

Supporting Information

Trimetallic Spinel $\text{NiCo}_{2-x}\text{Mo}_x\text{O}_4$ Oxygen Evolution Catalyst for Bias-Free Solar Water Splitting with Inverted Perovskite Solar Cells

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Experimental section

Synthesis of $\text{NiCo}_{2-x}\text{Mo}_x\text{O}_4$ spinel oxide. Fluorine-doped tin oxide (FTO, 1 x 1.2 cm) glass substrates were firstly cleaned with deionised water, ethyl alcohol and acetone in an ultrasonic bath for 15 minutes each. The substrates were dried with stream of N_2 . The precursor solution was prepared by mixing metal nitrates precursors and molybdate tetrahydrate ($\text{Ni}(\text{NO}_3)_2$; $\text{Co}(\text{NO}_3)_2$; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) with the desired ratios with urea (0.2 M) and ammonium fluoride (0.08 M) in 10 mL of water. This solution is transferred into the autoclave reactor (Teflon-lined stainless-steel vessel, 20 mL volume) together with the cleaned FTO substrates. The conductive side face down the solution with an angle of 45° . The autoclave reactor was placed in the oven at 120°C for 4 hours. The hydrothermally grown crystals on the substrate were cleaned with water and further annealed in air at 400°C for 4 hours to result in $\text{NiCo}_{2-x}\text{Mo}_x\text{O}_4$ spinel oxide grown on the FTO substrate. The ramping rate for each annealing step was 300°C/h .

Deposition of Oxides on Ni Foam. Ni foam was first cleaned in 3 M HCl for 15 minutes, followed by ultrasonic cleaning in acetone, ethanol, and water for 15 minutes each. The oxides were deposited on Ni foam using the same method as for the FTO substrates. The mass loading of oxides on Ni foam was $\approx 2 \text{ mg/cm}^2$.

Synthesis of perovskite solar cell device:

FTO substrate. First, FTO substrates were partially etched using HCl and zinc. Following the etching process, the substrates underwent cleaning by ultrasonication in a soap solution followed by an ethanol bath. The cleaned substrates were then dried with compressed air. Finally, UV–ozone treatment was performed on the substrates to remove any organic residue from the FTO surface.

Perovskite Device Fabrication

NiO Film Fabrication. The precursor solution was prepared by mixing 0.1×10^{-3} M nickel acetate and 0.1×10^{-3} M ethanolamine in 1 mL of 2-methoxyethanol. The mixture was heated on a hotplate at 70°C , until a clear, homogeneous green colour solution was formed.

For the deposition of the NiO layer, the cleaned FTO substrates were placed in the spin coater holder, and 50 μL of the prepared solution was dripped onto a substrate. The NiO film was deposited at 3000 rpm spin speed for 30 sec. Spin coating was initiated immediately after dripping the solution. The NiO film was then annealed at 325°C for 60 min under ambient conditions. When the samples cooled, they are transferred to the glovebox for the deposition of perovskite and other layers.

To prepare perovskite solution, 1.1 M PbI_2 , 0.22 M PbBr_2 , 1 M FAI, and 0.2 M MABr in were mixed in 1 mL of 4:1 dimethylformamide/dimethyl sulfoxide (DMF/DMSO) solvent with a 10% excess $\text{PbI}_2/\text{PbBr}_2$. The mixture was heated at 70°C on a hotplate until a clear solution formed. Then, 42.4 μL of 1.5 M CsI solution (dissolved in DMSO) was added to the FA–MA–Pb–I–Br solution. This

perovskite precursor solution was kept on the hotplate at 70 °C for 30 min. The perovskite coating was applied using a two-stage spin-coating process. Initially, the solution was spread at 2000 rpm for 10 s, followed by a rotation at 6000 rpm for 30 s. A 40 µL drop of the perovskite precursor solution was placed on the substrate, and rotation began immediately. Five seconds before the end of the spin-coating process, 120 µL of antisolvent (chlorobenzene) was rapidly dripped into the rotating substrate. After that the perovskite film was transferred to a hotplate and was annealed at 100 °C for 30 min. Next, a PCBM layer (ETL) was spin-coated using a 20 mg/mL PCBM solution in chlorobenzene at 1500 rpm for 40 seconds. This layer was annealed at 95°C for 15 min. Following this, a BCP layer was deposited by spin-coating a 0.5 mg/mL BCP solution in isopropyl alcohol at 5000 rpm for 30 s. The BCP layer was annealed at 60 °C for 5 min. Finally, a 100 nm thick Ag layer was deposited via thermal evaporation to complete the device. To connect two devices in series on the same substrate, the bottom FTO layer was patterned using a specially designed mask, and a silver electrode was evaporated using another mask to create a series-connected configuration. The geometric area is 1.8 cm².

Characterization. XRD patterns were characterized using Shimadzu thin film X-ray diffractometer with CuK α radiation of $\lambda = 0.15406$ nm, from 15° to 70° at a scan rate of 5°/min and step size of 0.02. SEM images were collected using FE-SEM (JEOL-6700F). The elemental composition of oxides was determined by EDX (Table S1).

XPS analysis was carried out utilizing a VGESCLAB 2201-XL instrument featuring a base pressure below 5×10^{-10} mbar and employing a monochromatic Al K α X-ray source.

Electrochemical measurements. Linear sweep voltammetry was performed on NiCo_{2-x}Mo_xO₄ spinel oxide in a three-electrode setup with Ag/AgCl (KCl, 3.0 M) as the reference and Pt wire as the counter electrode, 1M KOH was used as the electrolyte. Potential values are expressed in terms of reversible hydrogen electrode (RHE) using the following equation:

$$E_{\text{RHE}} = E^{\circ}\text{Ag/AgCl} + E_{\text{Ag/AgCl}} + 0.059 \text{ pH}$$

where E_{RHE} represents the potential vs. RHE, $E^{\circ}_{\text{Ag/AgCl}} = 0.1976$ V, and $E_{\text{Ag/AgCl}}$ denoting the experimentally measured potential vs Ag/AgCl.

Electrochemical active surface area (ECSA) is determined from cyclic voltammetry (CV) measurements, conducted in non-Faradic region at different scan rates. Initially, the double-layer capacitance (C_{dl}) is calculated first by plotting the differences in charging current density ($\Delta J = J_{\text{a}} - J_{\text{c}}$) against the scan rate, where the linear slope is twice of C_{dl} value. J_{a} and J_{c} represent the anodic and cathodic current densities, respectively and their values were extracted at specific potential value.

The ECSA of a catalyst is calculated from the capacitance of double layer (C_{dl}) as follows:

$$ECSA = C_{dl}/C_s$$

where C_s is the specific capacitance, and the average value of C_s is 0.04 mF cm^{-2} .¹

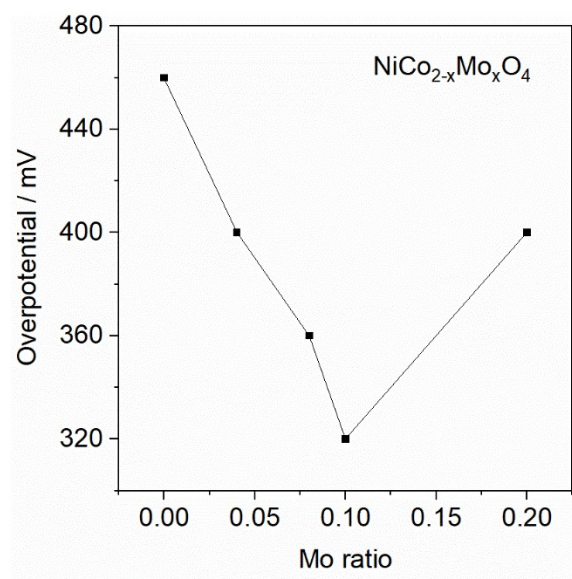


Fig. S1. Overpotential value as a function of Mo concentration in $\text{NiCo}_{2-x}\text{Mo}_x\text{O}_4$.

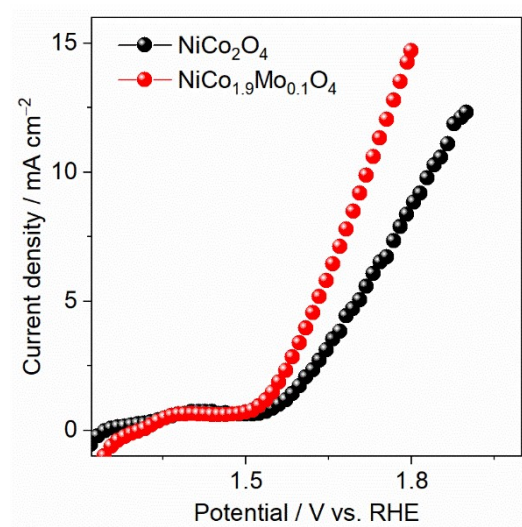


Fig. S2. Polarization curves of oxides without iR correction.

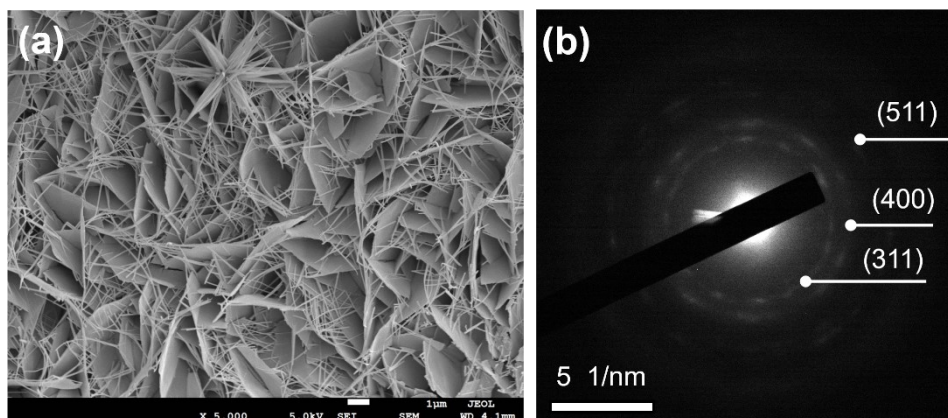


Fig. S3. (a) SEM image of NiCo_2O_4 (low magnification). (b) SAED of NiCo_2O_4 .

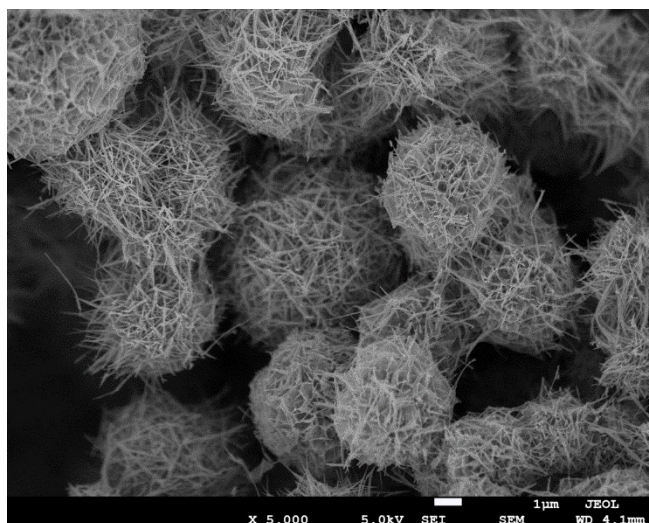


Fig. S4. SEM image of $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ (low magnification).

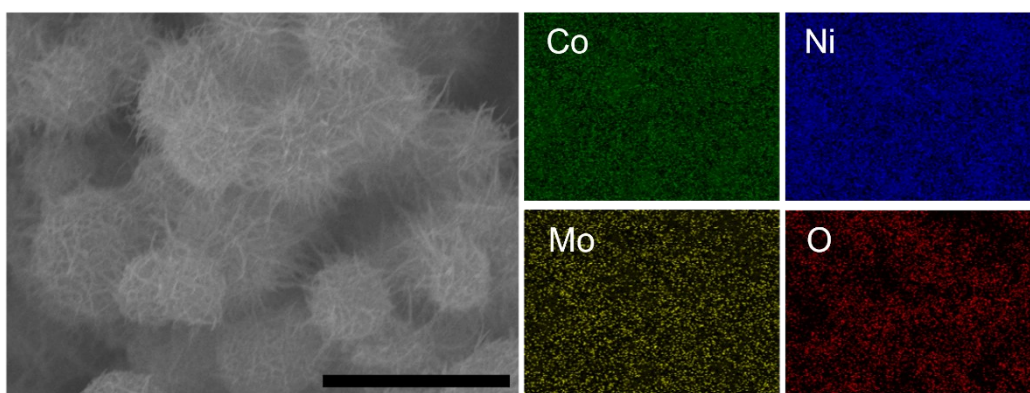


Fig. S5. SEM-EDS mapping of Co, Ni, Mo and O in trimetallic $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$, scale bar: 50 μm .

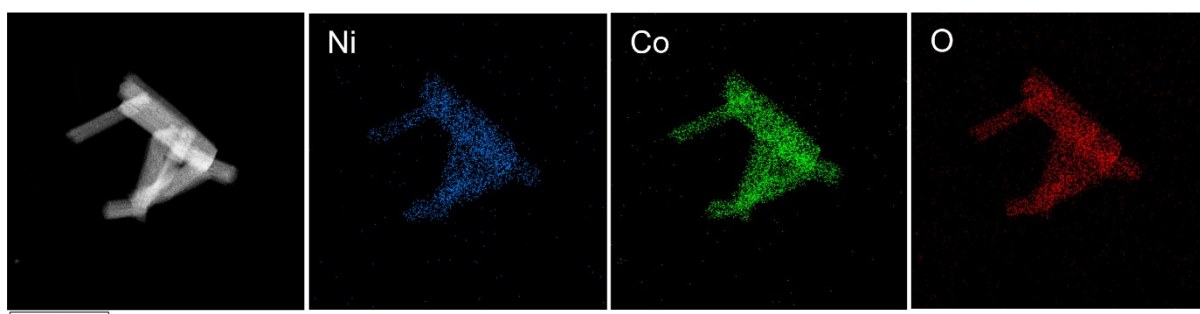


Fig. S6. TEM-EDS mapping of Co, Ni and O in bimetallic NiCo_2O_4 .

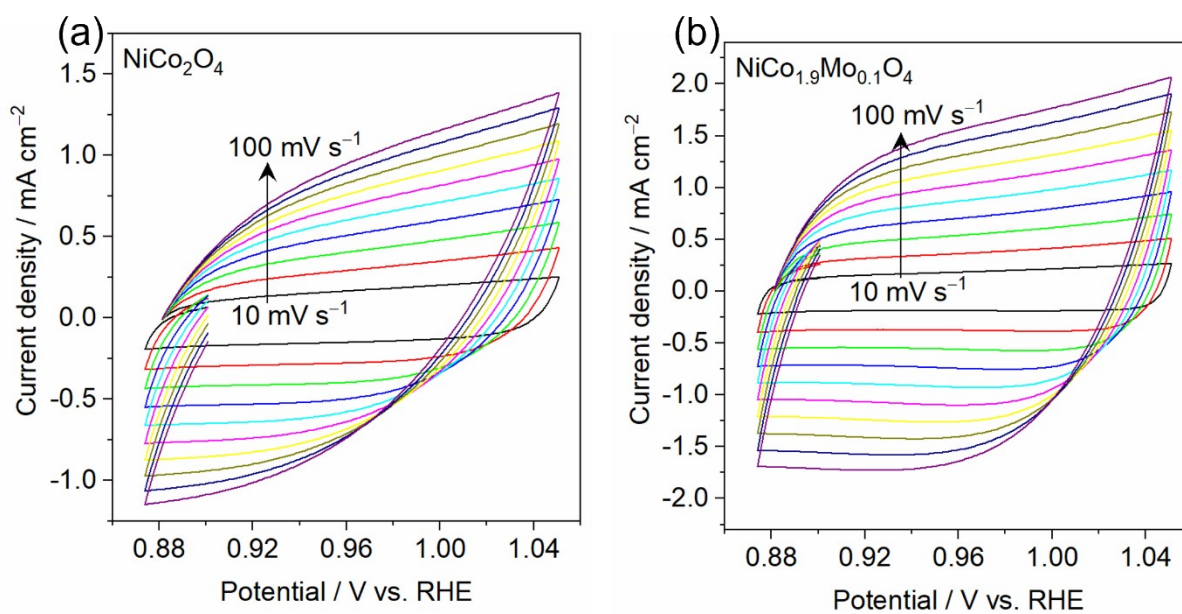


Fig. S7. Cyclic voltammetry of (a) NiCo_2O_4 and (b) $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ deposited on FTO substrate at different scan rates, interval: 10 mV.

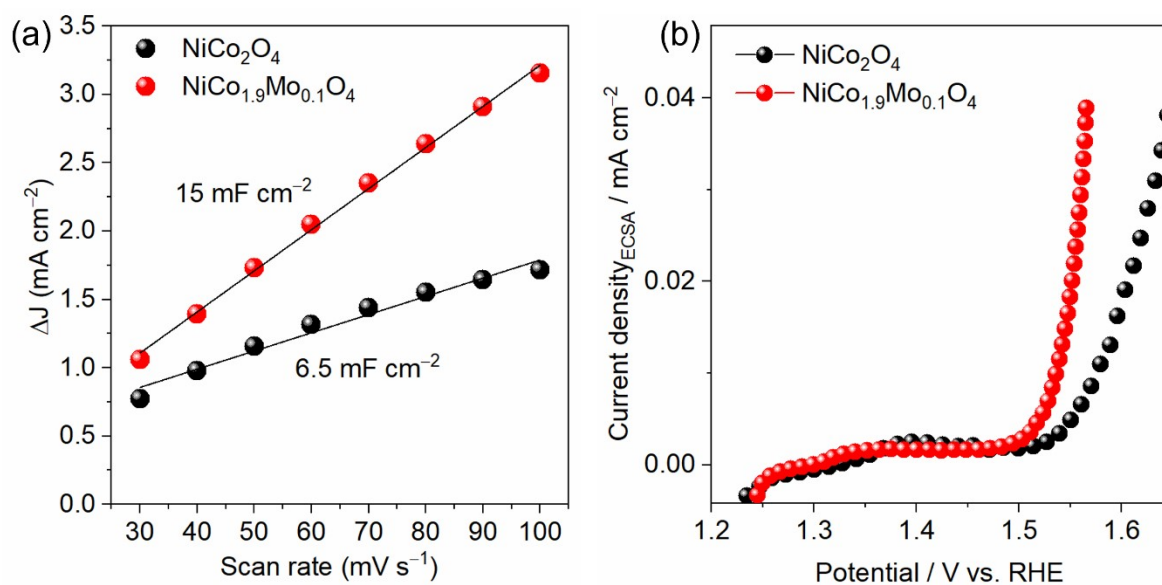


Fig. S8. (a) Current density vs. scan rate for NiCo₂O₄ and NiCo_{1.9}Mo_{0.1}O₄ on FTO substrate extracted from CV measurements and the slope is C_{dl} . (b) Normalized polarization curves by ECSA.

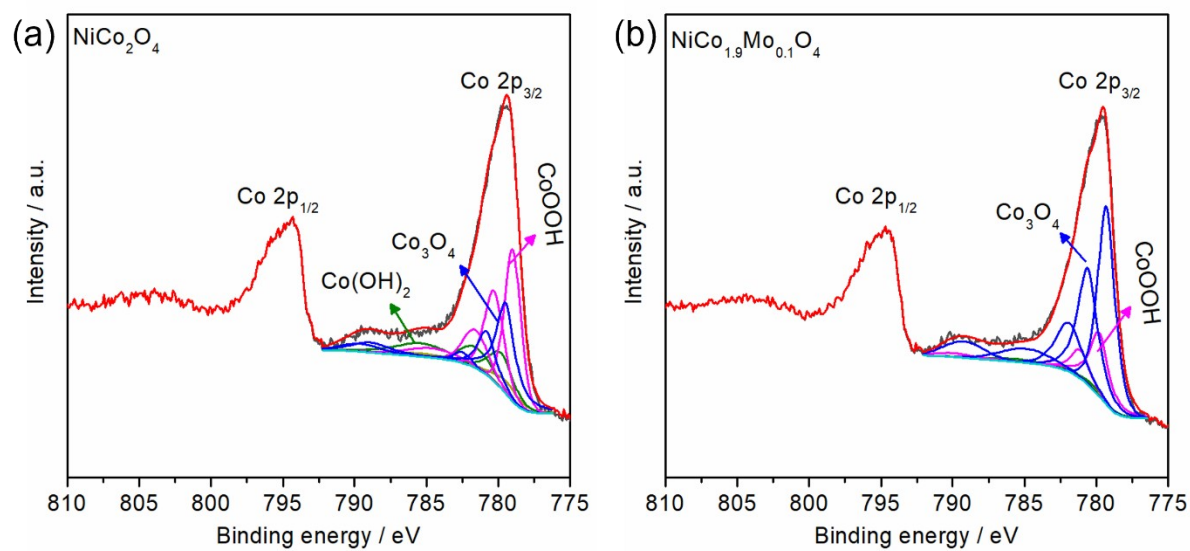


Fig. S9. XPS fitting of Co 2p in (a) NiCo_2O_4 and (b) $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$.

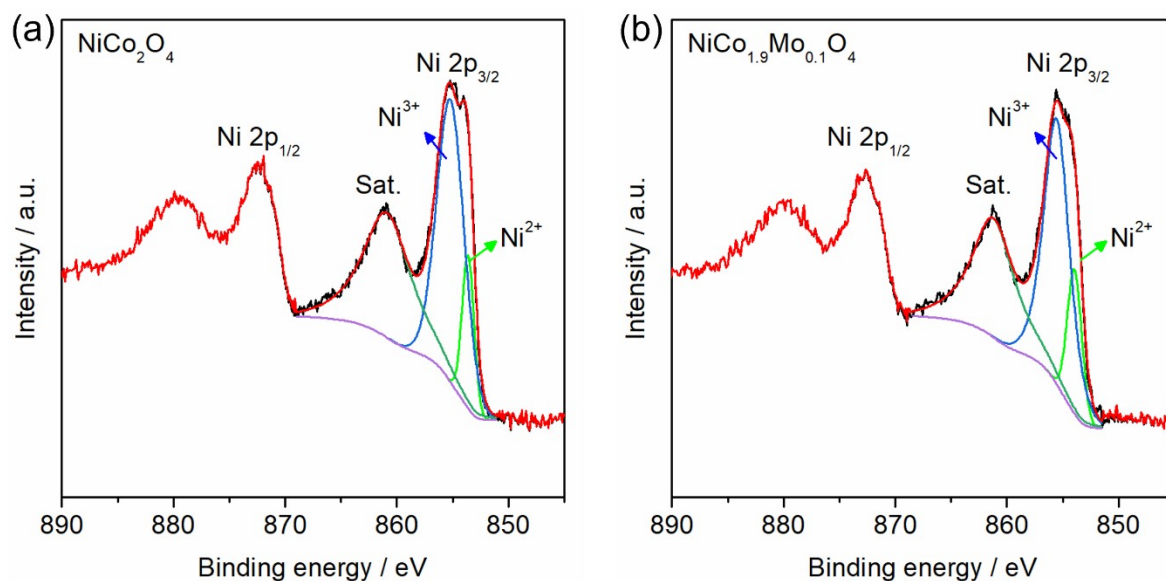


Fig. S10. XPS fitting of Ni 2*p* in (a) NiCo₂O₄ and (b) NiCo_{1.9}Mo_{0.1}O₄.

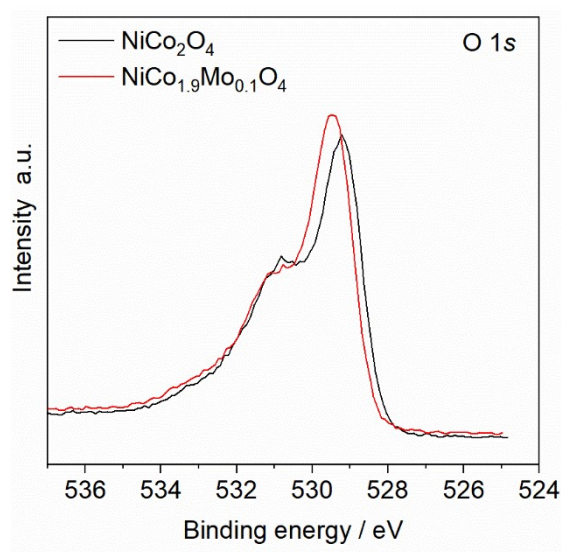


Fig. S11. O 1*s* XPS in NiCo₂O₄ and (b) NiCo_{1.9}Mo_{0.1}O₄.

The shift in binding energy (BE) for oxygen in NiCo_{1.9}Mo_{0.1}O₄ to higher values can be explained by the possibility of interacting bridged oxygen with cations of different electronegativity values (i.e., Ni (Co)-O-Ni(Co) and Ni(Co)-O-(Mo)). In general, the binding energy of inner electrons appears at high BE values if the electronegativity of surrounding connected atoms is high. Given the electronegativity values, the electronegativity of Mo is higher than that of Ni and/or Co. This further reveals strong interaction of Mo with Ni(Co) via bridged oxygen.

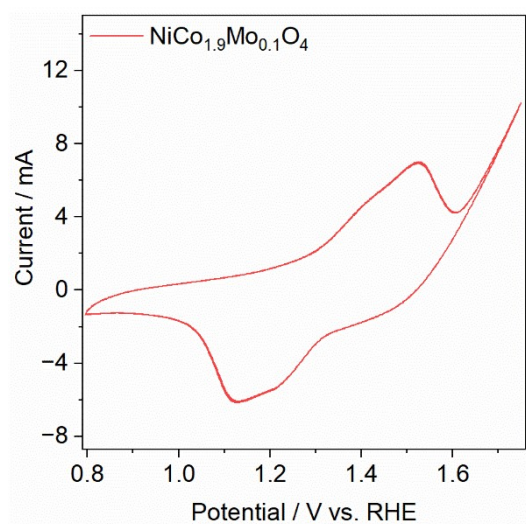


Fig. S12. CV cycles of $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ (cycle = 48, 49 and 50).

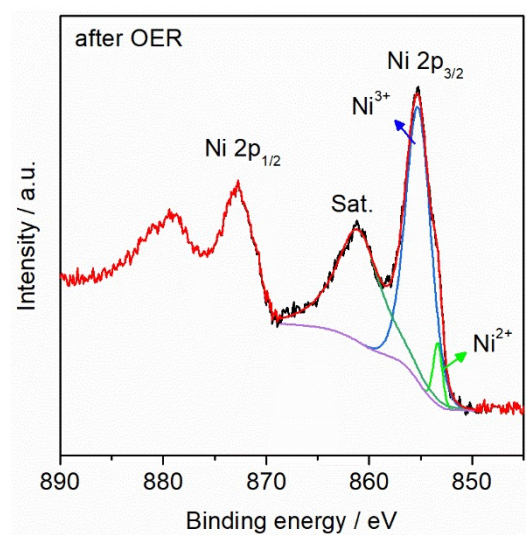


Fig. S13. XPS fitting of Ni 2p in $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ after OER.

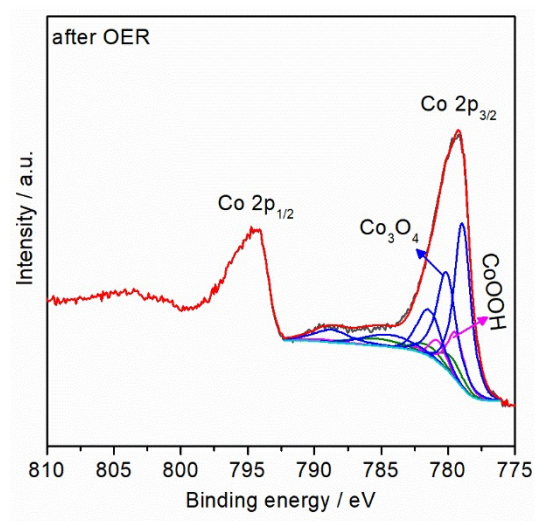


Fig. S14. XPS fitting of Co 2p in $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ after OER.

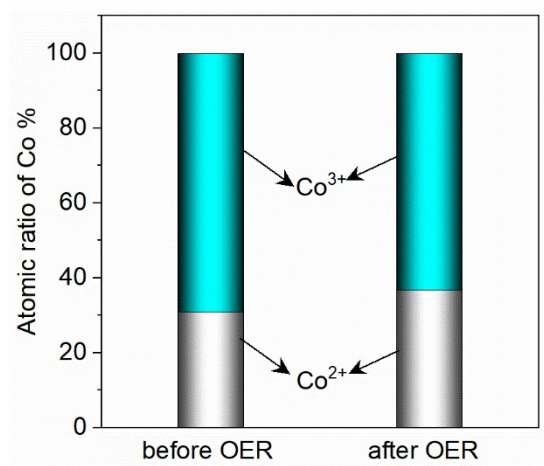


Fig. S15. Atomic ratios of Co^{2+} and Co^{3+} in $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ before and after OER.

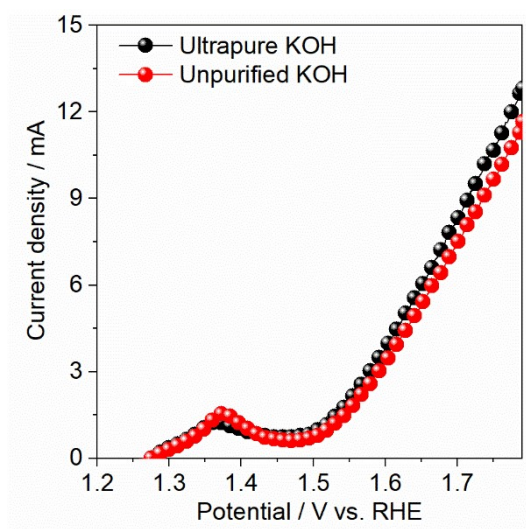


Fig. S16. Polarization curves of spinel oxides on nickel foam recorded in 0.1 M KOH, comparing measurements in ultrapure and unpurified electrolyte.

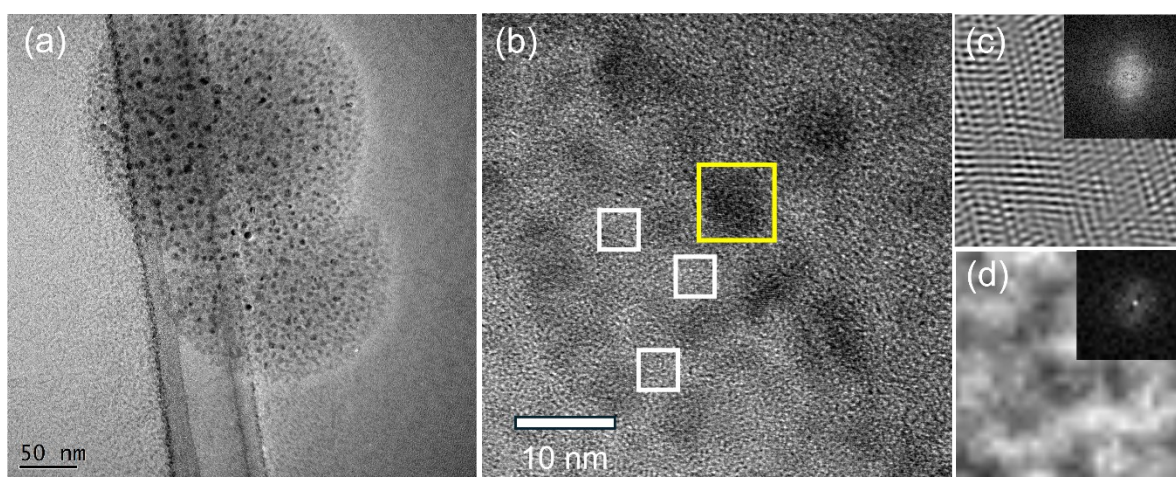


Fig. S17. HR-TEM image of $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ after OER (a) an overview displaying crystalline dark regions and an amorphous light region, (b) a magnified view, (c) a mask-filtered HR-TEM image obtained from inverse FFT of the yellow square, and (d) a mask-filtered HR-TEM image obtained from inverse FFT of the light region within one the white square.

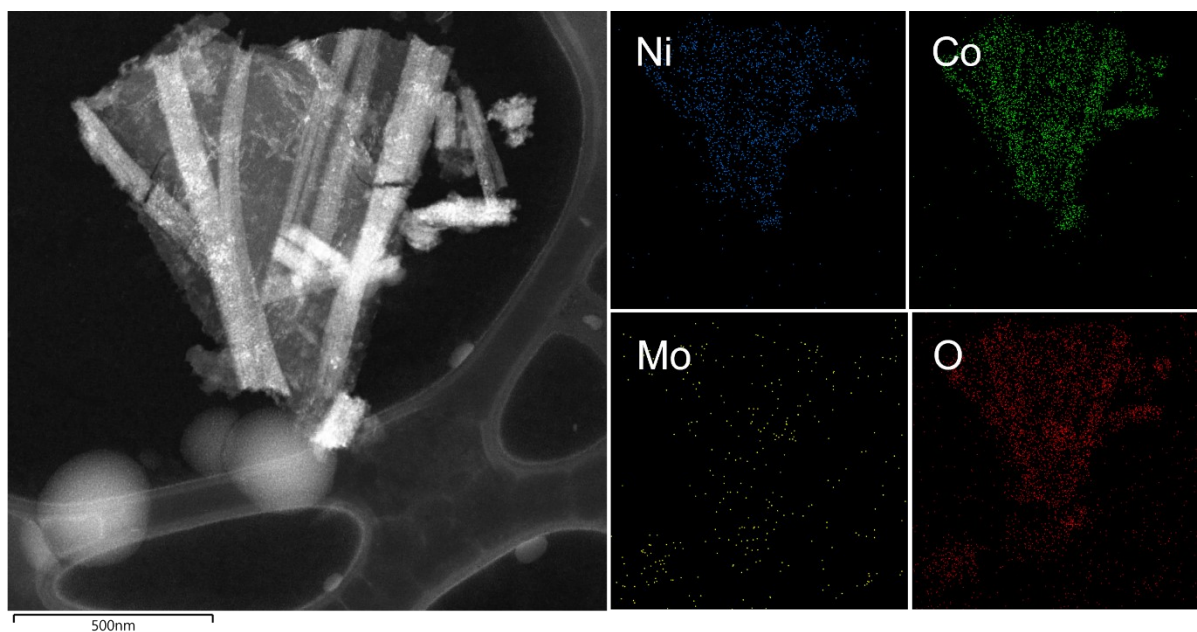


Fig. S18. TEM-EDS mapping of $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ after OER.

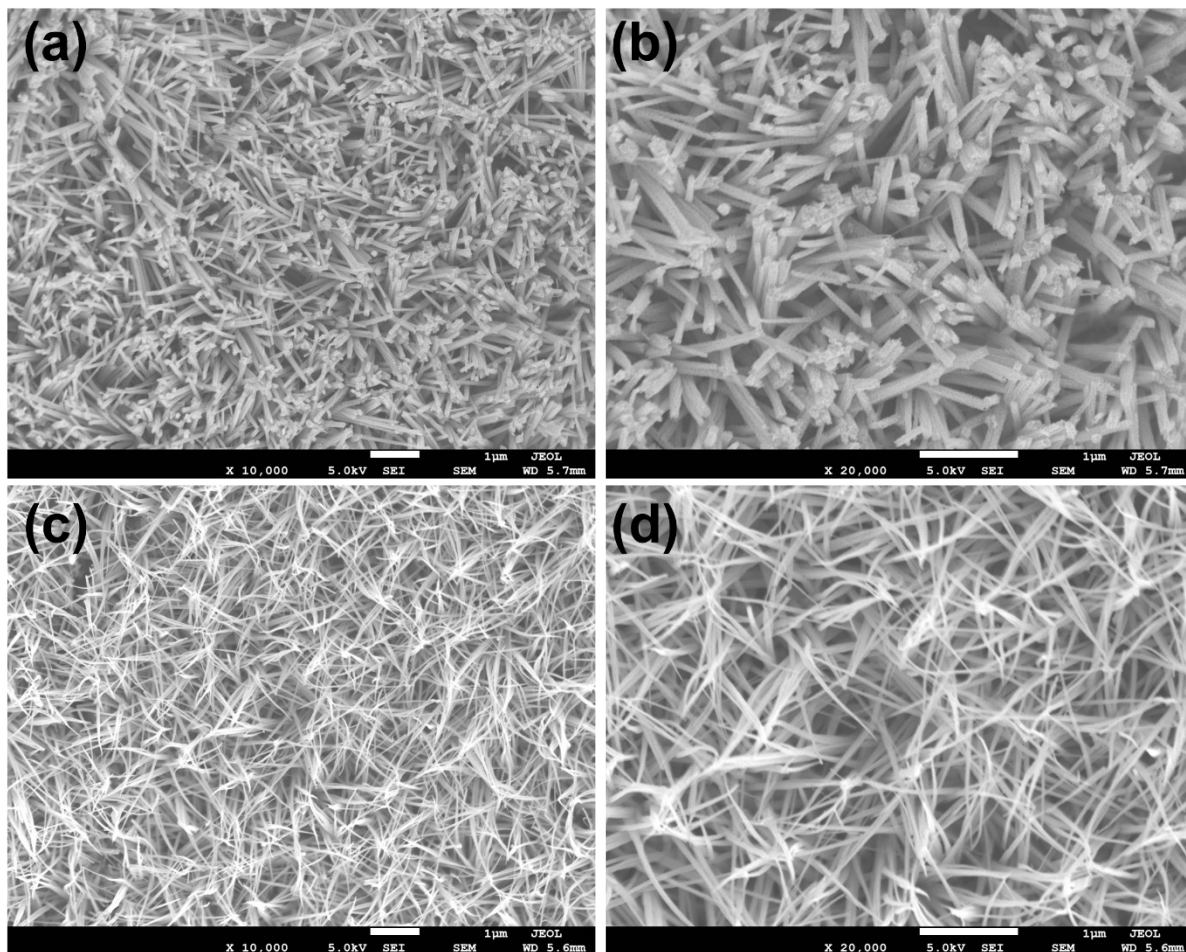


Fig. S19. SEM images of (a,b) NiCo_2O_4 and (c,d) $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4$ deposited on nickel foam. (a,c) and (b,d) represent low and high magnification resolution, respectively.

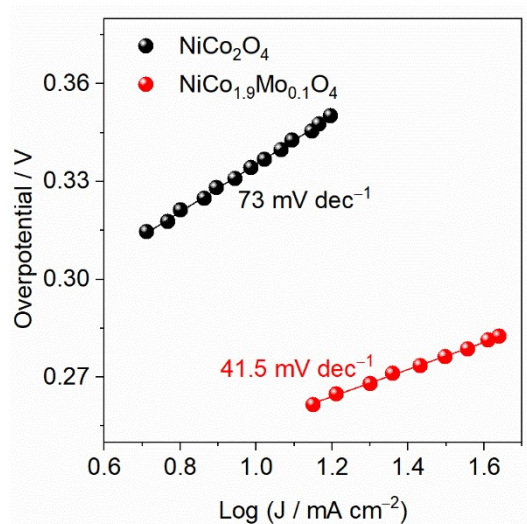


Fig. S20. Tafel plots of $\text{NiCo}_2\text{O}_4/\text{NF}$ and $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4/\text{NF}$.

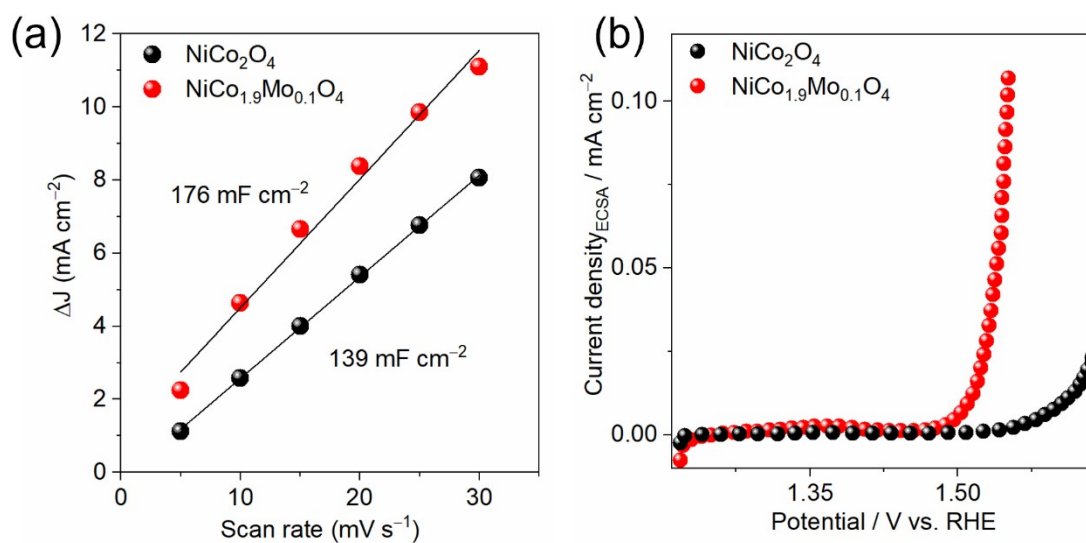


Fig. S21. (a) Current density vs. scan rate for $\text{NiCo}_2\text{O}_4/\text{NF}$ and $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4/\text{NF}$ (b) Normalized polarization curves by ECSA.

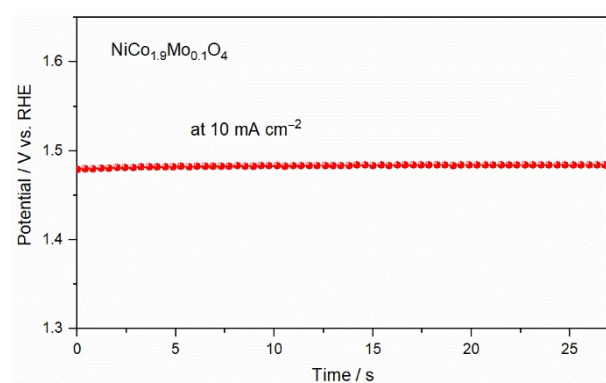


Fig. S22. Chronopotentiometry curve of $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4/\text{NF}$ at constant current density 10 mA cm^{-2} .

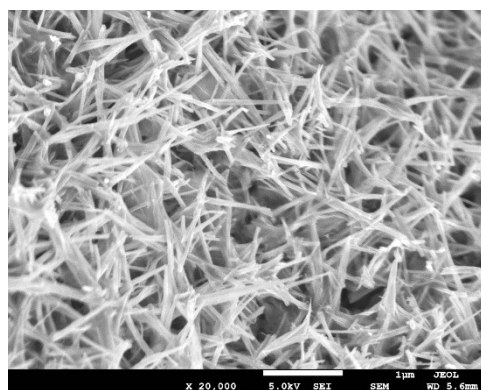


Fig. S23. SEM images of $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4/\text{NF}$ after stability test.

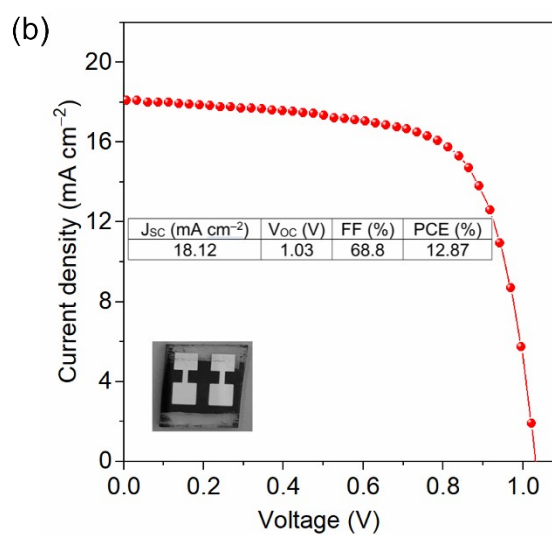
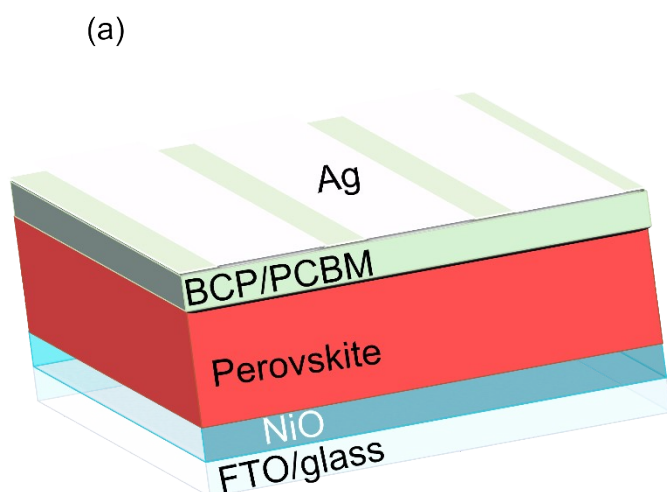


Fig. S24. (a). Schematic illustration of perovskite solar cell device. (b) J–V curve of perovskite solar cell device measured under 1 sun illumination.

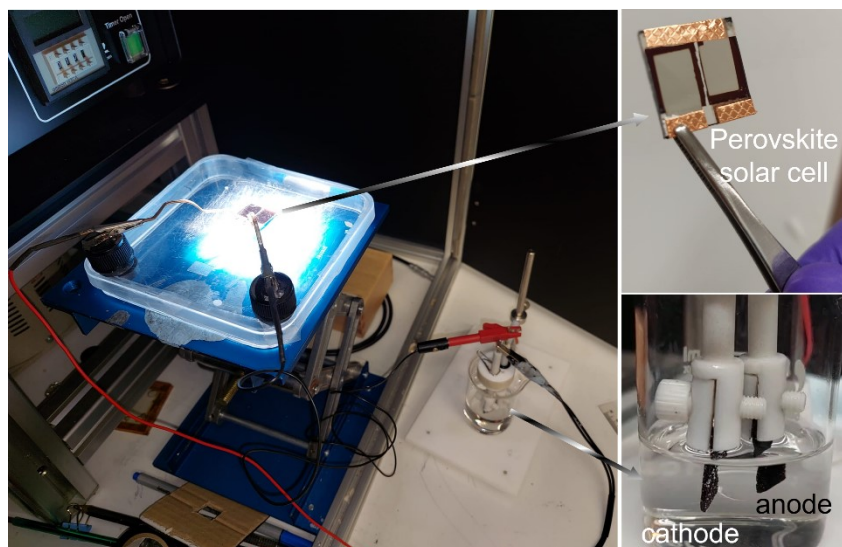


Fig. S25. A real image of perovskite solar cell connected to water electrolyzer system, where $\text{NiCo}_{1.9}\text{Mo}_{0.1}\text{O}_4/\text{NF}$ is the anode and Pt/NF is the cathode.

Table S1. Elemental ratio in spinel oxides estimated by EDX.

	Ni	Co	Mo	Ni:Co:Mo
NiCo ₂ O ₄	33.5	66.5	0	1:2:0
NiCo _{2-x} Mo _x O ₄	33.44	62.92	3.64	1:1.9:0.1

Table S2. Comparison of electrochemical activity of spinel oxide with recently reported catalysts for overall water splitting.

	Configuration	Electrolyte	Cell voltage at 10 mA cm ⁻²	Reference
1	Pt/NF//NiCo _{1.9} Mo _{0.1} O ₄ /NF	1.0 M KOH	1.53	This work
2	Co ₄ S ₃ /Mo ₂ C-N SC-2/NF// Co ₄ S ₃ /Mo ₂ C-N SC-2C/NF	1.0 M KOH	1.62	²
3	Commercial Pt/C//RuO ₂	1.0 M KOH	1.62	³
4	Ru-HPC//P-RuO ₂	1.0 M KOH	1.53	³
5	NiCo ₂ S ₄ /NF//NiCo ₂ S ₄ /NF	1.0 M KOH	1.61	⁴
6	FeCo// FeCoNi-2	1.0 M KOH	1.687	⁵
7	Co-NC@CC// Co-NC@CC	1.0 M KOH	1.57	⁶
8	FeNi@N-CNT// FeNi@N-CNT	1.0 M KOH	1.6	⁷
9	Co-P@PC-750// Co-P@PC-750	1.0 M KOH	1.6	⁸
10	Ru-NiCo ₂ O ₄ // Ru-NiCo ₂ O ₄	1.0 M KOH	1.55	⁹

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