

## II.G.5 Solar Water Splitting: Photocatalyst Materials Discovery and Systems Development

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(AC) Device Configuration Designs

(AD) Systems Design and Evaluation

### Technical Targets

This project is conducting fundamental studies of oxide and non-oxide photocatalysts to understand the nature of bandgap engineering as it relates to PEC splitting of water. In addition, bio-inspired electron and hole transfer catalysts are being studied in order to gain insight into the development of robust and low-cost non-precious metal catalysts for PEC systems. Insight gained from these studies will be applied toward the design and synthesis of PEC systems that meet the DOE 2018 PEC production targets, especially bandgap, durability, and systems-level efficiency.

### Accomplishments

- Successfully synthesized Ta<sub>3</sub>N<sub>5</sub> photocatalyst in both thin-film and powder form.
- Demonstrated un-biased PEC activity in Ta<sub>3</sub>N<sub>5</sub> thin-films.
- Developed comprehensive in-house PEC testing capabilities.
- Identified several potential oxynitride photocatalysts of the general formula ATaO<sub>2</sub>N (A= Ca, Sr, Ba).
- Measured valence/conduction-band levels via ultraviolet photoelectron spectroscopy (UPS).



### Objectives

- Develop and optimize novel photocatalyst(s) with bandgap(s) engineered for unbiased solar splitting of water.
- Develop bio-inspired metal complex catalysts to reduce the overpotential required for efficient solar splitting of water.
- Demonstrate a chemical conversion process efficiency of >8% for a photoelectrochemical (PEC) system.
- Demonstrate a pilot-scale PEC hydrogen system with >1,000 hours life.

### Technical Barriers

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

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AB) Bulk Materials Synthesis

### Introduction

The present work is focused on development of systems that use incident solar radiation to split water molecules into their hydrogen and oxygen constituents. Termed photoelectrochemical (PEC) systems, these systems rely entirely on renewable solar energy in the production of hydrogen. The system can be described as a combination of a conventional photovoltaic (PV) cell, where incident solar radiation creates electron flow in a semiconductor, and an electrolyzer, where hydrogen and oxygen are formed by subjecting an electrolyte to an electrical bias. In the case of PEC systems, the entire process is carried out in a single PEC element, significantly reducing the cost/complexity of the overall system.

In particular, the focus of this project is the development of photocatalysts suitable for the efficient

production of hydrogen over a design lifetime >1,000 hours. This requires that the photocatalyst not only be efficient, but also robust with respect to chemical attack while immersed in the electrolyte. To date, a photocatalyst meeting all criteria has not been identified. By screening materials based on compositional, electrical, and physical characteristics, we aim to identify and develop suitable candidates for this purpose.

## Approach

The approach taken for this project is two-fold. Photocatalyst development, led by GE Global Research, is focused on the development of photocatalysts suitable for unbiased water splitting. The technical focus is sub-divided into materials synthesis, electrical characterization, optical characterization, and electrochemical characterization. For the materials synthesis sub-task, materials are first synthesized in powder form using both conventional and novel synthesis techniques. Powders are then analyzed for optical properties. Provided the optical properties prove encouraging, candidates are then synthesized in thin-film form for electrical and electrochemical characterization.

The second approach is transfer catalyst development, led by Caltech. Due to the fundamental nature of this research, approach with respect to design, synthesis, and characterization varies. However, the overarching goal of this portion of the research is the development of electron catalysts that reduce the kinetic barrier to electron transfer. Using ligand design and molecular synthesis, electron transfer catalysts are characterized with respect to efficacy in an aqueous PEC system.

## Results

As mentioned briefly in the accomplishments, interest has evolved towards both nitride and oxynitride-based photocatalysts, primarily due to the potential for improved bandgap alignment compared to traditional oxide photocatalysts. This research was inspired by the work of Domen and Marchand [1-7], who performed much of the early work on nitride and oxynitride synthesis. Figure 1 shows the band structure as measured by UPS of several candidate materials. As seen from the diagram, each material straddles the redox potential of water. Furthermore, the bandgaps vary in magnitude from 2.5 to 2.2 eV, making them suitable for capturing a significant portion of the incident radiation spectra. However, synthesis of these materials in thin-film form (for PEC characterization) is a challenge; to date only  $Ta_3N_5$  has been successfully synthesized. The samples in this study were made via reactive plasma sputtering. The key to synthesis is achieving the  $Ta^{5+}$  cation, which is conveniently done by nitridation of the oxide. First, a precious metal (i.e. Pt) back contact

is applied to an alumina substrate. Then, a tantalum layer is applied. This tantalum layer is oxidized at 1,000°C in oxygen. Then the layer is nitrided in an  $NH_3$  atmosphere at 1,100°C.

$Ta_3N_5$  thin-films were tested in a nitrogen-sparged KOH solution. The results are shown in Figure 2. As seen from the data, the sample is indeed photoelectrochemically active (no external bias applied). However, the estimated efficiency is quite low (less than 0.1%). This can be attributed to many factors. First, like any semiconductor, the photocatalyst is expected to be very sensitive to processing. Furthermore, purity, especially with respect to electrically active impurities, is critical. Finally, it is well known that photoelectrochemical processes are kinetically hindered, thus requiring anodic and cathodic overpotentials as well as electron/hole transfer catalysts to work efficiently.

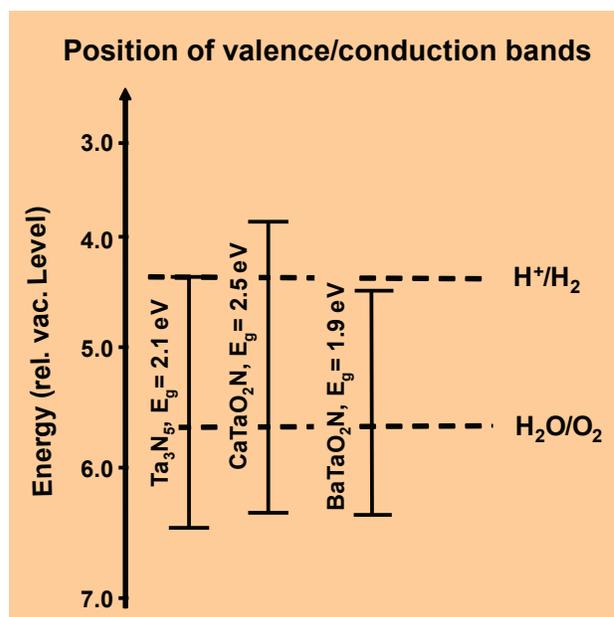


FIGURE 1. Band Structure of Several Nitride/Oxynitride Photocatalysts as Measured via UPS

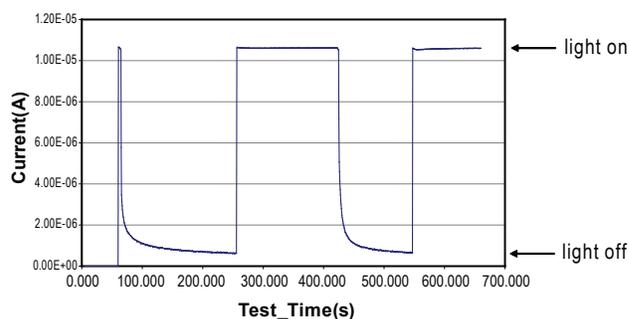


FIGURE 2. Light-Induced Photocurrent vs. Time for  $Ta_3N_5$  PEC Cell

One significant deficiency of  $Ta_3N_5$  is the relatively low anodic overpotential with respect to the reduction potential of water. Without efficient electron/hole transfer catalysts, it's difficult to ascertain the magnitude of this deficiency. A comprehensive assessment will require transfer catalysts. On a positive note, the material showed no measurable photodegradation effects. Future work will focus on improving the quality of thin-film specimens. That, combined with careful electronic property characterization, will give greater insight into the potential efficacy of such a system.

Significant improvements were also made to our ability to characterize photocatalysts. Specifically, we constructed a laboratory-scale system for evaluating performance of photocatalysts that includes gas chromatography analysis of  $H_2$  production. From this, we can measure both evolved hydrogen and electronic transport *in situ*. This will allow us to make real-time measurements of efficiency as well as photodegradation effects. This apparatus is shown in Figure 3.

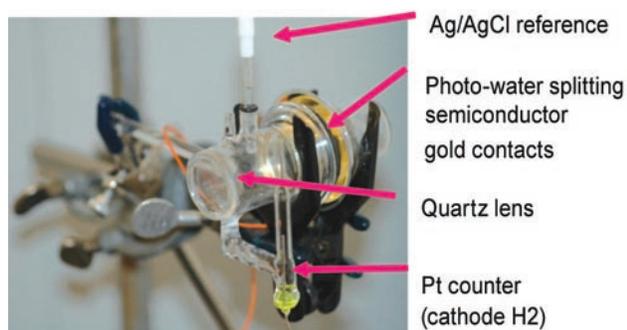


FIGURE 3. GEN-II PEC Testing Apparatus

## Conclusions and Future Directions

- $Ta_3N_5$  and  $ATaO_2N$  (A= Ca, Sr, Ba) have been synthesized.
- Bandgaps vary from 2.5-2.2 eV, with good alignment with the redox potential of water.
- $Ta_3N_5$  has been synthesized and characterized in thin-film form.
- $Ta_3N_5$  has been shown to photoelectrochemically split water under incident solar radiation.
- Thin-film examples of the oxynitride candidates  $ATaO_2N$  (A= Ca, Sr, Ba) have yet to be synthesized.
- Focus will shift towards optimization of the candidate species:
  - Electronic properties (carrier concentration, carrier lifetime, etc.).
  - Chemical properties (purity).
  - Physical properties (film morphology, phase, uniformity).
- Continued fundamental research into transfer catalysts.
- Systems-level studies with a baseline goal of >1% PEC efficiency and >1,000 hrs lifetime.

## References

1. *J. Phys. Chem. B*, **2003**, *107*, pp. 13441-13445.
2. *J. Phys. Chem. B*, **2004**, *108*, pp. 11049-11053.
3. *J. Phys. Chem. B*, **2003**, *107*, pp. 1798-1803.
4. *J. Mater. Chem.*, **2001**, *11*, pp. 1248-1252.
5. *J. Solid State Chem.*, **2003**, *171*, pp. 143-151.
6. *J. European Cer. Soc.*, **1991**, *8*, pp. 197-213.
7. *J. Phys. Chem. Solids*, **2003**, *64*, pp. 281-286.