
II.K.9 A Combinatorial Approach to Realization of Efficient Water Photoelectrolysis

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we seek. Nonetheless, concentrating efforts on newly discovered lower band gap oxides appears to be a fruitful endeavor and our methodology gives a rational approach for future discovery and optimization of such materials. Our results have highlighted the difficulty of developing a new material from its discovery to its deployment in an optimized, efficient and useful device. Not only will the composition and nanostructure need to be optimized but, in addition, inexpensive, stable, and perhaps transparent substrates that are compatible with the material's morphology and chemical makeup must also be found.

Objectives

Our first objective is to discover many new semiconducting oxides that have the required, band gap, band positions, low cost, catalytic activity and stability to efficiently photoelectrolyze water with solar illumination. When such materials are identified we then aim to configure them in a nanostructured film that will be able to harvest all solar photons with energies greater than the band gap and to efficiently collect the resulting photogenerated carriers to photoreduce and photooxidize water.

Technical Barriers

The main technical barrier is the vast number of possible combinations of metal oxides that must be produced and screened. In addition once promising materials are identified it is quite challenging and time consuming to investigate the composition, band structure and morphologies of the material in order to configure it into a photoelectrode that can efficiently photoelectrolyze water.

Abstract

We have developed a methodology to discover new materials useful for the photoelectrolysis of water. We determined the optimum composition and solid-state structure of one newly identified potential photocatalyst. The material contains cobalt, aluminum and iron in a Co_3O_4 spinel structure with Fe and Al substituted into Co sites with a nominal stoichiometry of $\text{Co}_{3-x-y}\text{Al}_x\text{Fe}_y\text{O}_4$ where x and y are about 0.18 and 0.30 respectively. It is a p -type semiconductor with an indirect band gap of around 1.5 eV, a value that is nearly ideal for the efficient single photoelectrode photoelectrolysis of water. This new cobalt iron aluminum oxide is most likely not the "holy grail" of photoelectrochemistry that

Progress Report

Since receiving funding for our combinatorial search for metal oxide semiconductors that can photoelectrolyze water efficiently with sunlight we have made substantial progress in both developing the techniques and protocols for the search. In addition we have discovered several promising and unexpected metal oxide compositions that have activity for water photoelectrolysis using visible light. Although the newly discovered materials are probably not the "holy grail" of photoelectrolysis, we have followed up on one compound in detail as much to develop a methodology for material optimization as the actual performance. This photocatalyst is a cobalt iron aluminum oxide that has interesting solid-state chemistry and a band gap of about 1.6 eV. Our studies have already produced a published electronic structure calculation focusing on this material [1].

We have used a consumer level ink jet printer to print and screen hundreds of different material combinations using the four-metals-taken-three-at-a-time pattern used to screen fuel cell catalysts [2]. Most of the material combinations show no or very little photoresponse while a few have performed significantly better than the internal reference materials ($\alpha\text{-Fe}_2\text{O}_3$ and CuO for n - and p -type photoactivity, respectively). One of the materials discovered in our search has reproducibly shown substantial p -type photoactivity. Figure 1 shows the photocurrent map done in 0.1-M NaOH without an externally applied bias of a "four-metals-taken-three-at-a-time" printed and fired film using Fe, Co, Al and Cs. The dark regions represent areas where the photocurrent is in the anodic direction whereas the bright regions show areas of p -type photocurrent response that are 2 to 2.5 times larger than the CuO internal standard (upper left triangle). The regions of high activity are found in the Co rich regions of the Co-Al-Fe and Co-Al-Cs triangles. Although we can tell

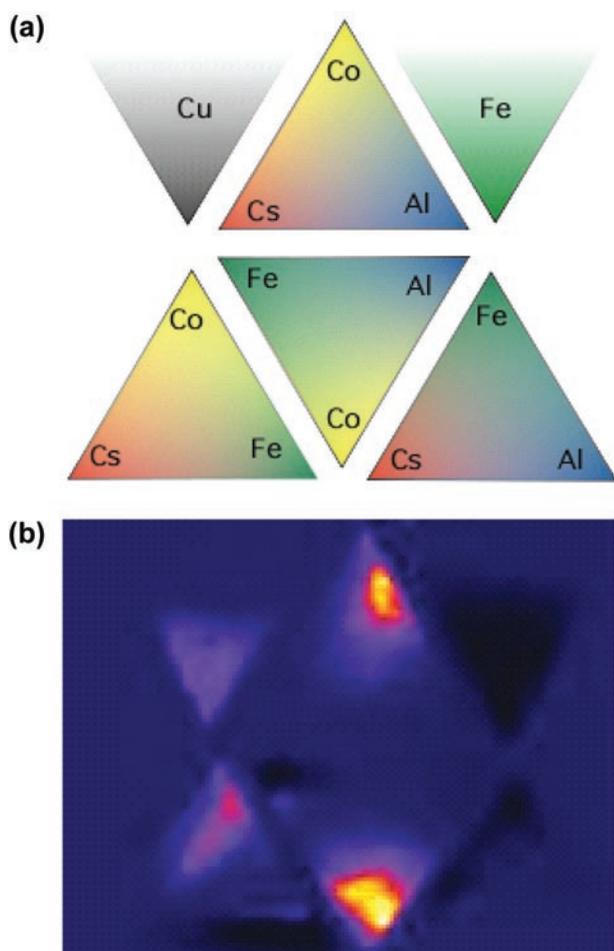


FIGURE 1. A. Template showing the gradient pattern used for printing the metal nitrate precursors for the Al-Co-Cs-Fe system (Fe and Cu triangles are internal standards for n- and p- type photoactivity, respectively). B. Laser screening at 532 nm with no applied bias in a 0.1-M NaOH solution. Qualitatively, it can be seen that the highest activity is associated with primarily Co and small amounts of Fe and Al. The printed triangles have a height of 1.9-cm.

from the gradient printing that the active phase is cobalt rich, the exact proportions of the metal components in the active mixture are unknown since we do not know the exact amounts of the various “inks” delivered by the printer driver software as its usual function has been optimized for visual aesthetics when printing conventional inks.

Future Directions

In the next funding cycle of our project entitled “A Combinatorial Approach to Realization of Efficient Water Photoelectrolysis”, we plan to continue to use and further develop our ink jetting printing techniques and protocols for high-throughput combinatorial screening and optimization of metal oxide semiconductors useful

for splitting water with solar energy. We will improve upon our metal oxide precursor “ink” formulations with the goal of achieving an easy to formulate, stable, safe and easily printed “ink” formulation for every metal. This will greatly facilitate the high-throughput combinatorial screening and the distributed screening project that is being independently developed.

We will also begin to explore the influence of the morphology of the metal oxide semiconductor photocatalysts on the efficiency of water photoelectrolysis. We will begin by synthesizing different diameters and shapes of monodisperse metal oxide nanoparticles and investigate their incident photon current efficiencies (IPCE) and absorbed photon current efficiencies (APCE) for photoredox reactions in both monolayer and multilayer films deposited on transparent conducting oxide substrates. Fundamentally, a decrease in APCE is expected as the nanoparticle diameter increases beyond the diffusion length of the photogenerated carriers but a rigorous examination of this behaviour has not yet been carried out. The performance of the nanoparticle films will be compared and contrasted to the behavior of thin films of materials with a uniform thickness produced by atomic layer deposition (ALD). Comparing the IPCE and APCE values of the two morphologies will provide insight into the surface and bulk recombination processes that can limit collection of photogenerated carriers in the semiconductor. The ability of multilayer nanoparticle films to transport charge, like TiO_2 in the nanocrystalline dye sensitized solar cell, will be studied by measuring APCE and IPCE values as a function of thickness of the nanoparticle films. Initially these studies will be performed on $\alpha\text{-Fe}_2\text{O}_3$, an n-type semiconducting oxide, and our newly discovered p-type cobalt aluminum iron oxide with a stoichiometry near $\text{Co}_{2.5}\text{Al}_{0.2}\text{Fe}_{0.3}\text{O}_4$. These two prototypical materials will serve as model systems for determining the processes limiting the efficiency of photoelectrolysis reactions in nanostructured oxide photoelectrodes.

Slow electron transfer kinetics of the multielectron water oxidation or reduction reactions can also limit the efficiency of a water photoelectrolysis system. Therefore we will also explore the use of ALD to deposit conformal films of catalysts onto the nanoparticles and planar ALD films to investigate their effect on photoelectrolysis efficiencies. Again we will use $\alpha\text{-Fe}_2\text{O}_3$ and our newly discovered p-type cobalt aluminum iron oxide as prototypical stable oxide semiconductors where reduction of overpotential losses should improve their performance. The goal is to develop these techniques as standard tools for evaluating and improving the performance of the many new semiconducting oxide materials that have been and will be discovered by our high-throughput combinatorial search.

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