$BiVO_4$ Film Preparation in $WO_3/BiVO_4/NiO$ Heterojunctions for Photoelectrochemical TEMPO-Mediated Oxidations

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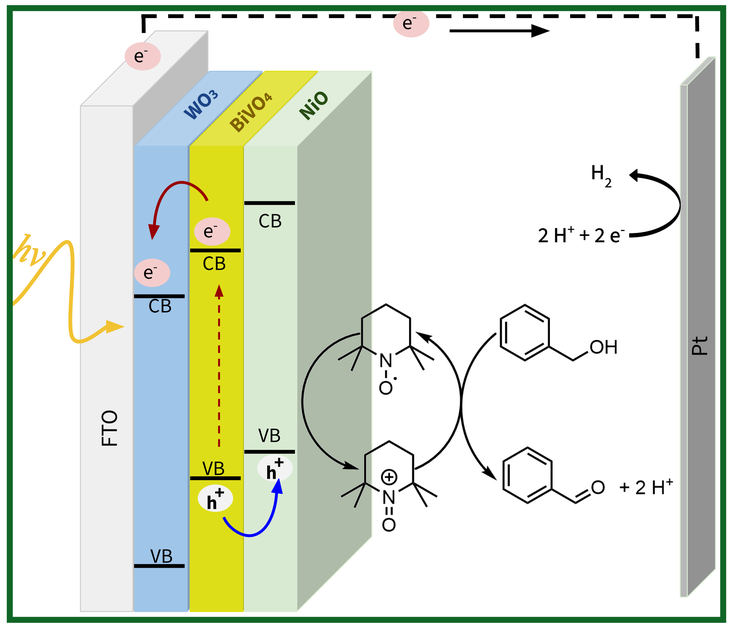
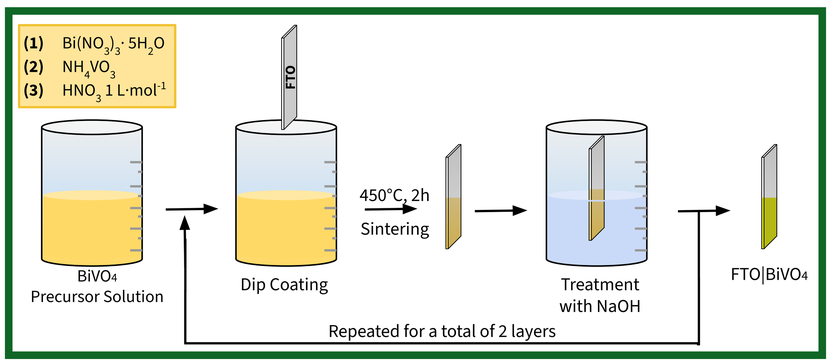
Introduction

$BiVO_4$ has been widely studied as a photoanode material due to its ability to absorb visible light and suitable band gap for photoelectrochemical oxidation. However, deposition of uniform and stable films play a large role in its performance. Initial efforts focused on optimizing $BiVO_4$ deposition on FTO by refining precursor concentration, dipping frequency, drying conditions, and post-treatment to develop a reproducible method with consistent film thickness. While $BiVO_4$ alone demonstrates promising PEC activity, further improvement has been well documented with the addition of a WO_3 base layer to enhance charge separation.[1] An additional NiO layer to $WO_3/BiVO_4$ heterjuctions is hypothesized to improve PEC performance by enhancing catalytic efficiency and charge seperation, reducing recombination and stabilizing the photoanode. This work focuses on optimizing $BiVO_4$ deWposition as part of a larger effort to develop an efficient triple-layer heterojunction for PEC TEMPO oxidation.



Methods



Results

A. Thickness and Uniformity

Table 1. Summary of $BiVO_4$ sample conditions and resulting film thickness

Set	Bi:V (mmol)	Dipping Cycles	Drying Conditions	Thickness (nm)
1	1.63 : 2.00	2	RT-O[1]	504 (70)
2	1.63 : 2.00	1	RT-O	306 (50)
3	1.63 : 2.00	1	RT-C[2]	324 (50)
4	1.63 : 2.00	2	RT-C	407 (140)
5	2.00 : 2.00	2	RT-C	-
6A	2.00 : 2.00	2	OVN[3]	-
6B	2.00 : 2.00	2	HUM[4]	-
7	2.00 : 2.00	2	RT-K[5]	299 (30)
8	2.00 : 2.00	2	RT-K	310 (50)

[1] **RT-O:** Dried in open air at room temperature
[2] **RT-C:** Dried at room temperature while covered with a dish
[3] **OVN:** Dried in an oven at 108°C
[4] **HUM:** Dried under conditions of elevated humidity
[5] **RT-K:** Dried in open air at room temperature on a cold countertop

B. UV-Visible Spectra

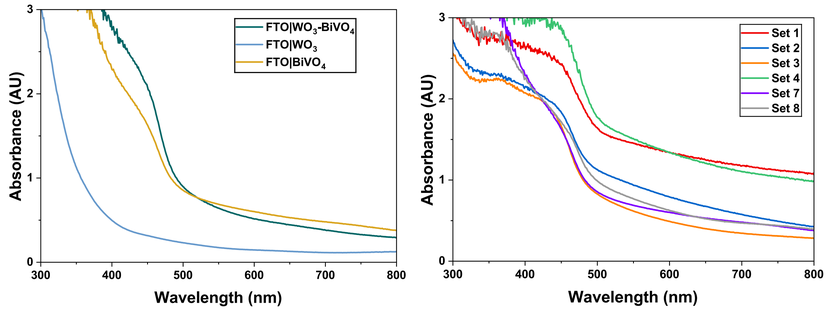


Figure 1. UV-Vis absorbance spectra of $BiVO_4$ samples from Sets 1 through 8 (right) and comparative UV-Vis spectra for $FTO|WO_3$, $FTO|BiVO_4$, and $FTO|WO_3$-$BiVO_4$ electrodes (left).

C. Current-Voltage Characterization

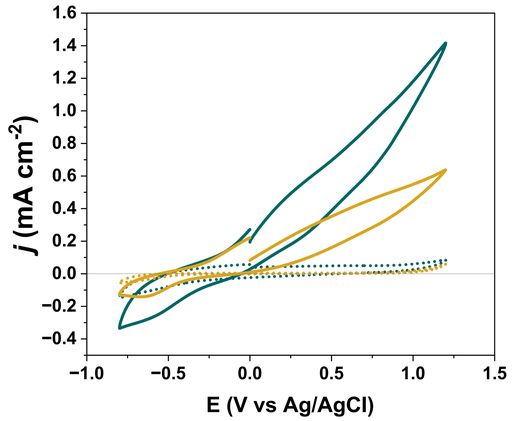


Figure 2. Cyclic voltammograms of $FTO|BiVO_4$ (yellow) and $FTO|WO_3$-$BiVO_4$ (teal) electrodes under dark (dashed) and illuminated (solid) conditions. Scans were recorded at 50 mV s^{-1} in acetonitrile containing 0.1M $TBAPF_6$ and 5 mM TEMPO. Illumination was provided at 100 mW cm^{-2}.

D. Transient Characterization

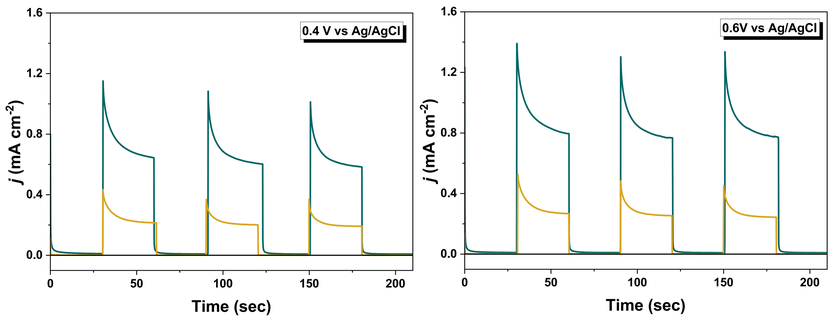
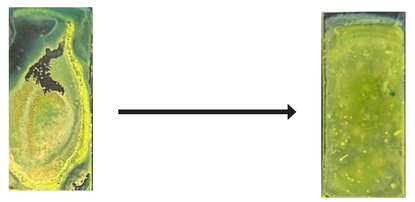


Figure 3. Transient photocurrent measurements of $FTO|BiVO_4$ (yellow) and $FTO|WO_3$-$BiVO_4$ (teal) electrodes under 30 s illumination intervals in 0.1M $TBAPF_6$ electrolyte with 5 mM TEMPO. Photocurrents were recorded under an applied bias of 0.4 V vs Ag/AgCl (left) and 0.6 V vs Ag/AgCl (right).

Conclusions

A reproducible protocol for $BiVO_4$ film deposition was developed, yeilding uniform and consistent films suitable for heterojunction integration. Drying rate was identified as a critical factor influencing film quality - rapid drying led to uneven depostion and thickness variation, while slow drying comprimised adhesion. UV-Vis spectroscopy confirmed $BiVO_4$ absoption in the visible range, supporting its role as a photoactive material. PEC measurments revealed enhanced photocurrent response for $WO_3/BiVO_4$ heterjunctions compared to $BiVO_4$ alone, attributed to improved charge seperation and reduced recombination.



Future Work

- Ongoing work focuses on preparing and characterizing the following electrodes:
  - » $FTO|WO_3$-$BiVO_4$-NiO
  - » $FTO|BiVO_4$-NiO
  - » $FTO|WO_3$-NiO
- Optimal NaOH treatment duration to balance $BiVO_4$ film preservation and removal of excess V_2O_5

References

1.McMillan, N. K., et al. (2023). Heterojunction WO_3-$BiVO_4$ photoanodes for TEMPO-mediated benzyl alcohol dehydrogenation in organic media. *ACS Appl. Eng. Mater.*, 1(11), 3122-3133