Supporting Information

Fabrication of BiVO₄ submicron rod photoanode through phase transition assisted by Mo doping

Shuang Zhao, ^a Haipeng Zhang, ^a Zhaoqi Wang, ^b Deifei Xiao, ^a Xianbin Xu, ^a Peng Wang, ^a Zhaoke Zheng, ^a Yuanyuan Liu, ^a Ying Dai, ^c Hefeng Cheng, ^a Zeyan Wang^{*a} and Baibiao Huang^{*a}

S. Zhao, H. Zhang, Z. Wang, D. Xiao, X. Xu, P. Wang, Z. Zheng, Y. Liu, Y. Dai, H. Cheng, Z. Wang, B. Huang

^a State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

E-mail: <u>wangzeyan@sdu.edu.cn</u> (Z. Wang); <u>bbhuang@sdu.edu.cn</u> (B. Huang) ^b Center for Gene and Immunotherapy, The Second Hospital, Cheeloo College of Medicine, Shandong University

^c School of Physics, Shandong University, Jinan 250100, China

Photoelectrochemical measurements:

The prepared photoanodes, a Pt sheet, and a saturated calomel electrode (SCE) were utilized as the working electrode, counter electrode, and reference electrode, respectively. The photoelectrochemical measurements were conducted using a CHI660E electrochemical workstation. A 0.1 M potassium phosphate electrolyte (KPi) (pH=7) was employed as an electrolyte. A 300 W Xe arc lamp coupled with an AM 1.5 G filter served as the light source, providing an intensity of 100 mW cm⁻². All measurements were performed with an SCE reference electrode, and the potentials were converted into reversible hydrogen electrode (RHE) by the following equation: $E_{RHE} = E_{SCE} + 0.241 + 0.059pH$

the photocurrent density potential curves (J-V) were measured in a three-electrode cell of 0.1 M KPi, under AM 1.5 G irradiation at a scan rate was 20 mV/s.

Electrochemical impendence spectra (EIS) were utilized as an efficient method for analyzing the characteristics of charge separation during photochemical water splitting. In the Nyquist plots, a semicircle at high frequencies serves as a feature of the charge transfer process, where the diameter of the semicircle corresponds to the charge transfer resistance. To determine the donor density (N_d), Mott-Schottky measurements were carried out at a frequency of 1 KHz in a 0.1 M KPi with a pH of 7 under dark conditions. A positive slope of Mott-Schottky indicates that the sample is an n-type semiconductor.

Incident-photocurrent-conversion efficiency (IPCE) was measured at 1.23 V vs. RHE. The instruments used are an electrochemical workstation and a 300 W Xe arc lamp with a grating monochromator. The IPCE calculation equation was as follows:

$$IPCE = \frac{1239.8 \times |j_{ph}|}{\lambda \times P_{mono}} \times 100\%$$

here j_{ph} indicates photocurrent density, λ means incident wavelength, and P_{mono} is the illumination power intensity calibrated for different wavelengths.

Mott–Schottky plots were carried out at a frequency of 1 kHz in the dark. The donor densities of N-type semiconductor material were calculated employing the Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{2}{e_0 \varepsilon \varepsilon_0 N_d} [(V - V_f) - \frac{kT}{e_0}]$$
$$N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} [d\left(\frac{1}{C^2}\right)/dV]^{-1}$$

Where C represents the capacitance of the space charge layer, e_0 stands for the electron charge, ε is the relative permittivity of BiVO₄ ($\varepsilon = 68$), ε_0 denotes the permittivity of vacuum, N_d symbolizes the donor density, V corresponds to the applied bias at the electrode, V_f is the flat-band potential.

The charge separation and injection efficiencies were calculated using the following equations:

$$\eta_{bulk} = J_{ph}^{Na_2SO_3} / J_{abs}$$
$$\eta_{interf} = J_{ph}^{H_2O} / J_{ph}^{Na_2SO_3}$$

Where $\int_{ph}^{Na_2SO_3} ph$ represents the photocurrent density measured with Na₂SO₃ as a hole scavenger, while $\int_{ph}^{H_2O} ph$ is measured in KPi. J_{abs} is calculated by: $J_{abs} = \frac{q}{hc} \int_{\lambda} \lambda \cdot \phi_{\lambda} \cdot \eta_{abs} d\lambda$, indicates the photon absorption rate as a function of photocurrent density. Where *q* is used to indicate the charge of an electron, *h* signifies the Plank constant, *c* represents the light speed, ϕ_{λ} is photon flux of the AM 1.5 G solar

spectrum, η_{abs} denotes the absorbance of the photoanodes.

	a / Å	b / Å	c / Å	α/°	β / °	γ / °	V / Å ³
t-BVO	15.08	15.08	13.52	90.00	90.00	90.00	2964.48
BVO	10.44	10.40	24.02	90.00	90.00	89.91	2615.20
Mo: t-BVO	10.44	15.05	13.10	90.00	90.00	90.00	2972.37
Mo: BVO	14.77	24.05	10.43	90.00	134.67	90.00	2637.74

Table S1 Optimized geometries of pure BiVO₄ and Mo doping BiVO₄ system values.

Computational details:

The computational part was implemented by using the first-principles calculation of CASTEP.¹ The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) formula was applied to the exchange-correlation potential in association with the DFT-D correction.^{2, 3} To search for the ground state of the supercells, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method was used, and the convergence tolerance was set to the energy change below 10^{-5} eV per atom, stress less than 0.05 GPa, force less than 0.02 eV Å⁻¹ and displacement change less than 0.001 Å. The cutoff energy of the atomic wave functions was set to 450 eV. The phase structure has remained unchanged when constructing a 2*2*2 supercell, despite the doping model calling for swapping out one of the V atoms for a Mo atom. As shown in **Table S1**, Mo doping leads to a diminished disparity in cell volume, which is conjectured to result in a reduction of the transition barrier. Due to the low dopant concentration within the supercell, the calculations were carried out utilizing a primitive cell without introducing alterations in the underlying physical phase structure.



Fig. S1 TG-DSC curves of the t-BVO and Mo: t-BVO.



Fig. S2 (a) XRD patterns of the t-BVO. (b) SEM image of the t-BVO from the top perspective.



Fig. S3 (a) TEM image and EDS mapping images of the Mo:1D-BVO corresponding to the elemental distribution are included in (b-e).



Fig. S4 The crystallographic unit cells for tetragonal zircon $BiVO_4$ and monoclinic scheelite $BiVO_4$.



Fig. S5 (a) UV-via DRS spectrum and the inserted Tauc-plot of the t-BVO.



Fig. S6 (a) J-V curve of the t-BVO in 0.5 M KPi solution under AM 1.5 G irradiation from the backside. (b) IPCE curve of the t-BVO measured at a potential of 1.23 V vs. RHE.



Fig. S7 (a) Reflection spectra of the BVO and Mo:1D-BVO.



Fig. S8 (a) Survey spectra, (b) Bi 4f, (c) V 2p, and (d) O 1s XPS peaks of the Mo:1D-BVO.



Fig. S9 Exploration of (a) different annealing temperatures, (b) different annealing times, and (c) different concentrations of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

Number of samples	1		
Sample volume $m_0(g)$	0.0275		
Constant volume V_0 (mL)	25		
Test element	Мо		
Test solution element concentration $C_0 (\mu g / L)$	66.687		
Dilution ratio f	200		
Digestion solution/elemental concentration of			
original sample solution	13337.400		
C ₁ (µg / L)			
Sample element content $C_S (\mu g / kg)$	12124909.1		
Sample element content W (%)	1.21		

Table S2 Molybdenum content was detected by ICP-MS.



Fig. S10 SEM images of (a) molybdenum powder (Mo) and (b) molybdenum trioxide (MoO₃).



Fig. S11 (a) Mott-Schottky plots of the BVO and Mo: BVO measured at a frequency of 1 KHz in the dark, and the inset shows the SEM image of the Mo: BVO. (b) Nyquist plots of the BVO and Mo: BVO measured at 1.23 V vs. RHE under AM 1.5 G irradiation from the backside. (c) J-V curves of the BVO and Mo: BVO in 0.5 M KPi solution under AM 1.5 G irradiation from the backside. (d) Charge separation efficiency

of the BVO and Mo: BVO in 0.5 M KPi solution under AM 1.5 G irradiation from the backside.



Fig. S12 PL spectra of the BVO and Mo:1D-BVO.



Fig. S13 (a) Reflection spectra of the Mo: BVO and Mo:1D-BVO. (b) Absorption spectra of the Mo: BVO and Mo:1D-BVO.



Fig. S14 (a) Co 2p and (b) P 2p XPS peaks of the Co-Pi/Mo:1D-BVO.



Fig. S15 TEM image and corresponding EDS mapping images of the Co-Pi/Mo:1D-BVO.



Fig. S16 (a) Mott-Schottky plots of the BVO, Mo:1D-BVO, and Co/Pi-Mo:1D-BVO measured at a frequency of 1 KHz in the dark. (b) Nyquist plots of the BVO, Mo:1D-BVO, and Co/Pi-Mo:1D-BVO measured at 1.23 V vs. RHE under AM 1.5 G irradiation from the backside.. (c) Comparisons of ABPE curves calculated from J–V curves. (d) Photocurrent density versus the BVO, Mo:1D-BVO, and Co-Pi/Mo:1D-BVO time curves measured at 1.23 V vs. RHE.



Fig. S17 Theoretical and practical H_2 and O_2 production of the Co-Pi/Mo:1D-BVO measured at 1.23 V vs. RHE in 0.5 M KPi solution.

References

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