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Supporting information

Photochemical and electrochemical co-regulation BiVO₄ photoanode

for solar-driven water splitting

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1 Equations used in this work

The obtained potentials (vs Ag/AgCl) can be converted to RHE scale with the Nernst equation:^[1]

$$E_{RHE} = E_{Ag/AgCl} + pH \times 0.059 + E_{Ag/AgCl}^{0} \tag{1}$$

 E_{RHE} represents the converted potential vs. RHE. The value of $E_{Ag/AgCl}^{0}$ (saturated KCl) is 0.197 V at 25 °C. $E_{Ag/AgCl}$ is the obtained potential vs. Ag/AgCl, and the pH of the electrolyte was 9.3.

Charge separation efficiency (η_{sep}) and charge transfer efficiency (η_{trans}) of the all samples photoanodes, can be calculated using the following equations:^[1]

$$\eta_{trans} = \frac{J^{H_2 0}}{J^{N a_2 S 0_3}}$$
(2)

$$\eta_{sep} = \frac{J^{Na_2 SO_3}}{J_{abs}} \tag{3}$$

Applied bias photon-to-current efficiency (ABPE) can be calculated using the following equation:^[2]

$$APBE(\%) = \frac{J \times (1.23 - V_b)}{P_{total}}$$
(4)

J refers to the photocurrent density (mA cm⁻²) obtained from the electrochemical workstation. V_b is the applied bias (vs RHE), and P_{total} is the total light intensity of 100 mW cm⁻².

According to the MS curves, charge carrier density (Nd) can be calculated using the following equation:^[3]

(5)

$$N_{d} = \frac{2}{e\varepsilon_{o}\varepsilon} \times \left(\frac{d\left(\frac{1}{C^{2}}\right)}{dV_{s}}\right)^{-1} = \left(\frac{2}{e\varepsilon_{0}\varepsilon}\right)\left[\frac{1}{slope}\right]$$

The electronic charge (e) is 1.6×10^{-19} C, vacuum permittivity (ϵ_0) is 8.86×10^{-12} F m⁻¹, and relative permittivity (ϵ) is 68 for BiVO₄.^[4] C (F cm⁻²) is the space charge capacitance in the semiconductor (obtained from MS curves), and Vs (V) is the applied potential for MS curves.

2 Material

F-doped SnO₂ coated glass (FTO) were purchased from Wuhan Jinge-solar Energy Technology Co. Ltd, potassium iodide (KI, AR), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, AR), nitric acid (HNO₃, AR), vanadyl acetylacetonate (VO(acac)₂, 99%), p-benzoquinone (C₆H₄O₂, AR), dimethyl sulfoxide (DMSO, AR), ethanol (C₂H₆O, AR), borate acid (H₃BO₃, 99%), Nickel sulfate (NiSO₄•6H₂O, 98.5%), Ferrous sulfate (FeSO₄•7H₂O, AR), sodium hydroxide (NaOH, 99%), Sodium sulfite (Na₂SO₃, 98%) and potassium hydroxide (KOH, 99%), all materials were purchased from Sinopharm, and deionized water was used without further purification.

3 Methods

Preparation of BiVO₄ : BiVO₄ was prepared according to previous report. Firstly, dissolve 0.4 mol KI in 50 mL aqueous solution, and 0.04 mol Bi(NO₃)₃·5H₂O was added to it after the dissolution was complete. Then, dilute nitric acid was added to adjust the pH of the solution to 1.7 resulting in a clear orange-red solution. Finally, added 20 mL of anhydrous ethanol containing 0.23 mol p-benzoquinone into the above solution. BiOI was prepared in a three-electrode system with Ag/AgCl, Pt wire, and FTO as reference, counter, and working electrodes, respectively. BiOI was obtained by electrodeposition under bias (-0.1 V vs. Ag/AgCl) for 5 minutes, then washed with deionized water. Next, dissolve 0.2 mol/L VO(acac)₂ in 0.2 mL DMSO, and slowly drop the solution on the surface of BiOI with a dropper. The samples were annealed in a muffle furnace at 450 °C for 2 h. After that, the excess V₂O₅ on the surface of the film were removed with 1 M NaOH solution, and the BiVO₄ film was finally fabricated.

Photochemical and electrochemical treating: Firstly, BiVO₄ is immersed in 1 M KBi buffer solution (pH 9.3) containing 0.2 M Na₂SO₃ with simulated 100 mW cm⁻² illumination for 12 min, which is defined as photochemical treatment, and photochemical treated BiVO₄ (P-BiVO₄) is achieved. Then, the P-BiVO₄ sample was electrochemically treated at -0.1 V (vs RHE) for 10 s (defined as electrochemical (E) treatment) in the same buffer solution containing 0.2 M Na₂SO₃ without 100 mW cm⁻² illumination to prepare PE-BiVO₄ sample. Under the same conditions, EP-BiVO₄ was obtained by electrochemical treatment first and then photochemical treatment.

Synthesis of PE-BVO/NiFeO_x: The NiFeO_x cocatalyst was deposited using a photo-assisted linear sweep voltammogram (LSV) process under 100 mW cm⁻² illumination. Briefly, a 0.5 M borate buffer solution was prepared by dissolving 0.1 mol of H₃BO₃ in 200 mL ionized water, followed by adding KOH to achieve a pH of 8.3. Then, 20 mg Fe(SO₄)₂•7H₂O and 2 mg Ni(SO₄)₂•6H₂O were dissolved in the above borate buffer solution previously purged with N₂ for 20 min. Under 100 mW cm⁻² illumination from the FTO side, LSV was performed from -0.3 to 0.5 V versus

Ag/AgCl with a scan rate of 50 mV s⁻¹ for 3, 5, 7, and 8 cycles (Fig. S2), respectively. The optimized condition for the deposition of NiFeO_x is 7 cycles, and PE-BiVO₄/NiFeO_x is achieved.

4 Characterization

The crystallinity and structure of simples was investigated by X-ray diffractometer (XRD, Bruker D8 Advance), Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F30 S-TWIN). The morphology and composition analyses were conducted by field emission scanning electron microscope (FESEM, Hitachi S3400e-N microscope, LEO 1530, Japan) and a JEM-2100F electron microscope (JEOL, Japan) with an energy dispersive X-Ray spectroscopy (EDX). The chemical composition for these photoanodes was studied by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250 XPS system, UK). Optical characteristic was recorded by Ultraviolet-visible spectrometer (Shimadzu UV-3100, Japan).

5 Photoelectrochemical characterization

All the PEC measurements were measured in a three-electrode quartz cell, including a 1 cm² window to facilitate illumination (100 mW/cm²). The illumination source is aligned with the electrochemical quartz cell, and light vertically irradiated through the substrate side (back-side). The linear sweep voltammogram (LSV) was measured in a potential from -0.4 to 1.2 V (vs Ag/AgCl) using CHI 852 (CH Instruments, China) workstation with a scan rate of 50 mV s⁻¹. The incident photonto-current conversion efficiency (IPCE) curves were received under monochromatic light (Newport 69920, 300 W Xe lamp) by external quantum efficiency measurement system (Newport/Oriel, QEPV-SI). Charge separation efficiency and charge injection efficiency were conducted in 1 M potassium borate solution with/without 0.2 M Na_2SO_3 as the hole scavenger. The photoelectrochemical impedance spectra (PEIS) was performed over a frequency range from 10^{-2} Hz to 10^6 Hz (Princeton, Versa STAT 3), and Mott-Schottky (MS) plots were tested by means of an electrochemical analyzer (CHI 760).

6 Supplemental data



Fig. S1 (a) Photocurrent densities of BVO at 1.23 V vs. RHE under 100 mW cm⁻² illumination after photochemical treatment for different time. (b) Photocurrent densities of BVO at 1.23 V vs. RHE under 100 mW cm⁻² after photochemical and electrochemical treatment at different potentials for 8s. (c) Photocurrent densities of BVO at 1.23 V vs. RHE under 100 mW cm⁻² illumination after photochemical and electrochemical treatment at 0.1 V vs. RHE for different time.



Fig. S2. Photocurrent densities of the PE-BVO/NiFeO_x-3, PE-BVO/NiFeO_x-5, PE-BVO/NiFeO_x-7, and PE-BVO/NiFeO_x-8 films in a 1 M borate buffer electrolyte at 1.23 V versus RHE under 100 mW cm⁻² illumination.

Fig. S3 SEM images of (a) $BiVO_4$, (b) P- $BiVO_4$, (c) PE- $BiVO_4$ and (d) PE- $BiVO_4$ /NiFeO_x. (e) XRD patterns of $BiVO_4$ (I), PE- $BiVO_4$ (II) and PE- $BiVO_4$ /NiFeO_x (III).

Fig. S4. High resolution XPS spectra of (a) Fe 2p, (b) Ni 2p.

Fig. S5. α and β represent the relative concentration of the oxygen vacancies and the lattice oxygen, respectively. The peak with lower binding energy (~529.4 eV) is assigned to the lattice oxygen (O_{lat}²⁻), while the peak at higher binding (~531.4 eV) energy is related to oxygen vacancies (O_{vac})^[4].

Fig. S6. EPR spectra of BiVO₄ and PE-BiVO₄.

Fig. S7. Photocurrent density of BVO, P-BVO, E-BVO, PE-BVO, and PE-BVO/NiFeO_x in a 1 M borate buffer electrolyte under 100 mW cm⁻² illumination.

Fig. S8. H_2 and O_2 evolution of PE-BVO/NiFeO_x photoanode detected by GC.

Fig. S9. UV-vis light absorption curves (Inset: Tauc plot versus the energy spectra)

Fig. S10. (a) ABPE of the BVO, PE-BVO and PE-BVO/NiFeO_x photoanodes, (b) J-t curve of the PE-BVO/NiFeO_x photoanode, (c) EIS curves of the BVO, PE-BVO and PE-BVO/NiFeO_x photoanodes at the open circuit potential under 100 mW cm⁻² illumination, (d) Mott-Schottky curves, of BVO, PE-BVO and PE-BVO/NiFeO_x photoanodes in 1 M borate buffer electrolyte under 100 mW cm⁻² illumination.

Table S1. Photocurrent density of reported BVO-based anodes (all data obtainedusing 100 mW/cm² solar illumination)

BVO Material	Photocurrent density (mA cm ⁻²)	Journal	Year
PE-BiVO ₄ /NiFeO _x	6.42	Present work	
BiVO ₄ /Ni-N ₄ -O/FeOOH	6.0	Journal of the American Chemical Society	2021 ^[5]
NiOOH/FeOOH/CQDs/Bi VO ₄	~6.0	Energy & Environmental Science	2017 ^[6]
La:BaSnO3-Mo:BiVO4	6.22	Nature Communications	2019 ^[7]
Ov-BiVO ₄ /NiFeO _x	5.54	Advanced Materials	2020 ^[8]
BiVO ₄ /FeOOH/NiOOH	5.87	Advanced Materials	2018 ^[9]
V ₁₃ O ₁₆ -BiVO ₄ /CoPi	5.0	Advanced Materials	2019 ^[10]
BiVO4/NiOOH/FeOOH	4.7	Nature Energy	2017 ^[11]
OEC/MoOx/MQD/BiVO ₄	5.85	Angewandte Chemie- International Edition	2022 ^[12]
R-BiVO4/CoPy/FN-H	4.75	Angewandte Chemie- International Edition	2019 ^[13]
E-BiVO4/CoBi	3.2	Angewandte Chemie- International Edition	2017 ^[14]

FePi/BiVO ₄	2.28	Applied Catalysis B: Environmental	2018 ^[15]
F-BiVO4/NiFe-LDH	2.67	Applied Catalysis B: Environmental	2020 ^[16]
Co-Pi/Mo:meso-BiVO ₄	4.57	Applied Catalysis B: Environmental	2018[17]
BiVO ₄ /FeCoO _x	4.82	Advanced Functional Materials	2018 ^[4]
CoFe-H/BiVO ₄	2.48	Advanced Functional Materials	2017 ^[18]

$N_d/10^{17} \text{ cm}^{-3}$		
BVO	1.86	
P-BVO	2.78	
E-BVO	3.45	
EP-BVO	3.89	
PE-BVO	4.83	
PE-BVO/NiFeO _x	7.82	

Table S2. Carrier densities (N_d) of BVO, P-BVO, E-BVO, PE-BVO and PE-BVO/NiFeO_x.

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