Liquid Phase Deposition of Nickel Oxide as a Hole Transport Layer for Light Driven TEMPO-Mediated Oxidation

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1. Introduction

TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) -mediated benzyl alcohol oxidation is a green, sustainable alternative to traditional oxidation methods[1], which often generate hazardous waste. By improving the efficiency of this process, we can reduce environmental impact in industrial and synthetic chemistry applications. NiO films, as hole transport layers, are key to enhancing the performance of photoelectrochemical systems used in these processes. Incorporating NiO onto FTO|WO_3-$BiVO_4$ electrodes can improve charge separation and oxidation efficiency, leading to more cost-effective and environmentally friendly oxidation reactions. Our research focuses on optimizing the liquid phase deposition of NiO films for improving light driven TEMPO oxidation, exploring the impact of several deposition conditions on film quality and thickness.

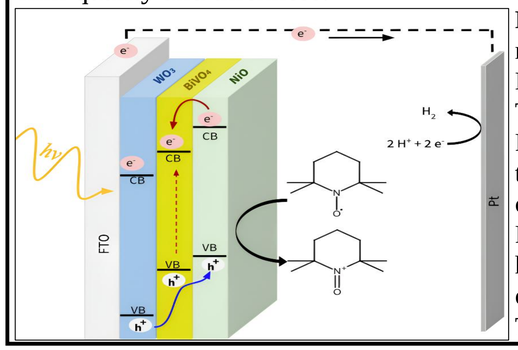


Figure 1. Charge transfer mechanism in a FTO|WO_3-$BiVO_4$ -NiO photoanode for TEMPO mediated oxidation. Photogenerated electrons transfer through the conduction bands towards the Pt counter-electrode, while holes in NiO facilitate the oxidation of TEMPO to $TEMPO^+$.

2. Methods

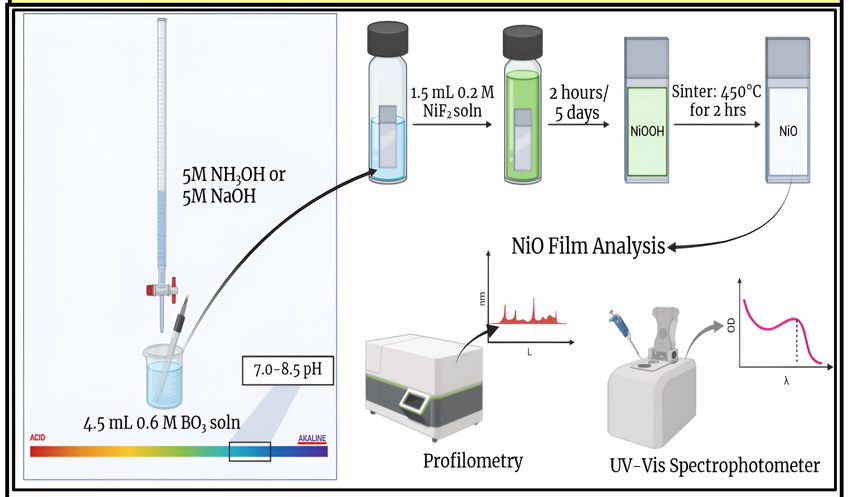


Figure 2. NiO Deposition Procedure. The 0.6 M BO_3 solution is titrated with 5 M NaOH or 5 M NH_3OH until pH range between 7.0-8.5. FTO substrate and 1.5 mL of 0.2 M NiF_2 solution is added; deposition process occurs for 4 days. FTO is removed, sintered at 450 ◦C for two hours, and the resulting NiO film is analyzed using a profilometer and UV-Vis spectrophotometer

3. Results

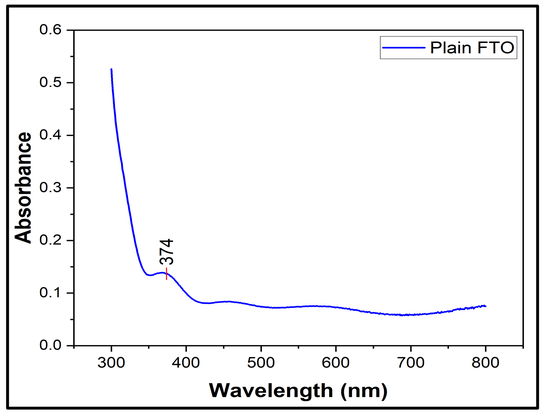


Figure 3. Absorption spectrum of FTO glass.

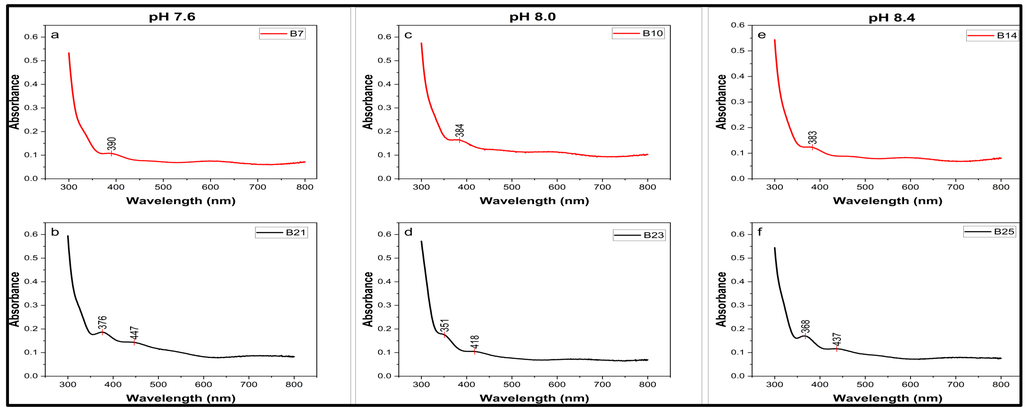


Figure 4. NiO absorbance spectra across different pH and titrants. *a,c,e*: 5 M NaOH; *b,d,f*: 5M NH_3OH at 7.6, 8.0, 8.4 pH (left-right).

Figure 5. NiO film deposition on plain FTO. 5 M NaOH treated at 7.6 pH (left) and 5 M NH_3OH treated at 7.6 pH (right.)

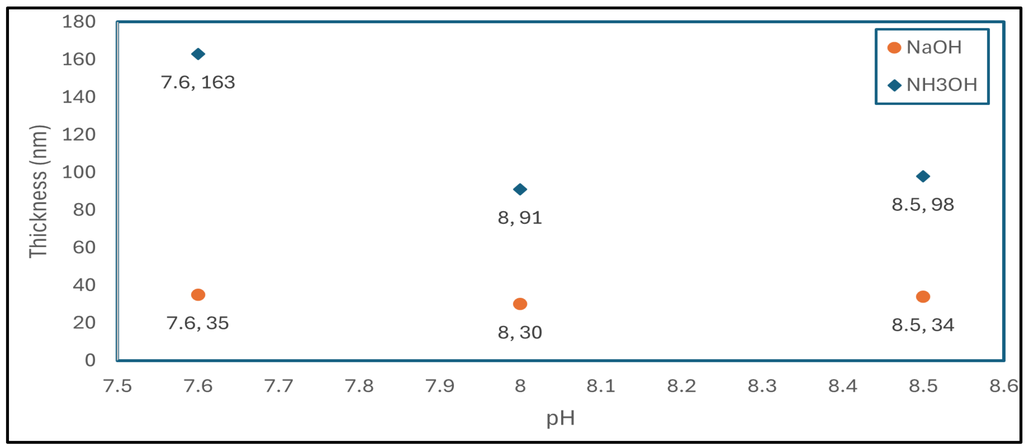
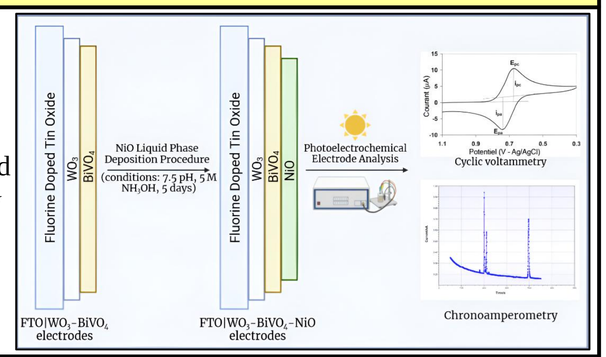


Figure 6.. pH vs. Thickness comparison among the different titrants. Blue diamonds represent 5 M NH_3OH, and orange circle represent 5 M NaOH titrant solutions.

4. Conclusion

Our experiments indicates that the uniformity and quality of NiO films are affected by the pH of the BO_3 precursor, and the type of base employed for titration. Characterization by profilometry reveals that maintaining a pH of 7.5 consistently produces uniform films with thicknesses in the range of 100–200 nm. UV–Vis spectroscopic analysis confirms the expected optical absorption of NiO in the near-ultraviolet region, with sharp peaks observed in NH_3OH samples. Further photoelectrochemical characterizations via cyclic voltammetry and chronoamperometry will further assess hole transport efficiency of the NiO films. This work establishes a scalable approach for NiO film fabrication that will enhance the performance of FTO | WO_3–$BiVO_4$ photoanodes in TEMPO-mediated oxidation processes, advancing sustainable, solar-driven alcohol oxidation with reduced environmental impact.



References:

[1]Heterojunction WO_3–$BiVO_4$ Photoanodes for TEMPO-Mediated Benzyl Alcohol Dehydrogenation in Organic Media. *ACS Applied Engineering Materials* **2023**, *1* (11), 3122–3133.