Supplementary Information

Polydopamine-mediated hydrogen bond network promotes hole extraction in BiVO₄ photoanodes for efficient photoelectrochemical water oxidation

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Experimental Section

Chemical reagents

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99.0%), potassium iodide (KI, 99.0%), p-benzoquinone (C₆H₄O₂, 99.0%), dimethyl sulfoxide solution (C₂H₆OS, DMSO, 99.7%), nitric acid (HNO₃, 65% ~ 68%), vanadyl acetylacetonate (C₁₀H₁₄O₅V, VO(acac)₂, 97.0%), sodium hydroxide (NaOH), dopamine–HCl (DA-HCl), tris(hydroxymethyl)aminomethane, and iron chloride hexahydrate (FeCl₃·6H₂O, 99%) were purchased from Macklin Reagent Co., Ltd. All chemicals were directly used without further purification. Deionized water was used in whole process.

Synthesis of BiOI and BiVO4 photoanodes

The BiOI nanofilms on FTO substrate were synthesized via the electrodeposition approach, according to statements in previous literature.^{1, 2} In the typical synthesis procedure, 0.4 M potassium iodide (KI) powder is firstly dissolved in 50 mL of deionized water. Then, the pH value of the resulting solution is then adjusted to 1.7 by adding nitric acid (HNO₃). Subsequently, a 0.04 M bismuth nitrate (Bi(NO₃)₃·5H₂O)

solution is introduced to the KI solution. In parallel, a 0.23 M p-benzoquinone is dissolved in 20 mL of ethanol solution and added to the above mixture, which is then stirred for 20 min to obtain a homogenous electrodeposition solution. Using a standard three-electrode system, a BiOI film is deposited at a constant potential of -0.1 V vs. Ag/AgCl for 200 s. Following this, approximately 180 µL of dimethyl sulfoxide (DMSO) containing 0.2 M vanadium acetylacetonate (VO(acac)₂) is uniformly spin-coated onto the BiOI film, and then placed it in a tube furnace and heated to 450 °C for 2 h with a ramping rate of 2 °C/min to obtain BiVO₄ photoanode. Finally, residual V₂O₅ on the surface of the BiVO₄ is removed by immersing it in 0.1 M NaOH for 40 min, followed by repeated rinsing with deionized water and drying at 60 °C.

Characterizations

The X-ray diffraction (XRD) was used to characterize the crystal structure of photoanodes by Bruker D8 advance X-ray instrument equipped with Cu Kα radiation (40 kV and 30 mA). Raman spectra were conducted to further explore the chemical composition and crystallinity of the photoanodes. Surface morphology was characterized by Scanning electron microscopy (SEM, Zeiss sigma300). The hydrophilicity of all the photoanodes was characterized by water contact angle (OCA15EC, Dataphysics, Germany). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive Xray spectroscopy (EDS) was also conducted by using JEOL-2010 TEM. X-ray photoelectron spectra (XPS) was collected for the identification of elemental constituents and valence states. Ultraviolet Visible (UV-Vis) absorption spectra and Fourier transform infrared (FT-IR) spectra were recorded by PerkinElmer Lambda 750 S UV-Vis-NIR spectrophotometer and Thermo Scientific Nicolet 6700 spectrometer. The photoluminescence (PL) spectra were performed at room temperature using a ZLX-PL-I PL system.

Equations used in this work

The measured potential values (vs Ag/AgCl) can be transformed to RHE scale by using the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E^{0}_{Ag/AgCl}$$
(S1)

Where $E_{Ag/AgCl}$ is the applied potential vs. Ag/AgCl and $E^{0}_{Ag/AgCl} = 0.1976$ V at

25 °C.

Applied bias photon-to-current conversion efficiency (ABPE) was calculated using the following Equation:

$$ABPE = (1.23 - E_{RHE}) \times J/P_{AM 1.5}$$
(S2)

Where J is the measured photocurrent density (mA cm⁻²), E_{RHE} is the measured applied voltage, $P_{AM 1.5}$ is the illumination power density of 100 mW cm⁻² (AM 1.5 G). IPCE measurement:

$$IPCE = (1240 \times J)/(\lambda \times P) \times 100\%$$
(S3)

Where *J* is the photocurrent density at a specific wavelength (mA cm⁻²), *P* is the measured optical power density (mW cm⁻²), and λ is the wavelength of the incident light (nm).

LHE =
$$1-10^{-(\lambda)}$$
 ((λ) is the absorbance at wavelength λ) (S4)

$$APCE = IPCE/LHE$$
(S5)

Calculation of the bulk charge separation efficiency (η_{sep}) and charge injection efficiency (η_{inj}) :

PEC measurements in a 0.2 M Na₂SO₄ electrolyte with 0.2 M Na₂SO₃ as a hole scavenger were recorded. Bulk charge separation (η_{bulk}) was the charge separation efficiency corresponding to the arrival of photogenerated holes at the electrode/electrolyte surface, and surface injection efficiency (η_{surface}) was the efficiency of hole injection from the electrode into the electrolyte, both of which can be calculated according to the following equations:

$$J_{\text{water}} = J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{inj}} \tag{S6}$$

$$\eta_{\rm sep} = J_{\rm Sulfite}/J_{\rm abs}$$
 (S7)

$$\eta_{\rm inj} = J_{\rm water} / J_{\rm sulfite}$$
 (S8)

Where $J_{Sulfite}$ and J_{water} are the photocurrent density values obtained in 0.2 M Na₂SO₄ with and without the addition of 0.2 M Na₂SO₃ as a hole scavenger. J_{abs} is the photocurrent density resulting from the complete conversion to absorbed irradiation; therefore, J_{abs} for BiVO₄ photoanodes was taken to be 7.5 mA cm⁻² under one sun illumination.

UV-vis light absorption:

$$\alpha h v = A (h v - E_g)^{n/2}$$
(S9)

Where α , h, v, A, and E_g are the absorption coefficient, Planck's constant, light frequency, proportionality constant, and band gap energy, respectively. n is the characteristic integer, depending on the characteristics of the optical transition in a semiconductor. Because BiVO₄ is a direct semiconductor, the value of n is 1.

Mott-Schottky (M-S) measurements:

M-S plots were measured in a 0.2 M Na₂SO₄ solution at a frequency of 1000 Hz and an amplitude of 10 mV under dark addition. The type of semiconductor, flat-band potential, and carrier density can be determined using the following M-S equation:

$$C = -1/(wZ'') = -1/2\pi f Z''$$
(S10)

Where *f* is the frequency.

$$N_{d} = (2/e\varepsilon\varepsilon_{0}) \left[d(1/C^{2})/dV \right]^{-1}$$
(S11)

Where $e = 1.6 \times 10^{-19} \text{ C}$, $\varepsilon_0 = 8.85 \times 10^{-14} \text{ F cm}^{-1}$, and $d(1/C^2)/dV$ is the slope of the M-S plot. The relative dielectric constant ε of the BiVO₄ photoanode is 68. The space charge capacitance C (F/cm²) and bias V of BiVO₄ are obtained from the Mott-Schottky curve.

Cyclic voltammetry (CV) curves were measured in the potential range of -0.08 to $0.04 \text{ V}_{Ag/AgCl}$ at scan rates from 0.06 to 0.12 V s⁻¹ with an increment of 0.02. To obtain the electrochemical active surface area (ECSA), the double-layer capacitance (C_{dl}) was obtained from the CV curves, which is proportional to ECSA.

Actual amount of gas produced = The amount of gas detected by meteorological chromatography

Theoretical amount of gas
$$(O_2) = [i(A) \times t(s)(C)]/96500(C) \times 1/4$$
 (S12)

Oxygen evolution reaction: $2H_2O + 4h^+ \rightarrow 4H^+ + O_2$

Theoretical amount of gas $(H_2) = [i(A) \times t(s)(C)]/96500(C) \times 1/2$ (S13)

Hydrogen evolution reaction: $2H^+ + 2e^- \rightarrow H_2$

Computational details

The model constructions were processed with Materials Studio (MS), and geometry optimization was performed with the density functional theory (DFT)-based DMol3 module. The specific calculation function is selected as GGA, and the base group is chosen as PBE. All atoms were fully relaxed until the residual force per atom was as small as 0.001 eV. Electronic properties are calculated, such as adsorption energies, electron density, density of states (DOS), and Bader charge.

In detail, the model established contains BiVO₄ (001) and dimer PDA. To obtain the optimized geometry configurations, we adopted an energy convergence criterion of 1.0×10^{-6} eV/atom, giving a force convergence tolerance of below 0.01 eV/Å. The calculations of BiVO₄ and BiVO₄/PDA, a 2 × 2 × 1 supercell of the BiVO₄ (001) slab, were constructed from the primitive cell of monoclinic BiVO₄. The vacuum space is set to 20 Å to ensure that the interaction between adjacent layers can be ignored. consideration. The cutoff energies of plane waves were set to 500 eV to ensure calculation accuracy.



Fig. S1. XRD pattern of β -FeOOH powder collected after the oil bath impregnation engineering reaction.



Fig. S3. FTIR spectra comparison of BiVO₄/PDA/ β -FeOOH photoanode with β -FeOOH.



Fig. S4. SEM image of precursor BiOI.



Fig. S5. (a) SEM image, (b-g) elemental mapping images of BiVO₄/PDA.



Fig. S6. XPS survey spectra of BiVO₄, BiVO₄/PDA, and BiVO₄/PDA/β-FeOOH



Fig. S7. PDA polymer placed horizontally on the BiVO₄ surface a-b) before optimization and c-d) after optimization.



Fig. S8. PDA polymer placed vertically on the BiVO₄ surface a-b) before

optimization and c-d) after optimization. **b**⁵⁰ a ^{0.0} $E_{\rm F}$ Bi 2p 40 O 2p Adsorption energy (eV) -0.4 (eV) -1.5 -1.6 V 3d 30 Total 20 DOS 10 0 -10 -20 -30 -2.0 -40 -2 -1 -5 -4 -3 0 1 2 3 4 5 -6 Energy (eV)

Fig. S9. a) Adsorption energy of BiVO₄ and PDA placed horizontally and vertically and b) DOS of BiVO₄.



Fig. S10. a) Bi 4f, b) V 2p and c) O 1s high resolution XPS spectra of BiVO₄/PDA/β-

FeOOH.



Fig. S11. Enlarged C 1s high resolution XPS spectra of Fig. 4a.



Fig. S12. (a-b) HRTEM images of BiVO₄/PDA/ β -FeOOH.



Fig. S13. EDX mapping of Cl element.



Fig. S15. Mott-Schottky curve of a) BiVO₄/PDA/β-FeOOH, b) BiVO₄/PDA and c)

BiVO₄.



Fig. S16. Carrier lifetime derived from OCP-decay curve at the transient when illumination is removed.



Fig. S17. LSV curves of BiVO₄ under varying the self-polymerization time of DA.



Fig. S18. LSV curves of $BiVO_4/PDA$ after dipping into $FeCl_3$ solution at 90 °C for



Fig. S19. (a) LSV curves, (b) ABPE values and (c) chopped photocurrent density– potential curves of BiVO₄/β-FeOOH in 0.2 M Na₂SO₄ solution.



Fig. S20. Cyclic voltammetry curves measured in a non-Faradaic region at different scan rates for a) BiVO₄/PDA/β-FeOOH, b) BiVO₄/PDA, and c) BiVO₄. (d) The



Fig. S21. (a) η_{sep} and (b) η_{inj} curves of the BiVO₄, BiVO₄/PDA, and BiVO₄/PDA/ β -FeOOH photoanodes.



Fig. S22. a) The light harvesting efficiency (LHE) and b) APCE curves of the BiVO₄,



BiVO₄/PDA and BiVO₄/PDA/ β -FeOOH photoanodes.

Fig. S23. The natural seawater used in our manuscript was from west coast of the

Yellow Sea.



Fig. S24. LSV of (a) BiVO₄, (b) BiVO₄/PDA and (c) BiVO₄/PDA/ β -FeOOH in

natural SW without and with the addition of 0.2 M Na₂SO₃.



Fig. S25. a) XRD patterns and b) Raman spectra of BiVO₄/PDA/ β -FeOOH before and after 8 h of i–t tests.



Fig. S26. Optical images of a) BiOI, b) BiVO₄, c) BiVO₄/PDA and d) BiVO₄/PDA/ β -FeOOH materials.

Table S1. Contact angle of different photoanodes. The volume of the test droplet was 2 μ L, and 3 areas were tested on the same photoanode.

Photoanodes	Contact angle (°)
BiVO ₄	78.13±0.7
BiVO4/PDA	46.38±1.3
BiVO4/PDA/β-FeOOH	25.05±3.15

Supplementary References

- 1. K. J. McDonald and K.-S. Choi, *Energy & Environ. Sci.*, 2012, **5**, 8553-8557.
- K. Xue, L. Yu, C. Liu, H. Luo, Z. Li, Y. Zhang and H. Zhu, J. Colloid Interface Sci., 2025, 680, 771-784.