3 M H₂A/HA· at pH 4. The black spectrum produced immediately after the laser pulse had characteristic ground state bleach centered around 450 nm and broad excited state absorbance peaking at 520 nm. The cage escape for the radical anion [Ru(BPS)_3]^{5-} and oxidized HA· (HA·) was found to be ~ 20 ± 5 % versus 55 ± 5 % for [[Ru(bpy)_3]^+, HA·], Figure 5.S33-5.S36. The smaller Φ_{cage} in the case of [[Ru(BPS)_3]^{5-}, HA·] relative to [[Ru(bpy)_3]^+, HA·] accounts for the slower kinetics
of hydrogen production observed in Figure 5.10.

**Figure 5.11.** (a) Transient absorption spectra recorded after a delay time following laser excitation (452 nm, 5 mJ/pulse). Conditions: 2.9 x 10^-4 M Co(bpyPY2Me), 1.3 x 10^-5 M [Ru(BPS)_3]^{4+}, in 0.3 M H_2A/HA^- at pH 4. (b) Rate constant of electron transfer from [Ru(BPS)_3]^{5-} to Co(II) taken as the slope of the inverse of [Ru(BPS)_3]^{5-} lifetime as a function of Co(II) concentration.

In the absence of Co(II), [Ru(BPS)_3]^{5-} recombines with HA^- following diffusion controlled kinetics, Figure 5.S36. However, in the presence of Co(II), [Ru(BPS)_3]^{5-} radical anion, which had an absorption peak ~ 520 nm (Figure 5.11a, red spectrum), transferred an electron to produce a Co(I) species which possessed a broadband absorbance in the visible spectrum (Figure 5.11a, brown spectrum). The rate of electron transfer between the [Ru(BPS)_3]^{4+} and Co(II) was found to be 3.8 x 10^9 M^{-1} s^{-1}, Figure 5.11b. As we expected, the negative charge imparted on the Ru(II) PS by the sulfonated ligand enhanced the rate constant of electron transfer between the [Ru(BPS)_3]^{5-} and Co(II) by a factor of 2 relative to [Ru(bpy)_3]^{2+} (2 x 10^9 M^{-1} s^{-1}). In addition, it was found that the cage escape yield of [[Ru(BPS)_3]^{4+}, Co(I)] to be ~ 85% which is identical to [[Ru(bpy)_3]^{2+}, Co(I)] within the experimental error. As a result, the quantum yield of charge separated species following the second electron transfer didn’t seem to be limiting the rate of hydrogen production in any significant way. These results suggested that the “amphiphilic” [Ru(BPS)_3]^{4+} utilizing a
rigid phenanthroline ligand was more stable PS in water than the “hydrophilic” [Ru(bpy)₃]²⁺.

5.5 CONCLUSIONS

A series of tetradentate Co(bpyPY2) water reduction catalysts have been synthesized and characterized. Complex 1 bearing a Me group significantly outperformed all other complexes which was attributed to the electronic structure of the catalyst. [Ru(bpy)₂HA]⁺ was found to be the decomposition product of [Ru(bpy)₃]²⁺. All turnover parameters were strongly dependent on the conditions used, and 1 achieved a TON of ~ 4200 (H₂/Co) and a TOF of ~ 3160 (H₂/Co/hr) under simulated sunlight (AM 1.5G, 100 mW/cm²) at 1 µM of Co. A deuteration test was performed on the system and showed > 90% D incorporation in the gaseous product, indicating that the protons reduced by the catalyst come predominantly from water. Another series of pentadentate Co(bpyPY2Me) was investigated. Complex 3 displayed dramatically improved catalytic performance for H₂ production as compared to the earlier reported Co catalysts of the redox inert PY5Me₂ family. The introduction of an electron withdrawing CF₃ group into the pyridine moiety of the ligand in 4 was shown to have a negative effect on the catalytic performance for photocatalytic H⁺ reduction in aqueous media. This effect was explained by the reduced σ donating ability of the CF₃ substituted pyridine group which stabilized the Co(I) complex and reduced π-back-bonding interactions between Co(I) and the π* ligand orbitals because Co(I) species is too strongly stabilized in 4. We have investigated a series of Ru(II) PS in the quest for molecules more stable than [Ru(bpy)₃]²⁺. We have found that an “amphphilic” compound possessing a hydrophobic core with hydrophilic solubilizing groups was less prone to ligand loss than [Ru(bpy)₃]²⁺. The stability of this compound was also thought to be enhanced by the presence of a phenanthroline ligand which is relatively more rigid than bipyridine. The PS, bearing
an overall negative charge, possessed a faster rate constant of electron transfer to the positively charged cobalt catalyst. The concept of cage escape yields role in dictating the overall rate of hydrogen production was manifested in the compositions investigated here. The overall TOF was lower in the case of [Ru(BPS)₃]⁺⁺ as compared to [Ru(bpy)₃]^{2+} due to a > 2 fold decrease in the initial quantum yield of formation of charge separated ruthenium radical anion and HA⁻. [Ru(phen)₃]^{2+} surprisingly had a cage escape yield less than 2% for the initial electron transfer product leading to no hydrogen being produced despite its favorable energetics. The combined data in this chapter represents important advancement towards the design of molecular hydrogen evolution systems that can operate in pure water.

5.6 SUPPORTING INFORMATION

**Figure 5.S1.** pH dependence on H₂ production collected after hydrogen production ceases. Conditions: 2.0 x 10^{-5} M 1 (a) or 2 (b), 3.3 x 10^{-4} M [Ru(bpy)₃]^{2+} and 0.1 M H₂A/HA⁻.
Figure 5.S2. H₂ production kinetic curves (a), initial rate of hydrogen production (b) and total H₂ produced collected after the reactions cease (c) as a function of H₂A/HA⁻ concentration. Conditions: 2.0 x 10⁻⁵ M I, 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ at pH 4.

Figure 5.S3. pH dependence on H₂ production collected after H₂ production ceases for Co(bpyPY2OH) (a) and Co(bpyPY2OMe) (b). Conditions: 2.0 x 10⁻⁵ M Co(II), 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ and 0.3 M H₂A/HA⁻.
Figure 5.S4. This experiment was performed with a solution of $4 \times 10^{-5}$ M 1, $1.5 \times 10^{-5}$ M $[\text{Ru(bpy)}_3]^{2+}$ and 0.5 M $\text{H}_2\text{A}/\text{HA}^-$ at pH 4. Measurements were taken before and after 1.5 hours of irradiation using LED light (452 ± 10 nm, 540 mW). HPLC was performed on a Shimadzu instrument equipped with a PDA detector, using C18 analytical column for separation. Mobile phase: H$_2$O and MeOH containing 0.1 % trifluoroacetic acid (TFA). Gradient: 10-90 % MeOH over a period of 40 min, the flow rate was 0.1 mL/min.
Figure 5.S5. ESI-positive (LC-MS) of a photocatalytic sample after 18 h of photocatalysis indicating the presence of [Ru(bpy)$_2$HA]$^+$. Initial conditions: 2 x $10^{-5}$ M 1, 1 x $10^{-4}$ M [Ru(bpy)$_3$]$^{2+}$ and 0.3 M H$_2$A/HA$^-$, pH 4.

Figure 5.S6. UV-Vis of the photocatalytic composition before (black) and after (red) ~ 18 h of photocatalysis (a). Normalized absorbance of [Ru(bpy)$_3$]$^{2+}$ (black) and [Ru(bpy)$_2$HA]$^+$ (red) (b). Initial conditions: 2 x $10^{-5}$ M 1, 1 x $10^{-4}$ M [Ru(bpy)$_3$]$^{2+}$ and 0.3 M H$_2$A/HA$^-$ at pH 4.
Figure 5.S7. Regeneration of photocatalysis after the addition of a fresh aliquot of \([\text{Ru(bpy)}_3]^{2+}\). Initial conditions: \(2 \times 10^{-5} \text{ M } 1, 2 \times 10^{-5} \text{ M } [\text{Ru(bpy)}_3]^{2+}\) and \(0.3 \text{ M } \text{H}_2\text{A}/\text{HA}^-\) at pH 4.

Figure 5.S8. Mercury poisoning test performed on a sample containing \(2.5 \times 10^{-5} \text{ M } 1, 3.3 \times 10^{-4} \text{ M } [\text{Ru(bpy)}_3]^{2+}\) and \(0.1 \text{ M } \text{H}_2\text{A}/\text{HA}^-\) at pH 4.
Figure 5.9. Dynamic light scattering (DLS) before (cyan) and after (green) a 30 minutes of irradiation of a solution containing $1.5 \times 10^{-5} \text{ M} \left[ \text{Ru(bpy)}_3 \right]^{2+}$ and $4 \times 10^{-5} \text{ M} \text{ I}$ in 0.5 M H$_2$A/HA$, pH 4$. The Pt(0) nanoparticles (black) were grown chemically by chemical reduction (NaBH$_4$) of platinum precursor in water and used as standards at $\sim 10^{-5}-10^{-4} \text{ M}$.

Figure 5.10. Linear dependence of final hydrogen produced as a function of $[\text{Ru(bpy)}_3]^{2+}$ concentration at $2.0 \times 10^{-5} \text{ M I}$ (a), and as a function of I concentration at $3.3 \times 10^{-4} \text{ M} [\text{Ru(bpy)}_3]^{2+}$ (b). These experiments were performed in 0.1 M H$_2$A/HA$^{-}$ at pH 4 in water. Under these conditions, the rate of hydrogen production is independent on the concentration of PS and catalyst, the rate is mainly limited by light absorption and subsequent electron transfer. However the stability and the overall hydrogen produced after the reaction ceases increases with the increase of I and $[\text{Ru(bpy)}_3]^{2+}$. 
Figure 5.S11. Hydrogen production as a function of time in the presence of 25 mL of solution containing $1 \times 10^{-6}$ M I, $3.3 \times 10^{-4}$ M [Ru(bpy)$_3$]$_{2}^{2+}$ and 0.3 M H$_2$A/HA$^-$ at pH 4 under 1 sun illumination (AM 1.5G, 100 mW/cm$^2$).

5.6.1 Quantum Yield of Hydrogen Production.

These measurements have been conducted over 12 samples. The first 9 samples were excited using the LED light sources (452 ± 10 nm), and 3 other samples were excited using the 442nm line isolated from a He/Cd laser. For each light source the power density was varied and measurements were taken at 3 different incident power densities. For the LED, both diluted (15 µM) and concentrated samples (%T = 0, [Ru(bpy)$_3$]$_{2}^{2+}$ = $3.3 \times 10^{-4}$ M) gave similar results. The concentration of I was 40 µM in all QY experiments and [H$_2$A/HA$^-$] = 0.5 M, pH 4 to ensure ~ 88% quenching of [Ru(bpy)$_3$]$_{2}^{2+}$. For the laser measurement, the power density before and after the sample was measured to get the absorbed power by the system. Since two photons are needed to produce one H$_2$, these quantum yields are based on two photons absorbed.

$$\Phi = 2 \times n_{H_2} \times n \ (\text{photons})^{-1}$$
Where \( n_{\text{H}_2} \) is the number of hydrogen produced as measured in the headspace of the reactors, and \( n_{\text{photons}} \) is the number of photons absorbed by the samples as calculated from the following formula: \( n_{\text{photons}} = P_{\text{abs}} \times t \times E_{\text{photon}}^{-1} \times N_a^{-1} \); where \( P_{\text{abs}} \) is the power absorbed (W), \( t \) is irradiation time in (s) and \( E_{\text{photon}} \) is the energy of a photon (J) assuming monochromatic light, and \( N_a \) is Avogadro’s number.

\[ \Phi = 7.5 \pm 0.8 \% \text{ (LED)} \] and \[ \Phi = 7.6 \pm 0.6 \% \text{ (laser)} \].

\textbf{Figure 5.S12.} Hydrogen produced as a function of optical power absorbed by the samples using LED as light source (452 ± 10 nm), 4 \( \times 10^{-5} \text{ M } \textbf{1} \), 3.3 \( \times 10^{-4} \text{ M } [\text{Ru(bpy)}_3]^{2+} \) and 0.5 M \( \text{H}_2\text{A}/\text{HA}^- \) at pH 4 \( \textbf{a} \) He/Cd as light source (442 nm), 1.5 \( \times 10^{-5} \text{ M } [\text{Ru(bpy)}_3]^{2+} \), 4 \( \times 10^{-5} \text{ M } \textbf{1} \), 0.5 M \( \text{H}_2\text{A}/\text{HA}^- \) at pH 4 \( \textbf{b} \).
Figure 5.S13. Transient absorption of $[\text{Ru(bpy)}_3]^{2+}$ in water ($A_{452\,\text{nm}} \sim 0.35, \text{H}_2\text{O}$), excited with a 452 nm laser Nd:YAG ($\sim 5\,\text{mJ/pulse}$) (a). Ground-state bleach recovery measured at 460 nm with lifetime of $\sim 0.6\,\mu\text{s}$ (b) and excited state absorption decay at 370 nm where the $\Delta\varepsilon_{\text{max}} \sim 22,000\,\text{M}^{-1}\text{cm}^{-1}$ (c).
Figure 5.S14. Dynamic photoluminescence quenching of the emission intensity vs time measured at 610 ± 2 nm in H$_2$O as a function of added H$_2$A/HA$^-$ from a stock solution at pH 4 (a). Stern-Volmer plot of the lifetime data (b).

Figure 5.S15. Spectroelectrochemical spectra of 2.8 x 10$^{-4}$ M [Ru(bpy)$_3$]$^{2+}$ in ACN (0.1 M TBAPF$_6$ supporting electrolyte) as a function of time of electrolysis (a). Extinction coefficient of [Ru(bpy)$_3$]$^{2+}$ deduced from the SEC data after the end of electrolysis following the Beer-Lambert law (b).
Figure 5.S16. Transient absorption of \([\text{Ru(bpy)}_3]^{2+}\) in \(0.3 \text{ M H}_2\text{A/HA}^-\) (\(A_{452 \text{ nm}} \sim 0.35\), pH 4), excited with a 452 nm laser Nd:YAG (~ 5 mJ/pulse) (a). Kinetic decay of the \([\text{Ru(bpy)}_3]^-\) radical anion at 505 nm (b) along with the second order equal kinetic fit which indicates a diffusion limited process with a rate constant between \(10^9\) - \(10^{10}\) M\(^{-1}\)s\(^{-1}\) (c).
**Figure 5.S17.** Spectroelectrochemical spectra of $6.8 \times 10^{-4}$ M 1 in ACN (0.1 M TBAPF$_6$ supporting electrolyte) as a function of time of electrolysis (a). Extinction coefficient of Co$^{I}$(bpyPY2Me) deduced from the SEC data after the end of electrolysis following the Beer-Lambert law (b).

**Figure 5.S18.** Kinetic transient absorption decay monitored at 505 nm (a) and 650 nm (b). Conditions: $4.4 \times 10^{-4}$ M 1, $2.5 \times 10^{-5}$ [Ru(bpy)$_3$]$^{2+}$ in 0.3 M H$_2$A/HA$^{-}$ at pH 4.
5.6.2 Cage Escape Calculations.

The cage escape yield ($\Phi_{CE}$) was calculated from transient absorption kinetic decay analysis using [Ru(bpy)$_3$]$^{2+}$ in water as actinometer.$^{81,82}$

$$\Phi_{CE} = \frac{\Delta A_{sample}}{\Delta \varepsilon_{sample}} \times (1 - 10^{-A_{actinometer}})$$

Where $\Delta A_{sample}$ is the maximum of the decay of the radical anion, $\Delta \varepsilon_{sample}$ was estimated from spectroelectrochemical measurement leading to the extinction coefficient at a particular wavelength, $\Delta A_{actinometer}$ is the maximum transient observed for the [Ru(bpy)$_3$]$^{2+}$ actinometer under identical excitation conditions and $\Delta \varepsilon_{actinometer} \sim 22,000$ M$^{-1}$cm$^{-1}$ as previously reported.$^{81,82}$ Both sample and actinometer had absorbance $\sim 0.35$, and the fraction quenched was calculated by extrapolation from the Stern-Volmer constant.

Figure 5.S19. The pH dependence of Co(bpy2PYMe) (a) and Co(bpy2PYMe-CF$_3$) (b) catalysts on H$_2$ production with the totals collected after hydrogen production ceased using $3.3 \times 10^{-3}$ M [Ru(bpy)$_3$]$^{2+}$ and $2.0 \times 10^{-5}$ M catalyst in 0.1 M H$_2$A/HA$^-$ in water.
Figure 5.S20. Mercury poisoning test performed on Co(bpy2PYMe), pH 4 (a) and Co(bpy2PYMe-CF₃), pH 4.5 (b) at 2.0 x 10⁻⁵ M catalyst and 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ in 0.1 M H₂A/HA⁻ in water.

Figure 5.S21. Linear dependence of hydrogen produced as a function of [Ru(bpy)₃]²⁺ concentration at 2.0 x 10⁻⁵ M Co(bpy2PYMe) (a), and as a function of Co(bpy2PYMe) concentration at 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ (b). These experiments were performed in 0.1 M H₂A/HA⁻ at pH 4 in water.
**Figure 5.S22.** Linear dependence of hydrogen produced as a function of [Ru(bpy)$_3$]$^{2+}$ concentration with $2.5 \times 10^{-5}$ M Co(bpy2PYMe-CF$_3$) (a), and as a function of Co(bpy2PYMe-CF$_3$) concentration with $3.3 \times 10^{-4}$ M [Ru(bpy)$_3$]$^{2+}$ (b). These experiments were performed in 0.1 M H$_2$A/HA$^-$ at pH 4.5 in water.

**Figure 5.S23.** H$_2$A/HA$^-$ concentration dependence of H$_2$ production collected after hydrogen production ceased utilizing $3.3 \times 10^{-4}$ M [Ru(bpy)$_3$]$^{2+}$ and $2.0 \times 10^{-5}$ M Co(bpy2PYMe) at pH 4 (a), Co(bpy2PYMe-CF$_3$), pH 4.5 (b).
Figure 5.S24. The pH dependence of H₂ production with Co(PY5Me2) (a) and Co(CF₃-PY5Me2) (b) collected after hydrogen production ceased in a composition of 3.3 x 10⁻⁴ M [Ru(bpy)₃]²⁺ and 2.0 x 10⁻⁵ M catalyst in 0.3 M H₂A/HA⁻ in water.

Figure 5.S25. Normalized UV-Vis before and after catalysis of [Ru(BPS)₃]⁺ (a) and [Ru(bpy)₃]²⁺ (b). Conditions: 2 x 10⁻⁵ M Co(bpyPY2Me), 6.7 x 10⁻⁵ M Ru(II), 1 M H₂A/HA⁻ at pH 4.
**Figure 5.S26.** Kinetic analysis of hydrogen evolution at different initial H$_2$A/HA$^-$$^-$ concentration (a) and final amount of hydrogen produced as a function of H$_2$A/HA$^-$$^-$ concentration (b). Conditions: 6.7 x 10$^{-5}$ M [Ru(BPS)$_3$]$^{4+}$, 2 x 10$^{-5}$ M Co(bpyPY2Me) at pH 4.

**Figure 5.S27.** Kinetic analysis of hydrogen evolution at different initial [Ru(BPS)$_3$]$^{4+}$ (a) and final turnover number vs Ru (b). Conditions: 2 x 10$^{-5}$ M Co(bpyPY2Me) and 1 M H$_2$A/HA$^-$$^-$ at pH 4.
Figure 5.S28. Kinetic analysis of hydrogen evolution at different initial Co(bpyPY2Me) (a) and final turnover number vs Co (b). Conditions: $1.34 \times 10^{-4}$ M [Ru(BPS)$_3$]$^{3+}$ and 1 M H$_2$/HA$^-$ at pH 4.

Figure 5.S29. Transient absorption of [Ru(phen)$_3$]$^{2+}$ in water ($A_{452\text{ nm}} \sim 0.35$, H$_2$O), excited with a 452 nm laser Nd:YAG ($\sim 5$ mJ/pulse) (a). Excited state absorption decay at 540 nm (b), Ground-state bleach recovery measured at 440 nm with lifetime of $\sim 1$ µs (c).
Figure 5.S30. Dynamic photoluminescence quenching of \([\text{Ru(phen)}_3]^2+\) at \(\lambda_{\text{emission}} = 610 \pm 2\) nm in H\(_2\)O as a function H\(_2\)A/HA\(^-\) concentration at pH 4 (a). Stern-Volmer analysis extracted from lifetime data (b).

Figure 5.S31. Spectroelectrochemistry performed on \([\text{Ru(phen)}_3]^2+\) in ACN containing 0.1 M TBAPF\(_6\) at different time of bulk electrolysis (a). Extinction coefficient of \([\text{Ru(phen)}_3]^+\) calculated from the SEC data by taking the sum of the initial and final spectrum to obtain the absorption of the product formed (b).
**Figure 5.S32.** Transient absorption of [Ru(phen)$_3$]$^{2+}$ in 0.3 M H$_2$A/HA$^-$ at pH 4 ($A_{452\text{ nm}}$ ~ 0.35), excited with a 452 nm laser Nd:YAG (~ 5 mJ/pulse) (a). Overlap of the excited state decay and kinetic decay of the [Ru(phen)$_3$]$^+$ radical anion at 520 nm (b).

**Figure 5.S33.** Transient absorption of [Ru(BPS)$_3$]$^{4-}$ in water ($A_{452\text{ nm}}$ ~ 0.35, H$_2$O), excited with a 452 nm laser Nd:YAG (~ 5 mJ/pulse) (a). Ground-state bleach recovery measured at 460 nm with lifetime of ~ 3.5 µs (b).
Figure 5.S34. Dynamic photoluminescence quenching of $[\text{Ru(BPS)}_3]^4-$ at $\lambda_{\text{emission}} = 610 \pm 2$ nm in $\text{H}_2\text{O}$ as $\text{H}_2\text{A}/\text{HA}^-$ concentration increases at pH 4 (a). Stern-Volmer analysis extracted from the lifetime data (b).

Figure 5.S35. Spectroelectrochemistry performed on $[\text{Ru(BPS)}_3]^4+$ in ACN containing 0.1 M TBAPF$_6$ at different time of bulk electrolysis (a). Extinction coefficient of $[\text{Ru(BPS)}_3]^5-$ calculated from the SEC data by taking the sum of the initial and final spectrum to obtain the absorption of the product formed (b).
Figure 5.S36. Transient absorption of $\text{[Ru(BPS)₃]}^{4-}$ in 0.3 M H₂A/H₂A⁻ at pH 4 ($A_{452 \text{ nm}} \sim 0.35$), excited with a 452 nm laser Nd:YAG (~ 5 mJ/pulse) recorded after < 1 µs delay (a). Transient absorption recorded after > 10 µs delay (b). $\text{[Ru(BPS)₃]}^{5-}$ kinetic decay at 520 nm (c). Second order equal kinetic fit of (c) which indicates a diffusion limited process with a rate constant ~ $10^5$–$10^{10}$ M⁻¹s⁻¹ (d).
Figure 5.S37. $^1$H NMR of Na$_4$[Ru(BPS)$_3$] in MeOD performed on 500 MHz Bruker instrument.
Figure 5.S38. $^{13}$C NMR of Na$_4$[Ru(BPS)$_3$] in MeOD performed on 500 MHz Bruker instrument.

Figure 5.S39. Lifetime measurement of [Ru(BPS)$_3$]$^{4-}$ ($\tau = 3.8 \mu$s) monitored at $\lambda_{\text{emission}} = 610 \pm 2$ nm (a). Normalized absorbance and photoluminescence spectra of [Ru(BPS)$_3$]$^{4-}$ in water (b).
5.7 REFERENCES


CHAPTER VI

CONCLUSIONS

6.1 CONCLUSIONS AND FUTURE PERSPECTIVE

Solar energy represents a viable alternative to fossil fuels, providing “clean” and sustainable energy to future generations. An attractive strategy gleaned from nature is to store this energy in the form of chemical bonds by running water splitting catalysis, Chapter 1. In this dissertation comprehensive approaches towards photocatalytic water splitting has been presented. A large body of data on topics ranging from heterogeneous to homogeneous compositions has been collected and analyzed. We have found that platinum(II) complexes, long thought to be active molecular catalysts for hydrogen production, actually decompose into Pt(0) nanoparticles which are responsible for proton reduction on the titania surface, Chapter 2.\(^1\),\(^2\) This methodology of growing Pt nanoparticles on titania (TiO\(_2\)) from surface-anchored molecular precursors furnished highly segregated and active catalysts that were shown to be superior to the benchmark platinized materials grown from the traditional chloride salt precursors. This effect was attributed partly to the small size of nanocrystals grown by the former method. As a matter of fact, our methodology has been recently utilized to grow superior Pt catalysts on the surface of dye-sensitized TiO\(_2\) towards visible light induced hydrogen production.\(^3\) We have also photochemically deposited water oxidation catalysts on the surface of titania composed of cobalt and phosphate (CoPi), Chapter 3.\(^4\) This catalyst is self-assembled from earth-abundant elements, with a structure consisting of a series of molecular cobaltate compounds composed of Co atoms connected by bridging oxygen ligands. This oxygen evolving complex operated at neutral pH to
catalyze water oxidation with small overpotentials and near unity Faradaic efficiency for oxygen formation. We have found that the photodeposited catalyst on TiO$_2$ and the already reported electrodeposited catalyst$^{5,6}$ have the identical structure$^7$ and mechanism$^8$ for oxygen production. These results are important to bridge the gap between well studied electrocatalysts and the photodeposited materials utilized in photoelectrochemical devices.$^{9-11}$ Given the wide bandgap of the semiconductors utilized in the solar energy storage schemes like WO$_3$ and TiO$_2$, their inherent efficiency is limited to way below 10% due to the so-called Shockley-Queisser limit of these materials, with most of the limit being imposed by solar photon capture at and above the bandgap.$^{12}$ A strategy was developed over the years in the Castellano laboratory to overcome this limit without chemical modification of the semiconductor surface or bulk properties. This technique relies on the upconversion of low energy photons into higher energy capable of sensitization of semiconductors below their respective bandgaps. In Chapter 4 we have provided the first proof-of-concept that upconversion can indeed extend the photoaction of semiconductors to below their bandgap.$^{13}$ Importantly, we have found that this photochemistry can occur utilizing non-coherent light at low power densities which is important for its application to solar energy conversion schemes.$^{14}$ Based on our work, several groups reported enhanced materials and integrated systems where upconversion was utilized for solar energy harvesting.$^{15,16}$ Besides developing materials for water splitting applications, we have also worked on molecular systems that are capable of converting visible light energy into hydrogen in pure water, Chapter 5. We have constructed a high-throughput apparatus in order to rapidly screen photocatalytic compositions and assess their performance metrics. This approach led to unprecedented understanding of compositions that function in pure water, a Holy Grail in the field of molecular photocatalysis. A structure-activity relationship was obtained for a series of
Co(II) water reduction catalysts and Ru(II) photosensitizers. We have achieved the highest reported turnover numbers in the field of photocatalysis in pure water partly owing to the comprehensive understanding of the systems investigated. We strongly believe that a breakthrough in the field of solar fuels is necessary to solve climate and energy problems currently impacting present and future generations. For this reason, more work must be done on energy-relevant projects as these important problems can likely be solved using creative scientific concepts. Our findings in all the research areas discussed here shed light on important aspects of the solar energy conversion schemes, representing a step forward towards the development of integrated devices that might solve future energy and environmental problems.

6.2 REFERENCES


