Supplementary Information

Chemical reduction-induced surface oxygen vacancies of $BiVO_4$ photoanodes with enhanced photoelectrochemical performance

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1. Preparation of pristine $BiVO_4$ films

$BiVO_4$ films were synthesized based on electrodeposition [1]. First, the pH of 50 mL of water in a beaker was adjusted to 1.7 by adding around 70 μL of 65% HNO_3. Next, 3.32 g of KI (0.4 M) was added to the solution which was stirred for 5 min to dissolve KI (for stabilizing $Bi(NO_3)_3$). After that, 0.97 g of $Bi(NO_3)_3 \cdot 5H_2O$ (0.04 M) was added to this solution which was stirred vigorously until total dissolving. Besides, 0.497 g of *p*-benzoquinone (0.23 M) was added to 20 mL of ethanol (99.8%) which was stirred for at least 30 min. The *p*-benzoquinone in ethanol was then mixed with the KI/$Bi(NO_3)_3$ solution by stirring for 2 min which was used as electrolyte for electrodeposition.

Cathodic deposition was carried out using a three-electrode system in which FTO glass (sonicated in acetone, ethanol and water each for 20 min, and dried with compressed air) was as working electrode, Pt wire as counter electrode and Ag/AgCl (3 M KCl) as reference electrode. Amperometric i-t technique was employed, and the potential was set at -0.1 V vs. Ag/AgCl. Each electrodeposition was last for 5 min, and a total charge of around 0.13 C cm^{-2} was finally accumulated to electrodeposit BiOI films on FTO glass. To obtain $BiVO_4$ films, 300 μL of 0.2 M $VO(acac)_2$ in DMSO was added on each BiOI film and heated at 85 ^oC for 30 min to vaporize DMSO. The samples were then calcined at 450 ^oC for 2 h in air using a muffle furnace (ramp rate 2 $^oC\ min^{-1}$). Finally, $BiVO_4$ films were treated in 1 M NaOH for 30 min with gentle stir to remove V_2O_5, and then rinsed with water and dried overnight in air.

2. Electrochemically active surface area (EASA) measurements

The EASA of bare $BiVO_4$ and S-$BiVO_4$ photoandoes was estimated according to a double-layer capacitance method [2, 3]. The change of current density in the dark under the bias ptoential is attributed to capacitive charging and not relevant to faradaic current since there is no redox couple in the electrolyte (Figure S2a and b) [2, 3]. The calculated C_{dl} values, representing the capacitance of double-layer at material surface, are 98 and 131 μF cm^{-2} for bare $BiVO_4$ and S-$BiVO_4$ photoanodes, respectively (Figure S2c). The corresponding EASA could be estimated according to the below equation (Table inserted in Figure S2c).

$$\text{EASA} = \frac{C_{dl}}{C_s}$$

Where C_s is the capacitance of smooth planar surface of the material in the same electrolyte. Since both photoanodes basically contain $BiVO_4$, they are assumed to have the same C_s.

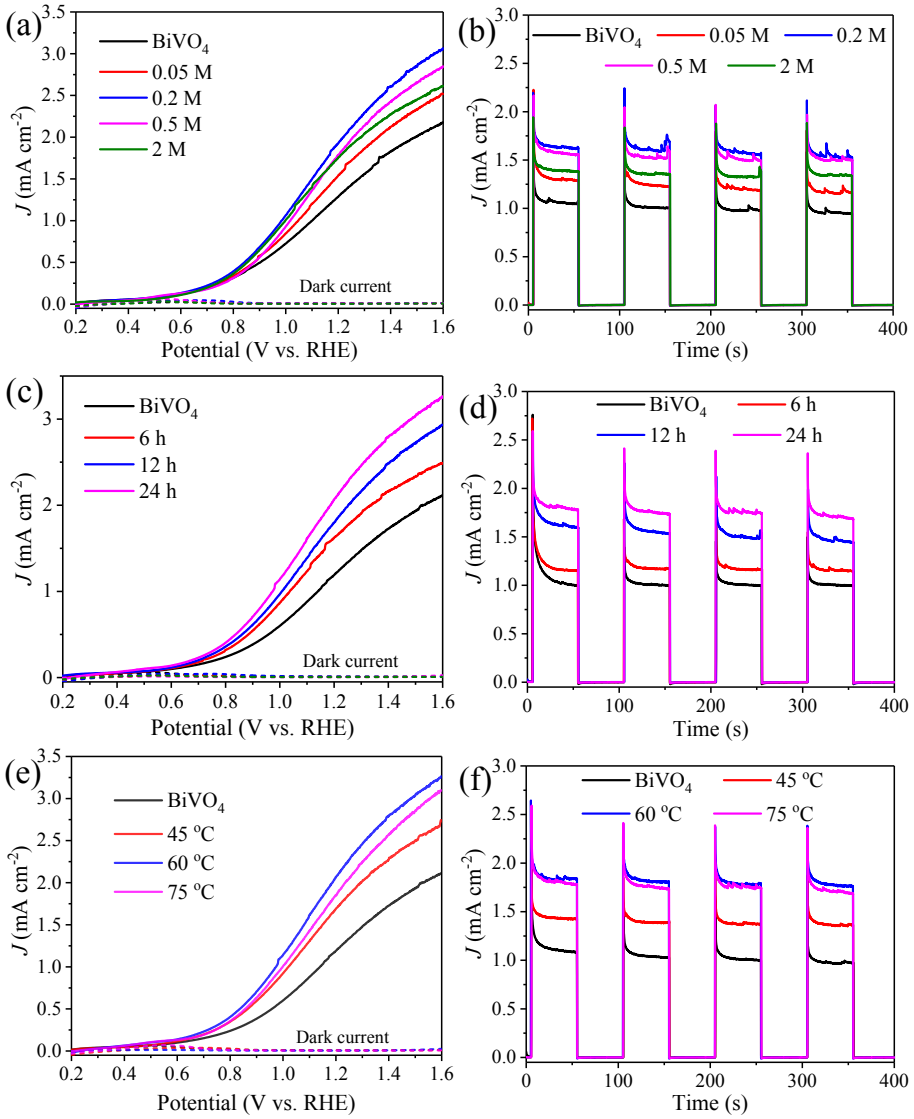

Figure S1. (a) LSV and (b) I-t responses of sulfite-treated $BiVO_4$ prepared by the reactions with different concentrations of Na_2SO_3 at 60 °C for 9 h. (c) LSV and (d) I-t results of sulfite-treated $BiVO_4$ prepared by the reactions with 0.2 M Na_2SO_3 for different times at 60 °C. (b) LSV and (d) I-t results of sulfite-treated $BiVO_4$ prepared by the reaction swith 0.2 M Na_2SO_3 for 24 h at various temperatures.

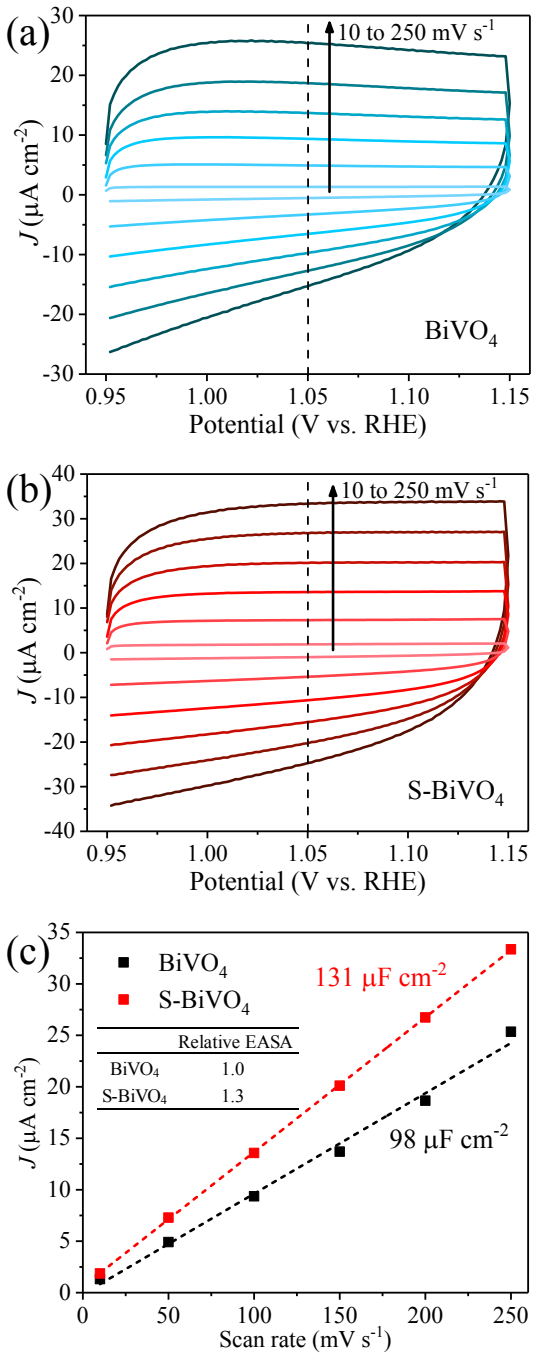

Figure S2. Cyclic voltammetry curves of (a) $BiVO_4$ and (b) S-$BiVO_4$ photoanodes at various scan rates (10, 50, 100, 150, 200 and 250 mV s^{-1}) in dark. (c) Charging current density at the potential of 1.05 V vs. RHE against scan rate.

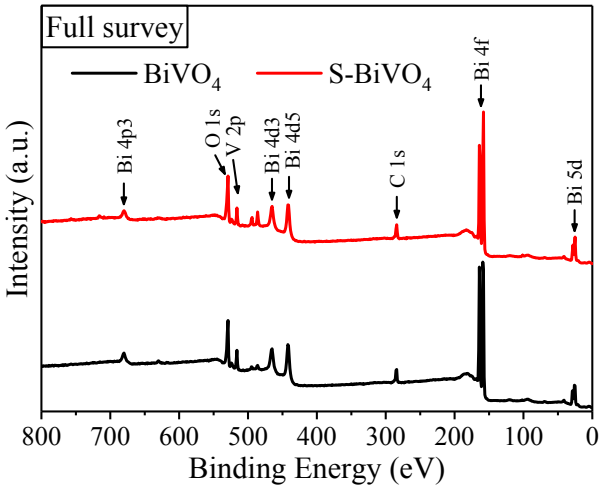

Figure S3. XPS full survey spectra of bare $BiVO_4$ and S-$BiVO_4$ photoanodes.

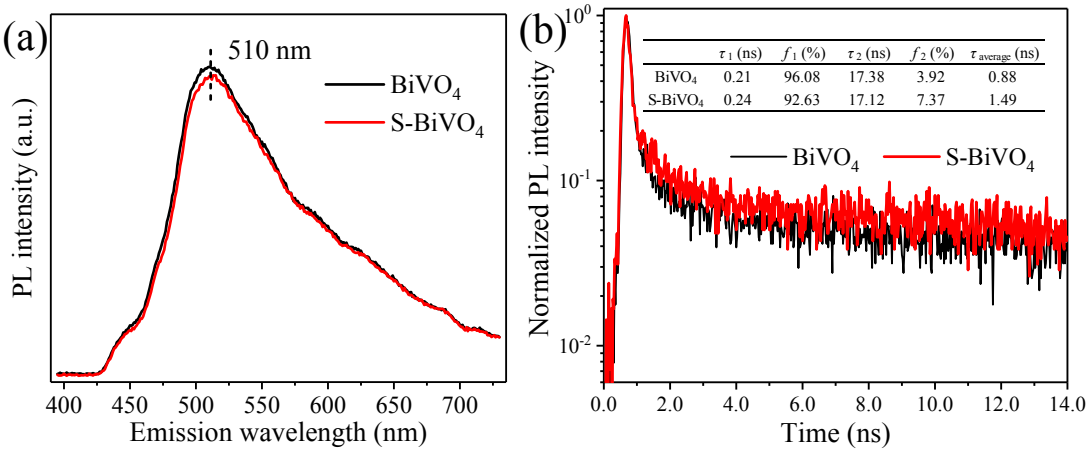

Figure S4. (a) Photoluminescence (PL) spectra of $BiVO_4$ and S-$BiVO_4$ photoanodes excited at 375 nm, and (b) Time-resolved photoluminescence (TRPL) spectra of bare $BiVO_4$ and S-$BiVO_4$ photoanodes.

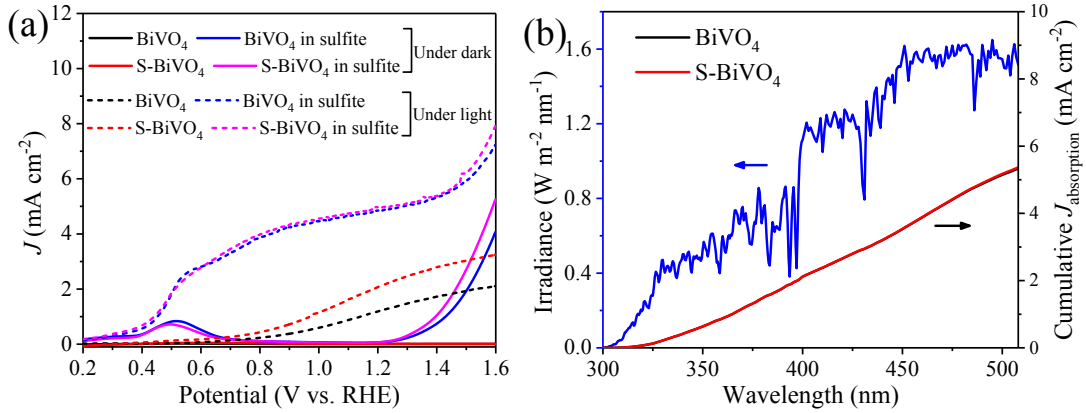

Figure S5. (a) LSV responses of $BiVO_4$ and S-$BiVO_4$ photoanodes in Na_2SO_4 (pH 6.6) and Na_2SO_3 (as hole scavenger, pH 10.6) electrolytes, respectively, under dark (solid curves) or illumination (dash curves) condition. (b) Theoretical cumulative photocurrent density from integrating light absorptance ($J_{absorption}$).

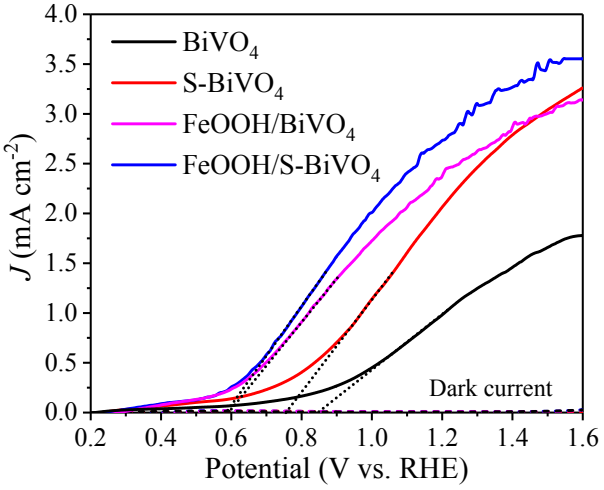

Figure S6. LSV responses of bare $BiVO_4$, S-$BiVO_4$, $BiVO_4$ coated by FeOOH and S-$BiVO_4$ coated by FeOOH.

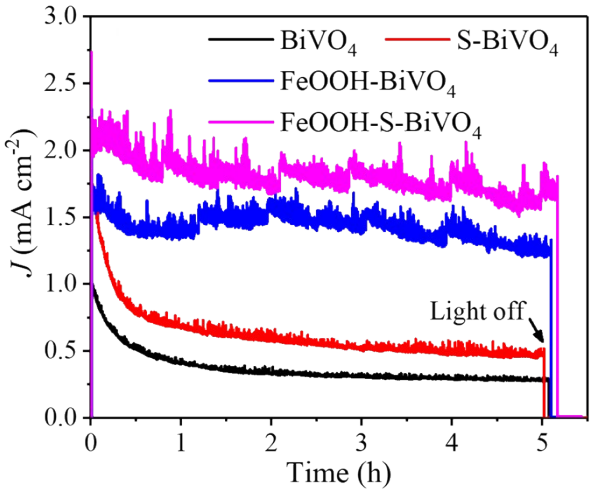

Figure S7. Amperometric i-t measurements of bare $BiVO_4$, S-$BiVO_4$, FeOOH-$BiVO_4$ and FeOOH-S-$BiVO_4$ photoanodes under 5-h illumination.

Table S1. Fitting parameters for electrochemical impedance spectra (EIS) of $BiVO_4$ and S-$BiVO_4$ photoanodes.

	R_s (Ω)	R_{ct} (Ω)	CPE-T (F)	CPE-P
$BiVO_4$	58	851	4.8×10^{-5}	0.75
S-$BiVO_4$	54	654	4.6×10^{-5}	0.77

Table S2. Calculated donor density of $BiVO_4$ and S-$BiVO_4$ photoanodes at various frequencies.

Sample	Donor density ($\times 10^{-26}$ m^{-3})			
	1000 Hz	2000 Hz	4000 Hz	Average
$BiVO_4$	2.88	2.48	1.76	2.37
S-$BiVO_4$	5.61	4.05	3.41	4.36

Reference

[1] T.W. Kim, K.-S. Choi, Nanoporous $BiVO_4$ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting, Science 343 (2014) 990-994.

[2] H.S. Han, S. Shin, D.H. Kim, I.J. Park, J.S. Kim, P.-S. Huang, J.-K. Lee, I.S. Cho, X. Zheng, Boosting the solar water oxidation performance of a $BiVO_4$ photoanode by crystallographic orientation control, Energy Environ. Sci. 11 (2018) 1299-1306.

[3] X. Yin, W. Qiu, W. Li, C. Li, K. Wang, X. Yang, L. Du, Y. Liu, J. Li, High porosity Mo doped $BiVO_4$ film by vanadium re-substitution for efficient photoelectrochemical water splitting, Chem. Eng. J. 389 (2020) 124365.