Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Hierarchically Fractal Co with Highly Exposed Active Facets and Directed Electron-Transfer Effect

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1. Materials and methods

1.1. Reagents and materials

All chemicals were analytical grade and procured from Sinopharm Chemical Reagent Co., Ltd. without any treatment. Deionized (DI) water (> 18 MΩ) was purified by a Wuhan Pinguan instrument water purification system.

1.2. Preparation of fractal Co and sphere Co

The fractal Co and sphere Co were synthesized according to previous literature, but slightly modified.[1, 2]

Typically, 2 mL $CoCl_2 \cdot 6H_2O$ (0.84 M) was dispersed into 6.5 mL DI, then 0.5 mL NaOH (20 M) and 1.5 mL $N_2H_4 \cdot H_2O$ (85 wt. %) were added in sequence. After constantly stirring for 30 min, the solution was put in an autoclave at 200 °C for 1.5 h. The precipitate was washed with deionized water for several times and collected by suction filtration. Finally, the sample was dried by freeze-drying equipment for 12 h, and then fractal Co was obtained.

Sphere Co was synthesized by the same method except for adding 0.457 g $NaH_2PO_2 \cdot H_2O$ and 1 mL NaOH (25 M) into 10 mL $CoCl_2 \cdot 6H_2O$ (0.1 M) in sequence.

1.3. Preparation of CoMn, CoFe, CoNi, CoCu, CoMo, CoMnFe, CoMnCu, CoFeNi, CoNiCu and CoMnFeNiCu.

To synthesize CoMn, 1 mL $MnCl_2 \cdot 4H_2O$ (0.1 M), 0.5 mL NaOH (25 M) and 1.5 mL $N_2H_4 \cdot H_2O$ (85 wt. %) were added into 9 mL $CoCl_2 \cdot 6H_2O$ (0.1 M). After constantly stirring for 30 min, the solution was put in an autoclave at 200 °C for 1.5 h. The precipitate was washed with deionized water for several times and collected by suction filtration. Finally, the sample was dried by freeze-drying equipment for 12 h, and then CoMn was obtained.

CoFe, CoNi, CoCu, CoMnFe, CoMnCu, CoFeNi, CoNiCu and CoMnFeNiCu were synthesized by the same method using corresponding metal salts.

CoMo was synthesized by the same method using $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and further reduction.

1.4. Characterization

X-ray diffraction (XRD) patterns were recorded by D8 Advance X-ray diffractometer (Bruker) equipped with Cu Kα radiation. Scanning electron microscopy (SEM) images were collected using a field-emission instrument of the HITACHI S-4800 electron microscope. Transmission electron microscopy (TEM) images were collected using a FEI Talos microscope.

1.5. Density Functional Theory (DFT) calculations

DFT calculation was conducted using the Cambridge Sequential Total Energy Package (CASTEP) code in the Materials Studios package[3]. The electron exchange correlation potential is calculated using the generalized gradient approximation PBE function, the kinetic energy cutoff value of the plane wave basis set is set at 400 eV, and the van der Waals interaction is treated by the density functional theory dispersion correction method[4].

1.6. Electrochemical measurements

Electrochemical experiments were performed using an electrochemical station (Autolab PGSTAT302N) with a three-electrode system at room temperature in 1.0 M KOH electrolyte. A glassy carbon (GC) electrode, standard Hg/HgO electrode, and graphite rod were used as the working, reference, and counter electrode, respectively. To prepare the ink, 10 mg of catalyst and 30 µL of 5 wt % Nafion were dispersed in 970 µL of isopropanol and ultrasonicated for 30 min. Then, 5 µL of the ink (containing 50 µg catalyst) was added dropwise onto the GC electrode (5 mm diameter, 0.196 cm^2) and dried at ambient conditions.

The linear sweep voltammetry (LSV) curves were measured at a scan rate of 5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) data were collected at −0.2 V vs reversible hydrogen electrode (RHE) from 100 kHz to 0.1 Hz with an AC amplitude of 10 mV. The accelerated degradation tests (ADTs) were measured by performing cyclic potential sweeps between 0.07 and −0.47 V vs RHE with 100 mV s^{-1} sweep rate for 2000 cycles. The chronopotentiometric measurements were conducted for 10 and 6 h at 10 mA cm^{-2} current density.

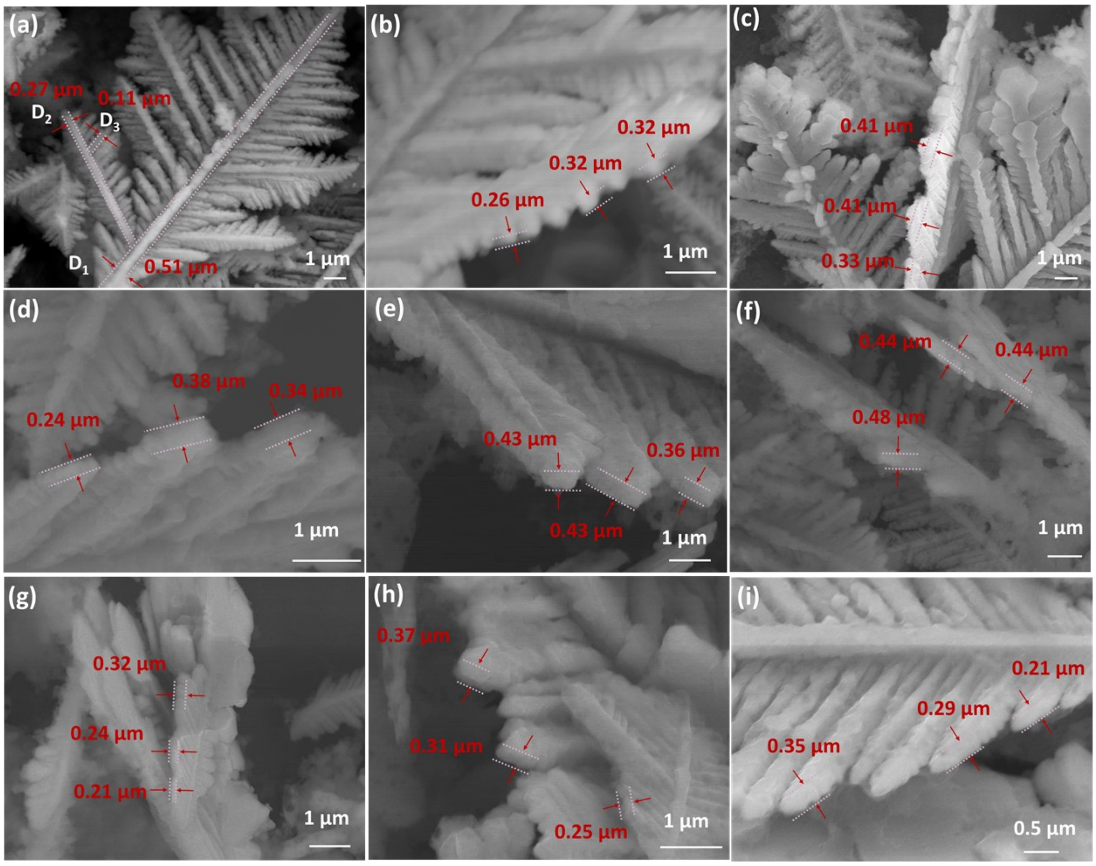


Figure S1. (a-i) SEM images of fractal Co at 20.0 KV.

It suggests that $D_1 > D_2 > D_3$ and the thickness of fractal Co is about 0.34 µm.

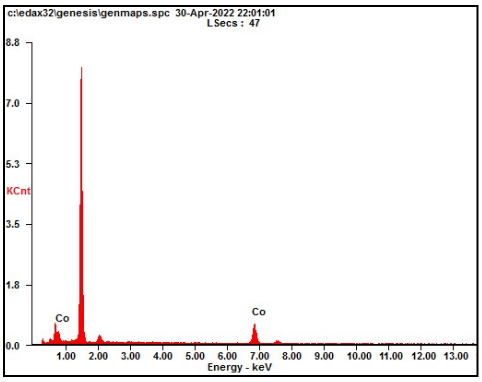


Figure S2. The EDS spectrum of fractal Co.

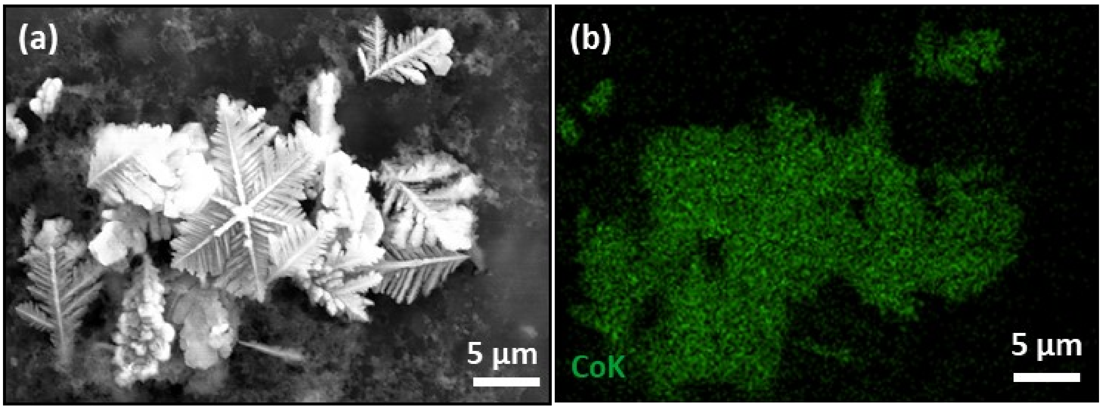


Figure S3. (a, b) SEM image of fractal Co and corresponding elemental mapping result.

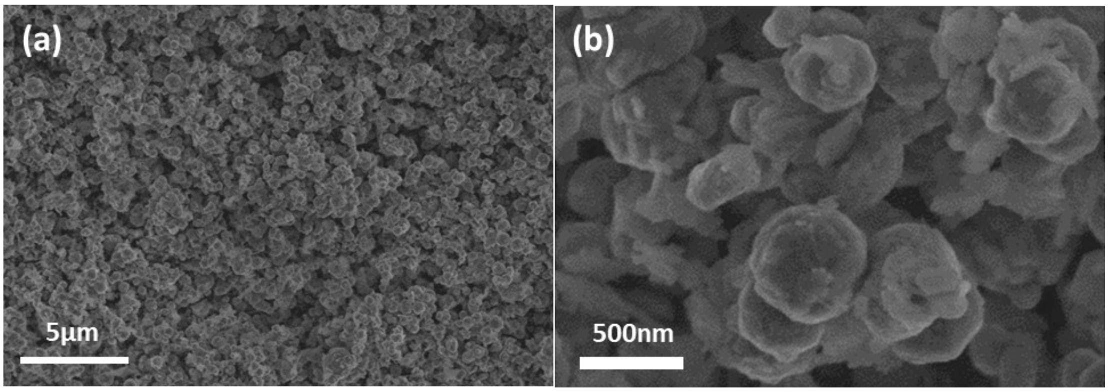


Figure S4. (a, b) SEM images of spherical Co with different magnifications.

$$\cos\varphi = \frac{h_1h_2 + k_1k_2 + \frac{1}{2}\left(h_1k_2 + h_2k_1\right) + \frac{3a^2}{4c^2}l_1l_2}{\sqrt{\left(h_1^2 + k_1^2 + h_1k_1 + \frac{3a^2}{4c^2}l_1^2\right)\left(h_2^2 + k_2^2 + h_2k_2 + \frac{3a^2}{4c^2}l_2^2\right)}}$$

$$d_{\mathrm{hkl}} = \frac{1}{\sqrt{\frac{4}{3}\frac{h^2 + hk + k^2}{|a|^2} + \left(\frac{l}{|c|}\right)^2}}$$

Figure S5. Dihedral angle formula and interplanar spacing formula (where h, k, l are Miller indices, a, c are axes, d is the interplanar distance and φ represents the angle between two facets).

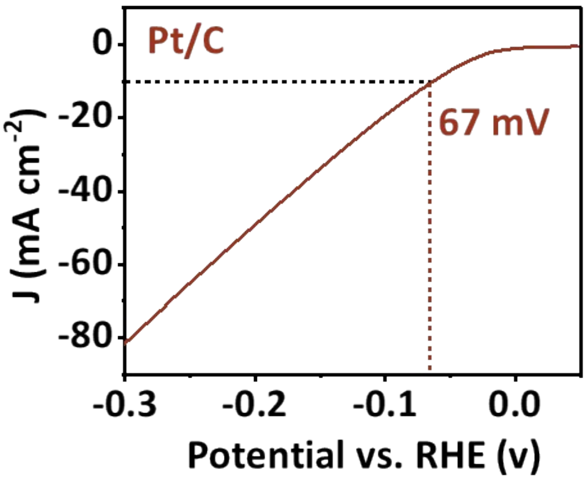


Figure S6. LSV curve of commercial Pt/C for HER in 1.0 M KOH electrolyte. The loading is 3 μg 0.196 cm^{-2}.

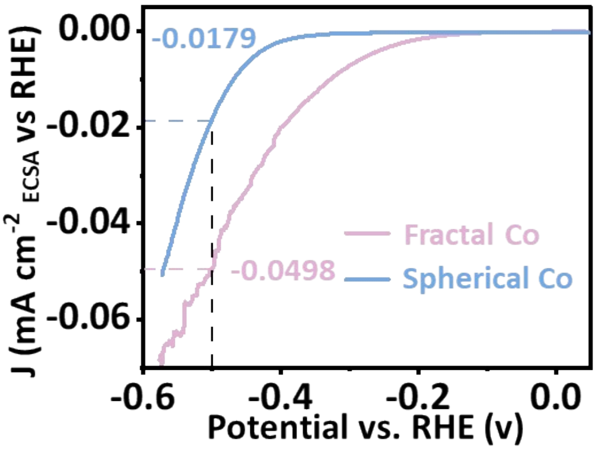


Figure S7. Specific HER activity of fractal Co and spherical Co in 1.0 M KOH.

For the calculation of electrochemical active surface area (ECSA), the value of specific capacitance for a flat surface (1 cm^2) is assumed as 40 μF cm^{-2} and the ECSA is calculated according to the following equation$^{5-7}$:

$$\mathrm{ECSA} = \frac{\mathrm{C}_{\mathrm{d}l}}{C_s}$$

Taking fractal Co as an example, it can be calculated as:

$$A_{ECSA} = \frac{614\,\mu F\ cm^{-2}}{40.0\,\mu F\ cm^{-2} \times 0.196 cm^2} = 78.3 cm^2_{ECSA}$$

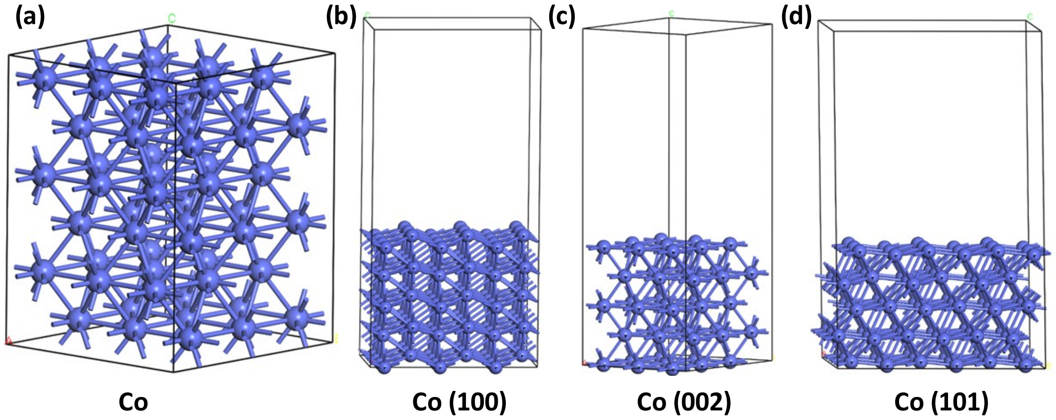


Figure S8. (a) Periodic slab model of fractal Co electrocatalyst. (b-d) Periodic slab model of fractal Co electrocatalyst with different facets, (100), (002) and (101), respectively.

Optimized by Materials Studios, the lattice parameters, a=b=2.489 Å, c=4.013 Å, match well with experiment results, a=b=2.503 Å, c=4.061 Å.

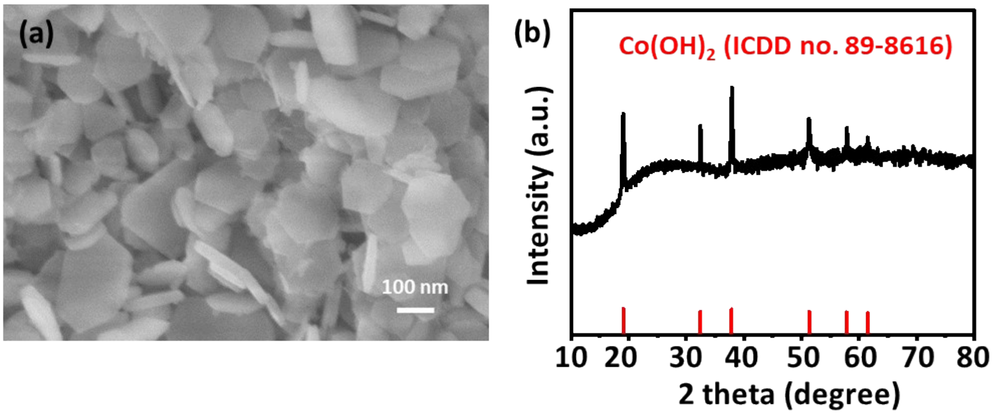


Figure S9. (a,b) SEM image and XRD pattern of Co(OH)$_2$

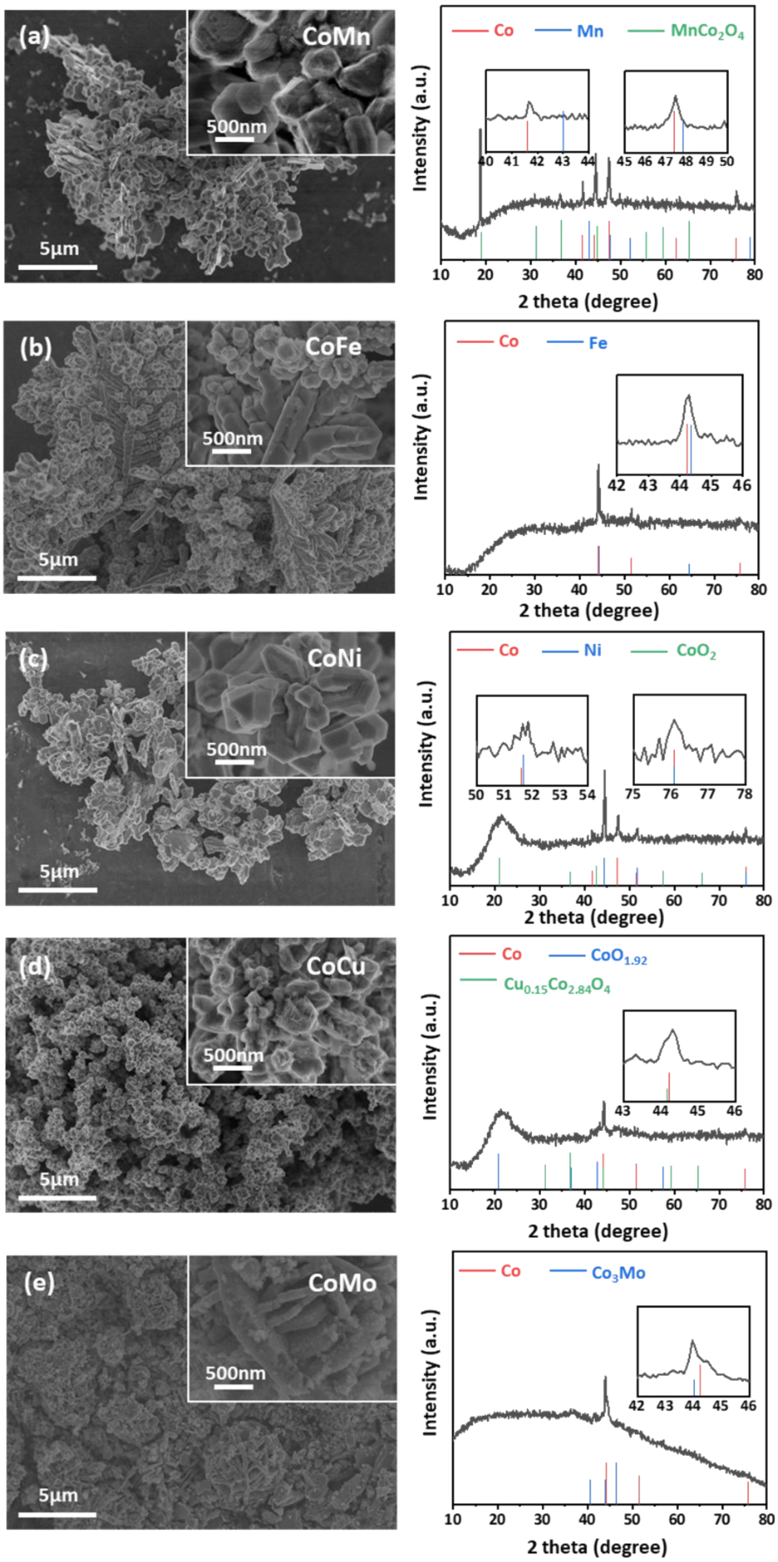


Figure S10. (a-e) SEM images with different magnifications and corresponding XRD patterns of CoMn, CoFe, CoNi, CoCu and CoMo electrocatalysts, respectively.

In XRD patterns, all Co-based compositions show strong Co peaks, indicating the main component is Co, which is consistent with the initial ratio of the raw salts of Co and other metals. The inserted images show peaks containing Co element and other metal elements.

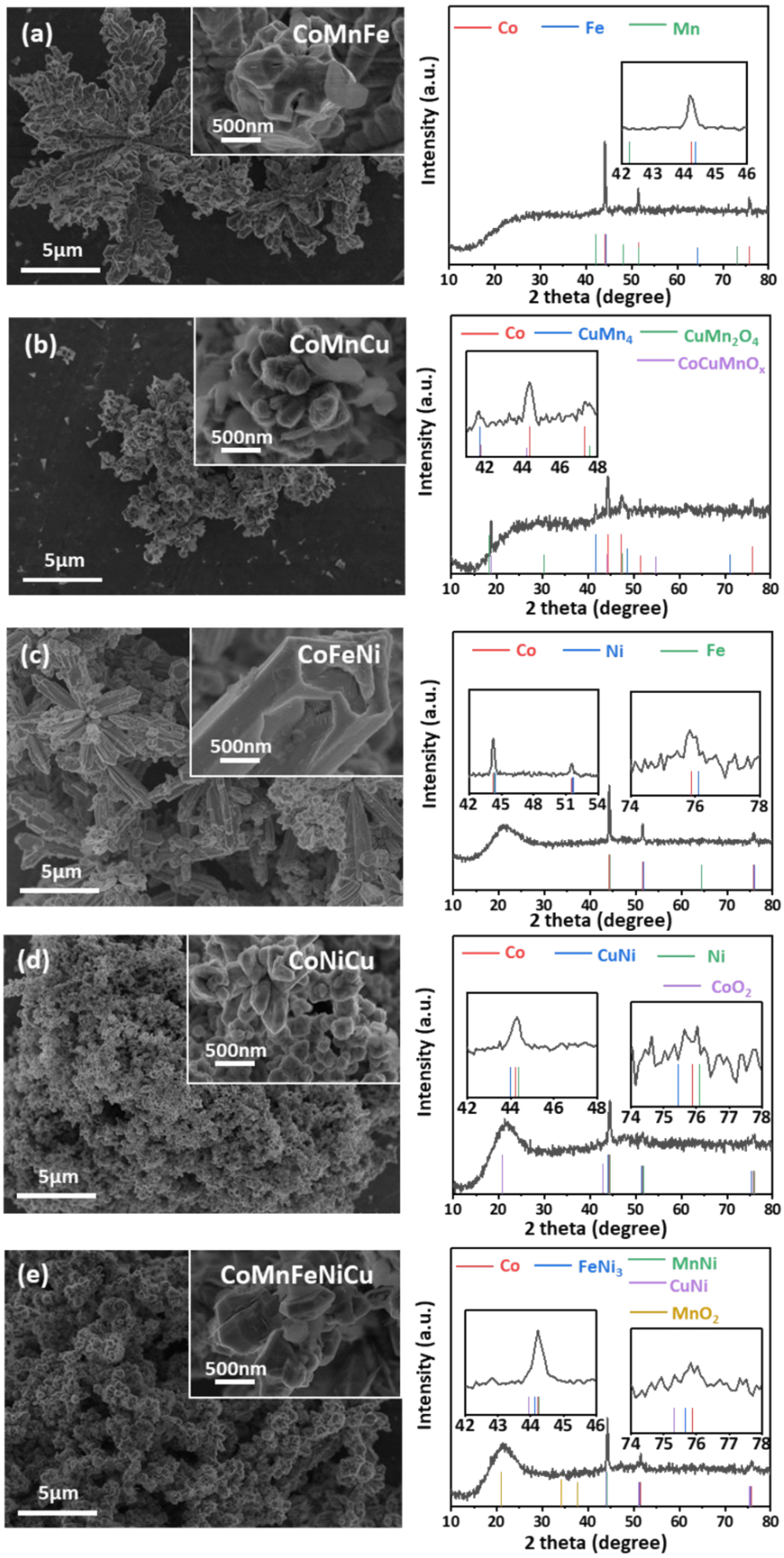
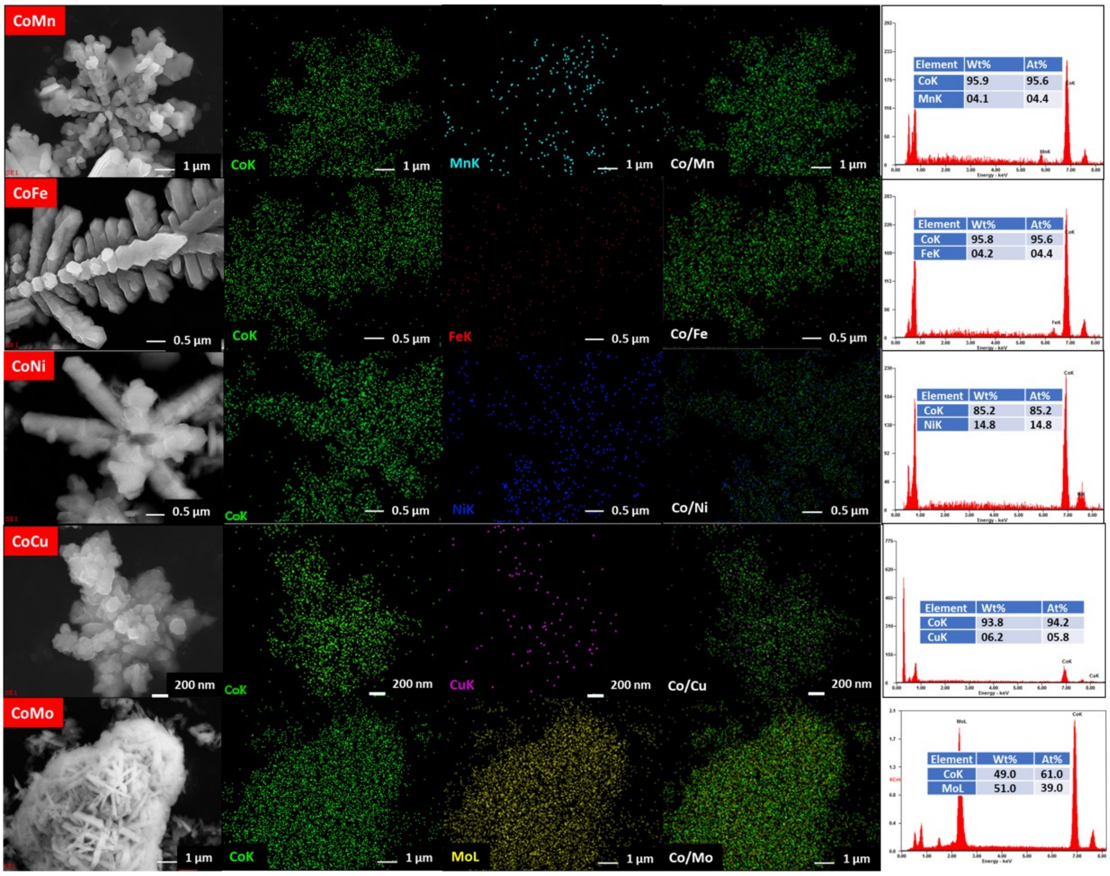


Figure S11. (a-e) SEM images with different magnifications and corresponding XRD patterns of CoMnFe, CoMnCu, CoFeNi, CoNiCu and CoMnFeNiCu electrocatalysts, respectively.

In XRD patterns, all Co-based compositions show strong Co peaks, indicating the main component is Co, which is consistent with the initial ratio of the raw salts of Co and other metals. The inserted images show Co element and other metal elements.



Element	Wt%	At%
CoK	95.9	95.6
MnK	04.1	04.4

Element	Wt%	At%
CoK	95.8	95.6
FeK	04.2	04.4

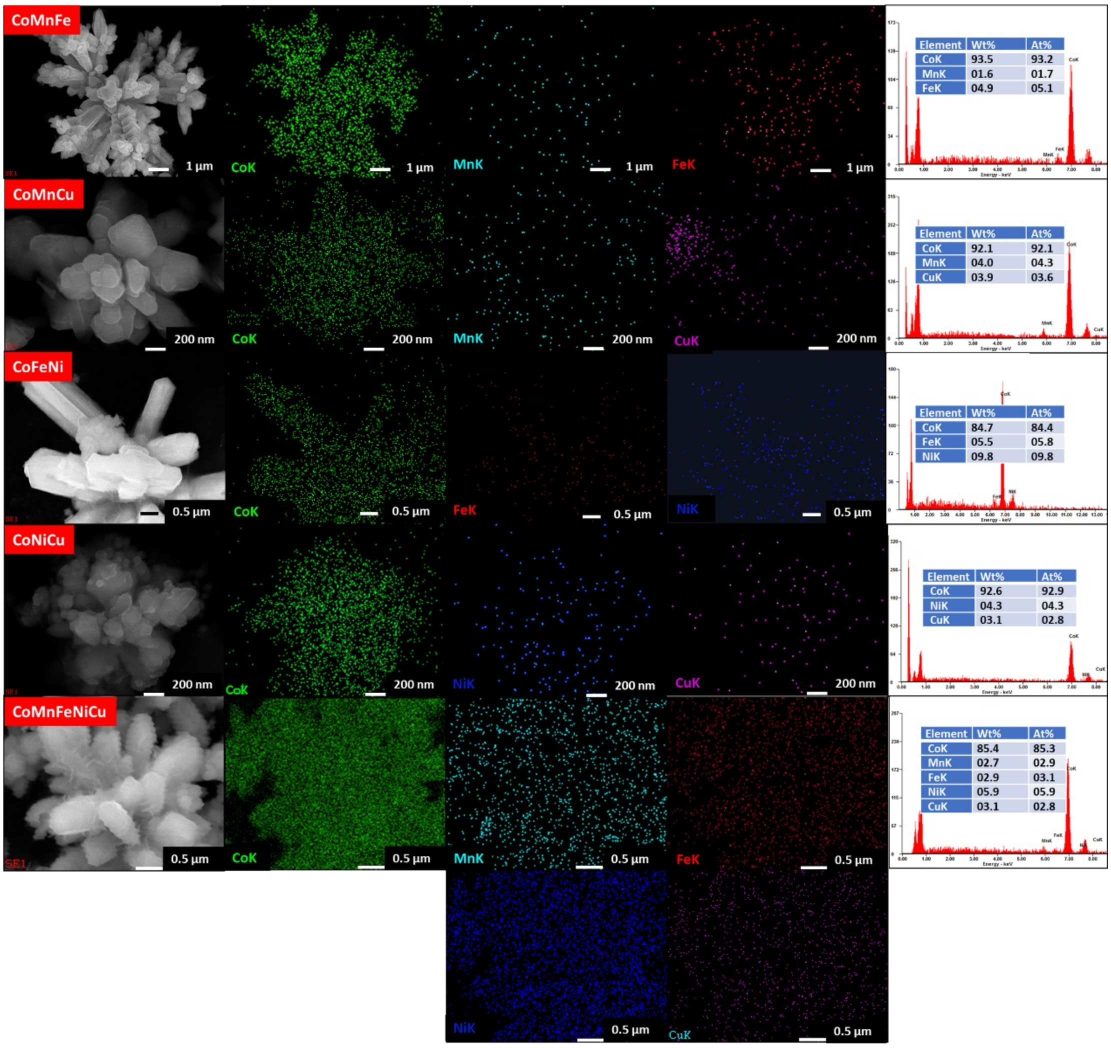
Element	Wt%	At%
CoK	85.2	85.2
NiK	14.8	14.8

Element	Wt%	At%
CoK	93.8	94.2
CuK	06.2	05.8

Element	Wt%	At%
CoK	49.0	61.0
MoL	51.0	39.0

Figure S12. Mapping images and element contents of CoMn, CoFe, CoNi, CoCu, CoMo electrocatalysts, respectively.

The EDS element mapping results indicate the homogenous dispersion of Co and other metal elements.



Element	Wt%	At%
CoK	93.5	93.2
MnK	01.6	01.7
FeK	04.9	05.1

Element	Wt%	At%
CoK	92.1	92.1
MnK	04.0	04.3
CuK	03.9	03.6

Element	Wt%	At%
CoK	84.7	84.4
FeK	05.5	05.8
NiK	09.8	09.8

Element	Wt%	At%
CoK	92.6	92.9
NiK	04.3	04.3
CuK	03.1	02.8

Element	Wt%	At%
CoK	85.4	85.3
MnK	02.7	02.9
FeK	02.9	03.1
NiK	05.9	05.9
CuK	03.1	02.8

Figure S13. Mapping images and element contents of CoMnFe, CoMnCu, CoFeNi, CoNiCu and CoMnFeNiCu electrocatalysts, respectively.

The EDS element mapping results indicate the homogenous dispersion of Co and other metal elements.

References

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