

## Electronic Supplementary Information

### **A molten-salt protected pyrolysis approach for fabricating ternary nickel-cobalt-iron oxide nanomesh catalyst with promoted oxygen-evolving performance**

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## **1. Experimental section**

### **1.1 Materials**

The chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification.

### **1.2 Synthesis of binary NiCo LDH and ternary NiCoFe LDH nanosheets**

The binary NiCo LDH and ternary NiCoFe LDH nanosheets were prepared by a hydrothermal method. Typically, certain amounts of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with total metal content of 4 mmol were dissolved in 30 mL deionized water containing 8 mmol hexamethylenetetramine (HMT) by vigorous stirring for 10 min. After forming a transparent solution, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and maintained at 100 °C for 10h. Then, the reaction system was allowed to cool to room temperature naturally. The as-obtained powdery products were rinsed with deionized water and absolute ethanol for several times, and finally dried under vacuum. By changing the molar ratios of the metals in the precursors (Ni:Co:Fe=0.33:0.67:0; 0.30:0.60:0.10; 0.27:0.53:0.20), binary or ternary LDH nanosheets with Fe concentrations of 0%, 10% and 20% can be obtained.

### **1.3 Molten-salt protected pyrolysis method for fabrication of metal oxide nanomesh**

Typically, 1.325 g  $\text{KNO}_3$ , 0.175 g  $\text{NaNO}_3$  and 1.000 g  $\text{NaNO}_2$  (mass ratio: 53:7:40) were mixed and grinded, and the mixed salts were placed in a porcelain crucible and transferred into a muffle furnace with temperature of 300 °C. After heating for 10 min, homogeneous molten salt can be formed, and 100 mg as-synthesized LDH precursors were added into the molten salt and maintained at 300 °C for 15 min. Then, the porcelain crucible was taken out from the muffle furnace and cooled to room temperature. Finally, the products were washed with deionized water for several times to remove the salt contaminants and dried under vacuum.

### **1.4 Synthesis of the polycrystalline NiCoFe oxide nanosheets by calcination in air**

In contrast to the molten-salt protected pyrolysis method, 100 mg as-synthesized

NiCoFe LDH nanosheets were placed in a porcelain crucible and calcined in a muffle furnace at 300 ° C for 15 min in air. After cooled down to room temperature, the powdery products were collected and named as MO-CA-10.

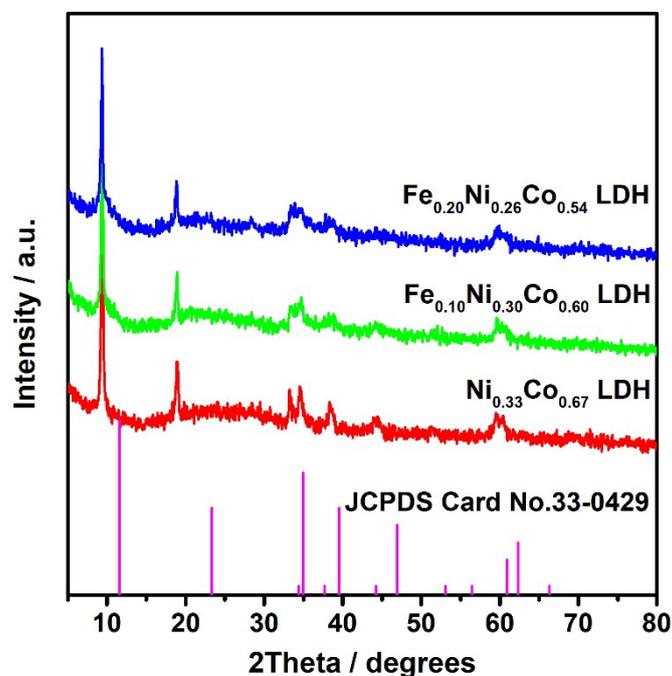
### **1.5 Structural characterizations**

X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and corresponding elemental mapping analyses were performed on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. Nitrogen adsorption-desorption isotherms were carried out by using a Micromeritics ASAP 2000 system, and all the gas adsorption experiments were performed at liquid-nitrogen temperature (77 K) after degassed at 200 °C for 6 h. The content of metals for the samples were determined by inductively coupled plasma optical emission spectrum (ICP-OES) on a Perkin Elmer Optima 7300DV ICP emission spectroscope. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg K $\alpha = 1253.6 \text{ eV}$ , and the resolution level was lower than 1 atom%.

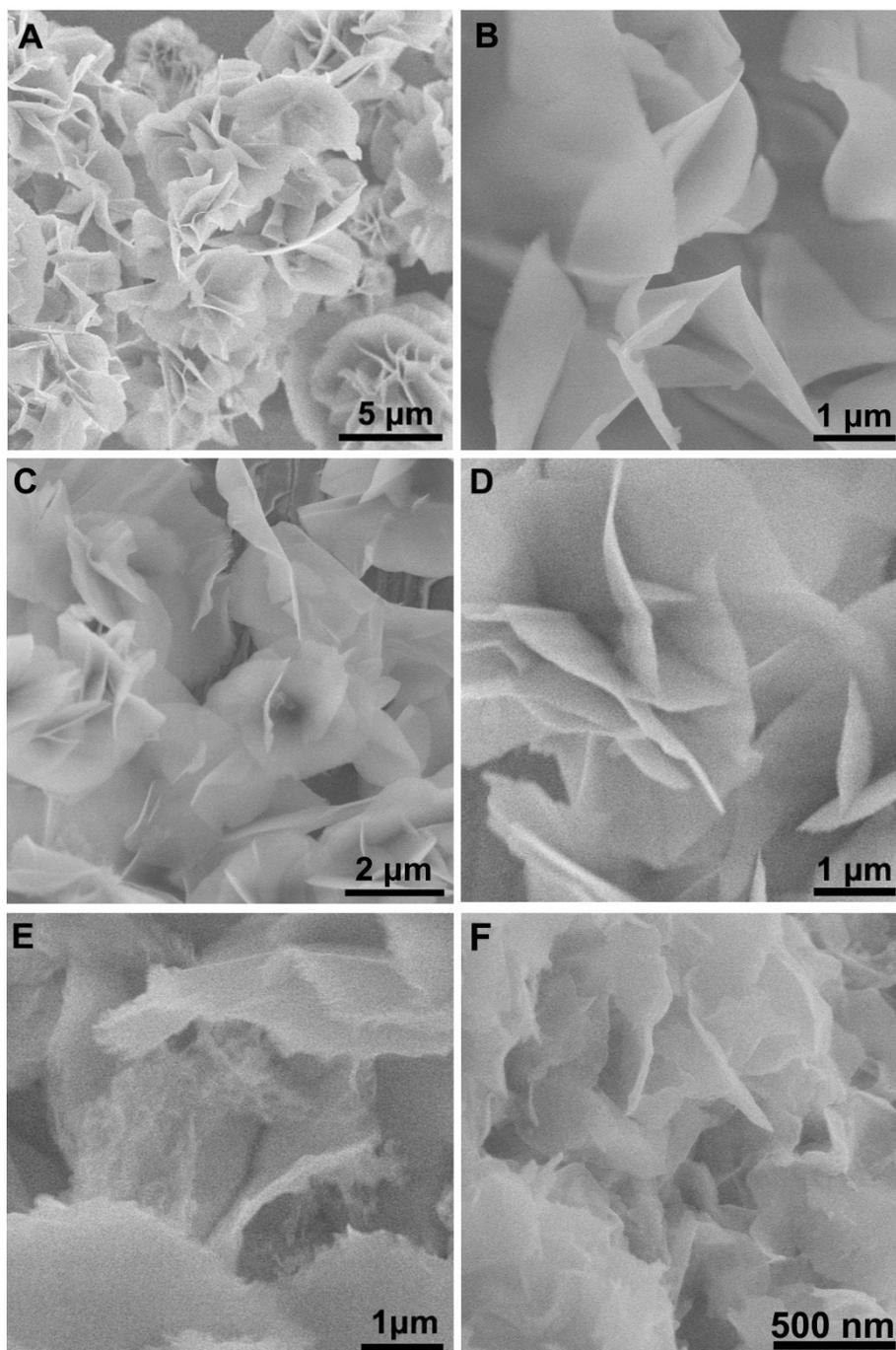
### **1.6 Electrocatalytic study**

All the electrochemical measurements were performed in a three-electrode system linked with an electrochemical workstation (CHI660E) at room temperature. All potentials were calibrated to a reversible hydrogen electrode (RHE) and the data are presented without iR correction. Typically, 4 mg of catalyst and 50  $\mu\text{L}$  Nafion solution (Sigma Aldrich, 5 wt%) were dispersed in 1 mL water-isopropanol mixed solution (volume ratio of 3:1) by sonicating for at least 30 min to form a homogeneous ink. Then 5  $\mu\text{L}$  of the dispersion (containing 20  $\mu\text{g}$  of catalyst) was loaded onto a glassy carbon electrode with 3 mm diameter, leading to a catalyst loading of 0.285  $\text{mg cm}^{-2}$ . The as-prepared catalyst film was allowed to be dried at

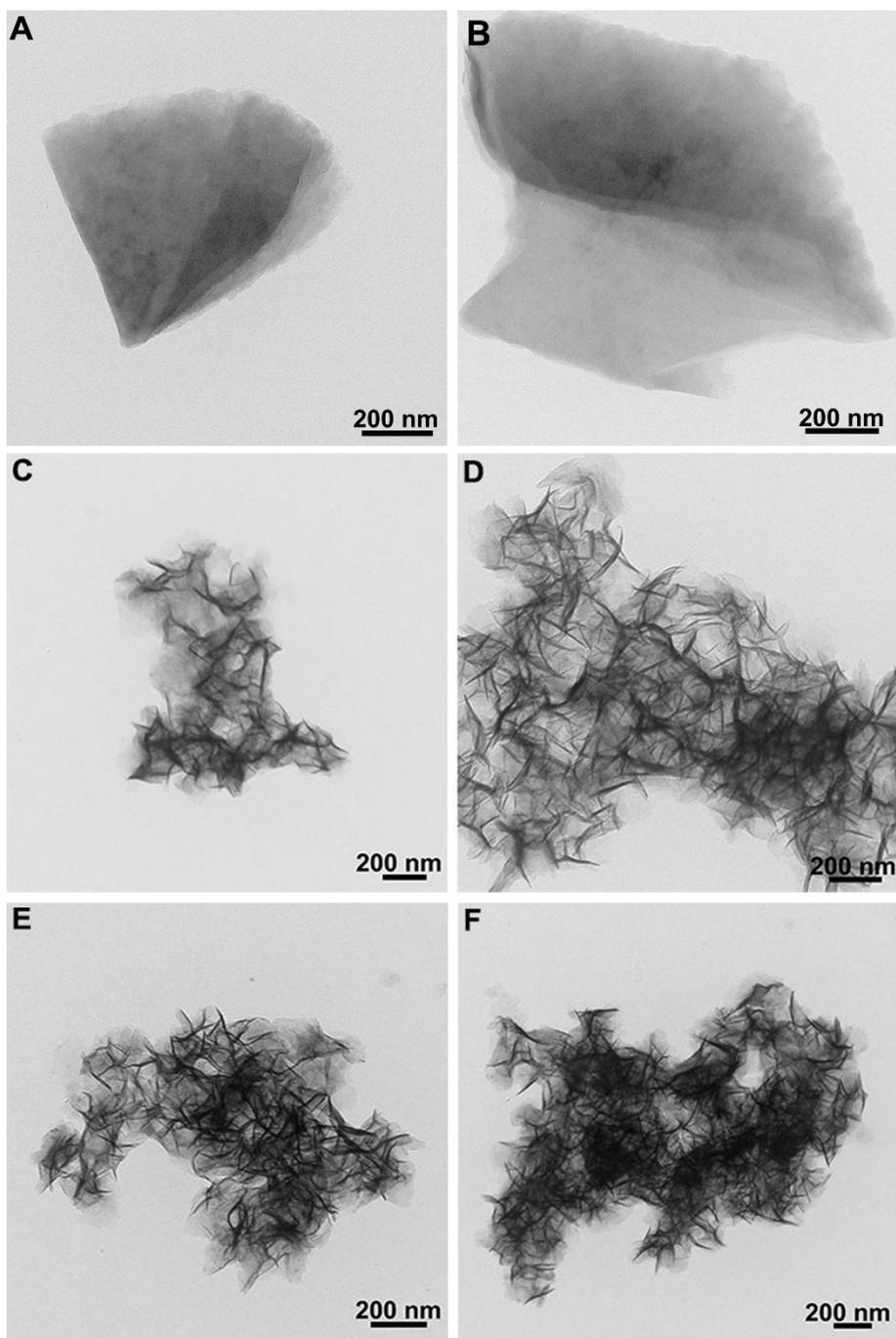
room temperature. The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) with a scan rate of  $5 \text{ mV s}^{-1}$  were conducted in  $\text{O}_2$ -purged 1 M KOH solution. A Hg/HgO electrode was used as the reference electrode, a platinum gauze electrode ( $2 \text{ cm} \times 2 \text{ cm}$ , 60 mesh) was used as the counter electrode, and the glassy carbon electrodes loaded with various catalysts were served as the working electrodes. For the chronoamperometry test, a static potential of 1.53 V vs. RHE was applied. The electrochemical impedance spectroscopy (EIS) measurements were operated in the same configuration at 1.5 V vs. RHE from  $10^{-2}$ - $10^5$  Hz.



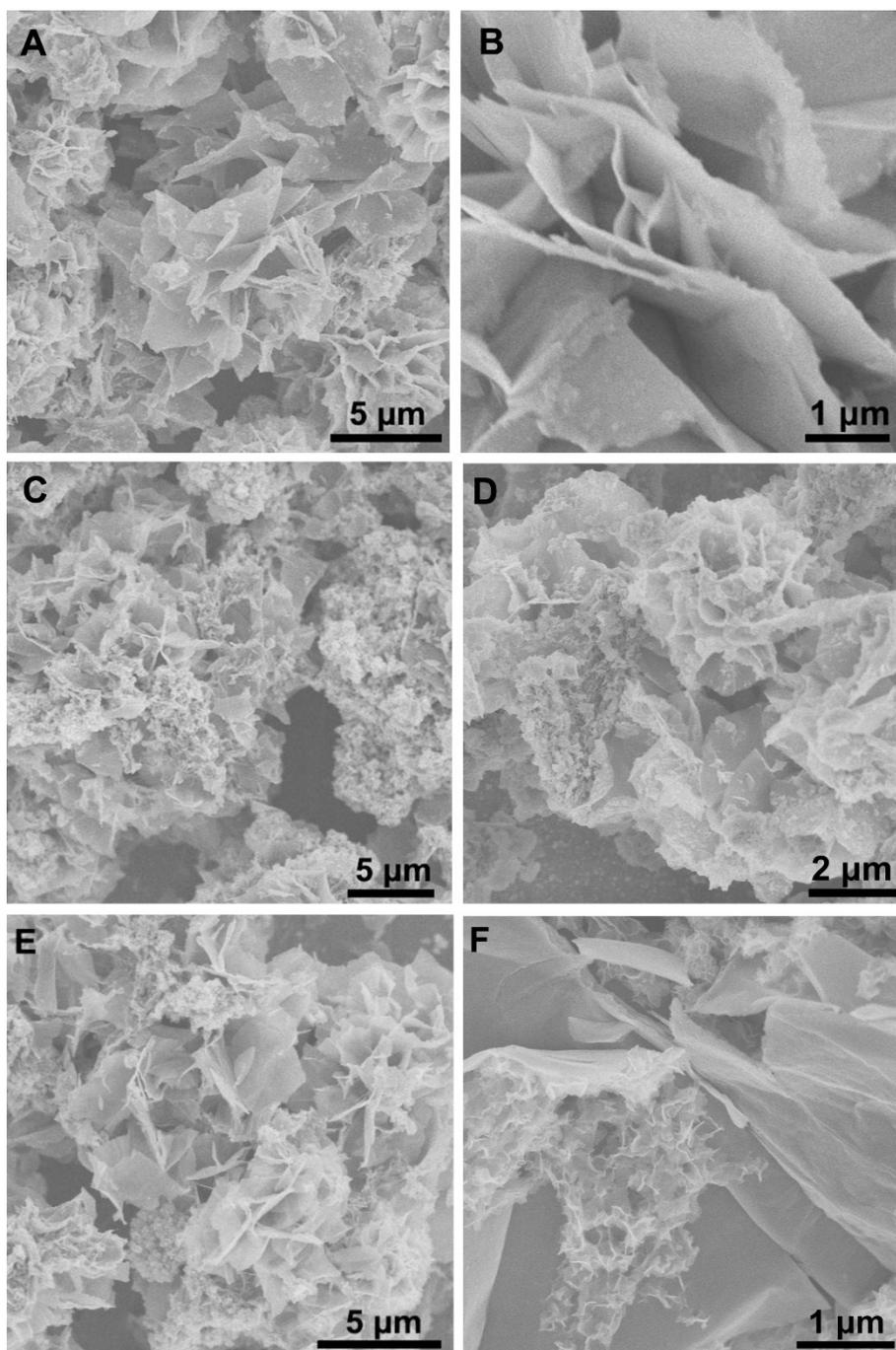
**Fig. S1** XRD patterns of the as-synthesized LDH nanosheets with the standard pattern of the typical intercalated hydroxide -  $\alpha$ - $\text{Ni}(\text{OH})_2$  (JCPDS card No. 33-0429).



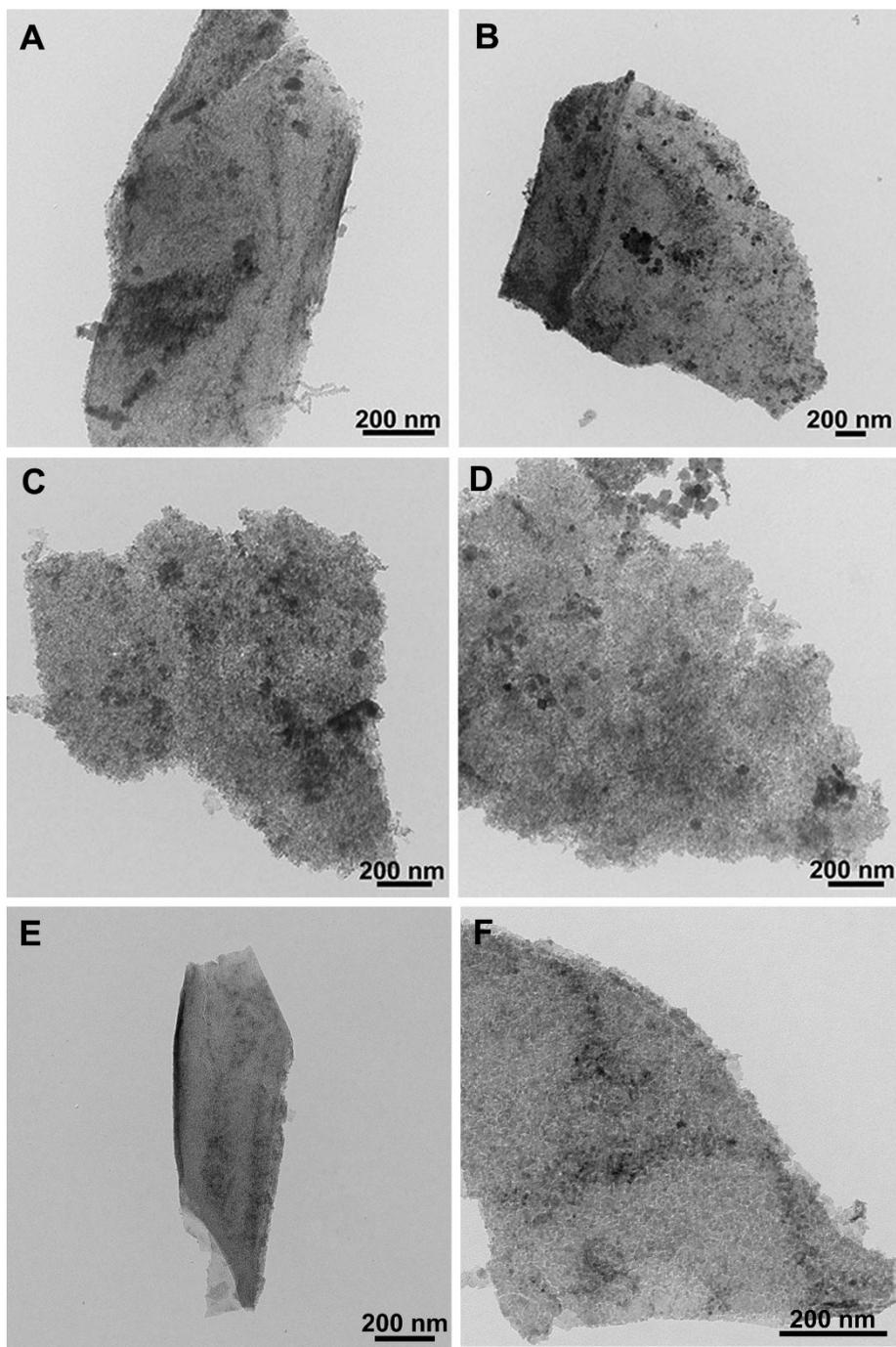
**Fig. S2** (A-B) SEM images of binary NiCo LDH nanosheets. (C-D) SEM images of ternary NiCoFe LDH nanosheets with Fe content of 10%. (E-F) SEM images of ternary NiCoFe LDH nanosheets with Fe content of 20%.



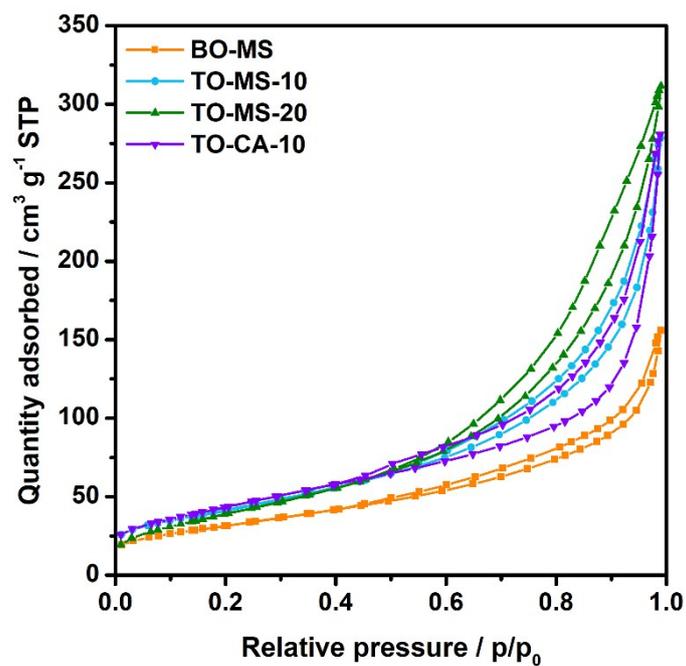
**Fig. S3** (A-B) TEM images of binary NiCo LDH nanosheets. (C-D) TEM images of ternary NiCoFe LDH nanosheets with Fe content of 10%. (E-F) TEM images of ternary NiCoFe LDH nanosheets with Fe content of 20%.



**Fig. S4** (A-B) SEM images of BO-MS. (C-D) SEM images of TO-MS-20. (E-F) SEM images of TO-CA-10.



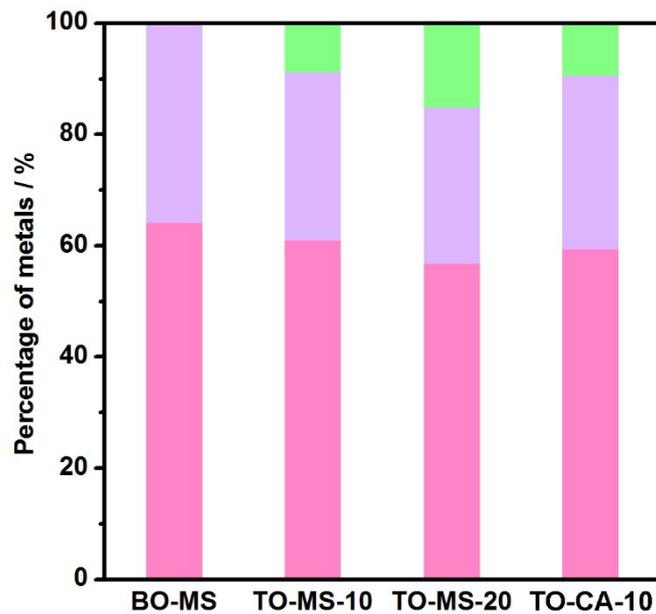
**Fig. S5** (A-B) TEM images of BO-MS. (C-D) TEM images of TO-MS-20. (E-F) TEM images of TO-CA-10.



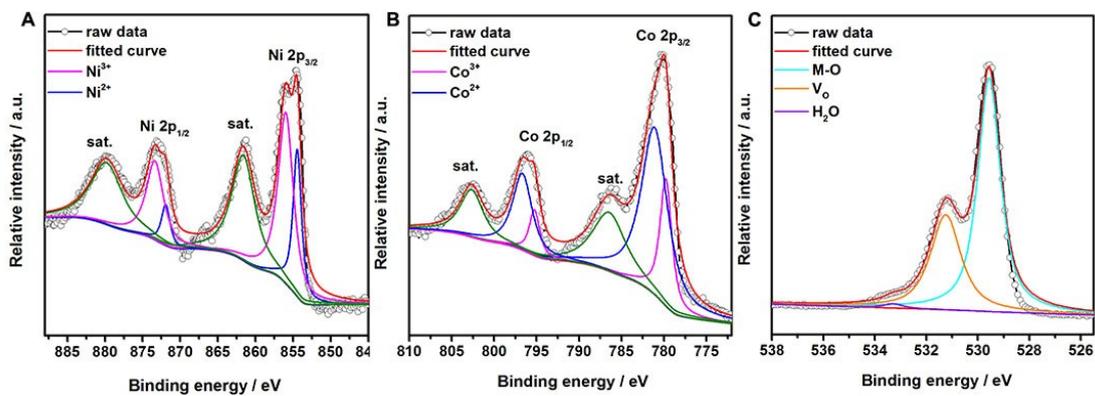
**Fig. S6** Nitrogen adsorption-desorption isotherms of the catalysts.

**Table S1.** BET specific surface area and ICP results of various catalysts.

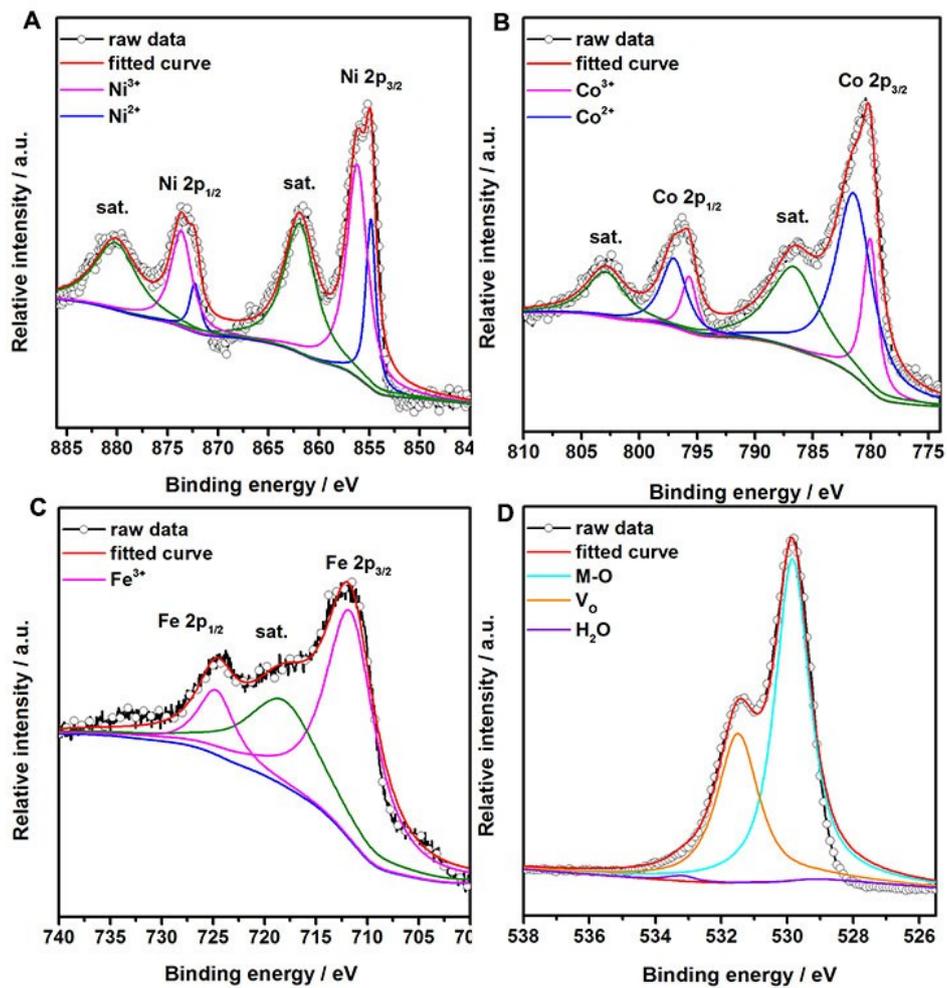
Materials	BET specific surface area [m <sup>2</sup> g <sup>-1</sup> ]	Ni (atom% per total metal)	Co (atom% per total metal)	Fe (atom% per total metal)
BO-MS	114.6	35.8	64.2	0
TO-MS-10	151.5	30.2	61.1	8.7
TO-MS-20	150.3	28.0	56.9	15.1
TO-CA-10	160.6	31.3	59.4	9.3



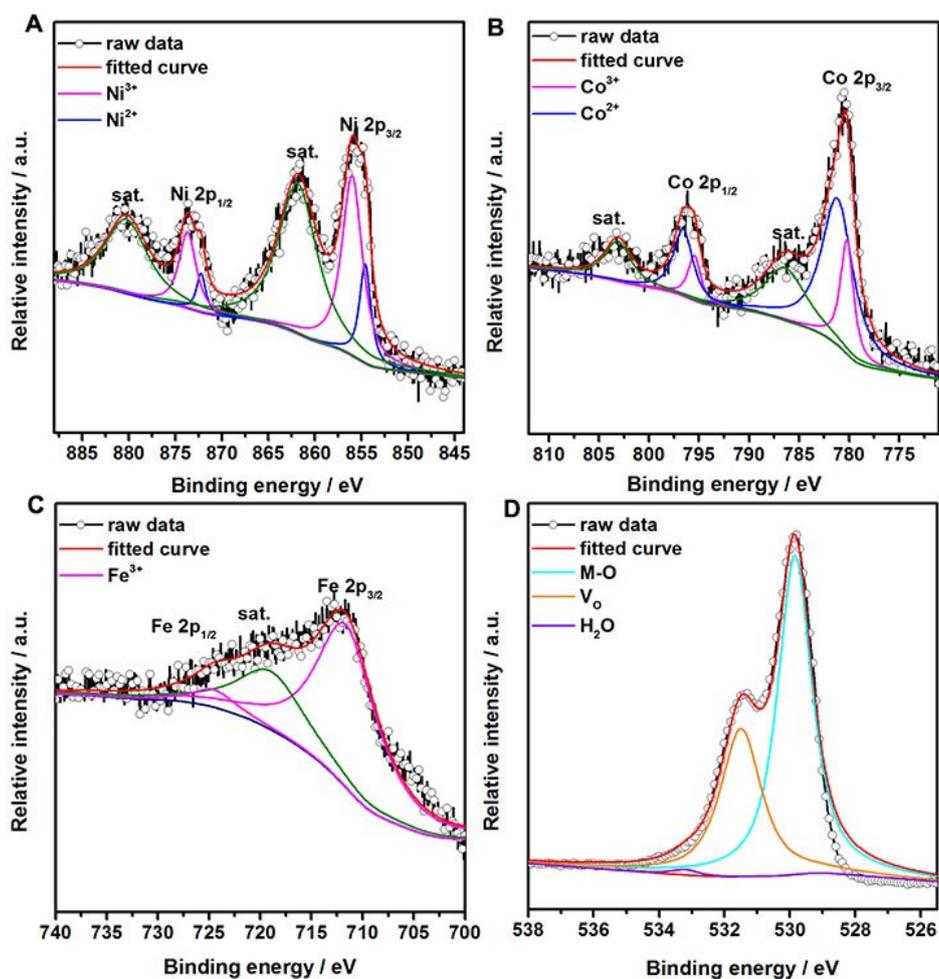
**Fig. S7** ICP results of the as-synthesized catalysts, where red represents cobalt, purple represents nickel and green represents iron.



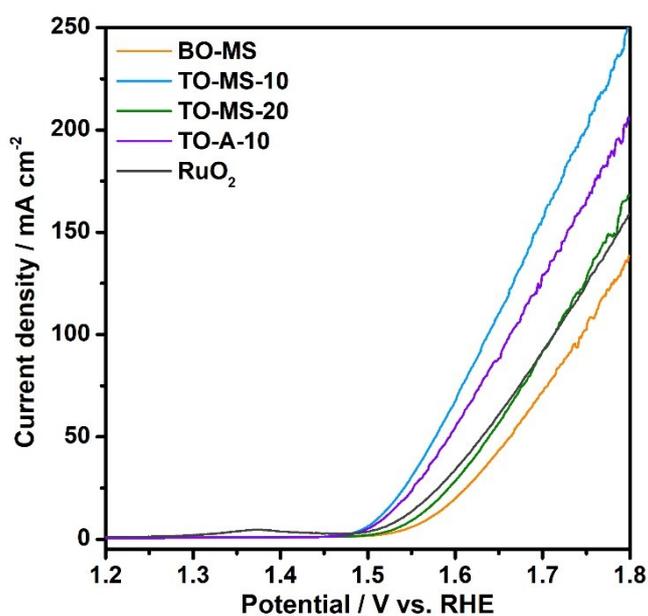
**Fig. S8** XPS spectra of (A) Ni, (B) Co and (C) O for BO-MS.



**Fig. S9** XPS spectra of (A) Ni, (B) Co and (C) Fe and (D) O for TO-MS-20.



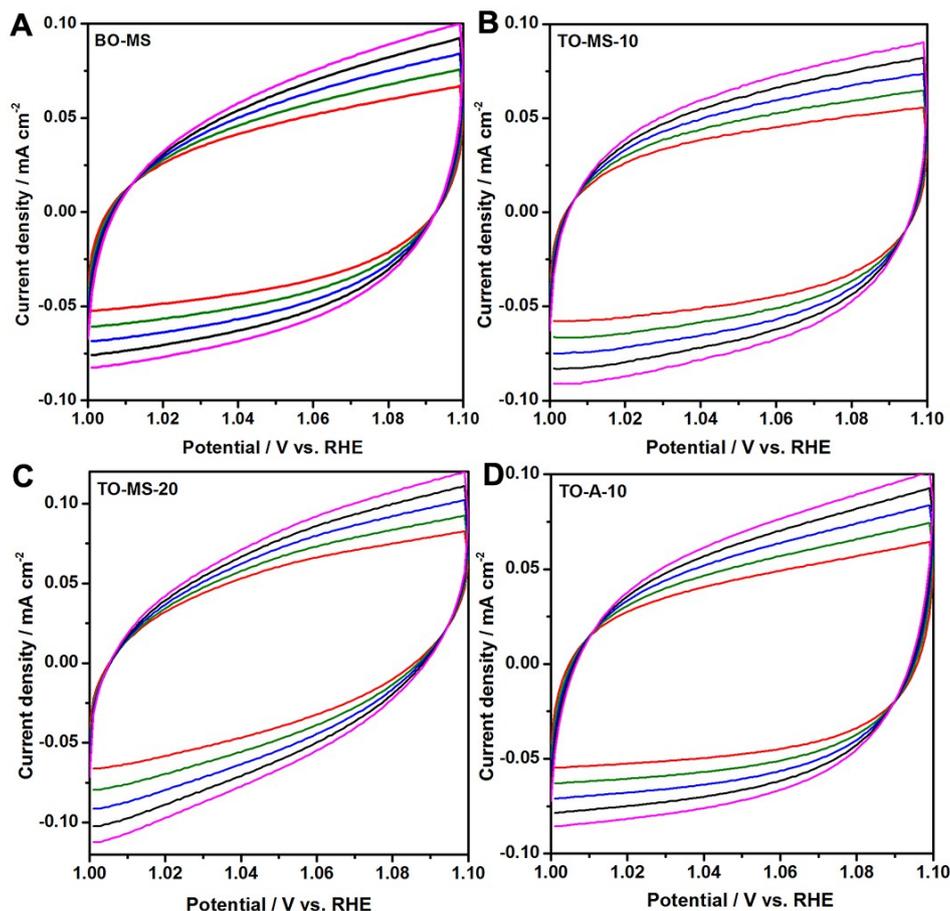
**Fig. S10** XPS spectra of (A) Ni, (B) Co and (C) Fe and (D) O for TO-CA-10.



**Fig. S11** LSV curves of the synthesized catalysts and commercial  $\text{RuO}_2$ .

**Table S2.** Electrochemical parameters of the catalysts.

	$j_{\text{geo}}$ @1.8 V vs. RHE [mA cm <sup>-2</sup> ]	Required potential for 10 mA cm <sup>-2</sup> [V vs. RHE]	$R_{\text{ct}}$ [ $\Omega$ ]	$C_{\text{dl}}$ [mF cm <sup>-2</sup> ]	$j_{\text{cat}}$ @1.6 V vs. RHE [A F <sup>-1</sup> ]
<b>BO-MS</b>	136.8	1.570	45.7	2.68	7.1
<b>TO-MS-10</b>	255.2	1.509	35.3	3.10	22.5
<b>TO-MS-20</b>	165.3	1.555	37.8	3.01	9.2
<b>TO-CA-10</b>	202.4	1.520	38.2	3.61	14.7

**Fig. S12** Cyclic voltammograms of (A) BO-MS, (B) TO-MS-10, (C) TO-MS-20 and (D) TO-CA-10 in a non-redox region.

The estimation of the effective active surface area of the samples was carried out according to literature.<sup>1,2</sup> Cyclic voltammetry (CV) were conducted at various scan rates (12, 14, 16, 18, 20 mV s<sup>-1</sup>) in the region of 1.0-1.1 V vs. RHE where no redox reaction occurs, which can be considered as the double-layer capacitive behavior. The electrochemical double-layer capacitance ( $C_{\text{dl}}$ ) of various catalysts can be identified

from the cyclic voltammograms, which is expected to be linearly proportional to the electrochemically active surface area. The  $C_{dl}$  value is estimated by plotting the  $\Delta j$  ( $j_a - j_c$ ) at 1.05 V vs. RHE against the scan rate, where the slope is twice  $C_{dl}$ . The  $C_{dl}$  values were calculated to be 2.68 mF cm<sup>-2</sup>, 3.10 mF cm<sup>-2</sup>, 3.01 mF cm<sup>-2</sup> and 3.61 mF cm<sup>-2</sup> for BO-MS, TO-MS-10, TO-MS-20 and TO-CA-10, respectively, revealing the similarly high  $C_{dl}$  value of the as-obtained porous nanosheets.

## Reference

- [1] M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, *J. Am. Chem. Soc.* **2013**, *135*, 10274-10277.
- [2] J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan and Y. Xie, *J. Am. Chem. Soc.* **2013**, *135*, 17881-17888.