Electronic Supplementary Information

Enhanced Solar Water Splitting of $BiVO_4$ Photoanode by in situ Surface Band Edge Modulation

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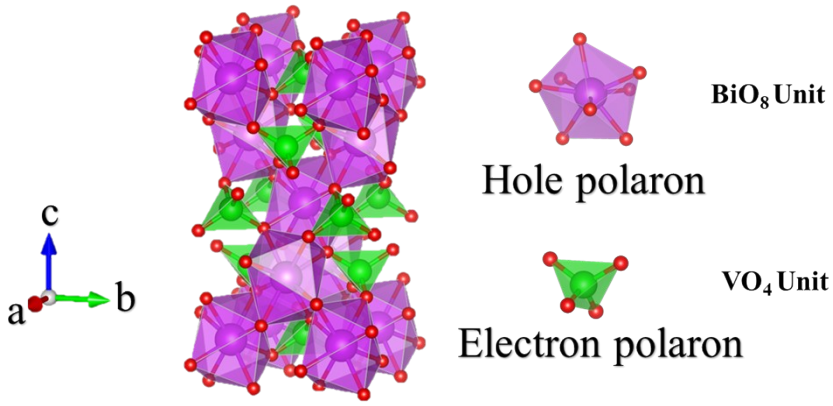

Fig. S1. Crystal structure of monoclinic $BiVO_4$.

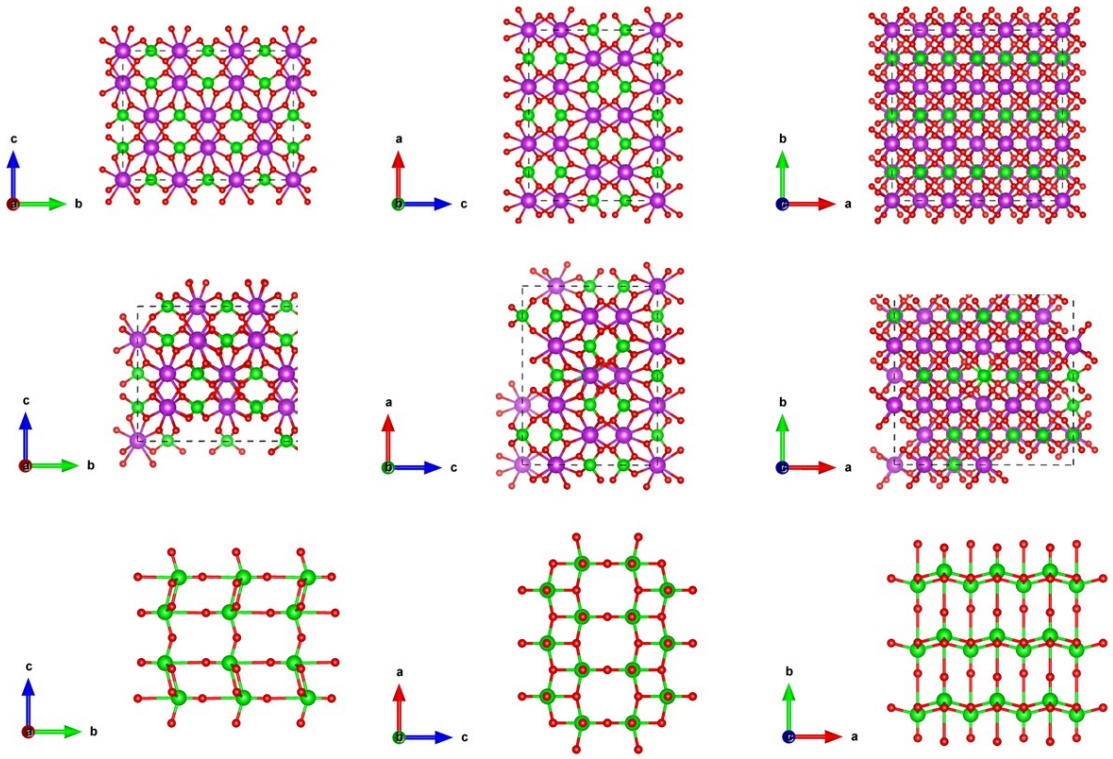

Fig. S2. From top to bottom are the atomic structure models of $BiVO_4$, $BiVO_4$-V_{Bi}, and V_2O_5 used for DFT calculations. (Purple, green, and red represent Bi, V, O atoms, respectively)

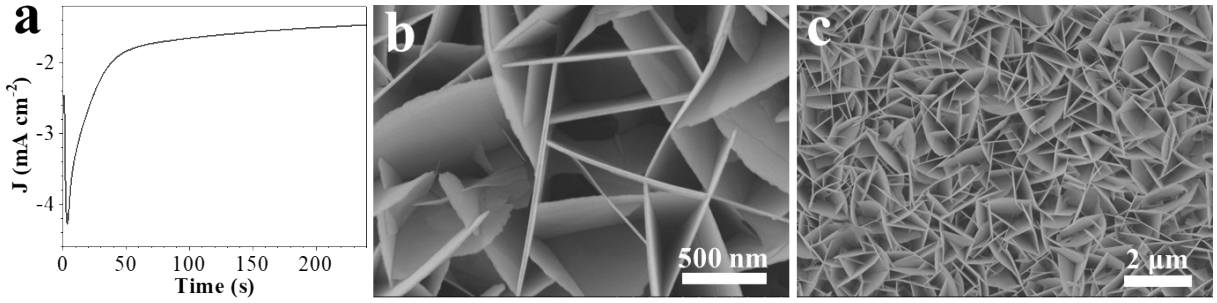

Fig. S3. (a) Electrochemical curves of electrodeposited BOI. (b-c) SEM images of BOI at different magnifications.

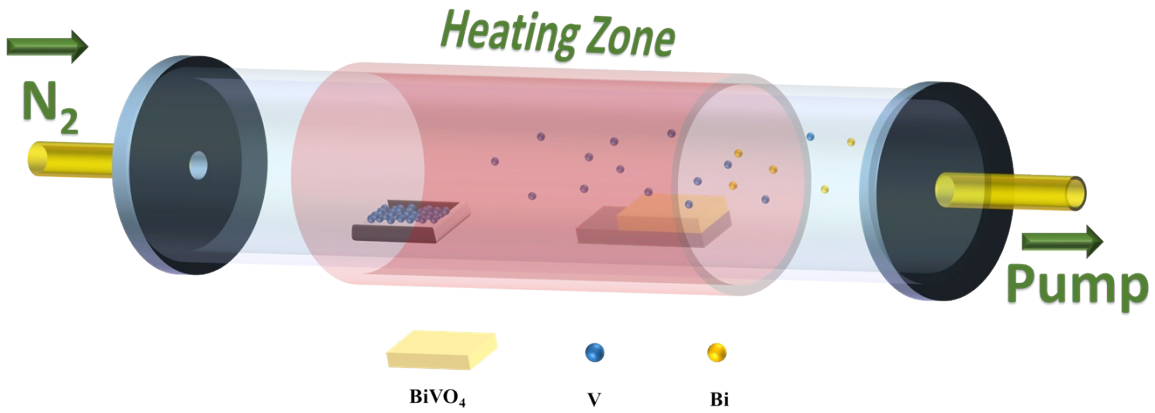

Fig. S4. Schematic diagram of the experimental setup for gas-phase cation exchange.

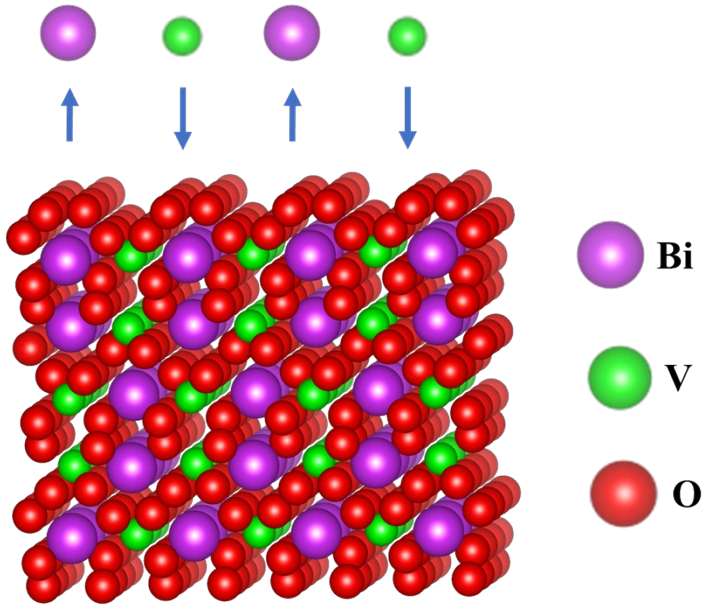

Fig. S5. Schematic diagram of the atomic structure of $BiVO_4$ for gas-phase cation exchange.

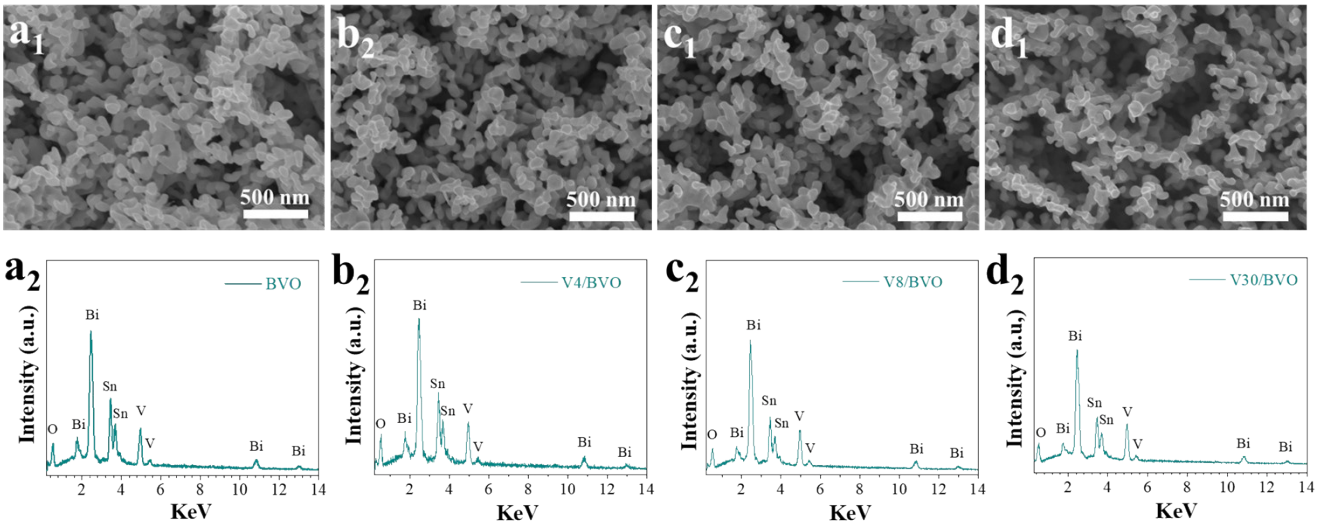

Fig. S6. SEM and EDS spectra of V/BVO electrodes with different cation exchange time.

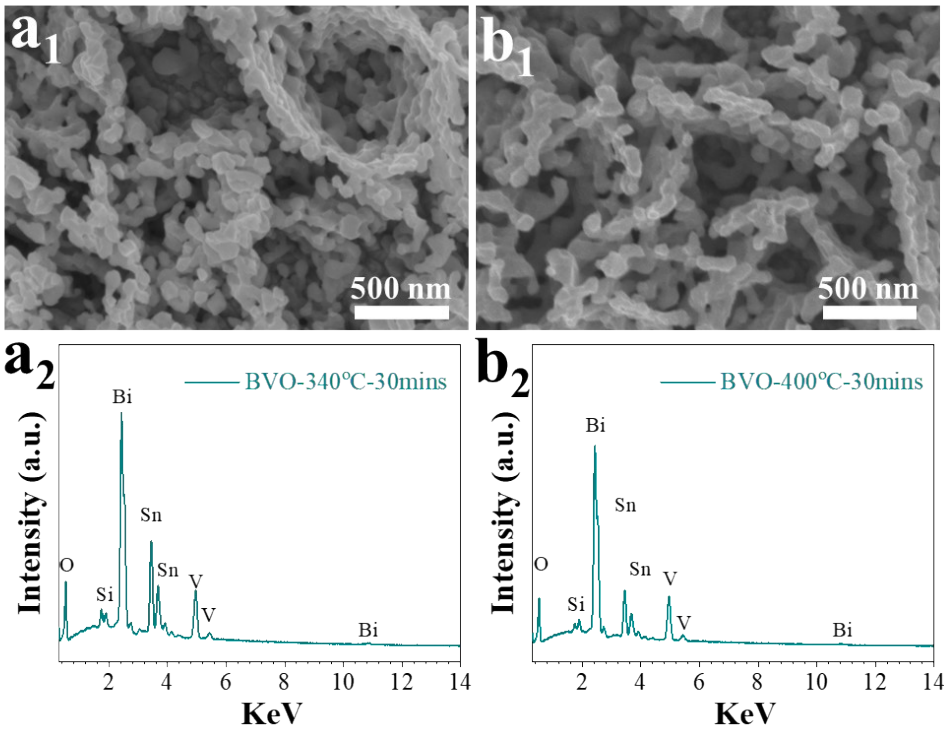

Fig. S7. SEM and EDS spectra of BVO-340 °C-30 mins (a_1, a_2) and BVO-400 °C-30 mins (b_1, b_2).

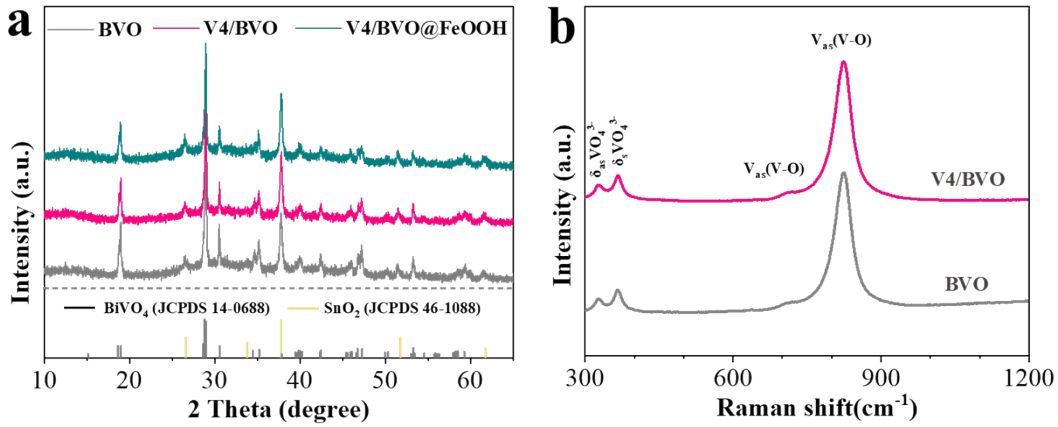

Fig. S8. (a) XRD patterns of BVO, V4/BVO, V4/BVO/FeOOH electrodes. (b) Raman spectra of BVO, V4/BVO electrodes.

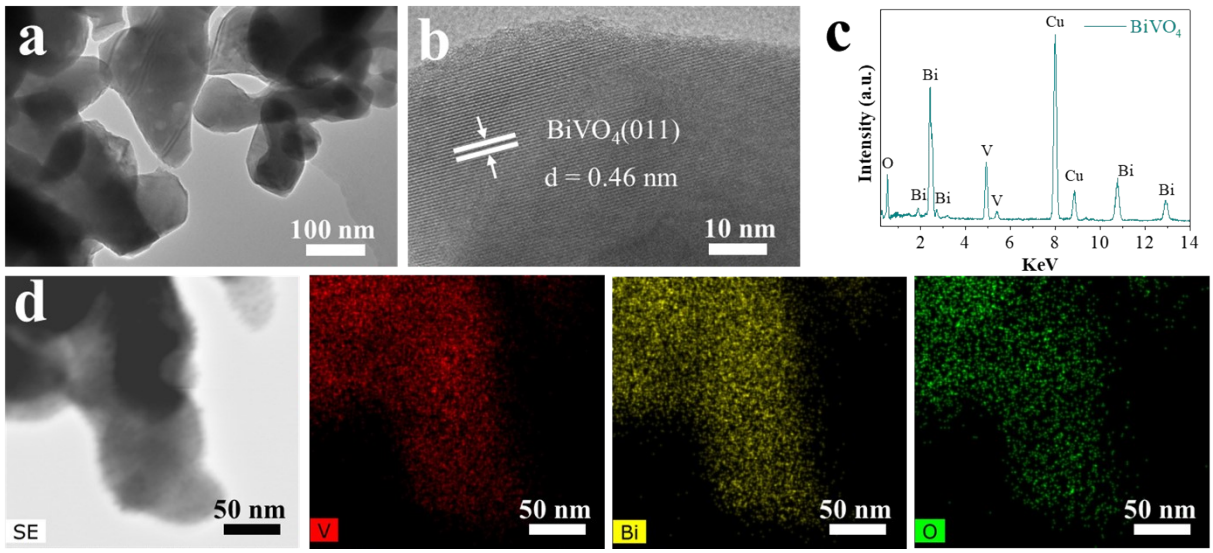

Fig. S9. (a-c) TEM image (a), HRTEM image (b) and EDS patterns (c) of the pristine $BiVO_4$ electrode, respectively. (d) Energy spectrum mapping of V, Bi, O elements of pristine $BiVO_4$ electrode.

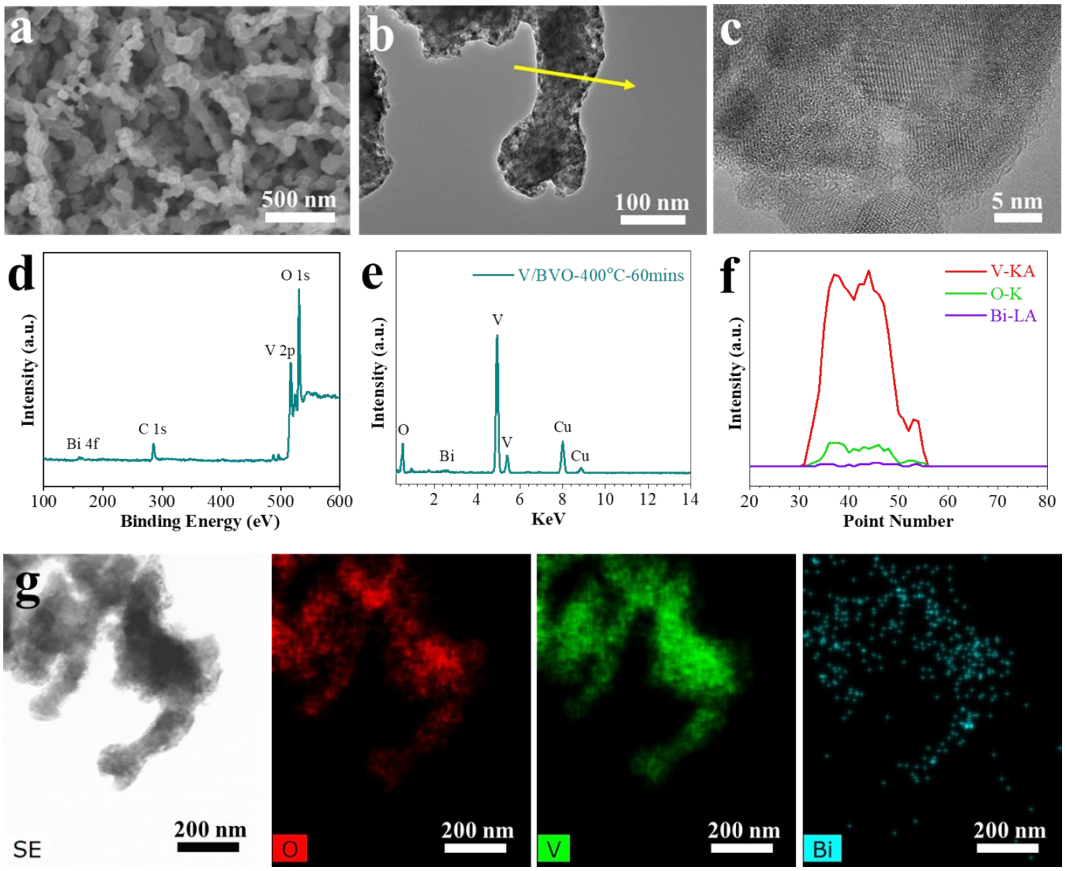

Fig. S10. SEM image (a), TEM image (b), HRTEM image (c), XPS spectrum (d), EDS energy spectrum (e), EDS line scanning spectrum (f) Elements mapping (g) of V/BVO-400℃-60mins photoanode.

As shown in Fig. S8a, the morphology of the sample V/BVO-400℃-60mins maintain the mesoporous structure of BVO. However, it is observed that a large number of defects appeared in the sample after replacement, which is caused by the replacement process (Fig. S8b). From the HRTEM image, it can be seen that the sample has a certain degree of crystallinity (Fig. S8c). XPS full spectrum (Fig. S8d) and EDS (Fig. S8e) can confirm that there is almost no Bi element in the sample, which proves that Bi has been completely replaced. In order to further confirm this result, we performed the line scan energy spectrum as shown in Fig. S8f and the result proved that Bi was almost detected. In addition, EDS mapping also confirmed the uniform distribution of V, O and the presence of a small amount of Bi. The above characterization and analysis prove that V can completely replace the Bi on the BVO surface.

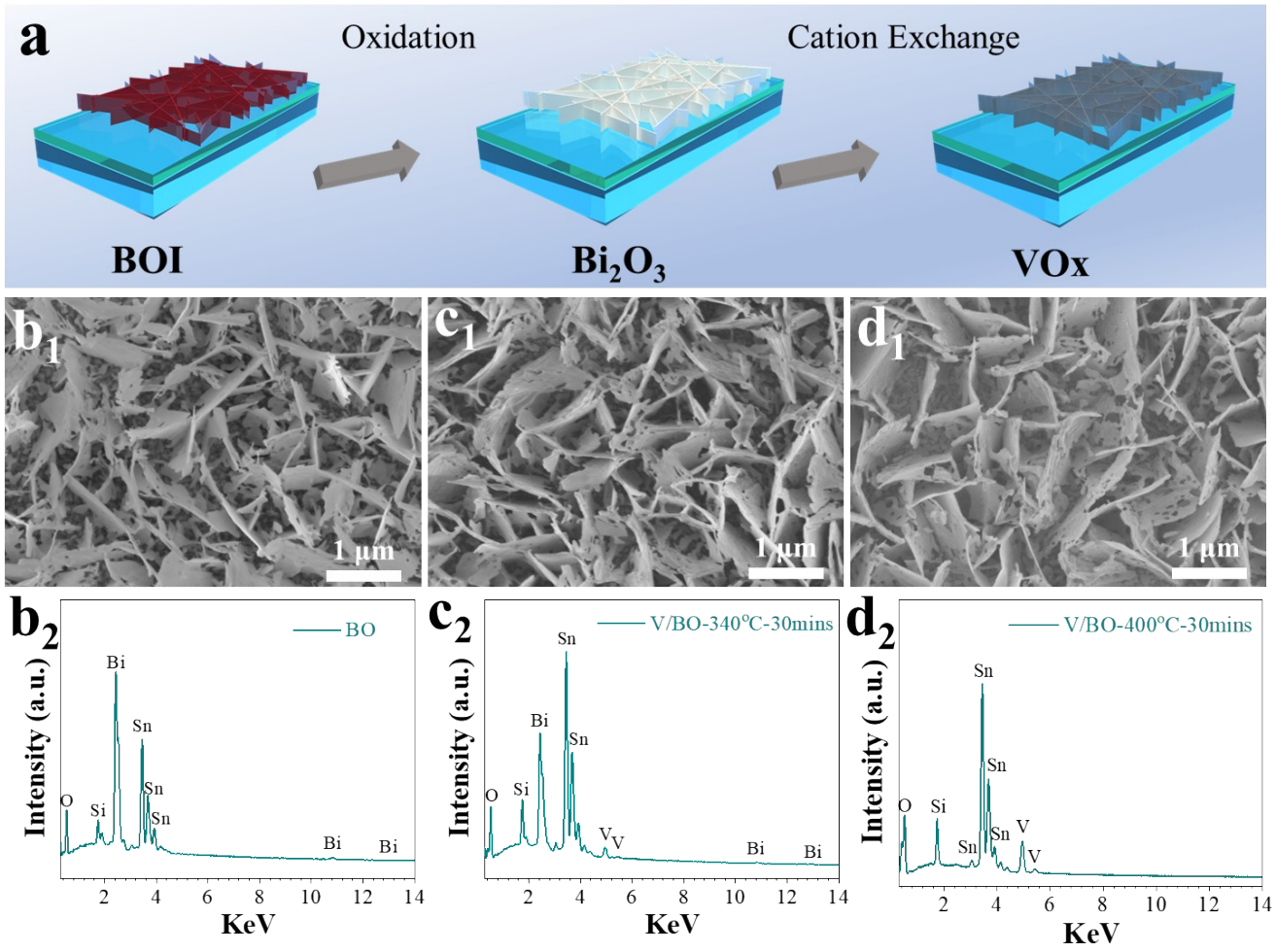

Fig. S11. (a) Schematic diagram of preparation of BO and VOx samples. (b1-d2) SEM images and EDS spectra of BO, V/BO-340 °C-30 mins, V/BO-400 °C-30 mins samples, respectively.

The Bi_2O_3 photoelectrode was obtained through the calcination of BOI electrode in air. Then, two samples were prepared by adding V resource in the chamber through the gas-phase cation exchange reaction at 340 and 400 °C, respectively. The reaction time was also set to 30 mins. The obtained samples were appointed as BO-340 °C-30 mins and BO-400 °C-30 mins, respectively.

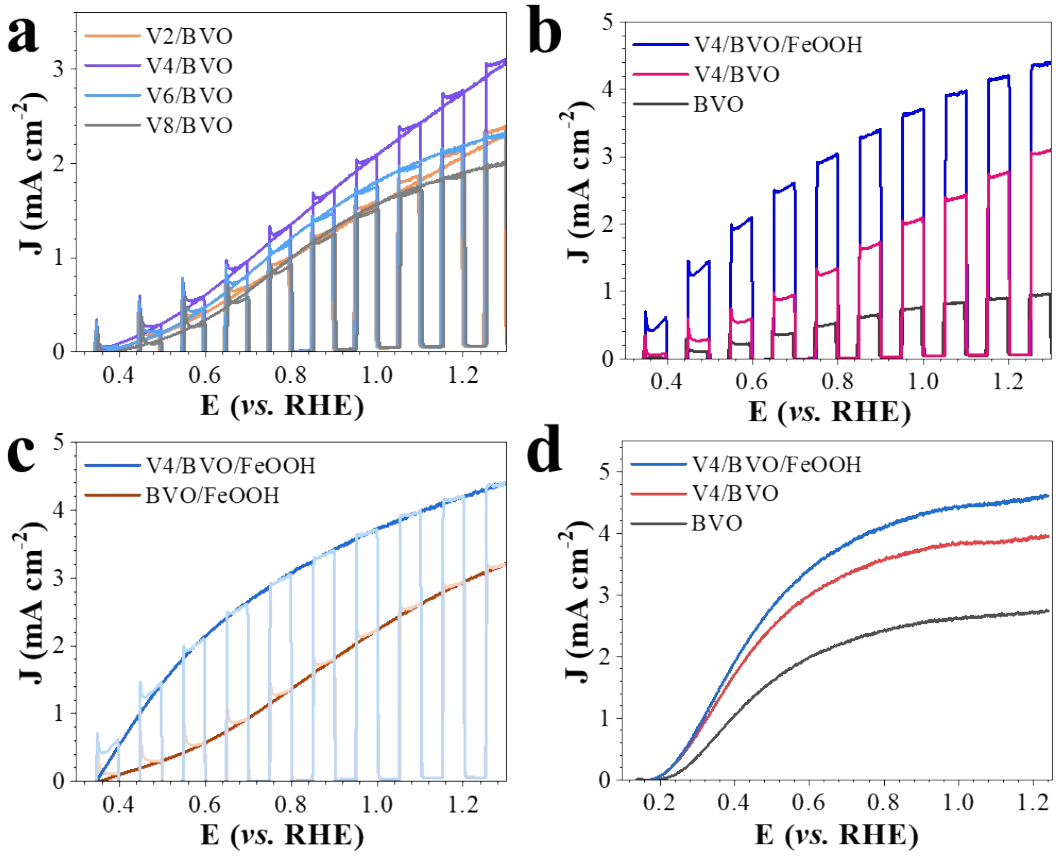

Fig. S12. (a) Long-illuminated photocurrent and transient photocurrent LSV spectra of electrodes with different cation exchange times. (b) Photocurrent LSV spectra of BVO, V4/BVO, V4/BVO/FeOOH electrodes under transient illumination. (c) Photocurrent LSV spectra of BVO/FeOOH, V4/BVO/FeOOH electrodes under transient and continuous illumination. (The above tests are carried out in 0.2M KBI solution under AM 1.5G light.) (d) LSV photocurrent curves of BVO, V4/BVO, V4/BVO/FeOOH electrodes tested in the presence of sacrificial agent. (0.2M KBi contains 0.2M Na_2SO_3 as sacrificial electrolyte, under AM 1.5G light.)

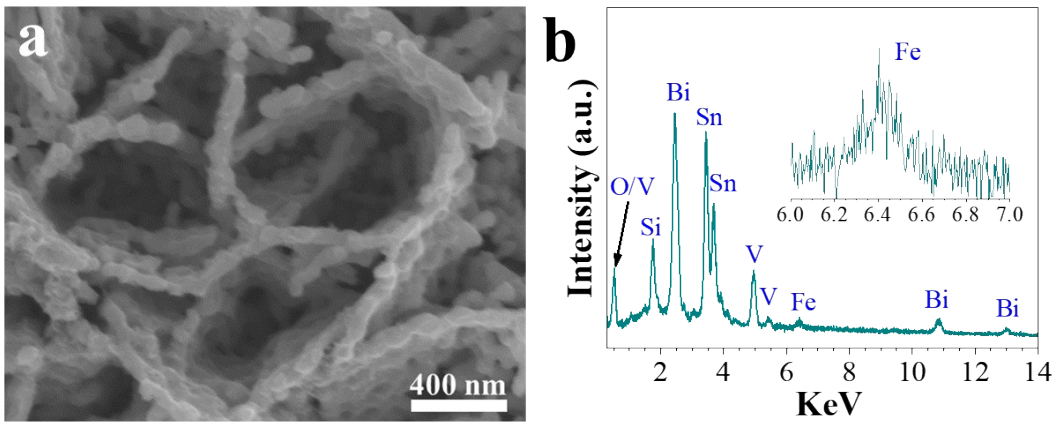

Fig. S13. SEM image and EDS spectrum of V4/BVO/FeOOH electrode.

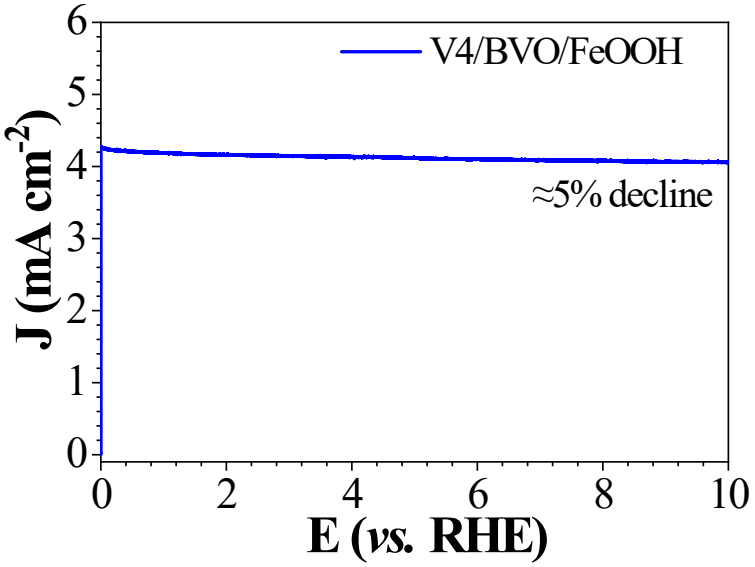

Fig. S14. Time course curves of H_2 and O_2 evolution of V4/BVO/FeOOH photoanode in a PEC cell at 1.23 V (vs. RHE) under AM 1.5G irradiation and the corresponding faradaic efficiency curves.

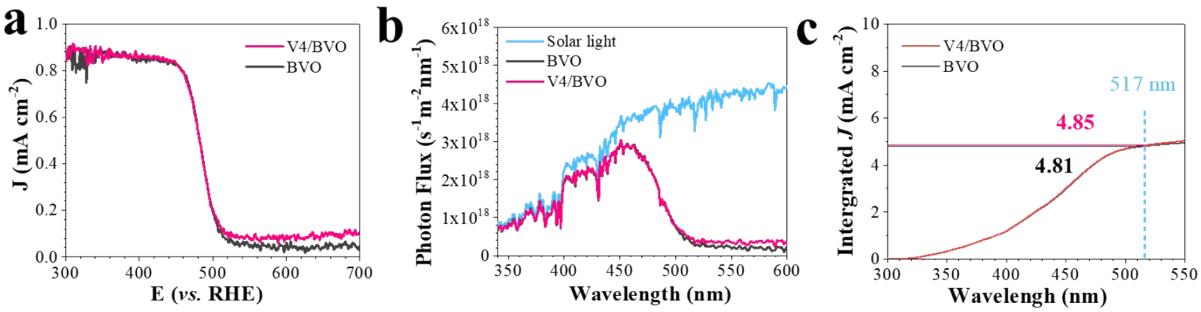

Fig. S15. (a) Light harvesting efficiency LHE of BVO and V4/BVO photoanodes. (b) Spectra of the solar irradiance of AM 1.5G and modulated photoanode absorption spectra of BVO and V4/BVO photoanodes. (c) Calculated J_{abs} based on the LHE spectra of the BVO and V4/BVO photoanodes.

Light harvesting efficiency (LHE) can be calculated by the following equation:

$$LHE = 1\text{-}10^{-A(\lambda)}$$

where $A(\lambda)$ is absorbance, λ is wavelength.

Table S1. EDS quantification of Bi, V elements.

Sample	Bi(at.%)	V(at.%)	N_{Bi}/N_V
BVO	50.38	49.62	1.02
V4/BVO	48.27	51.73	0.93
V8/BVO	46.59	53.41	0.87
V30/BVO	44.10	55.90	0.79
BVO-340 ^{o}C-30 mins	50.3	49.70	1.01
BVO-400 ^{o}C-30 mins	45.68	54.32	0.84

Table S2. Quantitative element ratio XPS analysis.

Sample	Bi(at.%)	V(at.%)	N_{Bi}/N_V
BVO	56.23	43.77	1.28
V4/BVO	32.57	67.43	0.48
V8/BVO	29.27	70.73	0.41

Table S3. The comparison of PEC performance for some reported single $BiVO_4$ based photoanodes (under the bias of 1.23 V_{RHE}).

Sample	Photo Current ($mA\ cm^{-2}$)	Journal	Years	References
V4/BVO/FeOOH	4.26			**This Work**
BV-V_O-FeNiOOH	3.76	Small	2022	1
$Bi_{1-X}VO_4$/Co-Bi	4.50	Advanced Materials	2022	2
MoB/BVO	4.30	Applied Catalysis B: Environmental	2022	3
Vo/BVO/FeOOH	4.71	Chemical Engineering Journal	2022	4
OEC/MoO_x/MQD/$BiVO_4$	5.85	Angewandte Chemie International Edition	2022	5
CoAl-LDH/$BiVO_4$	3.50	Applied Catalysis B: Environmental	2021	6
BV/Co(OH)x-Ag	3.95	Advanced Energy Materials	2021	7
BVO/F_1N_3-H	3.65	Angewandte Chemie International Edition	2021	8
Ar-BVO	4.32	Applied Catalysis B: Environmental	2021	9
R-TiO_2@$BiVO_4$	2.10	ACS Catalysis	2021	10
BiVO4/ZnO QDs	5.5	Applied Catalysis B: Environmental	2021	11
OEC/Ni-N_4-O/$BiVO_4$	6.00	Journal of the American Chemical Society	2021	12

Table S4. Summarized parameters of EIS for the photoanodes at 2.0 V_{RHE}.

Sample	$R_s(\Omega)$	$R_{ct}(\Omega)$	$C_{ct}(\mu F/cm^2)$
BVO	17.92	1647	14.88
V4/BVO	19.28	1544	53.38
V4/BVO/FeOOH	20.5	146.3	26.6

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