*Supplementary Materials*

# Tuning Electrochemical Hydrogen-Evolution Activity of $CoMoO_4$ through Zn Incorporation

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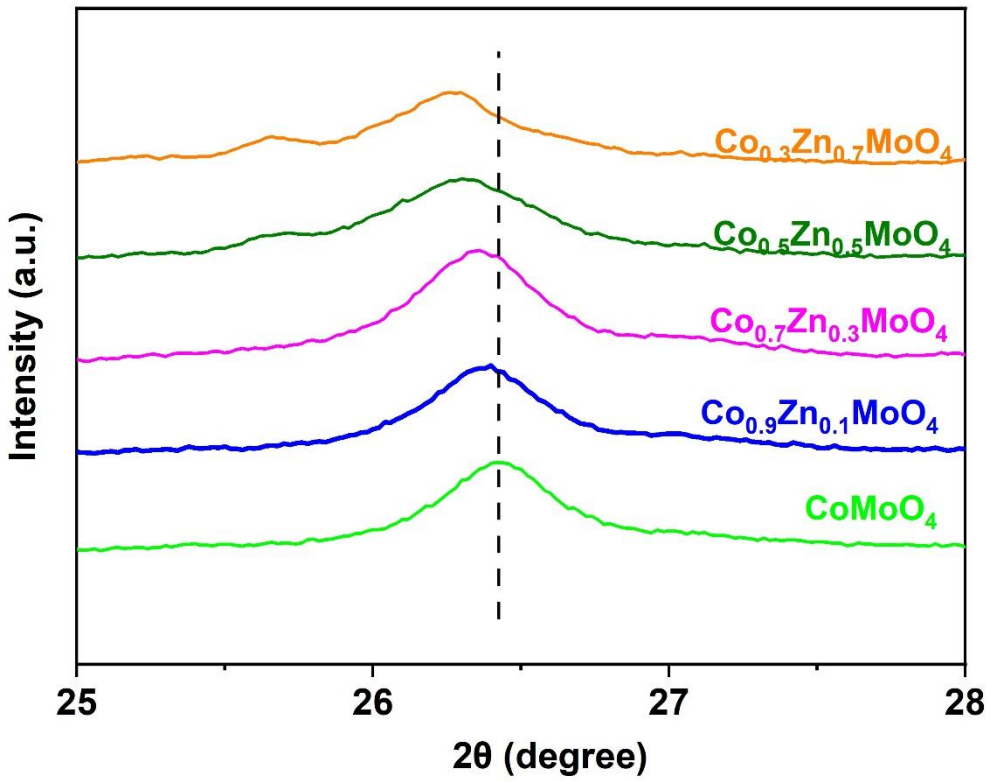


**Figure S1.** The shift of XRD (220) peaks for the prepared $Co_{1-x}Zn_xMoO_4$ samples.

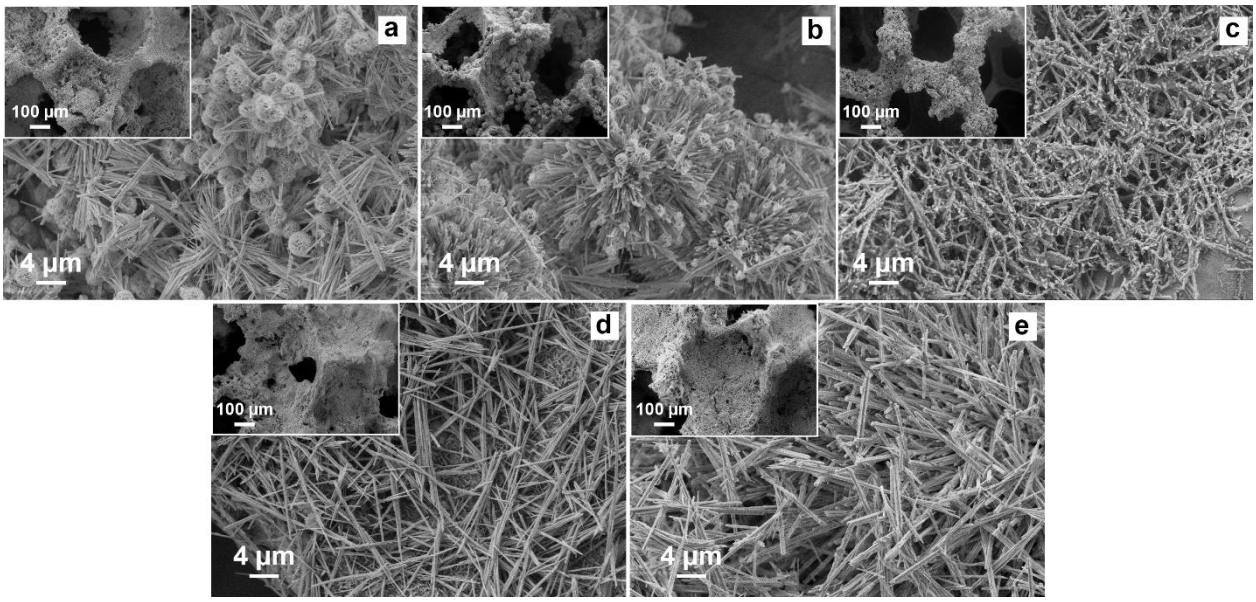


**Figure S2.** Depiction of the homogenous proliferation of catalysts on the backbone of NF substrate, (**a**) $CoMoO_4$, (**b**) $Co_{0.9}Zn_{0.1}MoO_4$, (**c**) $Co_{0.7}Zn_{0.3}MoO_4$, (**d**) $Co_{0.5}Zn_{0.5}MoO_4$, and (**e**) $Co_{0.3}Zn_{0.7}MoO_4$.

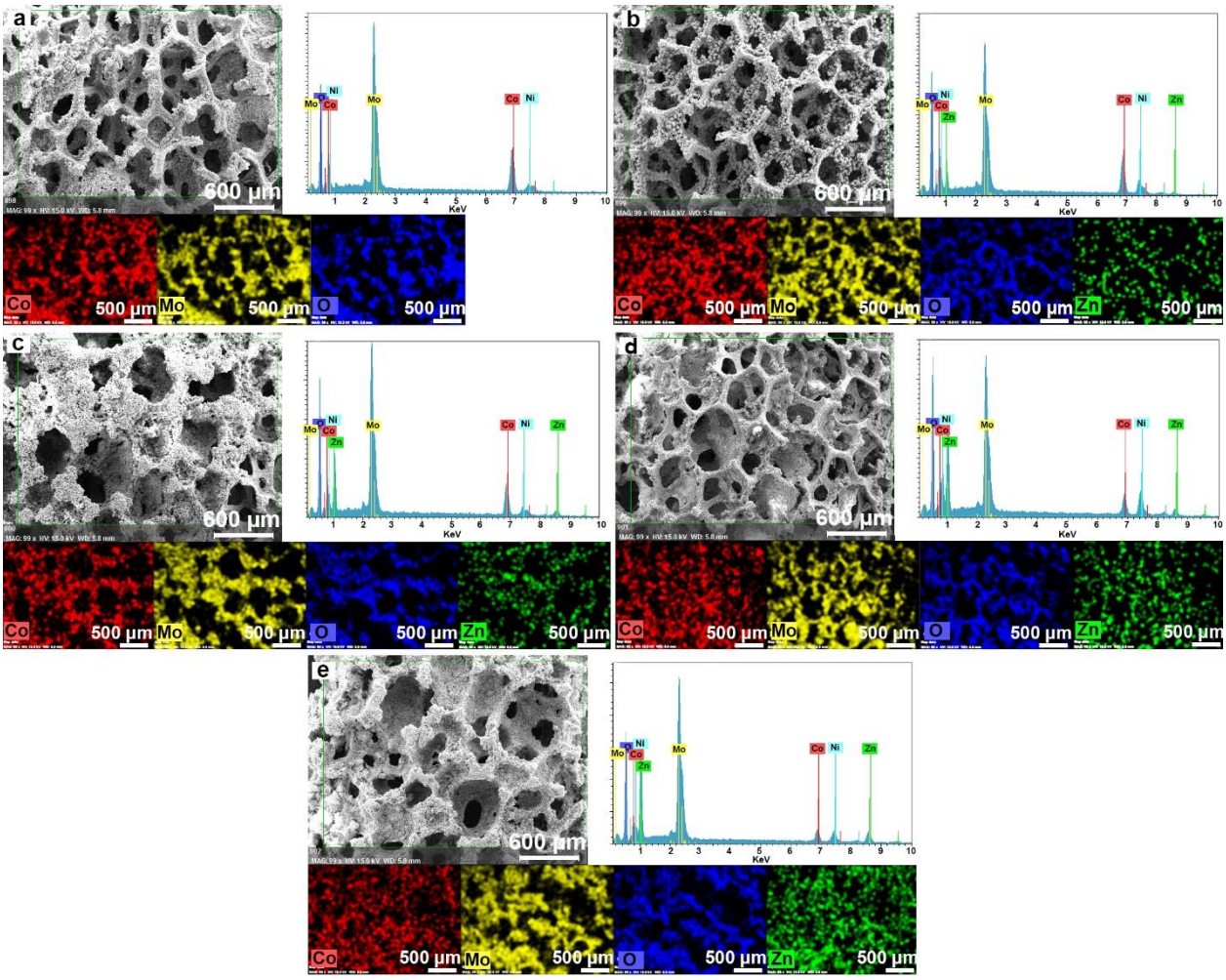


**Figure S3.** SEM/EDS and elemental mappings of (**a**) $CoMoO_4$, (**b**) $Co_{0.9}Zn_{0.1}MoO_4$, (**c**) $Co_{0.7}Zn_{0.3}MoO_4$, (**d**) $Co_{0.5}Zn_{0.5}MoO_4$, and (**e**) $Co_{0.3}Zn_{0.7}MoO_4$ on NF, respectively.

**Table S1.** EDS elemental composition of $Co_{1-x}Zn_xMoO_4$ ($x$ = 0, 0.1, 0.3, 0.5, and 0.7).

| Sample | At.% | | | |
|---|---|---|---|---|
| | Co | Zn | Mo | O |
| $CoMoO_4$ | 20.54 | - | 20.93 | 58.53 |
| $Co_{0.9}Zn_{0.1}MoO_4$ | 21.23 | 2.59 | 24.25 | 51.93 |
| $Co_{0.7}Zn_{0.3}MoO_4$ | 11.30 | 3.81 | 12.34 | 72.55 |
| $Co_{0.5}Zn_{0.5}MoO_4$ | 10.38 | 10.81 | 17.86 | 60.95 |
| $Co_{0.3}Zn_{0.7}MoO_4$ | 5.98 | 12.91 | 20.48 | 60.63 |

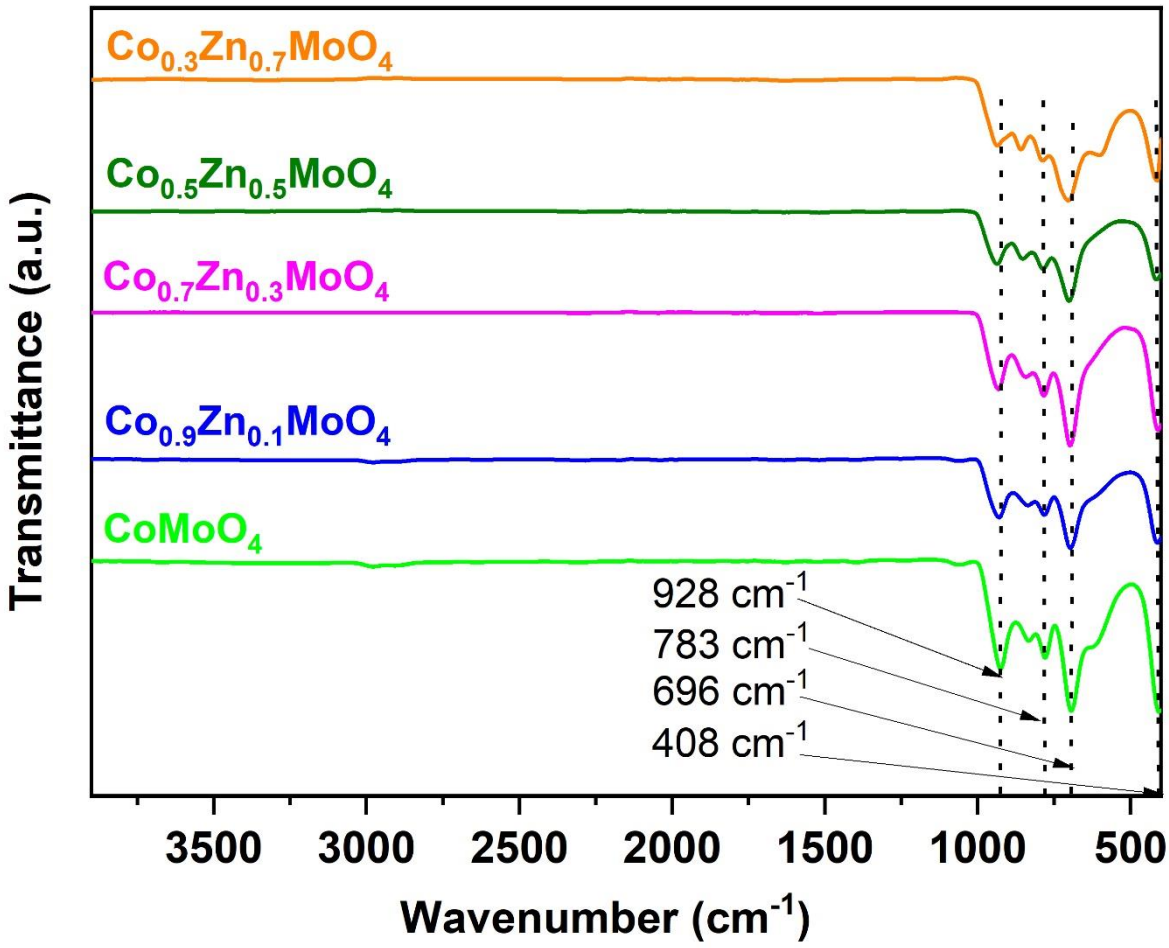


**Figure S4.** FT-IR Spectra of prepared $Co_{1-x}Zn_xMoO_4$.

**Table S2.** The XPS binding energy values for $CoMoO_4$, $Co_{0.5}Zn_{0.5}MoO_4$, and $Co_{0.5}Zn_{0.5}MoO_4$ after HER stability.

| Sample | Co 2p | | Mo 3d | | O 1s | | | Zn 2p |
|---|---|---|---|---|---|---|---|---|
| | $Co^{2+}$ | $Co^{3+}$ | $Mo^{4+}$ | $Mo^{6+}$ | $O_{latt}$ | $O_v$ | $O_{ads}$ | $Zn^{2+}$ |
| $CoMoO_4$ | 780.68 | 784.59 | 231.81 | 233.77 | 530.14 | 533.54 | 537.06 | - |
| $Co_{0.5}Zn_{0.5}MoO_4$ | 782.76 | 787.09 | 232.84 | 234.05 | 530.97 | 532.17 | 534.12 | 1022.84 |
| $Co_{0.5}Zn_{0.5}MoO_4$ after HER satability | 780.00 | 781.83 | 231.64 | 232.19 | 529.60 | 530.74 | 531.85 | 1021.10 |

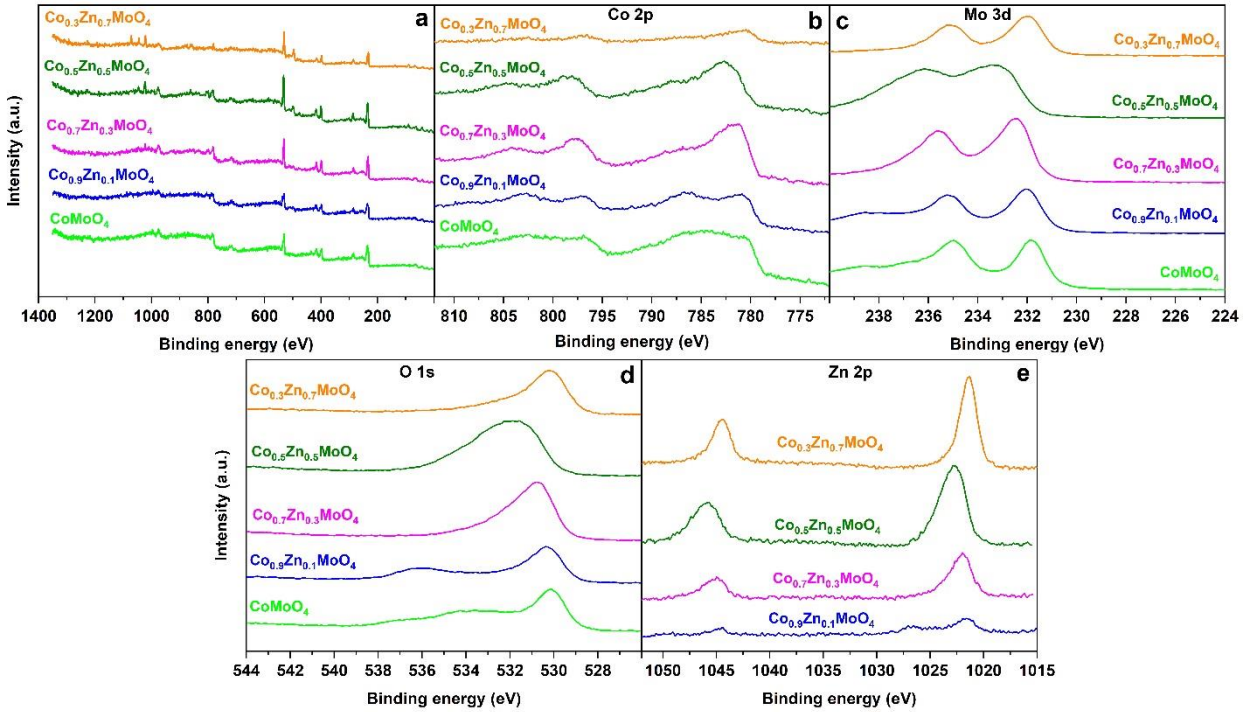


**Figure S5.** (**a**) XPS survey, (**b**) Co 2p, (**c**) Mo 3d, (**d**) O 1s, and (**e**) Zn 2p for $Co_{1-x}Zn_xMoO_4$ (x = 0, 0.1, 0.3, 0.5, and 0.7).

**Table S3.** Comparing the HER performance of present work with previous studies.

| Electrocatalyst | Electrolyte | $\eta_{HER}$ (mV) | Ref. |
|---|---|---|---|
| $ZnO@ZnMoO_4$ | KOH | $\eta^{10}$ = 360 | Reference [49] in the manuscript |
| $ZnWO_4$ | $H_2SO_4$ | $\eta^{10}$ = 372 | Reference [50] in the manuscript |
| $Ppy/ZnWO_4$ | $H_2SO_4$ | $\eta^{10}$ = 543 | Reference [50] in the manuscript |
| $Cu_{0.4}Ni_{0.6}WO_4$ | $H_2SO_4$ | $\eta^{10}$ =463 | Reference [51] in the manuscript |
| $CuWO_4$ | $H_2SO_4$ | $\eta^{10}$ = 574 | Reference [51] in the manuscript |
| β-$NiMoO_4$ | KOH | $\eta^{10}$ =238 | Reference [52] in the manuscript |
| $NiMoO_4$ | KOH | $\eta^{10}$ =339 | Reference [53] in the manuscript |
| $NiWO_4/Ni_3S_2$ | KOH | $\eta^{10}$ =136 | Reference [54] in the manuscript |
| $CoMoO_4$ | KOH | $\eta^{10}$ =353 | Reference [18] in the manuscript |
| $CoMoO_4/Co_9S_8$ | KOH | $\eta^{10}$ =173 | Reference [55] in the manuscript |
| $CoMoO_4$ | KOH | $\eta^{10}$ =275 | Reference [20] in the manuscript |
| $NiCo_2O_4$ | KOH | $\eta^{10}$ = 251 | Reference [20] in the manuscript |
| $CoMoO_4$ | KOH | $\eta^{10}$ =288 | This work |
| $Co_{0.5}Zn_{0.5}MoO_4$ | KOH | $\eta^{10}$ =204 | This work |

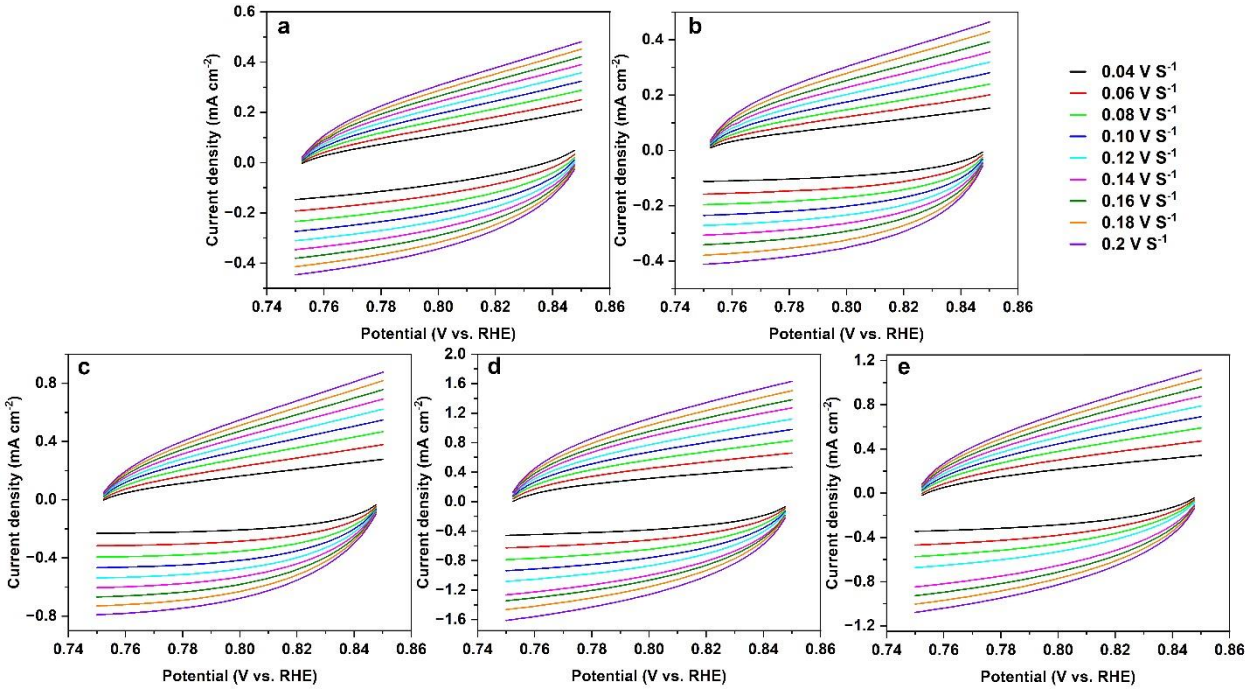


**Figure S6.** Typical cyclic voltammetry (CV) curves obtained at different scan rates (0.04–0.2 V $s^{-1}$) within the potential window 0.75–0.85 V vs RHE for (**a**) $CoMoO_4$, (**b**) $Co_{0.9}Zn_{0.1}MoO_4$, (**c**) $Co_{0.7}Zn_{0.3}MoO_4$, (**d**) $Co_{0.5}Zn_{0.5}MoO_4$, and (**e**) $Co_{0.3}Zn_{0.7}MoO_4$.

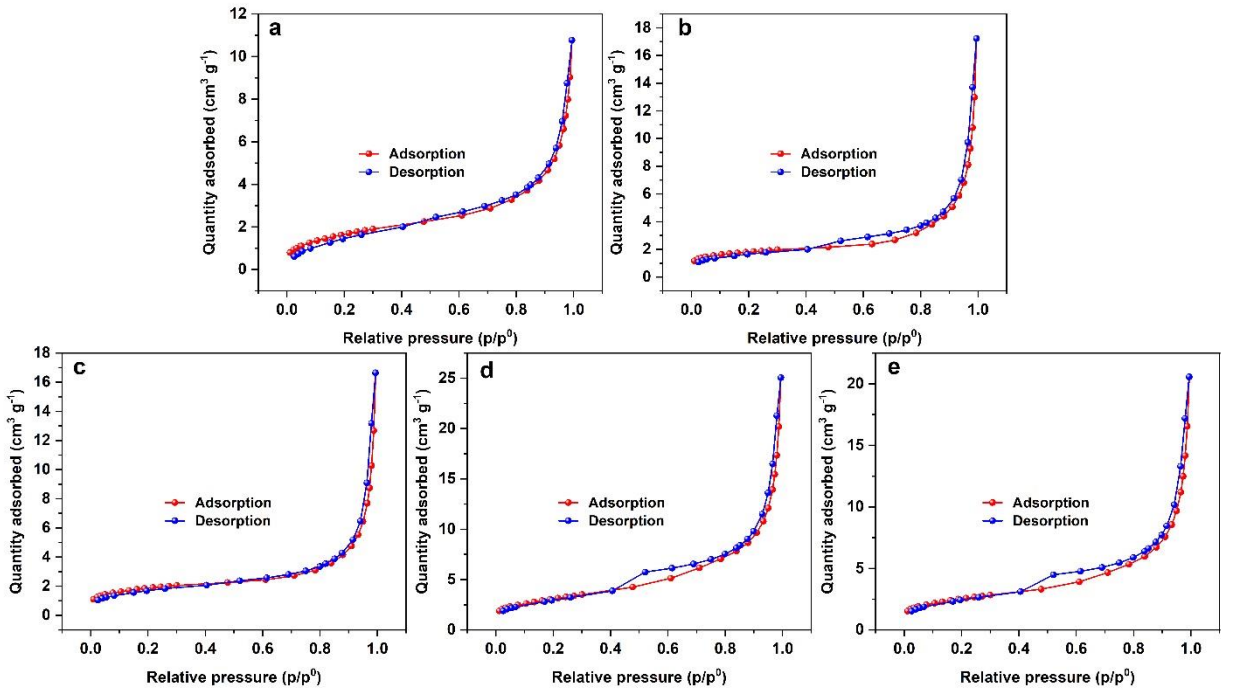


**Figure S7.** $N_2$ adsorption-desorption isotherms of (**a**) $CoMoO_4$, (**b**) $Co_{0.9}Zn_{0.1}MoO_4$, (**c**) $Co_{0.7}Zn_{0.3}MoO_4$, (**d**) $Co_{0.5}Zn_{0.5}MoO_4$, and (**e**) $Co_{0.3}Zn_{0.7}MoO_4$.

**Table S4.** Further details derived from BET analysis of the samples.

| Sample | BET surface area ($m^2/g$) | External surface area ($m^2/g$) | Average pore diameter (nm) |
|---|---|---|---|
| **$CoMoO_4$** | 6.10 | 6.87 | 10.9 |
| **$Co_{0.9}Zn_{0.1}MoO_4$** | 6.05 | 4.06 | 19.9 |
| **$Co_{0.7}Zn_{0.3}MoO_4$** | 6.39 | 5.27 | 21.4 |
| **$Co_{0.5}Zn_{0.5}MoO_4$** | 10.95 | 10.65 | 13.1 |
| **$Co_{0.3}Zn_{0.7}MoO_4$** | 8.84 | 7.97 | 14.1 |

**Table S5.** Fit parameters for the samples derived from EIS experiments.

| Samples | $R_s$ ($\Omega$) | $R_p$ ($\Omega$) | CPE-T ($F^{-1}\ s^{1-n}$) | $R_{ct}$ ($\Omega$) | $C_{dl}$-T ($F^{-1}\ s^{1-n}$) |
|---|---|---|---|---|---|
| $CoMoO_4$ | 2.374 | 140.7 | 0.011576 | 326.5 | 0.0052934 |
| $Co_{0.9}Zn_{0.1}MoO_4$ | 2.165 | 96.2 | 0.013613 | 306.4 | 0.007181 |
| $Co_{0.7}Zn_{0.3}MoO_4$ | 2.134 | 73.28 | 0.025863 | 285.6 | 0.008915 |
| $Co_{0.5}Zn_{0.5}MoO_4$ | 2.74 | 5.982 | 0.0027973 | 133 | 0.0032147 |
| $Co_{0.3}Zn_{0.7}MoO_4$ | 2.021 | 33.28 | 0.014376 | 260.6 | 0.011665 |

**Table S6.** The defined molar ratios of initial materials for the fabrication of $Co_{1-x}Zn_xMoO_4$ ($x$= 0, 0.1, 0.3, 0.5, 0.7).

| Sample | $Na_2MoO_4.2H_2O$ | $Co(NO_3)_2.6H_2O$ | $Zn(NO_3)_2.6H_2O$ |
|---|---|---|---|
| **$CoMoO_4$** | 2 mmol | 2 mmol | - |
| **$Co_{0.9}Zn_{0.1}MoO_4$** | 2 mmol | 1.8 mmol | 0.2mmol |
| **$Co_{0.7}Zn_{0.3}MoO_4$** | 2 mmol | 1.4 mmol | 0.6 mmol |
| **$Co_{0.5}Zn_{0.5}MoO_4$** | 2 mmol | 1 mmol | 1 mmol |
| **$Co_{0.3}Zn_{0.7}MoO_4$** | 2 mmol | 0.6 mmol | 1.4 mmol |