

## Electronic Supplementary Material (ESI)

### **Remarkable synergy of borate and interfacial hole transporter on BiVO<sub>4</sub> photoanodes for photoelectrochemical water oxidation**

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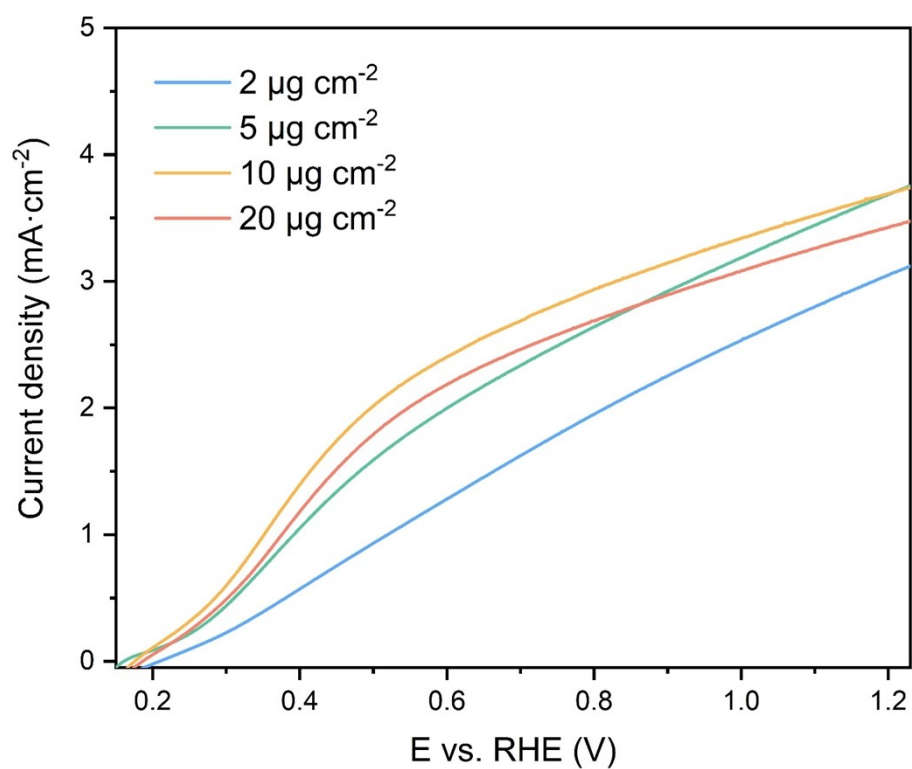
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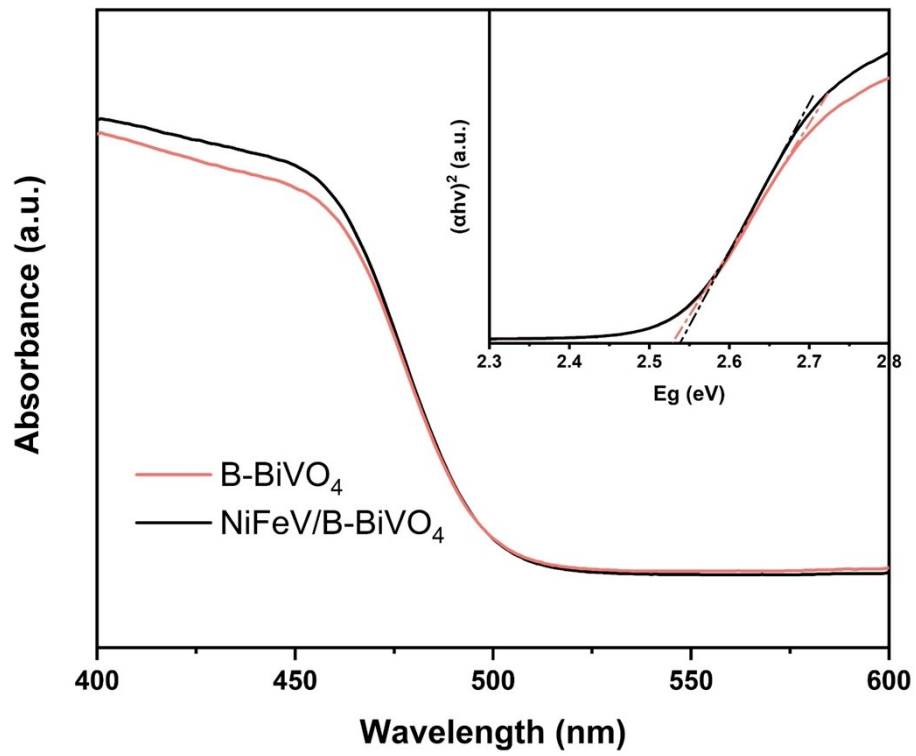
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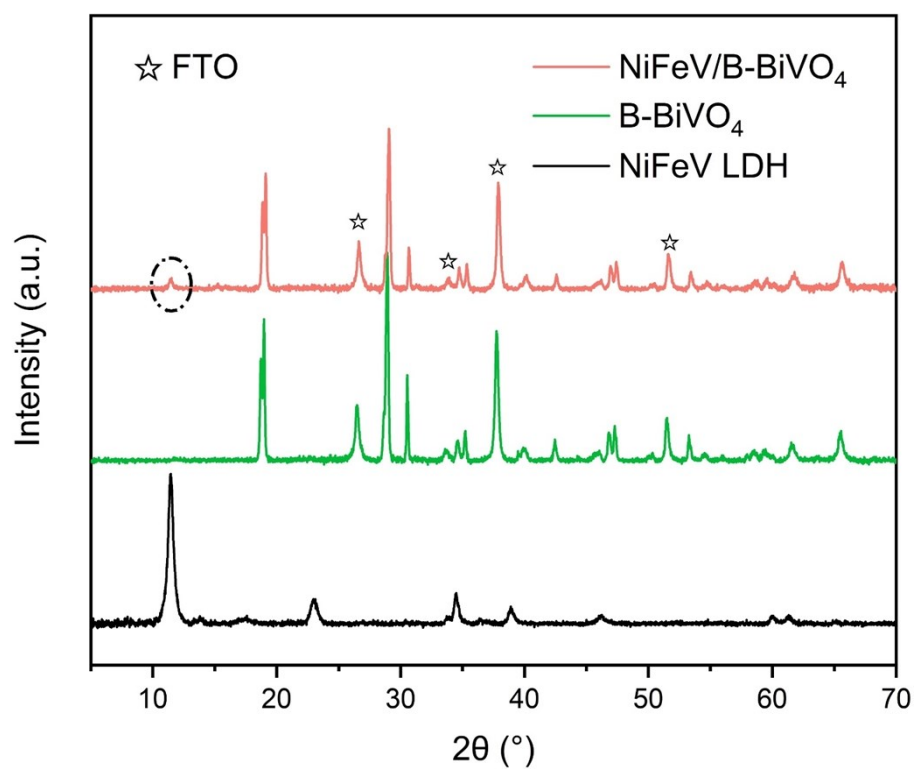
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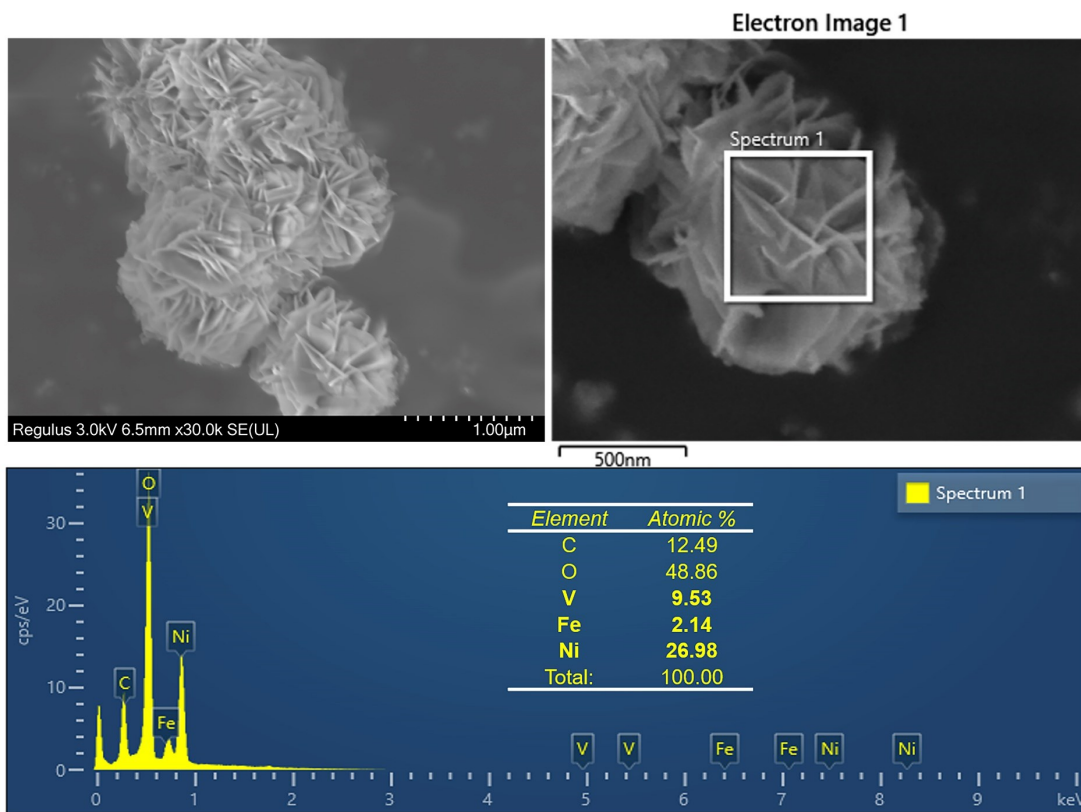
**Fig. S1.** LSV curves for NiFeV/BiVO<sub>4</sub> photoanodes with a series of catalyst mass loading measured under AM 1.5G illumination in a 1.0 M potassium borate buffer at pH 9.3 (scan rate: 10 mV s<sup>-1</sup>).



**Fig. S2.** UV-Vis diffuse spectra of B-BiVO<sub>4</sub> and NiFeV/B-BiVO<sub>4</sub> photoanodes, and the inset are corresponding Tauc plots



**Fig. S3.** XRD spectra of NiFeV LDH, BiVO<sub>4</sub>, B-BiVO<sub>4</sub> and NiFeV/B-BiVO<sub>4</sub> photoanodes.



**Fig. S4.** FE-SEM images (upper) and EDX patterns (bottom) with corresponding element ratio of NiFeV LDHs.

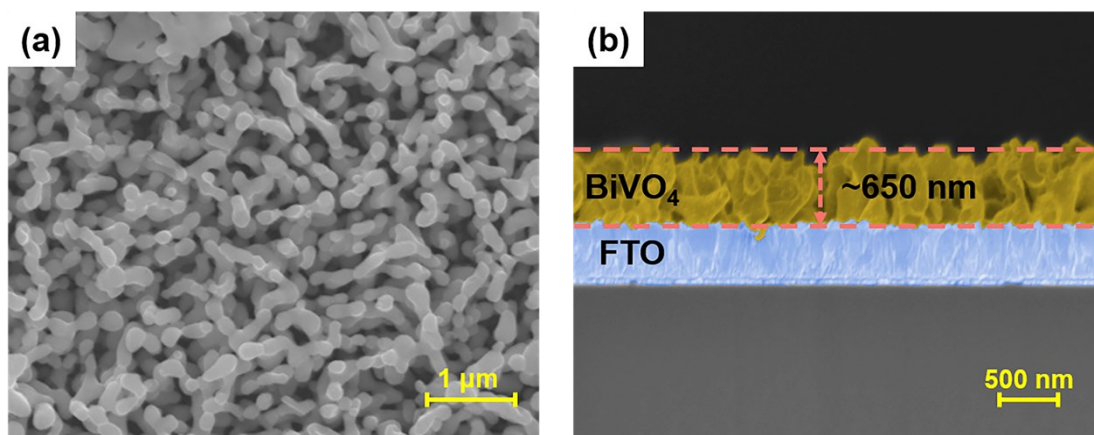
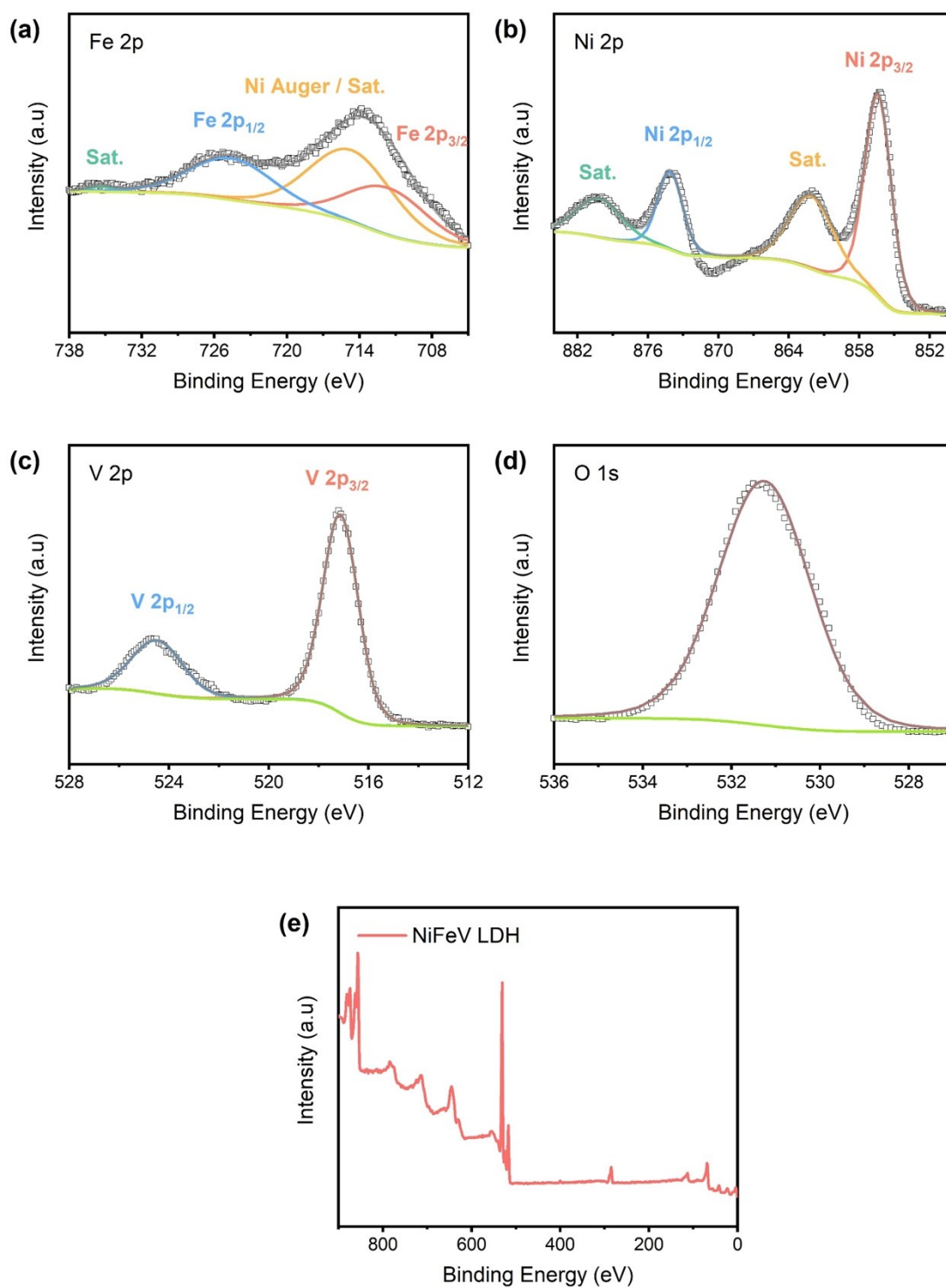
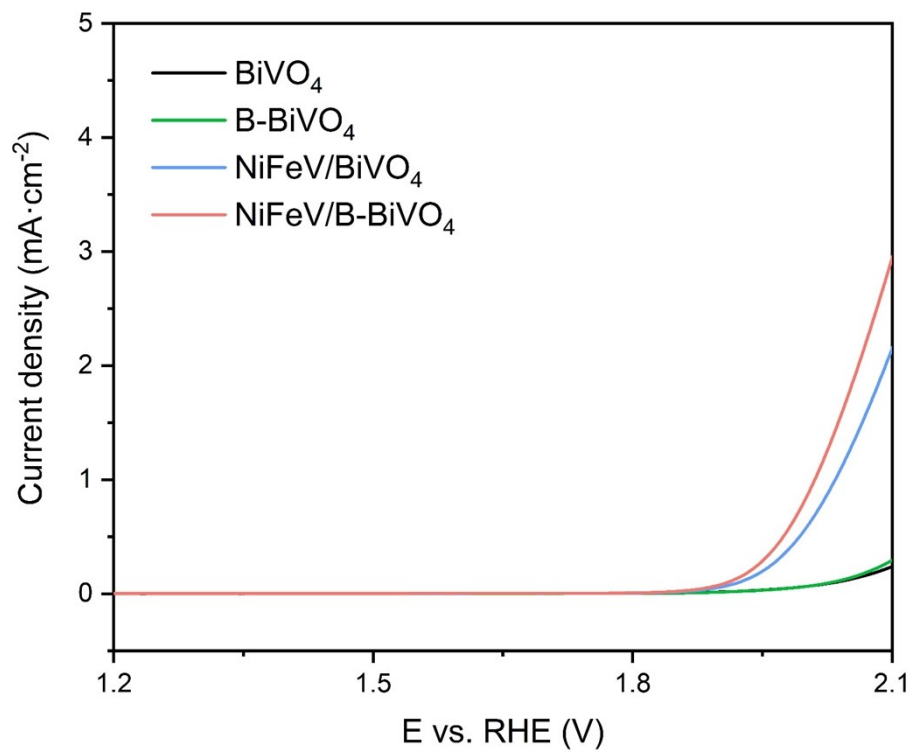


Fig. S5. (a) The top-view and (b) cross-sectional SEM images of the bare BiVO<sub>4</sub> photoelectrode.

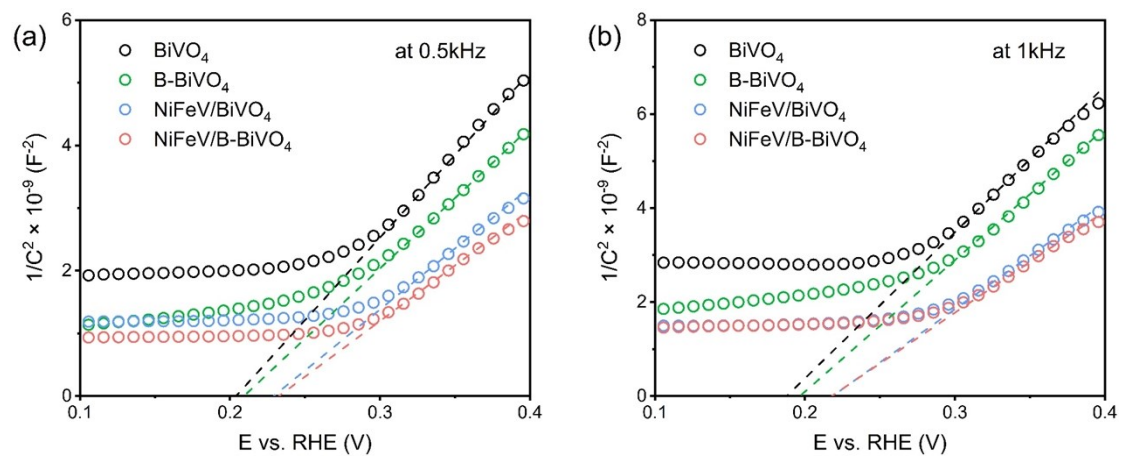


**Fig. S6.** XPS high-resolution spectra of pure NiFeV LDHs: (a) Ni 2p, (b) Fe 2p, (c) V 2p, (d) O 1s, and (e) the corresponding XPS survey.

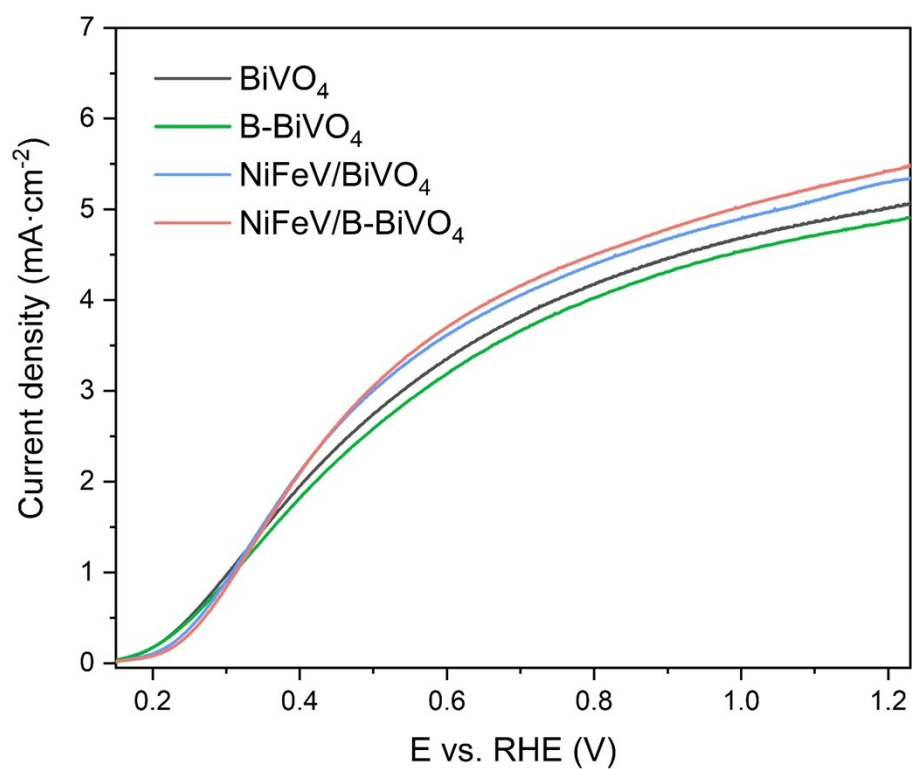


**Fig. S7.** LSV curves of BiVO<sub>4</sub>, B-BiVO<sub>4</sub>, NiFeV/BiVO<sub>4</sub>, and NiFeV/B-BiVO<sub>4</sub> photoanodes in dark in a 1.0 M potassium borate buffer at pH 9.3 (scan rate: 10 mV s<sup>-1</sup>).

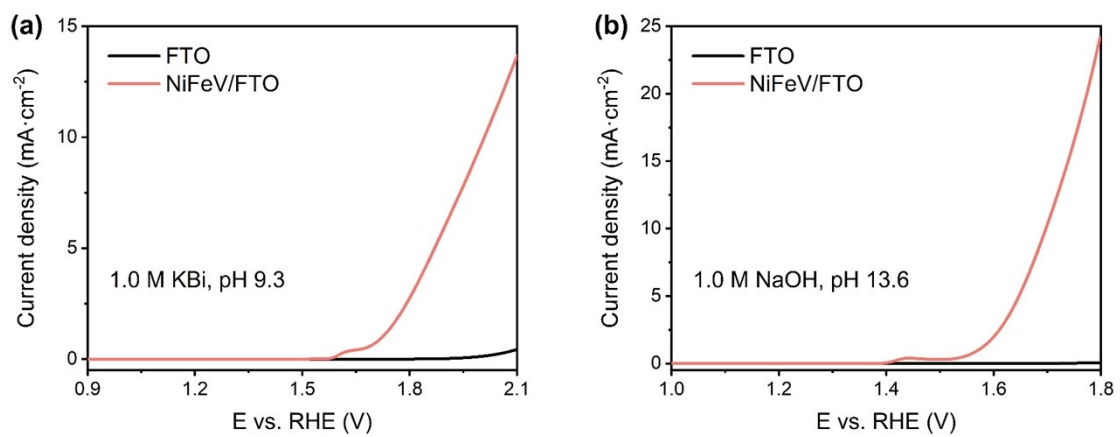




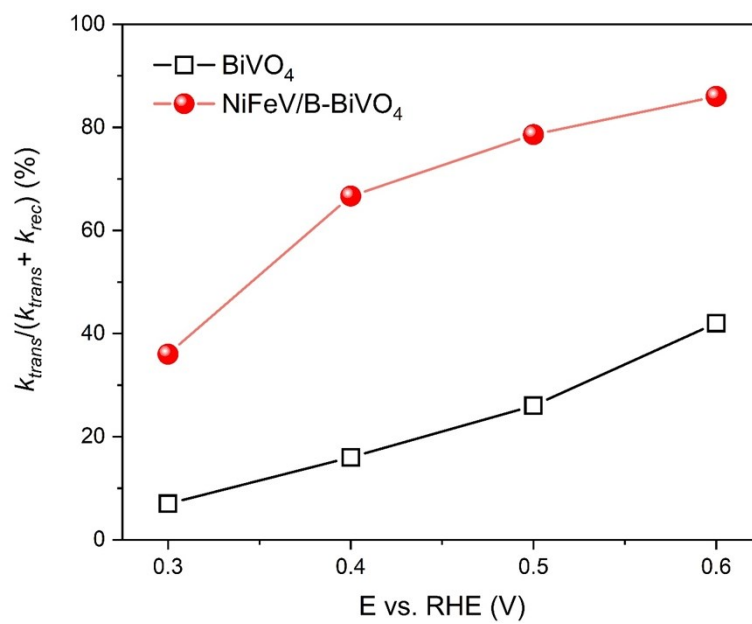
**Fig. S8** Mott-Schottky (MS) plots of photoanodes in dark at **(a)** 0.5 kHz and **(b)** 1 kHz.



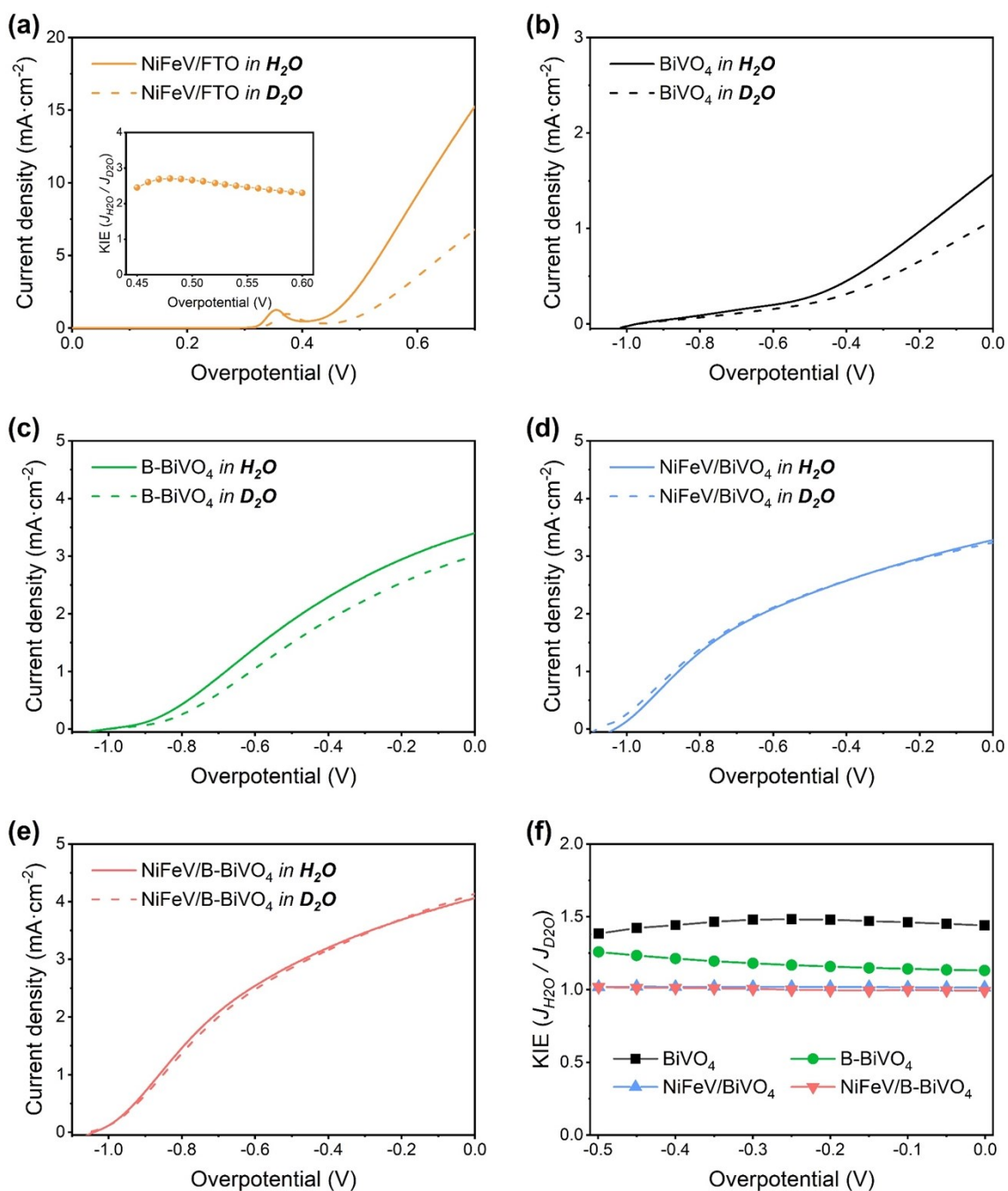
**Fig. S9.** LSV curves of BiVO<sub>4</sub>, B-BiVO<sub>4</sub>, NiFeV/BiVO<sub>4</sub>, and NiFeV/B-BiVO<sub>4</sub> photoanodes under AM 1.5G illumination in a 1.0 M potassium borate buffer (pH 9.3) with 0.2 M Na<sub>2</sub>SO<sub>3</sub> (scan rate: 10 mV s<sup>-1</sup>).



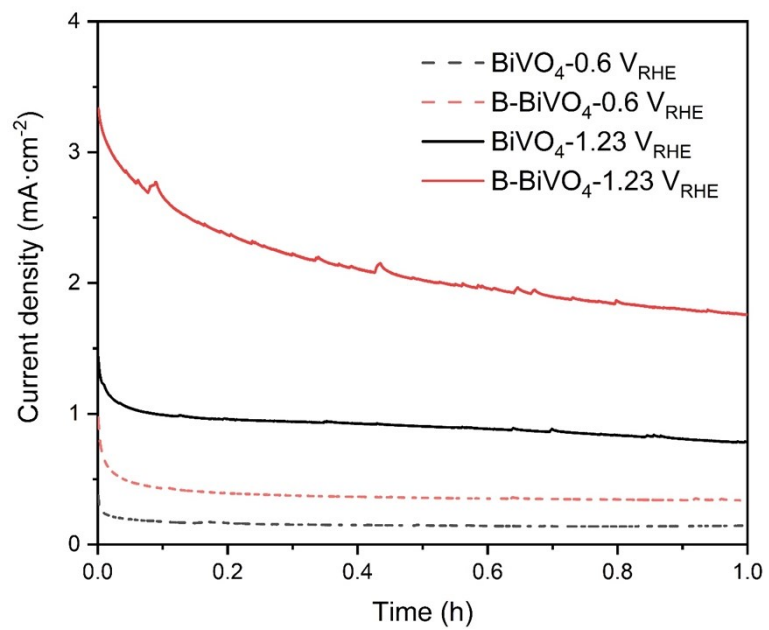
**Fig. S10.** The LSV measurements of NiFeV/FTO in (a) 1.0 M potassium borate buffer (pH 9.3) and (b) 1.0 M NaOH solution (pH 13.6) at a scan rate of  $50 \text{ mV s}^{-1}$  with 95% iR compensation.



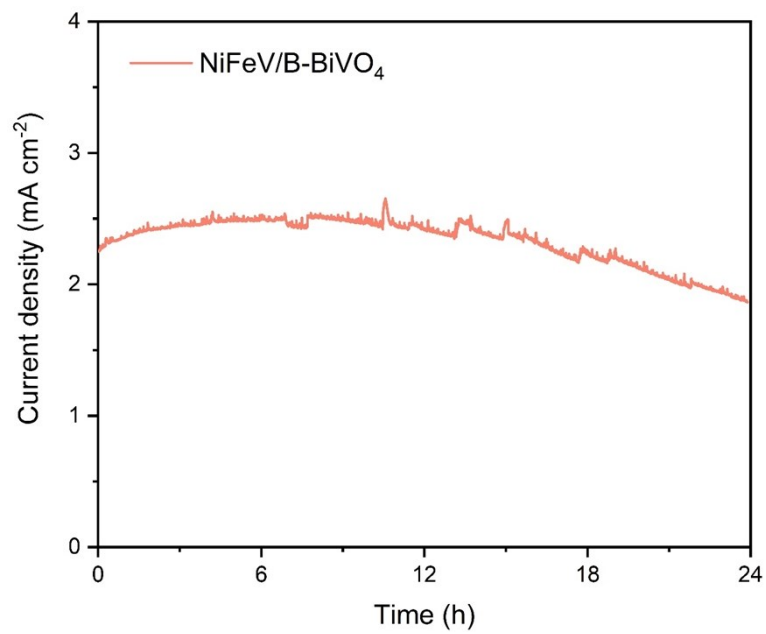
**Fig. S11.** The surface charge transfer efficiency, in terms of  $k_{trans}/(k_{trans}+k_{rec})$  for the  $\text{BiVO}_4$  and  $\text{NiFeV/B-BiVO}_4$  photoanodes obtained from IMPS analysis.



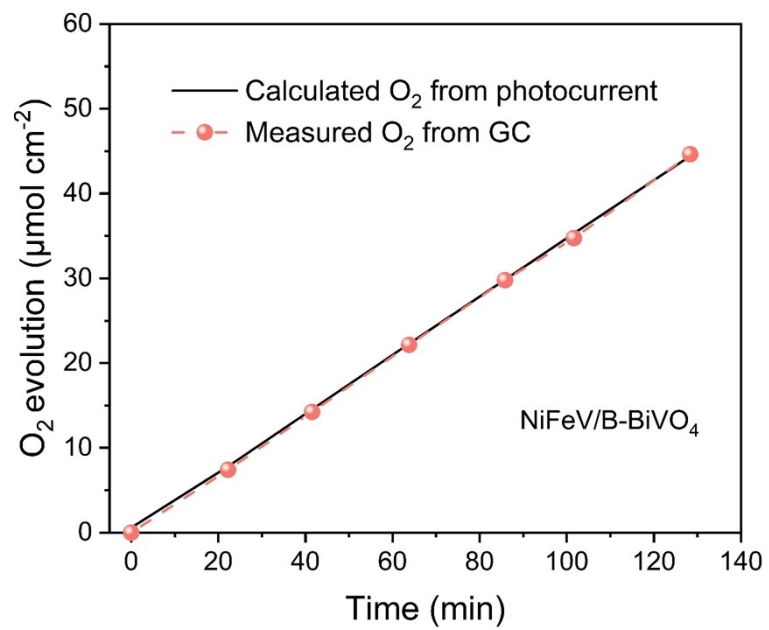
**Fig. S12.** (a) LSV curves of NiFeV/FTO in 0.1 M sodium borate  $H_2O$  (solid line) and  $D_2O$  (dash line) solutions, respectively (scan rate of  $10 \text{ mV s}^{-1}$  and 95% iR compensation); and the inset exhibits the corresponding KIEs at different overpotentials. (b)  $BiVO_4$ , (c) B- $BiVO_4$ , (d) NiFeV/ $BiVO_4$  and (e) NiFeV/B- $BiVO_4$  photoanodes tested under light illumination in 0.1 M sodium borate  $H_2O$  (solid line) and  $D_2O$  (dash line) solutions, respectively. (f) Corresponding KIE values of photoanodes versus overpotential.



**Fig. S13.** *J-t* curves of BiVO<sub>4</sub> and B-BiVO<sub>4</sub> tested in a 1.0 M potassium borate buffer (pH 9.3) at 0.6 V<sub>RHE</sub> and 1.23 V<sub>RHE</sub>, respectively.

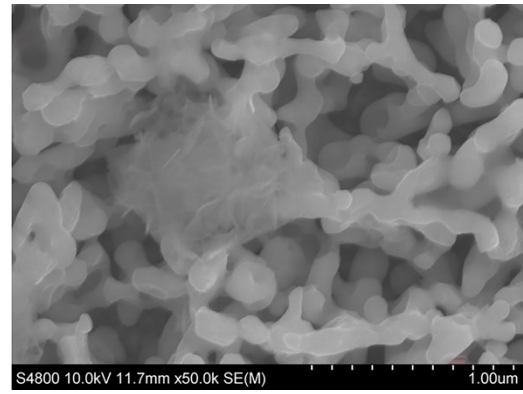
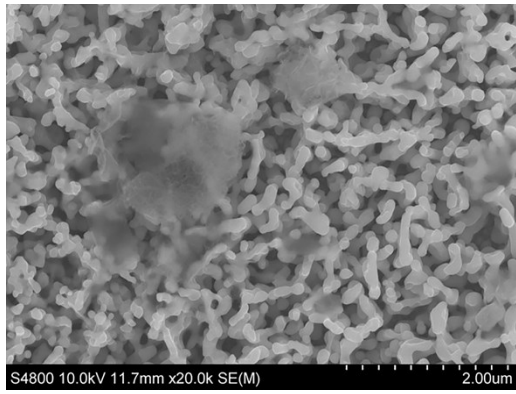


**Fig. S14.** The  $J-t$  curve of NiFeV/B-BiVO<sub>4</sub> tested in a 1.0 M potassium borate buffer (pH 9.3) at 0.6 V<sub>RHE</sub> for 24 h.

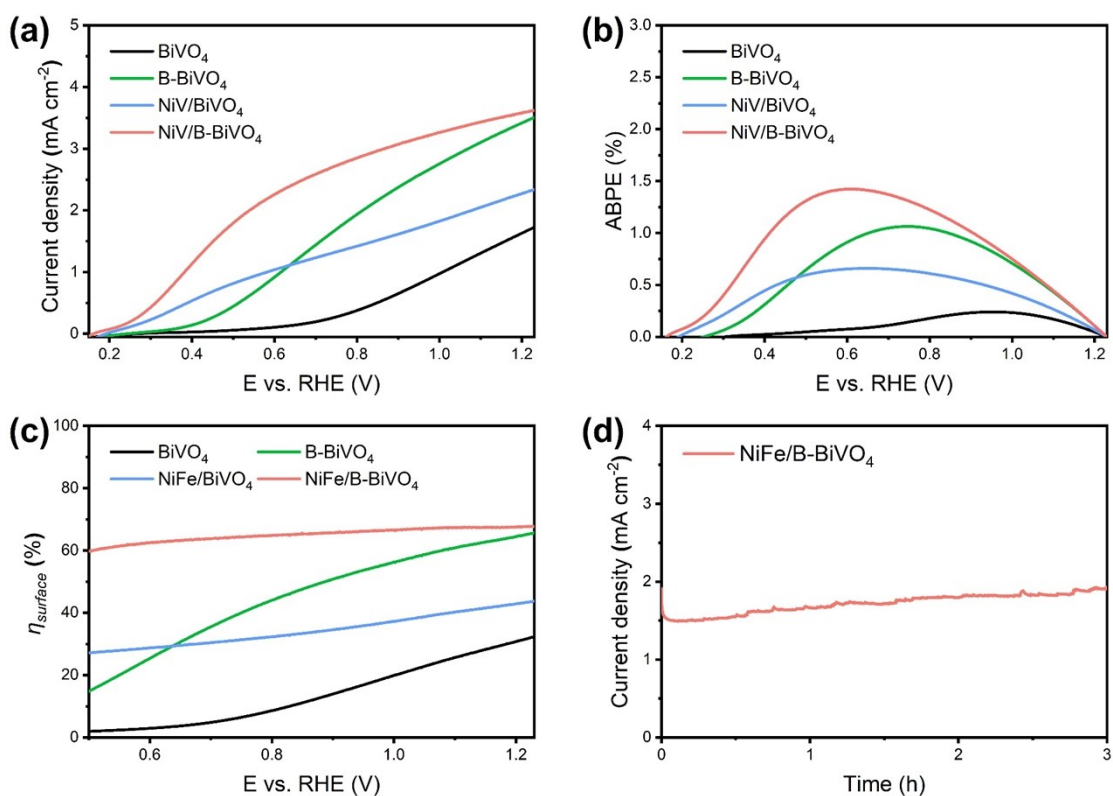


**Fig. S15.** Oxygen evolutions detected by gas chromatography and calculated from photocurrent during the photolysis of NiFeV/B-BiVO<sub>4</sub> photoanode at 0.6 V<sub>RHE</sub>.

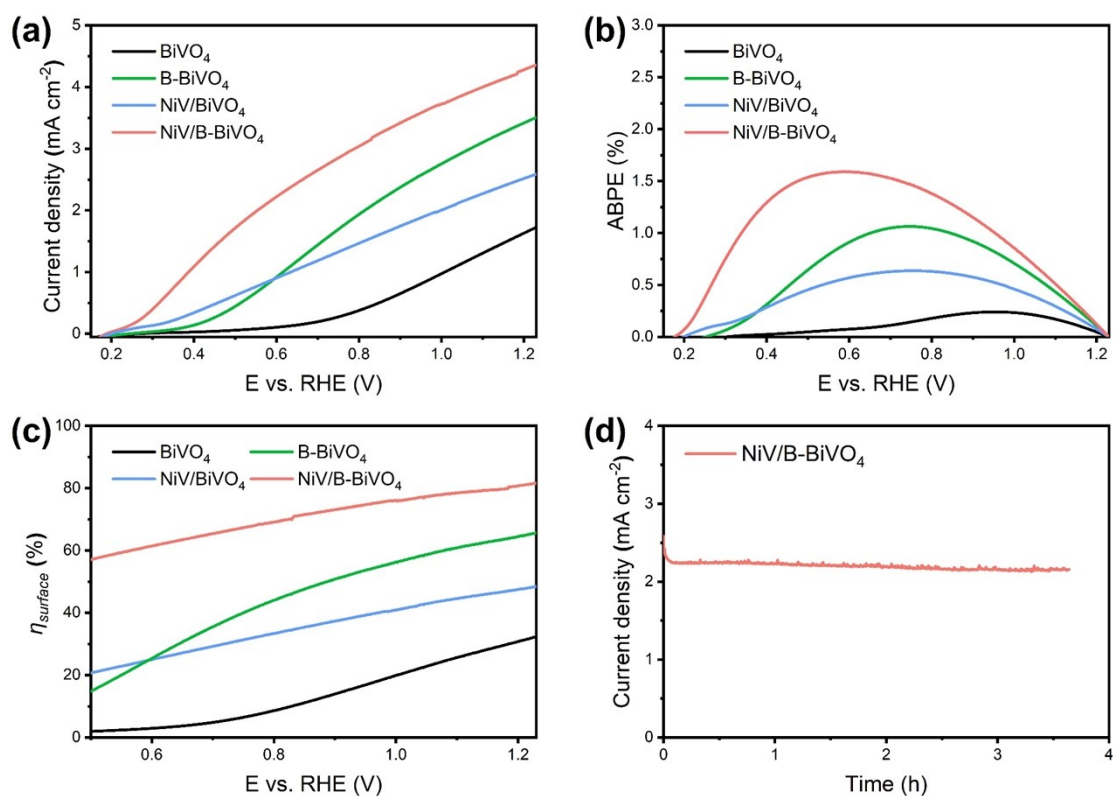




**Fig. S16.** The top-view SEM images of NiFeV/B-BiVO<sub>4</sub> at different magnifications after *J-t* testing at 0.6 V<sub>RHE</sub> for 8 h.



**Fig. S17.** (a) LSV curves of BiVO<sub>4</sub>, B-BiVO<sub>4</sub>, NiFe/BiVO<sub>4</sub>, and NiFe/B-BiVO<sub>4</sub> photoanodes under AM 1.5G illumination in a 1.0 M potassium borate buffer at pH 9.3 (scan rate: 10 mV s<sup>-1</sup>); (b) ABPE curves of photoanodes calculated from LSV curves; (c) Surface charge transfer efficiency ( $\eta_{surface}$ ) of photoanodes obtained from LSV curves of water oxidation and sulfite oxidation; (d) Long-term  $J-t$  curves at a constant bias of 0.6 V<sub>RHE</sub>.



**Fig. S18.** (a) LSV curves of BiVO<sub>4</sub>, B-BiVO<sub>4</sub>, NiV/BiVO<sub>4</sub>, and NiV/B-BiVO<sub>4</sub> photoanodes under AM 1.5G illumination in a 1.0 M potassium borate buffer at pH 9.3 (scan rate: 10 mV s<sup>-1</sup>); (b) ABPE curves of photoanodes calculated from LSV curves; (c) Surface charge transfer efficiency ( $\eta_{surface}$ ) of photoanodes obtained from LSV curves of water oxidation and sulfite oxidation; (d) Long-term  $J-t$  curves at a constant bias of 0.6 V<sub>RHE</sub>.

**Table S1.** PEC performance of LDH/BiVO<sub>4</sub> based photoanodes.

BiVO <sub>4</sub> photoanode	LDH co-catalyst loading method	$J_{ph}$ @1.23 V <sub>RHE</sub> (mA·cm <sup>-2</sup> )	Onset potential (V <sub>RHE</sub> )	Test condition <sup>[a]</sup>	Year
NiFeV/B-BiVO <sub>4</sub>	Drop casting (10 μg cm <sup>-2</sup> )	4.6	0.21	1.0 M KBi, pH 9.3	This work
CoAl/BiVO <sub>4</sub> <sup>1</sup>	Electrodeposition	3.5	0.41	0.5 M Na <sub>2</sub> SO <sub>4</sub> , pH 7.35	2021
NiFeY/BiVO <sub>4</sub> <sup>2</sup>	Hydrothermal	5.2	0.31	1.0 M KBi, pH 9.5	2020
Fe <sub>x</sub> Ni <sub>4-x</sub> -H/BiVO <sub>4</sub> <sup>3</sup>	Electrodeposition	3.65	0.53	0.5 M Na <sub>2</sub> SO <sub>4</sub> , pH 7	2020
ZnCoV/BiVO <sub>4</sub> <sup>4</sup>	Electrodeposition	2.55	0.33	0.1 M NaBi, pH 9.4	2020
NiFe/rGO/BiVO <sub>4</sub> <sup>5</sup>	Electrodeposition	3.26	0.4	1.0 M KBi, pH 9.33	2020
CoCe/BiVO <sub>4</sub> <sup>6</sup>	Hydrothermal	3.74	0.2	0.5 M KBi, pH 11	2020
NiCo/BiVO <sub>4</sub> <sup>7</sup>	Electrodeposition	2.95	0.4	0.5 M Na <sub>2</sub> SO <sub>4</sub> , pH 7.3	2020
CoMn/BiVO <sub>4</sub> <sup>8</sup>	Electrodeposition	2.69	0.31	0.5 M KP <sub>i</sub> , pH 7	2020
CoAl/GDY/BiVO <sub>4</sub> <sup>9</sup>	Hydrothermal	3.15	0.46	0.1 M Na <sub>2</sub> SO <sub>4</sub> , pH 6.8	2019
NiOOH/BP/BiVO <sub>4</sub> <sup>10</sup>	photodeposition	4.48	0.4	0.5 M KP <sub>i</sub> pH 7.1	2019
NiFe/BiVO <sub>4</sub> <sup>11</sup>	Drop casting	1.2	0.3	0.1 M KBi, pH 9.2	2018
CDs/NiFe/BiVO <sub>4</sub> <sup>12</sup>	Electrodeposition	2.84	0.5	0.5 M PBS, pH 7).	2018
CoPO <sub>3</sub> /pGO/NiFe/BiVO <sub>4</sub> <sup>13</sup>	Hydrothermal	4.45	0.17	1.0 M KBi, pH 9	2018
NiFe/BiVO <sub>4</sub> <sup>14</sup>	Hydrothermal	2.49	0.62	0.5 M Na <sub>2</sub> SO <sub>4</sub> , pH 7.3	2018
β-FeOOH/BiVO <sub>4</sub> <sup>15</sup>	Immersion	4.3	0.5	0.2 M Na <sub>2</sub> SO <sub>4</sub> pH 7	2018
CoOOH/BiVO <sub>4</sub> <sup>16</sup>	Spin coating	4.0	0.2	0.2 M KP <sub>i</sub> pH 7	2018
NiFe/BiVO <sub>4</sub> <sup>17</sup>	Hydrothermal	4.02	0.40	0.1 M KHCO <sub>3</sub> , pH 8.6	2017
CoLa/BiVO <sub>4</sub> <sup>18</sup>	Electrodeposition	2.02	0.19	0.5 M KP <sub>i</sub> , pH 7	2017

NiFe/BiVO <sub>4</sub> <sup>19</sup>	Electrodeposition	1.21	0.32	0.5 M Na <sub>2</sub> SO <sub>4</sub> , pH ~7	2017
CoFe/BiVO <sub>4</sub> <sup>20</sup>	Electrodeposition	2.48	0.23	0.5 M KPi, pH 7	2017
Ferrihydrite/BiVO <sub>4</sub> <sup>21</sup>	Hydrothermal	4.78	0.25	0.4 M NaBi pH 9	2017
QD/CoAl/BiVO <sub>4</sub> <sup>22</sup>	Hydrothermal	2.23	0.3	0.1 M KPi, pH 7	2016
CoAl/BiVO <sub>4</sub> <sup>23</sup>	Hydrothermal	1.1	0.41	0.1 M KPi, pH 7	2015
NiOOH/FeOOH/BiVO <sub>4</sub> <sup>24</sup>	Photodeposition	4.5	0.23	0.5 M KPi pH 7	2014

<sup>[a]</sup> NaBi= sodium borate; KPi= potassium phosphate; KBi= potassium borate; PBS=phosphate buffer solution.

\* Photocurrent density or onset potential was obtained from the *J-V* curves in the corresponding reference paper.

**Table S2.** Fitted results of the EIS curves in Fig. 3g

	BiVO <sub>4</sub>	B-BiVO <sub>4</sub>	NiFeV/BiVO <sub>4</sub>	NiFeV/B-BiVO <sub>4</sub>
R <sub>s</sub> /Ω	55.3	57.2	54.9	54.4
R <sub>ct</sub> /Ω	1398.2	518.1	372.6	289.2

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