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Band-Gap-Narrowed Semiconductors (Part 1.  
Overview)***

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# Catalyzed Water Oxidation by Solar Irradiation of Band-Gap-Narrowed Semiconductors (Part 1. Overview)

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## Objectives

- *Investigate the catalysis of water oxidation by cobalt and manganese hydrous oxides immobilized on titania or silica nanoparticles, and dinuclear metal complexes with quinonoid ligands in order to develop a better understanding of the critical water oxidation chemistry, and rationally search for improved catalysts.*
- *Optimize the light-harvesting and charge-separation abilities of stable semiconductors including both a focused effort to improve the best existing materials by investigating their structural and electronic properties using a full suite of characterization tools, and a parallel effort to discover and characterize new materials.*
- *Combine these elements to examine the function of oxidation catalysts on Band-Gap-Narrowed Semiconductor (BGNSC) surfaces and elucidate the core scientific challenges to the efficient coupling of the materials functions.*

## Technical Barriers

- *While there are a few reports, that have not yet been independently confirmed, on efficient BGNSCs for solar-driven water splitting, we need to design and characterize stable, low-cost and efficient light absorbing materials as photoanodes.*
- *There are no thermodynamically efficient and kinetically robust interface-bound oxidation catalysts that can facilitate efficient charge transfer of holes from the semiconductor and catalyze water oxidation at the modest potentials associated with efficient utilization of solar radiation.*
- *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 continue to attack the three major barriers hindering the realization of high-efficiency devices for 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 developing viable catalysts for the difficult four-electron water oxidation process by exploring the catalytic activity and mechanisms of two promising systems: transition-metal hydrous oxides immobilized on nanoparticle substrates, and dinuclear transition-metal complexes with quinonoid ligands. Second, we are tuning band energies to optimize the light-harvesting and charge-separation abilities of known photostable semiconductors in order to improve the existing materials through

a better understanding of their structural and electronic properties, and in addition, we are characterizing new classes of photoactive semiconductors. Finally, we are exploring the interfacial water-decomposition reactions that occur at bare and catalyst-functionalized semiconductor surfaces using carriers generated by dark- and photo-currents with the goal of maximizing semiconductor  $\rightarrow$  catalyst  $\rightarrow$  substrate charge transport.

## Progress Report

Our research has resulted in a number of advances in both immobilized and homogeneous water oxidation catalysis. In the area of BGNSC materials, we made a considerable contribution to understanding the nature of N-doped TiO<sub>2</sub>. However, our experimental and theoretical studies, as well as results elsewhere, have cast doubt on whether such a material can be made controllably and reproducibly by anion substitution with N concentrations above a few percent. Therefore, we have strategically redirected our efforts towards other very promising materials,<sup>1</sup> solid solutions of GaN/ZnO.

### 1. Water Oxidation Catalysis: Mechanism and Development.

**1.1. Immobilized Transition-Metal Hydrous Oxides.** A highly selective, non-noble metal catalyst for water oxidation has been developed based on Co hydrous oxide immobilized on titania nanoparticles. With Ru(bpy)<sub>3</sub><sup>3+</sup> as a one-electron oxidant, stoichiometric oxygen evolution is obtained at Co concentrations as low as 5 μM, indicating the very efficient catalysis of water oxidation and no Co oxidation states in excess of 1.3 V during the catalytic cycle. Co K-edge EXAFS analysis shows formation of clusters (Co–Co, 2.79 Å), suggesting a possibility for participation of binuclear Co structures in water oxidation. A 100% O<sub>2</sub> yield has allowed overall reaction rate measurements from the oxidant consumption. The rates are proportional to concentrations of both the catalyst and the oxidant and increase exponentially with pH, indicating that the rate-limiting step is one of the catalyst oxidation steps (not the steps of O<sub>2</sub> formation or release) that also requires either proton removal or hydroxide addition. The Co atom turnover frequencies calculated from initial reaction rates exceed 50 s<sup>-1</sup>. Adsorption of Co cations on silica nanoparticles also produces an efficient catalyst. When the Ru(bpy)<sub>3</sub><sup>3+</sup> oxidant is generated photochemically using a flash photolysis system equipped for O<sub>2</sub> detection, water oxidation is observed in parallel with the oxidant decay (Fig. 1). Notably, the oxidant consumption occurs on a time scale similar to that for oxygen production by the TiO<sub>2</sub>-supported catalyst with remarkable catalyst stability. (*SL with Shafirovich*)

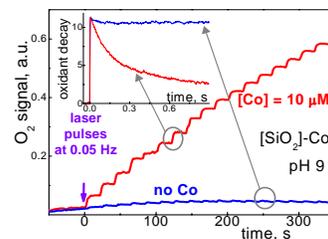


Fig. 1. O<sub>2</sub> generation by a photo-produced oxidant

**1.2. Dinuclear Ru Molecular Catalysts with Quinonoid Ligands.** The Tanaka catalyst [Ru<sub>2</sub>(OH)<sub>2</sub>(Q)<sub>2</sub>(btpyan)]<sup>2+</sup> (Fig. 2, R = *t*Bu), that contains redox active quinonoid ligands, has an excellent electrocatalytic activity for water oxidation (TN ≈ 30,000 per catalyst molecule in 40 hr) when immobilized on an indium-tin-oxide (ITO) electrode. Our experimental and theoretical investigation of this catalyst shows the striking features that it seems to maintain predominantly Ru(II) centers while the quinone ligands and water moieties are involved in redox reactions throughout the entire catalytic cycle for water oxidation. Our gas-phase theoretical study identifies triplet [Ru<sub>2</sub>(O<sub>2</sub><sup>-</sup>)(Q<sup>-1.5</sup>)<sub>2</sub>(btpyan)]<sup>0</sup> as a key intermediate that is formed by removal of all four protons before four-electron oxidation takes place. A proposed catalytic pathway for water oxidation is shown in Fig. 3. This is an entirely different mechanism than those proposed for extensively investigated μ-oxo ruthenium dinuclear complexes, or any other known water oxidation catalysts, in which higher oxidation states such as Ru(V) or Mn(IV) were considered to be essential. (*EF, JTM with Tanaka, Polyansky*)

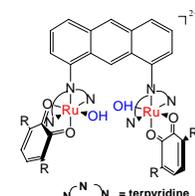


Fig 2. Structure of [Ru<sub>2</sub>(OH)<sub>2</sub>(Q)<sub>2</sub>(btpyan)]<sup>2+</sup>

## 2. Design and Characterization of BGNSCs for Solar Water Splitting

**2.1. N-Doped Titania.** The electronic and structural properties of N-doped rutile TiO<sub>2</sub>(110) and the powders prepared by dry or sol-gel methods were investigated together with DFT calculations. Our attempts showed no clear evidence of enhanced photoactivity for O<sub>2</sub> production. (JR, EF)

**2.2. GaN/ZnO Solid Solutions.** Because of the low N-substitution level and the lack of photocatalytic activity toward water oxidation in our N-doped TiO<sub>2</sub>, we changed our focus toward an oxynitride species with more promising photocatalytic activity, GaN/ZnO.<sup>1</sup> The lattice constants, band gap, and the overall activity of this photocatalyst for water splitting have been shown to depend strongly on the zinc concentration, *x*. We therefore initiated coordinated experimental and theoretical studies of (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>). The detailed results are shown in our other report entitled “Catalyzed Water Oxidation by Solar Irradiation of Band-Gap-Narrowed Semiconductors (Part 2. Some Details).” (JAR, EF, JTM, with Newton)

### Future Directions

**1. Immobilized Transition-Metal Hydrous Oxides.** During the previous project period we have introduced novel, efficient water oxidation catalysts based on cobalt hydrous oxide. Here, we propose research toward: (a) optimization of the Co-based catalysts, especially with respect to their stability, (b) extending studies to include Mn, which is of special interest because of its role in Photosystem II and our previous results on water oxidation catalysis by organic matrix-stabilized Mn hydrous oxide, and (c) mechanistic understanding.

**2. Dinuclear Ru Molecular Catalysts with Quinonoid Ligands.** Our experimental and theoretical studies have demonstrated that the catalytic activity is controlled by a delicate balance in the charge distribution over the Q–Ru–OH framework and the design of improved catalysts that work without large overpotentials is possible through the fine tuning of electronic properties of the quinonoid ligands. We propose to prepare dinuclear Ru complexes with 2-aminophenol and its analogues (with *t*Bu, Cl, NO<sub>2</sub>, etc.), which can also be designated as *o*-iminobenzo-quinone, -semiquinone, and -catecholate, and investigate their catalytic properties.

**3. Design and Characterization of BGNSCs for Solar Water Splitting.** We will prepare and characterize properties of oxychlorides, oxysulfides, oxynitrides, split-band transition metal oxides, and mixed-metal semiconductors with *d*<sup>0</sup> and *d*<sup>10</sup> elements. The cornerstone of this effort will be measuring the absolute band energies of the synthesized materials.

**4. Behavior of BGNSC Crystals and Films at the Liquid Water Interface.** We will also investigate the behavior at the liquid water interface using ATR-FTIR and *in situ* STM as a function of pH, ionic strength and applied potential. Our aim is to elucidate the details of how the oxygen formation occurs.

**5. Water Oxidation by Electrodes Chemically Modified with Dinuclear Ru Catalysts.** We plan to prepare chemically modified metal-oxide electrodes with the dinuclear Ru complex attached

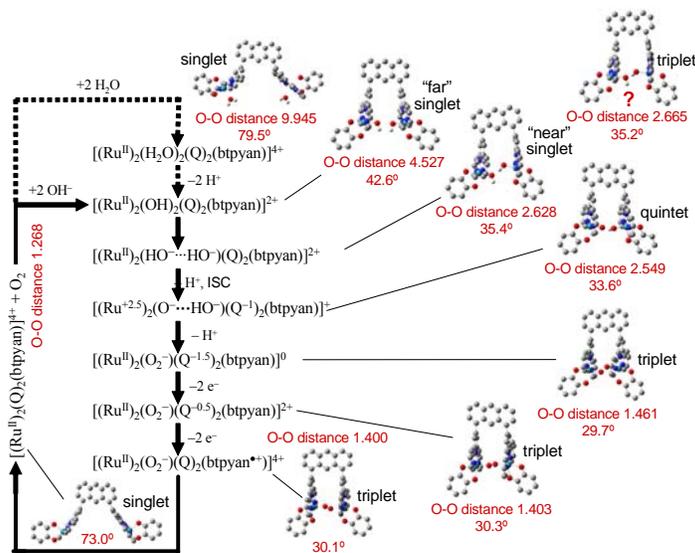


Fig. 3. Proposed catalytic pathway for H<sub>2</sub>O oxidation by [Ru<sub>2</sub>(OH)<sub>2</sub>(Q)<sub>2</sub>(btpyan)]<sup>2+</sup> showing calculated structures. Listed for each species is the calculated O-O distance and the Ru-C-Ru angle, where the carbon atom is at the top center of the anthracene moiety.

through a phosphonate (or carboxylate) group on the anthracene moiety of the btpyan ligand, to carry out a detailed kinetic and mechanistic investigation including the O–O bond formation step using spectroscopic techniques.

6. *Irradiation of MHO-Attached BGNCS Films with Visible Light*. We will address very important questions regarding the more ill-defined, yet possibly more practical, MHO-attached BGNCS systems: Can photogenerated holes of BGNCSs oxidize these attached catalysts and subsequently produce O<sub>2</sub> from water upon visible irradiation? To this end, we will assemble three types of electrodes: (i) MHOs immobilized on thin films of TiO<sub>2</sub> attached to optically transparent ITO electrodes; (ii) thin films of BGNCSs supported on ITO electrodes; and (iii) MHO immobilized on thin films of BGNCSs supported on ITO electrodes. The electrochemical characterization of assemblies will be tested with and without irradiation of visible light while immersed in aqueous solutions.

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