

II.D.1 New Metal Oxides for Efficient Hydrogen Production via Solar Water Splitting

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Overall Objectives

The main objectives for this project have been focused into four specific categories which are designed to adhere to National Science Foundation and DOE's technological pathway to photoelectrochemical (PEC) production of renewable hydrogen fuel as well as disseminate knowledge and awareness of renewable energy principles and research.

- Design new metal oxides with physical, optical, chemical and electronic properties optimized for PEC hydrogen production
- Develop approaches for synthesizing designed metal oxides in bulk and thin film form with appropriate phase and grain/film structure for incorporation into PEC water-splitting devices
- Fabricate cells/systems using new metal oxides and characterize to determine overall PEC performance as well as fundamental junction, interface, and device properties and new metal oxide stability
- Instruction of post-doctoral researchers, graduate, and undergraduate students in principles and techniques relevant to renewable energy research and education/outreach activities for K-12 students and the general public regarding renewable energy awareness

Fiscal Year (FY) 2015 Objectives

- Development of design principles and performing density-functional calculations to identify appropriate novel metal oxide materials
- Synthesis of novel metal oxides in bulk and thin film forms
- Create necessary testing station(s) for PEC water-splitting performance evaluation and use to characterize small cells made from novel metal oxides

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (AE) Materials Efficiency – Bulk and Interface
- (AF) Materials Durability – Bulk and Interface
- (AJ) Synthesis and Manufacturing

Technical Targets

This project is focused on identifying, designing, and synthesizing new semiconducting materials which may be successfully employed as light-absorbing materials that will drive the water-splitting reaction with a PEC water-splitting device. The insights and developments obtained from this work should prove useful towards meeting the following 2020 targets established by DOE for PEC hydrogen production in systems with solar concentration [1].

- PEC H₂ cost: \$5.70/kg
- Annual electrode cost tons per day (TPD) H₂: \$255,000/yr-TPD H₂
- Solar-to-hydrogen (STH) energy conversion ratio: 20%
- 1-Sun hydrogen production rate: 1.6 x 10⁻⁶ kg/s-m²

FY 2015 Accomplishments

The accomplishments completed during the current reporting period are summarized below:

- The composition and crystal structure of a new metal oxide material, BBNO, was identified which could serve as a PEC photoanode. Density functional theory calculations suggest a direct bandgap of approximately 1.9 eV, which should be sufficient to drive a PEC reaction cell.

- Bulk BBNO material was successfully synthesized from a mixture of metal oxide precursor materials via solid-state reactions. This material showed coloration and X-ray diffraction patterns consistent with theoretical expectations for this material.
- Thin films of BBNO were successfully synthesized using multiple techniques (radio frequency [RF] sputtering, spin/dip coating), which can be incorporated into a photoelectrode.
- Initial PEC performance data was acquired for a BBNO photoanode which demonstrates over $100 \mu\text{A}/\text{cm}^2$ photocurrent at a bias voltage of 1.0 V vs a Ag/AgCl reference electrode under 1-Sun illumination using sodium sulfite as the oxidation reagent, corresponding to an H_2 production rate of over $1.04 \times 10^{-8} \text{ kg}/\text{s}\cdot\text{m}^2$. Although this production rate is $\sim 100\times$ lower than the 2020 technical target, further optimization is expected to improve this performance measure. These initial tests have also shown that the oxide exhibits short-term stability (several hours) in aqueous electrolyte solutions.



INTRODUCTION

Direct PEC water splitting has shown promise for producing hydrogen fuel in renewable and scalable manner [2,3], with technical/economic analysis showing that an STH energy conversion efficiency of at least 15% is necessary for economic viability [4]. It has been determined that a tandem device using two separate semiconducting absorbing layers (one n-type with negative charge carriers and one p-type with positive charge carriers), each with complimentary light absorption features, is needed to achieve this efficiency threshold [5–7]. While some of these types of devices have reached efficiencies of over 18% [8], a key problem is that most n-type materials, used in the photoanodes for O_2 generation in the PEC reactor, are not stable enough to sustain long-term operation at high efficiencies [9–15]. The most stable materials for O_2 producing photoanodes are metal oxides, although all of the metal oxides explored thus far [16,17] have underperformed due to inappropriate combinations of material properties such as optical bandgaps, light absorption coefficients, electrical conductivity, and carrier diffusion lengths. This project is intended to design, synthesize, and evaluate a new metal oxide photoanode material which will have a superior combination of materials properties that will permit high efficiency tandem PEC devices to be created that also demonstrate long-term stability.

APPROACH

The University of Toledo has identified several new metal oxide materials with the following desired combination of physical characteristics (1) direct optical bandgaps in the range of 1.6–1.8 eV for ideal PEC performance [7] and strong photon absorption, (2) low charge carrier effective masses, (3) low non-radiative recombination which results from material defects, (4) band edge energies which can drive O_2 evolution reactions, and (5) thermodynamic stability in oxidizing aqueous conditions. The design principles used to identify this metal oxide composition and microstructure were based upon theoretical material principles that predict higher rates of photogenerated charge carriers and transport within the material due to favorable combinations of electron bonding orbitals and crystal symmetry within the microstructure. The additional consideration of using elements that are earth-abundant and have relatively low toxicity was also included in the material design principles. The University of Toledo is able to leverage prior experience in materials synthesis and thin film deposition techniques used in the course of various thin film photovoltaic research efforts to fabricate these materials in both bulk powder and thin film forms. Thin films of these materials could then be deposited onto glass substrates with transparent conductive oxide coatings, or other suitable substrates, to create photoanode electrodes for additional performance evaluation and characterization. Information obtained from these initial photoanodes will guide further efforts towards adjusting the material synthesis and electrode fabrication techniques to optimize the PEC performance.

RESULTS

Using the design principles previously described, a number of metal oxides having either the perovskite or spinel crystal structures were identified that contain Sn, Sb, and/or Bi. The band structure for BBNO was calculated and is shown in Figure 1. The information contained in the band structure revealed an expected bandgap of 1.9 eV and electron transitions which should correspond to high optical absorption, thus increasing the likelihood of producing successful thin films for PEC photoelectrodes. Bulk powder synthesis was performed by annealing a stoichiometric mixture of oxide precursors in a closed crucible in air at temperatures between 600°C and 900°C for several hours. The resulting powder mixture had changed in color from light yellow to brown after annealing and X-ray diffraction patterns from the annealed powders revealed the presence of a single phase with perovskite structure consistent with that expected for BBNO, as shown in Figure 2. Closed crucibles were required during annealing at these temperatures to mitigate loss of Bi, the oxide of which has higher vapor pressure than the other two metal oxide precursors. Films were prepared from this annealed powder by creating a ball milled suspension

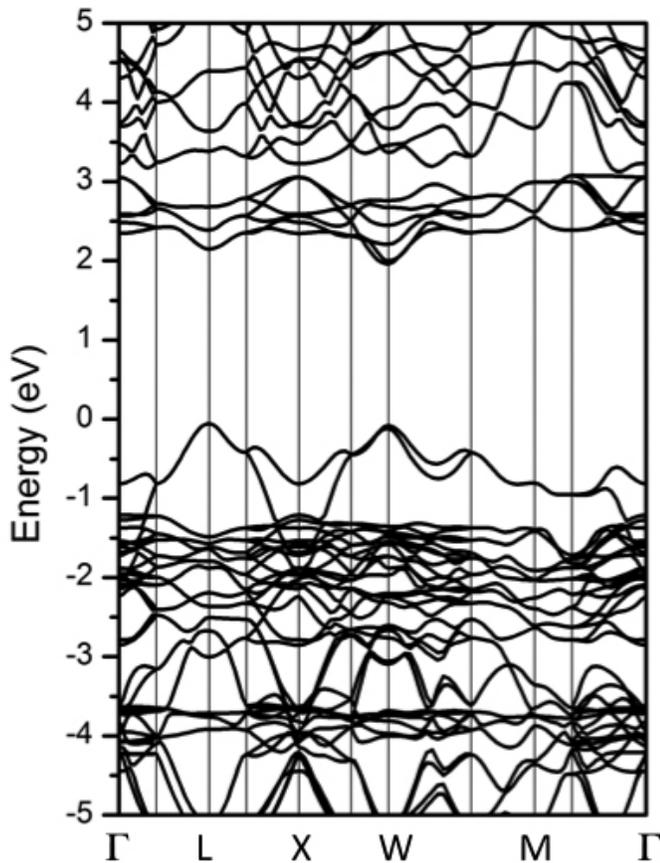


FIGURE 1. Calculated density functional theory band structure of BBNO

in solvents, such as acetone or ethanol, which was then applied to various substrates using dip coating or spin coating methods. The resulting films were several micrometers in thickness and had highly porous microstructures which were relatively unaffected by subsequent thermal processing (not shown). Alternatively, much thinner (<1 μm) films with more compact microstructures were obtained via two independent methods: RF sputtering and sol-gel reaction. Sputtered films were obtained from targets prepared in-house that were either mixed precursor powders (described earlier) or single phase annealed powder. A representative cross-sectional image of the RF sputtered films on a fluorine-doped tin oxide (FTO) coated glass substrate is shown in Figure 3. The sol-gel method involved dissolving metal oxide precursors, in a mixture of acetic acid, 2-methoxyethanol and pentane-2,4-dione. The resulting sol-gel was deposited via spin coating and annealed in air at temperatures between 500°C and 600°C for periods less than two hours. The film changed from light yellow to dark brown in color and was found to exhibit a band gap of nearly 1.9 eV, as expected. Preliminary evaluation for PEC photoanode activity was determined by illuminating films with a 300 W Xe arc lamp while immersed in solutions of 1 M sodium sulfite (after purging with nitrogen for over 30 minutes). It was found that the highly porous films drop spin/dip coating the ball milled powder suspension yielded almost no photocurrent, most likely due to poor electrical contact between individual grains and possibly high defect concentrations at the grain boundaries. The films deposited via RF sputtering and sol-gel spin coating

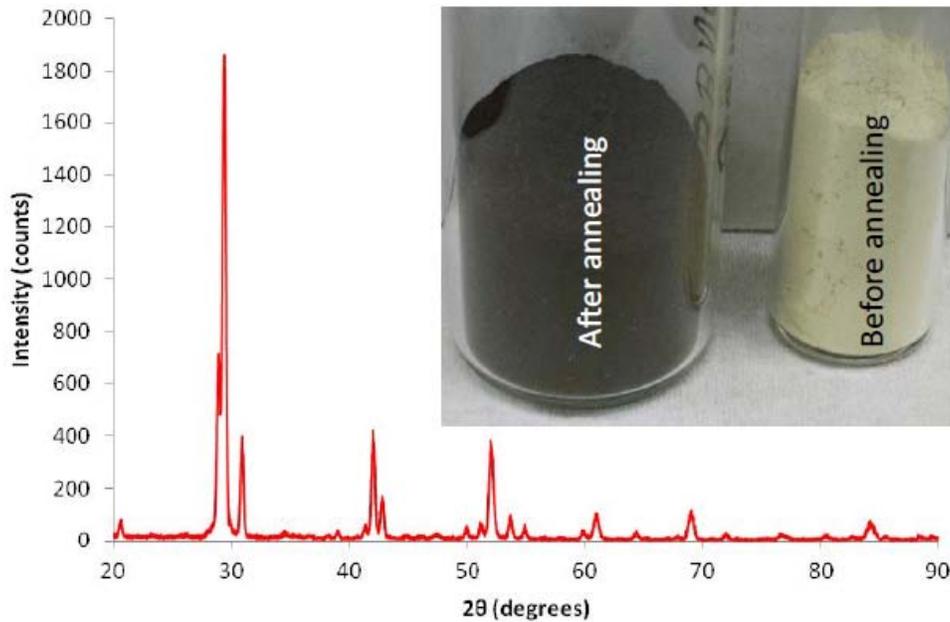


FIGURE 2. X-ray diffraction pattern for air annealed BBNO powder

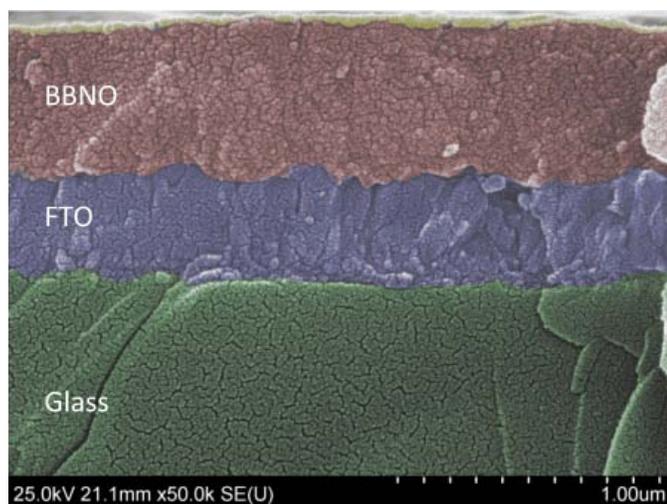


FIGURE 3. Cross-sectional scanning electron microscope image of RF sputtered BBNO film

showed higher photocurrents, although these were only on the order of $100 \mu\text{A}/\text{cm}^2$ at bias voltages near 1.0 V versus an Ag/AgCl reference electrode, as shown in Figure 4. Further characterization of the films from the photoanode samples revealed that they had p-type character, which was confirmed by both open-circuit photovoltage versus illumination intensity measurements and Mott-Schottky analysis using capacitance-voltage measurements (not shown here). The carrier concentrations of these films were on the order of 10^{16}cm^{-3} from the Mott-Schottky analysis. Investigations on manipulating the carrier type and concentration by varying the Bi:Nb ratios as well as incorporating dopant atoms such as Cl and F are underway but are still incomplete. Changing the carrier type is especially important since photoanodes operate most effectively when they have n-type character. Finally, all films appear to be stable in the aqueous electrolytes (without applied bias) for several hours without any visible signs of degradation. It was also discovered that the films are stable with the application of positive voltages (vs Ag/AgCl) up to the onset of O_2 evolution in the dark, while all films displayed degradation (in the form of brown-to-black color change and delamination) upon the application of negative bias beginning around -0.6 V (versus Ag/AgCl) and could be from reduction of the Bi and/or Nb cations. For photoanode applications, the negative bias potentials are unlikely to be experienced and should not be a significant concern.

The photocurrents observed are now about 100x lower than what is required for the technical targets, but adjustments to the material electronic characteristics (by altering carrier type/concentration), improving film interface quality, and application of suitable catalyst materials may possibly yield significant improvements. The initial observations for the film stability are encouraging for the ultimate lifetime requirements of a PEC water-splitting system.

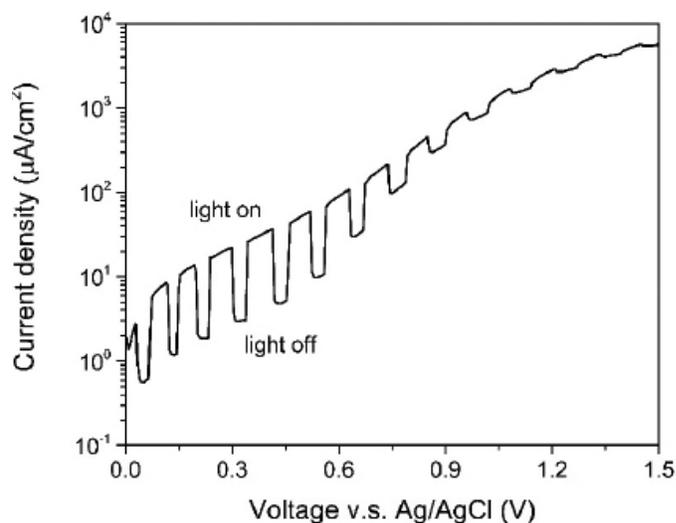


FIGURE 4. Preliminary J-V curve for BBNO film photoanode prepared via sol-gel method

CONCLUSIONS AND FUTURE DIRECTIONS

The conclusions obtained from the FY 2015 period are as follows:

- New metal oxide materials for PEC photoanodes were identified using well defined design principles, and the electronic band structure of one oxide, BBNO, was found to be a promising candidate for this application.
- BBNO was successfully synthesized in both bulk powder and thin film forms, the latter of which was successfully applied to FTO coated glass substrates to form PEC water-splitting photoanodes.
- Preliminary PEC photoanode performance and electrode stability was obtained for an aqueous solution with 1 M sodium sulfite oxidation reagent. While the observed photocurrent was much lower than the technical target, the film stability appears favorable for long term PEC operation.
- The observed conductivity of the BBNO films prepared is p-type with concentrations of approximately 10^{16}cm^{-3} , which is not ideal for photoanode operation.

Future work directions for the next reporting period include, but are not limited to:

- Exploring various changes to the material composition, such as adjusting the Bi:Nb ratio and incorporating dopants such as Cl and F, in order to change the conductivity to n-type.
- Investigating various interface treatments (such as oxygen plasma cleaning) to reduce the presence of defects (possible recombination centers) at the

metal oxide/substrate and metal oxide/electrolyte interfaces.

- Creation of nano-structured surfaces of the BBNO films which can increase the electrochemical surface area of the electrodes.
- Addition of water oxidation catalysts to metal oxide surface to reduce the reaction overpotentials.
- Synthesis and thin film fabrication of additional metal oxide materials suggested by the design principles but not yet explored.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Yanfa Yan, "Metal oxides for PEC water splitting," Invited talk at 227th ECS Meeting, Chicago, Illinois, 5/25/2015.
2. Yanfa Yan, "Band gap engineering of metal oxide for better water splitting," Invited talk at 2015 Spring MRS Meeting, San Francisco, 4/10/2015.

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