# **Supplementary Material**

# High ratio of Ni<sup>3+</sup> and Co<sup>3+</sup> facilitated by Mn-adding for enhanced oxygen evolution reaction and ethanol oxidation reaction

Yi-Nuo Zhen, Ruo-Yao Fan, Xin-Yin Jiang, Ning Yu, Yong-Ming Chai \*, Bin Dong\*

State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering,

China University of Petroleum (East China), Qingdao 266580, PR China

\* Corresponding author. Email: ymchai@upc.edu.cn(Y.M. Chai); dongbin@upc.edu.cn (B. Dong)

Tel: +86-532-86981156, Fax: +86-532-86981156

### **Experimental section**

Nickel foams (thickness: 1.5 mm) were purchased from Kunshan Lvchuang Electronic Technology Co. Ltd., China. Anhydrous ethanol ( $\geq$ 99.7 wt.%) was sourced from Shanghai Titan Scientific Co. Ltd., China. Cobalt (II) nitrate [Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O] ( $\geq$ 98.5 wt.%), nickel nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O] ( $\geq$ 98.5 wt.%), manganese (II) chloride [MnCl<sub>2</sub>•4H<sub>2</sub>O] ( $\geq$ 98.5 wt.%), potassium hydroxide (KOH) ( $\geq$ 85.0 wt.%), and N,N'-Dimethylformamide (DMF) ( $\geq$ 99.5 wt.%) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Terephthalic acid ( $\geq$ 99.0 wt.%) was procured from Shanghai Macklin Biochemical Co. Ltd., China. All experimental chemicals and materials used possess analytical purity and do not require further post-treatment before use.

## Synthesis of comparison samples in supplementary material

Co<sub>1</sub>Ni<sub>1</sub>Mn<sub>1</sub>BDC@NF-A: Adjusting Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O to 1 mmol and PTA to 1.5 mmol; Co<sub>1</sub>Ni<sub>1</sub>Mn<sub>2</sub>BDC@NF-A: Adjusting Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O to 1 mmol, MnCl<sub>2</sub>•4H<sub>2</sub>O to 2 mmol and PTA to 1.5 mmol; Co<sub>1</sub>Ni<sub>0.25</sub>Mn<sub>1</sub>BDC@NF-A: Adjusting Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O to 0.25 mmol and PTA to 1.125 mmol; Co<sub>1</sub>Ni<sub>0.75</sub>Mn<sub>1</sub>BDC@NF-A: Adjusting Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O to 0.75 mmol and PTA to 1.375 mmol.

Co<sub>1</sub>Ni<sub>1</sub>BDC@NF-A: 1 mmol Co + 1 mmol Ni +1 mmol PTA; Co<sub>1.5</sub>Mn<sub>0.5</sub>BDC@NF-A: 1.5 mmol Co + 0.5 mmol Mn + 1 mmol PTA; Co<sub>0.5</sub>Mn<sub>1.5</sub>BDC@NF-A: 0.5 mmol Co + 1.5 mmol Mn +1 mmol PTA; Co<sub>2</sub>BDC@NF-A: 2 mmol Co +1 mmol PTA; Mn<sub>2</sub>BDC@NF-A: 2 mmol Mn +1 mmol PTA; Ni<sub>1.5</sub>Mn<sub>0.5</sub>BDC@NF-A: 1.5 mmol Ni + 0.5 mmol Mn +1 mmol PTA; Ni<sub>0.5</sub>Mn<sub>1.5</sub>BDC@NF-A: 0.5 mmol Ni + 1.5 mmol Mn +1 mmol PTA; Ni<sub>2</sub>BDC@NF-A: 2 mmol Ni +1 mmol PTA.

#### **Materials characterization**

The scanning electron microscope (SEM) (Quanta FEG 250 and ZEISS sigma500) and transmission electron microscope (TEM) (JEM-2100F) were utilized to collect morphological and structural information for all samples. High-resolution transmission electron microscopic (HRTEM) images were taken on JEM-2100F. The crystal phases of the obtained catalysts were studied via X-ray diffraction (XRD) using a Germany-Bruck-D8 Advance device with Cu K $\alpha$  radiation. Fourier transform infrared (FT-IR) spectras were acquired using a Thermo Fisher IS20 Nicolet IS20 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Fisher Scientific II spectrometer equipped with an Al K $\alpha$  source. The inductively coupled plasma optical emission spectrometry (ICP-OES) (optima 8000) was utilized to characterize the proportion of metal element.

#### **Electrochemical measurements**

In a standard three-electrode cell configuration using Gamry Reference 1000 electrochemical equipment, the basic OER performance of all catalysts was evaluated in 1M KOH, and the EOR performance of all catalysts was evaluated in 1M ethanol in 1M KOH at room temperature. Throughout all testing processes, the saturated calomel electrode (SCE) and Pt wire were employed as reference and counter electrodes, respectively. Cyclic Voltammetry (CV) data were obtained under the same conditions with a scan rate of 10 mV s<sup>-1</sup> and 30 mV s<sup>-1</sup>. Linear sweep voltammetry (LSV) measurements were also conducted under identical conditions with scan rates of 2 mV s<sup>-1</sup> and 10 mV s<sup>-1</sup>. Using the Nernst equation  $E_{RHE}=E_{SCE}+0.059pH+0.243$ , all potentials associated with SCE were converted to those relative to a standard reversible hydrogen electrode (RHE). During activation by CV, the scanning rate was set at 30 mV s<sup>-1</sup>. The EIS Nyquist plot of the synthesized sample was measured over a frequency range of 100 kHz to 0.1 Hz. In the equivalent circuit, Rs represents the solution resistance, CPE represents the constant phase element, and Rct represents the charge transfer resistance. The durability of activated catalysts in 1M KOH and 1M ethanol in 1M KOH was assessed using chronopotentiometric measurements. To ensure objectivity, measurements of all reference samples were conducted under the same conditions and using the same measurement procedure at room temperature.



Fig. S1 Schematic diagram of preparation route for Co1Ni0.5Mn1BDC@NF-A.



Fig. S2 CV activation curve at  $30 \text{ mV s}^{-1}$ .



Fig. S3 XRD spectrum of Co1Ni0.5Mn1BDC@NF-A.



Fig. S4 FT-IR spectrum of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$ ,  $Co_1Ni_{0.5}BDC@NF-A$ ,  $Ni_1Mn_1BDC@NF-A$  and  $Co_1Mn_1BDC@NF-A$ .



Fig. S5 SEM of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$ .



Fig. S6 SEM of (a)  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  (b)  $Co_1Ni_{0.5}Mn_1BDC@NF$ .



Fig. S7 SEM of Co<sub>1</sub>Ni<sub>0.5</sub>BDC@NF-A.



Fig. S8 EDS results of  $Co_1Ni_{0.5}Mn_1BDC@NF$  and corresponding element contents.



Fig. S9 EDS results of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  and corresponding element contents.



**Fig. S10** Annular dark-field TEM image of Co<sub>1</sub>Ni<sub>0.5</sub>Mn<sub>1</sub>BDC@NF-A and the corresponding element mappings of Ni, Co, Mn, C and O.

		Co	Elements	Wt%	At%
	6-		СК	13.51	34.85
			ОК	13.69	26.52
		Ni	Mn K	7.78	4.39
		Ϋ́	Co K	39.84	20.95
	4-		Ni K	25.18	13.29
¢			10	1 1 1	1 · · · 1 14 10

Fig. S11 EDS results of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  and corresponding element contents.



Fig. S12 The XPS spectrum of Co1Ni0.5Mn1BDC@NF-A and Co1Ni0.5BDC@NF-A.



Fig. S13 The Comparison of fine XPS spectra of the Co1Ni0.5Mn1BDC@NF-A and Co1Ni0.5Mn1BDC@NF of (a) Co 2p, (b) Ni 2p.



Fig. S14 The percentage of near-surface elements in  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  and  $Co_1Ni_{0.5}BDC@NF-A$  obtained by XPS analysis.



Fig. S15 High-resolution spectrum of Mn 2p of Co<sub>1</sub>Ni<sub>0.5</sub>Mn<sub>1</sub>BDC@NF.



**Fig. S16** Electrocatalytic OER in 1 M KOH. (a and d) The cyclic voltammetry curves of different catalysts. (b and e) The corresponding Tafel plots from (a and d). (c and f) EIS Nyquist plots.



**Fig. S17** Electrocatalytic OER in 1 M KOH. (a and d) The cyclic voltammetry curves of different catalysts. (b and e) The corresponding Tafel plots from (a and d). (c and f) EIS Nyquist plots.



Fig. S18 The cyclic voltammetry curves of different catalysts.



**Fig. S19** XRD spectrum of Co<sub>1</sub>Ni<sub>0.5</sub>Mn<sub>1</sub>BDC@NF-A after long-term stability testing for OER.



**Fig. S20** SEM images of Co<sub>1</sub>Ni<sub>0.5</sub>Mn<sub>1</sub>BDC@NF-A samples (a, c) before long-term stability measurement and (b, d) after long-term stability measurements for OER.



Fig. S21 (a) Co 2p and (b) Ni 2p comparative spectra of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  after long-term stability measurements for OER.



Fig. S22 Electrocatalytic EOR in 1 M KOH with 1 M ethanol. (a) The polarization curves of different catalysts at 10 mV s<sup>-1</sup>. (b) The corresponding Tafel plots from (a).
(c) EIS Nyquist plots.



Fig. S23 Electrocatalytic EOR in 1 M KOH with 1 M ethanol. (a) The polarization curves of different catalysts at 10 mV s<sup>-1</sup>. (b) The corresponding Tafel plots from (a).
(c) EIS Nyquist plots.



**Fig. S24** XRD spectrum of Co<sub>1</sub>Ni<sub>0.5</sub>Mn<sub>1</sub>BDC@NF-A after long-term stability testing for EOR.



Fig. S25 SEM images of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  after long-term stability measurements for EOR.



Fig. S26 (a) Co 2p and (b) Ni 2p comparative spectra of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  after long-term stability measurement for EOR.



Fig. S27 The polarization curves of different catalysts in (a, b) OER at 10 mV s<sup>-1</sup>.(c, d) EOR at 10 mV s<sup>-1</sup>.



Fig. S28 The polarization curves of S, Fe-CoP@IF in HER.

Table S1 The content of Co, Ni and Mn in Co $_1Ni_{0.5}Mn_1BDC@NF-A$  measured

Elements	Intensity	Conc. Units/(mg/L)
Со	849101.6	6.355
Ni	1101116.6	6.270
Mn	8692238.1	2.499

Table S2 The percentage of near-surface elements in  $Co_1Ni_{0.5}Mn_1BDC@NF-A$ 

Materials	Со	Ni	Mn	0	С
Co1Ni0.5Mn1BDC@NF-A	3.17%	9.73%	6.05%	38.37%	42.68%
Co1Ni0.5BDC@NF-A	7.31%	10.03%	_	42.58%	40.07%

and Co1Ni0.5BDC@NF-A obtained by XPS analysis.

	-		
Catalysts	Electrolyte	Overpotential (mV)	References
Co1Ni0.5Mn1BDC@NF-A	1 M KOH	298@100 mA cm <sup>-2</sup>	This work
Co-Ni <sub>2</sub> P-N/NF	1 M KOH	329@100 mA cm <sup>-2</sup>	[1]
F-NiP <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> -NF	1 M KOH	370@100 mA cm <sup>-2</sup>	[2]
Co <sub>3</sub> Mo/Mo <sub>2</sub> C@NC	1 M KOH	355@100 mA cm <sup>-2</sup>	[3]
FeCoMo <sub>3</sub> O <sub>8</sub>	1 M KOH	361@100 mA cm <sup>-2</sup>	[4]
BCoPi	1 M KOH	357@100 mA cm <sup>-2</sup>	[5]
NiFe LDH@NiCoP	1 M KOH	350@100 mA cm <sup>-2</sup>	[6]
PEG/TU-NiFeCoMnAl	1 M KOH	317@100 mA cm <sup>-2</sup>	[7]
Co-Ni <sub>3</sub> S <sub>2</sub> /NF	1 M KOH	368@100 mA cm <sup>-2</sup>	[8]
N-CoO@CoP	1 M KOH	332@100 mA cm <sup>-2</sup>	[9]
Co-NiSe-2	1 М КОН	380@100 mA cm <sup>-2</sup>	[10]

Table S3 Comparison of OER performance of  $Co_1Ni_{0.5}Mn_1BDC@NF-A$  with

other reported catalysts.

Materials	$ m R_s/\Omega$	$R_{ct}$ / $\Omega$
Co1Ni0.5Mn1BDC@NF-A	0.78	0.021
Co <sub>1</sub> Mn <sub>1</sub> BDC@NF-A	0.84	0.028
Ni1Mn1BDC@NF-A	0.84	0.17
Co1Ni0.5BDC@NF-A	1.40	0.030

 Table S4 The detailed data of Impedance simulation in OER

Table S5 Com	parison of EOR pe	erformance of C	$Co_1Ni_{0.5}Mn_1BDO$	C@NF-A with

Catalysts	Substrate/concentration	Potential / (V)	References
Co1Ni0.5Mn1BDC@NF-A	Ethanol / 1M	1.30@100 mA cm <sup>-2</sup>	This work
WeCoMoO <sub>4</sub> /CF	Ethanol / 1M	1.40@100 mA cm <sup>-2</sup>	[11]
CuCo <sub>2</sub> S <sub>4</sub> /CC	Ethanol / 1M	1.38@10 mA cm <sup>-2</sup>	[12]
Co-S-P/CC	Ethanol / 1M	1.38@10 mA cm <sup>-2</sup>	[13]
NiO@CeO <sub>2</sub>	Ethanol / 1M	1.37@10 mA cm <sup>-2</sup>	[14]
NiFe-0.10F	Ethanol / 1M	1.39@10 mA cm <sup>-2</sup>	[15]
Co <sub>2</sub> -NiSe/NF	Ethanol / 1M	1.30@10 mA cm <sup>-2</sup>	[16]
CoNi hydroxide	Ethanol / 1M	1.39@10 mA cm <sup>-2</sup>	[17]
ZnSe-MnSe	Ethanol / 1M	1.39@10 mA cm <sup>-2</sup>	[18]

other reported catalysts.

Materials	$R_s/\Omega$	$R_{ct}$ / $\Omega$
Co1Ni0.5Mn1BDC@NF-A	1	0.015
Co <sub>1</sub> Mn <sub>1</sub> BDC@NF-A	1.15	0.020
Ni1Mn1BDC@NF-A	0.95	0.050
Co1Ni0.5BDC@NF-A	2.14	0.033

 Table S6 The detailed data of Impedance simulation in EOR

#### Reference

1. M. Kim, K. Min, D. Ko, H. Seong, S. Shim and S. Baeck, Regulating the electronic structure of Ni<sub>2</sub>P by one-step Co, N dual-doping for boosting electrocatalytic performance toward oxygen evolution reaction and urea oxidation reaction, *J. Colloid Interface Sci.*, 2023, **650**, 1851-1861.

2. K. Li, Y. Tong, D. Feng and P. Chen, Fluorine-anion engineering endows superior bifunctional activity of nickel sulfide/phosphide heterostructure for overall water splitting, *J. Colloid Interface Sci.*, 2022, **625**, 576-584.

3. X. Wang, L. Sun, L. Yang, J. Zhao and Q. Xu, Hybrid Zeolitic Imidazolate Framework-Derived Co<sub>3</sub>Mo/Mo<sub>2</sub>C Heterostructure for Enhanced Oxygen Evolution Reaction, *Adv. Funct. Mater.*, 2024, 2314247.

4. C. Hao, X. Li, H. Huang, L. Ge, Z. Fu, Ya. Lu, Y. Wang, S. Zhang and Z. Cheng, Simultaneous Activation of Different Coordination Sites in Single-Phase FeCoMo<sub>3</sub>O<sub>8</sub> for the Oxygen Evolution Reaction, *ACS Energy Lett.*, 2023, **8**, 4506-4513.

5. B. Pratihar, O. Roy, A. Jana and S. De, Mixed-valent cobalt phosphate/borophene nanohybrids for efficient electrocatalytic oxygen evolution reaction, *J. Colloid Interface Sci.*, 2024, **661**, 279-288.

6. H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin, S. Azimi, S. L. Schweizer, A.
W. Maijenburg and R. B. Wehrspohn, Bifunctional Heterostructure Assembly of NiFe
LDH Nanosheets on NiCoP Nanowires for Highly Efficient and Stable Overall Water
Splitting, *Adv. Funct. Mater.*, 2018, 28, 1706847.

7. S. Guan, B. Xu, J. Wu, J. Han, T. Guan, Y. Yang, K. Li and J. Wang, High-entropy

materials based on deep eutectic solvent for boosting oxygen evolution reaction, *Fuel.*, 2024, 358, 130315.

8. M. Yue, X. He, S. Sun, Y. Sun, M. Hamdy, M. Benaissa, A. Salih, J. Liu and X. Sun, Co-doped Ni<sub>3</sub>S<sub>2</sub> nanosheet array:A high-efficiency electrocatalyst for alkaline seawater oxidation, *Nano. Res.*, 2024, **17(3)**: 1050–105.

9. M. Lu, L. Li, D. Chen, J. Li, N. Klyui and X. Han, MOF-derived nitrogen-doped CoO@CoP arrays as bifunctional electrocatalysts for efficient overall water splitting, *Electrochim. Acta.*, 2020, **330**, 135210.

10. D. Liang, J. Mao, P. Liu, J. Li, J. Yan and W. Song, In-situ doping of Co in nickel selenide nanoflower for robust electrocatalysis towards oxygen evolution, *Int. J. Hydrog. Energy.*, 2020, **45**, 27047-27055.

 D. Feng, X. Ren and Y. Tong, Rational design of tungsten-doped cobalt molybdate nanosheet arrays for highly active ethanol-assisted hydrogen production, *Int. J. Hydrogen Energy.*, 2023, 48, 34244 e34254.

12. S. Sheng, K. Ye, Y. Gao, K. Zhu, J. Yan, G. Wang and D. Cao, Simultaneously boosting hydrogen production and ethanol upgrading using a highly-efficient hollow needle-like copper cobalt sulfide as a bifunctional electrocatalyst, *J. Colloid Interface Sci.*, 2021, **602**, 325-333.

13. S. Sheng, D. Ye, D. Sha, K. Zhu, D. Gao, J. Yan, G. Wang and D. Cao, Rational design of Co-S-P nanosheet arrays as bifunctional electrocatalysts for both ethanol oxidation reaction and hydrogen evolution reaction, *Inorg. Chem. Front.*, 2020, **7**, 4498.

14. X. Zhu, N. Wang, W. Xu, W. Zhou, M. An, D. Zhao, Y. Zhou and L. Li, NiO

coupled with CeO<sub>2</sub> as an efficient electrocatalysts for ethanol oxidation in hybrid water splitting, *Int. J. Hydrogen Energy.*, 2024, **51**, 1451-1455.

15. J. Shi, H. He, Y. Guo, F. Ji, J. Li, Y. Zhang, C. Deng, L. Fan and W. Cai, Enabling high-efficiency ethanol oxidation on NiFe-LDH via deprotonation promotion and absorption inhibition, *J Energy Chem.*, 2023, **85**, 76–82.

16. J. Xu, J. Ruan, Y. Jian, J. Lao, Z. Li, F. Xie, Y. Jin, X. Yu, M. Lee, Z. Wang, Nan Wang and H. Meng, Cobalt-Doping Induced Formation of Five-Coordinated Nickel Selenide for Enhanced Ethanol Assisted Overall Water Splitting, *Small.*, 2023, 2305905.

17. W. Wang, Y. Zhu, Q. Wen, Y. Wang, J. Xia, C. Li, M. Chen, Y. Liu, H. Li, H.A.Wu and T. Zhai, Modulation of Molecular Spatial Distribution and Chemisorption withPerforated Nanosheets for Ethanol Electro-oxidation, *Adv. Mater.*, 2019, **31**, 1900528.

18. L. Hu, P. Zhong, X. Sang, A.Ze, X. Lin, Y. Tong and H.Yang, Integrating dual active sites on heterogeneous bimetallic selenide to facilitate hydrogen evolution and ethanol oxidation, *Appl. Surf. Sci.*, 2023, **637**, 157912.