Supplementary Materials

Boosting Photoelectrochemical Water Oxidation by Sandwiching Gold Nanoparticles between BiVO₄ and NiFeOOH

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Experimental Procedures

Materials: Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99%), sodium borohydride (NaBH₄, 98%), and ascorbic acid (C₆H₈O₆, 99%) were purchased from Sigma-Aldrich. Hexadecyltrimethylammonium bromide (CTAB, 98%) was obtained from Alfa Aesar. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99%), potassium iodide (KI), p-benzoquinone, vanadium acetylacetone oxygen (VO(acac)₂), iron chloride hexahydrate (FeCl₃·6H₂O, 99%), nickel chloride hexahydrate (NiCl₂·6H₂O, 99%), dimethylsulfoxide (DMSO), ethyl alcohol, nitric acid (HNO₃), mercaptoethanol (C₂H₆OS), and sodium hydroxide (NaOH, 99%) were purchased from Aladdin Chemical. Deionized water used in all reactions has a resistivity of 18.25 MΩ·cm obtained from a Milli-Q ultrapure water purification system. Fluorine-doped tin oxide (FTO) conductive glass was carefully washed by ultrasonic concussion in ethanol and deionized water.

Characterization: Scanning electron microscopy (SEM) images were taken on an FEI Quanta 250. Transmission electron microscopy (TEM) images were obtained on an FEI Tecnai Spirit 12 with an applied acceleration voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and

elemental mapping images were acquired on an FEI Tecnai F20 microscope with an acceleration voltage of 200 kV. The extinction spectra were recorded on a Hitachi U-4100 ultraviolet/visible/NIR spectrophotometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed on PHI5000 Versaprobe (Japan) with an Al Ka X-ray source. The X-ray diffraction (XRD) pattern was monitored by the Bruker D8 Advance Instrument, irradiated with monochromatic Cu K α radiation ($\lambda = 0.154061$ nm) as an X-ray source.

Preparation of Au nanosphere: Au nanospheres were prepared according to a seedmediated growth method with slight modification.^[1] Typically, for the preparation of the seed solution, 0.25 mL of HAuCl₄ solution (0.01 M) was added into 9.75 mL of CTAB solution (0.1 M), followed by the rapid injection of a freshly prepared, ice-cold NaBH₄ solution (0.01 M, 0.6 mL) under vigorous stirring. The resultant solution was kept undisturbed in an oven at 30 °C for 4 h. Then, 0.25 mL of the seed solution was rapidly injected into a growth solution made of CTAB (0.1 M, 9.75 mL), water (190 mL), HAuCl₄ (0.01 M, 4 mL), and ascorbic acid (0.1 M, 15 mL). The mixture solution was gently shaken for 30 s and then left undisturbed overnight at 30 °C. The resultant Au nanospheres were centrifuged and washed by water twice and finally re-dispersed into water for further use.

Preparation of porous BiVO₄ photoanode: Porous BiVO₄ photoanodes were obtained via a BiOI-assisted method according to the previous report.^[2] Specifically, 0.9701 g of Bi(NO₃)₃·5H₂O was dissolved in 50 mL of KI solution (0.4 M). Then, HNO₃ solution was added to adjust its pH to 1.6-1.7. The solution quickly changed from feculent orange to clear and transparent orange red. Subsequently, 20 mL of ethanol solution containing 0.497 g of pbenzoquinone was dropped into the above solution with vigorous stirring for 10 min to acquire the electrodeposited solution. The electrodeposition process was carried out using a typical three-electrode cell. FTO, Ag/AgCl (4 M KCl), and platinum were used as working electrode, reference electrode, and counter electrode, respectively. The cathodic deposition was performed at a constant potential of -0.1 V vs. Ag/AgCl for 240 s at room temperature to obtain the BiOI electrodes. Then, the BiOI electrode was covered with DMSO solution (75 µL cm⁻²) containing VO(acac)₂ (0.2 M). The conversion of BiOI to BiVO4 was through a thermal treatment at 450 °C with a heating rate of 5 °C/min for 2 h in air. After calcination, the excess V₂O₅ on the BiVO₄ electrodes was removed by impregnating into NaOH (1 M) solution for 30 min with gentle stirring. The as-resulted BiVO₄ electrodes were rinsed with DI water and dried in oven at 80 °C for 12 h.

Preparation of BiVO₄/NiFeOOH and BiVO₄/Au/NiFeOOH photoanodes: The BiVO₄/NiFeOOH and BiVO₄/Au/NiFeOOH photoanodes were prepared through a pH-

controlled solution immersion method.^[3] BiVO₄ and BiVO₄/Au electrodes were first dipped into the mixed solution of FeCl₃·6H₂O (10 mM, 2.5 mL) and NiCl₂·6H₂O (10 mM, 7.5 mL) solution for 15 min. Then, 2 M NaOH solution was added to adjust its pH to ~8. The electrodes were kept in the solution for 45 min at room temperature for the NiFeOOH growth. All electrodes were washed with deionized water and blow-dried by N₂ to obtain the samples. **Photoelectrochemical measurements:** PEC performances of all photoelectrodes (1 × 1 cm²) were measured using a standard three-electrode electrochemical workstation (CHI 760E) at room temperature with Ag/AgCl reference electrode and Pt counter electrodes in 0.5 M K₃BO₃ electrolyte (pH = 9). The photoanodes were irradiated under AM 1.5G simulated sunlight (100 mW cm⁻²). All potentials in the experiment were converted to the reversible hydrogen electrode (RHE) according to the following Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197 \tag{1}$$

The electrochemical impedance spectroscopy (EIS) measurements were carried out with an alternative current amplitude of 5 mV in the frequency range of 10⁻² to 10⁵ Hz, and the measured spectra were fitted with Zview software. Mott-Schottky measurements were performed with a voltage of 10 mV at a frequency of 1 kHz under dark conditions. The incident photon to current efficiency (IPCE) were determined using a full solar simulator (CEL-QPCE3000, CEAULIGHT) at 0.6 V vs. RHE in 0.5 M K₃BO₃ electrolyte. The applied bias photon-to-current efficiency (ABPE) of each photoelectrode was calculated by following equation:^[4]

$$ABPE = \frac{J \times (V_{\text{redox}} - V_{\text{bias}})}{P_{\text{light}}}$$
(2)

where J is the photocurrent density, V_{redox} is the applied potential, and P_{light} is the incident illumination power density (100 mW cm⁻²). Photocarrier bulk separation efficiency (η_{sep}) and surface charge transfer efficiency (η_{trans}) of different photoelectrodes can be calculated through the following equation:^[5]

$$\eta_{\rm sep} = J_{\rm Na_2SO_3} / J_{\rm abs} \tag{3}$$

$$\eta_{\rm trans} = J_{\rm H_2O} / J_{\rm Na_2SO_3} \tag{4}$$

 J_{H_2O} and $J_{Na_2SO_3}$ are the photocurrent densities obtained in 0.5 M K₃BO₃ electrolyte without and with Na₂SO₃, respectively. The maximum theoretical photocurrent (J_{abs}) is obtained by the following formula:^[6]

$$J_{\rm abs}(\lambda) = \int_{300}^{\Lambda_{\rm max}} N_{\rm ph}(\lambda) \cdot \eta_{\rm abs}(\lambda) \cdot \mathbf{e} \cdot \mathrm{d}\lambda \tag{5}$$

$$\eta_{\rm abs} = \left(1 - 10^{-A(\lambda)}\right) \times 100\% \tag{6}$$

wherer λ_{max} is the maximum light absorption edge of a photoelectrode (nm), λ is the wavelength (nm), $N_{\text{ph}}(\lambda)$ is the photon flux (s⁻¹ cm⁻² nm⁻¹), e is the elementary charge (1.602 × 10⁻¹⁹ C), $\eta_{\text{abs}}(\lambda)$ is the light harvesting efficiency, A(λ) is the absorbance at wavelength. The evolution of gases was performed in 0.5 M K₃BO₃ at 1.23 V vs. RHE under AM 1.5 G illumination (100 mW cm⁻²) and the gases were detected by gas chromatography (GC-7920, China) with Ar as a carrier gas.

Density functional theory calculations: Spin-polarized density functional theory (DFT) calculations were implemented in the Vienna ab initio simulation package code (VASP).^[7,8] The Perdew-Burke-Ernzerhof (PBE) within the generalized gradient approximation (GGA) was adopted to examine the electronic exchange-correlation function of the interacting electrons.^[9] The van der Waals interactions were described by the zero damping DFT-D3 method of Grimme scheme.^[10] The energy cut-off is set to 400 eV. The Brillouin zone is sampled by a Monkhorst-Pack $3 \times 3 \times 1$ K-point grid. The periodic structure of the two phases can avoid interaction by a vacuum thickness larger than 15 Å. All the geometries were fully optimized until the atomic forces and energy were smaller than 0.02 eV $Å^{-1}$ and 10^{-5} eV, respectively. The Au/NiFeOOH heterojunction was constructed with Au (111) surface and NiFeOOH (001) surface. The BiVO₄/NiFeOOH heterojunction was modeled with NiFeOOH (001) surface and BiVO₄(010) surface. During the structure optimization, the metal atoms in the top and bottom two layers were fixed at their bulk position, while the atoms in the middle four layers were relaxed. The system energy reaches the lowest value at the surface distance of 2.8 Å. The free energy change (ΔG) is calculated from the ZPE-corrected total energies as $\Delta G = \Delta E + \Delta E_{ZPE}$ - T ΔS , where ΔE_{ZPE} and ΔS are the zero-point energy difference and the entropy difference, respectively, and T is the system temperature (298.15 K).



Fig. S1 (a) Extinction spectra of Au nanospheres in water. (b) Histogram of the size distribution of the Au NPs. (a) TEM image of the Au nanospheres.



Fig. S2 SEM images of BiVO₄/Au photoanodes with different deposition times of Au nanospheres. (a) 60 s. (b) 120 s. (c) 180 s. (d) 300 s.



Fig. S3 SEM image of BiVO4/NiFeOOH photoanode.



Fig. S4 XRD patterns of different samples.



Fig. S5 Wide-range XPS spectrum of BiVO₄/Au/NiFeOOH.



Fig. S6 Tauc plots of different samples.



Fig. S7 J–V curves of BiVO₄/Au photoanodes with different deposition time of Au nanospheres under light illumination.



Fig. S8 J-V curves of BiVO₄/Au/NiFeOOH under back and front illumination.



Fig. S9 (a) J–V curves of BiVO₄/Au/NiFeOOH and BiVO₄/NiFeOOH/Au under back illumination. (b) Chronoamperometric curves of BiVO₄/Au/NiFeOOH and BiVO₄/NiFeOOH/Au at 1.23 V (vs. RHE) under back illumination.



Fig. S10 (a) Chronoamperometric curves of different photoanodes at 1.23 V (vs. RHE) under light illumination. (b) H_2 and O_2 evolution on BiVO₄/Au/NiFeOOH photoanode measured at 1.23 V vs. RHE.



Fig. S11 EIS Nyquist plots measured at 1.8 V (vs. RHE) in dark.



Fig. S12 (a) Light harvesting efficiency. (b) The photon flux spectrum of the AM 1.5G, the calculated current density flux and integrated current density.



Fig. S13 J–V curves of different photoanodes in the electrolytes of K₃BO₃ and K₃BO₃ + Na₂SO₃. (a) BiVO₄. (b) BiVO₄/Au. (c) BiVO₄/NiFeOOH. (d) BiVO₄/Au/NiFeOOH.



Fig. S14 Polarization curves of BiVO₄/Au/NiFeOOH in the electrolytes of K₃BO₃ + Na₂SO₃.



Fig. S15 Convergence test for the distance between Au and NiFeOOH in a heterogeneous structure.



Fig. S16 Atomic configurations of OER process on (a) Au/NiFeOOH. (b) NiFeOOH. (c) Au.(d) BiVO4 and (e) BiVO4/NiFeOOH. The yellow, cyan, grey, red, pink, purple and tawny spheres represent Au, Ni, Fe, O, H, Bi and V, respectively.

 Table S1. PEC performances of BiVO4-based photoanodes under AM 1.5G simulated

 sunlight (100 mW cm⁻²).

Materials	Photocurret Density at 1.23 V vs. RHE	Electrolyte	Reference
BiVO ₄ /BP/NiOOH	4.48 mA cm ⁻²	$0.5 \text{ M KH}_2\text{PO}_4 \text{ and} \\ \text{K}_2\text{HPO}_4$	[11]
BiVO ₄ /CoNi-MOFs	3.20 mA cm ⁻²	$0.5 \text{ M} \text{ Na}_2 \text{SO}_4$	[12]
BiVO4/V-NiOOH/FeOOH	5.43 mA cm ⁻²	1 M K ₃ BO ₃	[13]
BiVO₄/NiFeY LDH	5.20 mA cm ⁻²	1 M K ₃ BO ₃	[14]
BiVO ₄ /N:NiFeO _x	6.40 mA cm ⁻²	0.5 M K ₃ BO ₃	[15]
BiVO ₄ /Fe _x Ni _{1-x} OOH	5.80 mA cm ⁻²	0.5 M K ₃ BO ₃	[3]
BiVO ₄ /MoO _x /MQD/NiFeOOH	5.85 mA cm ⁻²	0.5 M K ₃ BO ₃	[16]
BiVO ₄ /Bi/NiFeOOH	4.70 mA cm ⁻²	1.0 M K ₃ BO ₃	[17]
C-BiVO ₄ /CQDs	4.83 mA cm ⁻²	0.5 M K ₃ BO ₃	[18]
BiVO4/VO _x	6.29 mA cm ⁻²	1.0 M K ₃ BO ₃	[19]
BiVO ₄ /Co ₃ O ₄ /NiOOH	6.40 mA cm ⁻²	1.0 M K ₃ BO ₃	[20]
BiVO ₄ /N:MnCo ₂ O _x	6.50 mA cm ⁻²	0.5 M K ₃ BO ₃	[21]
BiVO₄/Au/NiFeOOH	5.30 mA cm ⁻²	0.5 M K ₃ BO ₃	This work

Table S2. Parameters used in EIS fitting for the photoanodes under light (AM 1.5G, 100 mW cm⁻²) irradiation.

Sample	<i>R</i> ₅/Ω·cm²	C _{ct} /10 ⁻⁴ S⋅sec ⁿ ⋅cm ⁻²	<i>R</i> _{ct} /Ω cm²	$C_{\rm sc}/10^{-6}$ S·sec ⁿ ·cm ⁻²	R _{sc} /Ω cm²	Equivalent circuit model
BiVO ₄	30.8	4.2	299.1			-
BiVO ₄ /Au	30.5	4.9	164.7			
BiVO₄/NiFeOOH	28.3	1.8	12.7	41.3	106.7	-Rs Ret Rsc
BiVO₄/Au/NiFeOOH	28.9	1.9	8.9	5.1	94.1	CPEH CPEsc

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