Supplementary Materials

Serial Hole Transfer Layers for BiVO₄ Photoanode with Enhanced Photoelectrochemical Water Splitting

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Methods

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Photodeposition of FeOOH and NiOOH.

The photo-/electrodeposition was carried out using a three-electrode PEC cell composed of a Fe₂O₃/BiVO₄ working electrode (WE), a platinum counter electrode (CE), and an Ag/AgCl reference electrode (RE). A 300 W Xe arc lamp (Shanghai Hualun Bulb Factory) with an AM 1.5G filter was used as the simulated solar light source. For FeOOH, electrodes were immersed in a 0.1 M FeSO₄ solution with gentle stirring. Prior to the photodeposition, the solution was purged with nitrogen gas for 1 h. An external bias of 0.25 V vs. Ag/AgCl, which was closed to the open circuit potential of the Fe₂O₃/BiVO₄ electrode in 0.1 M FeSO₄ solution without illumination, was applied. During illumination, the holes generated at the photoanode oxidized Fe²⁺ to Fe³⁺, which precipitated as FeOOH on electrode surface (Fe²⁺(aq) + h⁺ + 3OH⁻ + \rightarrow FeOOH(s) + H₂O)¹. Various deposition times (10, 15, and 20 min) were tested to optimize the best deposition amount. The photodeposition was followed by an electrodeposition at 1.2 V vs Ag/AgCl for 60 s. The resulting photoanodes are denoted as FeOOH /Fe₂O₃/BiVO₄.

For NiOOH, Fe₂O₃/BiVO₄ electrodes were immersed in 0.1 M Ni(NO₃)₂ solution with pH adjusted to 6.6 by adding 0.05 M NaOH. An external bias of 0.25 V vs. Ag/AgCl, which was closed to the open circuit potential of the Fe₂O₃/BiVO₄ electrode in 0.1 M Ni(NO₃)₂ solution without illumination, was applied. Just similar with FeOOH, NiOOH precipitated via the following reaction (Ni²⁺(aq) + h⁺ + 3OH⁻ \rightarrow NiOOH(s) + H₂O)². Various deposition times (150, 300, and 450 s) were tested for NiOOH. The photodeposition was followed by an electrodeposition at 1.2 V vs Ag/AgCl for 60 s. The resulting photoanodes are denoted as NiOOH/Fe₂O₃/BiVO₄.

FeOOH/NiOOH was also photodeposited as reversed layer on Fe₂O₃/BiVO₄ electrode in order to compare with NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode. A NiOOH layer was first photodeposited on Fe₂O₃/BiVO₄, then a FeOOH layer was photodeposited followed by additional electrodeposition of FeOOH at 1.2 V vs Ag/AgCl for 60 s. The resulting photoanodes are denoted as FeOOH/NiOOH/Fe₂O₃/BiVO₄.



Fig. S1. SEM-EDS spectrum and EDS atomic ratio of Bi, V, O, Fe, and Ni for (a and a') $BiVO_4$ photoanode, (b and b') $Fe_2O_3/BiVO_4$ photoanode and (c and c') $NiOOH/FeOOH/Fe_2O_3/BiVO_4$ photoanodes.



Fig. S2. (a) Particle size distribution measured from 100 particles and (b–f) the EDS elemental distribution maps of Bi, V, O, Fe, and Ni in NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode shown in SEM image (**Fig. 2c**).



Fig. S3. XRD patterns of BiVO₄ and NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanodes.



Fig. S4. X-ray photoelectron spectra of (a) Fe 2p, (b) Ni 2p, and (c) O 1s and (f) wide region for $BiVO_4$ (green), $Fe_2O_3/BiVO_4$ (black), $FeOOH/Fe_2O_3/BiVO_4$ (orange), $NiOOH/FeOOH/Fe_2O_3/BiVO_4$ (red) photoanodes. The dash lines in (c) represent peaks of Ni-O (black, 528.8 eV), both Fe-O and V-O (blue, 529.8 eV), O-H (red, 531.0 eV).

Parameters optimization for serial hole transfer layers.

1. Optimization of the Fe₂O₃ layer



Fig. S5. The influence of the thickness of Fe_2O_3 layer on (a) *J*-V curves, (b) EIS curves, (c) UV–vis absorption spectra, and (d) XRD patterns.

Since Fe₂O₃ had a short carrier diffusion length and excessive Fe₂O₃ would induce charge recombination³, the thickness of Fe₂O₃ layer would play an important role in the improvement of PEC performance. As shown in Fig. S5, different layers Fe₂O₃ (1 layer, 3 layers, 5 layers, and 7 layers) were investigated to demonstrate the effect of Fe₂O₃ thickness on the PEC properties of BiVO₄-based photoanodes. The Fe₂O₃/BiVO₄ photoanode modified with 1 layer, 3 layers, 5 layers, and 7 layers of Fe₂O₃ showed photocurrents of 0.78, 1.56, 1.48 and 1.30 mA/cm² at 1.23 V vs. RHE, respectively. The photocurrent of 1 layer Fe₂O₃/BiVO₄ was significantly lower than 3 layers Fe₂O₃/BiVO₄, which was possibly because the active sites for hole transfer in 1 layer Fe₂O₃/BiVO₄ were much less than those of 3 layers. With the layers increasing of Fe₂O₃, the photocurrents decreased for Fe₂O₃/BiVO₄ photoanodes with 5 and 7 layers of Fe₂O₃, suggesting the thickness of Fe₂O₃ was beyond the short carrier diffusion length, which would induce charge recombination and decrease the photocurrent. EIS was also measured and the Fe₂O₃/BiVO₄ photoanode with 3 layers Fe₂O₃ demonstrated the lowest resistance, which was consistent with the photocurrent results. In addition, the optical absorption behavior was measured by UV–vis absorption spectra (Fig. S5c). The Fe₂O₃/BiVO₄ photoanodes with different layers of Fe₂O₃ did not change the onset of light absorption (about 510 nm), while the optical absorption was slightly improved with the thickness of Fe₂O₃ increasing. As shown in Fig. S5d, XRD patterns for all BiVO₄ photoanodes showed no difference for the lower loading content of Fe₂O₃, which also suggested thin hole transfer layer of Fe₂O₃ did not change the crystal phase of BiVO₄.



Fig. S6. (a) *J*-V curves and (b) Schematics of the band structures of BiVO₄/Fe₂O₃ photoanode.

 $BiVO_4/Fe_2O_3$ was also tested to study the location of the Fe_2O_3 hole transfer layer on the performance of $BiVO_4$ photoanode. As shown in Fig. S6a, $BiVO_4/Fe_2O_3$ exhibited significantly lower photocurrents than the bare $BiVO_4$ electrode, not to mention the photocurrent generated by $Fe_2O_3/BiVO_4$ (1.55 mA/cm² at 1.23 V vs. RHE under front illumination). Actually, the valence band minimum of Fe_2O_3 is slightly higher than that of $BiVO_4$, and when $BiVO_4$ was later deposited on the surface of the Fe_2O_3 layer, photogenerated holes in the Fe_2O_3 layer could not transfer to the top $BiVO_4$ for water oxidation (Fig. S6b). In particular, the decreased photocurrent in our experiments was still higher than that of $Fe_2O_3/BiVO_4$ in previous reports (< 0.1 mA/cm² at 1.23 V *vs.* RHE under front illumination)³, which was possibly caused by the difference of Fe_2O_3 thickness (100 nm Fe_2O_3 strongly inhibited the charge transfer in previous reports, while 5-15 nm in our electrode had much less influence).

2. Optimization of the FeOOH and NiOOH layer



Fig. S7. *J*-V curves of BiVO₄-based photoanodes decorating with different time of FeOOH and NiOOH.

The deposition amounts of FeOOH and NiOOH may have an influence on the surface holes transfer process and thus change the PEC photocurrent performance. Various photodeposition times for FeOOH (10, 15 and 20 min) and NiOOH (150, 300 and 450 s) were tested on the Fe₂O₃/BiVO₄ electrode to optimize the performance (Fig. S7). The Fe₂O₃/BiVO₄ photoanodes modified with 0, 10, 15 and 20 min FeOOH showed a photocurrent density of 1.53, 1.82, 2.02 and 1.40 mA/cm² at 1.23 V vs. RHE, respectively. 20 min FeOOH decreased the photocurrent might be caused by excessive FeOOH deposition which increased holes transfer resistance. In addition, Fe₂O₃/BiVO₄ photoanodes modified with 150, 300 and 450 s NiOOH showed a photocurrent density of 1.82, 1.84 and 1.73 mA/cm² at 1.23 V vs. RHE, respectively. The most active

samples were those obtained at proper photodeposition time (15 min FeOOH and 300s NiOOH).



Fig. S8. SEM images of (a) FeOOH/Fe₂O₃/BiVO₄ photoanode (b) NiOOH /Fe₂O₃/BiVO₄ photoanode (c) FeOOH/NiOOH/Fe₂O₃/BiVO₄ (d) NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode

The SEM images of $Fe_2O_3/BiVO_4$ photoanodes with different strategies of photodepositing FeOOH and NiOOH were also shown in Fig. S8. Only NiOOH/Fe_2O_3/BiVO_4 showed an irregular morphology with lots of holes, while the other electrodes present similar surfaces. This might be caused by the better junction between FeOOH and $Fe_2O_3/BiVO_4$ photoanode than that between NiOOH and $Fe_2O_3/BiVO_4$.



Fig. S9. (a) LSV curves under chopped light illumination and (b) Electrochemical impedance spectroscopy (EIS) for the FeOOH/Fe₂O₃/BiVO₄ (orange), NiOOH/Fe₂O₃/BiVO₄ (oliver), FeOOH/NiOOH/Fe₂O₃/BiVO₄ (cyan), and NiOOH/FeOOH/Fe₂O₃/BiVO₄ (red) under AM 1.5G illumination in a three-electrode system with a platinum cathode as the counter electrode and a Ag/AgCl electrode as the reference electrode in 0.1 M KH₂PO₄ (pH 7) solution. The LSV curve of Fe₂O₃/BiVO₄ (green) was also showed in (a) for comparation.

To further study the surface hole transfer layer, FeOOH, NiOOH and FeOOH/NiOOH were also deposited on Fe₂O₃/BiVO₄ in order to get the best photoanode performance (Fig. S9). Upon photodepositing FeOOH and NiOOH, the photocurrent densities (J) of four photoanodes were superior to that of Fe₂O₃/BiVO₄ photoanode (Fig. S9a), which indicated that FeOOH and NiOOH might enhance the surface holes transfer and thus significantly improve the PEC activity of Fe₂O₃/BiVO₄ photoanode. Besises, the NiOOH/Fe₂O₃/BiVO₄ photoanode performed the best photocurrent density of 2.24 mA/cm² at 1.23 V vs. RHE, which was larger than both NiOOH/Fe₂O₃/BiVO₄ and FeOOH/Fe₂O₃/BiVO₄ photoanodes (Fig. S9). This was confirmed by a previous report that either Ni or Fe alone exhibited weaker activity for oxygen evolution than Ni-Fe catalysts⁴. In particular, NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode also exhibited better performance than FeOOH/NiOOH/Fe₂O₃/BiVO₄ (1.70 mA/cm² at 1.23 V vs. RHE) photoanode, which might be caused by the difference of FeOOH/Fe₂O₃ and NiOOH/electrolyte junctions. A similar result has already been reported in previous systems⁵, and further EIS data agreed with the photocurrent results (Fig. S9b).

Table S1. Flat Band Potential (EFB) and Donor Concentration (ND) Values Extrapolated from

Mott-Schottky Plots

Electrode type	BiVO ₄	Fe ₂ O ₃ / BiVO ₄	NiOOH/FeOOH /BiVO4	NiOOH/FeOOH /Fe ₂ O ₃ /BiVO ₄
E _{FB} (V vs. RHE)	0.260	0.279	0.238	0.299
$N_{\rm D} ({\rm cm}^{-3})$	2.386×10 ¹⁸	8.332×10 ¹⁸	2.158×10 ¹⁸	7.689×10 ¹⁸



Fig. S10. *J*-t curve of NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode for 12 hours. (Inset) *J*-t curve comparation of BiVO₄ and NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode for 2 hours. All measurements were conducted at 0.6 V vs. Ag/AgCl in 0.1 mol L⁻¹ Na₂SO₄ electrolyte under AM 1.5 G illumination.

To probe the stability of the photoelectrode, the change of the photocurrent was measured under constant working conditions for 2 hours. As shown in Fig. S10, the photocurrent of the bare BiVO₄ photoanode sharply decreased from 0.76 mA/cm² to 0.34 mA/cm² during the first 2000 s. After modifying the serial hole transfer layers, the NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode showed remarkable stability. Then, 12 hours of measurement was also conducted for NiOOH/FeOOH/Fe₂O₃/BiVO₄

photoanode for practical water splitting application. The photocurrent density only decreased from 2.25 mA/cm² to 2.21 mA/cm² after 12 hours measurement (Fig. S10). The results suggested that the serial hole transfer layers highly improved the durability of the bare BiVO₄ photoanode, which was stable enough for practical PEC water splitting. The increased stability might be attributed to the fact that the overlayers of Fe₂O₃ and NiOOH/FeOOH prevented the solution corrosion to the BiVO₄ electrode.



Fig. S11. Equivalent circuit of the charge transfer for BiVO₄-based photoanodes

Transient photocurrent (TPC) and Transient photovoltage (TPV) analyses

The decay curves were first normalized to the interval [0, 1] for TA and TPV analyses. Then,

the normalized data were fitted to a second-order exponential function as following^{6,7},

$$y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2}$$

where τ_1 and τ_2 are the time constants and A_1 and A_2 are the probability constants. The percentage of $\tau_1(\varphi_1)$ was calculated as

$$\varphi_1 = \frac{A_1}{A_1 + A_2} \times 100\%$$

and the percentage of $\tau_2 (\varphi_2)$ was calculated as

$$\varphi_2 = \frac{A_2}{A_1 + A_2} \times 100\%$$

The average decay time (τ) was calculated as

 $\tau = \tau_1 \varphi_1 + \tau_2 \varphi_2$

The calculated decay parameters of the TPC and TPV kinetics are presented in Table S3.

TPC kinetics parameters	$\tau_{1 \text{ (ms)}}$	τ_{2} (ms)	$\varphi_{1(\%)}$	$\varphi_{2}(\%)$	τ (ms)
BiVO ₄	0.55	1.85	47.1	52.9	1.24
NiOOH/FeOOH/Fe ₂ O ₃ /BiVO ₄	0.7	6.6	59.0	41.0	3.12
TPV kinetics parameters	$\tau'_{1(s)}$	$\tau'_{2(s)}$	$\varphi'_{1(\%)}$	$\varphi'_{2(\%)}$	τ' _(S)
TPV kinetics parameters BiVO ₄	τ' _{1 (s)} 0.217	τ' _{2 (s)} 2.00	φ' _{1 (%)} 31.6	φ' _{2 (%)} 68.4	τ' _(S) 0.79

Table S2. Decay parameters for both TPC and TPV kinetics.



Fig. S12. Digital photo of three types of Si PVC arrays, including Bi-cell, Tri-cell and tetra-cell Si. Every Si PVC array has a 2.5×5 cm² area with a function area of 8 cm².



Fig. S13. Assembling of composite electrode. (A) NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode (2.5×5 cm) (B) NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode with copper wire (C) commercial PVC cell (2.5×4 cm) positive and negative electrodes are given using + and - (D) the composite electrode sealed with resin. The copper wire connected with the FTO will finally connect with the wire of positive electrode.

The NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode was connected with copper wire by using high purity silver paint (SPI Supplies, USA). The back side of PVC (2.5×4 cm) was composed of the positive pole (indicated by +) and the negative pole (indicated by -), each of them was connected with copper wires by using tin solder. The positive pole was connected with the photoanode via copper wire, while the negative pole was connected with the Pt cathode. Finally, the PVC and NiOOH/FeOOH/Fe₂O₃/BiVO₄ photoanode were finally connected to fabricate a self-bias PEC water-splitting device using epoxy adhesive.



Fig. S14. The corresponding charge transfer diagram of the self-bias PEC water splitting device. FTO,

fluorine-doped tin oxide (data got reference⁸).



Fig. S15. Photograph of the characterization system for the PEC water splitting configuration.

References

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