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# *Toward Photochemical Water Splitting Using Band-Gap-Narrowed Semiconductors and Transition-Metal Based Molecular Catalysts*

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# TOWARD PHOTOCHEMICAL WATER SPLITTING USING BAND-GAP-NARROWED SEMICONDUCTORS AND TRANSITION-METAL BASED MOLECULAR CATALYSTS

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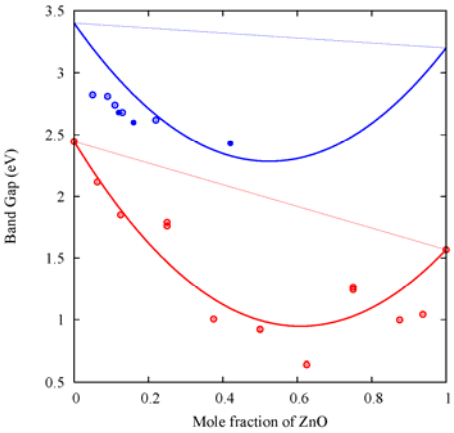
We are carrying out coordinated theoretical and experimental studies of toward photochemical water splitting using band-gap-narrowed semiconductors (BGNSCs) with attached multi-electron molecular water oxidation and hydrogen production catalysts. We focus on the coupling between the materials properties and the $H_2O$ redox chemistry, with an emphasis on attaining a fundamental understanding of the individual elementary steps in the following four processes:

(1) Light-harvesting and charge-separation of stable oxide or oxide-derived semiconductors for solar-driven water splitting, including the discovery and characterization of the behavior of such materials at the aqueous interface;
(2) The catalysis of the four-electron water oxidation by dinuclear hydroxo transition-metal complexes with quinonoid ligands, and the rational search for improved catalysts;
(3) Transfer of the design principles learned from the elucidation of the DuBois-type hydrogenase model catalysts in acetonitrile to the rational design of two-electron hydrogen production catalysts for aqueous solution;
(4) Combining these three elements to examine the function of oxidation catalysts on BGNSC photoanode surfaces and hydrogen production catalysts on cathode surfaces at the aqueous interface to understand the challenges to the efficient coupling of the materials functions.

**1. Elucidation and Characterization of the Structure, Band Gap and Interfacial Properties of the GaN/ZnO Solid-Solution Photocatalyst.** Domen *et al*. reported encouraging photocatalytic performance for the solid-sollution photocatalyst $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with mixed oxides of rhodium and chromium in overall water splitting. Perhaps most impressive was that if silver nitrate was used as a sacrificial electron acceptor, the quantum efficiency for oxygen evolution rose to 51% at 420–440 nm, which is 20 times higher than that for overall water splitting. We have carried out a systematic study of the structural and electronic properties of the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution as a function of zinc (oxygen) concentration, $x$, using density-functional theory (DFT). The DFT+$U$ approach has been adopted, and two different periodic supercells, the 16-atom $(Ga_{8-n}Zn_n)(N_{8-n}O_n)$ and 32-atom $(Ga_{16-n}Zn_n)(N_{16-n}O_n)$, have been used to model this solid solution.

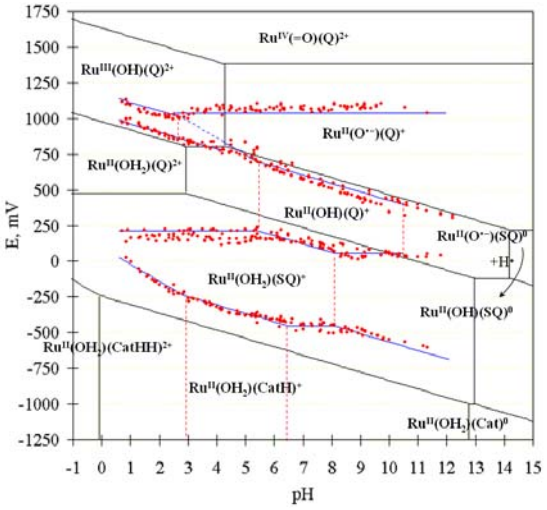



Variation of band gap as a function of Zn (O) concentration, $x$. Red: calculated BGs and smoothed $E_g(x)$ curve using the estimated bowing parameter $b$. Blue: experimental data for $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution and predicted experimental $E_g(x)$ behavior using the estimated $b$ and the limiting GaN and ZnO band gaps.

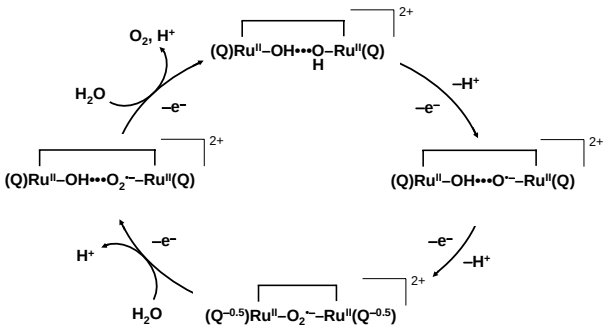
The calculated band gap as a function of ZnO content, $x$, is shown in the figure above as red points along with the red

curve showing the best fit a quadratic equation with a bowing parameter *b* indicating the leading term from ideal behavior. The blue curve shows the interpolation of the experimental band gaps for GaN and ZnO with the calculated value of *b*, and the blue points indicate experimental band gap measurements from Domen's group. Our prediction is that a minimum band gap of ca. 2.4 eV should occur at roughly $x = 0.5$. More recent theoretical work has shown that an $H_2O$ monolayer on the GaN(10$\underline{1}$0) surface dissociates completely, and that additional overlayers or MD simulations of the bulk $H_2O$ interface cause the structure of the surface monolayer to change. Future work will pursue $H_2O$ oxidation pathways at surfaces of GaN/ZnO with different compositon and exposed faces using DFT, first-principles MD and kinetic Monte Carlo techniques. Recent experimental work has elucidated the mechanism of GaN/ZnO synthesis from $Ga_2O_3$/ZnO mixtures and $NH_3$ using time-dependent powder XRD, and current work is exploring synthesis routes for producing GaN/ZnO solid solutions of arbitrary composition.

**2. Characterization of the electrochemistry of $Ru^{II}(OH_2)(Q)(tpy)$, the Tanaka catalyst and its monomer through construction of experimental and theoretical Pourbaix diagrams.** We have investigated the redox states of $Ru(OH_2)(Q)(tpy)^{2+}$ (Q = 3,5-di-*tert*-butyl-1,2-benzoquinone, tpy = 2,2′:6′,2″-terpyridine), the monomer of the Tanaka catalyst, $[Ru_2(OH)_2(Q)_2(btpyan)]^{2+}$ (Q = 3,6-di-*tert*-butyl-1,2-benzoquinone, btpyan = 1,8-bis(2,2′:6′,2″-terpyrid-4′-yl)-anthracene), containing non-innocent quinone ligands, through experimental and theoretical UV-vis spectra and Pourbaix diagrams. The electrochemical properties were determined for the species resulting from deprotonation and redox processes in aqueous solution. The formal oxidation states of the redox couples in the various intermediate complexes were systematically assigned using electronic structure theory. The various p$K_a$ values and reduction potentials, including the consideration of proton-coupled electron-transfer (PCET) processes, were calculated, and the theoretical version of the Pourbaix diagram was constructed in order to elucidate and assign several previously ambiguous regions in the experimental diagram (see figure above). Guided by the redox behavior of the monomer, we are constructing the Pourbaix of the dimer catalyst to aid the design of improved catalysts, and have tentatively proposed its water oxidation mechanism to be that shown in the figure at the right in which the oxidation state of the metal centers remains predominantly 2+ throughout the catalytic cycle. The O–O bond is formed by the reaction of two oxyl radicals to form a superoxide species.




An experimental and theoretical Pourbaix diagram of $Ru(OH_2)(Q)(tpy)^{2+}$. $E_{1/2}$ is relative to the SCE. The red dashed and solid blue lines correspond to the experimental p$K_a$ and redox potentials. The black lines are the theoretical predictions.




Proposed mechanism for water oxidation by the Tanaka catalyst in aqueous solution at pH 4.

**DOE Sponsored Publications: Hydrogen Fuel Initiative 2006-2008**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