Supporting Information

Nano-surface Monocrystalline $BiVO_4$ Nanoplate Photoanode for Enhanced Photoelectrochemical Performance

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Experimental Section

Preparation of $BiVO_4$ photoanode (BVO):

(1) Synthesize of $BiVO_4$-seeds FTO glass: First, the aqueous solutions of $Bi(NO_3)_3$ (0.01 M) and NH_4VO_3 (0.01 M) were prepared separately with EDTA (0.015 M) as the complexing agent and ammonia water to adjust the pH to 10, respectively. Then, the two solutions are mixed to obtain the precursor solution. Finally, the precursor solution was spin-coated on the FTO conductive glass. The spin-coated conductive glass was calcined at 500 ^oC for 2 h to obtian $BiVO_4$ seeds FTO glass.

(2) Synthesize of $BiVO_4$ photoanode: First, prepare an aqueous solution of 0.01 M $Bi(NO_3)_3$ with 0.015 M EDTA as a complexing agent, and adjust the pH to 10 with 2 M NaOH solution. After the solution is clear and transparent, 0.01 M ammonium metavanadate was added. Then, the 30 ml of the above solution was transfered into a teflon reactor, and the $BiVO_4$-seed FTO glass was placed in it. Next, the reactor was heated at 180 ^oC for 3 h. Finally, the FTO galss was taken out and calcined at 500 ^oC for 4 h to obtain The $BiVO_4$ photoanode.

Preparation of nano-surface $BiVO_4$ photoanode (NBV):

(1) Synthesize of $BiVO_4/SiO_2$ photoanode: First, the $BiVO_4$ photoanode is immersed in the 30 ml of ethanol solution with 0.5 ml tetraethyl orthosilicate at 60 ^oC for 30 min. Then, the photoanode is washed by ethanol and calcined at 300 ^oC for 1h to obtain the $BiVO_4/SiO_2$ photoanode.

(2) Synthesize of nano-surface $BiVO_4$ photoanode: First, the $BiVO_4/SiO_2$ photoanode is immersed in the solution of $H_2C_2O_4$ (0.01 M) for 10 min with illumination. Then, the photoanode is immersed in the solution of KOH (1 M) to remove the SiO_2. Finally, the photoanode is rinsed clean and the nano-surface $BiVO_4$ photoanode is obtained.

Characterization

The scanning electron microscope images (SEM) are obtained on the field emission scanning electron microscope (Hitachi, Co. S4800). The high-resolution transmission electron microscopy images (HRTEM) are collected by thhe transmission electron microscope (JEOL, 2100F). The X-ray diffractometer (Bruker, D8) with Cu Kα radiation is used to obtained the X-ray diffraction spectra (XRD). The diffuse reflectance ultraviolet-visible spectra (UV-Vis) is collected by the UV-Vis spectrophotometry (Shimadzu, UV-3600). The X-ray photoelectron spectroscopy (ESCALab220i-XL) is used to obtained the X-ray photoelectron spectra (XPS).

(Photo)electrochemical measurements

The electrochemical measurements are performed on the electrochemcial workstation (Zahner, IM6) with the platinum gauze electrode as the counter electrode, the saturated calomel electroed as the reference electrode and the as-prepared photoenode as the work electrode. The electrolyte is the phosphate buffer solution (0.2 M, pH=7). The illumination is provide by the xenon lamp (Perfectlight, PLS-SXE300D, China) with the AM 1.5 G lihjt filter.

The electrochemically active area of the photoanode is obtained by the cyclic voltammogram method. The electrolyte is 5mM $K_3Fe(CN)_6$ in 0.1 M KCl solution. The scan rate is set to 5, 10, 25, 50, 75, 100, 200 mV s^{-1}. The real electrochemically active area can be obtained by Randle-Sevcik equation:

$$I_p=2.69\times10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

Where I_p is the oxidation peak current, n is the electron transferred number (n =1), A is the electrochemically active area, D is the diffusion constant of ferrous cynide ($D=6.7\times10^{-6}$ cm^2 s^{-1}), C is the concentration of ferrous cyanide and the v is scan rate.

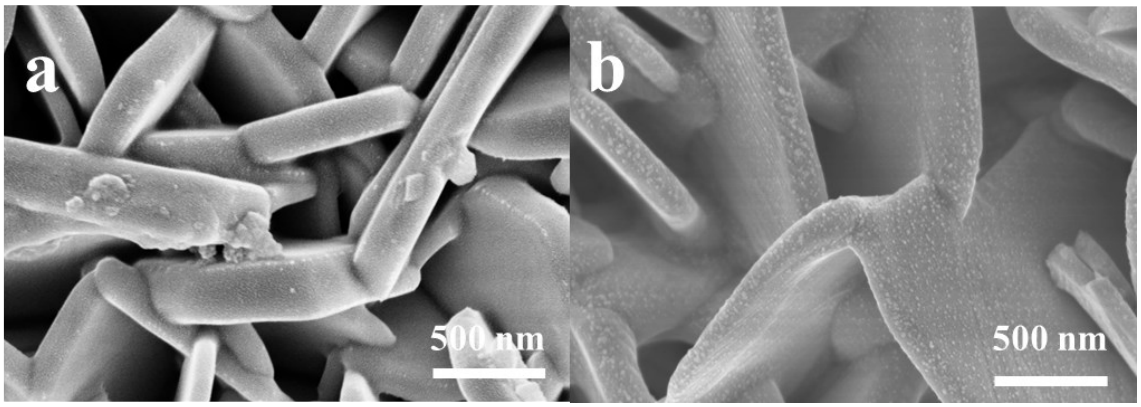

Figure S1. SEM image of $BiVO_4/SiO_2$ (a) and directly etched $BiVO_4$ (b).

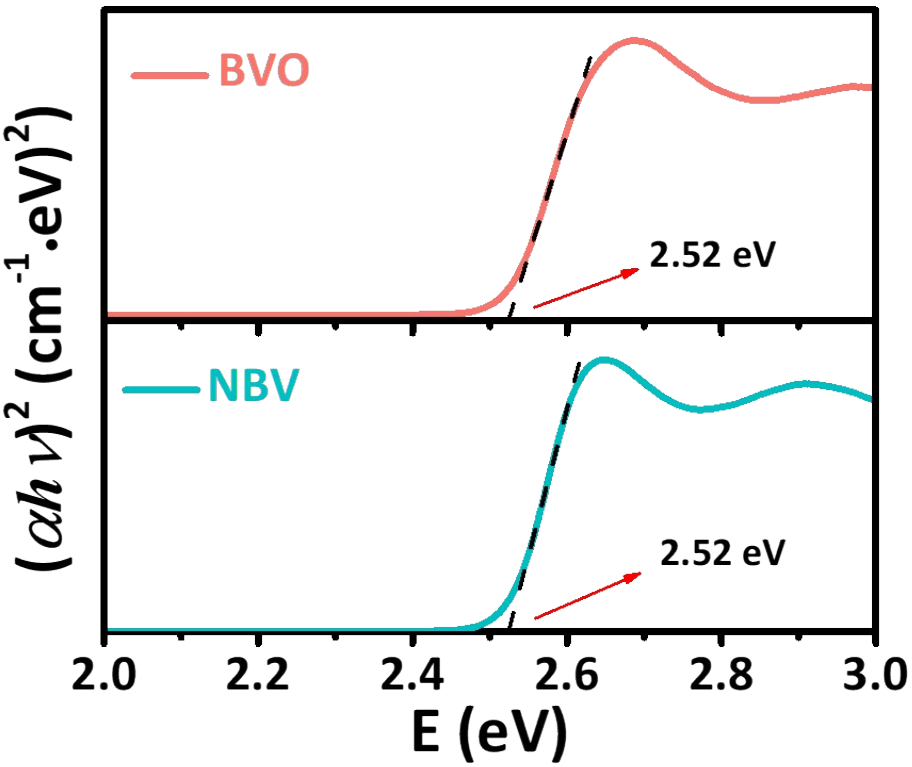

Figure S2. Tauc plots of BVO and NBV photoanodes.

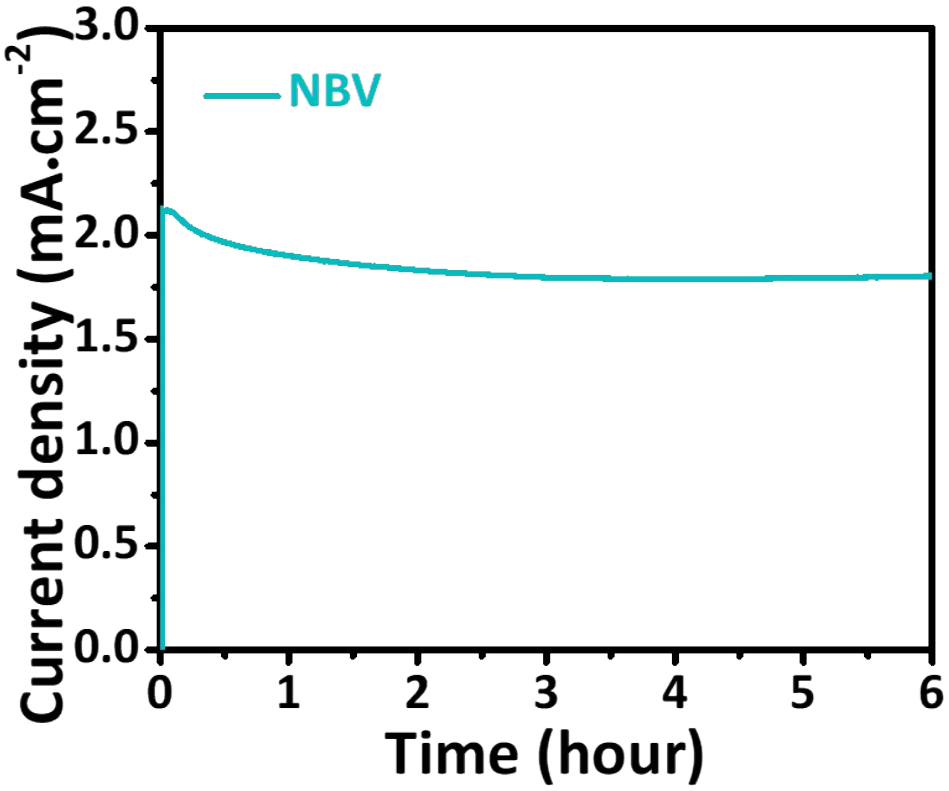

Figure S3. Stability test of NBV photoanode.

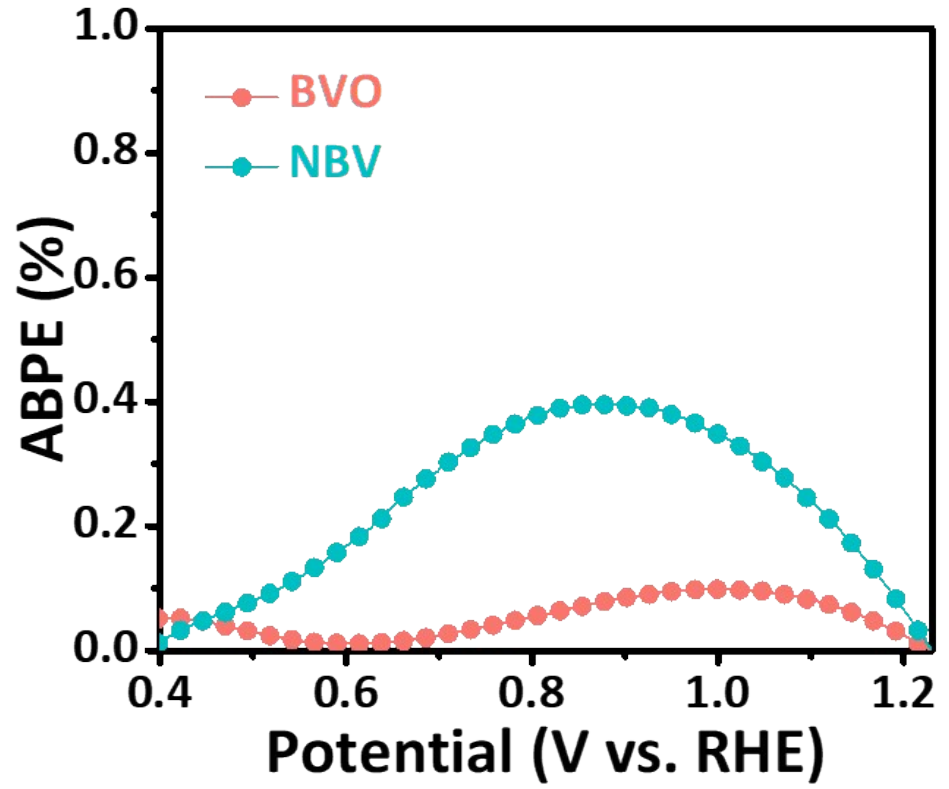

Figure S4. The applied bias photo-to-current efficiency (ABPE) of photoanodes.

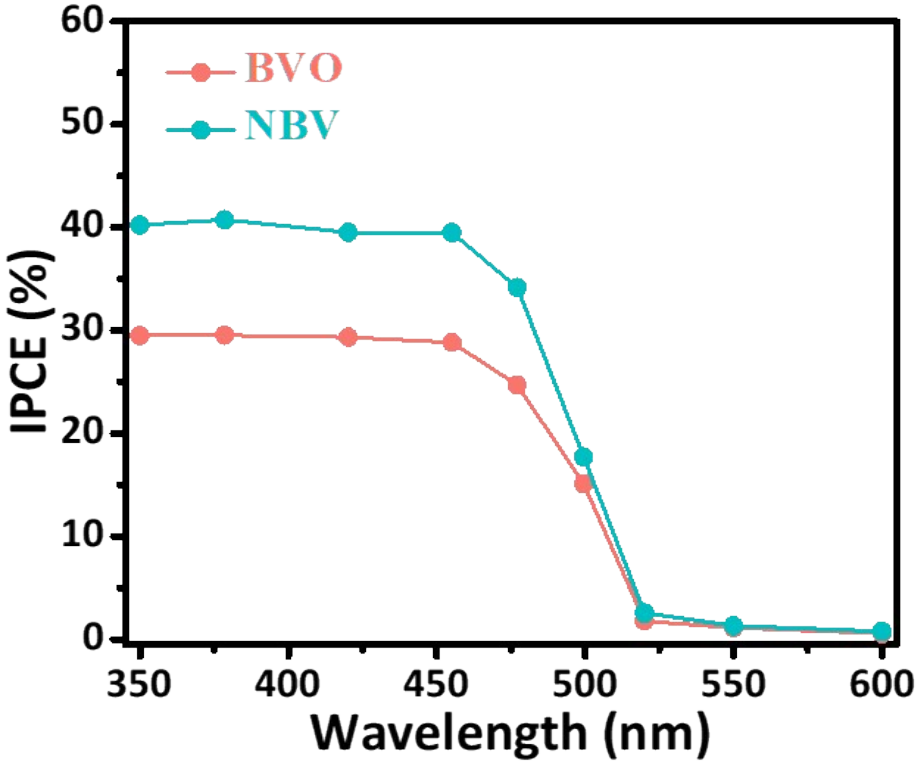

Figure S5. Incident photo-to-electron conversion efficiency (IPCE) of BVO and NBV photoanodes.

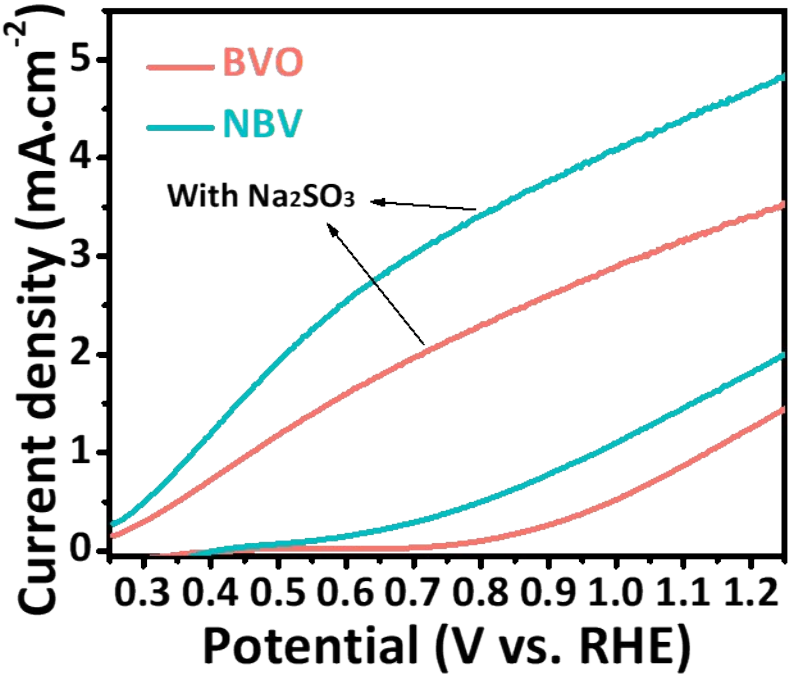

Figure S6. Sulfite oxidation and water oxidation curves of photoanodes.

Table S1 Summary of $BiVO_4$ photoanode with oxygen vacancies

Treatment method	Onset potential (V vs. RHE)	Onset potential with oxygen vacancies (V vs. RHE)	Photocurrent density (mA cm^{-2}, 1.23 V vs. RHE)	Photocurrent density with oxygen vacancies (mA cm^{-2}, 1.23 V vs. RHE)	Ref.
Hydrogenation	0.53	0.53	1.5	3	1
Electrochemically Treatment	None	None	0.25	2.5	2
Hydrogenation	None	None	0.2	2.1	3
Etch	0.7	0.4	1.5	2.0	This work

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3. G. Wang, Y. Ling, X. Lu, F. Qian, Y. Tong, J. Z. Zhang, V. Lordi, C. R. Leao, Y. Li, *J. Phys. Chem. C*, 2013, **117**, 10957-10964.