Modifications of Metal Oxide Semiconductors for Efficient Light Driven Water Oxidation

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Background Information

Solar energy holds great potential as the renewable energy source of the near future, however the largest hurdle remains finding an efficient way to store the energy and combat the intermittent and diffuse nature of sunlight.[1] Water-splitting dye sensitized photoelectrochemical cells (WS-DSPECs) provide one way to convert the energy of sunlight into chemical bonds, in this case in the form of hydrogen gas.[1]

WS-DSPECs have many different parts, as can be seen in the figure below, and each needs to be optimized to create an efficient system. The focus of this project is to explore novel, cheap, easily synthesized, easily modifiable, and efficient metal oxides for the photoanode.

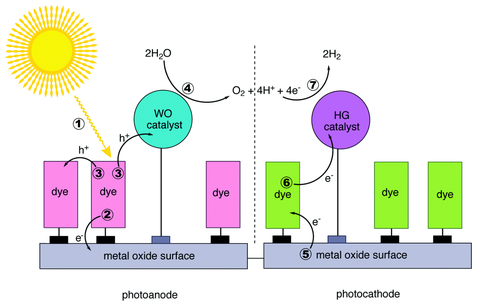


Figure from Reference 1

CuV_2O_6

In the literature different copper vanadate films have been modified via changes to the stoichiometric ratio of Cu and V, and by doping with various metals.[6]
For example, the figures shown below demonstrate that the best stoichiometry for high photocurrent for water oxidation occurs with $Cu_{11}V_6O_{26}$,[7] and the best photocurrent with chromium dopant is at 0.75% Cr.[8]

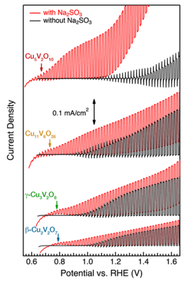


Figure from Reference 2

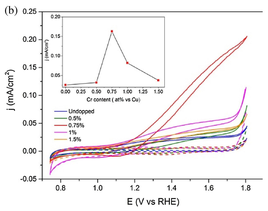


Figure from Reference 3

Heterogenized Molecular Catalysts

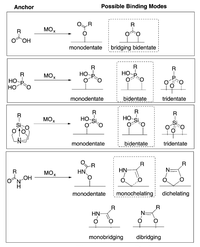


Figure from Reference 1

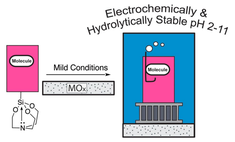


Figure from Reference 4

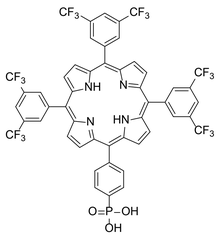
Metal oxide photoanodes can be modified by heterogenizing molecular catalysts via anchoring groups.[1,4] This method combines many of the benefits of heterogeneous and homogeneous catalysis including:

- High Selectivity
- High Stability
- A singular, well-defined active site

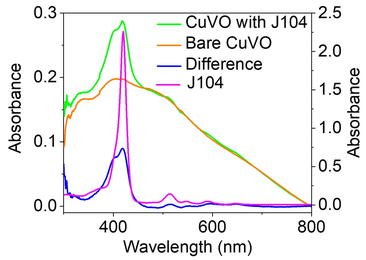
Loading on CuV_2O_6

In order to improve the performance of CuV_2O_6 we are looking into different methods of attaching a catalyst.

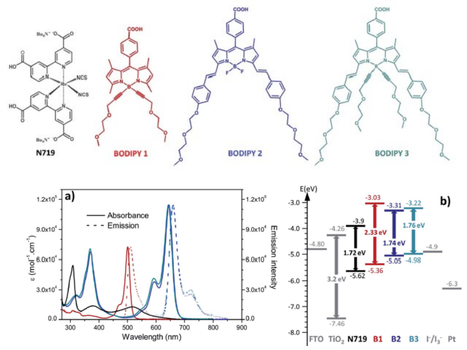
- There has been some success with the "blue solution" but there are issues with stability.
- Using anchoring groups, such as phosphonates, to attach a water oxidation catalyst can offer a solution to the stability problem.
- Porphyrin **J104** was used to observe the loading and as a proxy for catalyst loading UV-vis measurements show loading through increased absorbance at wavelengths which correspond with the same peaks of **J104** absorbance.



J104 Porphyrin
Synthesized by Jianbing Jiang



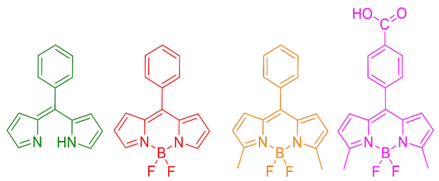
BODIPY as a photosensitizer

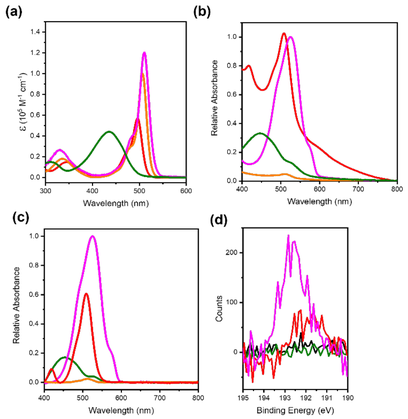


Figures from Reference 5

BODIPY is a common molecule used in a variety of fields including optoelectronics and biological imaging. It has also been used as a photosensitizer in DSSCs. In papers such as reference 5 seen above the molecules are attached to the metal oxide surface using carboxylic anchoring groups.

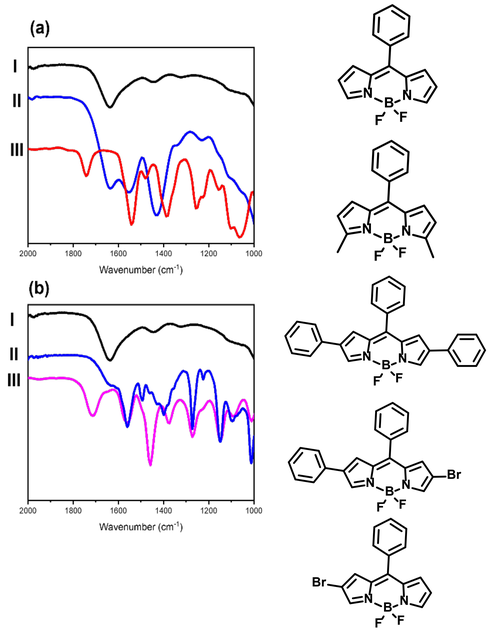
BODIPY loading





We have found that BODIPY is able to bind to metal oxide surfaces without synthetically adding an anchoring group. By UV-vis and XPS studies we were able to show that the Boron remains attached to the dyprrin ligand.

Future Work



We want to learn more about the binding mode of BODIPY onto TiO_2 by comparing the loading of a series of derivative molecules. We also want to look at spectroscopic techniques such as IR and XPS to help elucidate the mechanism of binding.

References

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