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Final Technical Report

Project Title: Development of Polycrystalline Photoelectrodes with Optimum Compositions and Morphologies for Solar Fuel Production via Electrochemical Synthesis

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Abstract

Photoelectrochemical cells (PECs) can utilize solar energy for water splitting to produce H_2 as a clean fuel. The most critical components of a water-splitting PEC are semiconductor electrodes (photoelectrodes) that absorb solar energy to generate photoexcited charge carriers and transport them to the electrode/electrolyte interface for water reduction and oxidation reactions. While efficient PEC hydrogen production has been successfully demonstrated on the laboratory scale, the commercial viability of PECs depends critically on the cost of H_2 produced by the PECs, which is affected by the cost of PEC construction. Therefore, identifying promising inexpensive semiconductor electrodes is important. The goal of this project was to bring an advancement in the synthesis and understanding of inexpensive polycrystalline photoelectrodes based on oxides. Oxide-based semiconductors are inexpensive, easy to fabricate, and relatively more stable in aqueous media compared to other types of semiconductors. This project developed new electrodeposition methods to produce a variety of oxide-based semiconductor electrodes with precisely controlled compositions and morphologies to enhance photon absorption, electron-hole separation, and the use of electrons and holes for desired chemical reactions. The resulting high-quality photoelectrodes were investigated to establish the structure-composition-morphology-photoelectrochemical property relationships to identify the advantages and limitations of each oxide semiconductor system.

Project Activities and Accomplishments

Solar water splitting using a photoelectrochemical cell (PEC) provides a viable option for the sustainable and environmentally benign production of H_2, which can be used as a clean fuel. The key components of a water splitting PEC are semiconductor electrodes (photoelectrodes) that utilize the solar spectrum to generate photoexcited charge carriers and transport them to the electrode/electrolyte interface for use in water reduction and oxidation reactions. Efficient hydrogen production by a PEC has already been successfully demonstrated on the laboratory scale. However, because the commercial viability of PECs depends critically on the cost of H_2 produced, practical PEC development requires developing inexpensive and robust semiconductor electrodes that can achieve a high solar-to-hydrogen efficiency at significantly reduced cost.

The goal of the project was to prepare and investigate oxide-based photoelectrodes for use in PECs. Among various semiconductors that have been considered as photoelectrodes for use in PECs, oxide-based photoanodes are particularly attractive because of their stability in aqueous media in addition to inexpensive and facile processing compared to other types of semiconductors. However, prior to this project, most oxides considered for solar water splitting were binary oxides such as TiO_2, ZnO, and Fe_2O_3, although there are numerous ternary oxides with potentially more promising bandgap energies and band positions for solar water splitting. This was because it is not easy to produce oxides with complex compositions as high-purity, high-quality photoelectrodes; when ternary and quaternary oxides are synthesized, the chances for simpler binary oxides, which are often thermodynamically more stable, to form as impurity phases are high. The formation of these impurity phases and the resulting nonstoichiometry of the desired phase leads to poor photocurrent and photovoltage performance of the sample. If these impurities and the nonstoichiometry of the samples are not well characterized and no deliberate effort is made to perfect the synthesis of these complex oxides, the true properties of these oxides cannot be revealed. Based on the poor performances of improperly prepared samples, an incorrect evaluation can be made, and further development of a potentially promising compound can often be discouraged.

Another challenge in preparing oxide-based photoelectrodes is that their nano-scale morphologies play a critical role in photocurrent generation. This is because charge transport in oxide photoelectrodes is slow due to the more ionic nature of the metal ion-oxide bonding, which results in considerable electron-hole recombination. To alleviate this issue, oxide photoelectrodes must be prepared with appropriate nanostructures so that the distance the minority carriers must travel to reach the semiconductor/water interface is shorter than their diffusion lengths.

In order to address these issues and produce compositionally more complex ternary oxides as high-quality photoelectrodes with desired nanostructures, this project used solution-based electrodeposition as the major synthesis tool. Through this project, numerous new electrochemical reactions and deposition conditions were developed to grow ternary oxides directly from the conducting substrate or deposit precursor materials on the conducting substrate that can be easily converted to target ternary oxide photoelectrodes through simple post-deposition thermal and chemical processes. During electrodeposition, deposition potential and current were used as additional synthesis parameters to finely control the nucleation and growth processes of desired materials, offering an exceptional level of morphology control (**Figure 1**). As a result,

photoelectrodes could be prepared with various nanostructures that can enhance electron-hole separation and therefore photocurrent generation. Furthermore, the solution-based electrodeposition methods allowed for facile and uniform composition tuning during the growth of semiconductor electrodes through doping and forming solid solutions, which is critical for tuning the charge transport properties of photoelectrodes.

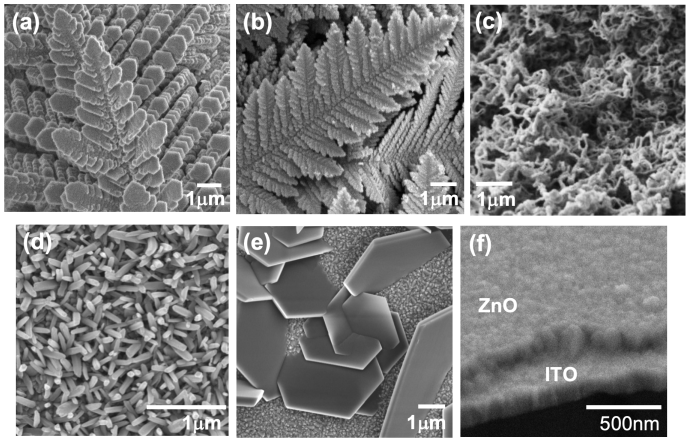

Figure 1. ZnO electrodes prepared with various controlled morphologies via electrodeposition-based synthesis.

Through the newly developed electrodeposition conditions, a variety of n-type semiconductors (e.g., $BiVO_4$, $CuWO_4$, Bi_2WO_6, $Bi_2Mo_3O_{12}$, $Cu_{11}V_6O_{26}$, $AgNbO_3$, $BiFeO_3$, and Fe_2TiO_5) that can be used as photoanodes[1,3,4,5,8-17,22,25,27,30,32] and p-type semiconductors (Cu_2O, CuO, $CuFeO_2$, $CuNb_2O_6$ $CuBi_2O_4$, $LaFeO_3$, and $Ca_2Fe_2O_5$) that can be used as photocathodes[1-2,6,11,12,14,18-21,23-24,26,30,32-33] were fabricated and investigated. The morphologies and compositions of these compounds were varied to identify optimal morphologies and compositions. Examples for composition tuning include Mo doping of $BiVO_4$,[8] Mo and W doping of $Cu_{11}V_6O_{26}$,[17] Ag doping of $CuBi_2O_4$,[14] Li doping of CuO,[19] and K doping of $LaFeO_3$,[23] all of which were performed to increase the majority carrier densities in the host photoelectrodes. The examples of morphology tuning include nanostructure variation of $CuBi_2O_4$ and ZnO using the variation of deposition conditions.[14,15] The resulting optimized photoelectrodes were investigated to establish the structure-composition-morphology-photoelectrochemical property relationships to evaluate the advantages and limitations of each oxide semiconductor system.

To aid the semiconductor electrodes in using photogenerated holes and electrons for desired oxidation and reduction reactions, depositing catalysts on top of the semiconductor electrodes is often needed (**Figure 2a**). Thus, this project also developed new (photo)electrodeposition conditions to deposit catalysts.[3,29,31] Examples include MoS_2 to facilitate the hydrogen evolution reaction and $CoSb_2O_6$ and $MnSb_2O_6$ to facilitate the oxygen evolution reaction.[7,28] Semiconductor electrodes may also require buffer or protection layers to enhance electron-hole separation or to enhance chemical and photo-electrochemical stabilities (**Figure 2b-c**). Thus, this project also developed electro-deposition conditions to uniformly deposit buffer and protection layers on the semiconductor electrodes. Examples include depositing a $ZnFe_2O_4$ layer on a $BiVO_4$ photoanode to protect it in basic media,[13] depositing a TiO_2 layer to suppress photocorrosion of a Cu_2O photocathaode,[33] and using

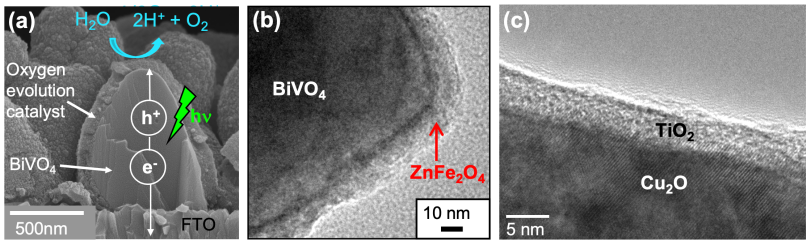

Figure 2. (a) An SEM image of $BiVO_4$ covered by an oxygen evolution catalyst (FeOOH) layer, (b) a TEM image of $BiVO_4$ covered by a $ZnFe_2O_4$ protection layer, and (c) a TEM image of Cu_2O covered by a TiO_2 protection layer.

ZnO and Al-doped ZnO as a buffer layer in solar cells.[15] For the deposition of catalyst, buffer, or protection layers on top of semiconductor electrodes, it is critical that their deposition conditions (e.g., potential, pH) are compatible with the underlying semiconductor electrodes, so as to not alter their compositions and morphologies. Thus, depending on which semiconductor electrode was used as the working electrode, the deposition conditions of the catalyst, buffer, or protection layers were customized.

Our efforts resulted in the successful construction of multilayer photoelectrodes that can enhance the overall performances of oxide-based semiconductor electrodes, which allowed us to accurately assess which limitations of each system can be mitigated. The synthesis ability and understanding we gained for producing and investigating oxide-based thin film electrodes (semiconductors, catalysts, buffer and protection layers) through this project has advanced the solar fuels field and broadly impacted various energy and catalysis fields requiring thin film-type oxide electrodes.

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