

Influence of a NiO Hole Transport Layer on Charge Separation in FTO|WO₃|BiVO₄ Photoanodes for TEMPO-Mediated Oxidation

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1. Background

- Photoelectrochemical (PEC) cells use sunlight to drive oxidation reactions at a semiconductor electrode with no toxic chemical oxidants required.
- Light generates electron-hole pairs in the photoanode; holes (h⁺) migrate to the surface to oxidize substrates while electrons (e⁻) travel through an external circuit.
- PEC systems offer a sustainable route to organic synthesis, reducing energy consumption and hazardous chemical waste.

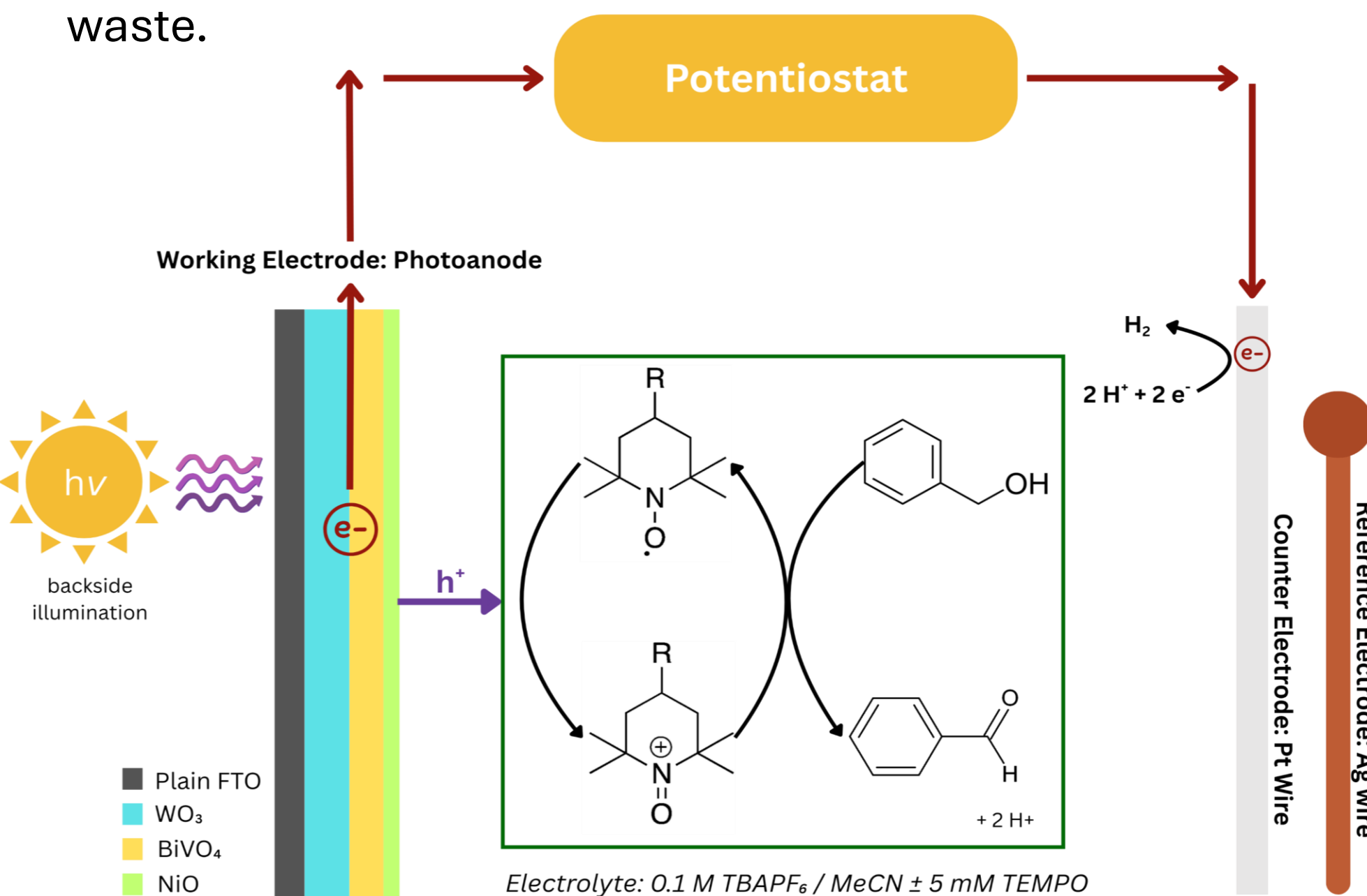


Fig. 1. Schematic of a three-electrode photoelectrochemical cell. The photoanode (WE) absorbs light to generate electron-hole pairs. Photogenerated holes oxidize TEMPO at the semiconductor-electrolyte interface while electrons flow through the external circuit to the Pt counter electrode (CE) and combines with protons to make H₂ gas. Potentials are measured against an Ag wire pseudo-reference electrode (RE).

- Conventional oxidants (PCC, CrO₃, KMnO₄) oxidize alcohols stoichiometrically and generates toxic, heavy-metal waste streams.
- TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) is a stable organic radical that selectively oxidizes benzyl alcohol to benzaldehyde without over-oxidation to benzoic acid.
- TEMPO is regenerated in every catalytic cycle, meaning no stoichiometric reagent is consumed and no metal waste is produced.

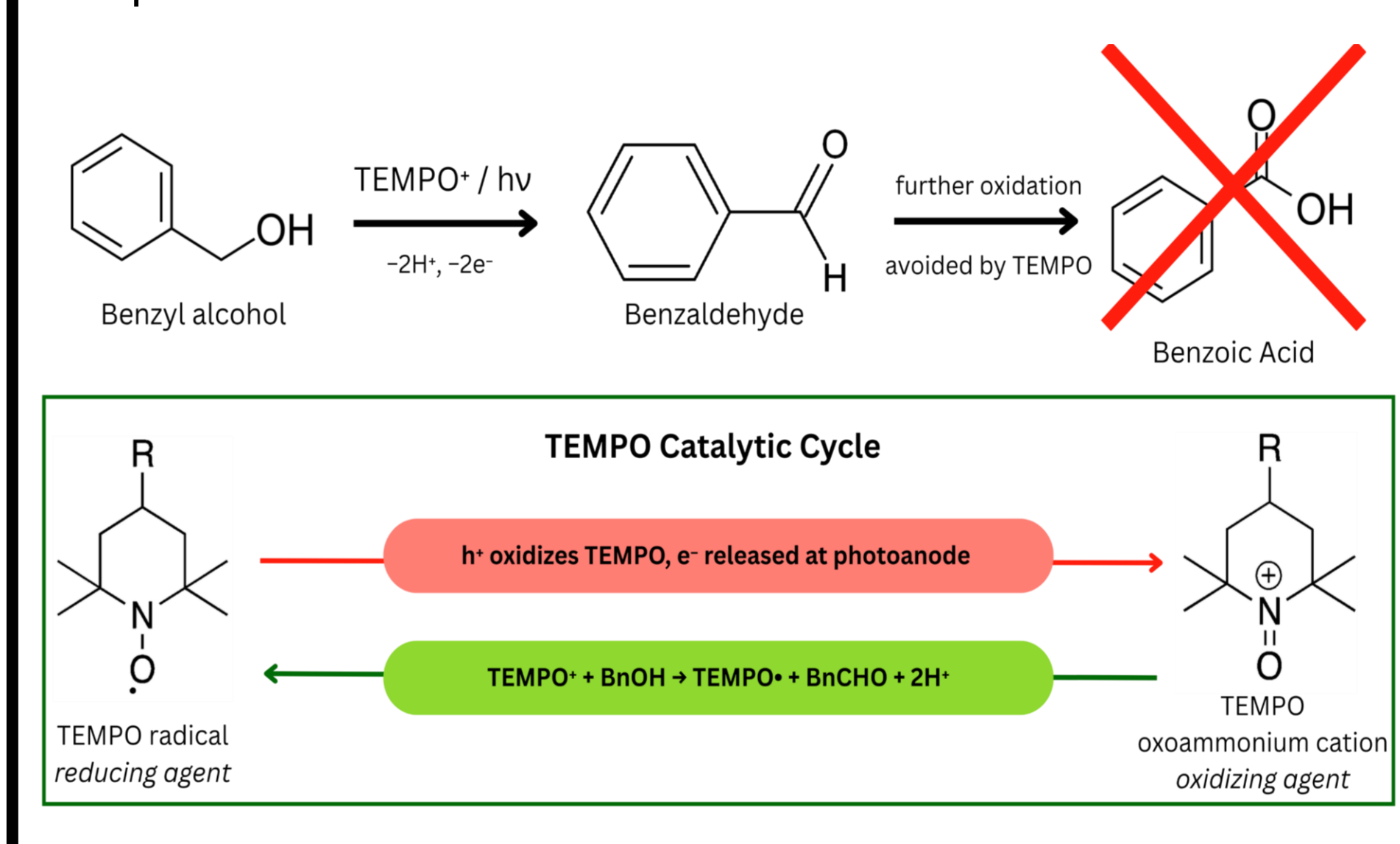


Fig. 2. TEMPO-mediated oxidation of benzyl alcohol to benzaldehyde. The upper panel shows the reaction scheme: TEMPO⁺ selectively oxidizes benzyl alcohol to benzaldehyde; further oxidation to benzoic acid is prevented by TEMPO selectivity. The lower panel details the catalytic cycle: TEMPO is oxidized to TEMPO⁺ at the photoanode surface via photogenerated holes (h⁺), and TEMPO⁺ subsequently oxidizes benzyl alcohol to regenerate TEMPO.

- BiVO₄ absorbs visible light, making it well-suited for solar-driven photo electrochemistry.
- The WO₃|BiVO₄ heterojunction promotes charge separation: electrons transfer from BiVO₄ into WO₃ while holes remain in BiVO₄ and migrate toward the surface.
- Despite this improvement, photogenerated holes accumulate at BiVO₄ surface defects and recombine with electrons before reaching TEMPO which limits photocurrent density and overall efficiency

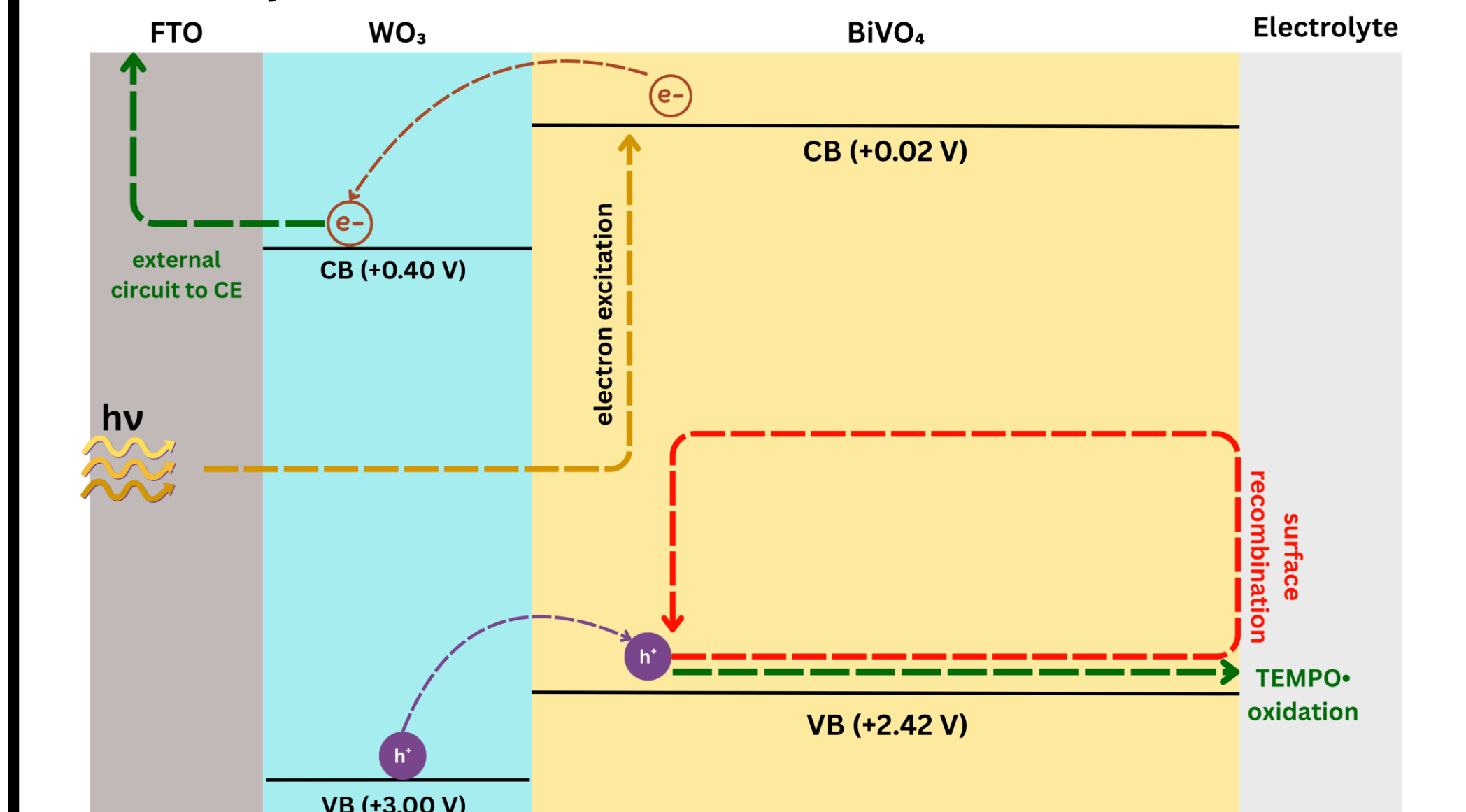


Fig. 3. Energy band diagram of the FTO|WO₃|BiVO₄ photoanode. Upon illumination, BiVO₄ absorbs visible light and generates electron-hole pairs. The favorable conduction band offset at the WO₃|BiVO₄ heterojunction drives electrons into WO₃ and toward FTO, while holes remain in BiVO₄ and migrate toward the electrolyte interface. Holes that do not reach the electrolyte interface recombine at surface defects reducing photocurrent.

2. Hypothesis

- NiO is a p-type semiconductor, transparent across the visible spectrum and Earth-abundant, making it a practical, scalable candidate.
- When deposited on BiVO₄, NiO forms a p-n junction that creates a built-in electric field, driving directional hole extraction toward the electrolyte and away from recombination sites.
- We hypothesize that incorporation of NiO will:
 - ↓ interfacial charge transfer resistance (R_{ct}),
 - ↑ steady-state photocurrent density in the presence of TEMPO, and
 - ↑ heterogeneous electron transfer rate constants (k₀).

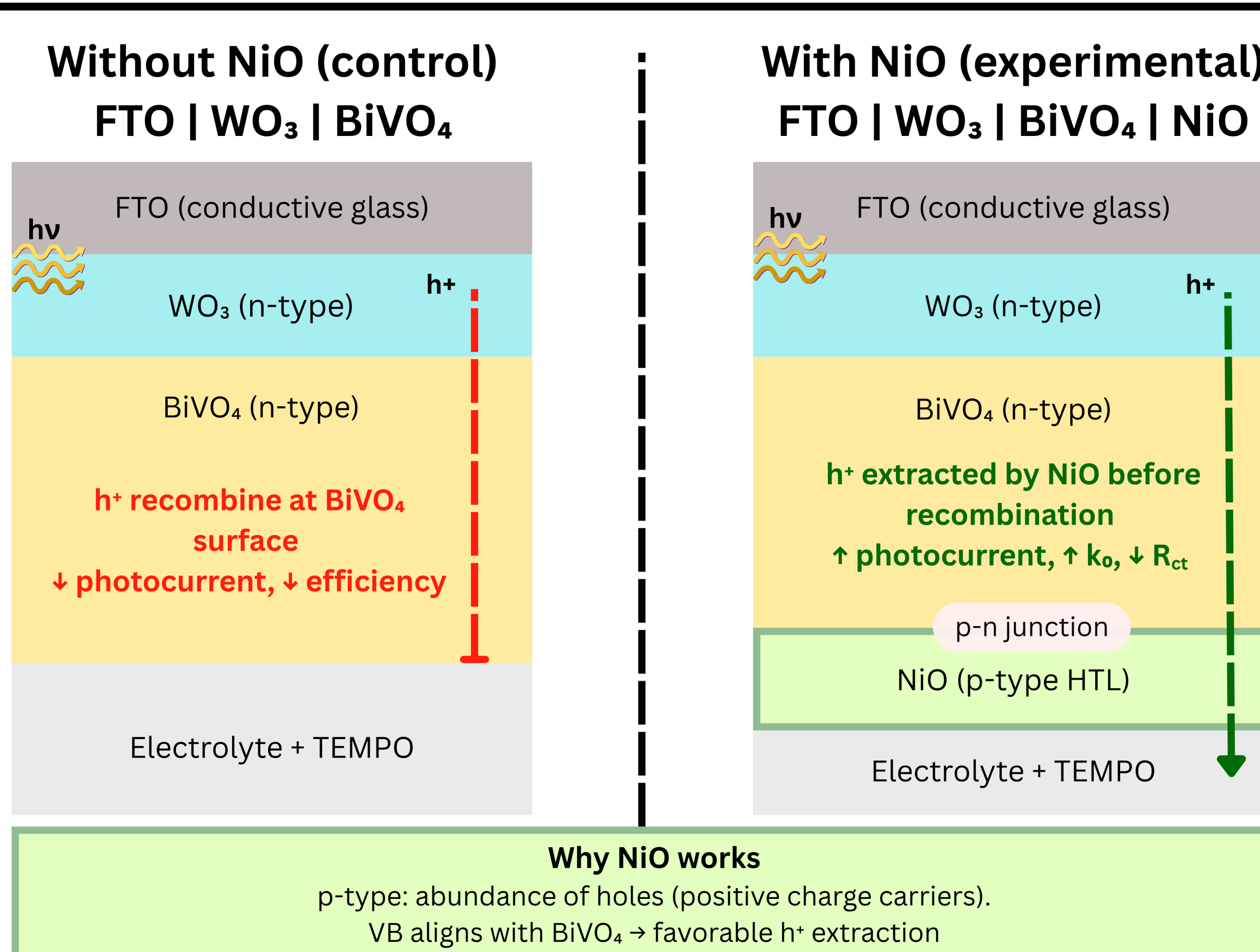


Fig. 4. Cross-sectional comparison of control (FTO|WO₃|BiVO₄) and experimental (FTO|WO₃|BiVO₄|NiO) photoanodes. In the control (left), photogenerated holes accumulate at BiVO₄ surface defects and recombine before reaching TEMPO, reducing photocurrent. In the experimental photoanode (right), the NiO hole transport layer (HTL) forms a p-n junction at the BiVO₄|NiO interface, driving directional hole extraction through NiO to the electrolyte where TEMPO oxidation occurs.

3. Methods

Fabrication of NiO Layer using Liquid Phase Deposition

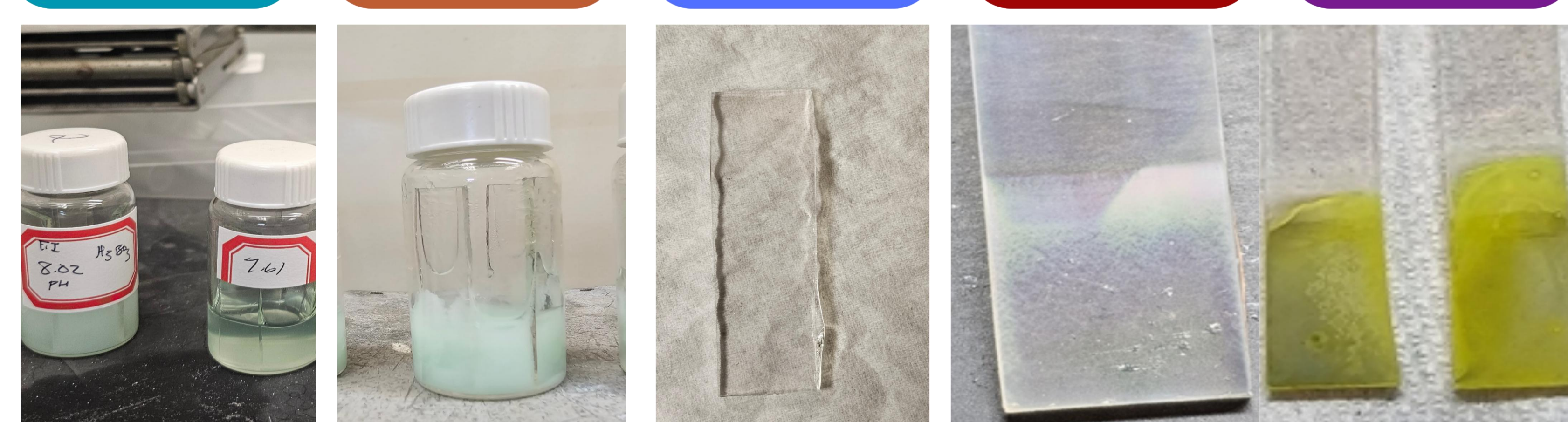
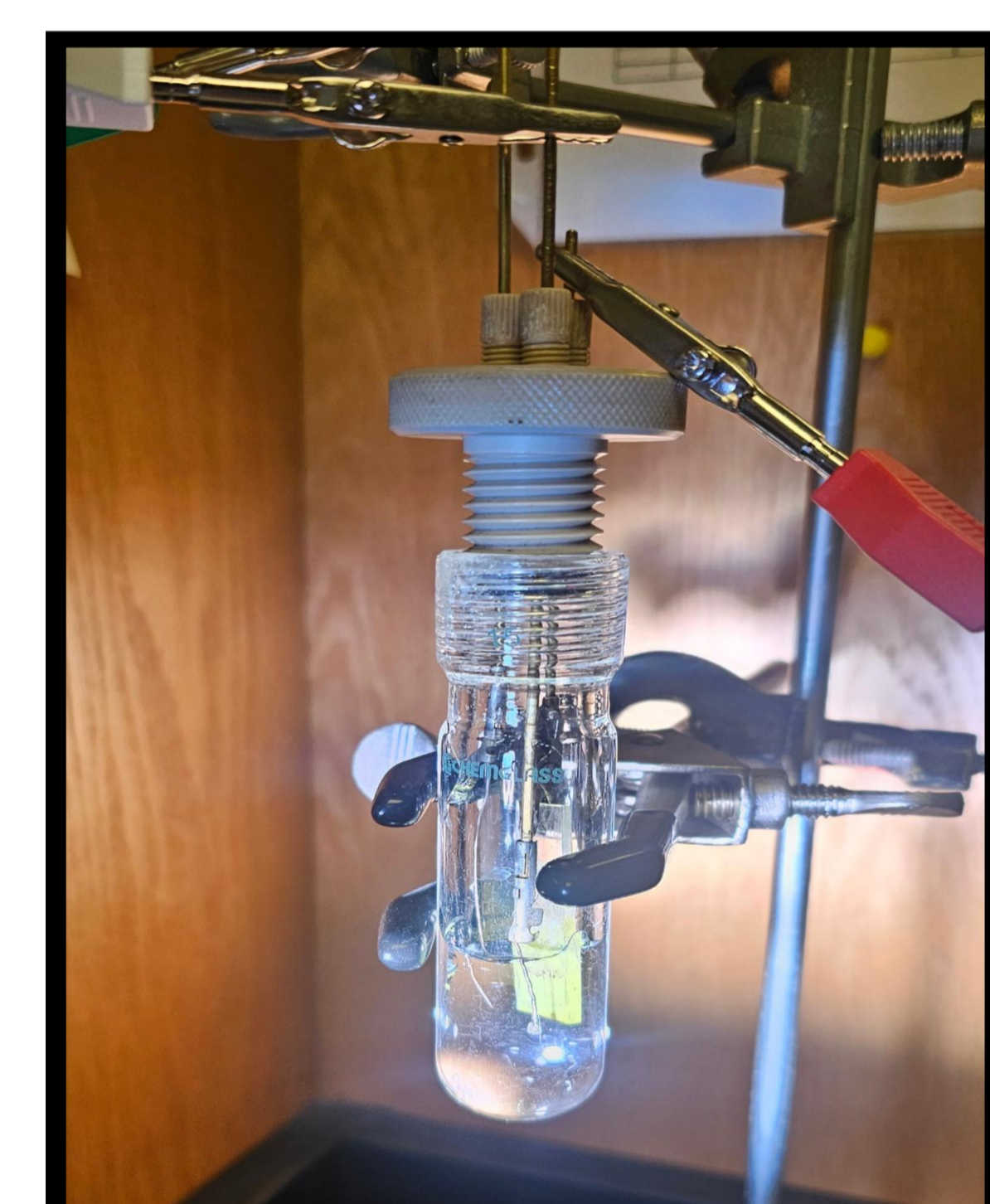


Fig. 5 : Step 1: Solution of 0.2 M NiF₂ and 0.6 M H₃BO₃ is prepared and titrated to pH 7.0 with NH₄OH. Step 2: Cleaned FTO is immersed conductive-side inward and left undisturbed at room temperature for 24 hours. Step 3: FTO is removed, the non-conductive side wiped and air-dried for 10 minutes; the deposited film is amorphous Ni(OH)₂. Step 4: Film is sintered at 450°C (ramp 1 hr, hold 2 hr, cool 1 hr), converting Ni(OH)₂ to crystalline NiO. Deposition chemistry: [NiF₂]²⁺ + 2H₂O → Ni(OH)₂ + 4HF; boric acid scavenges free F⁻, driving hydrolysis. Thermal conversion: Ni(OH)₂ → NiO + H₂O (450°C).

Electrochemical Characterization



- Cyclic Voltammetry (CV):**
 - Electron transfer rate constant (k₀)
 - Redox potentials
 - Reaction reversibility
- Chronoamperometry (CA):**
 - Stability of the electrode
 - Catalytic durability
 - Diffusion behavior
- Electrochemical Impedance Spectroscopy (EIS):**
 - Charge transfer resistance (R_{ct})
 - Interfacial kinetics
 - Resistive / capacitive components

Fig. 6. Three-electrode electrochemical cell configuration. The photoanode (working electrode, WE) is illuminated from the substrate side (backside illumination). A platinum wire serves as the counter electrode (CE) and an Ag wire pseudo-reference (RE) is used, calibrated against a standard. All measurements conducted in 0.1 M TBAPF₆/ACN at room temperature. Electrochemical characterization included cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS).

4. Key Results

A. Cyclic Voltammetry

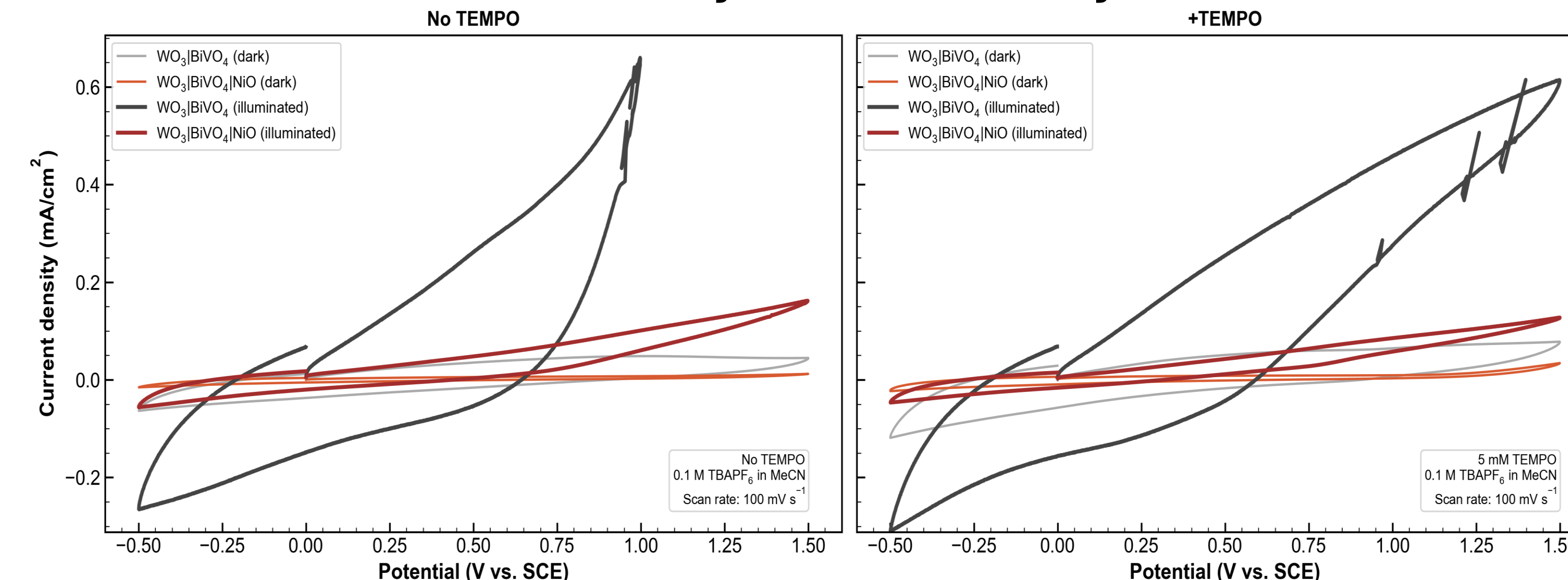


Fig. 7. Cyclic voltammograms of WO₃|BiVO₄ and WO₃|BiVO₄|NiO photoanodes under dark and illuminated conditions in 0.1 M TBAPF₆/MeCN (scan rate: 100 mV s⁻¹).

B. Chronoamperometry

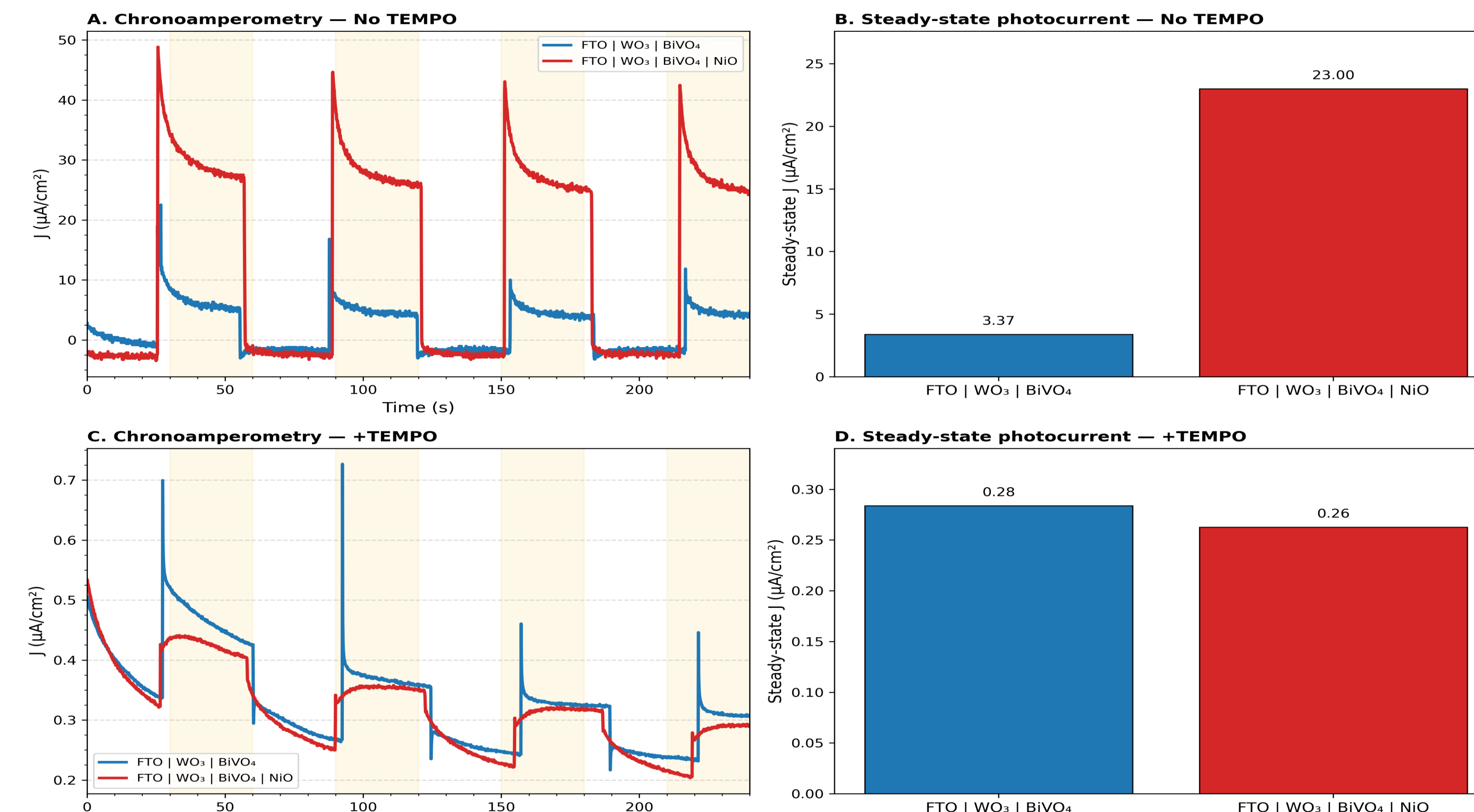


Fig. 8. Combined chronoamperometry and steady-state photocurrent data for FTO | WO₃ | BiVO₄ and FTO | WO₃ | BiVO₄ | NiO photoanodes in 0.1 M TBAPF₆/MeCN at 0.8 V vs. SCE. (A) Chronoamperometry of the photoanodes without TEMPO under chopped light conditions (30 s dark / 30 s light). (B) Corresponding steady-state photocurrent density extracted from the last 30 s of illumination without TEMPO. (C) Chronoamperometry of the photoanodes with TEMPO under the same chopped light conditions. (D) Steady-state photocurrent density with TEMPO. Light periods are shaded in yellow for clarity.

4. Key Results (Cont.)

C. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was attempted on the X5 WO₃|BiVO₄|NiO photoanode at 0.4 V vs SCE in both dark and illuminated conditions. However, only the dark measurement was successfully obtained, so full EIS analysis and k₀ calculation could not be performed.

5. Conclusions

This study establishes

- A reproducible liquid phase deposition (LPD) protocol for fabricating uniform NiO thin films on FTO substrates at room temperature
- NiO modification does not improve photocurrent behavior in cyclic voltammetry and shows reduced performance relative to the unmodified electrode.
- TEMPO does not enhance charge transfer and instead suppresses photocurrent response under the tested conditions.
- Chronoamperometry reveals stronger sustained photocurrent and photo-response for the NiO-modified electrode in the absence of TEMPO, highlighting a discrepancy between transient and steady-state behavior.
- Overall, NiO does not enhance interfacial charge transfer in this system, and EIS analysis was not completed to further resolve the mechanism.

Future work:

- Optimize NiO deposition or post-deposition treatments to improve interfacial charge transfer and photocurrent efficiency.
- Investigate alternative redox mediators or electrolyte conditions to enhance photo-response and stability.

6. References & Acknowledgements

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