Electronic Supporting Information

Nanotip effect assisted in-situ growth of ZIF-67 nanoflowers on BiVO$_4$ photoelectrode to boost photoelectrochemical water oxidation

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Experimental Section

The experimental procedure for preparation of nanoconical $BiVO_4$ is as following:

1. Deposition of $BiVO_4$ seed layer on FTO

Firstly, 0.01 mol of NH_4VO_3 and 0.01 mol of $Bi(NO_3)_3 \cdot 5H_2O$ were sequentially dissolved in a 30 ml mixed solution of nitric acid and deionized water with a volume ratio of 2:1. After complete dissolution, 0.01 mol of citric acid was added into above mixture solution under continuous stirring to obtain blue-colored solution. Afterwards, a certain volume (6 ml) of above solution was taken out to mix with 2 ml polyvinyl alcohol aqueous solution (0.05g/ml) under ultrasonic treatment to obtain precursor solution, which was then spin-coated onto FTO with 3000 rpm for 30 s. After finished, the FTO was further annealed under 450 °C for 2 h in air to obtain $BiVO_4$ seed film.

2. Preparation of $BiVO_4$ film

Procedurally, 0.002 mol NH_4VO_3 was firstly dissolved in a 12.5 ml mixed solution of nitric acid and deionized water with a volume ratio of 2:3, followed by the addition of 0.002 mol $Bi(NO_3)_3 \cdot 5H_2O$ under continuous stirring until completely dissolved. Then, 47.5 ml of DI water were added into the above solution followed by addition of 8.0 g of $NaHCO_3$. Subsequently, the above solution was transferred into a conical flask to be heated at 60 °C controlled by a water bath device. Next, the FTO substrate with pre-prepared $BiVO_4$ seed layer was immersed into the solution with seed layer side up. After reaction for 6 h, the FTO substrate covered with $BiVO_4$ film was move out, rinsed using DI water and dried naturally, and finally annealed at 420 °C for 30 min under natural air atmosphere with a heating rate of $3.5°C \cdot min^{-1}$ to obtain crystalline $BiVO_4$ nanocone film (marked as BVO).

Characterizations of Materials

The crystallographic structure of the as-obtained photoelectrode materials were detected by X-ray diffractometer (XRD, CuKα, 40 kV, 40 mA, PANalytical Corp). Scanning electron microscope (SEM, ZEISS Sigma 300) and transmission electron microscope (TEM, FEI Talos F200x) were operated to identify the surface

morphological and microstructural properties of materials. The chemical compositions and atomic chemical states of the materials were determined using an X-ray photoelectron spectrometry (XPS, Axis Ultra, Kratos, UK). The optical behavior for photoelectrodes were collected using a spectrophotometry (Hitachi U-4100). Raman spectrum were conducted using a LabRAM HR Evolution Raman spectroscope (HORIBA Jobin Yvon). The Fourier Transform Infrared (FTIR) spectra was acquired and analyzed by using a Nicolet is10 FT-IR spectrometer.

Photoelectrochemical measurements of materials

Photoelectrochemical performance was tested using a CHI 760D electrochemical workstation outfitted with a 3-electrode cell. A Pt plate and Ag/AgCl were respectively applied as counter and reference electrodes, and the $BiVO_4$-based films were served as working electrode (actual exposure area of 0.196 cm^2). Photocurrents were recorded at a scan rate of 10 mV/s using the back-side illumination of 100 mW·cm^{-2}, which is powered by a 500 W Xe lamp coupled with an AM 1.5 filter. The electrolyte was 0.5 M sodium sulfate solution (pH=6.8). The photoelectrochemical impedance spectroscopy (PEIS) was measured at 1.23 V versus RHE using a back-illumination mode with frequency of 10^5 Hz to 10^{-1} Hz. Intensity modulated photocurrent spectroscopy (IMPS) measurement were operated by using ModuLab XM photochemistry system equipped with an LED with a wavelength of 405 nm. During test, the amplitude of the modulated light intensity is 50% of the background light intensity with frequency of 10000 Hz-0.05 Hz. The data was recorded and processed by ModuLab XM light Chemical system.

The bias vs. Ag/AgCl ($E_{Ag/AgCl}$) were calibrated to the reversible hydrogen electrode (E_{RHE}) by applying the Nernst equation as following [1,2]:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197(V) \qquad (S1)$$

The applied bias photon to current efficiency (*ABPE*) of photoanodes were given according to the below formula [3,4]:

$$ABPE \ (\%) = J \times (1.23 - V)/P_{light} \qquad (S2)$$

Where, *J* is the photocurrent density (mA·cm^{-2}) at measured bias, *V* is the applied bias (versus RHE), P_{light} is the incident light intensity (100 mW·cm^{-2}).

As reported in the literature, the measured photocurrent for water oxidation (J_{H_2O}) can be calculated using the following equation [5,6]:

$$J_{H_2O} = J_{abs} \times \eta_{surf} \times \eta_{bulk} \tag{S3}$$

$$J_{abs} = \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{1240} LHE(\lambda)P(\lambda)d(\lambda) \tag{S4}$$

J_{abs} is the photocurrent density assuming the absorbed photons completely convert into current, η_{surf} and η_{bulk} are the charge separation efficiencies in the bulk and on the surface of photoanode, respectively. The photocurrent performance of BVO and BVO/ZIF-67 photoanode for Na_2SO_3 oxidation (J_{Na2SO3}) were tested in 0.5 M Na_2SO_4 containing 0.1 M Na_2SO_3 aqueous solution as electrolyte (pH=9.65). The $P(\lambda)$ represents the irradiation power at each monochromatic light wavelength (λ), LHE (λ) is the light harvest efficiency that can be collected from the light absorption spectrum.

The η_{surf} for Na_2SO_3 oxidation is assumed to be 100% because of the extremely fast oxidation kinetics with Na_2SO_3 as the hole scavenger. Therefore, the photocurrent for Na_2SO_3 oxidation can be calculated using the following formula [7]:

$$J_{Na_2SO_3} = J_{abs} \times \eta_{bulk} \tag{S5}$$

Accordingly, the η_{surf} and η_{bulk} are given by the following formulas [5]:

$$\eta_{surf} = \frac{J_{H_2O}}{J_{Na_2SO_3}} \tag{S6}$$

$$\eta_{bulk} = \frac{J_{Na_2SO_3}}{J_{abs}} \tag{S7}$$
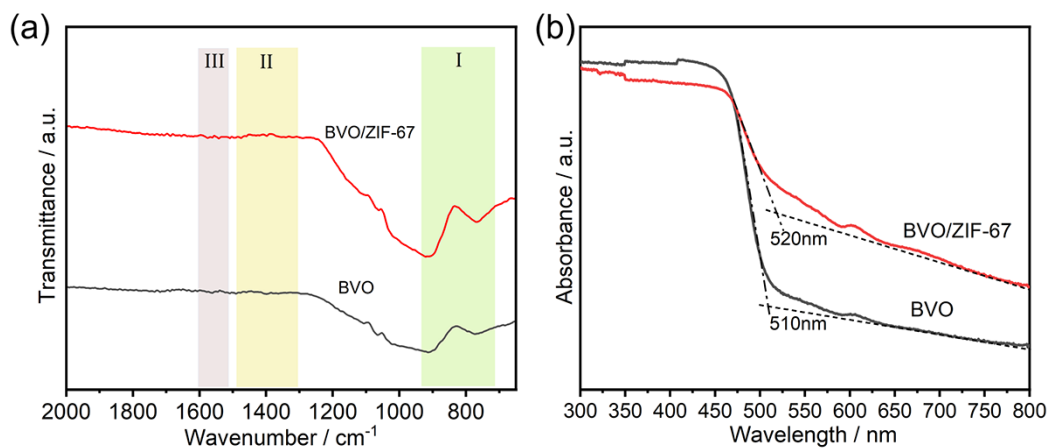
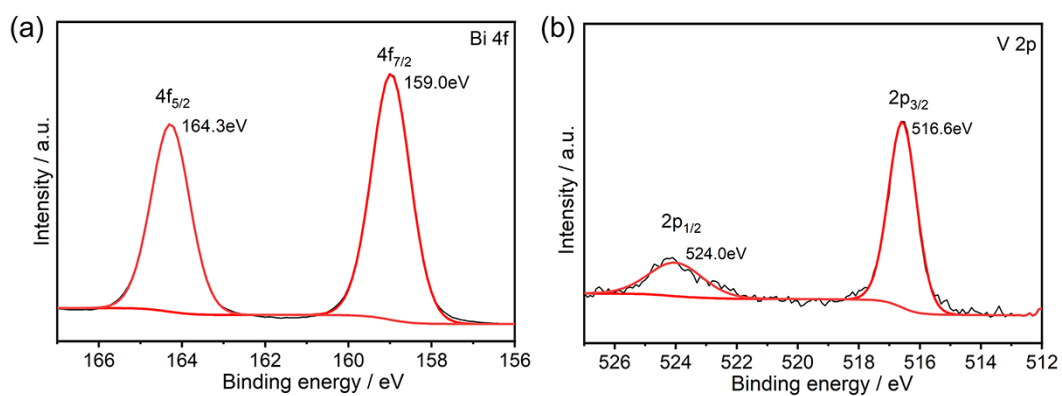Fig. S1 FT-IR spectrum (a) and UV-vis spectra (b) of BVO and BVO/ZIF-67 photoanode.

Fig. S2 XPS spectra of (a) Bi 4f and (b) V 2p in BVO/ZIF-67 composite
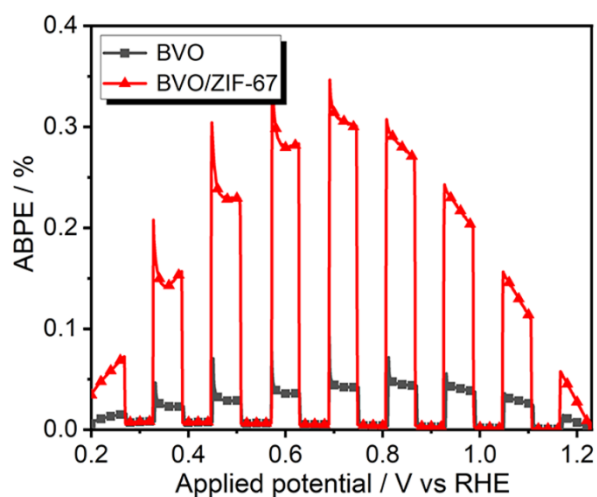
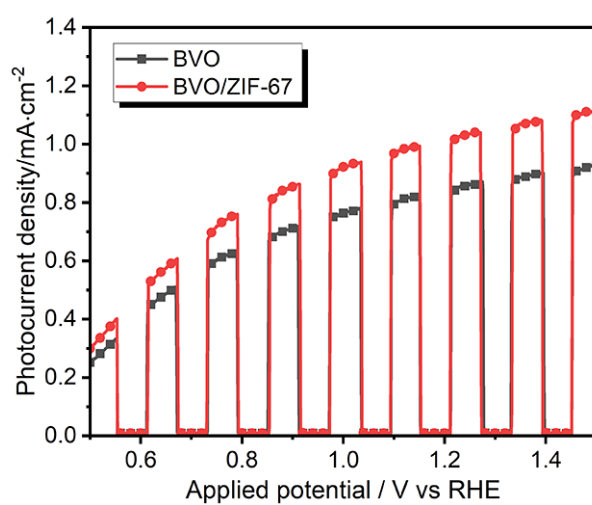Fig. S3 ABPE plots of BVO and BVO/ZIF-67 composite photoanode

Fig. S4 The photocurrent performance of BVO and BVO/ZIF-67 photoanode measured in 0.5 M Na_2SO_4 containing 0.1 M Na_2SO_3 aqueous solution as electrolyte.

Table S1. Calculated absorbed photocurrent density (J_{abs}) for BVO and BVO/ZIF-67 photoanodes.

Photoanodes	J_{abs} / mA·cm^{-2}
BVO	5.48
BVO/ZIF-67	5.95

The J_{abs} was calculated by using the equation S4. The LHE (λ) is the light harvest efficiency that can be collected from the light absorption spectrum shown in Fig. S1b. The optical absorption edge of BVO and BVO/ZIF-67 can be estimated to be 510 nm and 520 nm, respectively.
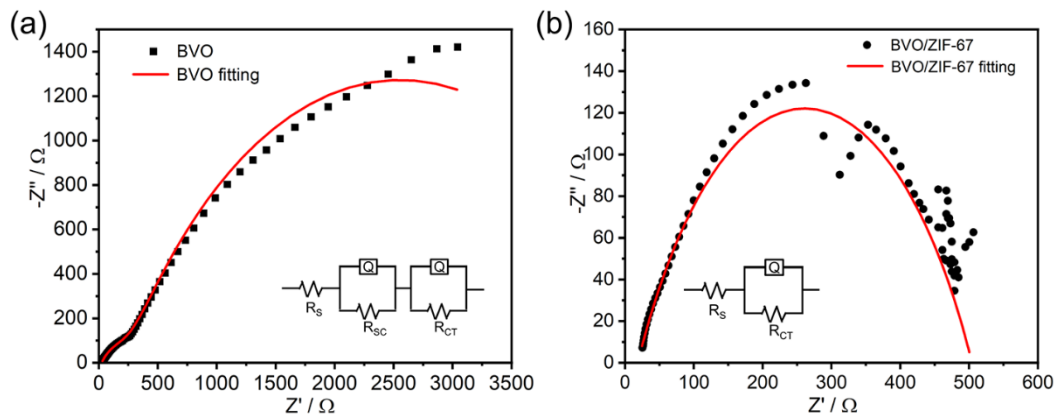

Fig. S5 The Nyquist plots of the BVO (a) and BVO/ZIF-67 (b) photoanodes (inset: the equivalent circuit, where R_S is the series resistance of electrolyte and external circuit; R_{SC} represents charge transport resistance in the bulk photoelectrode; R_{CT} shows the interfacial charge transfer resistance between the photoelectrode and electrolyte.) .

Table S2a The fitted values of R_S, R_{SC}, and R_{CT} of BVO photoanode

Photoanode	R_S / Ω	R_{SC} / Ω	R_{CT} / Ω
BVO	23.2	247.0	4584.0

Table S2b The fitted values of R_S, and R_{CT} of BVO/ZIF-67 photoanode

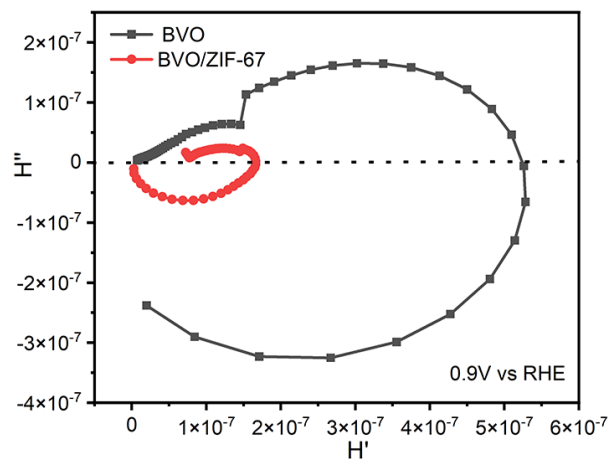| Photoanode	R_S / Ω	R_{CT} / Ω
BVO/ZIF-67	18.5	485.6

Fig. S6 IMPS plots for BVO and BVO/ZIF-67 measured at 0.9 V vs RHE under illumination by LED with wavelength of 405 nm

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