Electronic Supplementary Information

Sulfurization-Induced Edge Amorphization in Copper-Nickel-Cobalt Layered Double Hydroxide Nanosheets Promoting Hydrazine Electro-Oxidation

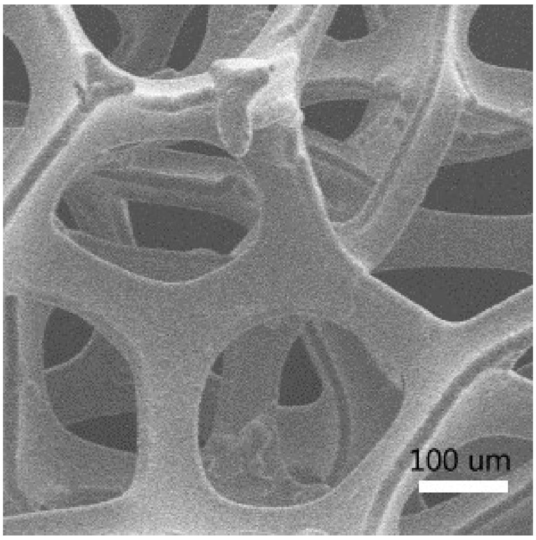

Fig. S1 SEM image of the bare nickel foam.

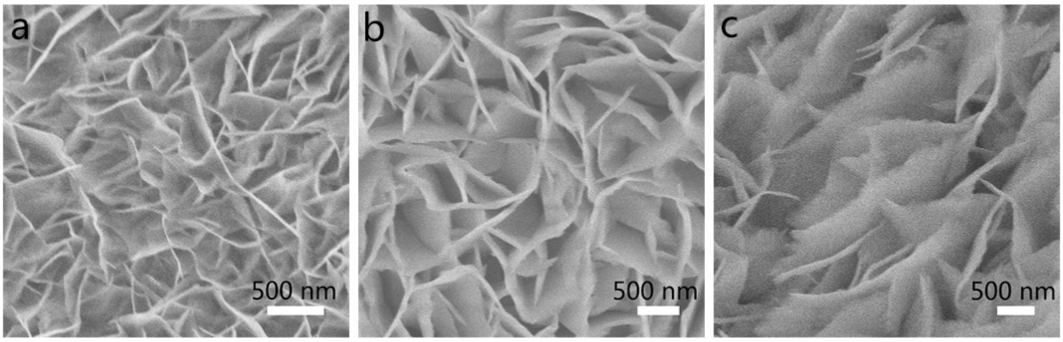

Fig. S2 SEM images of (a) LDH-1, (b) LDH-2 and (c) LDH-4.

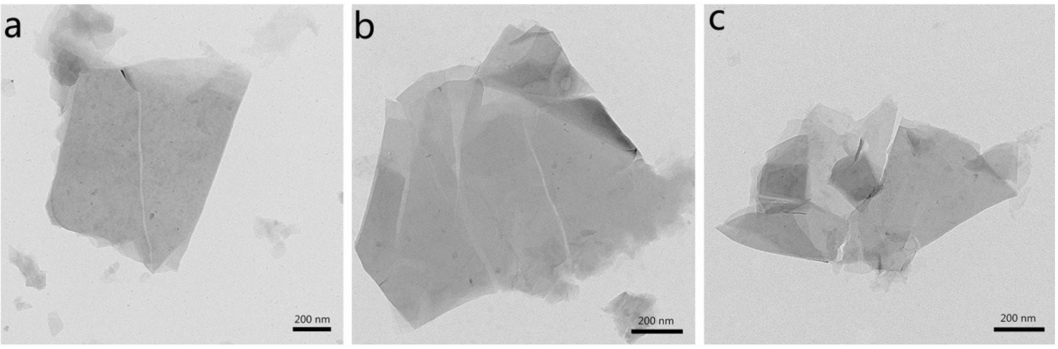

Fig. S3 TEM images of the LDH nanosheet with (a) 0%, (b) 1% and (c) 10% Cu.

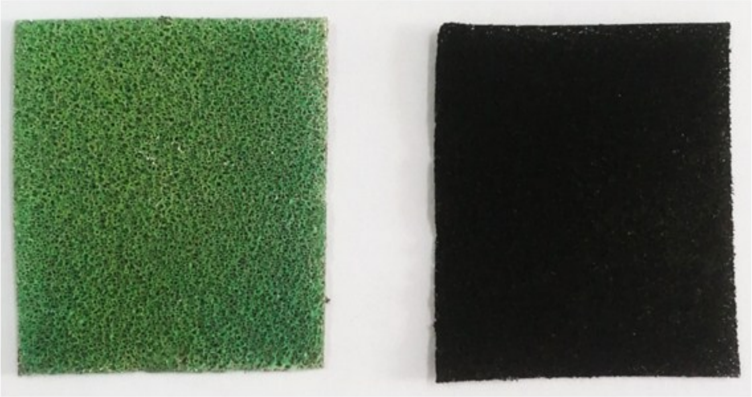

Fig. S4 Image of the LDH-3 (green) and S-LDH-3 (black).

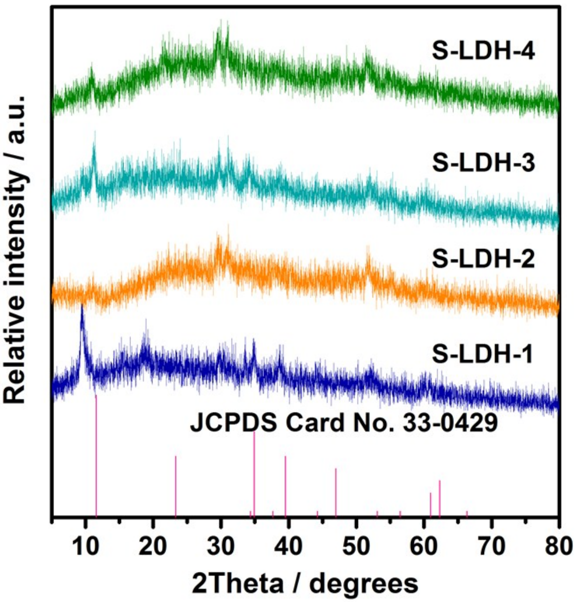

Fig. S5 XRD patterns of the S-LDH nanosheets separated from the nickel foam.

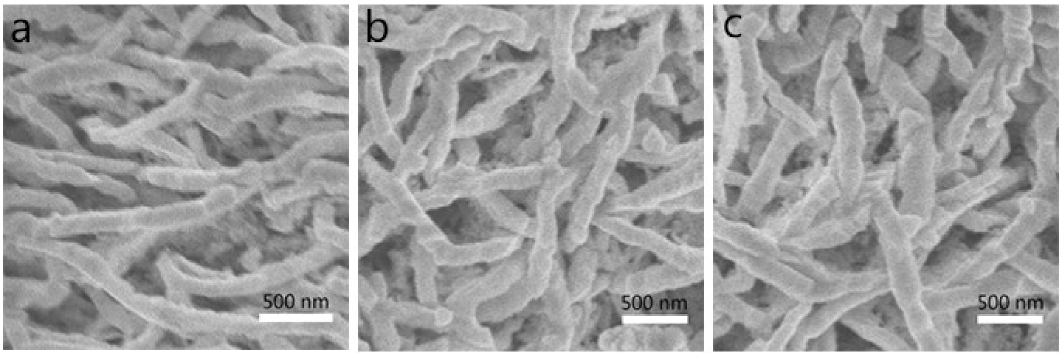

Fig. S6 SEM images of (a) S-LDH-1, (b) S-LDH-2 and (c) S-LDH-4.

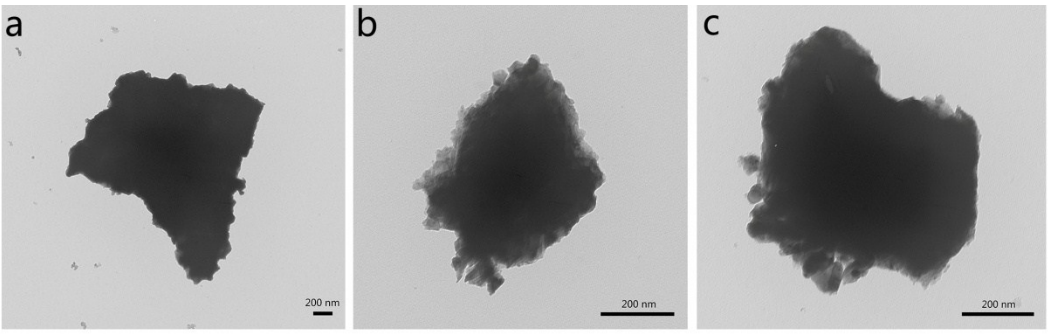

Fig. S7 (a-c) TEM images of the sulfurized samples with (a) 0%, (b) 1% and (c) 10% Cu.

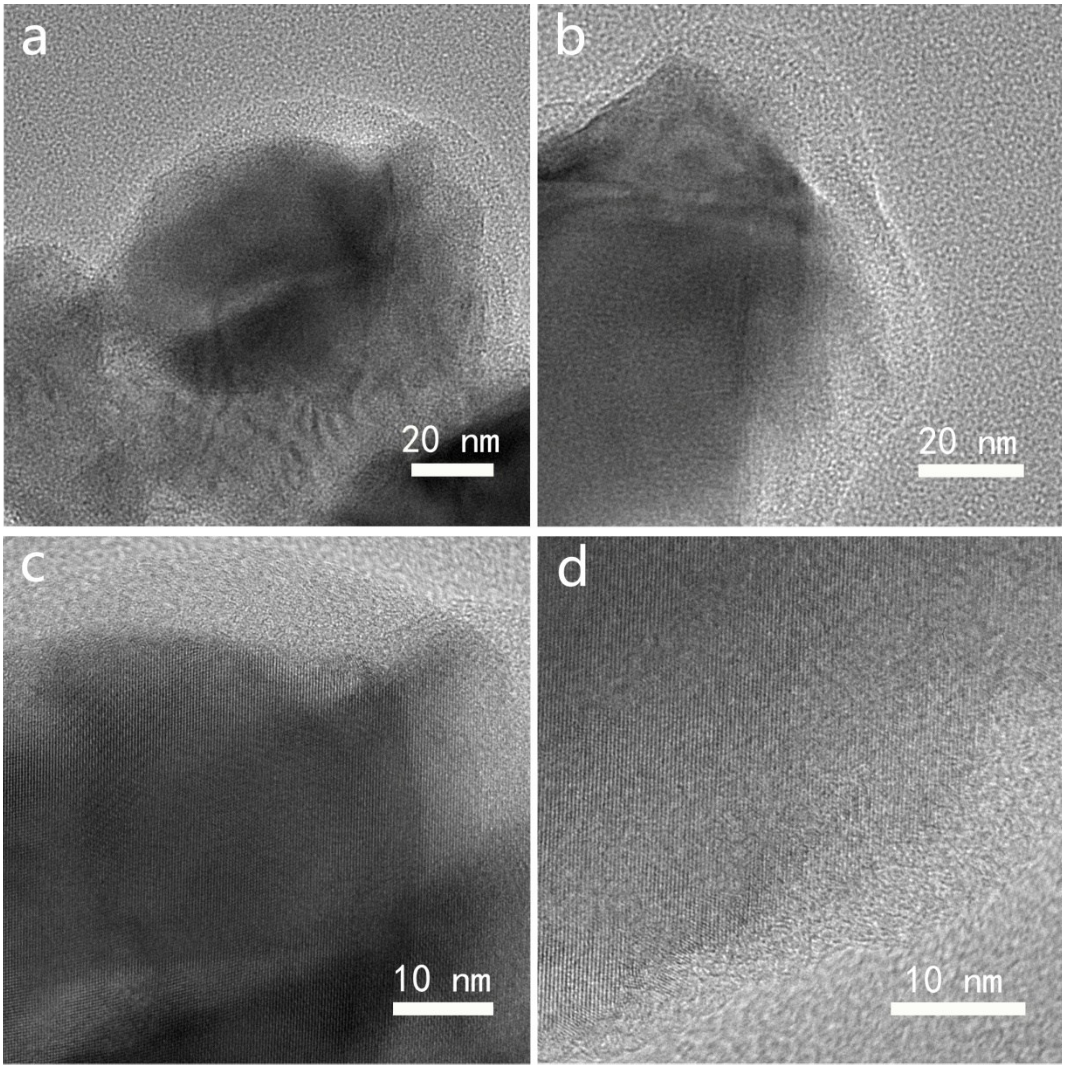

Fig. S8 Additional HRTEM images of the S-LDH-3, where the sulfurization-induced edge amorphization can be clearly revealed.

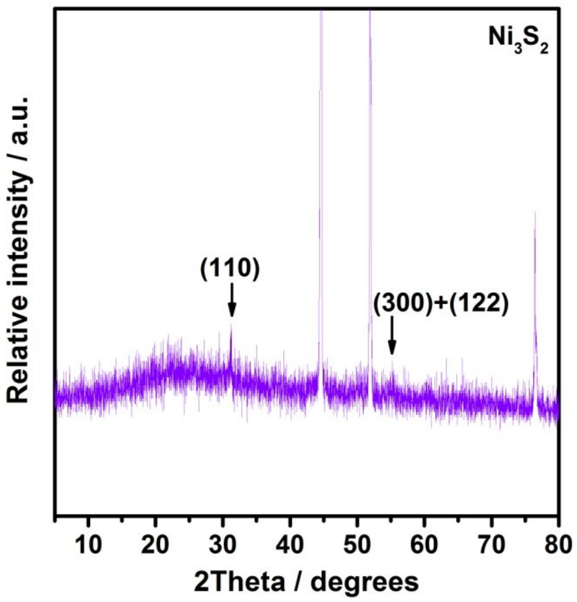

Fig. S9 XRD pattern of S-NF, from which the Ni$_3$S$_2$ phase can be identified.

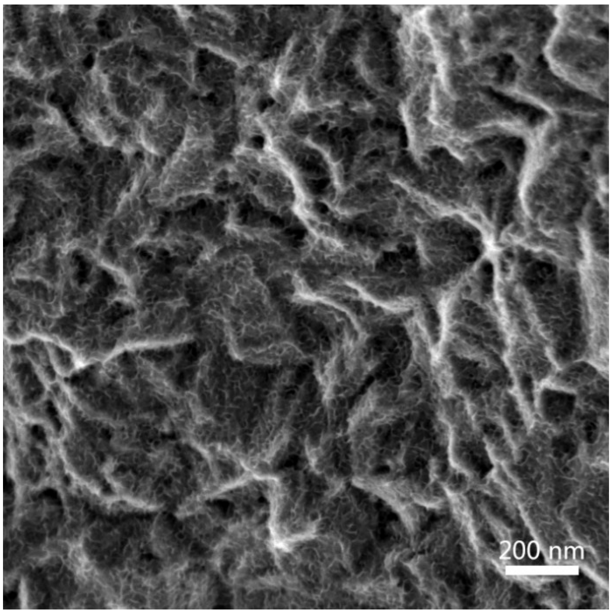

Fig. S10 SEM image of S-NF.

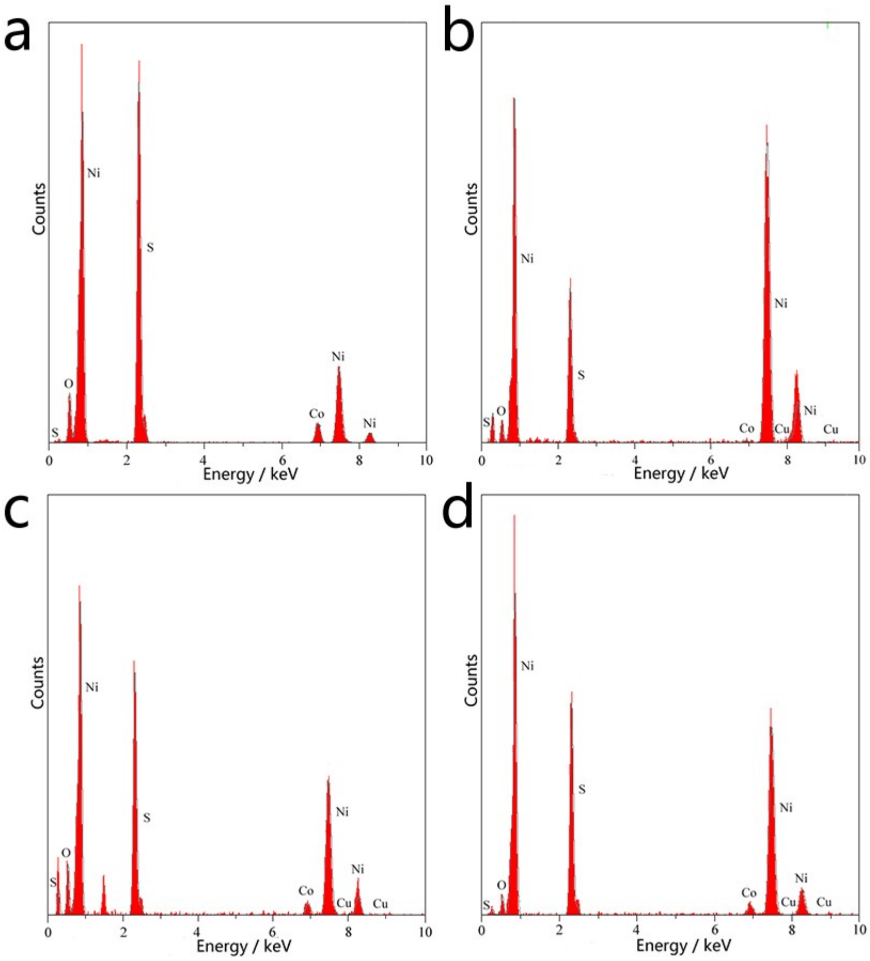

Fig. S11 (a-d) EDS spectra of sulfurized LDH nanosheet arrays with 0%, 1%, 5% and 10% Cu.

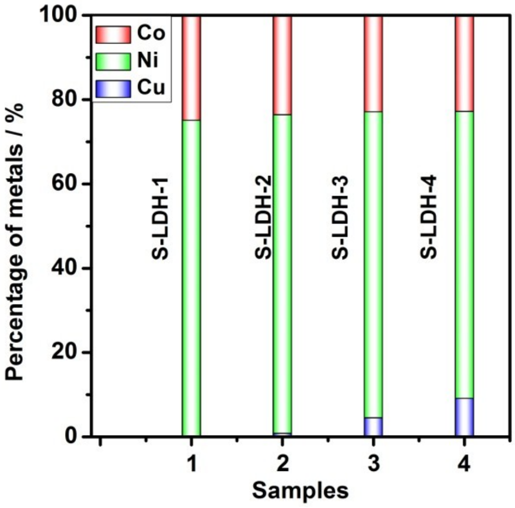

Fig. S12 The inductively coupled plasma optical emission spectrometry (ICP-OES) results of the sulfurized LDH nanosheet arrays.

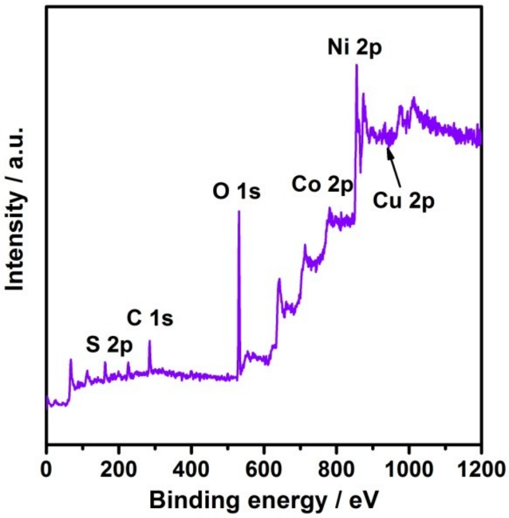

Fig. S13 XPS survey spectrum of the S-LDH-3.

Table S1 Loading weights of the samples.

Samples	mass /mg	Samples	mass /mg	Load weight / mg	Samples	mass /mg	Load weight / mg
bare NF-1	356.8	LDH-1	383.2	26.4	S-LDH-1	371.8	15.0
bare NF-2	332.1	LDH-2	366.9	34.8	S-LDH-2	349.7	17.6
bare NF-3	339.7	LDH-3	375.0	35.3	S-LDH-3	355.5	15.8
bare NF-4	322.8	LDH-4	353.7	30.9	S-LDH-4	337.5	14.7

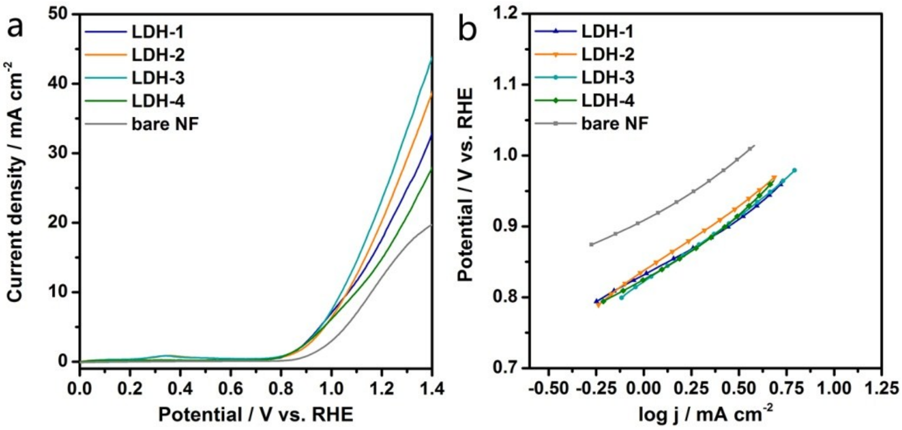

Fig. S14 (a) Polarization curves of CuNiCo LDH nanosheet arrays and (b) Corresponding Tafel plots.

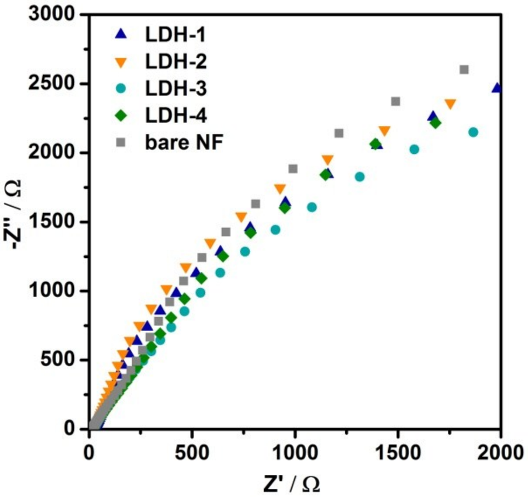

Fig. S15 Nyquist plots of CuNiCo LDH nanosheet arrays and bare nickel foam measured at 0.4 V vs. RHE.

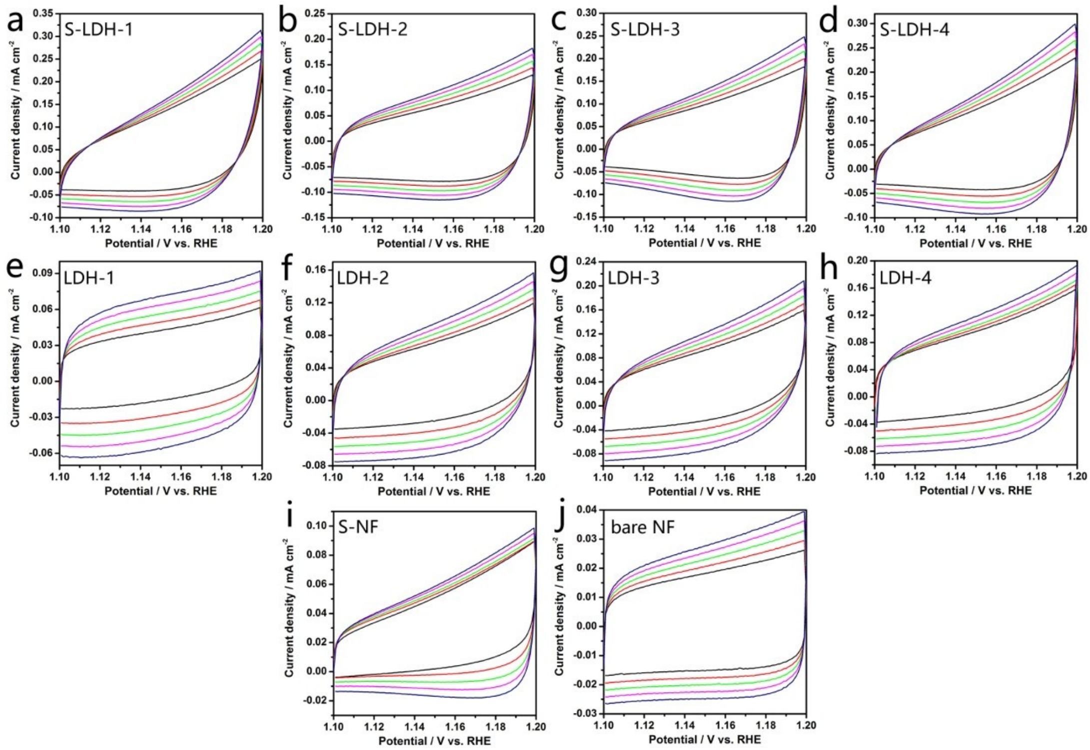

Fig. S16 (a-j) CV curves of various catalysts measured at a non-redox region in 0.1M KOH for the calculation of electrochemical double-layer capacitances.

The effective active surface area of the samples was estimated according to the literature.[1] Cyclic voltammetry (CV) was performed at various scan rates (12, 14, 16…20 mV s^{-1}, etc) in 1.1-1.2 V vs. RHE region. The electrochemical double-layer capacitance (C_{dl}) of various samples can be determined from the cyclic voltammograms, which is expected to be linearly to the effective surface area (Fig.

S16). The double-layer capacitance is estimated by plotting the ΔJ (J_a-J_c) at 1.15 V vs. RHE against the scan rate, where the slope is twice C_{dl}. The calculated values of electrochemical double-layer capacitance are listed in Table S2.

Table S2. List of the electrochemical double-layer capacitance (C_{dl}).

Samples	C_{dl} [mF cm^{-2}]
S-LDH-1	4.2
S-LDH-2	4.3
S-LDH-3	5.2
S-LDH-4	5.0
LDH-1	4.3
LDH-2	4.1
LDH-3	4.9
LDH-4	4.5
S-NF	1.6
bare NF	1.2

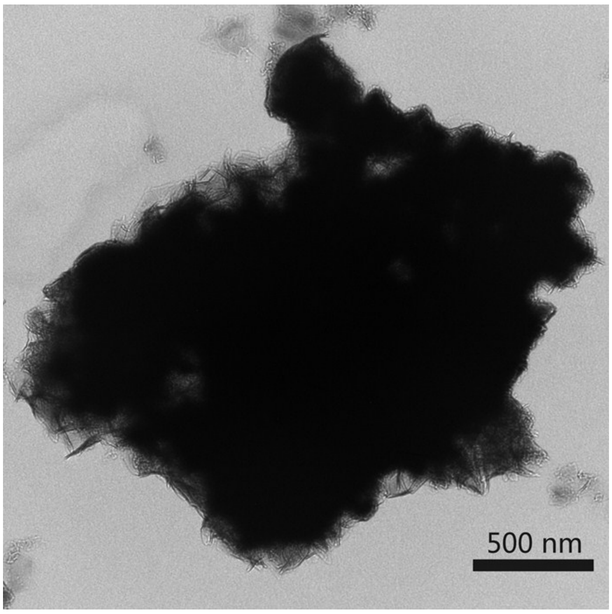

Fig. S17 TEM image of the S-LDH-3 after 20h stability test.

Reference

1. Xie, J.; Zhang, J.; Li, S.; Grote, F.; Zhang, X.; Zhang, H.; Wang, R.; Lei, Y.; Pan, B.; Xie, Y. *J. Am. Chem. Soc.* **2013**, *135*, 17881.