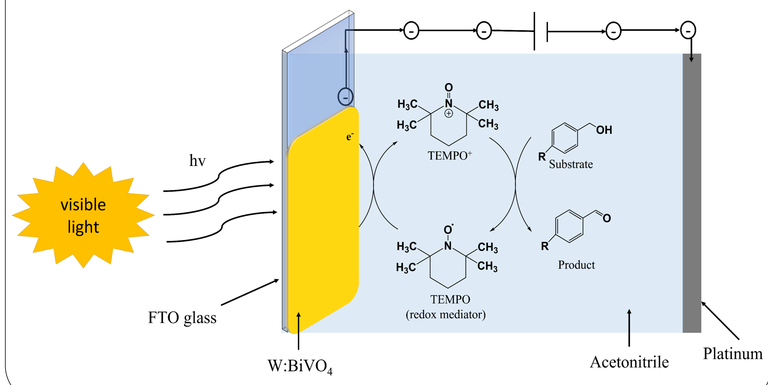
Polyethylene glycol (PEG)-assisted Morphology Control of Tungsten Doped Bismuth Vanadate (W:BiVO4) Materials and Their Application in Photoelectrochemical Reactions

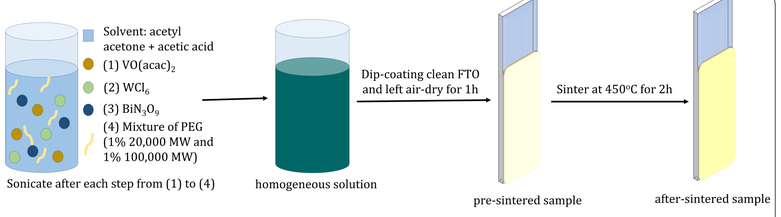
Khanh Nguyen, Nelli K. McMillan and Benjamin D. Sherman
Department of Chemistry & Biochemistry, Texas Christian University, TX 76129

Introduction

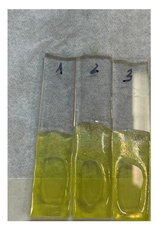
Various semiconductor metal oxides such as ZnO, TiO_2, WO_3, and $BiVO_4$ have been utilized for photoelectrochemical (PEC) water-splitting as well as for value added alternative reactions.[1-2] However, single-phase materials often face multiple challenges including poor charge separation efficiency and surface degradation especially in aqueous environment. $BiVO_4$ is a promising photoanode material, but the above-mentioned shortcomings are still present. We suggest to use $BiVO_4$ materials to perform alternative reactions at the anode that can yield a value-added products, i.e oxidation to primary alcohols to aldehydes. Therefore, in order to enhance the PEC performance of $BiVO_4$,our group has focused on doping techniques for $BiVO_4$ with tungsten (W) to yield tungsten doped $BiVO_4$ (W:$BiVO_4$). In addition, polyethylene glycol (PEG) has also been introduced to the material as a morphological control agent. The addition of polymer to the precursor solution helps to control the porosity of the resulting surface film by promoting a less porous and more compact formation of $BiVO_4$ on FTO.[3]



Method



- **Preparation of FTO|W:$BiVO_4$ + PEG.** Repeat dip-coating and sintering to obtain 2-layers-samples.
- **Preparation of FTO|W:$BiVO_4$ without PEG.** The procedure is the same as described above but without the addition of the mixture of PEG.
- Each photoanode is subjected to UV-Vis spectroscopy. Then, TAUC plots were constructed based on the UV-Vis data in order to obtain band gap of the materials.
- The photochemical oxidation of TEMPO: samples were illuminated from the back.

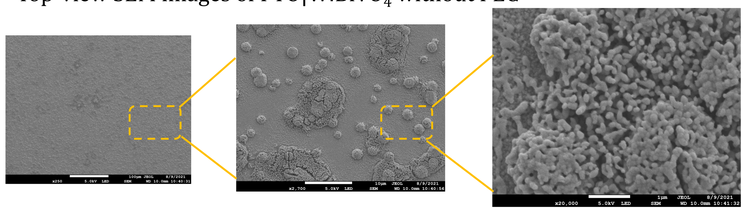


FTO:W:$BiVO_4$ + PEG (2L) after depositing epoxy

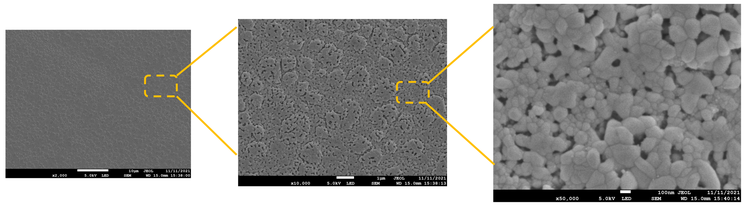
Results

A) Scanning Electron Microscopy (SEM) Images

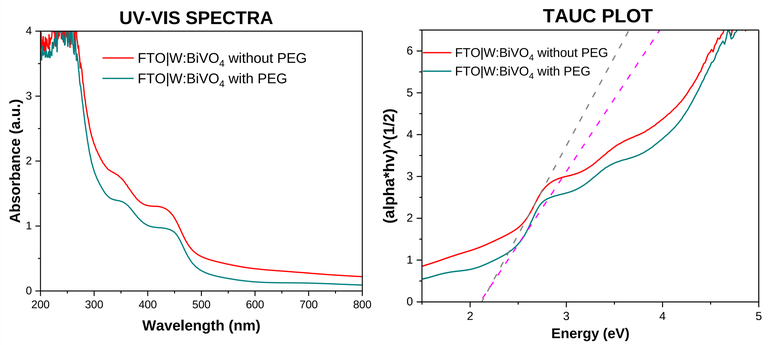
Top-view SEM images of FTO|W:$BiVO_4$ without PEG



Top-view SEM images of FTO|W:$BiVO_4$ with PEG

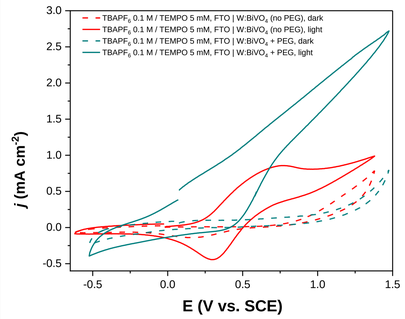


B) Ultraviolet-visible profiles and TAUC Plots

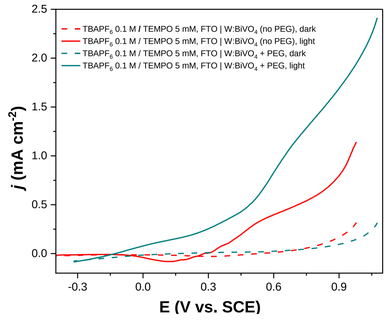


UV-Vis profiles of W:$BiVO_4$ electrodes with and without adding PEG (left) and the TAUC plot (right) constructed based UV-Vis data. Linear fitting the TAUC plot helps determine the band gap of FTO|W:$BiVO_4$ with and without PEG, which are 2.24 eV and 2.30 eV, respectively.

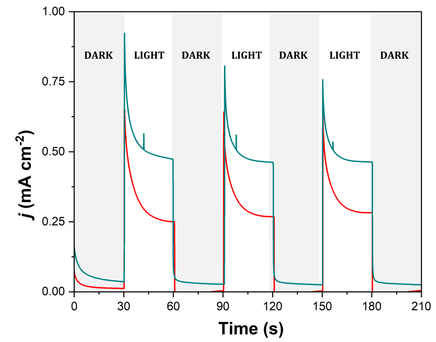
C) Photoelectrochemical Activity



CV in electrolyte (0.1 M $TBAPF_6$), with 5 mM TEMPO, Solid lines indicate photocurrents upon illumination and dashed lines- dark currents.



LSV in electrolyte (0.1 M $TBAPF_6$), with 5 mM TEMPO, Solid lines indicate photocurrents upon illumination and dashed lines- dark currents.



CA in electrolyte (0.1 M $TBAPF_6$), with 5 mM TEMPO with 30s dark-light intervals. Applied bias of 0.3 V vs. Ag/Ag^+ (calibrated to SCE with ferrocene, $E_{,Fc^+/Fc}$= 0.45 vs. SCE). Green line is the performance of W:BiVO4 with PEG while red line is the performance of W:BiVO4 without the addition of PEG.

References

1. Reid. M.L. *et al.* Sustainable Energy Fuels. 1905-1927.
2. Cao, Y. *et al*. Surface Engineering of WO3/BIVO4 to boost solar water-splitting. Catalysts 10, 556.
3. Li, T. *et al*. Photoelectrochemical oxidation of organic substrates in organic media. Nature Communications, 8(1).

The Michael and Sally McCracken Annual
Student Research Symposium

THE Welch FOUNDATION

Conclusion

- **SEM images** have shown that the surface of W:$BiVO_4$ with PEG is more compact than those without PEG.
- However, the addition of PEG did not produce any significant benefit in terms of band gap since samples with PEG have a **band gap** of 2.24 eV on average while samples without PEG have a band gap of 2.30 eV, on average.
- **Photocurrent density** of PEG (1% MW 100,000 : 1% M 20,000) - W:$BiVO_4$ (0.58 $mAcm^{-2}$ with an applied biased of 0.3 V vs. SCE) has outperformed that of W:$BiVO_4$ without PEG (0.30 $mAcm^{-2}$ with an applied biased of 0.3 V vs. SCE). Based on the data obtained, PEG(1% MW 100,000 : 1% MW 20,000) - W:$BiVO_4$ outperformed W:$BiVO_4$ by approximately 2 times.
- **Future work**: In the future, the best performing electrode samples will be studied for driving TEMPO-mediated benzyl alcohol oxidation.