Supporting Information (SI):

# Formation of porous NiCoV-LTH nanosheet arrays by *in-situ* etching of nickel foam for hydrogen evolution reaction at large current density

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## Experimental

### Chemicals and Reagents

All chemicals were of reagent grade and used without further purifications. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), Vanadium chloride ($VCl_3$), hexamethylenetetramine (abbreviation: HMT, $C_6H_{12}N_4$), $NH_4F$, potassium hydroxide (KOH) and ethanol absolute ($CH_3CH_2OH$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Nickel foam (NF), with a thickness of 1.5 mm, bulk density of 0.23 g/cm$^3$, and pore number per inch of 110, was acquired from Suzhou Jiashide Metal Foam Co., Ltd. (China). Ultrapure water (>18.2 MΩ cm) was provided by a PALL PURELAB Plus system.

### The synthesis of NiCoV-LTH/NF

Ni foam (1×4 cm$^2$) was cleaned ultrasonically with acetone, 3 M HCl solution, ultrapure water and ethanol for 15 min successively to obtain the clean surface. Then, 0.214g $CoCl_2 \cdot 6H_2O$, 0.425 g $VCl_3$, 2.1 g HMT and 0.2g $NH_4F$ were added to 30 mL of ultrapure water in turn to form a clear solution under magnetic stirring for 20 min. Afterwards, a piece of treated NF and the above solution were transferred into a 50 mL stainless–steel Teflon–lined autoclave and heat-treated at 120°C for 16 h. After that, the as-obtained sample was washed with ultrapure water and ethanol and dried in a vacuum at room temperature, named as NiCoV-LTH/NF.

### The synthesis of NiV-LDH/NF

For comparison, the NiV-LDH/NF sample was synthesized as followed as the procedure of NiCoV-LTH/NF apart from using the $CoCl_2 \cdot 6H_2O$.

**Characterizations**

X-ray diffraction patterns that reflecting phase composition and crystal structure were recorded by X-ray diffractometer with Cu Kα radiation (λ = 0. 15406 nm) at a scanning rate of 4°/min. Morphologic characteristics and microstructural evolution were characterized using field emission scanning electron microscope (FESEM, Hitachi, S-4800), together with transmission electron microscope (TEM, FEI Tecnai G2 F20STWIN) at an accelerating voltage of 200 kV. The surface elemental compositions and valence states of the samples were collected with X-ray photoelectron spectrometer (XPS, AXIS SUPRA).

**Electrochemical measurements**

All electrochemical tests were carried on an electrochemical workstation (CHI 660E, Shanghai Chen Hua) in a three-electrode system with an Hg/HgO electrode and a graphite rod were used as the reference electrode and the counter electrode, respectively. The recorded potentials were calibrated and subsequently converted into reversible hydrogen electrode (RHE) scale in accordance with the following equation: $E_{(RHE)} = E_{(Hg/HgO)} + 0.059 \times pH + 0.098$ V. The obtained samples with an area of 0.09 $cm^2$ were directly evaluated as working electrodes to characterize catalytic performance for Hydrogen Evolution Reaction (HER.) Linear sweep voltammetry (LSV) curves were recorded at a scanning rate of 5

mV $s^{-1}$ with 90% iR compensation. Tafel plot and corresponding Tafel slope values were obtained from LSV curves. The cyclic voltammetry (CV) was performed at different sweep rates, fitting a straight line between scanning rate and corresponding current density difference, and the half of the slope was recognized as electrochemical double-layer capacitance ($C_{dl}$) value. Electrochemical impedance spectroscopy (EIS) was executed within the frequency range from 0.1 Hz to 100 kHz at the overpotential of 280 mV. The long-term stability test was evaluated with amperometric i–t curve measurement.

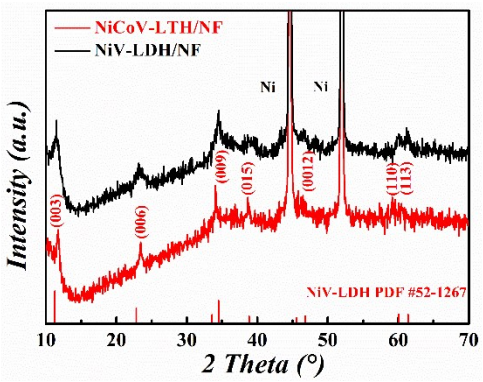


**Fig. S1** XRD pattern of NiV-LDH/NF and NiCoV-LTH/NF.

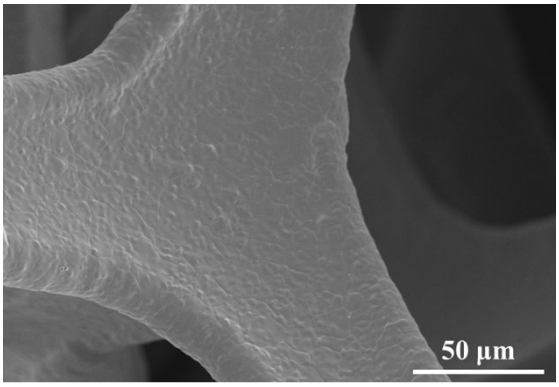


**Fig. S2** SEM image of pure NF.

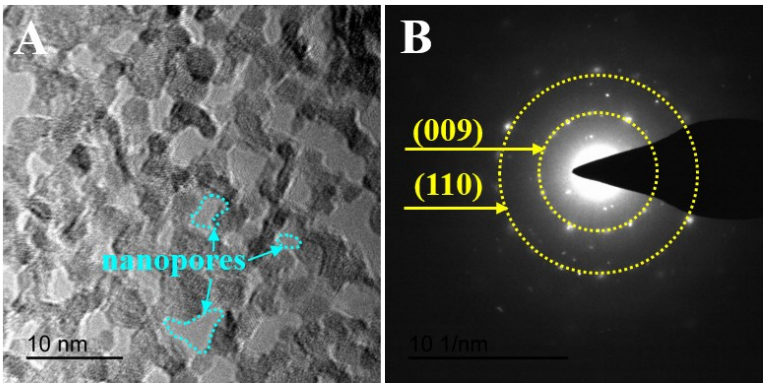


**Fig. S3** (A) TEM image and (B)SAED pattern of NiCoV-LTH/NF.

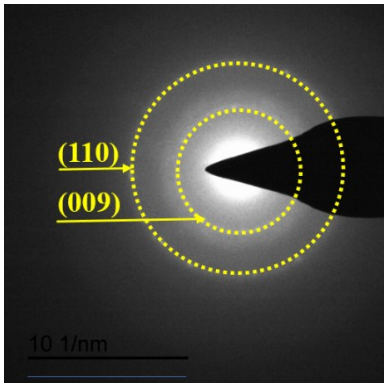


**Fig. S4** SAED pattern of NiV-LDH/NF.

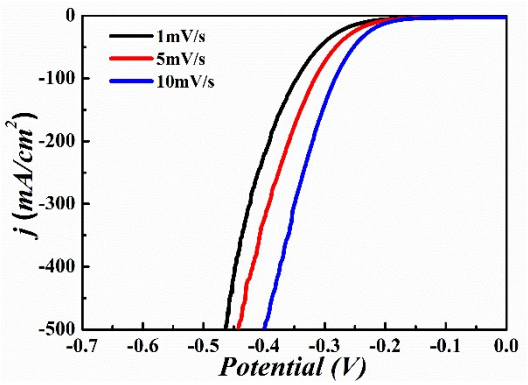


**Fig. S5** HER polarization curves of NiCoV-LTH/NF in 1.0 M KOH at different scan rates.

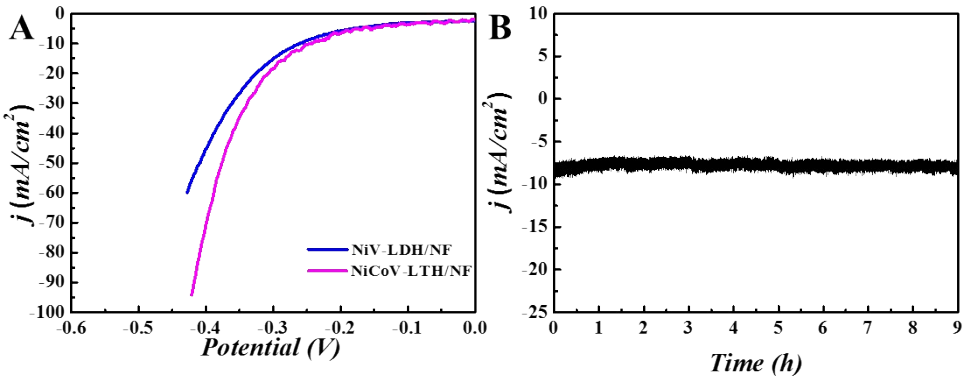


**Fig. S6** (A)HER polarization curves of NiV-LDH/NF and NiCoV-LTH/NF in 1.0 M PBS solution; (B) Chronoamperometric measurements of the NiCoV-LTH/NF electrode in 1.0 M PBS solution.

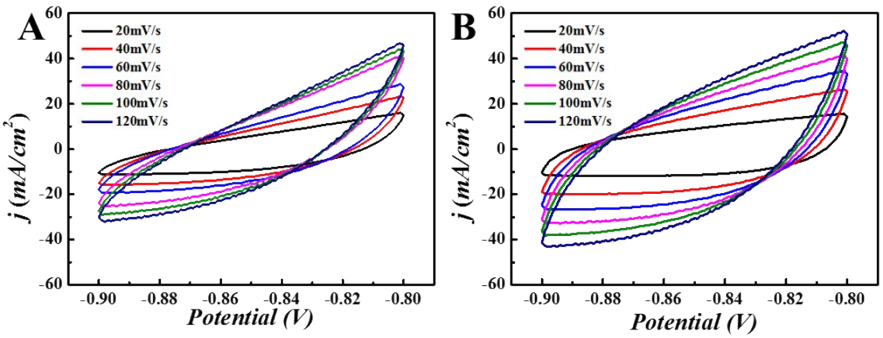

**Fig. S7** CV curves of (A) NiV-LDH/NF and (B) NiCoV-LTH/NF at different scan rates.

**Table S1.** Comparison of HER performance for LDH-based electrocatalysts in 1.0 M KOH.

| Catalyst | Electrolyte | Current density ($j$ (mA/cm$^2$)) | Overpotential at corresponding $j$ (mV) | Stability test | Tafel slope (mV/dec) | Reference |
|---|---|---|---|---|---|---|
| **NiCoV-LDH/NF** | **1 M KOH** | **10**<br>**100**<br>**500** | **175**<br>**308**<br>**428** | **20 h** | **142** | **This work** |
| Cu@CoFe-LDH/Cu | 1 M KOH | 10<br>100 | 171<br>200 | 48h | 36.4 | Nano Energy, 41, (2017) 327–336 |
| $Ni_3S_2$@NiV-LDH/NF | 1 M KOH | 10<br>100 | 126<br>256 | 100 h | 90 | Nanoscale 11 (2019) 8855-8863 |
| NiFeCo LDH/NF | 1 M KOH | 10<br>100 | 108<br>245 | 50 h | 73 | ACS Sustainable Chem. Eng. 7 (2019) 10035-10043 |
| CoMoV LDH/NF | 1 M KOH | 10<br>100 | 270<br>360 | 20 h | 182 | Chem. Commun. 55 (2019) 3521-3524 |
| $Zn_{1-x}Fe_x$–LDH/NF | 1 M KOH | 10<br>100 | 221<br>340 | 30 h | 110 | Small 14 (2018) 1803638 |
| $Ni_{0.75}Fe_{0.125}V_{0.125}$-LDHs/NF | 1 M KOH | 10<br>100 | 125<br>220 | 15 h | 62 | Small 14 (2018) 1703257 |
| $Ni_{1-x}Fe_x$-LDH | 1 M KOH | 10<br>50 | 242<br>319 | 36 h | 110 | ACS Appl. Mater. Interfaces 10 (2018) 42453−42468 |
| CoFe LDH-F | 1 M KOH | 10<br>100 | 255<br>352 | 35 h | 95 | ACS Appl. Mater. Interfaces 8 (2016) |

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