

## Supporting Information

# NiMoO<sub>x</sub> as a Highly Protective Layer against Photocorrosion for Solar Seawater Splitting

*Xiaotian Guo,<sup>[a]</sup> Xianhu Liu,<sup>[b]</sup> Lei Wang<sup>[a]\*</sup>*

*[a] School of Chemistry and Chemical Engineering & Inner Mongolia Engineering and  
Technology Research Center for Catalytic Conversion and Utilization of Carbon Resource  
Molecules, Inner Mongolia University, Hohhot 010020, China*

*E-mail: [wanglei@imu.edu.cn](mailto:wanglei@imu.edu.cn)*

*[b] Key Laboratory of Materials Processing and Mold, Ministry of Education, Zhengzhou  
University, Zhengzhou 450002, China*

## Experimental

### *Materials*

The nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were purchased from Tianjin Yongsheng Chemical Reagent Co., Ltd. The ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) were purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. The sodium hydroxide (NaOH), potassium iodide (KI), bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) were purchased from Beijing Innochem Technology Co., Ltd. The Fluorine-doped Tin Oxide (FTO) coated glasses as substrates were purchased from South China Science & Technology Co., Ltd. The P-benzoquinone ( $\text{C}_6\text{H}_4\text{O}_2$ ), vanadium acetylacetonate oxygen ( $\text{VO}(\text{acac})_2$ ), 304 stainless steel (304SS) and dimethyl sulfoxide (DMSO) were purchased from Alfa Aesar Chemical Co., Ltd. The natural seawater is collected from Xiamen, Fujian. All the chemical reagents used in the experiments were used without further purification

### *Materials preparation*

The as-formed BVO was prepared by an electrodeposition approach. 1.94 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was added in a mixed solution of 100 mL 0.4 M KI and nitric acid. 0.995 g  $\text{C}_6\text{H}_4\text{O}_2$  was dissolved in 40 mL ethanol solution, and mixed with the above solution to obtain electrodeposition solution. The FTO substrate was cleaned with acetone and ethanol. The FTO was electrodeposited at  $-0.1 \text{ V}_{\text{Ag}/\text{AgCl}}$  for 300 s to obtain BiOI/FTO film. 150  $\mu\text{L}$  DMSO solution with 0.2 M  $\text{VO}(\text{acac})_2$  was dropped on the top surface of BiOI/FTO, following with annealing at 450 °C for 2 h. The sintered sample was stirred in 1 M NaOH solution for 30 min to remove the excess  $\text{V}_2\text{O}_5$ . The nanoporous  $\text{BiVO}_4$  (noted as BVO) was obtained.

For the preparation of  $\text{NiMoO}_x/\text{BVO}$  sample, a piece of BVO electrode was immersed in 0.2 mM nickel nitrate solution for 6 h and then immersed in 0.05 mM ammonium molybdate solution for 15 min, following with Ar annealing at 400 °C for 1 h. For the synthesis of  $\text{NiO}_x/\text{BVO}$  or  $\text{MoO}_x/\text{BVO}$  sample, the BVO was immersed in nickel nitrate solution for 6 h or

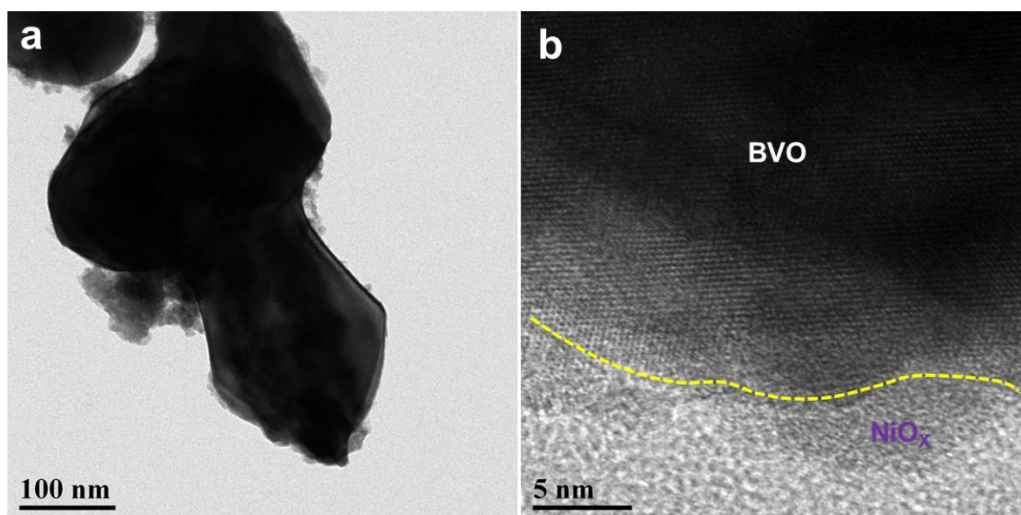
ammonium molybdate solution for 15 min, following with the subsequent thermal treatment.

#### *Photoelectrochemical (PEC) measurements*

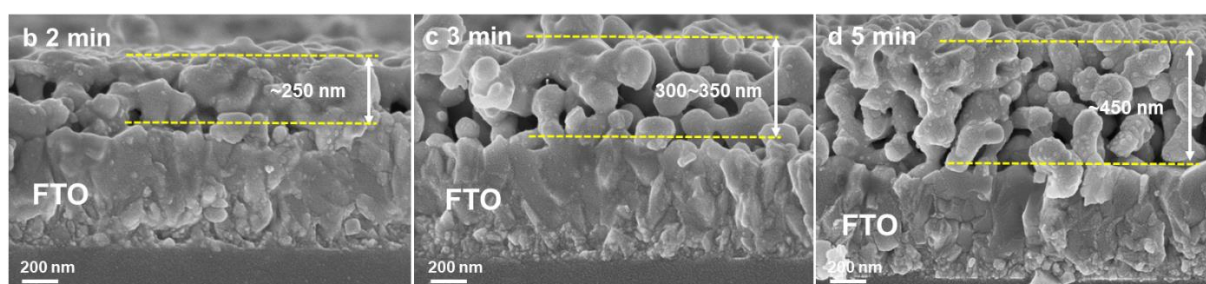
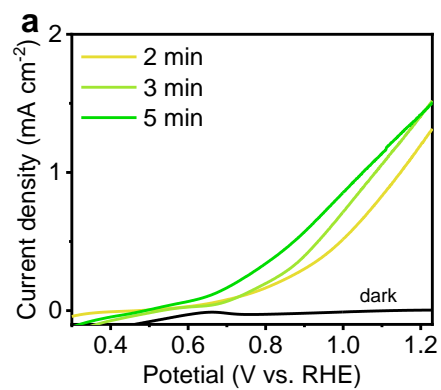
Both electrochemical measurement and photoelectrochemical measurement use CHI 760E electrochemical workstation and a standard three electrode system. Simulated seawater (SSW) and natural seawater (SW) were employed as the electrolyte. The SSW was prepared by the chemicals (NaCl, 27.159 g; MgCl<sub>2</sub>, 3.8983 g; MgSO<sub>4</sub>, 1.66 g; CaSO<sub>4</sub>, 01.404 g; K<sub>2</sub>SO<sub>4</sub>, 0.577g; K<sub>2</sub>CO<sub>3</sub>, 0.2124 g; NaBr, 0.0894 g) dissolved in 1 L distilled water. The pH value of SSW was 8.3. The AgCl electrode was used as the reference electrode and a Pt foil was as counter electrode. Natural seawater is collected from Xiamen, Fujian, the pH value at room temperature is 8.3. The current voltage (*J-V*) curves were performed at a rate of 10 mV s<sup>-1</sup> under AM 1.5G illumination (100 mW cm<sup>-2</sup>, Beijing Perfectlight Technology Co., Ltd.) All the measurements of stability were carried out under 1.23 V<sub>RHE</sub>. The incident photoelectron conversion efficiency (IPCE) was measured using a xenon lamp at a potential of 1.23 V<sub>RHE</sub>. The photoelectrochemical impedance spectroscopy (PEIS) was carried out at 0.8 V<sub>RHE</sub> in the frequency range of 10<sup>-2</sup>-10<sup>5</sup> Hz under AM 1.5 G back-side illumination.

#### *Characterization*

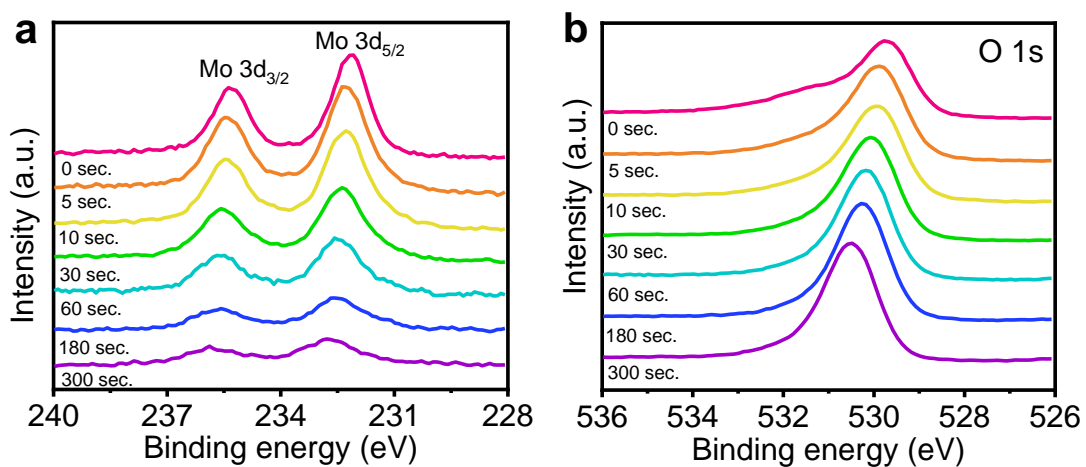
X-ray diffraction analysis (XRD, RIGAKU rint-2000) uses Cu K  $\alpha$  Radiation. Scanning electron microscopy (SEM) were conducted using FE-SEM-Supra 55 (Zeiss, Germany). Transmission electron microscopy (TEM) were carried out using JEM-2100F (JEOL, Japan) systems. Chemical state of sample surface was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250xi, Thermo Fisher Scientific). The UV-vis transmission spectrum was carried out with UV-2600 (Shimadzu) spectrometer and BaSO<sub>4</sub> as reference.



**Figure S1.** (a,b) TEM images of NiO<sub>x</sub>/BVO.



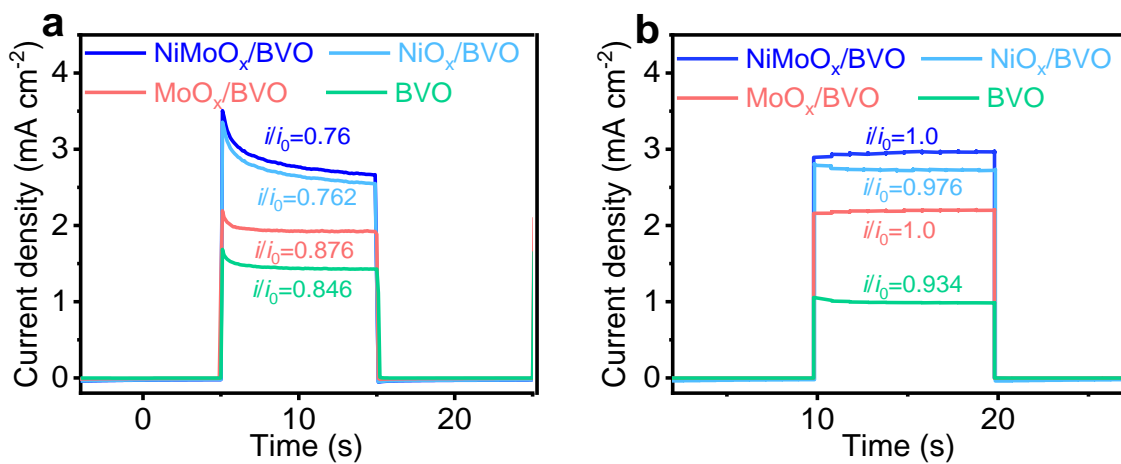
**Figure S2.** (a) LSV curves and (b-d) cross-sectional SEM images of BVO prepared under different deposition time (2 min, 3 min, and 5 min).



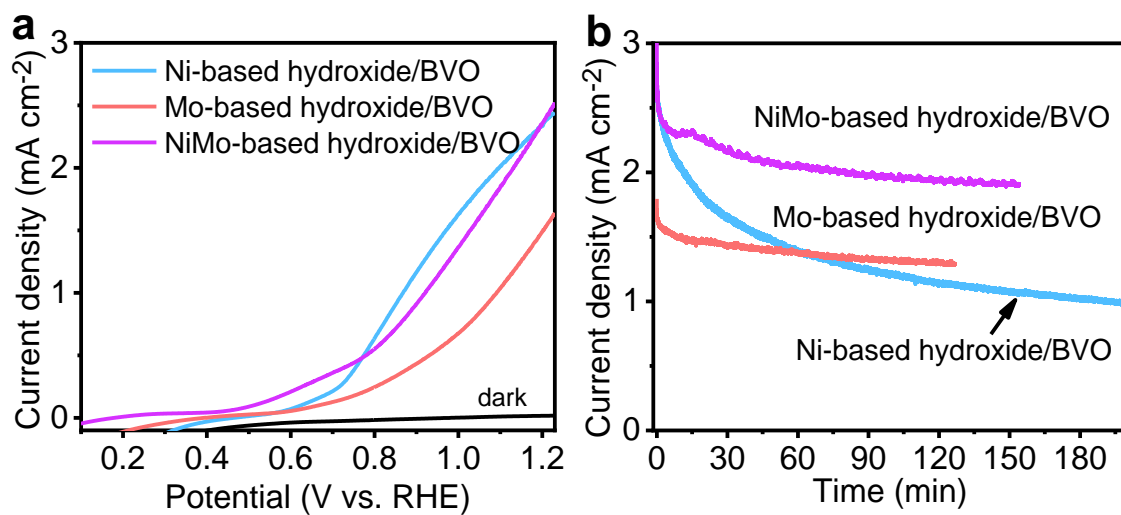
**Figure S3.** XPS depth profiles of MoO<sub>x</sub>/BVO. The etching time is 0, 5, 10, 30, 60, 180, and 300 sec., respectively.

**Table S1.** Elements atomic ratios for NiO<sub>x</sub>/BVO, MoO<sub>x</sub>/BVO, and NiMoO<sub>x</sub>/BVO from XPS analysis.

Element (at.%)	NiO <sub>x</sub> /BVO	MoO <sub>x</sub> /BVO	NiMoO <sub>x</sub> /BVO
Ni	14.02	—	12.03
Mo	—	3.33	3.62
Bi	10.56	15.77	10.4
V	5.82	8.4	4.83
O	69.6	72.5	69.12

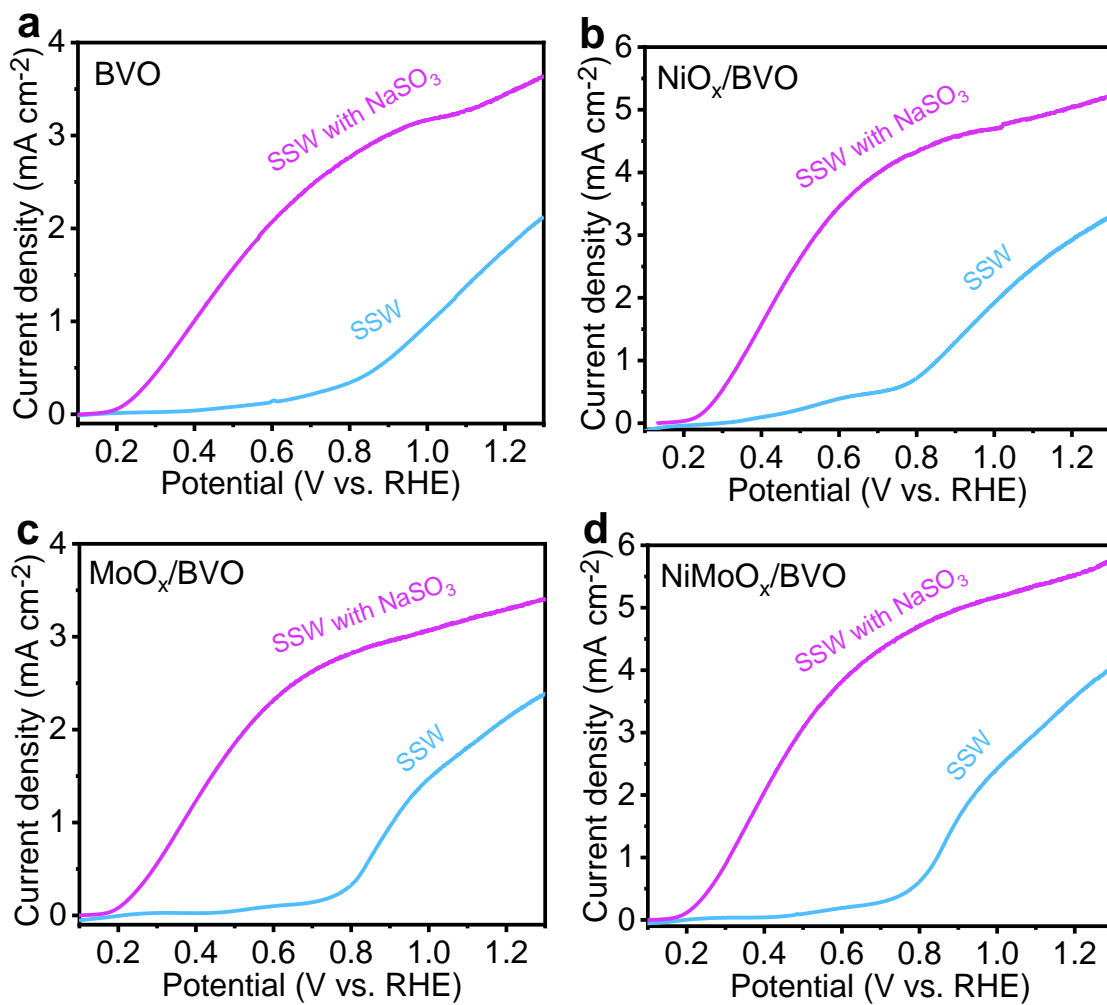


**Figure S4.** (a,b) Photocurrent of BVO, NiO<sub>x</sub>/BVO, MoO<sub>x</sub>/BVO, and NiMoO<sub>x</sub>/BVO at 1.23 V<sub>RHE</sub> in SSW under back-side one sun illumination at the initial time (a) and after several times for a relatively stable value.

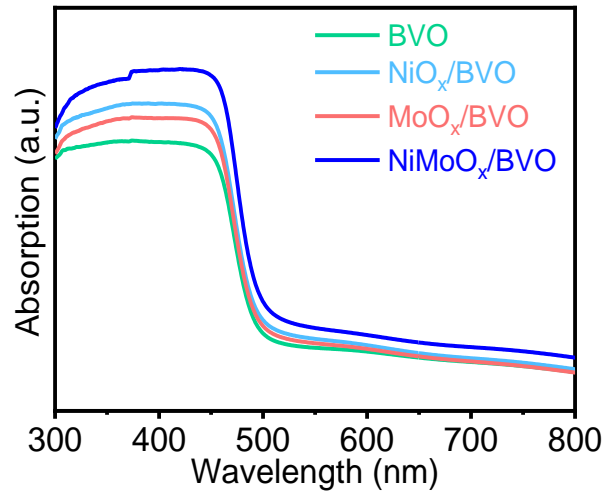


**Figure S5.** (a) LSV of NiMo-based hydroxides on BVO without annealing treatment in SSW; (b) *J-t* curves of corresponding samples applied at 1.23 V<sub>RHE</sub> in SSW. All measurements were performed under back-side one sun illumination.





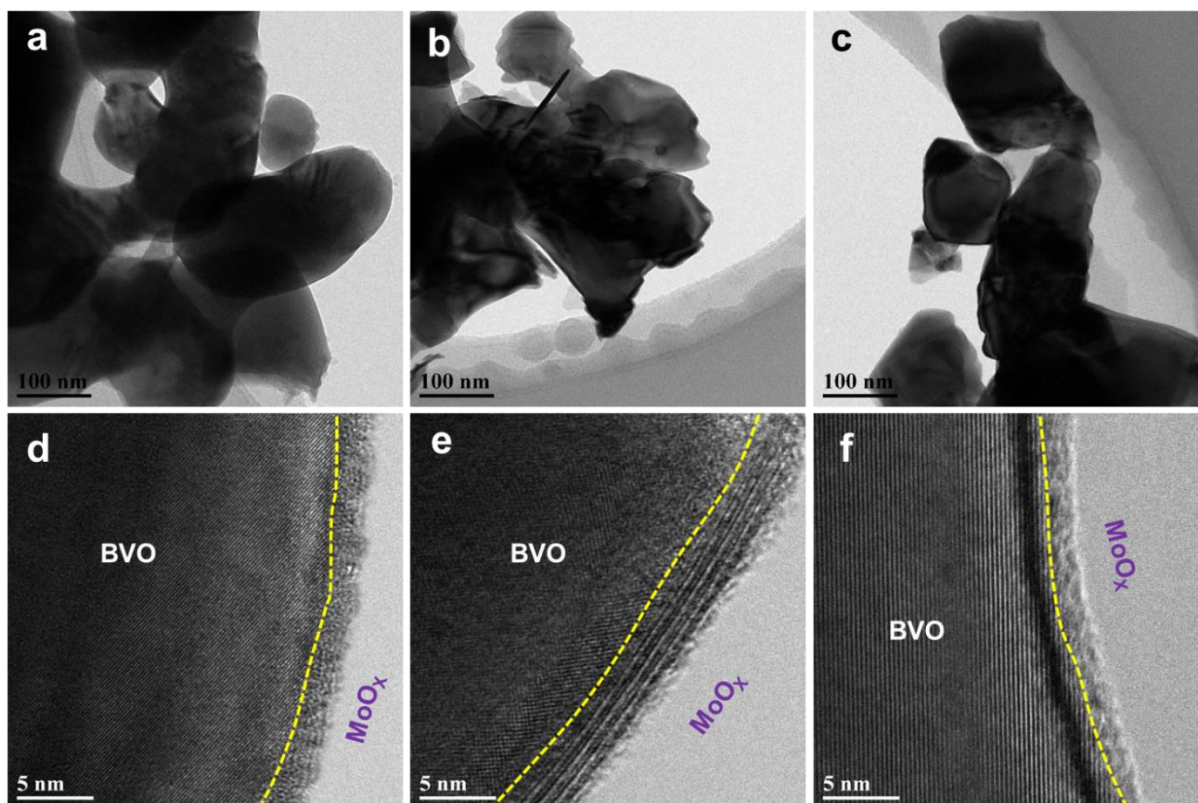
**Figure S6.** (a-d) LSV of BVO (a), NiO<sub>x</sub>/BVO (b), MoO<sub>x</sub>/BVO (c), and NiMoO<sub>x</sub>/BVO (d) in SSW without and with the addition of Na<sub>2</sub>SO<sub>3</sub> under back-side one sun illumination.



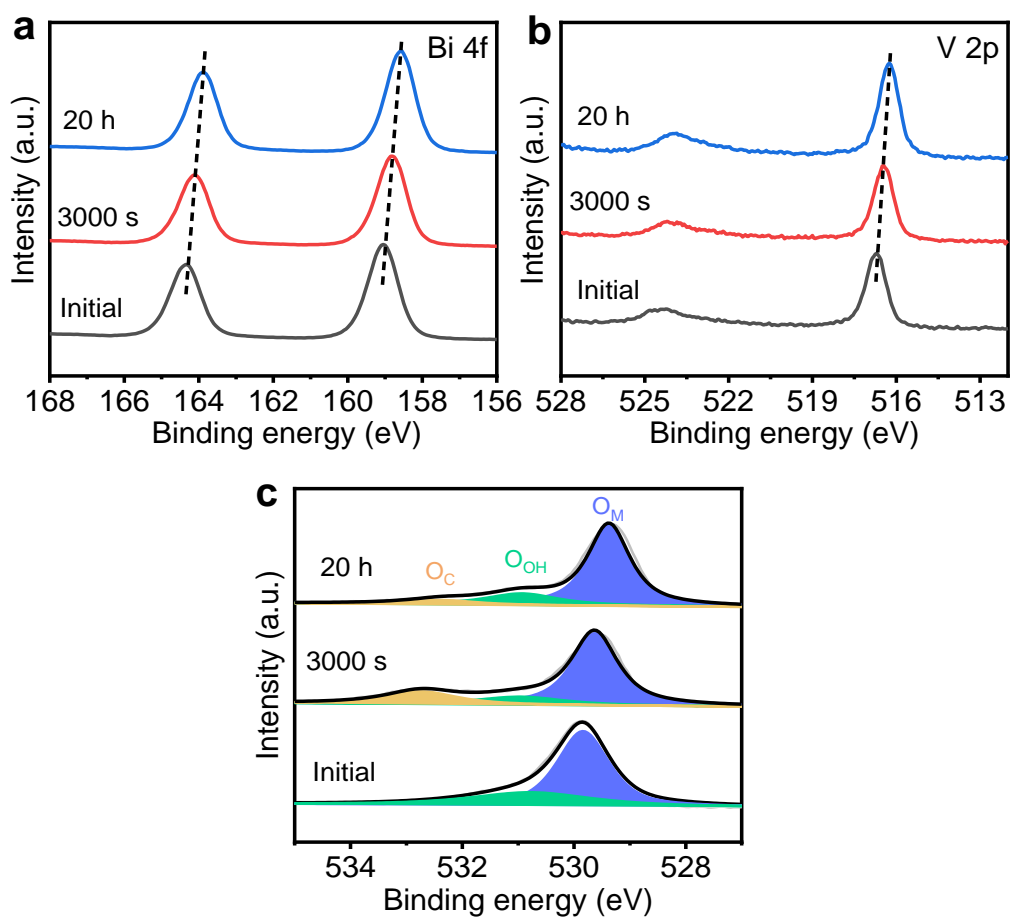
**Figure S7.** UV-Vis spectra of BVO, NiO<sub>x</sub>/BVO, MoO<sub>x</sub>/BVO, and NiMoO<sub>x</sub>/BVO.

**Table S2.** Comparison of recent key advances on photoelectrodes for PEC seawater splitting.

Catalysts	Photocurrent density @1.23V <sub>RHE</sub>	Electrolyte	Stability	Ref.
Bi <sub>x</sub> Fe <sub>1-x</sub> VO <sub>4</sub> @CNT hetero-nanostructure	0.04 mA cm <sup>-2</sup>	seawater	60 min	1
Co-Pi decorated TiO <sub>2</sub> @g-C <sub>3</sub> N <sub>4</sub> Nanorod Arrays	1.6 mA cm <sup>-2</sup>	Natural seawater	10 h	2
Ag/WO <sub>3</sub> /ZnFe-LDH nano-square arrays	0.96 mA cm <sup>-2</sup>	Natural seawater	24000 s	3
α-Fe <sub>2</sub> O <sub>3</sub> /WO <sub>3</sub>	1.0 mA cm <sup>-2</sup>	Natural seawater	5 h	4
RhO <sub>2</sub> /Mo-BiVO <sub>4</sub>	~4 mA cm <sup>-2</sup>	Natural seawater	270 min with high light intensity	5
NiMoO <sub>x</sub> /BiVO <sub>4</sub>	~3.0 mA cm <sup>-2</sup>	Natural seawater	190 h	This work



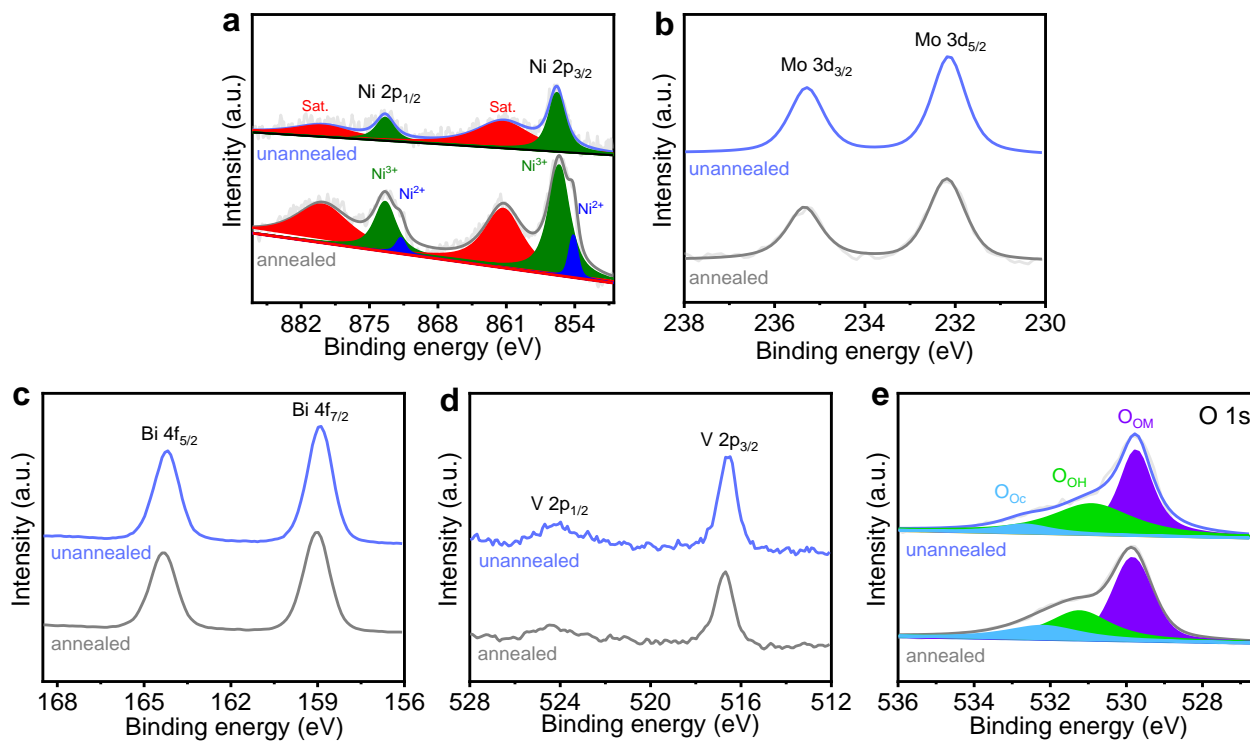
**Figure S8.** (a-f) TEM images of MoO<sub>x</sub>/BVO during stability measurement after various times: (a,d) initial, (b,e) 3000 s, and (c,f) 20 h.



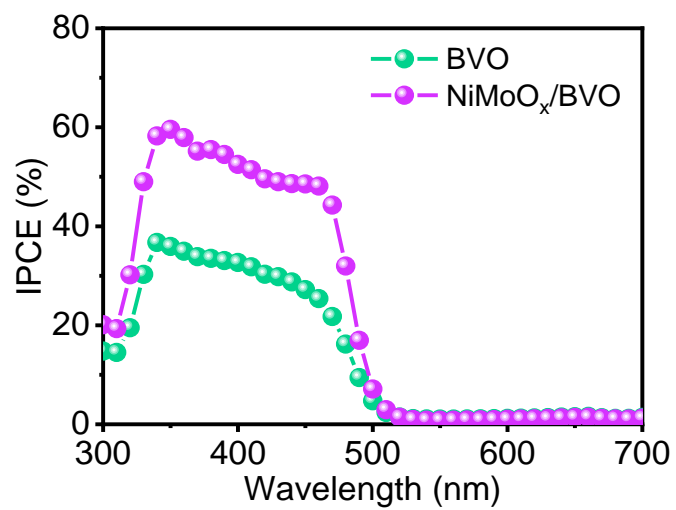
**Figure S9.** (a-c) XPS Bi 4f (a), V 2p (b), and O 1s (c) spectra for the NiMoO<sub>x</sub>/BVO after various times during stability measurement.

**Table S3.** Element atomic ratios NiMoO<sub>x</sub>/BVO after various times derived from XPS spectra of Figures 4h,i and S9.

Element (at.%)	0 s	3000 s	20 h
Ni	9.49	1.02	1.10
Mo	2.90	2.96	0.98
Bi	12.99	13.61	15.30
V	7.44	7.94	10.49
O	67.18	74.47	72.14

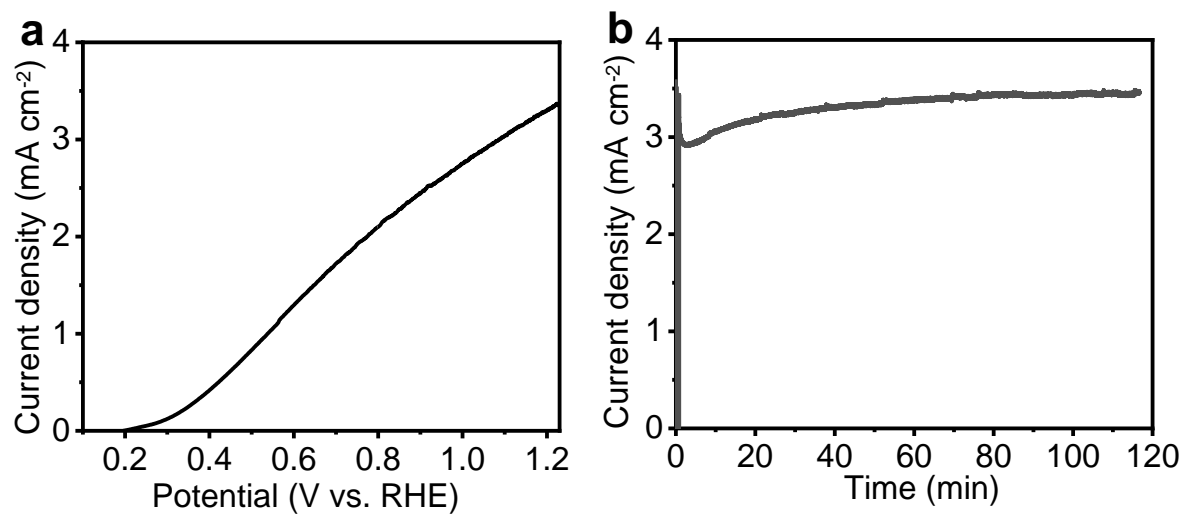


**Figure S10.** (a-e) XPS Ni 2p, Mo 3d, Bi 4f, V 2p, and O 1s spectra of NiMoO<sub>x</sub>/BVO without and with annealing treatment.

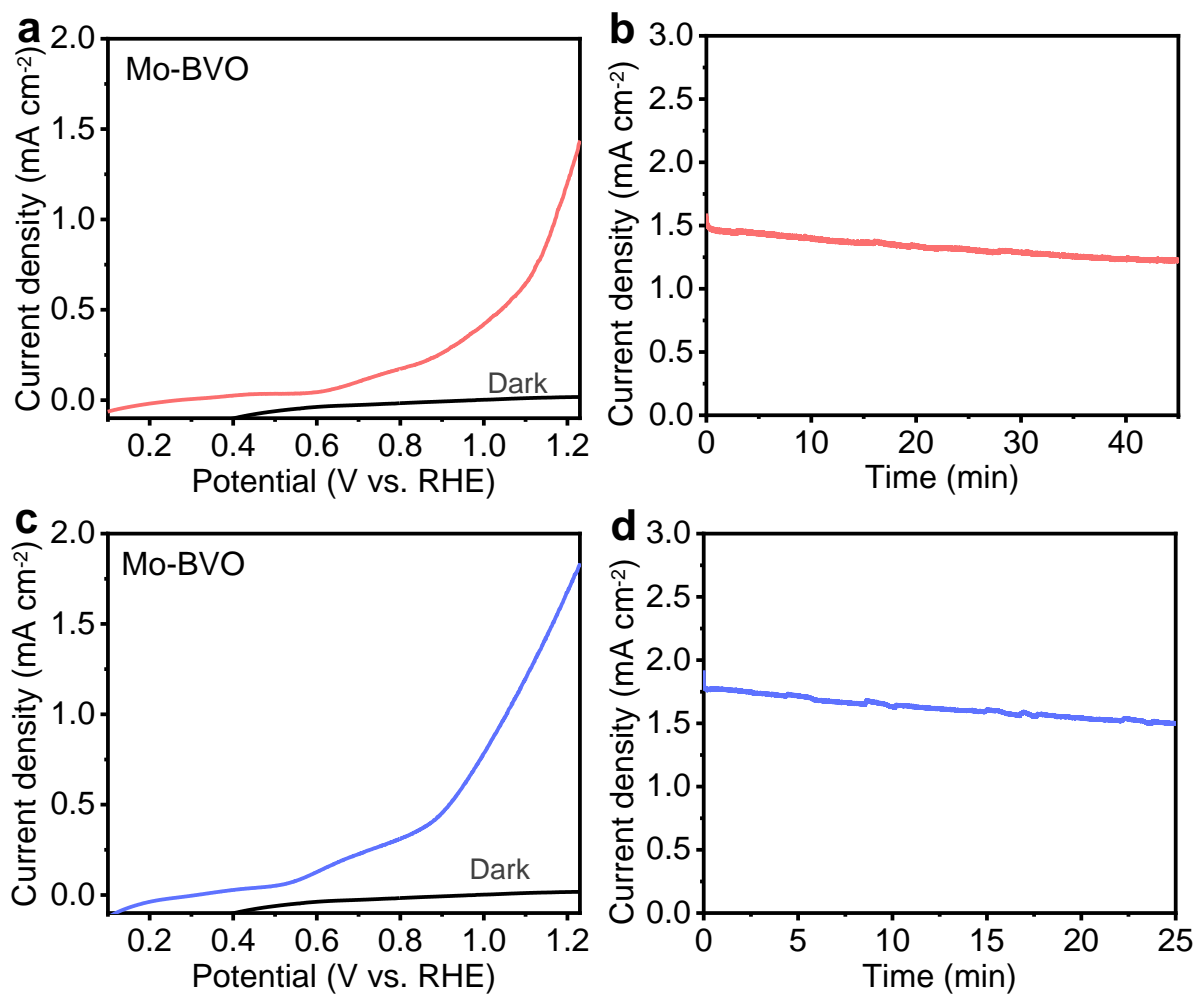


**Figure S11.** IPCE values of BVO and NiMoO<sub>x</sub>/BVO applied at 1.23 V<sub>RHE</sub> in SSW under back-side one sun illumination.

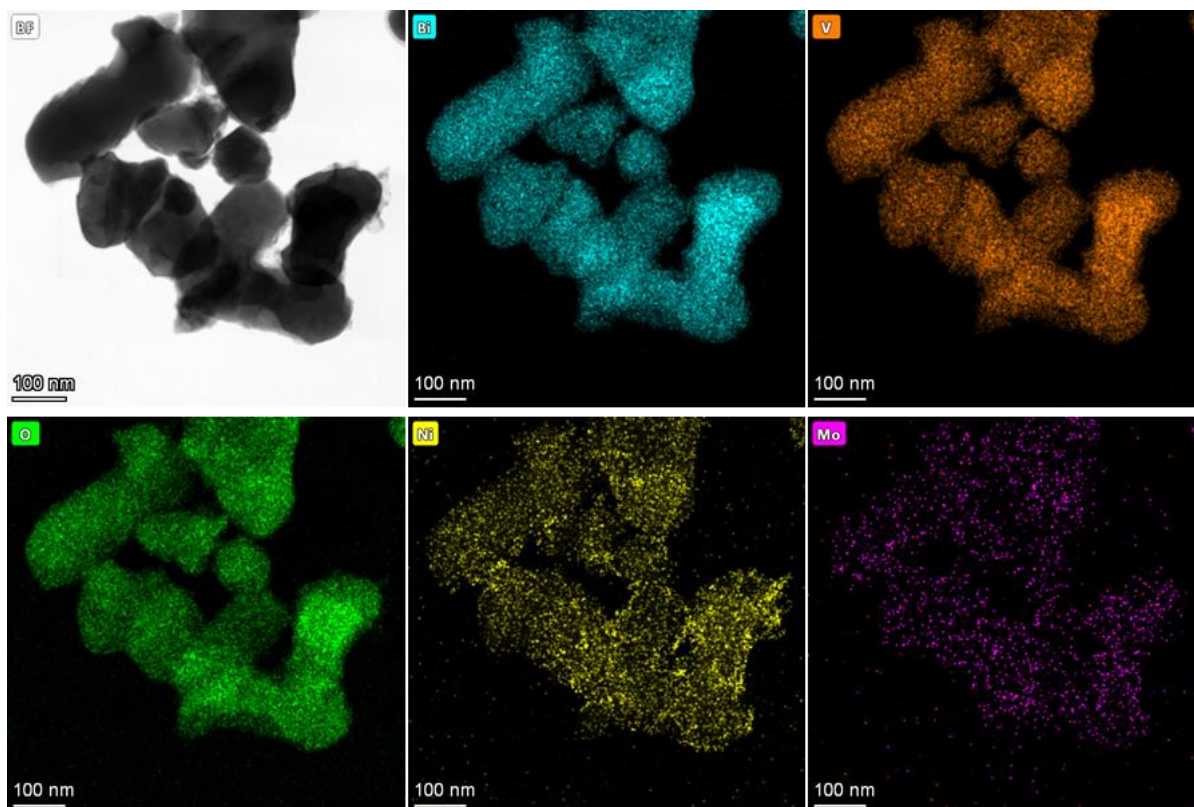




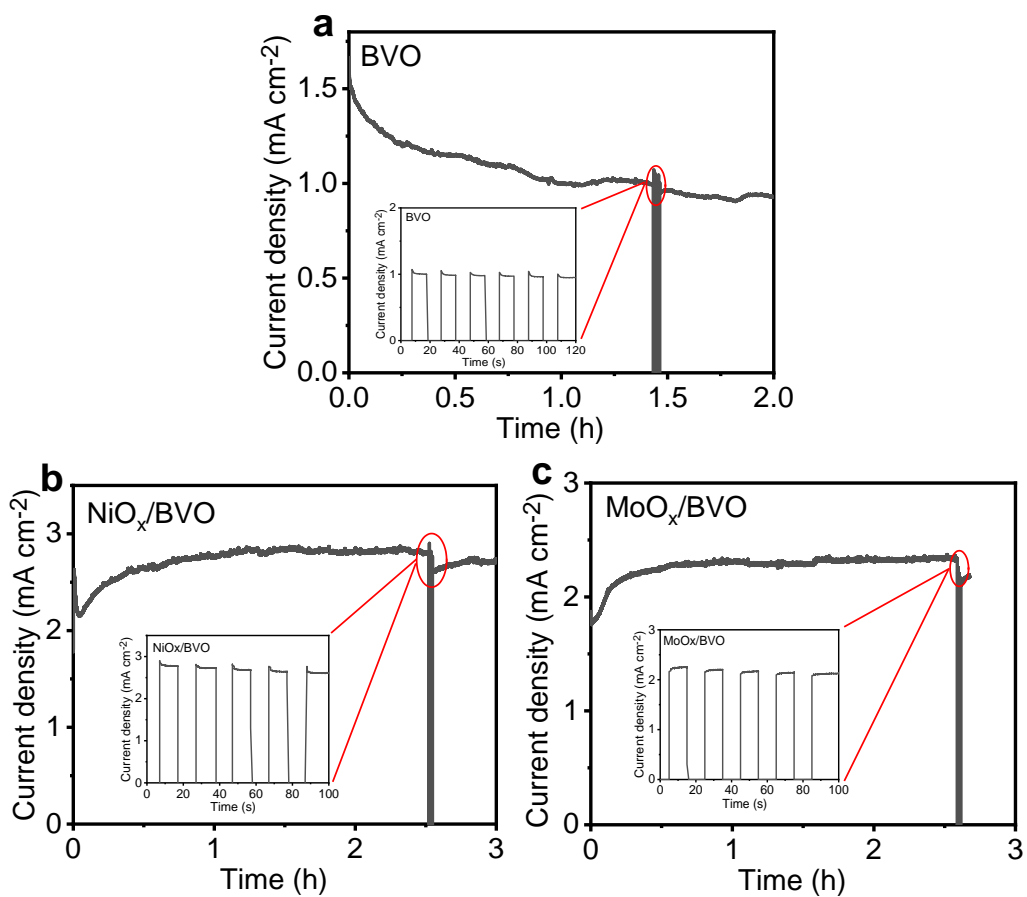
**Figure S12.** (a) LSV (a) and (b) *J-t* curves of Ni(OH)<sub>2</sub>/BVO in KBI under back-side one sun illumination.



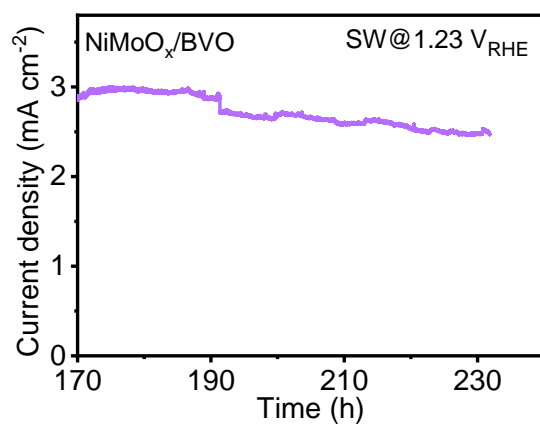
**Figure S13.** (a,c) LSV and (b,d) *J-t* curves of Mo-doped BVO in SSW under back-side one sun illumination. For the Mo-doped BVO, the  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  was added to DMSO (a,b) or the  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  was added to electrodeposition solution (c,d).



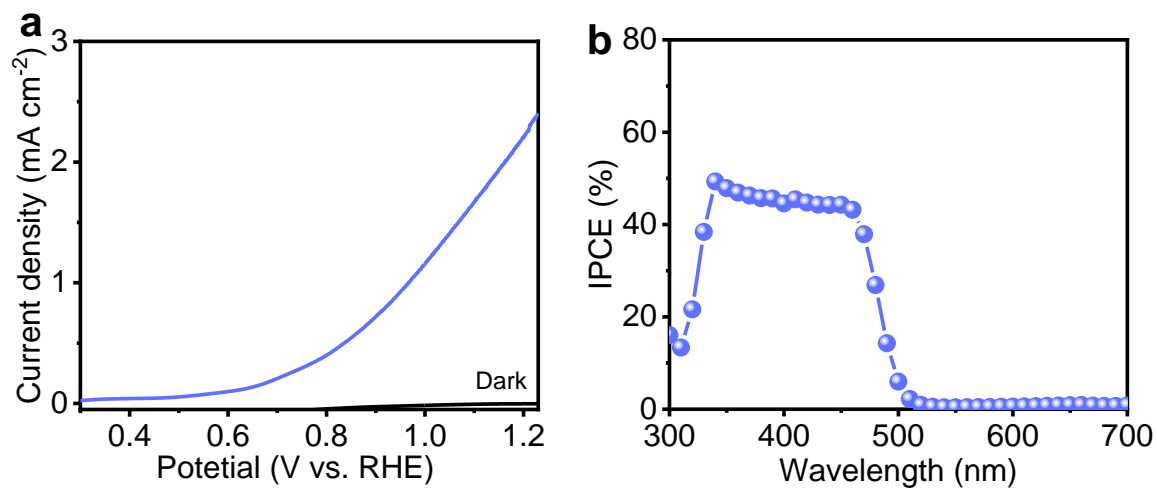
**Figure S14.** TEM-EDS mapping of NiMoO<sub>x</sub>/BVO.



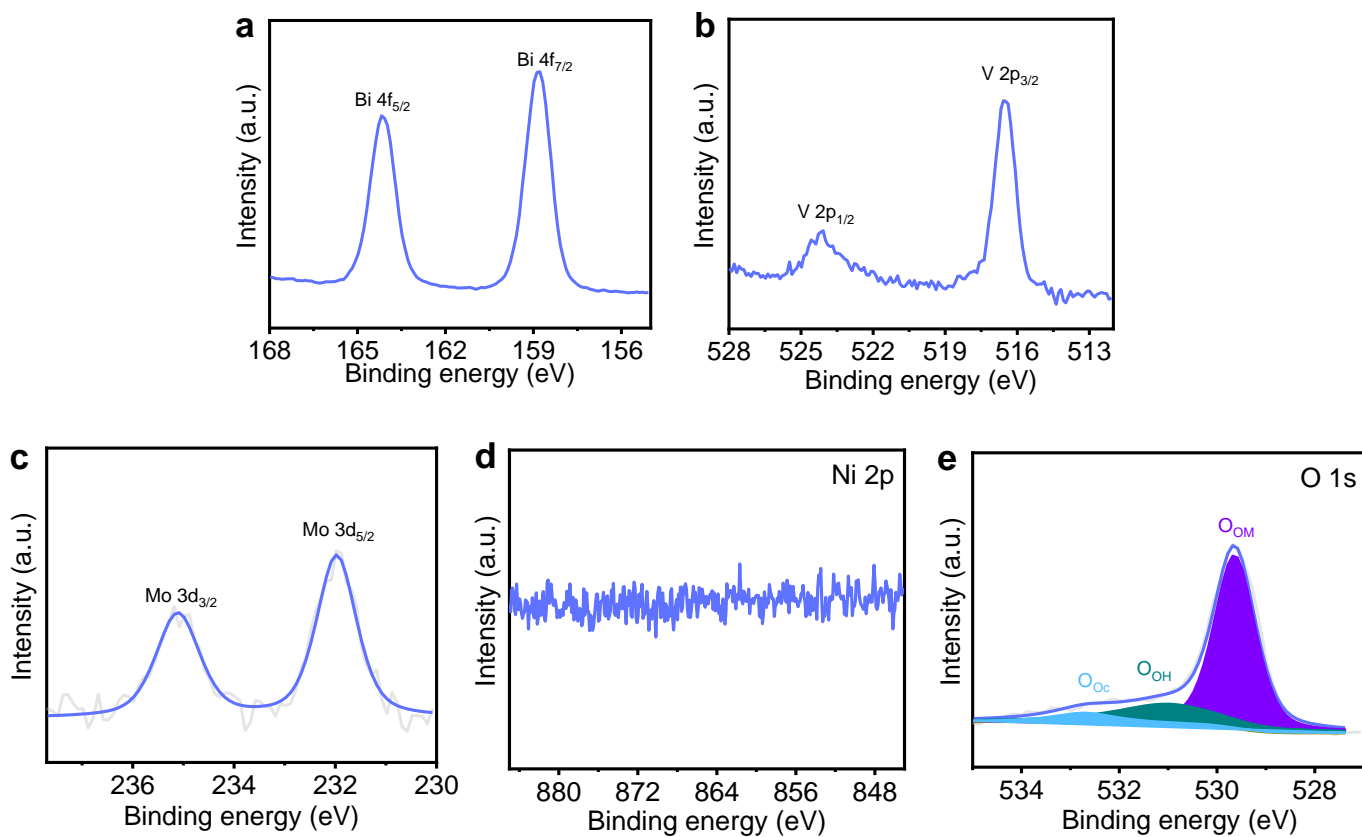
**Figure S15.** (a-c)  $J$ - $t$  curves of BVO (a),  $\text{NiO}_x/\text{BVO}$  (b), and  $\text{MoO}_x/\text{BVO}$  (c) at  $1.23 \text{ V}_{\text{RHE}}$  in SSW under back-side one sun illumination ( $100 \text{ mW cm}^{-2}$ ). Inset shows the photoresponses under chopped-light illumination.



**Figure S16.** The tail in the chronoamperometry for NiMoO<sub>x</sub>/BVO at 1.23 V<sub>RHE</sub> in SW under back-side illumination after 230 h stability.



**Figure S17.** (a) LSV curve and (b) IPCE value of NiMoO<sub>x</sub>/BVO sample after stability measurement of 230 h in SW.



**Figure S18.** (a-e) XPS Bi 4f (a), V 2p (b), Mo 3d (c), Ni 2p (d), and O 1s (e) spectra of NiMoO<sub>x</sub>/BVO after stability measurement of 230 h in SW.

## References:

- [1] X. She, G. Ma, L. Zhang, S. Jiao, G. Cheng and Z. Zhang, *Journal of Alloys and Compounds*, 2022, 893, 162146.
- [2] Y. Li, R. Wang, H. Li, X. Wei, J. Feng, K. Liu, Y. Dang and A. Zhou, *The Journal of Physical Chemistry C*, 2015, 119, 20283-20292.
- [3] J. Liu, S.-M. Xu, Y. Li, R. Zhang and M. Shao, *Applied Catalysis B: Environmental*, 2020, 264, 118540.
- [4] Y. Li, J. Feng, H. Li, X. Wei, R. Wang and A. Zhou, *International Journal of Hydrogen Energy*, 2016, 41, 4096-4105.
- [5] W. Luo, Z. Yang, Z. Li, J. Zhang, J. Liu, Z. Zhao, Z. Wang, S. Yan, T. Yu and Z. Zou, *Energy & Environmental Science*, 2011, 4, 4046-4051.