**Supporting Information for** 

## Facile Fabrication of BiVO<sub>4</sub> Nanofilms with Controlled Pore Size and their Photoelectrochemical Performances

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## **Experimental Section**

*Preparation of nanoporous BiVO<sub>4</sub> photoanodes*: Nanoporous BiVO<sub>4</sub> photoanodes were fabricated by drop-casting the precursor solution on FTO substrates. As the following, the preparation of precursor solution will be shown detailedly. At first, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> were dissolved separately in ethylene glycol (75 mM), 0.68 g PEG-600 was dissolved in 20 mL ethylene glycol as a structure controlling solution. Then, according to the desired volume ratio, these three solutions were mixed to create the precursor solution. 5 mL Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O solution, 5 mL NH<sub>4</sub>VO<sub>3</sub> solution and 2.5 mL PEG-600 solution were mixed to form a yellow precursor solution. Then, 0.2 mL precursor solution was drop-cast on FTO substrates (1×5 cm<sup>2</sup>). The sample was dried in an oven at 150 °C for 60 min and then annealed in a muffle furnace in air at 500 °C for 2.5 hours. Finally, a yellow BiVO<sub>4</sub> photoanode would generate on the FTO substrates. For comparison, different bore diameters of BiVO<sub>4</sub> films were synthesized via adjusting reaction conditions, the concentration of PEG-600. In detail, the precursor solution contains Bi, V and PEG-600 with Bi : V : PEG-600 (volume ratio) = 4 : 4 : 0, 4 : 4 : 1, 4 : 4 : 2, 4 : 4 : 3, 4 : 4 : 4. The samples were designated as BiVO<sub>4</sub>-a, BiVO<sub>4</sub>-b, BiVO<sub>4</sub>-c, BiVO<sub>4</sub>-d and BiVO<sub>4</sub>-e, respectively.

**Preparation of nanoporous BiVO**<sub>4</sub>/**CoPi photoanodes**: BiVO<sub>4</sub>-NP electrodes were loaded with CoPi cocatalyst by the in situ photochemical deposition method, carried out in a beaker in 0.1 M pH 7.0 potassium phosphate solutions containing 0.5 mM  $Co(NO_3)_2 \cdot 6H_2O$ , and illuminated from the top using a 300 W Xe lamp. CoPi/BiVO<sub>4</sub> electrodes with different loadings of CoPi cocatalyst were carefully prepared by controlling the photodeposition time (5, 10, 15 min). The samples were respectively denoted as BiVO<sub>4</sub> -NP/CoPiX.

**Preparation of nanoporous BiVO<sub>4</sub>-powders**: The pure BiVO<sub>4</sub> nanoparticles was synthesized via a typical procedure, 1 mmol of Bi(NO<sub>3</sub>)<sub>3</sub> • 5H<sub>2</sub>O and 1mmol of NH<sub>4</sub>VO<sub>3</sub> was added to 30 mL of 2M nitric acid solution at room temperature and remained continuous stirring for 30 minutes. Then, an appropriate amount of NH<sub>4</sub>OH ( $25\sim28\%$ ) was also added into the prepared solution to fit the pH value to 8. After stirring for 30 min, a clear orange solution was obtained. This solution was poured into a 50 mL Teflon-lined autoclave and maintained at 180°C for 24 h under autogenous pressure, and then naturally cooled to room temperature. The resulting precipitates

were collected and washed with ethanol and deionized water thoroughly and dried at  $80^{\circ}$ C in air. The as-obtained products were denoted BiVO<sub>4</sub>-powders.

*Characterization*: The X-ray diffraction spectra (XRD) measurements were performed on a Rigaku RINT-2000 instrument utilizing Cu K $\alpha$  radiation (40 KV). The XRD patterns were recorded from 10° to 90° with a scanning rate of 0.067°/s. Scanning electron microscopy (SEM) measurements were carried out on a field-emission scanning electron microscope (JSM-6701F. JEOL) operated at an accelerating voltage of 5 KV. Transmission electron microscopy (TEM) measurements were carried out by using a FEI Tecnai TF20 microscope operated at 200 kV. UV-vis diffuse reflectance spectra were taken on an UV-2550 (Shimadzu) spectrometer by using BaSO<sub>4</sub> as the reference.

Photoelectrochemical measurements: The Photoelectrochemical properties were measured by an electrochemical analyzer (CHI660D) in a standard three-electrode system with a working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The photoelectrodes were prepared by electrophoretic deposition on FTO substrate (1×5 cm<sup>2</sup>), as the working electrode, were cleaned by ultrasonication in distilled water, acetone and ethanol for 20 min sequentially. The illumination source was a 300 W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with  $\lambda \ge 420$  nm, and the power intensity of the incident light was calibrated to 200 mW/cm<sup>2</sup> at the surface of the working electrode. Illumination through the FTO side (back-side illumination) was used. A 0.5 M phosphate buffer (pH 7) containing 1 M Na<sub>2</sub>SO<sub>3</sub> as hole scavenger was used as the electrolyte. The pH of the solution was checked using a bench top pH meter. For light measurements the lamp was positioned to provide approximately 100 mW/cm<sup>2</sup> irradiation on the film as measured by athermopile detector (Newport, Models 1916C and 818-P). All potentials of the working electrode were presented against the reversible hydrogen electrode (RHE) for ease of comparison with H<sub>2</sub> and O<sub>2</sub> redox levels and other reports that used electrolytes with different pH conditions. The conversion between potentials vs. SCE and vs. RHE is performed using the equation below.

$$E_{RHE} = E_{SCE} + E_{SCE} \left( reference \right) + 0.0591 \times pH$$
(1)

 $(E_{SCE} \text{ (reference)} = 0.24 \text{ V vs. NHE at 25 °C})$  where pH is a pH value of the electrolyte.

The incident photon to current efficiency (IPCE) was determined using a full solar simulator (Newport, Model 9600, 300W Xe arc lamp) and a motorized monochromator (Oriel Cornerstone 130 1/8 m). IPCE was measured at 0.7 V vs. RHE in 0.5 M phosphate buffer (pH=7) using the same three-electrode setup described above for photocurrent measurements. IPCE was calculated as follows:

$$IPCE(\%) = \frac{1240 \times I(mA/cm^2)}{P_{light}(mW/cm^2) \times \lambda(nm)} \times 100$$
(2)

where I is the measured photocurrent density at a specific wavelength,  $\lambda$  is the wavelength of incident light and  $P_{\text{light}}$  is the measured light power density at that wavelength.

Supposing 100% Faradaic efficiency, the applied bias photon-to-current efficiency (ABPE) was calculated by following equation:

$$ABPE(\%) = \frac{I(mA/cm^2) \times (1.23 - V_{bias})(V)}{P_{light}(mW/cm^2)} \times 100$$
(3)

where *I* is the photocurrent density from the C-V curve shown in Figure 2,  $V_{\text{bias}}$  is the applied bias between WE and RHE,  $P_{\text{light}}$  is the incident illumination power density (100 mW cm<sup>-2</sup>).

Mott-Schottky plots were measured by an electrochemical analyzer (CHI660D) in a standard three-electrode system at frequencies of 1 and 5 kHz.

$$\frac{1}{C^2} = \frac{2}{N_D e \varepsilon_0 \varepsilon} \left[ \left( U_S - U_{FB} \right) - \frac{k_B T}{e} \right]$$
(4)

where *C* is the space charge layer capacitance,  $N_{\rm D}$  is the concentration of charger carriers,  $\varepsilon$  is the dielectric constant of the material,  $\varepsilon_0$  is the permittivity of vacuum, *e* is the elemental charge,  $U_{\rm S}$  is the applied potential,  $U_{\rm FB}$  is the flat band potential,  $k_{\rm B}$  is Boltzmann's constant, and *T* is temperature.

The electrochemical impedance spectroscopy (EIS) Nyquist plots were obtained at 0.7 V (vs. RHE) with small AC amplitude of 10 mV in the frequency range of 10<sup>-2</sup> to 10<sup>5</sup> Hz. The measured spectra were fitted with Zview.

*Photoelectrochemical*  $H_2$  *evolution*: was studied by applying 0.7 V (vs. RHE) in a self-made photoreactor, in which the photoanode and the counter electrode were separated by an Amberplex membrane. A 0.5 M phosphate buffer (pH 7) containing 1 M Na<sub>2</sub>SO<sub>3</sub> as hole scavenger was utilized as electrolyte, a nanoporous BiVO<sub>4</sub> film and Pt wire were used as photoanode and

photocathode, respectively, a saturated calomel electrode was used as reference electrode. According to the standard  $H_2$  evolution curve, the amount of generated  $H_2$  was measured by taking 30  $\mu$ L of gas from the headspace of the cell using a syringe and injecting it into the gas-sampling loop of the GC every 15 min.

In situ XPS experiments: System diagram of the in situ X-ray photoelectron spectroscopy (XPS) was shown in Figure S11 (Supporting Information). Different from the normal XPS, a 300 W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with  $\lambda \ge 420$  nm was used as illumination source. In the process of measurements, we can observe the changes of XPS spectra by controlling light on or off.

In the case of semiconductor samples, except for routine XPS measurements for the chemical binding states, the light irradiation could further induce the peak shifts of binding energy of various elements due to the electron transfer from the valence band (VB) to the conduction band (CB) and holes leave behind on the valence band. More specifically, the valence band and conduction band of semiconductors were composed of spin-orbits of various elements. Thereby, the charge transfer and electron density changes among various elements could be well and truly detected by XPS spectra. In contrast, when light irradiation was turned off, the excited electron on the conduction band will come back to the valence band and recombined with holes, and all the binding energy peaks of various elements will shift to their original positions. Therefore, this insitu XPS technique could truly reflect the charge transfer and electron density changes transfer and electron density changes of various elements in the semiconductors under light irradiation.

*Transmission of light*: Optical system diagram of the monochromatic light transmission has been shown in Figure S12 (Supporting Information). The illumination source is also a 300 W Xe arc lamp. The wavelength of incident light was adjusted by a motorized monochromator (Oriel Cornerstone 130 1/8 m), and the light intensity was measured by a light intensity meter (THORLABS) (Table S2, Supporting Information).

## Calculations

*Theoretical method*: First-principles calculations were performed using the GGA-PBE functional,<sup>1</sup> as implemented in CASTEP.<sup>2</sup> The ultrasoft pseudopotentials were applied to describe the interaction between core electrons and valence electrons. The valence electronic

configurations of Bi, V, and O are  $6s^26p^3$ ,  $3s^23p^63d^34s^2$ , and  $2s^22p^4$ , respectively. The cutoff energy of the plane-wave basis was 600 eV. A scissor of 0.316 eV was employed.

**Discussion:** The valence band of  $BiVO_4$  is mainly composed of O 2p, and the conduction band is formed by V 3d, O 2p, and Bi 6p. The photoexcited electrons are mostly transferred from O to V and Bi.

Table S1. Parameters of the nanoporous  $BiVO_4$  obtained from  $N_2$  adsorptiondesorption measurement.

Samples	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> /g)	Average pore size (nm)	
BiVO <sub>4</sub> -a	16.719	0.02	12.712	
BiVO <sub>4</sub> -b	20.765	0.08	14.617	
BiVO <sub>4</sub> -c	32.669	0.139	16.994	
BiVO <sub>4</sub> -d	26.238	0.126	17.264	
BiVO <sub>4</sub> -e	22.467	0.102	20.809	
BiVO <sub>4</sub> -Powders	2.495	0.0038	6.114	

Table S2. The light intensity of monochromatic light transmission before and after.

Wavelength	P <sub>iight</sub> (mW cm <sup>-2</sup> )				
(λ : nm)	No samples	Nanoporous BiVO <sub>4</sub>	Nanoparticles BiVO <sub>4</sub>		
400	3.64	0.42	0.011		
500	3.66	0.43	0.026		
600	3.42	0.35	0.054		
650	3.15	0.38	0.047		



Figure S1. Schematic representation of the synthesis procedure used in this study.



Figure S2. Pore diameter distribution of  $BiVO_4 - a$  (A), b (B), c (C), d (D) and e (E).



**Figure S3.** (A - C) TEM images of the BiVO<sub>4</sub> - c films on FTO substrate. (D) The SAED pattern. (E) EDX analysis. (F - I) Elemental mappings of (G) Bi, (H) V, (I) O elements.



Figure S4. Top (A) and side (B) view SEM images of BiVO<sub>4</sub> nanoparticle powders.



**Figure S5.** SEM images of BiVO<sub>4</sub> films. (A) BiVO<sub>4</sub>-a, (B) BiVO<sub>4</sub>-b, (C) BiVO<sub>4</sub>-d, (D) BiVO<sub>4</sub>-e.



Figure S6. XRD of BiVO<sub>4</sub> samples



**Figure S7.** Representative Mott-Schottky plots of  $BiVO_4$  films. All samples were measured in a 0.5 M phosphate buffer (pH 7) containing 1 M  $Na_2SO_3$  as hole scavenger in dark (black points: 5 kHz, red points: 1kHz).



**Figure S8.** Electrochemical impedance spectra of  $BiVO_4$  films measured at 0.7 V (vs. RHE) in a 0.5 M phosphate buffer (pH 7) containing 1 M Na<sub>2</sub>SO<sub>3</sub> as hole scavenger in dark. The inset shows an equivalent circuit for the photoanodes.



Figure S9. UV-vis absorption spectrum of BiVO<sub>4</sub> - c (A) and all samples (B).



**Figure S10.** Current-Potential characteristics of samples for water oxidation (A) and the production of  $H_2$  (B) at 1.23 V vs. RHE under visible light illumination (200 mW/cm<sup>2</sup>), current-potential characteristics of pure BiVO<sub>4</sub> nanoporous.



Figure S11. System diagram of the in situ X-ray photoelectron spectroscopy (XPS)



**Figure S12.** (A - C) In situ Bi 4f, V 2p, O 1s XPS spectra of  $BiVO_4$  powders films. All the samples were irradiated by visible light.



Figure S13. Optical system diagram of the monochromatic light transmission



**Figure S14.** Contactangle pattern of BiVO<sub>4</sub> films, (A) BiVO<sub>4</sub> nanoporous and (B) powders films.

Table S3. Best fitted parameters of time	e-resolved PL spectra.

Sample –	Decay life time (ns)		Relative amplitude (%)		Average lifetime	Goodness of fit parameter
	τ <sub>1</sub>	τ2	f <sub>1</sub>	f <sub>2</sub>	( <t>, ns)ª</t>	( <b>χ</b> ²)
BiVO₄-a	1.32	7.08	40.3	59.7	6.436	1.094
BiVO₄-b	1.61	7.31	36.7	63.3	6.662	1.076
BiVO4-c	2.17	7.72	31.2	68.8	7.093	0.986
BiVO4-d	1.92	7.56	33.5	66.5	6.920	1.005
BiVO <sub>4</sub> -e	1.55	7.25	37.5	62.5	6.602	0.993
BiVO <sub>4</sub> -Powders	0.95	5.84	43.4	56.6	5.298	1.038

<sup>a</sup> The average lifetime was calculated using equation:  $\langle T \rangle = (f_1T_1^2 + f_2T_2^2)/(f_1T_1 + f_2T_2)$ 



**Figure S15.** Time - resolved PL spectrum monitored at 575 nm under 370 nm excitation at 298 K for BiVO<sub>4</sub> nanoporous and powders photoanodes.

## **References:**

- 1 Perdew, J.P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996. 77, 3865-3868.
- 2 Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. Z. Kristallogr. 2005. 220, 567-570.