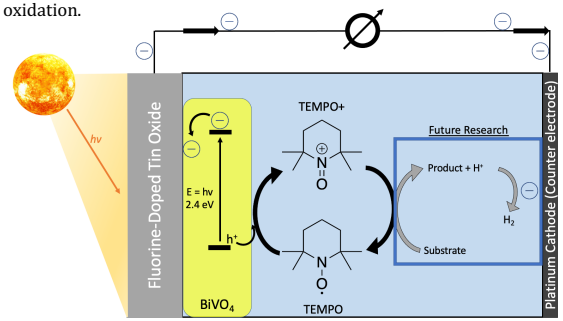
Effect of Polyethylene Glycol on the Fabrication of Nanostructured $BiVO_4$ Photoanodes for Photoelectrochemical TEMPO-Mediated Oxidations

Jacob N. Wortley, Nelli K. McMillan and Benjamin D. Sherman*
Department of Chemistry & Biochemistry, Texas Christian University, TX 76129

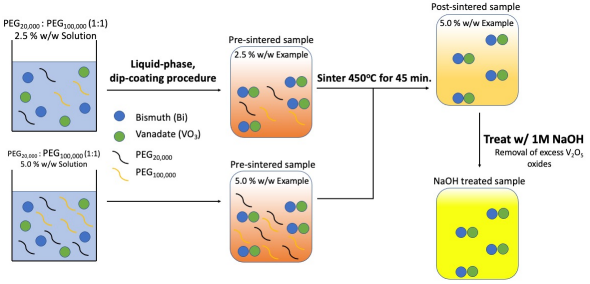
Introduction

Bismuth Vanadate ($BIVO_4$) is a promising semiconductor for solar energy conversion. Due to its non-toxic properties and ability to absorb in the visible light spectrum, $BiVO_4$ is of interest as an alternative to common silicon-based semiconductors. $BiVO_4$ offers an optimal band gap to perform water oxidation for hydrogen fuel production applications. This work focuses on the oxidation of the redox mediator, 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), to aid in oxidation of potential substrates for H_2 production. In this study, we examine the oxidative performance of $BiVO_4$ photoanodes under varying concentrations of the structure-directing polymer, Polyethylene glycol (PEG). PEG is a useful agent in altering film thickness, porosity, and surface area. Morphology and optical measurements were completed using FESEM and UV-Vis Spectrophotometry to understand effects of PEG on $BiVO_4$ deposition. Photoelectrochemical measurements using Linear Sweep Voltammetry and Chronoamperometry were utilized to measure resultant TEMPO oxidation.



PEC cell set up with $BiVO_4$ photoanode

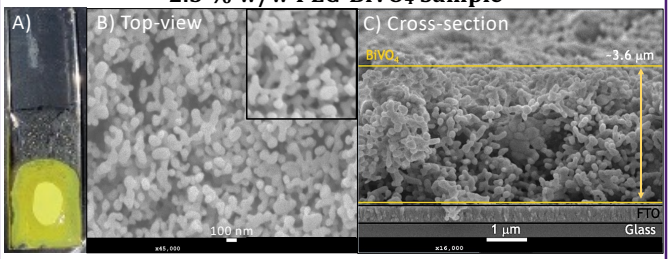
Research Method



Results

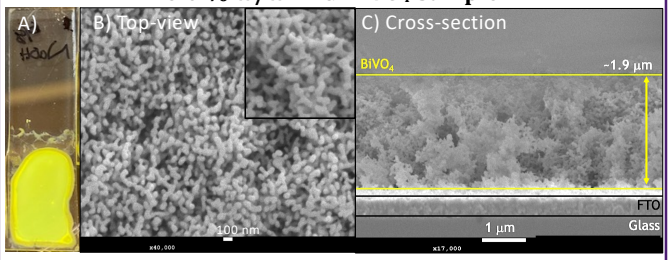
1. FESEM Characterization

2.5 % w/w PEG-$BiVO_4$ Sample



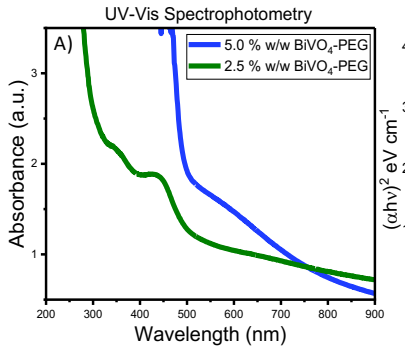
A. Optical image of photoanode with epoxy layer. B. Top view of $BiVO_4$ interface magnified 45,000x. C. Cross-section view of interface magnified at 16,000x with markers indicating deposition thickness.

5.0 % w/w PEG-$BiVO_4$ Sample

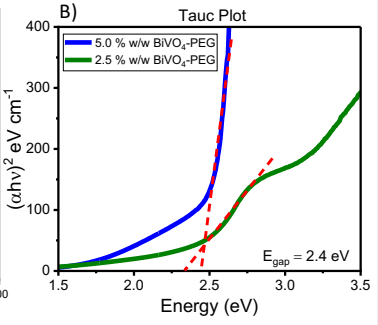


A. Optical image of photoanode without epoxy layer. B. Top view of $BiVO_4$ interface magnified 40,000x. C. Cross-section view of interface magnified at 17,000x with markers indicating deposition thickness.

2. Ultraviolet-Visible Measurements

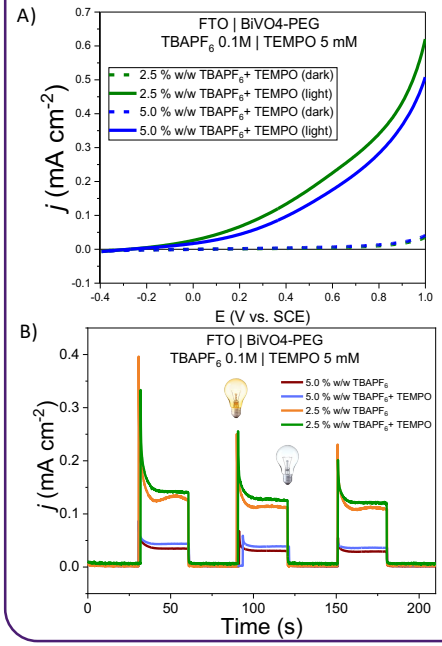


A) UV-Vis absorption spectrum of $BiVO_4$ electrodes based on composition of PEG.



B) Tauc plots extrapolated from UV-Vis measurements. $BiVO_4$'s direct band gap is typically reported as 2.4 eV.

3. PEC Measurements



A) Linear Sweep Voltammetry (LSV) taken under dark and light conditions. All measurements were recorded at 50 mV/s in acetonitrile solution containing 5 mM TEMPO in 0.1 M $TBAPF_6$.

B) Chronoamperometry (CA) taken under dark and light conditions. PEC conversion of TEMPO to $TEMPO^+$ under applied bias of 0.3 V vs SCE (calibrated from Ag/Ag^+ quasi-reference electrode). Measured in acetonitrile solution containing 5 mM TEMPO in 0.1 M $TBAPF_6$.

Conclusion

- $BiVO_4$-PEG photoanodes are easily produced via a dip-coating deposition method.
- Varying PEG concentration within $BiVO_4$ photoanodes directly effects film thickness.
- 2.5% w/w $BiVO_4$-PEG photoanodes obtained a higher photocurrent density than 5.0% w/w films.
- Lower PEG concentration photoanodes increases film thickness.

References

1. Park, Y., McDonald, K. J., et al. (2013). Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chemical Society Reviews, 42*(6), 2321-2337.
2. Mohamed, E. A., Zahran, et al. (2017). Simple preparation of highly active water splitting FTO/BiVO4 photoanode modified with tri-layer water oxidation catalysts. *Journal of Materials Chemistry., 5*(15), 6825-6831.
3. Barhdadi, R., Comminges, C., et al. (2007). The electrochemistry of TEMPO-mediated oxidation of alcohols in ionic liquid. *Journal of Applied Electrochemistry, 37*(6), 723-728.

Acknowledgments

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