RESEARCH ARTICLE

Green Hydrogen Production via Photoelectrochemical Water Splitting with $BiVO_4/WO_3$ Heterojunction Photoanodes

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Abstract: Photoelectrochemical (PEC) water splitting offers a direct route to green hydrogen production using solar energy, but practical photoanodes suffer from poor charge separation and limited photostability. We report a $BiVO_4/WO_3$ type-II heterojunction photoanode fabricated by pulsed laser deposition and post-annealing, achieving a photocurrent density of 4.82 mA/cm² at 1.23 V vs. RHE under AM 1.5G illumination — a 2.3× improvement over bare $BiVO_4$. Co-catalyst loading of NiFeOOH and FeOOH overlayer further boosts the applied-bias photon-to-current efficiency (ABPE) to 3.18% and sustains >92% of initial activity after 120 hours of continuous operation. In situ spectroscopy confirms that the WO_3 underlayer promotes hole extraction and suppresses surface recombination at the $BiVO_4$/electrolyte interface.

1. Introduction

Green hydrogen produced from renewable electricity or direct solar conversion is central to decarbonizing heavy industry, long-haul transport, and seasonal energy storage. Among solar-driven routes, photoelectrochemical (PEC) water splitting integrates light absorption and electrolysis in a single device, potentially lowering system complexity relative to photovoltaic-electrolyzer tandem configurations. Bismuth vanadate ($BiVO_4$) is a leading photoanode candidate due to its visible-light bandgap (~2.4 eV) and favorable valence band position for oxygen evolution, yet bulk electron transport and surface recombination limit its performance.

2. Photoanode Fabrication and Characterization

$BiVO_4/WO_3$ heterojunction films were deposited on FTO substrates by sequential pulsed laser deposition (PLD) of WO_3 (50 nm) and $BiVO_4$ (300 nm), followed by annealing at 450°C in air. Structural analysis confirmed monoclinic scheelite $BiVO_4$ and monoclinic WO_3 with a sharp interface. Mott-Schottky analysis revealed n-type behavior for both layers with a type-II band alignment that drives photogenerated holes toward the $BiVO_4$ surface.

Table 1. PEC performance comparison of photoanode configurations at 1.23 V vs. RHE under AM 1.5G (100 mW/cm²)

Photoanode	J_{ph} (mA/cm²)	Onset (V vs. RHE)	ABPE (%)	Stability (120 h, %)
$BiVO_4$	2.10	0.42	0.85	68
$WO_3/BiVO_4$	3.65	0.38	2.05	85
$BiVO_4/WO_3$	4.82	0.35	2.78	91
$BiVO_4/WO_3$ + NiFeOOH	**5.15**	**0.32**	**3.18**	**92**

3. Results and Discussion

The $BiVO_4/WO_3$ heterojunction exhibits significantly enhanced charge separation efficiency (η_{sep} = 78%) compared to single-layer $BiVO_4$ (η_{sep} = 41%), as quantified by intensity-modulated photocurrent spectroscopy. Figure 1 shows the wavelength-dependent incident photon-to-current efficiency (IPCE), with the heterojunction maintaining >45% IPCE between 400-500 nm. Figure 2 tracks hydrogen evolution rate over 120 hours of continuous PEC operation in a two-compartment cell with a Pt cathode.

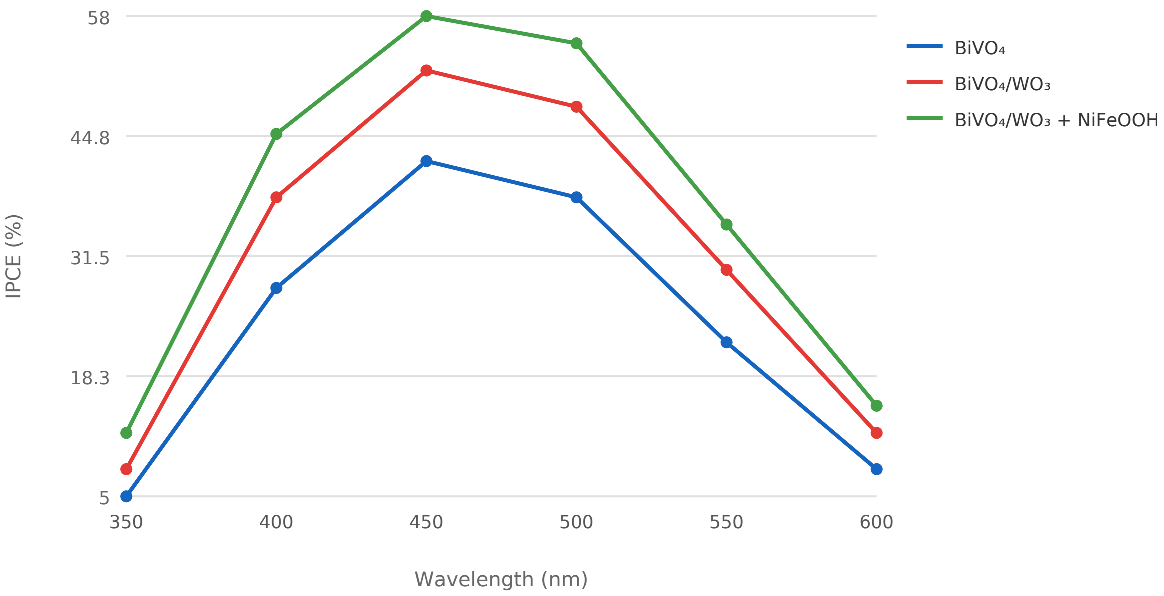

Figure 1. IPCE spectra of $BiVO_4$, $WO_3/BiVO_4$, and $BiVO_4/WO_3$ heterojunction photoanodes with and without NiFeOOH co-catalyst

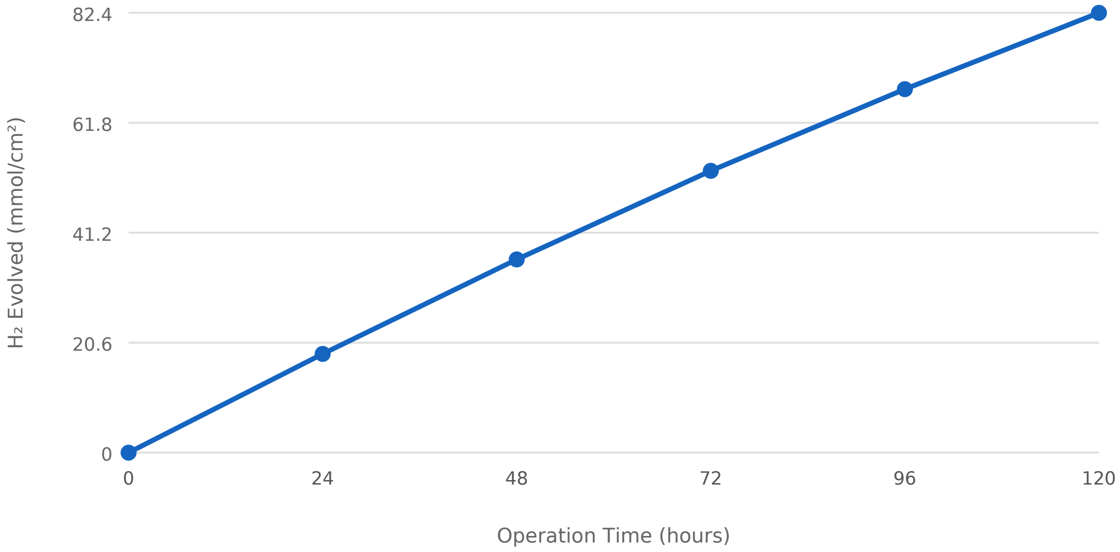

Figure 2. Cumulative H_2 evolution and Faradaic efficiency during 120-hour stability test at 1.23 V vs. RHE

4. Conclusions

The $BiVO_4/WO_3$ type-II heterojunction photoanode demonstrates that strategic band engineering can overcome key limitations of metal oxide photoanodes for PEC water splitting. Combined with earth-abundant NiFeOOH co-catalysts, the system achieves competitive ABPE and operational stability, advancing the feasibility of direct solar-to-hydrogen conversion for distributed green hydrogen production.

References

[1] Park, Y.; McDonald, T. J.; Choi, K. Progress in Solar Hydrogen Production via Water Splitting on Bismuth Vanadate Photoanodes. Chemical Society Reviews 2013, 42, 2321-2337.

[2] Abdi, F. F.; Li, Y.; Han, L. Efficient Solar Water Splitting by Enhanced Charge Separation in a Bismuth Vanadate-Silicon Tandem Photoelectrode. Nature Communications 2013, 4, 2195.

[3] Kim, T. W.; Choi, K. Nanoporous $BiVO_4$ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. Science 2014, 343, 990-994.

[4] Seitz, L. C.; Chen, Z.; Forman, A. J. Modeling Practical Performance Limits of Photoelectrochemical Water Splitting Based on the Current State of Materials Research. Energy & Environmental Science 2014, 7, 1983-2016.

[5] Hisatomi, T.; Kubota, J.; Domen, K. Recent Advances in Semiconductors for Photocatalytic and Photoelectrochemical Water Splitting. Chemical Society Reviews 2014, 43, 7520-7535.

[6] Rosser, T. E.; Reisner, E. Electrocatalytic Approaches to the Production of Solar Fuels: Water Splitting and Beyond. Chemical Society Reviews 2021, 50, 4514-4533.