# **Supplementary Information**

# Transition metal tailored $\delta$ -MnO<sub>2</sub> with optimized charge compensation for enhanced hydrogen evolution

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#### 1. Materials

All chemicals used in the experiment were analytical grade with no further purification. Potassium permanganate (KMnO<sub>4</sub>,  $\geq$ 98%) was purchased from Tianjin Damao Chemical Reagent Co., Ltd. Manganese sulfate monohydrate (MnSO<sub>4</sub>·H<sub>2</sub>O,  $\geq$ 99%), Nickel sulfate hexahydrate (NiSO<sub>4</sub>·6H<sub>2</sub>O, AR), Copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O,  $\geq$ 99%), Zinc sulfate heptahydrate (ZnSO<sub>4</sub>·7H<sub>2</sub>O, AR), Potassium hydroxide (KOH,  $\geq$ 85%) was purchased from Aladdin Reagent (Shanghai) Co., Ltd. Nickel foam (NF) was purchased from Taiyuan Lizhiyuan Technology Co., Ltd. Acetone and HCl were provided by Tianjin Kemeng Chemical Industry & Trade Co.

## 2. Characterization methods

The morphology and microstructure of the samples were marked using scanning electron microscopy (SEM, Zeiss sigma 300) and transmission electron microscopy (TEM, FEI Tecnai F20, 200 kV). X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi) was used to determine the electronic states of the samples, and all spectra were standardized with the C 1s peak of the non-constant carbon at 284.8 eV. Raman spectra (Thermo Fisher Scientific,

532 nm YAG laser) were recorded. X-ray diffraction (XRD-6100, Shimadzu) was used to study the phase and crystal structure of the materials with a Cu Ka ( $\lambda = 1.5405$  Å) radiation source (40 kV and 30 mA) at a scan rate of 10° min-1, working in the angular range of 5-80°. The Xray absorption fine structure (XAFS) spectra of Ni K-edge (8333 eV), Cu K-edge (8979 eV), and Zn K-edge (9659 eV) were collected in transmission mode on Table XAFS-500 (Specreation Instruments Co., Ltd.) at 25 kV and 20 mA. The acquired EXAFS data was extracted and processed according to the standard procedures using the ATENNA software. The EXAFS data were fitted using the ARTEMIS package[1].

#### 3. Electrochemical measurements

All measurement methods were performed using a CHI760E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China), including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). CV tests were generally performed at scan rates of 10, 25, 50, 80, 100, and 120 mV s<sup>-1</sup>. EIS spectra were measured in the frequency range of 0.01-100 kHz with an alternate current amplitude of 5 mV at open circuit voltage. In the catalytic testing system, a graphite rod and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and the reference electrode. The working electrode took  $0.5 \times 0.5$  cm<sup>2</sup> of X-MO/NF. The loadings of active substances were 2 mg cm<sup>-2</sup> for the X-MO/NF (X = Ni, Cu, Zn). In addition, 1 M KOH served as an electrolyte for catalytic research. The potential herein was referenced to the reversible hydrogen electrode (RHE) with Eq. (1)[2]:

$$E_{(RHE)} = E_{(Ag/AgCl)} + 0.197 + 0.059 \times pH$$
(1)

LSV curves were used to measure the electrocatalytic activity of the catalyst at a scan rate of 5 mV s<sup>-1</sup>, with all polarization curves 90% iR-compensated, where i is the current and R is the uncompensated electrolyte ohmic resistance measured by electrochemical impedance spectroscopy (EIS). The current density was calculated from the actual area of the prepared catalyst immersed in the electrolyte. According to the Tafel equation:  $\eta = a + b\log j$ , using the logarithm of the current density as the X-axis and the overpotential as the Y-axis, a Tafel plot is obtained, where *a* is the Tafel constant, *b* is the Tafel slope, *j* is the cathodic current density, and  $\eta$  is the overpotential.



Fig. S1. SEM images of samples: (a)  $\delta$ -MO/NF. (b) Ni-MO/NF. (c) Cu-MO/NF and (d) Zn-MO/NF.



Fig. S2. Ni-MO/NF: (a)TEM image, (b-c) HRTEM images, (d) Elemental mapping images of

Mn, O, and Ni.



**Fig. S3.** Cu-MO/NF: (a)TEM image, (b-c) HRTEM images, (d) Elemental mapping images of Mn, O, and Cu.



Fig. S4. (a) XRD patterns of  $\delta$ -MO/NF and X-MO/NF (X = Ni, Cu, Zn). (b) XRD partial magnification.



Fig. S5. XRD pattern of  $MnO_2$  powder nanostructures obtained by the hydrothermal reaction of KMnO<sub>4</sub> and MnSO<sub>4</sub> solution at 160 °C for 16 h.



Fig. S6. Raman spectra of the as-synthesized  $\delta$ -MO/NF (black), Ni-MO/NF (red), Cu-MO/NF (green) and Zn-MO/NF (blue).



Fig. S7. XPS spectrums of Ni-MO/NF: (a) Mn 2p. (b) Mn 3s. (c) O 1s. (d) Ni 2p.



Fig. S8. XPS spectrums of Cu-MO/NF: (a) Mn 2p. (b) Mn 3s. (c) O 1s. (d) Cu 2p.



**Fig. S9.** (a) Fitted EXAFS curves of Zn-MO/NF. (b) Zn K-edge EXAFS (points) and the curvefit (line) for Zn-MO/NF in k<sup>2</sup>-weighted *k*-space.



Fig. S10. (a) XANES spectrasof Ni K-edge and (b)  $k^2$ -weighted FT-EXAES spectra of Ni foils  $k(\mathbf{A}^{-1})$ NiO and Ni-MO/NF. (c) Fitted EXAES curves of Ni-MO/NF. (d) Ni K-edge EXAES (points) and the curvefit (line) for Ni-MO/NF, shown in  $k^2$ -weighted k-space. Wavelet transforms for  $k^2$ -weighted Ni K-edge EXAES of (e) NiO and (f) Ni-MO/NF.



Fig. S11. (a) XANES spectra of Cu K-edge and (b): FT-EXAES spectra of Cu foil, OuO, and 15 Cu-MO/NF. (c) Fitted EXAES curves of Cu-MO/NF. (d) Cu K-edge EXAES (points) and the curvefit (line) for Cu-MO/NF, shown in k<sup>2</sup>-weighted k-space. Wavelet transforms for k<sup>2</sup>-weighted Cu K-edge EXAES of (e) CuO and (f) Cu-MO/NF.



Fig. S12. CV curves of (a) δ-MO/NF, (b) Ni-MO/NF, (c) Cu-MO/NF and (d) Zn-MO/NF.



**Fig. S13.** Distribution of Mn 3d, O 2p, Zn 2p, and Zn 3d orbitals in the PDOS diagram of Zn-MO.

Sample	Mn at. %	O at. %	Ni/Cu/Zn at. %
δ-MO/NF	38.5	61.5	
Ni-MO/NF	29.3	67.2	3.5
Cu-MO/NF	34.0	63.9	2.1
Zn-MO/NF	32.0	67.1	0.9

**Tab. S1.** The atom percentage of all elements in the X-MO/NF (X=Ni, Cu, Zn) samples was measured by EDS.

Tab. S2. EXAFS fitting results of sample data.

Sample	Shell	CN	R (Å)	σ <sup>2</sup> (Å <sup>2</sup> )	$\Delta E_0 (eV)$	R factor
Ni foil	Ni-Ni	12*	2.49	0.0063	4.2	0.003
NiO	Ni-O	4.5	2.06	0.0030	( )	0.016
	Ni-Ni	11.0	2.95	0.0063	-0.3	
Ni-MO/NF	Ni-O	5.2	2.05	0.0038	0.7	0.007
	Ni-Ni	11.1	2.91	0.0150	-0.7	
Cu foil	Cu-Cu	12*	2.54	0.0088	4.4	0.002
CuO	Cu-O	4.1	1.95	0.0031	0.9	0.003
	Cu-Cu	3.8	2.91	0.0076	0.8	
Cu-	<b>C O</b>	2.0	1.05	0.0022	1 1	0.002
MO/NF	Cu-O	3.8	1.95	0.0022	1.1	0.003
Zn foil	Zn-Zn	6*	2.64	0.0103	0.4	0.008
ZnO	Zn-O	4.5	1.98	0.0043	5.3	0.016
Zn-MO/NF	Zn-O	3.6	1.99	0.0030	0.6	0.003

CN, coordination number; R, Distance between absorbing and backscattering atoms;  $\sigma^2$ , Debye-Waller factor, for considering the degree of thermal and structural disorder;  $\Delta E_0$ , Indicates a good or bad fit. S0<sup>2</sup> was fixed to 0.87 for Ni foil, 0.85 for Cu foil, and 0.82 for Zn foil, and CN was fixed to known crystallographic values based on EXAFS fitting experiments. Reasonable ranges for the EXAFS fit parameters are  $0.800 < S0^2 < 1.000$ ; CN > 0;  $\sigma^2 > 0$  Å<sup>2</sup>;

 $|\Delta E_0| < 10 \text{ eV}$ ; R factor < 0.02.

Tab. S3. Impedance fitting results.

Sample	$R_s(\Omega)$	$R_{ct}(\Omega)$
δ-MO/NF	2.85	19.41
Ni-MO/NF	2.71	13.36
Cu-MO/NF	2.49	12.41
Zn-MO/NF	2.42	10.96

Tab. S4. Literature data on HER activity of MnO<sub>2</sub>-based electrocatalysts.

Catalysts	Electrolyte	Tafel slope	η(mV)@j	Ref
		(mV dec <sup>-1</sup> )	(mA cm <sup>-2</sup> )	itei.
NS-MnO <sub>2</sub>	1 M KOH	62	167@10	[2]
Co-doped MnO <sub>2</sub> NSs	1 M KOH	122	218@10	[3]
Al-MnO <sub>2</sub>	1 M KOH	148	170@10	[4]
$rGO/MnO_2/MoS_2$	1 M KOH	75.13	205@10	[5]
$MnO_2$	1 M KOH	135	269@10	[6]
Ni-Fe-K <sub>0.23</sub> MnO <sub>2</sub>		103.9	116@10	[7]
CNFs-300	I M KOH			[/]
Zn-MO/NF	1 M KOH	109.8	115@10	This work

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