

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

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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. In this paper we will discuss design and characterization of BGNSCs for water splitting. Results and discussion on water oxidation catalysts are shown in our other report entitled “Catalyzed Water Oxidation by Solar Irradiation of Band-Gap-Narrowed Semiconductors (Part 1. Overview).”

## Progress Report

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.

## Design and Characterization of BGNSCs for Solar Water Splitting

**1. N-Doped Titania.** The electronic properties of N-doped rutile TiO<sub>2</sub>(110) have been investigated using synchrotron-based photoemission and density-functional (DF) calculations. Doping *via* N<sub>2</sub><sup>+</sup> ion bombardment leads to the implantation of N atoms (~5% saturation concentration) that coexist with O vacancies. The theoretical results are consistent with the existence of attractive interactions between the dopant and O vacancies, which stabilize the N impurities with respect to N<sub>2</sub>(g) formation. Without O vacancies, the amount of N that can be accommodated inside the titania lattice is quite small (< 2%).

The thermal introduction of nitrogen into titania powder (anatase and P25 mixtures) by reaction with ammonia was also investigated by *in situ* and *ex situ* characterizations with XPS, NEXAFS, and XRD. Above 750 °C, *in situ* XRD reaction studies revealed a smooth phase transition from anatase or P25 mixtures to cubic TiN. Incorporation of nitrogen into the interstitial sites of TiO<sub>2</sub> anatase is supported by Rietveld refinement of XRD data. N 1s XPS and N K-edge NEXAFS spectra support the idea that nitrogen present in titania may combine to form N<sub>2</sub> molecules evolving into the gas phase upon heating to elevated temperatures, a behavior that agrees with the results of DFT calculations. Nitrogen embedded in TiO<sub>2</sub> is unstable energetically and spontaneously forms trapped or gaseous N<sub>2</sub>. The N-doped TiO<sub>2</sub> nanoparticles prepared by sol-gel methods under various conditions along with N-doped Degussa P-25 TiO<sub>2</sub> (treated with triethylamine) were characterized by XPS. The observed N/Ti ratio was low (less than 1 %) and no TiN-like N 1s peak at 396 eV was observed in any sample investigated. Our attempts to photooxidize water (using the colloidal or suspended solutions with AgNO<sub>3</sub>) and to measure photocurrents with ITO electrodes coated with films of N-doped TiO<sub>2</sub> (> 400 nm) showed no clear evidence of enhanced photoactivity for O<sub>2</sub> production. (JR, EF)

**2. GaN/ZnO Solid Solutions.** Recently, a solid solution of GaN and ZnO, (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>), has been reported to be a stable photocatalyst that is capable of water splitting under visible light. Using time-resolved *in situ* X-ray diffraction (XRD), we have monitored the formation of (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) during the solid-state reaction of NH<sub>3</sub> with Ga<sub>2</sub>O<sub>3</sub>/ZnO and ZnGa<sub>2</sub>O<sub>4</sub>. Spinel ZnGa<sub>2</sub>O<sub>4</sub> was found to be an intermediate for the formation of wurtzite

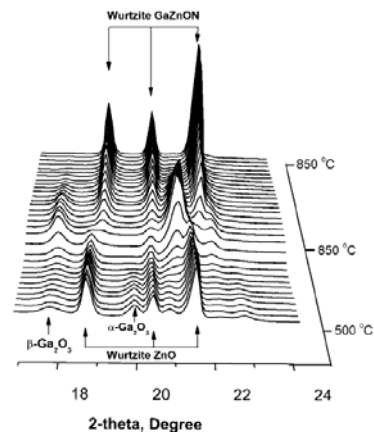


Fig. 1. *In situ* XRD patterns for the nitridation of a 1:1 Ga<sub>2</sub>O<sub>3</sub>/ZnO mixture by 5% NH<sub>3</sub> in He. The Ga<sub>2</sub>O<sub>3</sub> was present in its  $\alpha$  and  $\beta$  phases.

$(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$  and the conversion from  $\text{ZnGa}_2\text{O}_4$  to  $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$  was straightforward (Fig. 1). We have carried out a systematic study of the structural and electronic properties of this  $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$  solid

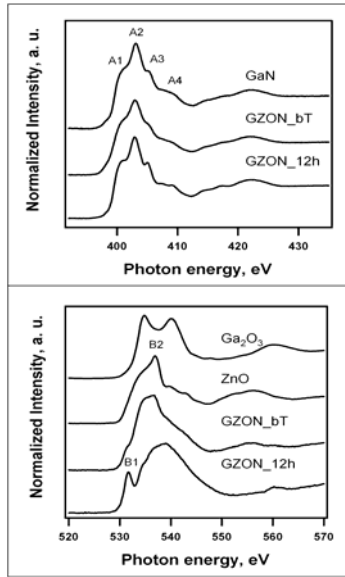


Fig. 3. NEXAFS spectra of the N K-edge (top) and O K-edge (bottom) of wurtzite gallium zinc oxynitride (GZON\_12h), a mixture of wurtzite gallium zinc oxynitride and spinel  $\text{ZnGa}_2\text{O}_4$  (dominant) denoted GZON\_bT, and  $\text{Ga}_2\text{O}_3$  along with GaN and ZnO references. The spectra were collected in partial electron yield mode and an e-gun was used to neutralize the surface charge.

solution as a function of zinc (oxygen) concentration,  $x$ , using density-functional theory (DFT). Downward bowing of the band gap over the entire composition range was observed, and the minimum “experimental” band gap is estimated to be about 2.29 eV for the intermediate  $x = 0.525$  (Fig. 2). X-ray absorption fine structure (XAFS) spectra of the zinc and gallium K-edges revealed that the local structure of the  $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$  is similar to that of GaN and ZnO, respectively, but there is more distortion from GaN when the zinc content is higher and from ZnO when the zinc content is lower. In terms of the inter-atomic distance of the first coordination shell, the  $R_{\text{Zn-O(N)}}$  is longer than the  $R_{\text{Ga-N(O)}}$ , indicating the preferred population of Zn-O(N) along the  $c$ -axis, in agreement with our theoretical calculations. The surface sensitive N K-edge NEXAFS data suggested that the local environment of the nitrogen on the  $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$  surface is the same as that of GaN. However, the oxygen K-edge spectra showed a pre-edge feature related to neither ZnO nor  $\text{Ga}_2\text{O}_3$ , indicating the presence of oxygen-related holes in the photocatalysts (Fig. 3). (JAR, EF, JTM, with Newton)

## Future Directions

1. *Design and Characterization of BGNSCs for Solar Water Splitting.* We will prepare and characterize properties of a wide range of oxychlorides, oxysulfides, oxy-nitrides, split-band transition metal oxides, and mixed-metal semiconductors with  $d^0$  and  $d^{10}$  elements. The cornerstone of this effort will be measuring the absolute band energies of the synthesized materials (See Fig. 4).

2. *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. We will also carry out molecular dynamics (MD) studies of this interface on New York Blue, a 36,864-processor IBM Blue Gene/L supercomputer at BNL. Our aim is to elucidate the details of how the oxygen formation occurs.

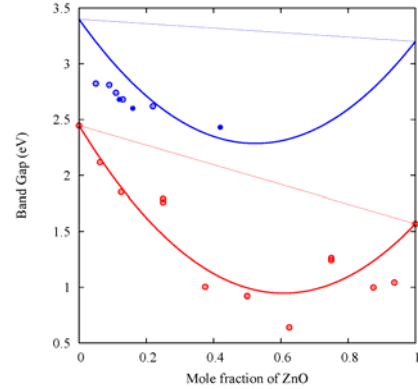


Fig. 2. Variation of band gap as a function of Zn (O) concentration,  $x$ . Red: calculated BGs and smoothed  $E_g(x)$  curve using the estimated bowing parameter  $b$ . Blue: experimental data for  $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$  solid solution and predicted experimental  $E_g(x)$  behavior using the estimated  $b$  and the limiting GaN and ZnO band gaps.

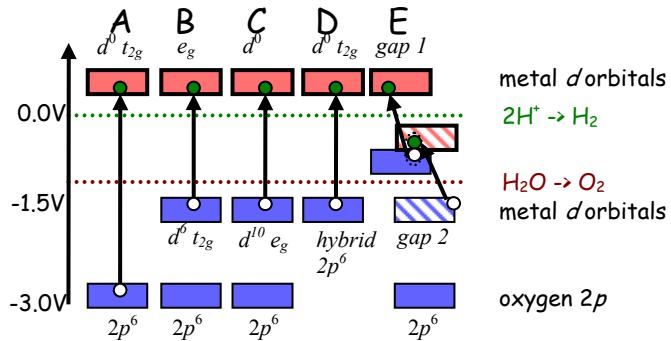


Fig. 4. Schematic conduction band (red) and valence band (blue) energies for (A) Traditional oxide semiconductors such as  $\text{TiO}_2$ . (B) Crystal field or Mott-Hubbard split bands (C) Mixed-metal oxides. (D) Hybrid anion semiconductors (oxychlorides, oxysulfides, oxynitrides). (E) Composite  $n$ - $p$  semiconductors pairs. Labels indicate the orbital origins of the state

2. *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 through a phosphonate (or carboxylate) group on the anthracene moiety of the btpyan ligand, to carry out a detailed kinetic and mechanistic investigation including o-o bond formation step with spectroscopic techniques.

3. *Irradiation of MHO-Attached BGNSC Films with Visible Light*. Three types of electrodes will be assembled: (i) MHOs immobilized on thin films of TiO<sub>2</sub> attached to optically transparent ITO electrodes; (ii) thin films of BGNSCs supported on ITO electrodes; and (iii) MHO immobilized on thin films of BGNSCs supported on ITO electrodes. The electrochemical characterization of assemblies will be tested with and without irradiation of visible light while immersed in aqueous solutions.

## **References**

1. Maeda, K.; Teramura, K.; Lu, D. L.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K., *Nature* **2006**, 440, (7082), 295-295.

## **Publications (including patents) acknowledging the grant or contract**

1. "N Doping of TiO<sub>2</sub>(110): Photoemission and Density-Functional Studies", A. Nambu, J. Graciani, J. A. Rodriguez, Q. Wu, E. Fujita, and J. Fdez Sanz, *J. Chem. Phys.* **125** (2006) 094706-1,8
2. "Anatase-TiO<sub>2</sub> Nanomaterials: Morphological/Size Dependence of the Crystallization and Phase Behavior Phenomena", M. Fernández-García, X. Wang, C. Belver, J. C. Hanson, and J. A. Rodriguez, *J. Phys. Chem. C*, **111** (2007) 674-682.
3. "Reaction of NH<sub>3</sub> with TiO<sub>2</sub>: N-doping and the formation of TiN", H. Chen, A. Nambu, J. Graciani, J. C. Hanson, E. Fujita, and J.A. Rodriguez, *J. Phys. Chem. C*, **111** (2007) 1366-1372.
4. "Interaction of oxygen with TiN(001): N↔O exchange and oxidation process", J. Graciani, J. Fdez. Sanz, T. Asaki, K. Nakamura, and J. A. Rodriguez, *J. Chem. Phys.*, **126** (2007) 244713-1,8
5. "Anatase-TiO<sub>2</sub> Nanomaterials: Analysis of Key Parameters Controlling Crystallization", M. Fernández-García, C. Belver, J. C. Hanson, X. Wang, and J. A. Rodriguez, *J. Am. Chem. Soc.* **129** (2007) 13604-13612.
6. "First-Principles Studies of the Structural and Electronic Properties of the (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) Solid Solution Photocatalyst", L. L. Jensen, J. T. Muckerman, and M. D. Newton, *J. Phys. Chem. C*, **112** (2008) ASAP DOI:10.1021/jp073554y.
7. "Water Oxidation by a Ruthenium Complex with Non-Innocent Quinonoid Ligands: Possible Formation of an O–O Bond at a Low Oxidation State of the Metal", J. T. Muckerman, D. E. Polyansky, T. Wada, K. Tanaka, and E. Fujita, An invited paper for Forum on "Making Oxygen" *Inorg. Chem.*, **47** (2008) 1787-1802.
8. "N Doping of Rutile TiO<sub>2</sub>(110) Surface. A Theoretical DFT Study", J. Graciani, L. J. Alvarez, J. A. Rodriguez, and J. F. Sanz, *J. Phys. Chem. C*, in press.
9. "Catalytic Reactions Using Transition-Metal-Complexes toward Solar Fuel Generation: Personal Views" E. Fujita and J. T. Muckerman, An invited review, *Bull. Jpn. Soc. Coord. Chem.* (2008) submitted.
10. "Preparation of (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) Photocatalysts from the Reaction of NH<sub>3</sub> with Ga<sub>2</sub>O<sub>3</sub>/ZnO and ZnGa<sub>2</sub>O<sub>4</sub>: In situ Time-Resolved XRD and XAFS Studies," H. Chen, W. Wen, Q. Wang, J. C. Hanson, J. T. Muckerman, E. Fujita, A. Frenkel, and J. A. Rodriguez, *J. Phys. Chem. C*, (2008) submitted.