

Electronic Supplementary Information

MOF derived bi-functional Electro-catalyst Ni₃ZnC_{0.7}-Mo₂C with enhanced performance for Overall Water Splitting

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Experiment Section

1. Medicines and materials

Zinc nitrate Hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Sodium Molybdat Dihydrat ($\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$), Ammonium fluoride (NH_4F), Urea (CON_2H_4), 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$), and Potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received, without further purification. All the water used in the experiments was purified using a microporous system.

2. Samples preparation

2.1 The synthesis of $\text{ZnMoO}_4 \cdot x\text{H}_2\text{O}$ on Ni foam ($\text{ZnMoO}_4 \cdot x\text{H}_2\text{O}/\text{NF}$)

Firstly, 0.15 mmol $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 25 mL solvent (H_2O : ethanol=2:1), then 6 mmol NH_4F and 7.5 mmol NH_4F were added, recorded as the solution A. 0.15 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL solvent (H_2O : ethanol=2:1), recorded as solution B. Solution B was dropped slowly into solution A and stirred. Ultrasonic treatment was then performed for 1 hour and a milky suspension was obtained. Secondly, the Ni foam (NF) 1.0 mm was cut into 2cm * 3 cm pieces and then treated ultrasonically for 15 minutes inside 3M HCl to remove the surface oxides, cleaned by ethanol and water. Thirdly, one piece Ni foam was put into 50 mL polytetrafluoroethylene reactor, and the solution mixed in step 1 was added into the reactor, reacting at 160 °C for 12 hours at the blast drying oven. After the reaction, the products were cleaned using ethanol and water, and dried at 60 °C for 12 hours. Finally, the $\text{ZnMoO}_4 \cdot x\text{H}_2\text{O}$ grown on Ni foam ($\text{ZnMoO}_4 \cdot x\text{H}_2\text{O}/\text{NF}$) was obtained.

2.2 The synthesis ZnMoO_4 -MOF(ZIF-8)/NF

A sealed quartz tank was used to perform Sublimation gas phase MOF reaction. To start with, 50 mg 2-Methylimidazole (2-MeIm) was spread on the bottom of quartz tank, the $\text{ZnMoO}_4 \cdot x\text{H}_2\text{O}/\text{NF}$ was cut into 1.8 cm * 0.7 cm pieces and put on the slot. The reaction was conducted at 200 °C for 2 hours, then ZnMoO_4 -MOF (ZIF-8)-50@NF was obtained. Besides, 20 mg and 80 mg 2-MeIm were used to prepare ZnMoO_4 -MOF(ZIF-8)-20, 80/NF.

2.3 The synthesis Ni₃ZnC_{0.7}-Mo₂C/NF

The ZnMoO₄-MOF-50/NF was put into a tube furnace, then it was heated to 600 °C at 10 °C/min and kept for 4 hours under the Ar atmosphere. After cooling down to 25 °C, the product, Ni₃ZnC_{0.7}-Mo₂C-T600/NF, was obtained, loading amount about 2.6 mg cm⁻².

Besides, 700 °C-4h were used to Ni₃ZnC_{0.7}-Mo₂C-T700/NF, then the products of 800 °C were pure Mo₂C because Zn atoms evaporate too fast and Ni₃ZnC_{0.7} can hardly generated.

2.4 Synthesis of Pure Ni₃ZnC_{0.7}

Pure Ni₃ZnC_{0.7} was prepared by NiZn-MOF annealing at 600°C-4h. NiZn-MOF was synthesized according to previous literature²⁰. Typically, 1.0 mmol of Zn(NO₃)₂, 3mmol of Ni(NO₃)₂ and 2 mmol of triethylenediamine dissolved in 50 mL DMF, and 4.2 mmol of 1,4-benzenedicarboxylic acid was dropped to the DMF solution, then transferred to 100 mL Teflon-lined autoclave, kept for 110°C-48h. After reaction, NiZn-MOF was got by centrifugation and being washed with DMF/ethanol.

Working electrode was prepared as follows: 10 mg of catalyst was dispersed in 1 mL of Isopropyl-alcohol solvent containing 10 μL of 5 wt% Nafion solutions with ultrasonic mixing for about 30 min. Then 400 μL of the catalyst ink suspension was loaded onto Ni foam and dried in air (loading ~2.4 mg cm⁻²).

3. Characterization

Transmission electron microscopy (TEM) and elements mapping were obtained through a JEM 2010 microscope at 200 kV. Samples were prepared by ultrasonic dispersion in ethanol and loaded on copper grids with a carbon film. The scanning electron microscope (SEM, Hitachi SU8010) was taken to inspect the samples' morphology. X-ray diffraction (XRD) patterns were conducted on an X-ray diffractometer (bruker-D8) using Cu K α radiation($\lambda=1.5418 \text{ \AA}$). Raman spectrum was conducted on a Micro Raman spectrometer (Reinshaw Raman Scope RM3000). X-ray photoelectron spectrometry (XPS, Kratos Axis Ultra DLD) was used to detect the chemical composition of the samples, then the binding energy was calibrated based on

C 1s peak at 284.8eV. Fourier transform infrared (FT-IR) spectra were obtained using a Thermo Nicolet AVATAR 370 FT-IR, the samples were revealed from Ni foam and mixed with KBr and then pressed into a disk. Afterward, the samples were revealed from Ni foam and a Thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449F3 DTA-TGA Jupiter analyzer from 100 °C to 900 °C, at a rate of 10 °C /min.

4 Electrochemical measurements

Electrochemical measurements were carried out in 1M KOH with a three-electrode cell (CHI 660B, CHI Instruments, Inc., Shanghai). The Ni₃ZnC_{0.7}@NF samples were cut into 0.5 cm * 0.5 cm. Hg/HgCl₂ and carbon rods were used as the reference electrode, counter electrode, and working electrode. The polarization curves were obtained with a scanning rate of 5 mV s⁻¹, with an electrode rotation to avoid the accumulation of H₂ or O₂ bubbles on the electrode surface. Electrochemical impedance spectroscopy (EIS) was performed at the Electrochemical workstation (PGSTAT302N) at an overpotential of 200 mV while sweeping the frequency from 10 kHz to 0.1 Hz. The electrochemical capacitance of the acquired samples was tested in 1 M KOH using cyclic voltammetry at different scan rates in the non-faradaic potential region. The capacitive current was obtained at the middle potential value for scan rate 10 mV s⁻¹, 20 mV s⁻¹, 30 mV s⁻¹, 40 mV s⁻¹, and 50 mV s⁻¹. The electrode stability was tested by chronoamperometry. The potentials reported in this paper were converted from vs. Hg/HgCl₂ to vs. RHE by $E(\text{RHE}) = E(\text{SCE}) + 0.241 \text{ V} + 0.059 \text{ pH}$.

Experiments details

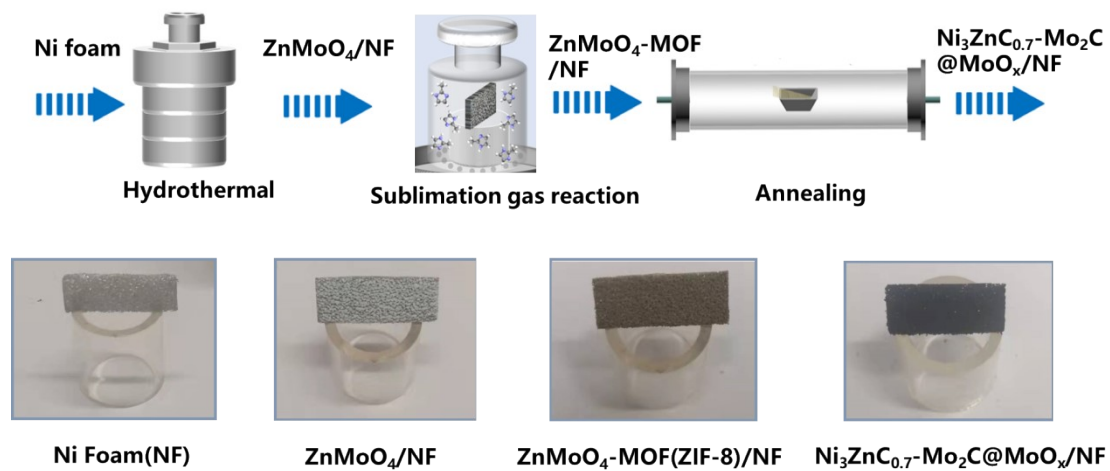


Figure S1. The detailed experiment parameters and the photos of the samples.

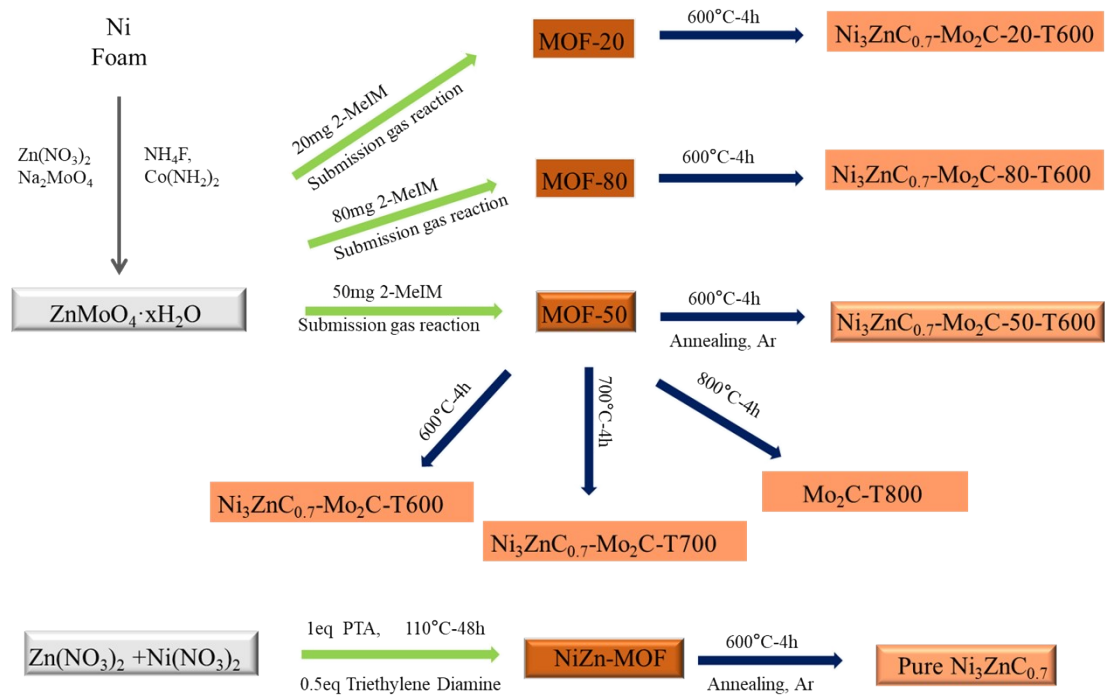
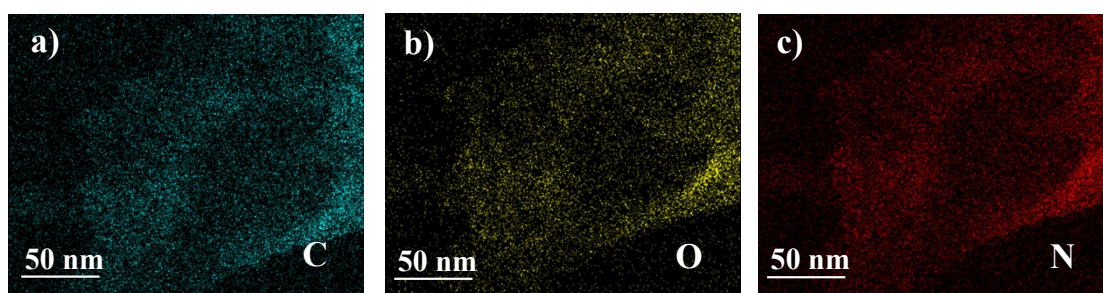


Figure S2. Conditions of different samples.



Sample quality m_0 (g)	Constant volume V_0 (mL)	Test element	Test solution element concentration C_0 (mg/L)	Dilution multiple of test solution-- f	Element concentration of original sample solution C_1 (mg/L)	Sample element content C_x (mg/kg)	Percentage of sample element content W%	Molecular Weight	Molecular ratio (Base on Zn)
0.0268	10	Mo	8.02	50	401.00	149626.87	14.9627%	96.0	1.0174
0.0268	10	Ni	17.56	50	878.08	327639.93	32.7640%	58.7	3.6435
0.0268	10	Zn	5.37	50	268.50	100186.57	10.0187%	65.4	1.0000

Figure S3. Element Mapping C, N, O and ICP result of $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C-T600}$.

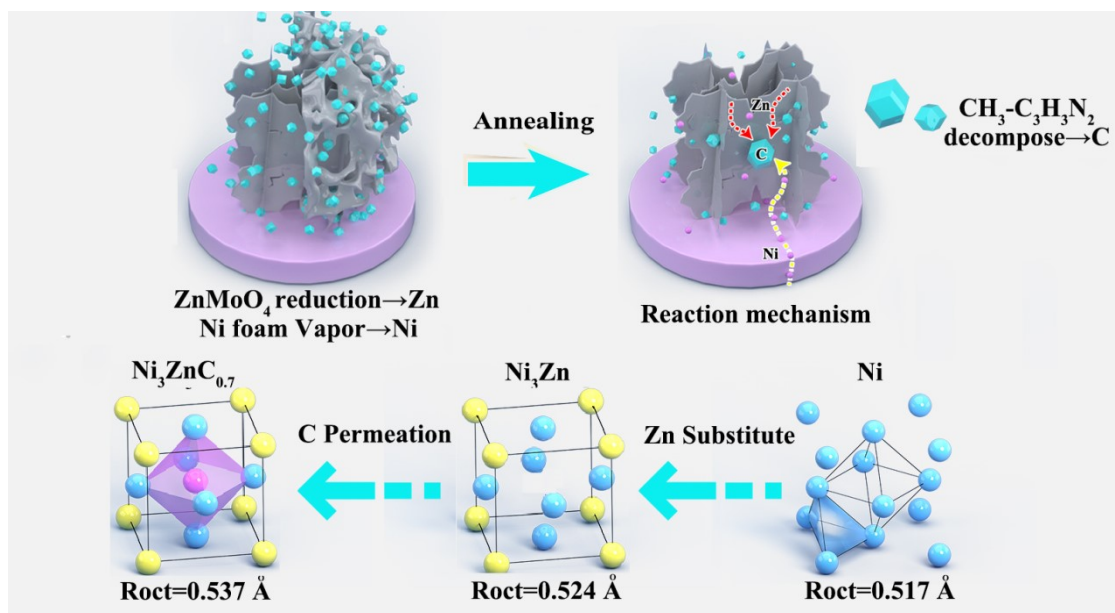


Figure S4. The generation details of Ni₃ZnC_{0.7} during annealing.

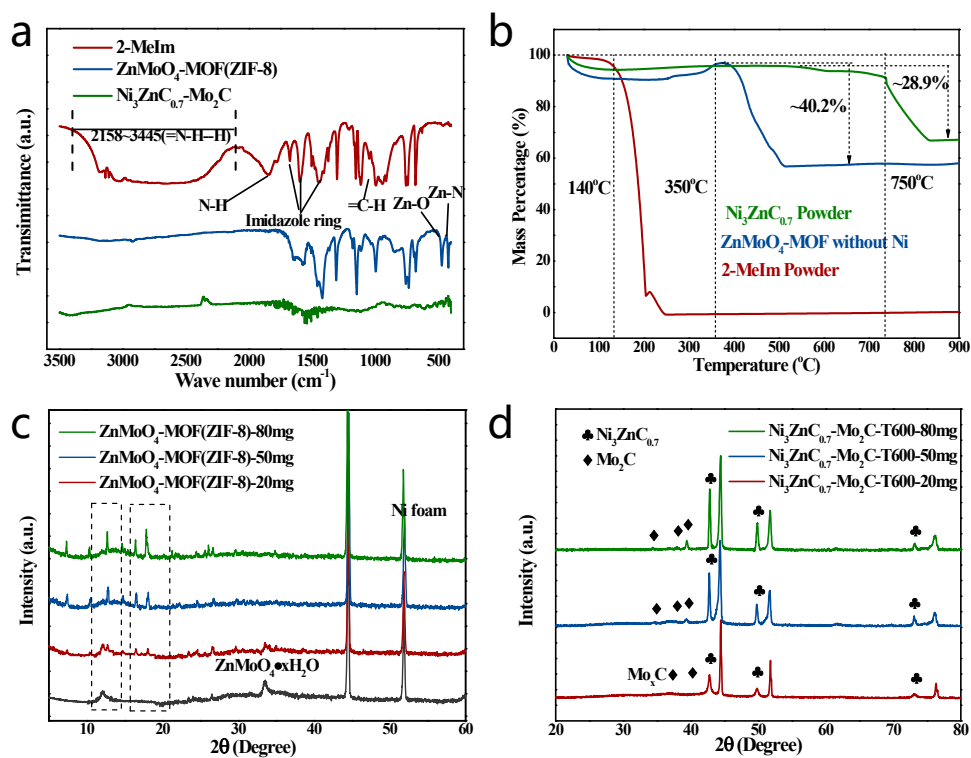


Figure S5. FTIR (a) and TGA (b) for 2-MeIm, $\text{ZnMoO}_4\text{-MOF(ZIF8)}$ and $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C}$. (c) XRD for MOF of different 2-MeIm, (d) XRD for $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C}$ of different amount of 2-MeIm.

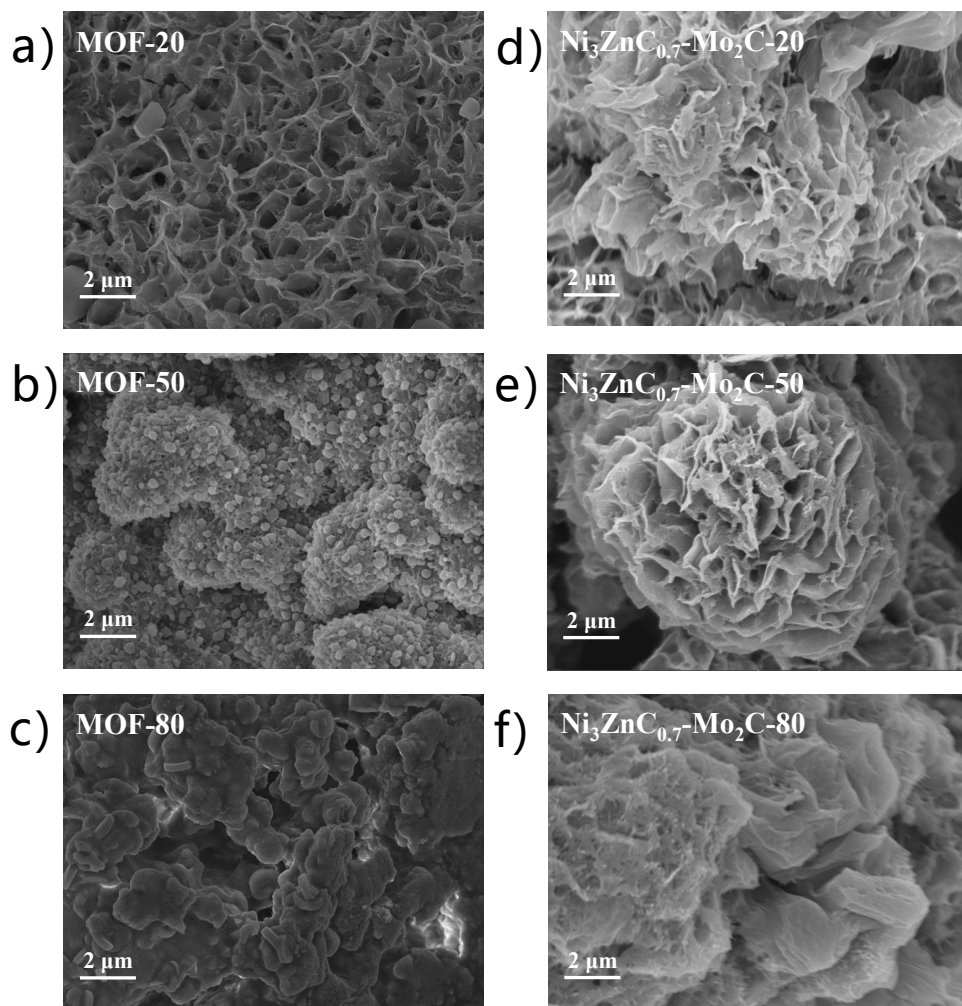


Figure S6. (a-c) SEM images of $\text{ZnMoO}_4\text{-MOF(ZIF8)}$ of different amount of 2-MeIm. (d-f) SEM images of $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C}$ of different amount of 2-MeIm.

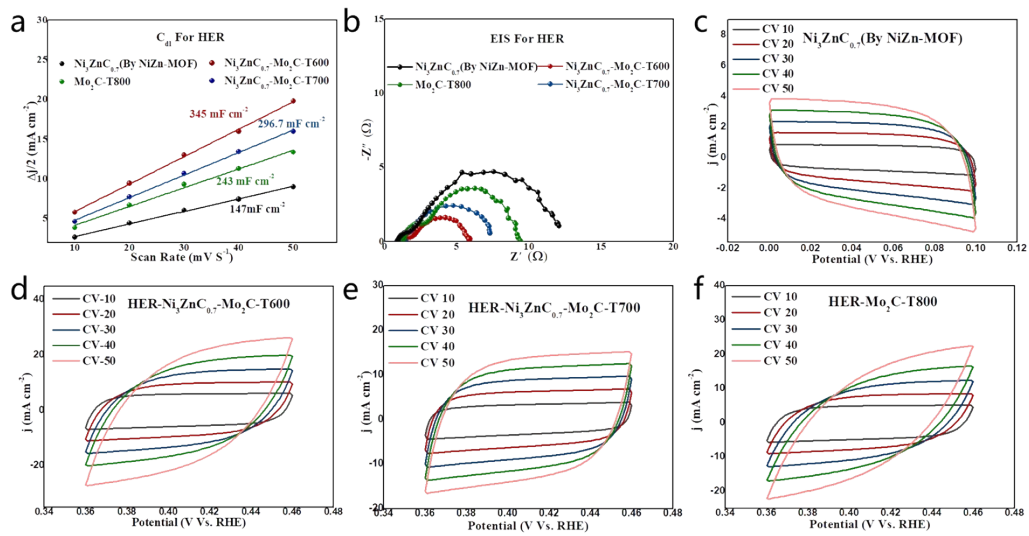


Figure S7. (a) C_{dl} for HER of $Ni_3ZnC_{0.7}$ - Mo_2C -T600, T700, $Ni_3ZnC_{0.7}$ (By NiZn-MOF), Mo_2C -T800, (b) EIS for HER of $Ni_3ZnC_{0.7}$ - Mo_2C -T600, T700, $Ni_3ZnC_{0.7}$ (By NiZn-MOF), Mo_2C -T800 (c-f) Corresponding CV curves.

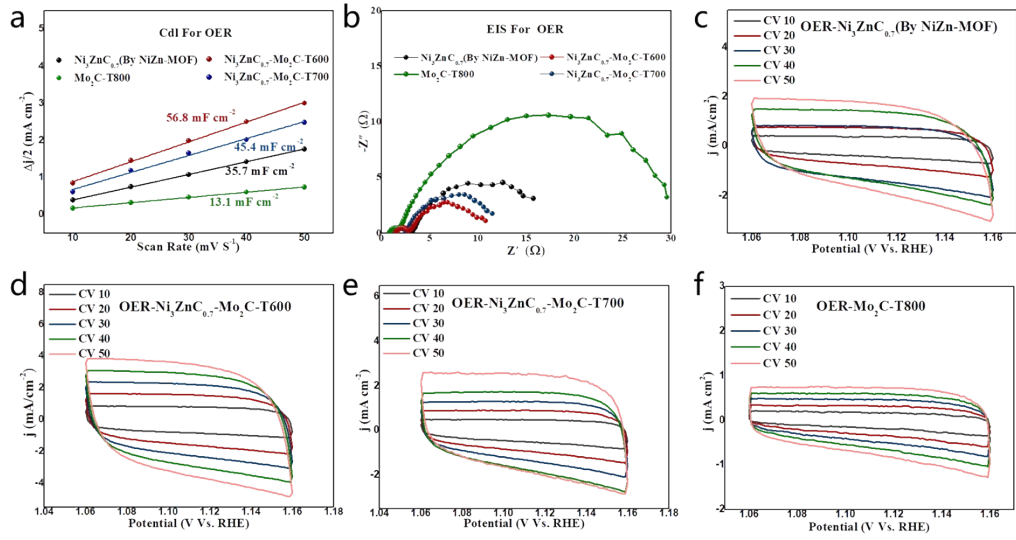


Figure S8. (a) C_{dl} for OER of Ni₃ZnC_{0.7}-Mo₂C-T600,T700, Ni₃ZnC_{0.7} (By NiZn-MOF), Mo₂C-T800, (b) EIS for OER of Ni₃ZnC_{0.7}-Mo₂C-T600,T700, Ni₃ZnC_{0.7} (By NiZn-MOF), Mo₂C-T800 (c-f) Corresponding CV curves.

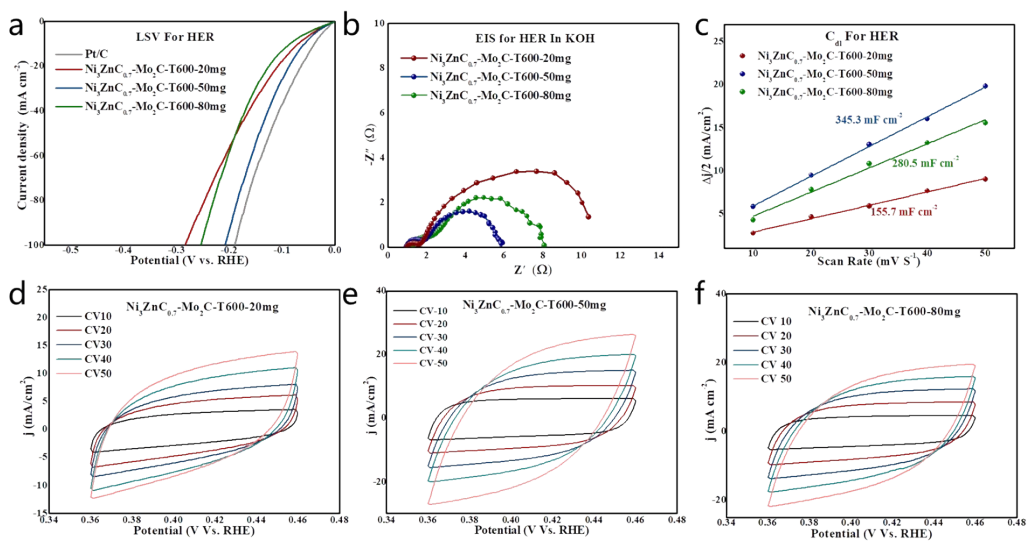


Figure S9. The HER contrast of $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C-T600}$ -20mg, 50mg, 80mg , (a) LSV curves (b) EIS curves (c) C_{dl} curves (d-f) corresponding CV curves.

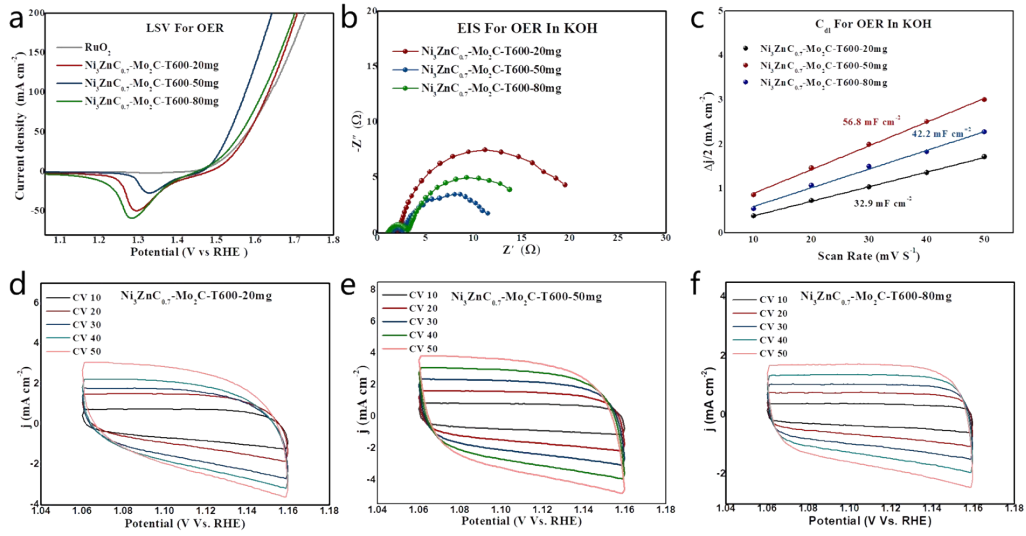


Figure S10. The OER contrast of $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C-T600}$ -20mg, 50mg, 80mg (a) LSV curves (b) EIS curves (c) C_{dl} curves (d-f) corresponding CV curves.

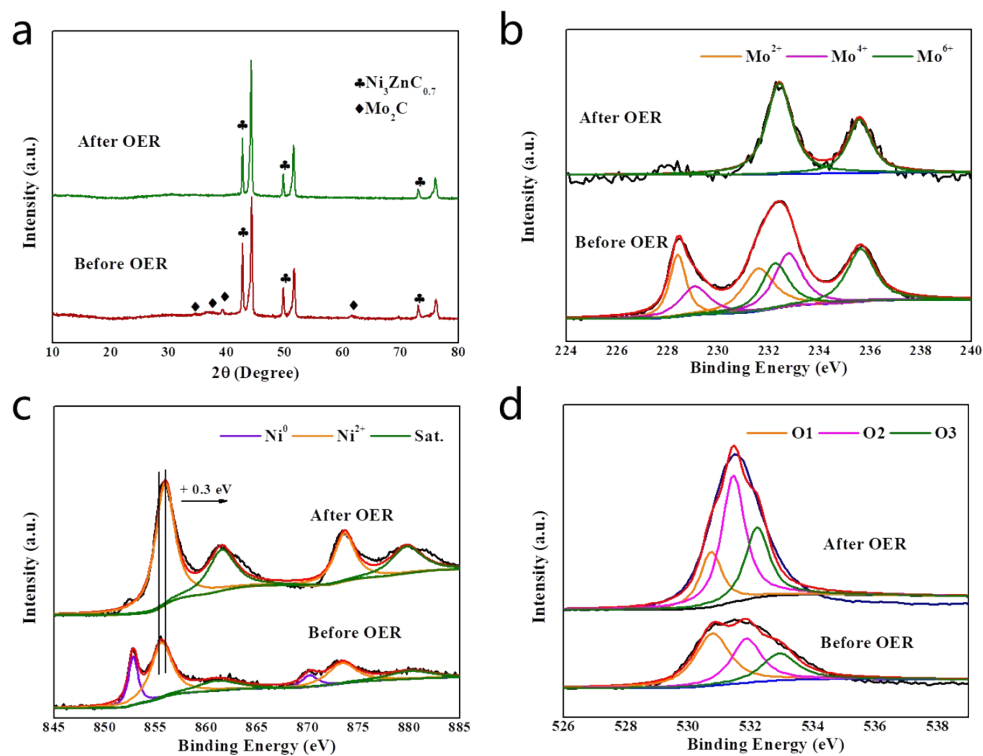


Figure S11. (a) XRD before and after OER of $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C-T600}$, (b) Mo 3d before and after OER, (c) Ni 2p before and after OER, (d) O 1s before and after OER of $\text{Ni}_3\text{ZnC}_{0.7}\text{-Mo}_2\text{C-T600}$.

Table S1. The comparison of overpotential with the reported bifunctional electrocatalysts at 10 mA cm⁻²

Samples	η_{10} for HER	η_{10} for OER	η_{10} for Water Splitting	References
Ni₃ZnCo_{0.7}-Mo₂C	58 mV	257 mV	1.56 V	This work
Ni ₃ ZnCo _{0.7}	203 mV	380 mV	1.67V	[19]
Ni-Ni ₃ C	98 mV	299 mV	1.64 V	[17]
Ni-Ni ₃ N	/	229 mV	/	[27]
Fe-Ni ₃ C	178 mV	275 mV	1.58 V	[15]
Co-Co ₂ C	96 mV	261 mV	1.63V	[32]
CoP-Co ₂ P	62.5 mV	280 mV	1.56 V	[37]
Co ₃ ZnCo-Co	188 mV	295 mV	1.65 V	[38]
Co ₆ W ₆ C	161 mV	310 mV	1.58 V	[25]
Co ₆ Mo ₆ C	59 mV	286 mV	1.59 V	[39]
Cu-CoWC	98 mV	238 mV	1.64 V	[40]
Ni-Mo _x C	162 mV	328 mV	1.72 V	[41]
Co-Mo ₂ C	121 mV	311 mV	1.67 V	[42]
NiS ₂ -MoS ₂	62 mV	278 mV	1.59 V	[43]
CoP(Hollow)	173 mV	333 mV	1.65 V	[44]