Catalyzed Water Oxidation by Solar Irradiation of Band-Gap-Narrowed Semiconductors

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Objectives

- **Learn to design improved band-gap-narrowed semiconductors:** Design and characterize BGNSCs that are stable toward photo-oxidation, yet efficiently absorb a large fraction of solar radiation and with bands positioned to generate sufficiently energetic electrons and holes to drive H_2 and O_2 production reactions.
- **Elucidate homogeneous water oxidation catalysis pathways:** Understand and improve homogeneous water oxidation catalysis, where defined structure and mechanistic studies can give deep insight the $4e^-$ water-oxidation pathways
- **Understand interface-bound water oxidation catalysts:** Elucidate the factors controlling kinetics and efficiency of interface-bound catalysts through study of immobilized molecular catalysts and nanostructured inorganic catalysts.
- **Develop insight on water interactions and reactivity at band-gap-narrowed semiconductors:** Understand water interactions and reactivity at BGNSC interfaces and differences from wide band-gap semiconductors. Characterize photocatalysis of water at BGNSC interfaces with and without attached water oxidation catalysts.

Technical Barriers

- We need to design and characterize stable, low-cost and light absorbing materials as photoanodes for solar-driven water splitting
- There are no thermodynamically efficient and kinetically robust interface-bound oxidation catalysts that can facilitate charge transfer of holes from the semiconductor and catalyze water oxidation.
- The breakthroughs in overall device efficiency needed to support a hydrogen economy require integrated expertise in the co-dependent areas of semiconductor and catalyst development.

Abstract

We are attacking four major issues hindering progress in solar-driven water splitting using an integrated experimental and theoretical approach that offers fundamental insights into the underlying photoelectrolysis processes occurring in band-gap-narrowed semiconductor and catalyst components. First, we are tuning known photostable semiconductors to control their light-harvesting and charge-separation abilities in order to achieve a better understanding of their structural and electronic properties, and, in addition, design and characterize new classes of visible-light photoactive semiconductors. Second, we are developing viable catalysts for the difficult four-electron water oxidation process by exploring the catalytic activity and mechanisms of molecular transition-metal complexes. Third, we have begun immobilizing molecular catalysts and (non-precious) metal oxide catalysts on electrodes and/or metal-oxide nanoparticles in order to determine the kinetics of electrochemical water oxidation in the absence of mass transport limitations, and identify the intermediates by spectroscopic techniques. Finally, we plan to explore the interfacial water-decomposition reactions that occur at bare and catalyst-functionalized semiconductor surfaces using carriers generated by visible-light irradiation with the goal of understanding semiconductor–catalyst–water charge transport.

Progress Report

The combined experimental and theoretical research in our second funding period has resulted in a number of advances in the following areas. We investigated: (1) the properties of solid solutions of GaN/ZnO; (2) preparation and characterization of epitaxial $LaTiO_2N$ electrodes; (3) a number of new pyrochlore and pyrochlore-related semiconductors such as $AgBiNb_2O_7$ with strong visible light absorption (E_g ~ 2.7 eV) and band edges appropriately positioned for overall water splitting; (4) the detailed mechanism for water oxidation by the so-called "Tanaka catalyst," $[(Ru^{II})_2(OH)_2(Q)_2(btpyan)]^{2+}$ (Q = 3,6-di-*tert*-butyl-1,2-benzoquinone; btpyan = 1,8-bis(2,2′:6′,2″-terpyrid-4′-yl)anthracene) (Fig. 1, left) that stands apart from other dinuclear ruthenium catalysts not only in its stability and high turnover number but in the respect that it functions in an entirely different manner involving its redox-active quinonoid ligands; and (5) characterization of intermediates

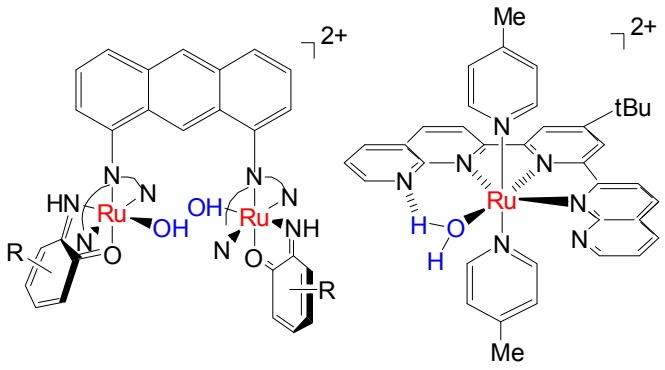

FIGURE 1. Structures of $[(Ru^{II})_2(OH)_2(Q)_2(btpyan)]^{2+}$ (left) and $[Ru(OH_2)(NPM)(pic)_2]^{2+}$ (right).

of Thummel's mononuclear water oxidation catalyst $[Ru(OH_2)(NPM)(pic)_2]^{2+}$ (NPM = 4-t-butyl-2,6-di-1′,8′-(naphthyrid-2′-yl)-pyridine, pic = 4-picoline) (Fig. 1, right). Furthermore, we demonstrated that the Co metal hydrous oxide can be immobilized on a suspension of TiO_2 or SiO_2 nanoparticles in basic aqueous solution, and that it is a very effective catalyst for water oxidation. Here we present some of our studies.

1. Photocatalytic Water Oxidation at the GaN (10$\bar{1}$0) – Water Interface. We constructed an atomistic model and proposed a sequence of intermediate steps for water oxidation at a pure GaN(10$\underline{1}$0)/water interface. Ab initio molecular dynamics simulations examined the fully solvated aqueous interface at ambient temperature. An appropriate cluster model, that includes a polarizable continuum in addition to explicit solvent water molecules, was cut out from snapshots of these AIMD simulations for additional DFT-based calculations of the water oxidation mechanism. The reaction intermediates follow a sequence of four proton-coupled electron transfers. Four UV photons are consumed to generate the four photo-holes which drive the oxidation, producing $4H^+ + O_2$ from $2H_2O$. Calculated standard free energies show that the photogenerated holes in GaN have sufficient energy to drive the overall water oxidation reaction. Implications for the operation of GaN/ZnO alloy photocatalysts, which absorb in the visible wavelength range, are presented. The calculated potentials show a remarkable parallelism to the known potentials for the sequential one-electron oxidation of water in homogeneous aqueous solution, suggesting that the proposed sequence may apply more generally than for the specific GaN (10$\underline{1}$0) surface catalyst.

2. Phase Diagram, Structure and Electronic Properties of $(Ga_{1-x}Znx)(N1-xOx)$ from DFT-Based Simulations. We constructed an accurate cluster expansion (CE) for the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution based on density functional theory (DFT). A subsequent Monte Carlo simulation revealed a phase diagram which has a wide miscibility gap and an $x = 0.5$ ordered compound. The disordered phase displays strong short range order (SRO) at synthesis temperatures. To study the influences of SRO on the lattice and electronic properties, we conducted DFT calculations on snapshots from the MC simulation. Consistent with previous theoretical and experimental findings, lattice parameters were found to deviate from Vegard's law with small upward bowing. Bond lengths depend strongly on local environment, with a variation much larger than the difference of bond length between ZnO and GaN. The downward band gap bowing deviates from parabolic by having a more rapid onset of bowing at low and high concentrations. An overall bowing parameter of 3.3 eV is predicted from a quadratic fit to the compositional dependence of the calculated band gap. Our results indicate that SRO has significant influence over both structural and electronic properties.

3. Characterization of the Intermediates Involved in Water Oxidation: A detailed characterization of intermediates in water oxidation catalyzed by a mononuclear Ru polypyridyl complex $[\mathbf{Ru}\text{–}OH_2]^{2+}$ (**Ru** = Ru(NPM)$(pic)_2$) (Fig. 1, right) has been carried out using electrochemistry, UV-vis and resonance Raman spectroscopy, pulse radiolysis, stopped flow, and ESI-MS with $H_2{}^{18}O$ labeling experiments, and theoretical calculations. The results reveal a number of intriguing properties of intermediates such as $[\mathbf{Ru}{=}O]^{2+}$ and $[\mathbf{Ru}\text{–}OO]^{2+}$. Two consecutive one-electron steps take place at the potential of the $[\mathbf{Ru}\text{–}OH]^{2+}/[\mathbf{Ru}\text{–}OH_2]^{2+}$ couple, which is higher than the potential of the $[\mathbf{Ru}{=}O]^{2+}/[\mathbf{Ru}\text{–}OH]^{2+}$ couple. While pH-independent oxidation of $[\mathbf{Ru}{=}O]^{2+}$ takes place at 1410 mV vs NHE, bulk electrolysis of $[\mathbf{Ru}\text{–}OH_2]^{2+}$ at 1260 mV vs NHE at pH 1 (0.1 M triflic acid) and 1150 mV at pH 6 (10 mM sodium phosphate) yielded a red colored solution with a Coulomb count corresponding to the *net four-electron oxidation*. ESI-MS with labeling experiments clearly indicate that this species has an O–O bond. This species required an additional oxidation to liberate an oxygen molecule, and without any additional oxidant it slowly decomposed to form $[\mathbf{Ru}\text{–}OOH]^{+}$ in 2 weeks. We have assigned this species as $^1[\mathbf{Ru}\text{–}\eta^2\text{-}OO]^{2+}$ based on our electrochemical, spectroscopic, and theoretical data alongside a previously published conclusion by T. J. Meyer's group (*J. Am. Chem. Soc.* **2010**, *132*, 1545-1557).

Future Directions

Our ***four-part plan*** for developing functional photocatalytic systems builds upon the advances we have made in water oxidation catalysis and the elucidation of the properties of appropriate band-gap-narrowed semiconductors for use as photoanodes. First, we will work towards identifying new and promising semiconductors to serve as photoanodes in our mechanistic water oxidation studies. This will involve not only tuning their band gaps and absolute band edge energies, but also consideration of their suitability for use in well-defined interfacial mechanistic studies (*e.g.*, single crystals vs. films of powders). Second, we will develop improved transition-metal based

molecular catalysts for mechanistic investigation of water oxidation. Third, we will compare their electrochemical water-oxidation activity when immobilized on conducting electrodes with that in homogeneous aqueous solution. Fourth, we will pursue advances in these areas to uncover the core scientific challenges to the efficient coupling of the catalytic functions at the water interface under irradiation. This will be accomplished through the study of water oxidation at complex aqueous interfaces following the transfer of stored photo-produced electrical energy from a semiconductor through a catalyst into water.

We will also engage in related collaborative research to address the origin of two enhancement effects (*i.e.*, Cs ion pretreatment of semiconductors and the addition of carbonate ion) on efficient solar water splitting, originally discovered by K. Sayama's group (AIST). Using funds from METI, Japan *via* a program called U.S.-Japan Cooperation on Clean Energy Technologies, the AIST researchers will be able to stay at BNL for an extended period to carry out that related proposed work.

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