DEPARTMENT OF
Chemistry
UNIVERSITY OF WISCONSIN–MADISON

Ph.D. Dissertation Defense

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"Development of Oxide-based Semiconductors as Photoanodes for Use in Photoelectrochemical Water Splitting Applications"

Alternatives to fossil fuel-based energy must be developed as fossil fuel sources deplete worldwide. Solar energy is an attractive choice for energy generation but is difficult to implement on a large scale since it can only be harnessed intermittently. One way to alleviate this concern is to use sunlight to directly catalyze the formation of fuel molecules that can be stored and utilized when necessary. Hydrogen gas is one such solar fuel that is clean-burning and environmentally benign and that can be generated from the sunlight-driven process of photoelectrochemical water splitting.

For photoelectrochemical water splitting to be a commercially competitive way of storing solar energy, semiconductor materials which can efficiently absorb sunlight, convert them into photo-excited electron-hole pairs, and use the electrons and holes to perform water reduction and water oxidation must be developed. Water oxidation reaction is the more kinetically limiting of the two half-reactions for water splitting, making the development of highly efficient photoanodes for the water oxidation reaction critical so as not to limit the overall efficiency of generating hydrogen. From a technoeconomic perspective, oxide-based photoanodes are the most promising to use as photoanodes because of their solution-based, scalable synthesis routes. However, they currently suffer from low efficiencies for solar water oxidation. The work presented herein was conducted to increase the efficiency of oxide-based photoanode $BiVO_4$, as well as the development of other promising but understudied photoanodes for photoelectrochemical water splitting. Studies on $BiVO_4$ focused on improving its charge transport properties by doping at the Bi-site with lanthanide ions, developing a new tandem device architecture which increased light harvesting capabilities, and evaluating its long-term chemical stability in near-neutral aqueous electrolytes. Studies were also conducted on $PbCrO_4$, Pb_2CrO_5, CoV_2O_6, and $BiMn_2O_5$ to evaluate their utility as photoanodes for water oxidation via new electrochemical synthesis routes.