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# P-Type Transparent Conducting Oxide Protection Layers for Sustainable Photoelectrochemical Water Oxidation

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In this paper, we propose that a p-type transparent conducting oxide (p-TCO) can function as a selective hole contact and corrosion protection layer on photoanodes used for light-driven water oxidation. To prove the concept, NiCo<sub>2</sub>O<sub>4</sub> was used as the p-TCO for n-Si protection in alkaline condition, and we show that this material has the requisite electronic structure, stability, transparency, and hole conductivity to achieve sustained and efficient solar water oxidation. The photoelectrochemical performance demonstrates the attractive combination of transparency and low-resistance hole conductivity in the NiCo<sub>2</sub>O<sub>4</sub>. Long-term testing indicates multi-day stability with minimal decrease in performance or observable corrosion of the Si photoanode. This work suggests that p-TCOs are promising as corrosion protection layers for stable water oxidation photoanodes.

## Introduction

For a z-scheme photoelectrochemical water splitting device, various photocathodes were developed with high photo-efficiency<sup>1,2</sup> and good stability in aquatic electrolyte with wide pH range by using TiO<sub>2</sub> as the protection layer.<sup>1</sup> However, we still struggle with the dilemma of photoanodes. On the one hand, the promising high efficiency photoanode candidates are not stable in aqueous electrolyte (e.g. GaAs and other III-V nanowires<sup>3</sup>) or aqueous electrolyte with extreme pH values (n-Si). On the other hand, the existing stable ones have various fundamental problems to be viable photoanodes (e.g. the short hole diffusion length of Fe<sub>2</sub>O<sub>3</sub> or the too-high bandgap of WO<sub>3</sub>, BiVO<sub>4</sub>, etc.). In this context, a new and innovative protection scheme would be “game changing” for artificial photosynthesis as it would greatly increase the space of available materials. To address this challenge, we propose investigating new group of materials for protecting

photoanodes. *These materials are wide bandgap, hole conducting, and stable in aqueous solution with wide pH range, including the strongly acidic and basic conditions required for proton conducting membranes and efficient OER catalysis.*

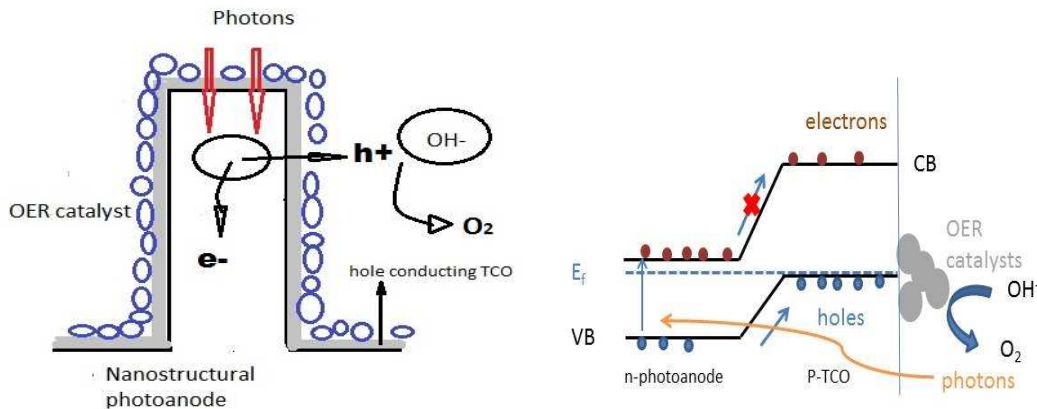


Figure 1. Scheme of an integrated half-cell with photoanode, hole conducting TCO and OER catalysts and idealized band diagram of photoanode and p-TCO protection layer.

To prove the concept, we selected  $\text{NiCo}_2\text{O}_4$  with the inverse spinel structure was used as the p-TCO and show that this material, when integrated with Si-based photoanodes, has the requisite electronic structure, stability, transparency, and hole conductivity to achieve sustained and efficient solar water oxidation.

## Results and discussion

$\text{NiCo}_2\text{O}_4$  was deposited on n-Si (100) and np-Si (100) by reactive sputtering at a substrate temperature of 70-100 °C. The film structure was amorphous, as shown by the lack of XRD and Raman features. P-type conductivity was confirmed by measurement of a positive Seebeck coefficient. Light transparency of >70% ( $\lambda > 400$  nm) was achieved with a  $\text{NiCo}_2\text{O}_4$  thickness of 40 nm. The hole conductivity was 50-60 S/cm and, as expected, p- $\text{NiCo}_2\text{O}_4$  forms a rectifying contact to n-Si.

Photoelectrochemical (PEC) evaluation was performed in aqueous 1M NaOH (pH 14) with simulated AM1.5 illumination; these conditions would rapidly corrode the n-Si photoanodes in the absence of a protection layer. PEC performance of the np-Si/p- $\text{NiCo}_2\text{O}_4$  structures is excellent, particularly when a thin NiFe oxygen evolving catalyst is applied (see Figure 2). An onset potential of 0.95 V vs. RHE is observed, which is one of the lowest reported for a Si-based photoanode. The current density at the reversible potential for water oxidation (+1.23 V vs. RHE) is >25  $\text{mA cm}^{-2}$ , and the current rises to a limiting value of 30  $\text{mA cm}^{-2}$  at more anodic potentials, which demonstrates the attractive combination of transparency and low-resistance hole conductivity in the  $\text{NiCo}_2\text{O}_4$ . Figure 3 shows the stability testing of the np-Si/40 nm a- $\text{NiCo}_2\text{O}_4$ /NiFe photoanode performed with simulated sunlight at pH 14. This long-term testing indicates multi-day stability with minimal decrease in performance or observable corrosion of the Si photoanode.

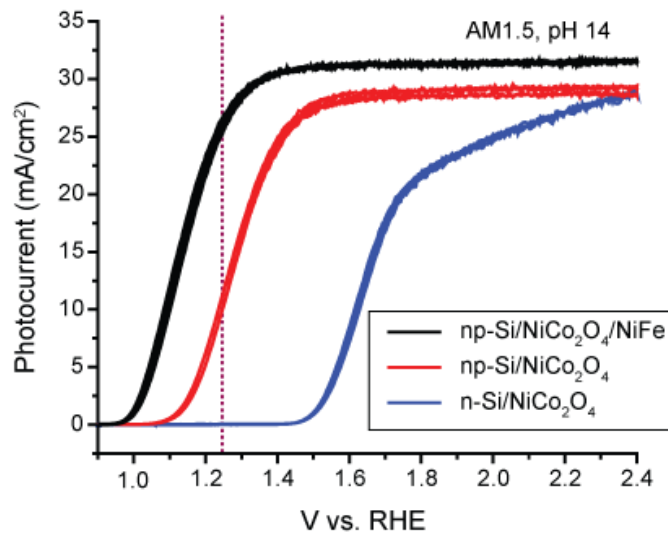


Figure 2. CV scans of n-Si and np-Si photoanodes protected with a 40 nm film of p-type  $\text{NiCo}_2\text{O}_4$ . The measurements were performed in 1 M KOH (pH 14) with simulated sunlight. The black trace is for a np-Si/p- $\text{NiCo}_2\text{O}_4$  structure with 2 nm coating of NiFe (50/50) serving as an oxygen evolving catalyst. For this film, the onset potential for OER is 0.95 V vs. RHE and the current density at the reversible potential for oxygen evolution is  $26 \text{ mA cm}^{-2}$ .

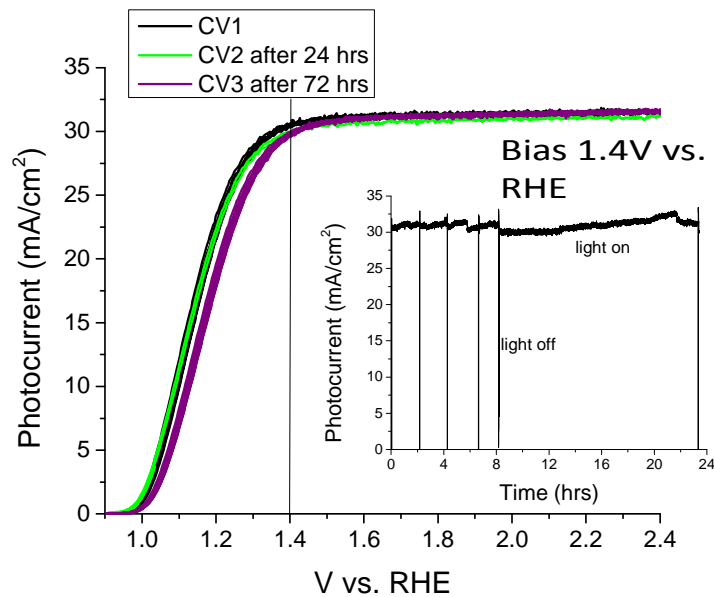


Figure 3. CV scans measured at the start of the test, after 24 hours, and after 72 hours. The inset shows the photocurrent measured at 1.4 V vs. RHE in the first 24 hours of a 72 hour test.

### Conclusion

We used  $\text{NiCo}_2\text{O}_4$  for Si photoanode protection as the concept-proof example to demonstrate that p-TCOs are promising as corrosion protection layers for stable water oxidation photoanodes.

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