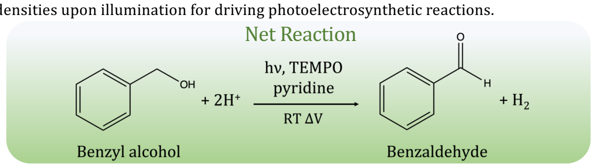
Fabrication and Characterization of WO_3-$BiVO_4$ Heterojunction Electrodes for Use in Photoelectrosynthetic Applications

Jacob N. Wortley, Khanh Nguyen, Nelli K. McMillan, and Benjamin D. Sherman

Department of Chemistry & Biochemistry, Texas Christian University, TX 76129

Introduction

Light-driven reactions, such as those utilized in photoelectrosynthetic applications, focus on capturing and transferring light energy to drive chemical reactions. For this purpose, light-active metal oxide semiconductor materials are used, such as $BiVO_4$, α-Fe_2O_3, and WO_3 to list a few. Previous work demonstrated the use of $BiVO_4$ electrodes to drive the oxidation of benzyl alcohol to benzaldehyde in the presence of a TEMPO (2,2,6,6-tetramethylpiperidine) mediator.[1] This study seeks to improve the photoelectrochemical performance of this reaction by using a heterojunction WO_3-$BiVO_4$ electrode. We hypothesize that the heterojunction would decrease charge carrier recombination and improve the photochemical yield of the reaction compared to a $BiVO_4$ electrode.[2,3] The WO_3-$BiVO_4$ interface forms a type II band alignment allowing electrons from photoexcited $BiVO_4$ to transfer into WO_3 and holes to accumulate at the $BiVO_4$-electrolyte interface.[4] Two techniques, UV-visible spectroscopy and incident photon-to-current efficiency (IPCE) measurements, were applied to better understand why the heterojunction improved the photocurrent density in the presence of reaction components in solution. UV-visible spectroscopy was used to determine the band gaps of the materials. Information about the efficiency of light energy conversion to chemical energy was obtained by IPCE measurements. IPCE values are determined by relating the proportion of incident light power to the current produced by illuminating the WO_3-$BiVO_4$ photoanode over a small wavelength range. Photoanodes exhibiting higher IPCE % are more effective at driving photoelectrosynthetic reactions.[1] To test the effect of WO_3 on the energy conversion efficiency, IPCE experiments were run for the WO_3-only, $BiVO_4$-only, and WO_3-$BiVO_4$ samples. Comparing IPCE values for WO_3-$BiVO_4$ samples shows a clear increase compared to $BiVO_4$-only photoanodes. These results demonstrate how coupled materials (WO_3-$BiVO_4$) can generate higher current densities upon illumination for driving photoelectrosynthetic reactions.



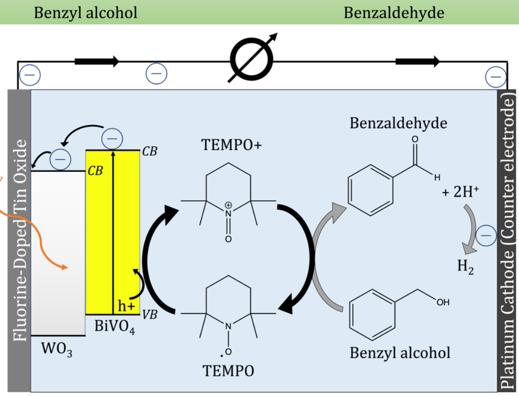


Figure 1. A general scheme of our photoelectrochemical cell with the type II band-aligned WO_3-$BiVO_4$ heterojunction used to drive the dehydrogenation of benzyl alcohol.

Results

1. Characterization of Electrodes

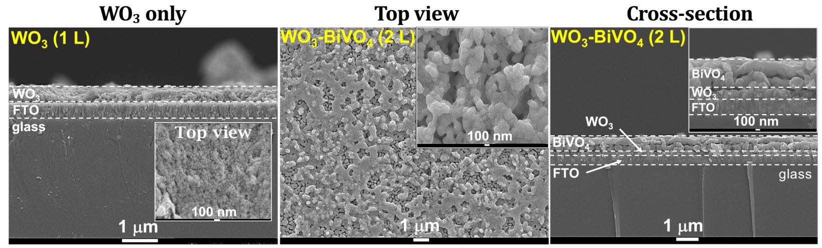


Figure 2. FESEM images of electrodes on FTO. (Left) Cross-section and top views of WO_3 with one layer (1L). (Middle) Top view of WO_3-$BiVO_4$ (2L). (Right) Cross-section of WO_3-$BiVO_4$ (2L)

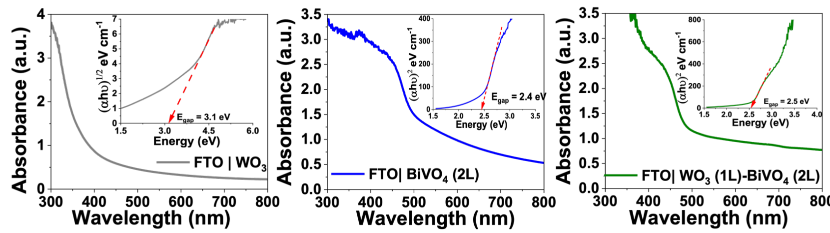


Figure 3. UV-visible absorption spectra of $FTO|WO_3$ (grey), $FTO|BiVO_4$ (2L) (blue), and $FTO|WO_3$–$BiVO_4$ (2L) (green) electrodes. The insets show corresponding Tauc plots with the indicated band gaps (E_{gap}).

2. Photoelectrochemical Measurements

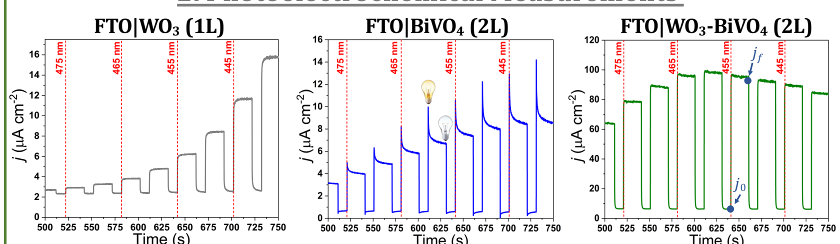
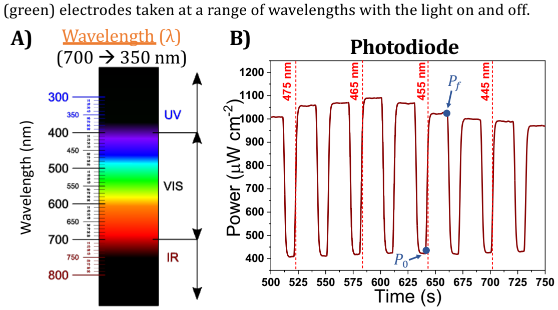


Figure 4. Transient photocurrent measurements of $FTO|WO_3$ (grey), $FTO|BiVO_4$ (2L) (blue), and $FTO|WO_3$–$BiVO_4$ (2L) (green) electrodes taken at a range of wavelengths with the light on and off.



Photocurrent Density (j)

$$j = \frac{j_f - j_0}{Electrode\ surface\ area}$$

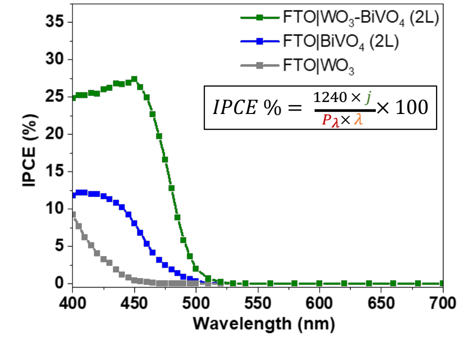
Power Density (P_λ)

$$P_\lambda = \frac{P_f - P_0}{Diode\ surface\ area}$$

$$IPCE\ \% = \frac{1240 \times j}{P_\lambda \times \lambda} \times 100$$

Figure 5. A) photoelectrochemical measurements occurred at visible light wavelengths from 700 → 350 nm.[5] B) Photodiode measurements of incident light power taken at a range of wavelengths with the light on and off.

3. Incident Photon-to-Current Efficiency



Sample type	IPCE % λ = 450 nm
WO_3	<1%
$BiVO_4$	5%
WO_3-$BiVO_4$	28%

Figure 6. Incident photon to current efficiency (IPCE) measured with the $FTO|WO_3$ (grey), $FTO|BiVO_4$ (2L) (blue), and $FTO|WO_3$–$BiVO_4$ (2L) (green) electrodes in an acetonitrile solution with 0.1 M $TBAPF_6$, 5 mM TEMPO, 25 mM benzyl alcohol, and 100 mM pyridine at 0.6 V vs. SCE applied potential.

Conclusion

- WO_3-$BiVO_4$ electrodes are easily produced at low cost via a liquid-phase deposition method.
- The band gap of WO_3-$BiVO_4$ electrodes is in between the E_{gap} for WO_3 and $BiVO_4$ alone.
- IPCE is an effective technique to measure the light-to-energy conversion of $BiVO_4$-based semiconductors.
- The WO_3-$BiVO_4$ heterojunction exhibited the highest IPCE of 28% at 450 nm light exposure.
- WO_3-$BiVO_4$ heterojunctions exhibit a higher photocurrent density upon illumination than WO_3 and $BiVO_4$ semiconductors.

References

1. McMillan, N.K., *et al. ChemPlusChem* **2022**, *87*, e202200187.
2. Tan, H.L., *et al. Particle Systems Characterization.* **2016**, *34*. 11-22.
3. Peter, L.M., *et al. Faraday Discuss.* **2012**, *155*, 309-322.
4. Zheng, Z., *et al. Materials Today Physics* **2020**, *15*, 100262.
5. Fulvio314. Light spectrum, retrieved April 10, **2023**.

Acknowledgements

The Welch Foundation

TCU College of Science & Engineering, Department of Chemistry & Biochemistry