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14. ABSTRACT Water oxidation catalysis by polypyridyl complexes of Ru(II) has been investigated mechanistically including studies in nonaqueous solvents with exploitation in electrocatalysis. Electrocatalysis studies have been extended to CO ₂ reduction to CO and, with added weak acids, to syngas (H ₂ :CO) production and to CO ₂ splitting into CO and O ₂ based on a single catalyst. The reduction chemistry has been similarly extended to H ₂ production in a dye sensitized photoelectrosynthesis cell (DSPEC). Studies on DSPECs have been extended to the demonstration of accumulated multiple oxidative equivalents at surface catalysts on mesoporous TiO ₂ and to the evaluation of the					
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Oxygen Activation and Photoelectrochemical Oxidation on Oxide Surfaces

ABSTRACT

Water oxidation catalysis by polypyridyl complexes of Ru(II) has been investigated mechanistically including studies in nonaqueous solvents with exploitation in electrocatalysis. Electrocatalysis studies have been extended to CO₂ reduction to CO and, with added weak acids, to syngas (H₂:CO) production and to CO₂ splitting into CO and O₂ based on a single catalyst. The reduction chemistry has been similarly extended to H₂ production in a dye sensitized photoelectrosynthesis cell (DSPEC). Studies on DSPECs have been extended to the demonstration of accumulated multiple oxidative equivalents at surface catalysts on mesoporous TiO₂ and to the exploration of the influence of Li⁺ doping. A new approach to surface-based assemblies based on phosphonate-derivatized porphyrins has been developed for creating antenna and chromophore-catalyst assembly structures by a layer-by-layer technique.

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08/27/2012 14.00	Wenjing Song, Zuofeng Chen, Christopher R. K. Glasson, Kenneth Hanson, Hanlin Luo, Michael R. Norris, Dennis L. Ashford, Javier J. Concepcion, M. Kyle Brennaman, Thomas J. Meyer. Interfacial Dynamics and Solar Fuel Formation in Dye-Sensitized Photoelectrosynthesis Cells, <i>ChemPhysChem</i> , (06 2012): 0. doi: 10.1002/cphc.201200100
08/27/2012 17.00	Dennis L. Ashford, David J. Stewart, Christopher R. Glasson, Robert A. Binstead, Daniel P. Harrison, Michael R. Norris, Javier J. Concepcion, Zhen Fang, Joseph L. Templeton, Thomas J. Meyer. An Amide-Linked Chromophore–Catalyst Assembly for Water Oxidation, <i>Inorganic Chemistry</i> , (06 2012): 6428. doi: 10.1021/ic300061u
08/27/2012 16.00	Aaron K. Vannucci, Zuofeng Chen, Javier J. Concepcion, Thomas J. Meyer. Nonaqueous Electrocatalytic Oxidation of the Alkylaromatic Ethylbenzene by a Surface Bound Ru, <i>ACS Catalysis</i> , (05 2012): 716. doi: 10.1021/cs300040m
08/27/2012 15.00	Christopher J. Gagliardi, Aaron K. Vannucci, Javier J. Concepcion, Zuofeng Chen, Thomas J. Meyer. The role of proton coupled electron transfer in water oxidation, <i>Energy & Environmental Science</i> , (01 2012): 7704. doi: 10.1039/c2ee03311a
08/31/2011 1.00	Zuofeng Chen, Paul G. Hoertz, Caleb A. Kent, Thomas J. Meyer. Application of High Surface Area Tin-Doped Indium Oxide Nanoparticle Films as Transparent Conducting Electrodes, <i>Inorganic Chemistry</i> , (09 2010): 8179. doi: 10.1021/ic100719r
08/31/2011 5.00	Wenjing Song, Christopher R. K. Glasson, Hanlin Luo, Kenneth Hanson, M. Kyle Brennaman, Javier J. Concepcion, Thomas J. Meyer. Photoinduced Stepwise Oxidative Activation of a Chromophore–Catalyst Assembly on TiO ₂ , <i>The Journal of Physical Chemistry Letters</i> , (07 2011): 1808. doi: 10.1021/jz200773r
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08/31/2011 2.00	Zuofeng Chen, Javier J. Concepcion, Thomas J. Meyer. Rapid catalytic water oxidation by a single site, Ru carbene catalyst, <i>Dalton Transactions</i> , (02 2011): 3789. doi: 10.1039/c0dt01178a
08/31/2012 21.00	Christopher Glasson, Javier Concepcion, Dennis Ashford, Wenjing Song, Patrick Holland, Thomas J. Meyer. Self-Assembled Bilayers on Indium-Tin Oxide (SAB-ITO) Electrodes: A Design for Chromophore-Catalyst Photoanodes, <i>Inorganic Chemistry</i> , (08 2012): 8637. doi:
10/28/2011 11.00	Zuofeng Chen, Chuncheng Chen, David R. Weinberg, Peng Kang, Javier J. Concepcion, Daniel P. Harrison, Maurice S. Brookhart, Thomas J. Meyer. Electrocatalytic reduction of CO ₂ to CO by polypyridyl ruthenium complexes, <i>Chemical Communications</i> , (09 2011): 0. doi: 10.1039/c1cc15071e

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- 12/04/2013 22.00 J. J. Concepcion, X. Hu, W. Yang, P. G. Hoertz, T. J. Meyer, Z. Chen. Concerted O atom-proton transfer in the O–O bond forming step in water oxidation, *Proceedings of the National Academy of Sciences*, (04 2010): 0. doi: 10.1073/pnas.1001132107
- 12/04/2013 23.00 Zuofeng Chen, Javier J. Concepcion, Jonathan F. Hull, Paul G. Hoertz, Thomas J. Meyer. Catalytic water oxidation on derivatized nanoITO, *Dalton Transactions*, (04 2010): 0. doi: 10.1039/c0dt00362j
- 12/04/2013 24.00 Z. Chen, A. K. Vannucci, J. J. Concepcion, J. W. Jurss, T. J. Meyer. Proton-coupled electron transfer at modified electrodes by multiple pathways, *Proceedings of the National Academy of Sciences*, (12 2011): 0. doi: 10.1073/pnas.1115769108
- 12/04/2013 25.00 Z. Chen, J. J. Concepcion, M. K. Brennaman, P. Kang, M. R. Norris, P. G. Hoertz, T. J. Meyer. Splitting CO_2 into CO and O_2 by a single catalyst, *Proceedings of the National Academy of Sciences*, (06 2012): 0. doi: 10.1073/pnas.1203122109
- 12/04/2013 26.00 Kenneth Hanson, Daniel A. Torelli, Aaron K. Vannucci, M. Kyle Brennaman, Hanlin Luo, Leila Alibabaei, Wenjing Song, Dennis L. Ashford, Michael R. Norris, Christopher R. K. Glasson, Javier J. Concepcion, Thomas J. Meyer. Self-Assembled Bilayer Films of Ruthenium(II)/Polypyridyl Complexes through Layer-by-Layer Deposition on Nanostructured Metal Oxides, *Angewandte Chemie International Edition*, (12 2012): 0. doi: 10.1002/anie.201206882
- 12/04/2013 27.00 Dennis L. Ashford, Wenjing Song, Javier J. Concepcion, Christopher R. K. Glasson, M. Kyle Brennaman, Michael R. Norris, Zhen Fang, Joseph L. Templeton, Thomas J. Meyer. Photoinduced Electron Transfer in a Chromophore–Catalyst Assembly Anchored to TiO_2 , *Journal of the American Chemical Society*, (11 2012): 0. doi: 10.1021/ja3084362
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- 12/04/2013 29.00 Zuofeng Chen, Thomas J. Meyer. Copper(II) Catalysis of Water Oxidation, *Angewandte Chemie*, (01 2013): 0. doi: 10.1002/ange.201207215
- 12/04/2013 30.00 Kenneth Hanson, M. Kyle Brennaman, Akitaka Ito, Hanlin Luo, Wenjing Song, Kelsey A. Parker, Rudresh Ghosh, Michael R. Norris, Christopher R. K. Glasson, Javier J. Concepcion, Rene Lopez, Thomas J. Meyer. Structure–Property Relationships in Phosphonate-Derivatized, Ru, *The Journal of Physical Chemistry C*, (07 2012): 0. doi: 10.1021/jp304088d
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- 12/04/2013 32.00 Hanlin Luo, Wenjing Song, Paul G. Hoertz, Kenneth Hanson, Rudresh Ghosh, Sylvie Rangan, M. Kyle Brennaman, Javier J. Concepcion, Robert A. Binstead, Robert Allen Bartynski, Rene Lopez, Thomas J. Meyer. A Sensitized Nb_2O_5 Photoanode for Hydrogen Production in a Dye-Sensitized Photoelectrosynthesis Cell, *Chemistry of Materials*, (01 2013): 0. doi: 10.1021/cm3027972
- 12/04/2013 33.00 Ming-Tian Zhang, Zuofeng Chen, Peng Kang, Thomas J. Meyer. Electrocatalytic Water Oxidation with a Copper(II) Polypeptide Complex, *Journal of the American Chemical Society*, (02 2013): 0. doi: 10.1021/ja3097515

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12/04/2013 35.00 Zuofeng Chen, Christopher R. K. Glasson, Patrick L. Holland, Thomas J. Meyer. Electrogenated polypyridyl ruthenium hydride and ligand activation for water reduction to hydrogen and acetone to isopropanol, Physical Chemistry Chemical Physics, (05 2013): 0. doi: 10.1039/c3cp51946e

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- 08/27/2012 19.00 Kenneth Hanson, Daniel Torelli, Aaron Vannucci, Matthew Kyle Brennaman, Hanlin Luo, Leila Alibabaei, Wenjing Song, Dennis Ashford, Michael Norris, Christopher Glasson, Javier Concepcion, Thomas J. Meyer. Self-assembled Bilayer Films of Ru(II) Polypyridyl Complexes by Layer-by-Layer Deposition on High-Surface Area Metal Oxides, Angewandte Chemie (08 2012)
- 08/31/2012 20.00 Hanlin Luo, Wenjing Song, Paul G. Hoertz, Kenneth Hanson, Rudresh Ghosh, Sylvie Rangan, M. Kyle Brennaman, Javier J. Concepcion, Robert A. Binstead, Robert Allen Bartynski, Rene Lopez, Thomas J. Meyer. A Sensitized Nb₂O₅ Photoanode for Hydrogen Production in a Dye-Sensitized Photoelectrosynthesis Cell, Chemistry of Materials (08 2012)
- 09/01/2011 8.00 Zuofeng Chen, Aaron Vannucci , Thomas Meyer . Proton coupled electron transfer at modified electrodes. Multiple pathways. , Proceedings of the National Academy of Sciences(US) (12 2011)
- 09/01/2011 9.00 Zuofeng Chen, Chuncheng Chen , David Weinberg, Peng Kang, Javier Concepcion . Electrocatalytic Reduction of CO₂ to CO by Polypyridyl Ruthenium Complexes, Chem. Commun. (09 2011)
- 09/01/2011 10.00 Zuofeng Chen, Thomas Meyer, et al. Electrochemical and Solar Splitting of CO₂ into CO and O₂. One Catalyst is Enough, IN PREP (09 2011)

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Paper

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Awards

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Kosolapoff Award, Auburn University (2012)

Honorary Doctor of Chemistry, Ohio University (May, 2013)

Honda-Fujishima Lectureship Award sponsored by the Japan Photochemical Association (September, 2013)

Graduate Students

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Post Doctorates

NAME

PERCENT SUPPORTED

Zuofeng Chen 0.50

Christopher Glasson 0.50

Animesh Nayak 0.50

Wenjing Song 0.50

Aaron Vannucci 0.50

FTE Equivalent: 2.50

Total Number: 5

Names of Faculty Supported

NAME

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Total Number:

Names of Under Graduate students supported

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Student Metrics

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NAME

Total Number:

Names of personnel receiving PHDs

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Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

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See Attachments Below

Technology Transfer

Oxygen Activation and Photoelectrochemical Oxidation on Oxide Surfaces
Agreement Number: W911NF0910426
Final Report

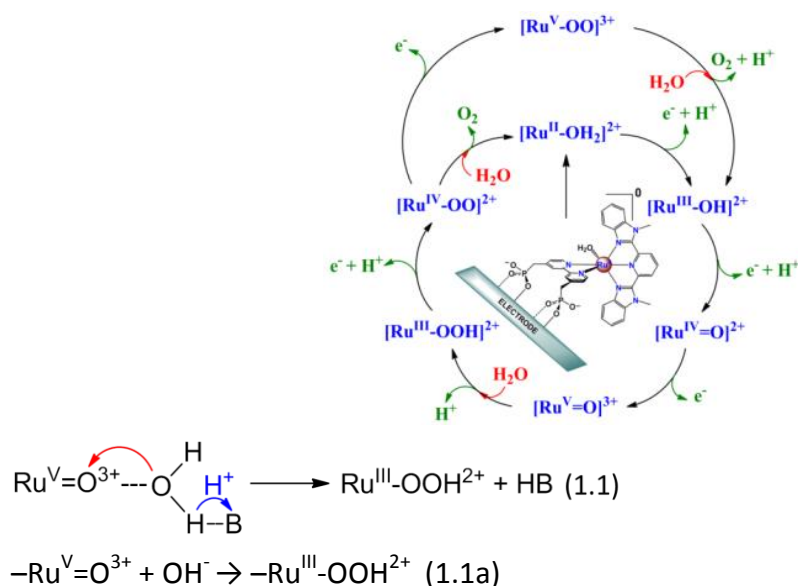
Foreword:

This report summarizes research findings based on Army Research Office support from August 20, 2009 to August 19, 2013 on grant W911NF0910426.

1. Water Oxidation Catalysts

Significant progress in water oxidation catalysis has been made with single-site Ru metal complex catalysts such as $[\text{Ru}(\text{Mebimpy})(\text{bpy})(\text{OH}_2)]^{2+}$ (**1**) (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine; bpy = 2,2'-bipyridine) in solution or on oxide surfaces with $[\text{Ru}(\text{Mebimpy})(4,4'-((\text{HO})_2\text{OPCH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$ where 4,4'-((HO)₂OPCH₂)₂bpy is 4,4'-bis-methylenephosphonato-2,2'-bipyridine (**1-PO₃H₂**) bound to ITO and *nanol*ITO electrodes as shown in Scheme 1.1. The overall mechanism in Scheme 1.1 has been established by mixing experiments with spectrophotometric monitoring. The key O–O bond forming step, analyzed by quantum mechanical simulations (QM/MM), features O-atom attack of $\text{Ru}^{\text{V}}=\text{O}$ on a H_2O molecule. Kinetic studies have identified a new pathway which utilizes added bases as proton acceptors and concerted atom-proton transfer (APT) in which O-atom transfer from the water molecule occurs in concert with proton transfer to added base (B), eq. 1.1, with considerable rate enhancements. A new pathway was also identified in which O-atom transfer to OH^- occurs (eq. 1.1a) under basic conditions with a kinetic rate increase of 10^6 compared to water oxidation in acid. These results have important implications for catalytic, electrocatalytic, and photoelectrocatalytic water oxidation.

Scheme 1.1. Water oxidation mechanism for *nanol*ITO|1-PO₃H₂.



Electrode Materials

Our catalysts are used in a heterogeneous catalytic system on prepared, optically transparent, conducting nanoparticles of tin-doped indium oxide (ITO), which we have termed nanoITO. Figure 1.1 shows scanning electron microscope images of the electrode materials. After fabrication, the electrodes are derivatized with surface-bound molecular catalysts at levels comparable to TiO_2 electrodes used in conventional Dye Sensitized Solar Cells (DSSC). The conductivity of the electrodes provides a basis for facile interfacial electron transfer and rapid, reversible, potential controlled color changes. This allows for direct spectral (rather than current) monitoring of voltammograms, and multi-layer catalysis of surface redox reactions.

NanoITO electrodes are prepared by spin-coating suspensions of ~ 40 nm ITO nanoparticles onto planar substrates (e.g. borosilicate glass, quartz, FTO (fluoride-doped SnO_2), or ITO). Once formed, films were annealed in air at 500°C for 1 hour and then at 300°C under 3% H_2/N_2 for an additional hour. Thickness was controlled by varying nanoparticle concentration in the suspension: $0.55\ \mu\text{m}$ for 12 wt%, $2.5\ \mu\text{m}$ for 22 wt%, $6.7\ \mu\text{m}$ for 29 wt%, and $15.7\ \mu\text{m}$ for 36 wt%. Top-down and cross-sectional field emission scanning electron microscope (FESEM) images demonstrate that the films are highly porous and uniform, allowing for the diffusion of solvent and electrolyte within the porous film structure, Figure 1.1.¹

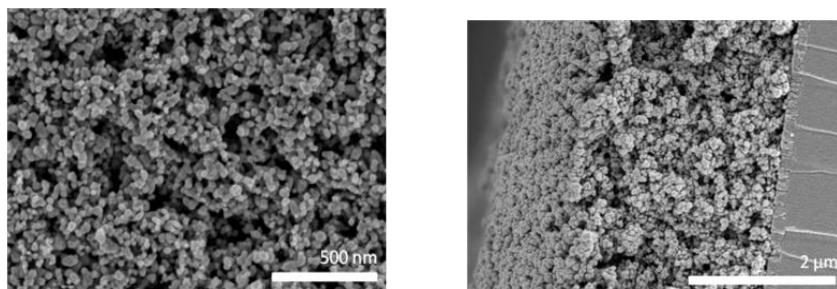
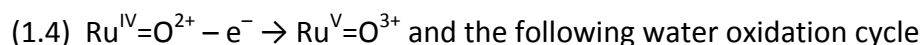
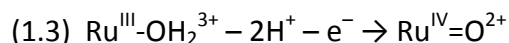
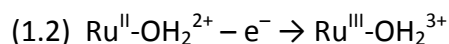


Figure 1.1. Top-down (left) and cross-sectional (right) field emission scanning electron microscopy (FESEM) images of an ITO|*nanoITO* slide ($2.5\ \mu\text{m}$) annealed in air at 500°C and under a steady flow of 3% H_2/N_2 at 300°C . For both images, a thin coating of Au/Pd was deposited prior to imaging.

It has been shown that redox potentials, pH dependences, catalytic properties, and water oxidation mechanism are all retained on oxide surfaces. We have obtained greatly enhanced rates for $\mathbf{1-PO_3H_2}$ on the surface of conductive *nanoITO* films under basic conditions and shown that surface binding provides a basis for sustained, electrocatalytic water oxidation over an extended pH range. We also used direct spectrophotometric monitoring to provide direct evidence for surface mechanism and observation of catalytic intermediates, eqs (1.2)-(1.9) and Figure 1.2.



(1.5) $\text{Ru}^{\text{IV}}(\text{OO})^{2+}$ as a stable intermediate on the surface

(1.6) $\text{Ru}^{\text{IV}}=\text{O}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{Ru}^{\text{III}}-\text{OH}_2^{3+}$

(1.7) $\text{Ru}^{\text{III}}-\text{OH}_2^{3+} + \text{e}^- \rightarrow \text{Ru}^{\text{II}}-\text{OH}_2^{2+}$

(1.8) $\text{Ru}^{\text{IV}}(\text{OO})^{2+} + \text{H}^+ + \text{e}^- \rightarrow \text{Ru}^{\text{III}}-\text{OOH}^{2+}$

(1.9) $\text{Ru}^{\text{III}}-\text{OOH}^{2+} + \text{H}^+ + \text{e}^- \rightarrow \text{Ru}^{\text{II}}(\text{HOOH})^{2+}$

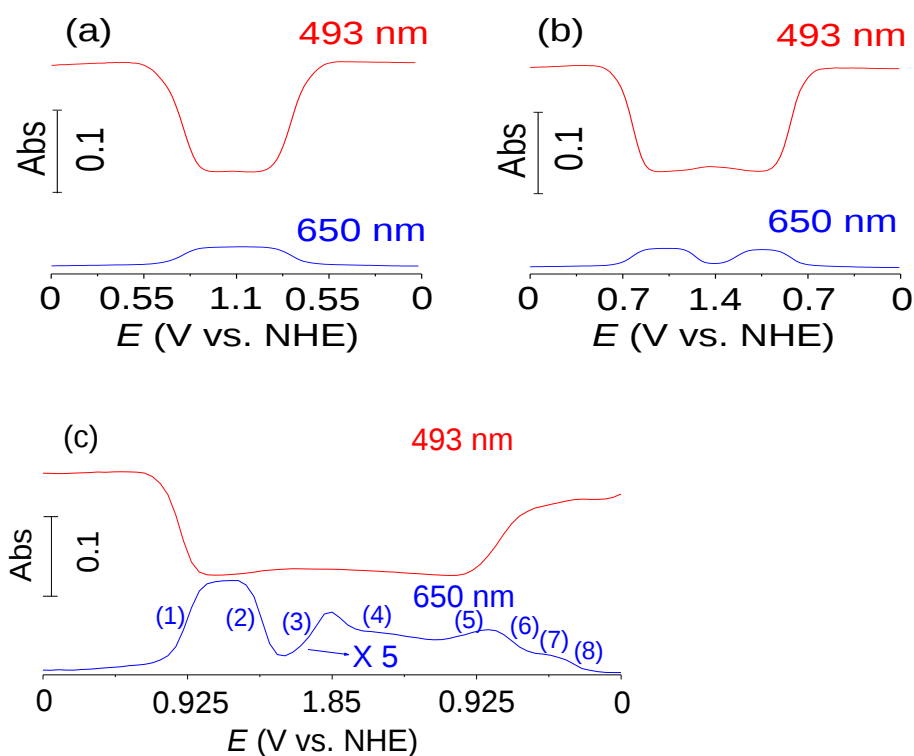


Figure 1.2. Spectral evolution of surface-bound 1- PO_3H_2 , $\text{ITO}|\text{nanolITO}|1\text{-PO}_3\text{H}_2$, at pH 1 (0.1 M HNO_3) during CV scans between: (a) 0 - 1.1 V, (b) 0 - 1.4 V, and (c) 0 - 1.85 V. The monitoring wave lengths were $\lambda_{\text{max}} = 493 \text{ nm}$ for $\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$ and $\text{Ru}^{\text{II}}(\text{HOOH})^{2+}$ (red line), and $\lambda_{\text{max}} = 650 \text{ nm}$ for $\text{Ru}^{\text{III}}-\text{OH}_2^{3+}$ and $\text{Ru}^{\text{III}}-\text{OOH}^{2+}$ (blue line). Scan rate, 10 mV/s. For clarity, the blue line in (c) was magnified by 5-fold. The sequence of electrochemical/chemical events was keyed to the scheme above and steps (2)-(9).

Water Oxidation Mechanism

The mechanism of interfacial water oxidation by $[\text{Ru}(\text{Mebimpy})(4,4'-((\text{HO})_2\text{OPCH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$ (Mebimpy is 2,6-bis(1-methylbenzimidazol-2-yl) and 4,4'- $((\text{HO})_2\text{OPCH}_2)_2\text{bpy}$ is 4,4'-bis-methylenephosphonato-2,2'-bipyridine) (**1- PO_3H_2**) bound to ITO and nanolITO electrodes is shown in Scheme 1.1. Key elements in the mechanism include stepwise proton coupled electron transfer (PCET) oxidation from nanolITO| $\text{Ru}-\text{OH}_2^{2+}$ to higher oxidation states $\text{Ru}^{\text{IV}}=\text{O}^{2+}$ and $\text{Ru}^{\text{V}}=\text{O}^{3+}$. This process occurs through $\text{Ru}^{\text{III}}-\text{OH}^{2+}$ or $\text{Ru}^{\text{III}}-\text{OH}_2^{3+}$ with a $\text{pK}_a = 2.3$ for the latter. In acidic solutions, oxidative activation from $\text{Ru}^{\text{III}}-\text{OH}^{2+}/\text{Ru}^{\text{III}}-\text{OH}_2^{3+}$ occurs through $\text{Ru}^{\text{IV}}(\text{OH})^{3+}$. Further oxidation to $\text{Ru}^{\text{V}}=\text{O}^{3+}$ followed by O-atom transfer from H_2O

gives $\text{Ru}^{\text{III}}\text{-OOH}^{3+}$, which can be further oxidized to the peroxide $\text{Ru}^{\text{IV}}(\text{OO})^{2+}$ followed by slow O_2 evolution. Additional oxidation of the Ru^{IV} peroxide to $\text{Ru}^{\text{V}}(\text{OO})^{3+}$ increases the lability of O_2 leading to re-entry into the catalytic cycle through O_2 loss and regeneration of $\text{Ru}^{\text{III}}\text{-OH}^{2+}$. Evidence has been obtained for intermediate $\text{Ru}^{\text{IV}}(\text{OO})^{2+}/\text{Ru}^{\text{III}}\text{-OOH}^{2+}$ and $\text{Ru}^{\text{III}}\text{-OOH}^{2+}/\text{Ru}^{\text{II}}(\text{HOOH})^{2+}$ couples both in solution and on electrode surfaces.

A kinetic bottleneck to water oxidation occurs in the oxidation of $\text{Ru}^{\text{III}}\text{-OH}^{2+}$ to $\text{Ru}^{\text{IV}}=\text{O}^{2+}$, Scheme 1.1. It arises from the large difference in $\text{p}K_a$ values between $\text{Ru}^{\text{III}}\text{-OH}^{2+}$ (> 14) and $\text{Ru}^{\text{IV}}=\text{OH}^{3+}$ (< 0). We have investigated $\text{Ru}^{\text{III}}\text{-OH}^{2+}$ or $\text{Ru}^{\text{III}}\text{-OH}_2^{3+} \leftrightarrow \text{Ru}^{\text{IV}}=\text{O}^{2+}$ interconversion on the surfaces of metal oxide electrodes by a combination of electrochemical and spectroelectrochemical measurements under a variety of conditions. In these experiments, the phosphonate-derivatized water oxidation catalyst, $\text{Ru}(\text{Mebimpy})(4,4'\text{-(PO}_3\text{H}_2\text{CH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$, shown in Scheme 1.1, was attached to the surfaces of three metal oxides: planar FTO (fluoride-doped SnO_2) and nanostructured, mesoporous films of ITO (nanoITO) both of which are conductive and function as electrodes, and nanostructured films of TiO_2 (nano TiO_2) which is a semiconductor. The results that we have obtained are revealing. They demonstrate participation by multiple pathways on the surface whose relative importance varies depending on solution composition, the nature of electrode, the extent of catalyst loading, and temperature. Pathways have been identified for direct, $\text{Ru}^{\text{III}}\text{-OH}^{2+} - \text{e}^- \rightarrow \text{Ru}^{\text{IV}}=\text{OH}^{3+}$ oxidation, indirect oxidation by cross-surface disproportionation of $\text{Ru}^{\text{III}}\text{-OH}^{2+}$, and concerted electron-proton transfer (EPT) with added acetate anion, equation 1.1. In propylene carbonate as solvent, evidence has been found for proton transfer to the surface-bound phosphonate groups and generalized solvation effects arising, for example, from loss of solvation energy for released protons. Reduction of $\text{Ru}^{\text{IV}}=\text{O}^{2+}$ to $\text{Ru}^{\text{III}}\text{-OH}_2^{3+}$ can occur by PT-ET with prior protonation and reduction of $\text{Ru}^{\text{IV}}=\text{OH}^{3+}$ in strongly acidic solutions. At higher pHs, with $\text{pH} \gg \text{p}K_a(\text{Ru}^{\text{IV}}=\text{OH}^{3+})$, autocatalytic reduction of $\text{Ru}^{\text{IV}}=\text{O}^{2+}$ to $\text{Ru}^{\text{III}}\text{-OH}^{2+}$ occurs by partial reduction to $\text{Ru}^{\text{III}}\text{-O}^+$ followed by rapid protonation, further reduction to $\text{Ru}^{\text{II}}\text{-OH}_2^{2+}$, and cross-surface comproportionation, resulting in narrow, kinetically skewed voltammetric waves.

Water oxidation in non-aqueous environments

Water oxidation in Photosystem II occurs at the Oxygen Evolving Complex (OEC) which is embedded in the hydrophobic thylakoid membrane with water a limiting reagent. We have demonstrated catalytic water oxidation in nonaqueous solvents with water as a limiting reagent by, $\text{Ru}(\text{Mebimpy})(\text{bpy})(\text{OH}_2)^{2+}$ **1** in solution and $\text{Ru}(\text{Mebimpy})(4,4'\text{-(PO}_3\text{H}_2\text{CH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$ **1-PO₃H₂**, on the surfaces of conductive, planar FTO (fluoride-doped SnO_2) and nanoITO Figure 1.3. The rate of water oxidation in propylene carbonate (PC) or trifluoroethanol (TFE) with added water is enhanced by a factor of 300 compared to water as solvent and occurs by a pathway first order in H_2O .

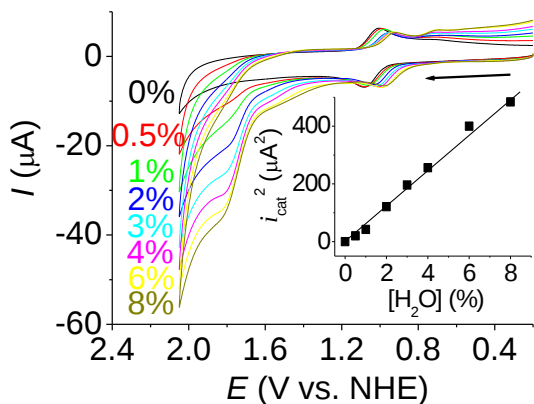


Figure 1.3. CVs of 1 mM **1** in 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{PC}$ with addition of increasing amounts of water as indicated in the figure. The inset shows a plot of i_{cat}^2 (background subtracted) at 1.85 V (vs NHE) vs $[\text{H}_2\text{O}]$, note eq 2. Electrode, GC; scan rate, 100 mV/s.

Water oxidation intermediates

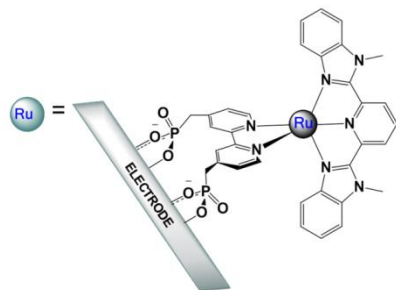
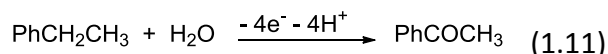
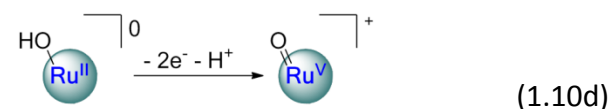
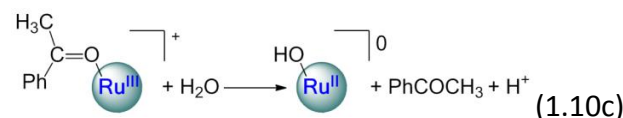
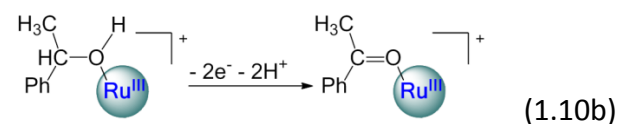
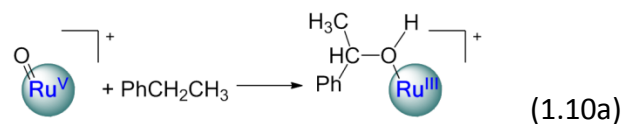
Any mechanism for water oxidation near the thermodynamic potential for the $\text{H}_2\text{O}/\text{O}_2$ couple is necessarily complex due to the requirement for $4e^-/4\text{H}^+$ loss and O-O bond formation. Mechanistic complexity, however, creates an opportunity to examine intermediates that appear in the catalytic cycle for possible catalytic activity with alternate substrates.

Catalyst **1-PO₃H₂** was utilized for the electrocatalytic oxidation of the alkylaromatic hydrocarbons toluene, ethylbenzene, and cumene. Oxidation of hydrocarbons has a direct relation to fuel cell development and conversion of natural gas to liquid fuels. Since the hydrocarbons were not miscible with aqueous solutions, a new solvent system composed of propylene carbonate (PC) and 1 % water by volume with 0.1M LiClO_4 as electrolyte was constructed to carry out the oxidations. PC was chosen due to its oxidative stability and miscibility with water and hydrocarbons, and water was added to the system as a source of oxygen atoms in order to propagate the catalytic cycle. Cyclic voltammetry and steady state current measurements were able to determine that the catalytic rate constant for the oxidation of ethylbenzene was $2.5 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$, which is comparable to the highest rate constants previously reported for hydrocarbon oxidations under similar conditions. Controlled potential electrolysis followed by product determination from mass spectroscopy showed that acetophenone was produced with a 95% Faradaic efficiency. The H/D kinetic isotope effect was determined by to be $k_{\text{C}_8\text{H}_{10}}/k_{\text{C}_8\text{D}_{10}} = 1.2 \pm 0.2$ in PC/1% H_2O ($I = 0.1 \text{ M LiClO}_4$, $23 \pm 2^\circ\text{C}$). The small magnitude of the KIE value is inconsistent with a mechanism involving hydride or hydrogen atom transfer (HAT) from ethylbenzene to the oxidant in the rate limiting step, however, direct O-atom insertion mechanisms with relatively small H/D KIE magnitudes have been reported.

A mechanism consistent with the experimental observations is shown in Scheme 1.2. The mechanism features rate limiting O-atom insertion into a C-H bond to give an intermediate with 1-phenylethanol in the coordination sphere (eq. 1.10a). Once formed, this $2e^-$ intermediate undergoes further $2e^-/2\text{H}^+$ oxidation to the coordinated ketone followed by hydrolysis. There is no evidence for buildup of the intermediate alcohol, 1-phenylethanol. Independent rate

measurements show that electrocatalytic oxidation of 1-phenylethanol occurs with $k_{cat} \approx 7.5 \text{ M}^{-1} \text{ s}^{-1}$, or $> 3\times$ that of ethylbenzene catalysis, are consistent with oxidation of the alcohol in the coordination sphere of the intermediate in eq. 1.10b before it undergoes hydrolysis eq. 1.10c.

Scheme 1.2. Proposed oxygen-atom insertion mechanism for electrocatalytic ethylbenzene oxidation by *nanoITO*|**1-PO₃H₂**.



Water Oxidation from Cu salts

In another aspect, our work highlights a remarkable and previously unexpected research finding, that simple Cu(II) salts in concentrated bicarbonate/carbonate and phosphate buffer solutions act as rapid, efficient electrocatalysts for water oxidation. As showed in **Figure 1.4**, the roles of $\text{HCO}_3^-/\text{CO}_3^{2-}$ or $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ are essential in avoiding precipitation of $\text{Cu}(\text{OH})_2$ ($K_{sp}(\text{Cu}(\text{OH})_2) = 4.8 \times 10^{-20}$), CuCO_3 ($K_{sp}(\text{CuCO}_3) = 1.4 \times 10^{-10}$) or $\text{Cu}_3(\text{PO}_4)_2$ ($K_{sp}(\text{Cu}_3(\text{PO}_4)_2) = 1.40 \times 10^{-37}$) and in coordination stabilization of higher oxidation state Cu(III) and/or Cu(IV) intermediates. Water oxidation occurs by kinetically well-defined pathways either first or second order in $[\text{Cu}(\text{II})]$, depending on solution conditions with evidence for oxidized, presumably peroxide, intermediates. The rate of water oxidation in 1 M CO_3^{2-} is especially rapid and sustained for extensive periods. These results open new doors in the emerging science and

technology of "solar fuel" production and should be of interest broadly and of great potential for practical application.

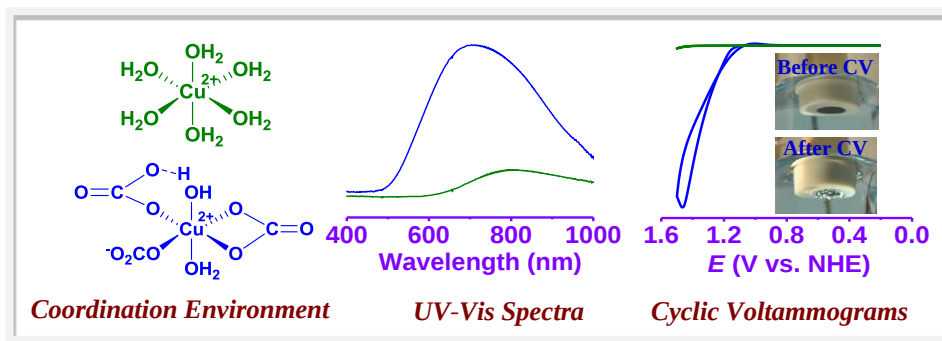


Figure 1.4. (Left) Proposals for the coordination environments of Cu(II) in water or CO₂/HCO₃⁻/CO₃²⁻ aqueous solution. (Middle) The corresponding UV-Vis spectra of 1 mM Cu(II) in water or in 1 M Na₂CO₃ (pH ~10.8). (Right) CVs in 1 M Na₂CO₃ (pH ~10.8) at a BDD electrode (0.071 cm²) with and without of added 3 mM CuSO₄.

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2. Electrocatalytic Hydrogen Evolution

In previous reports, we have shown that complex **1**, note Figure 2.1, is a robust electrocatalyst toward CO₂ reduction in acetonitrile^[1]. Here, we show that complex **1** is also a catalyst for water or proton reduction to hydrogen^[2]. With water added to acetonitrile, the initial step is ligand-based reduction followed by proton abstraction from water to give the hydride, [Ru^{II}(tpy)(bpy)(H)]⁺. The hydride is the active form of the catalyst toward H₂ evolution. Figure 2.2(a) shows CVs of Ar-deaerated solutions of **1** in 0.1 M ⁿBu₄NPF₆/CH₃CN with increasing amounts of added water at a glassy carbon electrode and Figure 2.2(b) a series of CVs with 10% added water obtained at different negative switching potentials. Waves O1 and O2 in the insets arise from the re-oxidation of intermediates that form in the hydrogen evolution scheme.

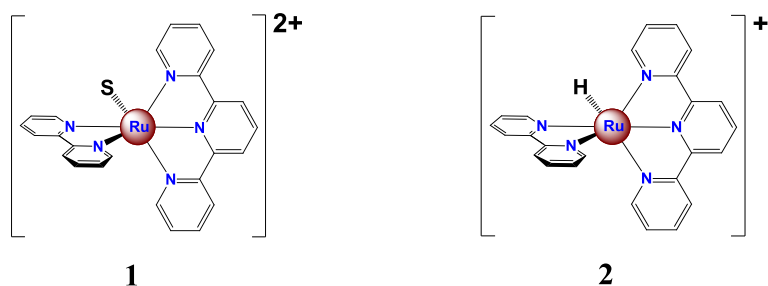


Figure 2.1. Structures of the polypyridyl Ru catalyst ($[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{S})]^{2+}$) **1** (S is solvent), and the Ru hydride ($[\text{Ru}^{\text{II}}(\text{bpy})(\text{bpy})(\text{H})]^+$) **2**.

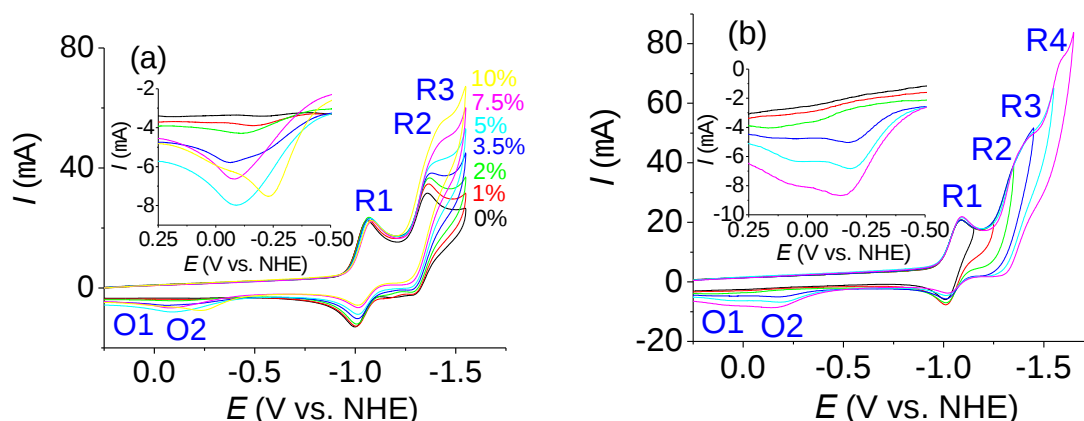
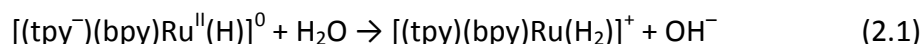


Figure 1.2. (a) Cyclic voltammograms of 1 mM **1** in 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ under Ar with addition of increasing amounts of water (0–10% v:v; 0–5.5 M). (b) Cyclic voltammograms of 1 mM **1** in 10 % H_2O (v:v, 5.5 M), 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ under Ar with reductive scans to increasingly negative potentials. The inset shows a magnified view of return, oxidative scans between -0.5 to 0.25 V following a reductive scan. Glassy carbon electrode; scan rate 100 mV/s.

The mechanism for electrocatalytic reduction of water and added weak acids to hydrogen is shown in Figure 2.3. As in CO_2 reduction, water reduction catalysis is initiated by reduction at the polypyridyl ligands. The *in situ* electrogenerated $[(\text{tpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{H})]^+$ is not sufficiently reactive to release hydrogen on the CV time scale with 10% added water. Hydrogen evolution is significantly promoted by tpy-based reduction to give $[(\text{tpy}^-)(\text{bpy})\text{Ru}^{\text{II}}(\text{H})]^0$ at $E_{\text{p,c}} = -1.41$ V (wave R3 in Figure 2.2b). It reacts with water in the rate limiting step with a $\text{H}_2\text{O}/\text{D}_2\text{O}$ kinetic isotope effect (KIE) of 3.7 to give an additional intermediate, presumably the dihydrogen complex, $[(\text{tpy})(\text{bpy})\text{Ru}(\text{H}_2)]^+$, eq 2.1. The intermediate undergoes a characteristic reduction at $E_{\text{p,c}} = -1.55$ V (wave R4). The catalytic cycle is completed by loss of hydrogen, solvolysis, and re-entry into the catalytic cycle.



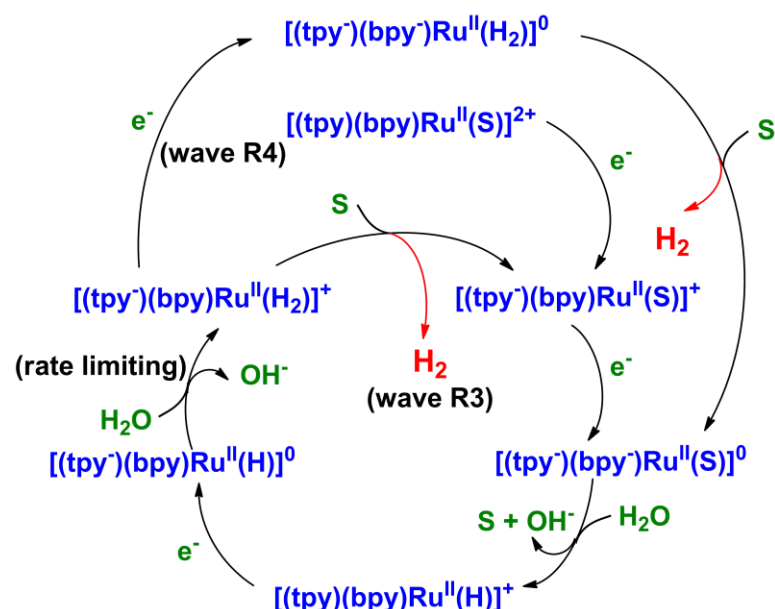


Figure 2.3. Proposed mechanism for electrocatalytic reduction of water by **1** (S = CH₃CN).

A considerable rate enhancement for hydrogen evolution by **1** was observed with added weak acids, qualitatively, with the extent of rate enhancement scaling with the strength of the acid and its pK_a . A series of CVs with added [ⁿBu₄N][H₂PO₄] ($pK_a = 7.2$ in water compared to $pK_a = 15.7$ for water in water) is shown in Figure 2.4. With > 10 mM added H₂PO₄[−], significant rate enhancements for hydrogen evolution are observed, by a factor of 10⁴ fold compared to water. Under these conditions, there is no evidence for re-oxidation of $[(\text{tpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{H})]^+$ at wave O1 or of the dihydrogen intermediate at wave O2. These observations point to hydrogen evolution with added H₂PO₄[−] by a second catalytic cycle, Figure 2.5. In this cycle, the rate limiting step is formation of the hydride following a second reduction at bpy. Once the hydride is formed, it undergoes a rapid reaction with H₂PO₄[−] to give hydrogen and the solvent-coordinated complex which re-enters the catalytic cycle.

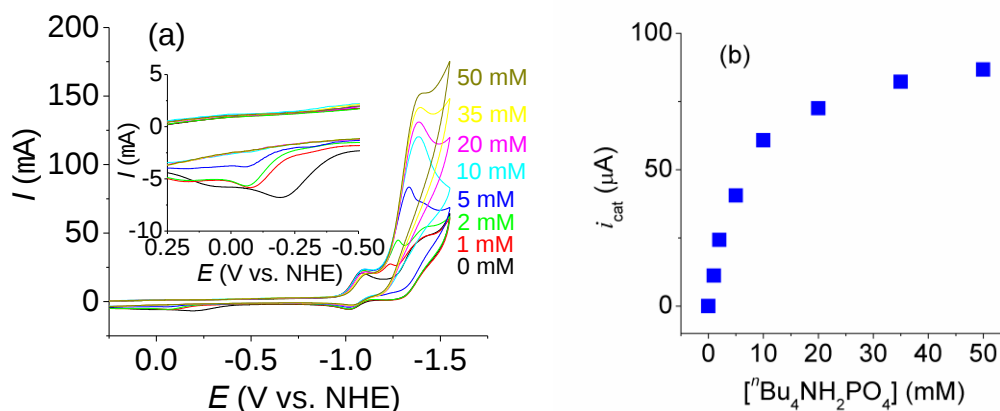


Figure 2.4. (a) Cyclic voltammograms of 1 mM **1** in 10% H₂O, 0.1 M ⁿBu₄NPF₆/CH₃CN under Ar with addition of increasing amounts of [ⁿBu₄N][H₂PO₄]. The inset shows a magnified view of return, oxidative scans between −0.5 to 0.25 V following a reductive scan. Glassy carbon

electrode: scan rate, 100mV/s. (b) Plot of catalytic currents during electrolysis at -1.38 V, i_{cat} (background subtracted), vs. concentration of added H_2PO_4^- .

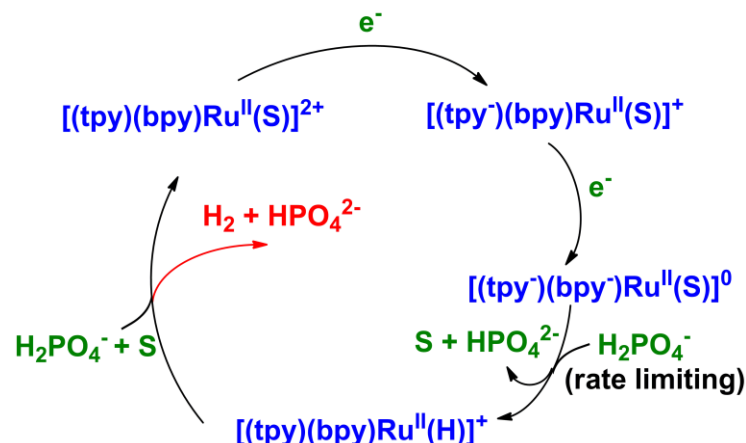


Figure 2.5. Proposed mechanism for electrocatalytic reduction of H_2PO_4^- by **1** ($\text{S} = \text{CH}_3\text{CN}$).

Hydrogen evolution also occurs with other added weak acids, *e.g.* $[\text{nBu}_4\text{N}][\text{HCO}_3]$ ($\text{pK}_a \sim 10.3$ in water) where there is evidence for both $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H})]^+$ and its reduced form as intermediates. Similar results were obtained for $[\text{Ru}(\text{tpy})(\text{bpy})\text{Cl}]^+$, following its reduction, solvolysis, and conversion to the hydride, and for other structurally related polypyridyl ruthenium complexes.

In the catalytic cycle in Figure 2.3, enhanced hydride donor reactivity of the hydride is induced by the electron reservoir effect and activation of the hydride by ligand-based reduction. As noted above, Creutz, *et al.*, had demonstrated an extensive hydride reactivity of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H})]^+$ toward a number of hydride acceptors, CO_2 , formaldehyde, *etc.* We extended this reactivity to the reduction of organic functional groups, in particular, to the reduction of acetone to *iso*-propanol. In 10% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ under Ar, no significant reaction is detected between $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H})]^+$ and acetone after 12 h. However, upon *in situ* electrochemical reduction, $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H})]^0$ is an active electrocatalyst toward reduction of acetone to *iso*-propanol in competition with hydrogen production.

Syngas Production

The electrochemical investigations on CO_2 and water reduction revealed well-defined mechanisms based on common intermediates. In these reactions electrocatalytic reduction of H_2O or CO_2 by $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ is initiated by ligand-based reduction which activates the metal toward displacement of bound CH_3CN by CO_2 in the dry solvent or, with added water, by proton abstraction from H_2O to give the hydride, $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{H})]^+$. In dry CH_3CN , ligand-based reduction of $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ induces coordination of CO_2 to give the metallocarboxylate, $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{CO}_2^{2-})]^0$ which undergoes further reduction and O^{2-} loss to CO_2 to give the corresponding CO complex. With added weak acids $-\text{H}_2\text{PO}_4^-$, HCO_3^- – the hydride protonates to give a dihydrogen intermediate, liberating H_2 .

In solutions saturated in CO_2 with 10% H_2O and added weak acid H_2PO_4^- , we found a competition exists between the H_2 evolution and CO_2 reduction pathways^[3]. In current

experiments, we have shown that electrocatalytic reduction under these conditions gives syngas mixtures of H₂ and CO with the ratio dictated by the relative amount of acid added. Given the importance of syngas mixtures as precursors to methanol and other hydrocarbons this is an important observation in demonstrating use of a single catalyst to carry out this important reaction with important implications for potential electrocatalytic and photoelectrocatalytic approaches to syngas production.

CO₂ splitting

In spite of formidable challenges in chemical reactivities for both water oxidation and CO₂ reduction, we illustrated that the transition metal complex $[(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{S})]^{2+}$ (tpy = 2,2':6',2''-terpyridine; Mebim-py = 3-methyl-1-pyridylbenzimidazol-2-ylidene; S = solvent) is a robust, reactive electrocatalyst both for water oxidation to O₂ in aqueous solution and for CO₂ reduction to CO in acetonitrile with the single catalyst applied to CO₂ splitting into CO and O₂ in a two-compartment electrochemical cell, as showed in Figures 2.6 and 2.7. In its simplicity, the contrast of the setup in Figure 2.6 with natural photosynthesis is striking. Photosynthesis in green plants involves thousands of atoms, five membrane-bound integrated assemblies, and the Calvin cycle and evolved over billions of years to achieve CO₂ splitting into oxygen and carbohydrates. In the electrochemical/photoelectrochemical approach, single catalysts or pairs of catalysts are combined with semiconductors, electrodes, wires, and membranes to connect the half reactions and exchange electrons and protons.

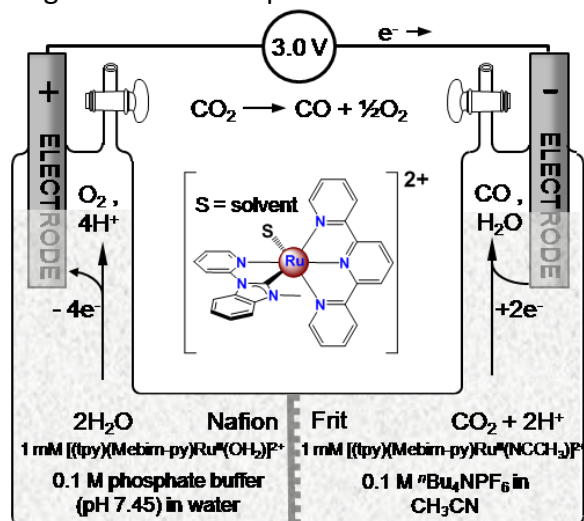


Figure 2.6 Schematic diagram for the two-compartment, Nafion|Frit-separated electrochemical cell for CO₂ splitting.

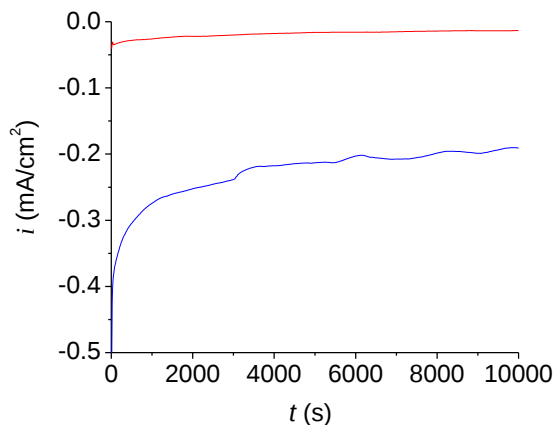


Figure 2.7. Blue line: As in Figure 2.6, controlled potential electrolysis at 3.0 V at two boron doped diamond electrodes ($\sim 0.85 \text{ cm}^2$). Red line: background current without added catalyst.

Although the above study was the first example of a single molecule catalyst for CO_2 splitting to the best of our knowledge, long term performance was limited by slow solvent inter-permeability across the membrane separator, slow carbene ligand oxidation at the anode, and catalyst precipitation at the cathode. As an extension of our Cu(II) catalysis of water oxidation, together with our interest in CO_2 splitting by single catalysts, we report here that, under appropriate solution conditions, simple Cu(II) salts are reactive as water oxidation electrocatalysts and its reduction form, Cu(0) film formed by electroplating from Cu(II) capable of CO_2 reduction in electrolysis cell of two compartments. The two half reactions provide a basis for net electrochemical and solar splitting of CO_2 into CO/HCOO^- and O_2 , as showed in Figure 2.8.

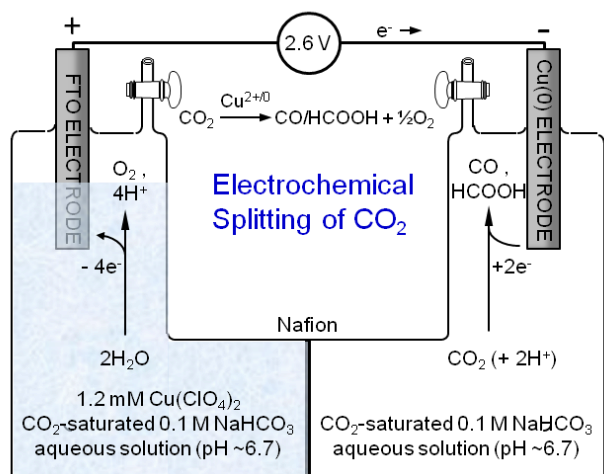


Figure 2.8. Schematic diagram for a two-compartment, two-electrode Nafion-separated electrochemical cell for CO_2 splitting by simple Cu(II) in CO_2 -saturated 0.1 M NaHCO_3 aqueous solution (pH ~ 6.7).

References:

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3. H₂ Production in Dye Sensitized Photoelectrosynthesis Cell(DSPEC): Interfacial Dynamics and Efficiencies

We explored Dye Sensitized-Photoelectrochemical Cell (DSPEC) configurations for important photochemical reactions such as water splitting, $2 \text{H}_2\text{O} + 4 h\nu \rightarrow \text{O}_2 + 2 \text{H}_2$, and organic dehydrogenation/oxidation, e.g., $\text{RR}'\text{CHOH} + 2 h\nu \rightarrow \text{RR}'\text{C}=\text{O} + \text{H}_2$ with visible light. This approach follows from the Dye Sensitized Solar Cells (DSSC) pioneered by Gratzel and coworkers. In our studies we focused on the relationship between interfacial photophysical dynamics and hydrogen production efficiencies in DSPEC.

Charge separation and recombination dynamics (eq 3.1 and figure 3.1) have been investigated in DSPEC cells with $\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-((\text{HO})_2\text{OP})_2\text{bpy})]^{2+}$ attached to FTO|TiO₂ substrates (**TiO₂-RuP**). Phosphonates are appealing compared to commonly used carboxylates functional group because of enhanced surface stability in aqueous media.

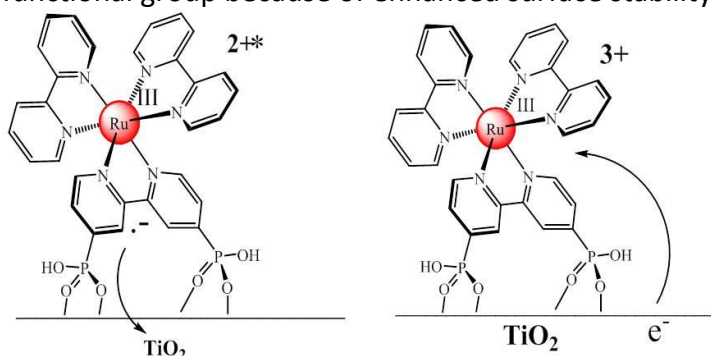


Figure 3.1. Interfacial electron-transfer dynamics and hydrogen formation at TiO₂-RuP photoanode



We have shown that the electron injection yield from **RuP** excited states to TiO_2 is favored by low pH, but back electron transfer kinetics is also enhanced in acidic media. In addition, back electron transfer can be tuned by applying external bias or reducing light intensity (Figure 3.2). These effects originate from combination of effects: (i) pH dependence of TiO_2 conduction band/trap states ($E = -0.16 - 0.059\text{pH}$ vs NHE); (ii) injected electron density in TiO_2 ; (iii) the quasi-Fermi level of TiO_2

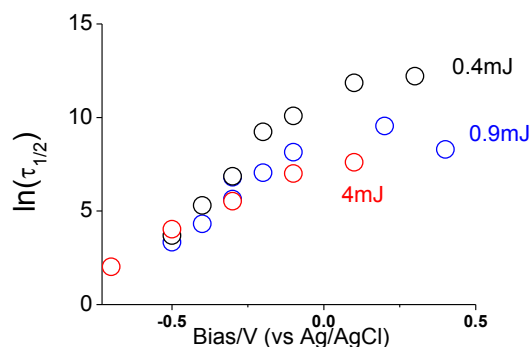
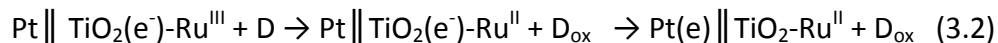


Figure 3.2. Half lifetime of photogenerated $\text{TiO}_2\text{-Ru}^{\text{III}}\text{P}$ at pH 1 in aqueous solution under various external bias and excitation intensities

We have investigated photoelectrochemical hydrogen generation in a DSPEC cell based on eq 1 with the photogenerated holes, as $\text{TiO}_2\text{-Ru}^{\text{III}}$, reduced by external donors, triethanolamine (TEOA) or ethylenediaminetetraacetate (EDTA) to provide reductive equivalents to a second, counter electrode for proton reduction to hydrogen, eq. 3.2 and 3.3. We explored this phenomenon by transient absorption (TA), transient photocurrent, photon-to-current conversion efficiency (IPCE) measurements, and by hydrogen production under steady state light illumination.



The reaction of TEOA and EDTA was monitored by transient absorption (TA). The observed rate constant for RuP regeneration reached a plateau at $\sim 10\text{mM}$ of TEOA at pH 6.7 (Figure 3.3A). The reduction of $\text{Ru}^{\text{III}}\text{P}$ by EDTA was more efficient (Figure 3.3B) due to its higher affinity to semiconductor surface, as well as a better pre-association with surface bond, photogenerated $\text{Ru}^{\text{III}}\text{P}$. In the presence of external donors, electron collection efficiencies were obtained by transient photocurrent measurements, as a function of applied potential (Figure 3.4A), with back electron transfer dynamics monitored simultaneously (Figure 3.4B). The conduction band potential of TiO_2 was slightly lower than potential of H^+/H_2 redox couple, therefore an positive bias was necessary for efficient proton reduction at the Pt counter electrode. Sufficient positive bias decreases the rate of back electron transfer to surface $\text{Ru}^{\text{III}}\text{P}$ and facilitates electron transport through TiO_2 film to external circuit. The interfacial dynamics data revealed optimized condition for long-lived charge separated states for hydrogen production. DSPEC performance (incident photon to current conversion, IPCE) under steady state light irradiation (Figure 3.5) agreed well with results obtained by transient measurements.

The with quantum yields for hydrogen generation approached 15% in DSPEC with 0.2 V bias in the presence of EDTA as electron donor.

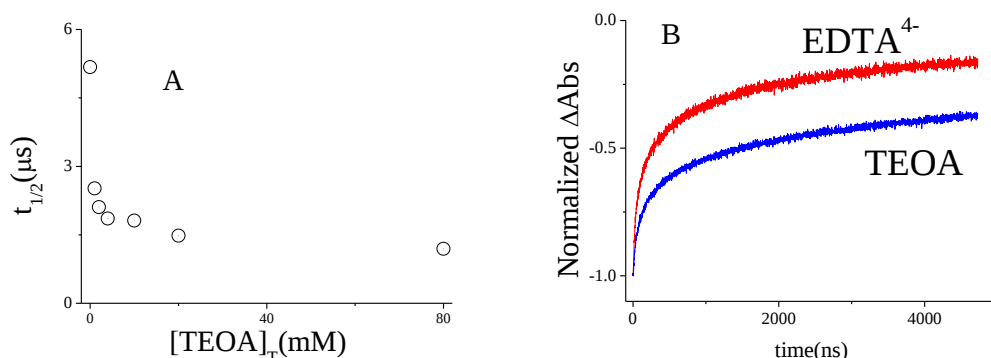


Figure 3.3. (A) Half lifetime ($t_{1/2}$) for Ru(III) following laser flash excitation in the presence of different concentration of TEOA. (B) Regeneration of $\text{TiO}_2\text{-Ru}^{\text{II}}\text{P}$ monitored by 450nm transient absorption in the presence of 80 mM TEOA and 20 mM EDTA under open circuit condition.

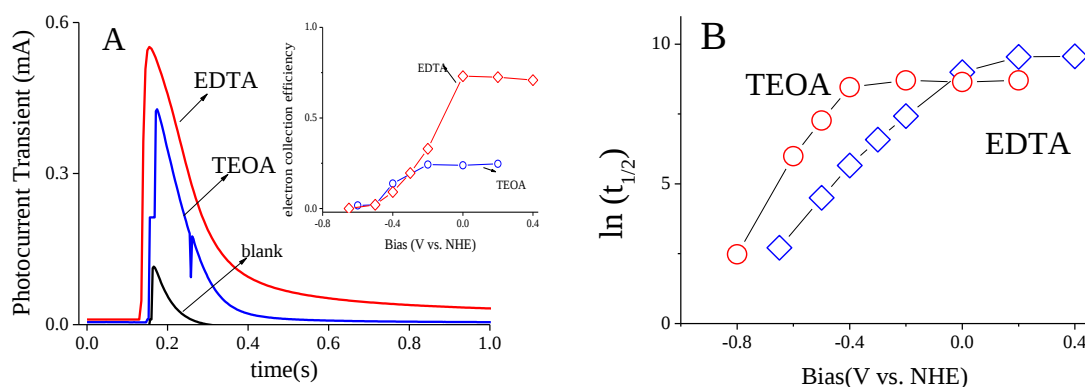


Figure 3.4. (A) Transient photocurrent induced by one laser pulse with TEOA or EDTA as electron donor in DSPEC with 0.2V bias vs. NHE. Insert, electron collection efficiency at different applying bias in the presence of both donors; (B) Plot of $\ln(t_{1/2}, \mu\text{sec})$ vs applied bias for $\text{TiO}_2(\text{e})\text{-Ru}^{\text{III}}\text{P}$ with added TEOA (o), pH 6.7, and EDTA^{4-} ($\diamond$), pH 4.5.

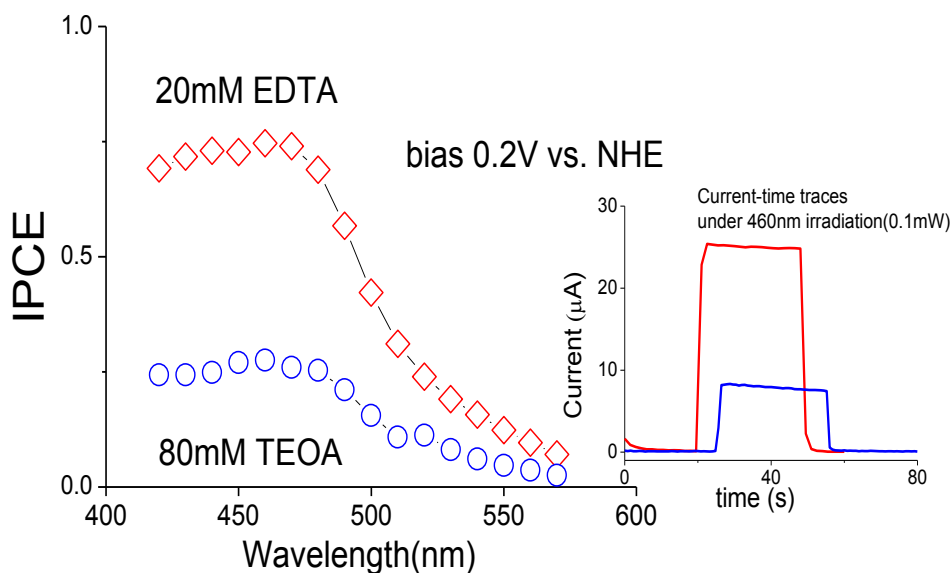
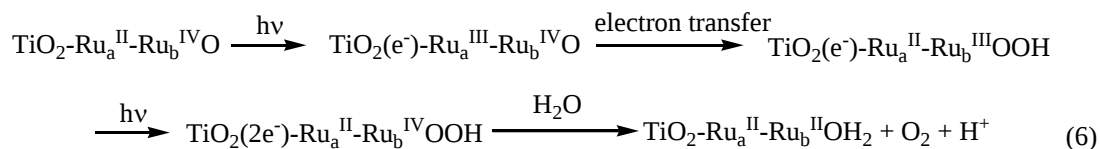
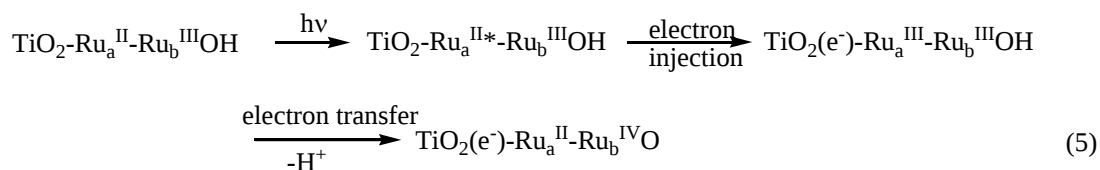
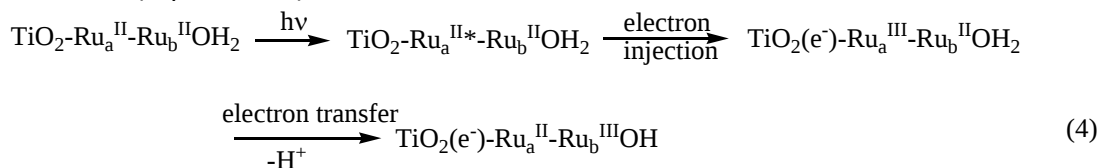


Figure 3.5. Incident photon to current efficiency (IPCE) for DSPEC with 0.2 V bias with TEOA or EDTA as electron donor.

Photo-Induced Multiple oxidative Equivalent Accumulation/Catalyst Activation of Chromophore-Catalyst Assembly $Ru_a-Ru_b-OH_2$ on TiO_2

A major challenge for water splitting, photochemical oxidation of organics, or CO_2 reduction in DSPEC cells exists due to the multi-proton/and multi-electron nature of the reactions. This requires multiple photon events, all of which are in competition with back electron transfer, to build up the required multiple redox equivalents. We are investigating a series of ruthenium polypyridyl assemblies which combine light harvesting and electron injection in TiO_2 with delivery of oxidative equivalents to a remote catalyst for water/organic oxidation (eq 3.4 – 3.6).



We have developed several chromophore catalyst assemblies with carboxylic or phosphonate functional group (Figure 3.6, 1C and 1P). In these molecular assemblies, $\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{OH}$ and $\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{IV}}\text{O}$ could be generated electrochemically on high surface area conducting In_2O_3 electrode, which provided spectral information for different oxidizing/activated states (Figure 3.7). The photoinduced generation of $\text{TiO}_2(\text{e}^-)\text{-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}$ and $\text{TiO}_2(\text{e}^-)\text{-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{IV}}$ were confirmed by transient absorption measurements (Figure 3.8).

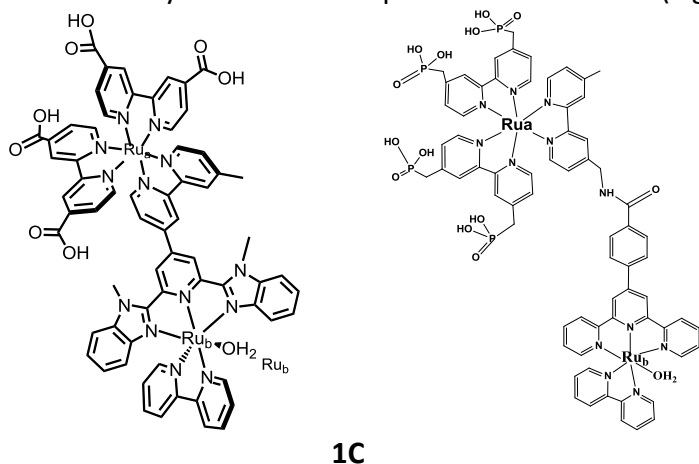


Figure 3.6. Structures of the assemblies

Compared to chromophore RuP , 1C has much lower injection efficiency ($\sim 20\%$) due to competition between injection and excited decay from the remote catalysts site. Injection efficiency was improved for molecular assembly 1P, which has non-conjugated bridging ligand between chromophore and catalyst. Rates of back electron transfer in these molecular assemblies were greatly decreased, compared to monomeric analogs (Table 1). It is worth noting that for 1P, the lifetime of photogenerated $\text{TiO}_2(\text{e}^-)\text{-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{OH}$ was extended to millisecond in pH 4.5 aqueous solution (Figure 3.9), which is a favored condition for light driven catalytic water oxidation.

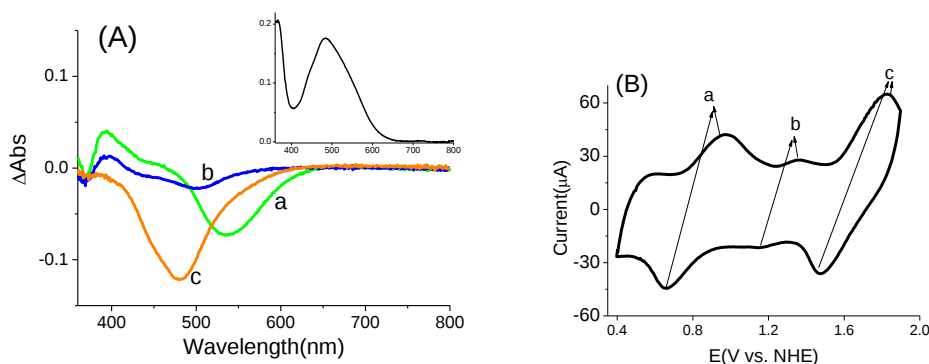


Figure 3.7. (A) Visible spectral changes accompanying reversible oxidation of $\text{nanoITO-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{II}}\text{OH}_2$ to $\text{nanoITO-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{OH}$ (a), to $\text{nanoITO-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{IV}}\text{O}$ (b) and to $\text{nanoITO-Ru}_a^{\text{III}}$

$\text{Ru}_b^{\text{IV}}=\text{O}$ (c). Insert: spectrum of $\text{nanoITO-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{II}}\text{-OH}_2^{2+}$. (B) Cyclic voltammogram of **1C** on nanoITO (10 mV/s).

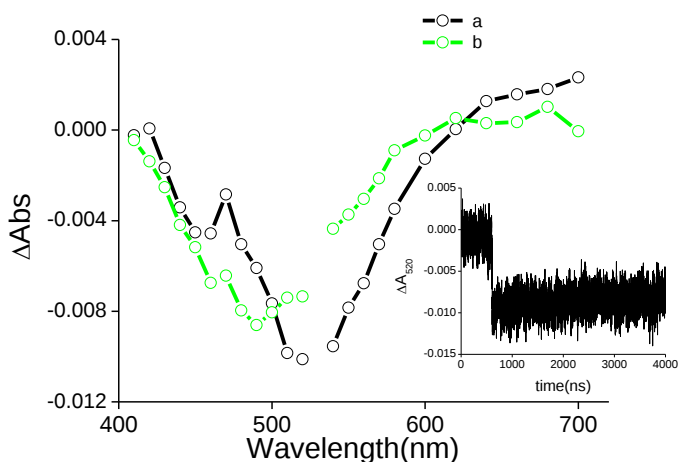


Figure 3.8. Transient absorption difference spectra obtained following 532 nm excitation of $\text{TiO}_2\text{-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{II}}\text{OH}_2$ (a) and $\text{TiO}_2\text{-Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{OH}$ (b) in propylene carbonate with 2% Insert: Plot of transient absorbance-time trace monitored at 520 nm.

Table 3.1. Back electron transfer dynamics obtained from stretched exponential fit ($\Delta OD = Ae^{-(t/\tau)^\beta}$) for molecular assembly **1P**, monomeric control chromophore and contral catalyst on TiO_2

Complex	Back Electron Transfer ^b	
	τ (μs)	β
1P	6.7	0.25
chromophore	1.8	0.29
catalyst	2.2	0.22

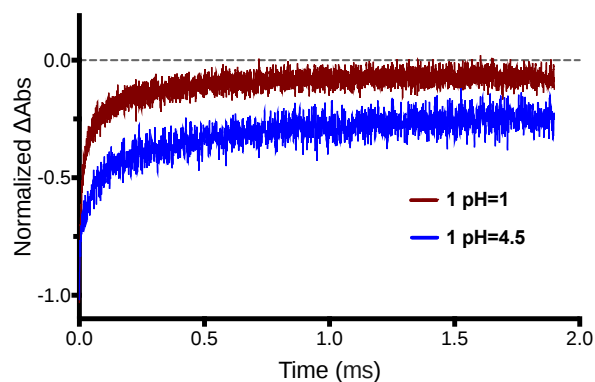


Figure 3.9. Absorbance-time traces for **1P** on TiO_2 following 532 nm laser flash (5.0 mJ) excitation with monitoring at 480 nm in 0.1 M HClO_4 (red) and at pH = 4.5 (0.18M LiClO_4 with 20mM NaOAc/HOAc buffer, blue).

Lithium intercalation dynamics at photoanode interfaces and effect of Lithium doping on dye sensitized photoelectrochemical cells (DSPECs)

Solar fuels production in dye sensitized photoelectrosynthesis cells (DSPEC) is a promising approach to solar energy conversion. The efficiency of DSPECs is highly dependent on small cations present at photoelectrode interfaces or doped into the semiconductor bulk, due to their impacts on the dynamics of photo-induced charge separation, recombination, and carrier transport at photoelectrode–electrolyte interfaces.

In our study, the dynamics of Li^+ diffusion at photoelectrodes/electrolyte interface was monitored *in situ* in a working DSPEC for hydrogen generation. The photoanode was TiO_2 mesoscopic film sensitized with $[\text{Ru}(\text{bpy})_2(4,4'\text{-PO}(\text{OH})_2\text{bpy})]^{2+}$ (**RuP**). As shown in **Figure 3.10**, **RuP** on TiO_2 was shown to be sensitive to the microscopic environments including external electric field (by electron injection into TiO_2) and local concentration of small cations including Li^+ and proton. Such spectral response of RuP was attributed to the change in metal to ligand charge transfer transition energy in the electric field (Stark effect), and the screening of electric field by cations. The spectral response provides simple method to time-resolve the cation diffusion dynamics.

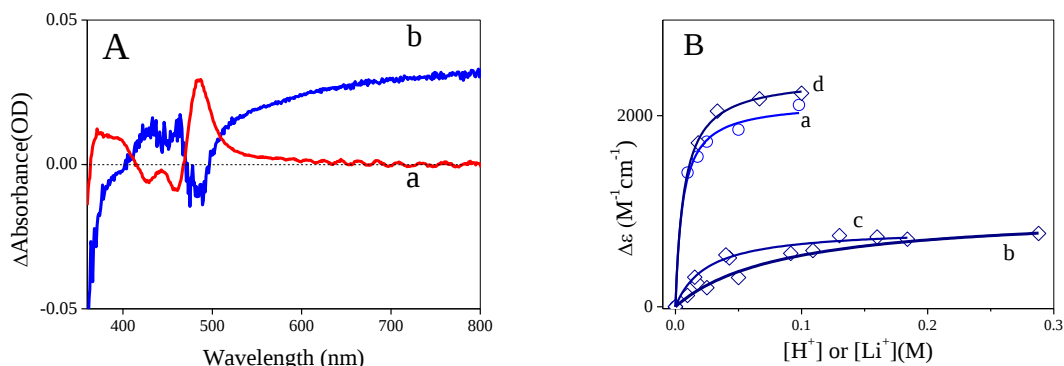
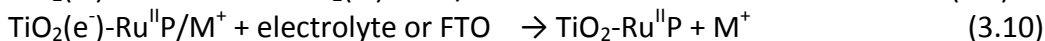
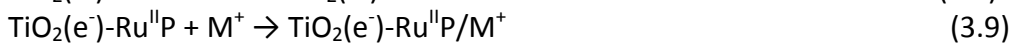
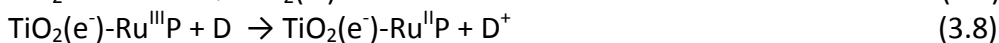


Figure 3.10. (A) Spectral change of TiO_2 -RuP in electrolyte with/without 0.1 M Li^+ (a, red), and after applying a -0.7 V bias vs. NHE to the electrode for ~30 s ((b, blue); (B) Change in molar absorptivity of TiO_2 -RuP at (482 ± 2) nm immersed in solutions with different concentrations of proton or Li^+ : (a) proton in aqueous solution; (b) Li^+ in aqueous solution; (c) Li^+ in propylene carbonate (PC) with 5% water; (d) Li^+ in PC. The solid curves are fit from Langmuir isotherm equation

In DSPECs for hydrogen production, sacrificial electron donors, such as EDTA were used to regenerate $\text{Ru}^{\text{III}}\text{P}$ after electron injection. The reactions at the photoanode are summarized in eqn (3.7)–(3.10), where M^+ is the cation in the electrolyte and D is the electron donor. Eq (3.9) and (3.10) demonstrate the charge compensation at TiO_2 surface, i.e., cation intercalation/re-release, *coupled* to electron injection, recombination and transport at the interfaces.



The cation intercalation, triggered by electron injection was confirmed by spectral change of **TiO₂-RuP** photoanode (consistent with Figure 3.1 A, a), in DSPEC under both open circuit condition, where injected electrons accumulated in TiO₂ conduction band/trap states(Figure 3.11), and with applied bias to extract electrons to external circuit (Figure 3.12). In addition, upon electron recombination, the intercalated Li⁺ diffuse back to electrolyte bulk. The apparent rate for intercalation was much faster than re-release under the DSPEC operating condition, with both rate constants strongly solvents dependent (water >propylene carbonate–water mixture > propylene carbonate (**Table 3.2**).

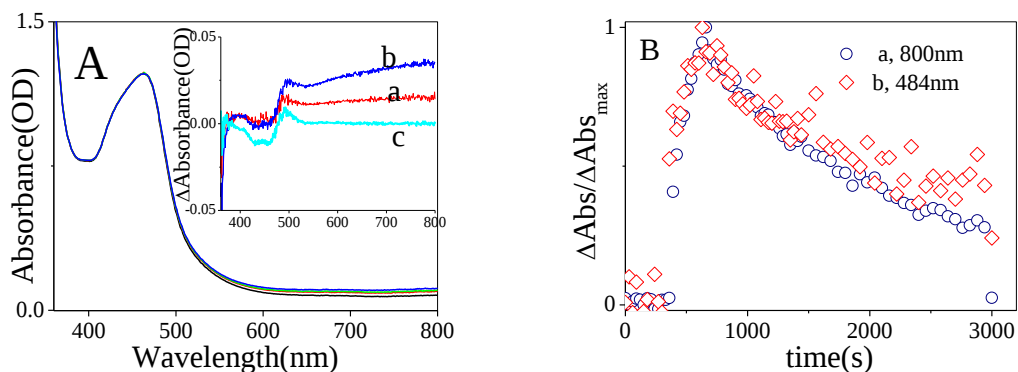


Figure 3.11. (A) Absorbance changes for **TiO₂-RuP** in a DSPEC under open circuit conditions. The electrolyte was 0.2 M LiClO₄ with 20 mM added EDTA⁴⁻ at pH 4.5. light source was 445 nm LED (7.2 mW). Insert: Absorbance difference spectra relative to initial spectrum following (a) 30 s, (b) 280 s photolysis periods and (c) after complete discharge of the original electrode. (B) The ratio of the absorption change to the maximum absorption changes at (a) 800 nm and (b) 489 nm extracted from the data in panel A.

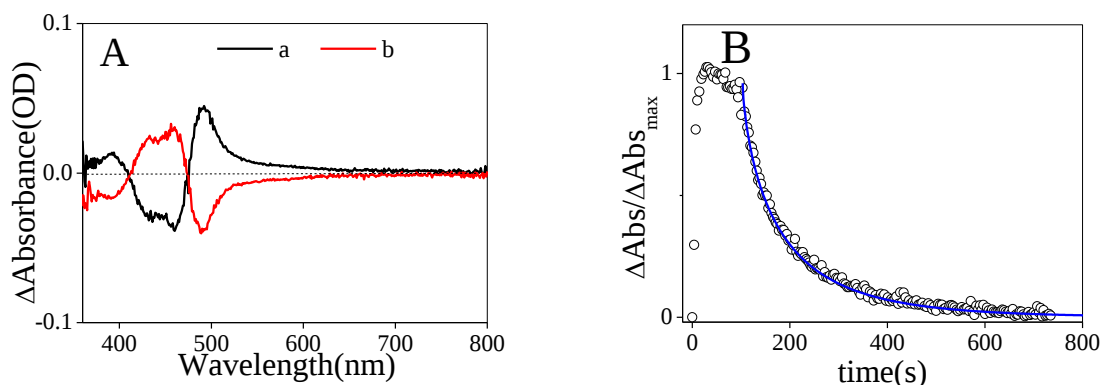


Figure 3.12. (A) Absorbance spectral changes for TiO₂-RuP in a DSPEC with 0.2 V applied bias vs. NHE: (a, black) difference between 120 s irradiation and before irradiation; (b, red) difference between 300 s and 10 s after the light was switched off. Light intensity at 445 nm was 7.2 mW. (B) Absorption-time change monitored at 489 nm under the same conditions as (A). The solid blue line on top is the stretched exponential fit to the decay data.

Table 3.2. Dynamics of Li⁺ intercalation and release.

Electrolyte	Donor	$t_{1/2}$ for intercalation (sec)	$t_{1/2}$ for release(sec)
Water, pH 4.5	EDTA	5.5	50
PC	4-methoxythioanisole	71	>5000
PC/5% water	4-methoxythioanisole	70	1740

Our results clearly show that lithium diffusion back dynamics are much slower than electron transport/recombination. The difference in intercalation/release dynamics resulted Li⁺ enrichment or doping in TiO₂ during DSPEC operation. This was supported by the change in the positive shift of TiO₂ conduction band/trap states, as shown in the cyclic voltammetry of TiO₂-RuP (**Figure 3.13**, a positive shift in the onset of the capacitive potential), as well as the increase in TiO₂ electron lifetime. Our results provided a mechanistic insight of the change in DSSC or DSPEC efficiency during long term operation which was observed in other research groups. The photodriven cation doping provides an alternative means for controlling DSPEC efficiencies.

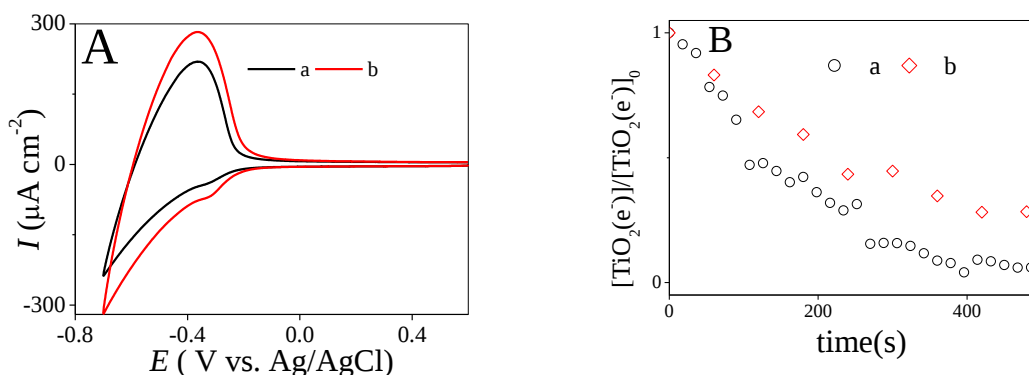


Figure 3.13. (A) Cyclic voltammograms of $\text{TiO}_2\text{-RuP}$ (a) before and (b) after photolysis at open circuit for 30 min (445 nm, 7.2 mW) (B) $\text{TiO}_2(e^-)$ density change with time in the dark after 300 s photolysis at open circuit: (a) 1st run (b) 5th run. The electrolyte was 0.2 M LiClO_4 with 20 mM EDTA, pH 4.5. Scan rate: 0.1 V s^{-1}

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4. Layer-by-Layer Synthesis of a Porphyrin and Ru(II) Water Oxidation Catalyst Assembly on Nanostructured Metal Oxides

Dye-sensitized solar cells (DSSC) and photoelectrosynthesis cells (DSPEC) provide viable strategies for solar-to-electricity or fuel using sunlight. In both a key is excitation and injection by surface-bound chromophores or chromophore-catalyst assemblies on nanostructured metal oxide surfaces. Organic chromophores are desirable in such applications given their potentially low cost, high light absorptivity, and ability to be modified systematically by chemical synthesis. Porphyrins with high light absorptivities in the visible are an advantageous choice in terms of

spectral coverage and energetic. Although reasonably large numbers of porphyrin have been studied for DSSC applications, there are few examples for DSPEC application.

In this report we describe the synthesis of an electron deficient porphyrin with phosphonate anchors and construction of chromophore-catalyst bilayer assemblies on nanostructured metal oxides by a layer-by-layer approach pioneered earlier for polypyridyl complexes of Ru. Relevant structures are shown in Figure 4.1. The free base porphyrin shown has two *meso* positions substituted with pentafluorophenyl and the other two *meso* positions are substituted with 4-phosphonated phenyl for surface binding and assembly formation. It was synthesized from 5-pentafluorophenyldipyrromethane and 4-(diethoxyphosphoryl)benzaldehyde by acid catalyzed condensation reaction. Metallation was carried out by treating the free base porphyrin with zinc(II) acetate.

Porphyrin-loaded nano-crystalline TiO₂ films were prepared by dipping ~70 nm thick nano-crystalline TiO₂ films in a 1.2 mM solution of hydrolyzed porphyrin **1** or **3** in 1:1 CH₂Cl₂/MeOH mixture. Adsorption of the porphyrin to the slide was monitored over time with surface saturation reached in ~2 h. From the adsorption isotherm, a maximum surface coverage of 6.3×10^{-8} mole.cm⁻² which is comparable to Ru-bipyridyl based chromophores.

Excited state energetics were estimated from solution phase electrochemistry and emission measurement. A simplified energy diagram is given in Figure 4.2. Emission quenching of both the free base and Zn-porphyrin derivatives bound to *nano*-TiO₂ was investigated in parallel with the porphyrin surface-bound in ZrO₂ films. A significant amount (~80%) of emission quenching is observed for the Zn-porphyrin bound to TiO₂ compared to ZrO₂ (Figure 4.3). However, almost no emission quenching was observed for free base porphyrin due to a lower excited state potential (-0.34 V vs NHE) of free base porphyrin than that of Zn porphyrin (-0.7 V vs NHE). However, on SnO₂ emission quenching is observed for both free base as well Zn-porphyrin (Figure 4.3).

A chromophore-catalyst assembly was prepared by previously demonstrated methods published from our group. In these experiments, TiO₂ slides were dipped in solutions of **1** (1.2 mM in MeOH), ZrOCl₂ (5mM in 0.1 M HClO₄) and **2** (350 μM in MeOH) successively for 4 h in each solution. Formation of assemblies was monitored by measuring absorption spectra of the slides (Figure 4.4). To check if the porphyrin formed a compact monolayer, a porphyrin-loaded TiO₂ slide was dipped in a solution of **2** and the change in absorption was observed within a 30 min time period. Absorption measurements on the resulting slides were consistent with co-deposition of **2** on surface-bound **1** but the extent of loading was small, not exceeding ~15% of the porphyrin loading as determined from absorption measurement and the increase in absorbance at 500 nm, a λ_{max} for the Ru(II) complex. The origin of the increased absorbance appears to be due to co-deposition of the Ru(II) catalyst directly on the electrode surface by surface phosphonate binding. Over extended periods, the extent of Ru(II) loading was observed to increase with concomitant decrease in porphyrin absorbance and the porphyrin was displaced from the surface.

By contrast, after dipping the porphyrin loaded slide in a ZrOCl₂-containing solution followed by the catalyst, a substantial change in absorption occurred consistent with formation of a -porphyrin-Zr-Ru(II) layer-by-layer structure. The absorbance at 500 nm was nearly

doubled after Zr(IV) treatment (Figure 4.4). Since both the porphyrin chromophore and the Ru(II) catalyst have comparable molar extinction coefficients from 450-700 nm, the absorbance doubling indicates formation of a 1:1 chromophore-catalyst assembly. Bilayer films of porphyrin and Ru(II) catalyst were similarly formed on nanocrystalline SnO₂ films with the absorbance behavior matched closely with that on TiO₂.

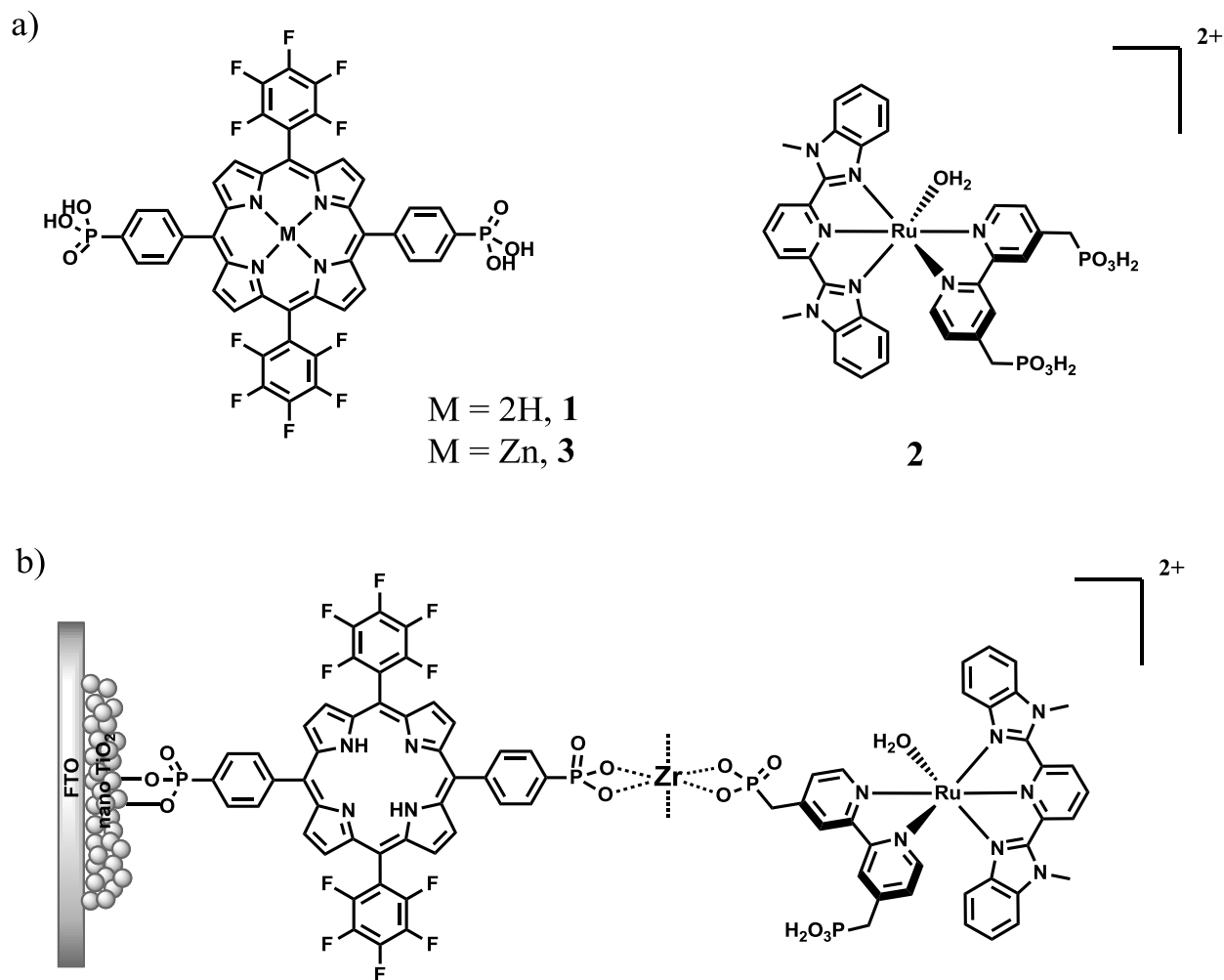


Figure 4.1. a) Porphyrin chromophores studied in this work and the appended water oxidation catalyst. b) Schematic representation of the bilayer chromophore-catalyst assembly

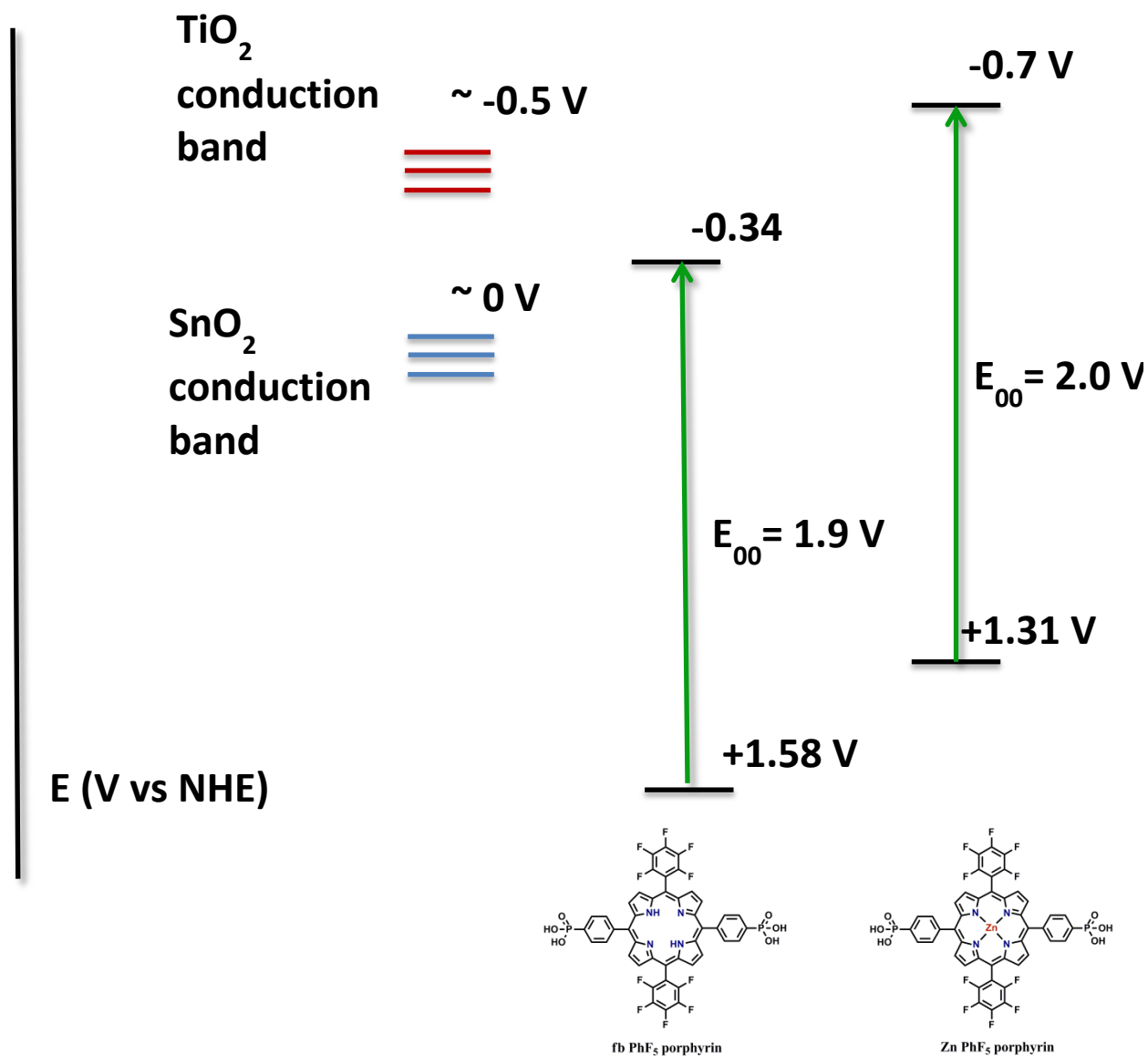


Figure 4.2 Redox potential level diagrams for the phosphonate derivatized porphyrins showing excited states suitable for injection into SnO₂ metal oxides.

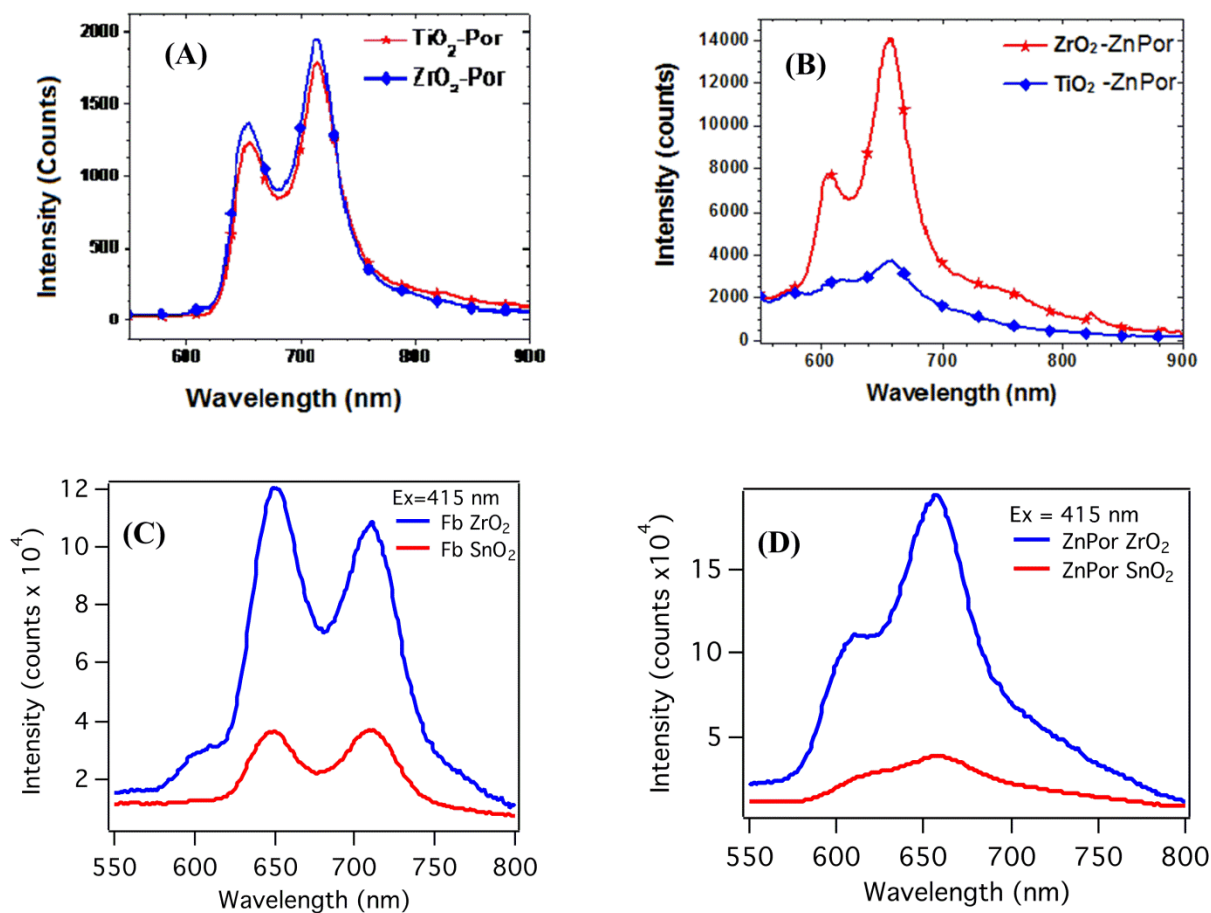


Figure 4.3 Emission quenching of porphyrin on metal oxides compared to ZrO₂. (A) free base porphyrin on TiO₂, (B) Zn(II)-porphyrin on TiO₂, (C) free base porphyrin on SnO₂ and (D) Zn(II)-porphyrin on SnO₂.

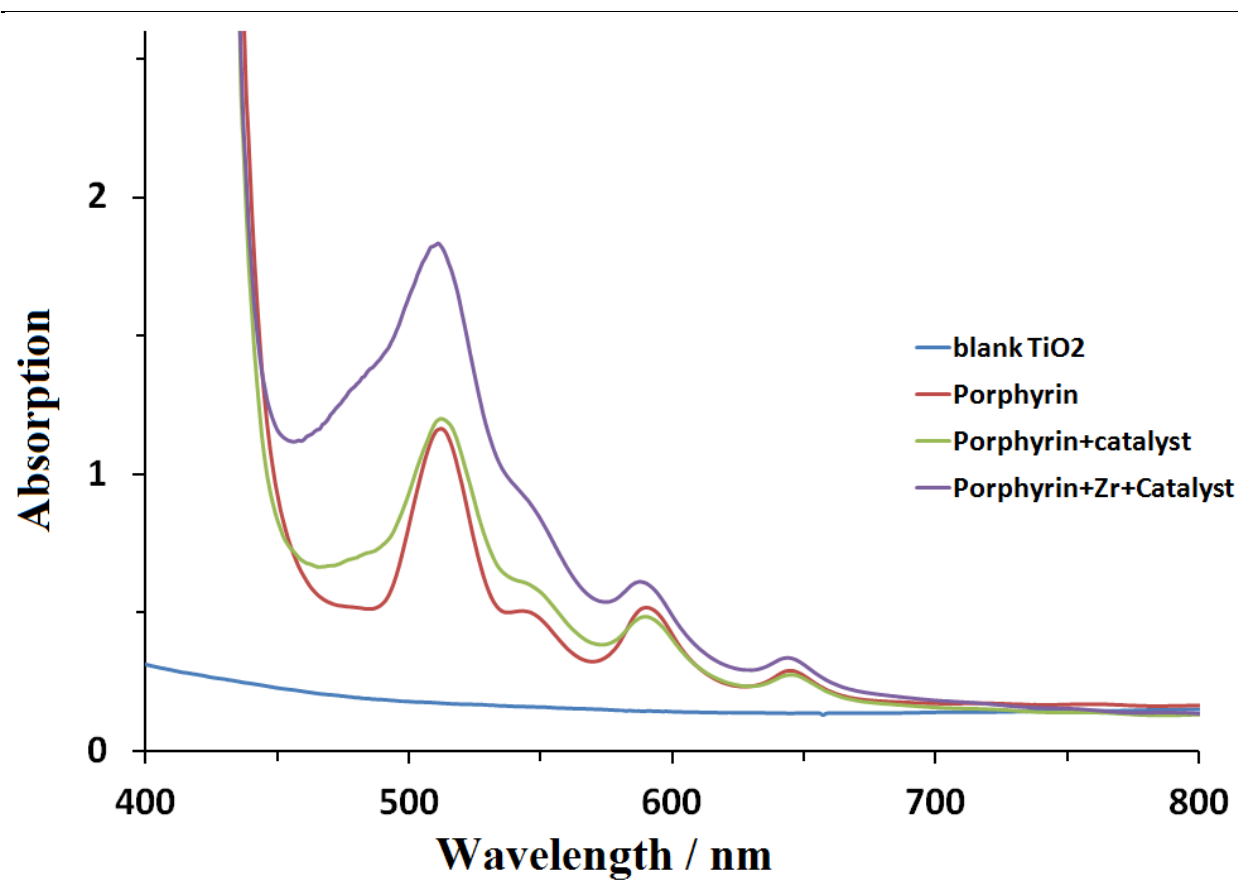


Figure 4.4. Absorption of bilayer assembly
