Supplementary Information (SI) for Dalton Transactions.

Synergistic Effect of Trimetallic Selenides (Co, Fe, Ni)Se_2/NF for Enhanced Electrocatalytic Oxygen Evolution Reaction and Urea Oxidation Reaction

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Chemicals

Nickel foam (NF) was provided by Changsha Lyrun Material Co., Ltd. Formic acid aqueous solution was purchased from the Tianjin Zhiyuan Chemical Reagent plant. Guanidine carbonate purchased from Tianjin Yongsheng Fine Chemical Co. Cobalt perchlorate and ferric perchlorate were purchased from Tokyo Chemical Industry. Selenium powder (Se) was obtained from Tianjin Chemical Reagent Research Institute. Ruthenium dioxide (RuO_2) was obtained from Beijing Inokai Technology Co., Ltd. Commercial platinum/ carbon (Pt/C) was purchased from Shanghai Aladdin Reagent Co., Ltd. Nafion solution was purchased from Alfa Aesar Chemicals Co., Ltd. All chemical reagents were used without further purification.

Material characterization

The phases of samples were recognized by X-ray diffraction (XRD, Bruker D8 advance diffractometer, λ=0.15405), using Cu K_α radiation. The crystal morphology was measured by transmission electronic microscopy (TEM, Hitachi H600 microscope) and field-emission scanning electronic microscopy (FESEM, Hitachi S-4800 microscope). The element contents of compounds were showed by energy-dispersive X-ray spectroscopy (EDS). The elemental states and chemical compositions were further analyzed by utilizing X-ray photoelectron spectroscopy (XPS). Element analysis was performed by inductively coupled plasma-mass spectrometry (ICP-MS) using Agilent 7900.

Electrochemical Measurement

Load calculation method: Weigh 10 pieces each of bare NF (1 cm × 2 cm) and the prepared electrodes (1 cm × 2 cm) separately, calculate the average weight difference, and the loading of the self-supporting electrode = weight difference (mg) / area (1 cm × 2 cm, calculated per single side). The (Co, Fe, Ni)Se_2/NF catalyst loading calculated by this method is 3.1 mg.

A CHI 760E electrochemical workstation were used to proceed electrochemical measurements. A typical three-electrode device with (Co, Fe, Ni)Se_2/NF as the working electrode, Ag/AgCl (saturated KCl) electrode as the reference electrode and graphite rod as the counter electrode was adapted for all electrochemical measurements.The Powder samples were used as working electrodes was attained by the following steps. Catalyst suspension was prepared by mingling 3.1 mg of electrocatalyst with 10 μL of 5 wt % Nafion solution and 490 μL of a mixture including 245 μL of absolute ethanol and 245 μL of deionized water. Then, the generated suspension was equably dispersed by ultrasound for 30 min. Next, 10 μL of completely dispersed electrocatalyst suspension was dropped onto the NF with an area of 1*0.5 cm^2 and waited to dry naturally. All of the recorded electrochemical datas were based on the reversible hydrogen electrode (RHE) by transformation using the Nernst equation.

$$E\ (RHE) = E\ (Ag/AgCl) + (0.1989 + 0.059\ PH)\ V$$

IR losses were not considered in this experiment. Using linear sweep voltammetry (LSV), the polarization curves were obtained in 1 M KOH at a certain sweep speed of 1 mV s^{-1}. Tafel plots were based on the above curves. In 1 M KOH, electrochemical impedance spectroscopy (EIS) was performed using a frequency range of 0.01 to 100000 Hz with an amplitude of 5 mV. Cyclic voltammetry (CV) at different sweep speed (20, 40, 60, 80, 100 mV s-1) was carried out from 0.18- 0.28 V versus RHE in 1 M KOH to obtain cyclic voltammograms. The doublelayer capacitance (Cdl) was estimated by above cyclic votammograms. The long time stability tests of the catalysts were obtained at a high sweep speed of 100 mV s^{-1} for 1000 cycles. The electrochemical surface area (ECSA) was estimated by the Cdl that was calculated by cyclic voltammetry at various scanning rates in the non-Faradic range. The calculation formula is：ECSA=Cdl/Cs*A, where Cs is the specific capacitance. In this work, 40 μF cm^{-2} was adopted as the value of Cs. The density of the ECSA-normalized OER LSV curves was calculated by the equation: ECSA-normalized current density = current density × Cs / Cdl.

For $CoSe_2$-$Ni_{0.85}Se$/NF

ECSA=21.4 mF cm^{-2}/40 μF cm^{-2}*1cm^2=535 cm^2

For (Co, Fe, Ni)Se_2/NF-2:1

ECSA=33.27 mF cm^{-2}/40 μF cm^{-2}*1cm^2=831.75 cm^2

For (Co, Fe, Ni)Se_2/NF-3:1

ECSA=42.03 mF cm^{-2}/40 μF cm^{-2}*1cm^2=1050.75 cm^2

For (Co, Fe, Ni)Se_2/NF-4:1

ECSA=23.08 mF cm^{-2}/40 μF cm^{-2}*1cm^2=577 cm^2

For (Fe, Ni)Se_2/NF

ECSA=24.38 mF cm^{-2}/40 μF cm^{-2}*1cm^2=609.5 cm^2

For RuO_2/NF

ECSA=29.4 mF cm^{-2}/40 μF cm^{-2}*1cm^2=735 cm^2

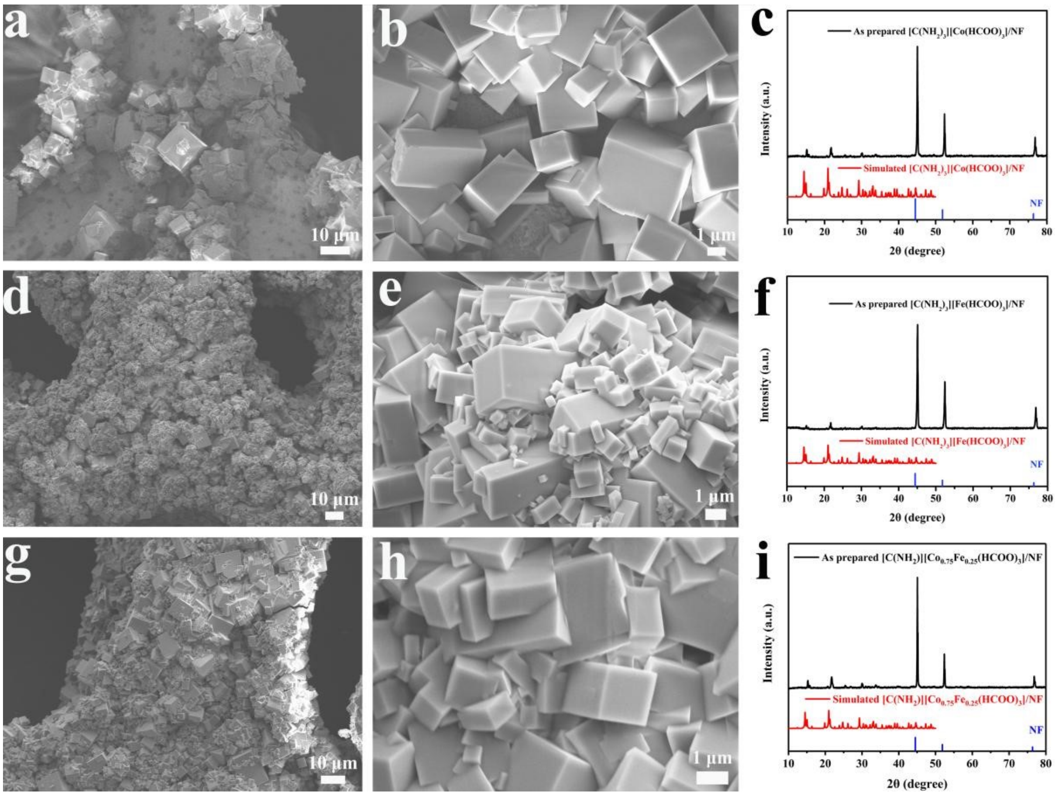

Figure. S1. SEM images (a, b, d, e, g, h) and X-ray powder diffraction patterns (c, f, i) of Co-MOFs/NF (a-c), Fe-MOFs/NF (d-f), Co-Fe(3:1)-MOFs/NF (g-i)

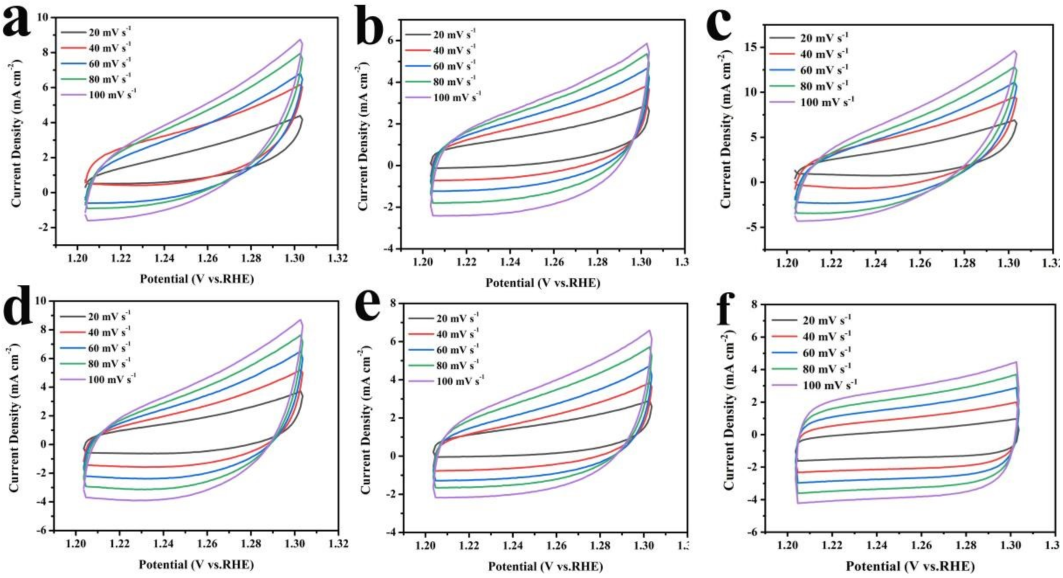

Figure. S2. CV curves of $CoSe_2$-$Ni_{0.85}Se$/NF (a), (Co, Fe, Ni)Se_2/NF-2:1 (b), (Co, Fe, Ni)Se_2/NF-3:1 (c), (Co, Fe, Ni)Se_2/NF-4:1 (d), (Fe, Ni)Se_2/NF (e) , RuO_2/NF (f) with increasing scanning rate (mV s^{-1})

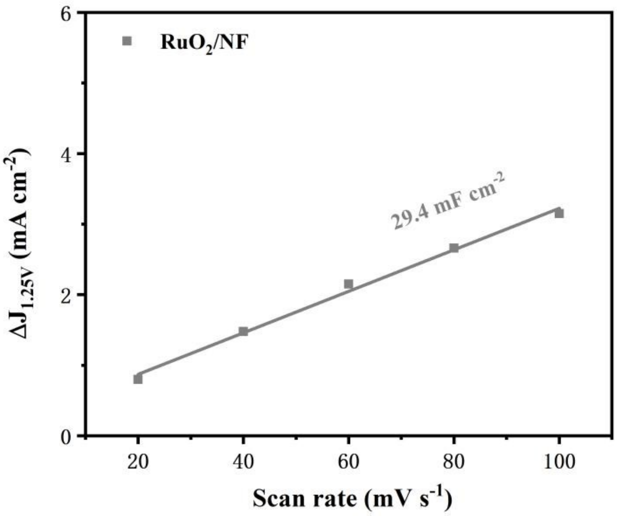

Figure. S3. The linear slope diagram of RuO_2 in 1 M KOH

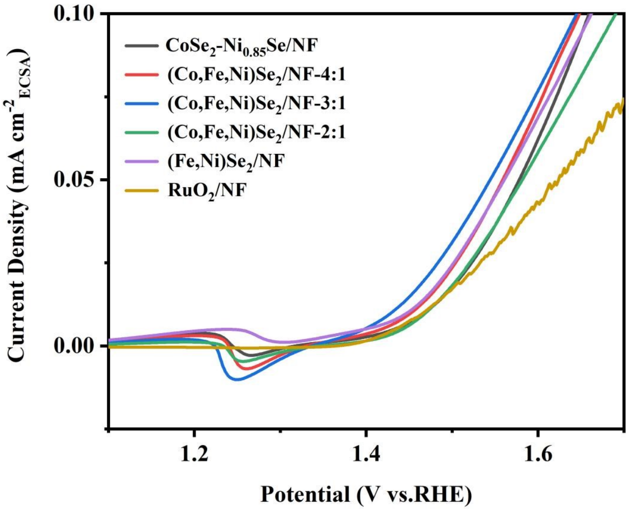

Figure S4. LSV curves of the catalysts normalized by the corresponding ECSA values.

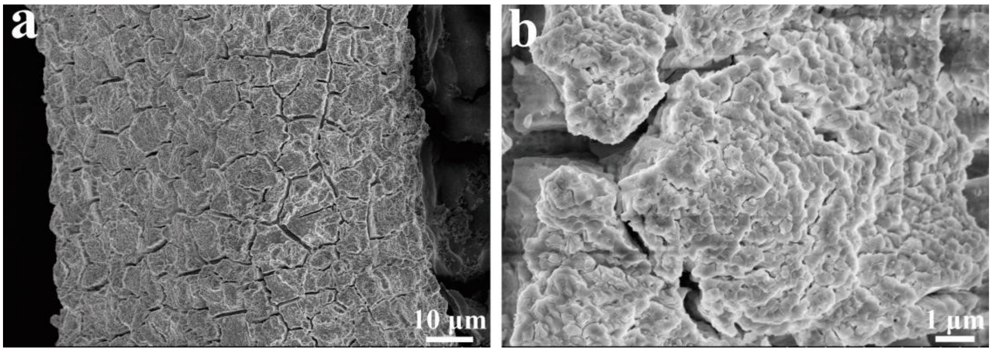

Figure. S5. SEM image of (Co, Fe, Ni)Se_2/NF-3:1 after i-t test in 1 M KOH

Table S1. Actual mass ratio of elements in catalysts acquired by ICP-MS.

Catalyst	**Ni /wt.%**	**Co /wt.%**	**Fe /wt.%**
(Co, Fe, Ni)Se_2/NF-3:1	0.78	0.16	0.06

Table S2. Comparison of OER and UOR activities of (Co, Fe, Ni)Se$_2$/NF-3:1 with recently reported TMSes electrocatalysts

Electrocatalyst	J (mA cm^{-2})	Urea concentration (M)	Overpotential (mV)	Reference
			UOR	
(Co, Fe, Ni)Se$_2$/NF-3:1	10	0.33	1.33	This work
Ni(OH)$_2$	10	0.33	1.42	[1]
NF/NiMoO$_4$	10	0.5	1.37	[2]
Fe$_{11.1\%}$-Ni$_3$S$_2$/Ni	10	0.33	1.35	[3]
Ni$_2$P/CFC	10	0.33	1.34	[4]
Ni$_3$N/CC	10	0.33	1.35	[5]
Ni(OH)$_2$-grephene	10	0.33	1.43	[6]
NiCo$_2$S$_4$/CC	10	0.33	1.35	[7]
Ni$_3$Se$_4$	10	0.5	1.38	[8]
MoS$_4$-LDH/NF	10	0.33	1.34	[9]
Ni$_2$P/NF	10	0.5	1.37	[10]
NiMoS/Ti	10	0.5	1.34	[11]

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