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Three-dimensional NiFe Layered Double Hydroxide Film for High-efficiency Oxygen Evolution Reaction

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Supporting Information.

Experimental Section:

NiFe-LDH nanoplate (NiFe-LDH NP) film on Ni foam was synthesized by a simple hydrothermal method. In a typical procedure, $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (0.5 mmol) and $CO(NH_2)_2$ (5 mmol) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Nickel foam (about 3 cm × 2 cm) was carefully cleaned with concentrated HCl solution (37 wt%) in an ultrasound bath for 5 min in order to remove the surface NiO layer, and then deionized water and absolute ethanol were used for 5 min each to ensure the surface of the Ni foam was well cleaned. The aqueous solution and the Ni foam were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 120 °C for 12 h, and then allowed to cool to room temperature naturally. A brown thin film on the metal substrate was formed and subsequently rinsed with distilled water, ethanol each for 5 minutes with the assistance of ultrasonication, and dried at 80 °C for 6 h. It is hard to measure the accurate mass-loading of the NiFe-LDH NPs on the Ni foam because some of the Ni substrate would be oxidized by the Fe^{3+} ion and dissolved in the solution. However, since the coverage and the size of the nanoplates were similar to the $Ni(OH)_2$ NP film, we believe the mass-loading of the NiFe-LDH NP film was comparable to the $Ni(OH)_2$ NP film.

$Ni(OH)_2$ NP film was synthesized by a similar procedure as mentioned above, but without adding $Fe(NO)_3 \cdot 9H_2O$, and changing the amount of $Ni(NO_3)_2 \cdot 6H_2O$ to 1 mmol. After carefully weighting the total mass of the film before and after hydrothermal growth, a mass-loading of 1 $mg \cdot cm^{-2}$ was achieved for $Ni(OH)_2$ NP film. Therefore, we loaded 1 $mg \cdot cm^{-2}$ of 20 wt% Ir/C catalyst on nickel foam as comparison.

X-ray powder diffraction patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10 (°)/min in the range from 5 to 90°. The size and morphology of the samples were characterized using a field-emission SEM (JEOL JSM6335) operating at 20 kV and a TEM system (H800) operating at 200 kV. XPS and Raman spectrums were carried out by using a model of ESCALAB 250 and LabRAMA ramis.

The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.) Prior to

the test measurements, H_2 was bubbled through the electrolyte solution to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H^+/H_2 redox couple. Cyclic voltammetry and linear sweep voltammetry with scan rates of 1 $mV \cdot s^{-1}$ were conducted in 0.1 M and 1 M KOH solution. Pt was used as the counter electrode. AC impedance measurements were carried out in the same configuration at open circuit voltage from 10^5-0.1 Hz with an AC voltage of 5 mV. In all measurements, we used saturated calomel electrode (SCE) as the reference. It was calibrated with respect to reversible hydrogen electrode (RHE) by using Pt electrode as standard electrode. All the potentials reported in our manuscript are against RHE. The stability testing of the three films were operated at constant overpotentials for achieving a high initial current density.

Figures:

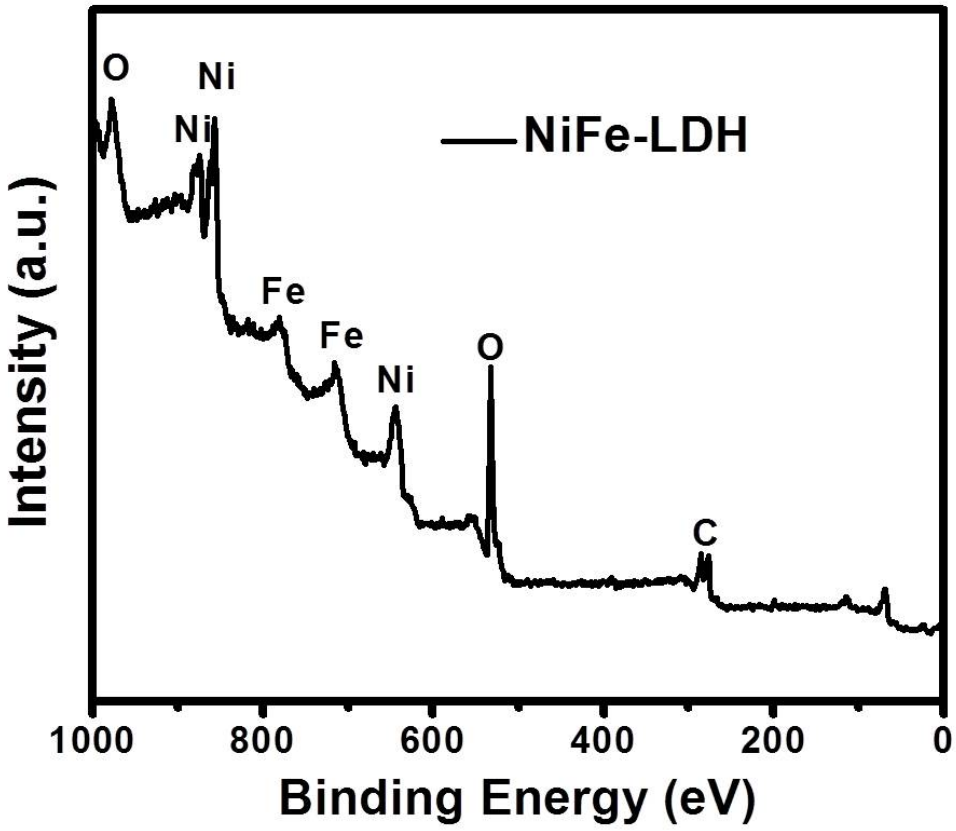

Figure S1. XPS spectra of NiFe-LDH NP film.

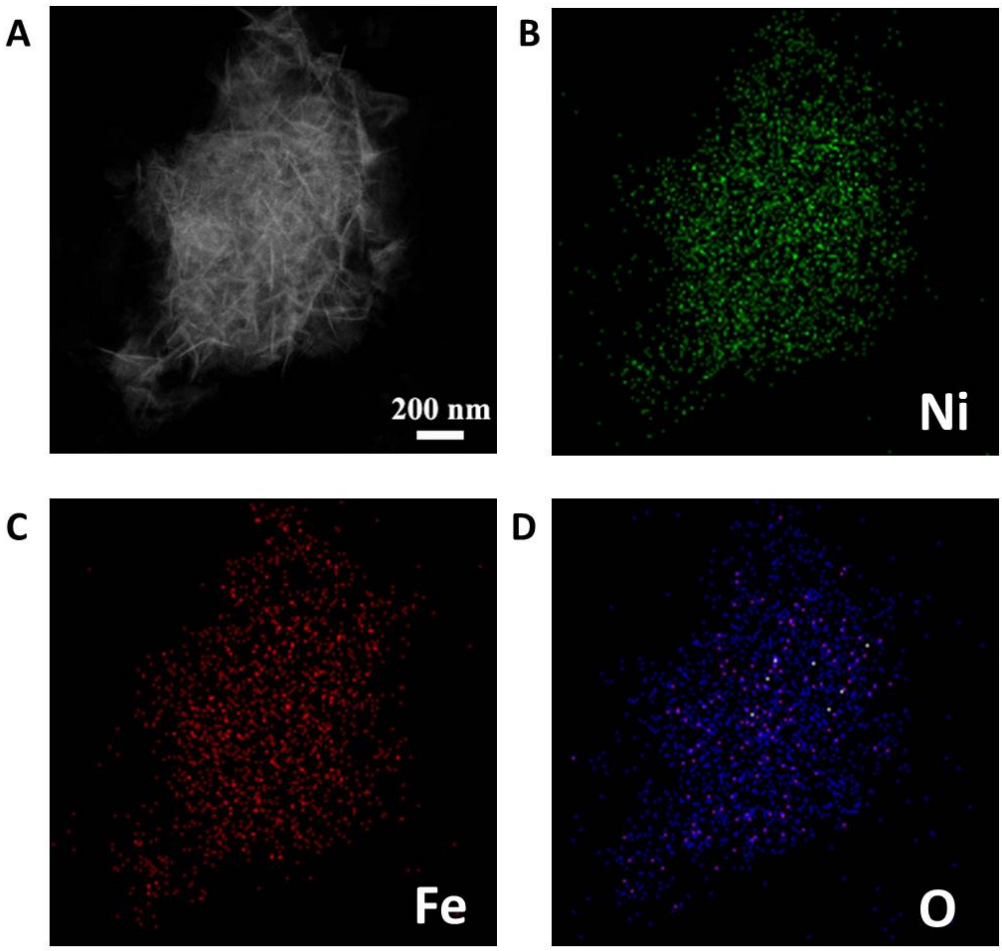

Figure S2. EDX mapping results of NiFe-LDH NP film.

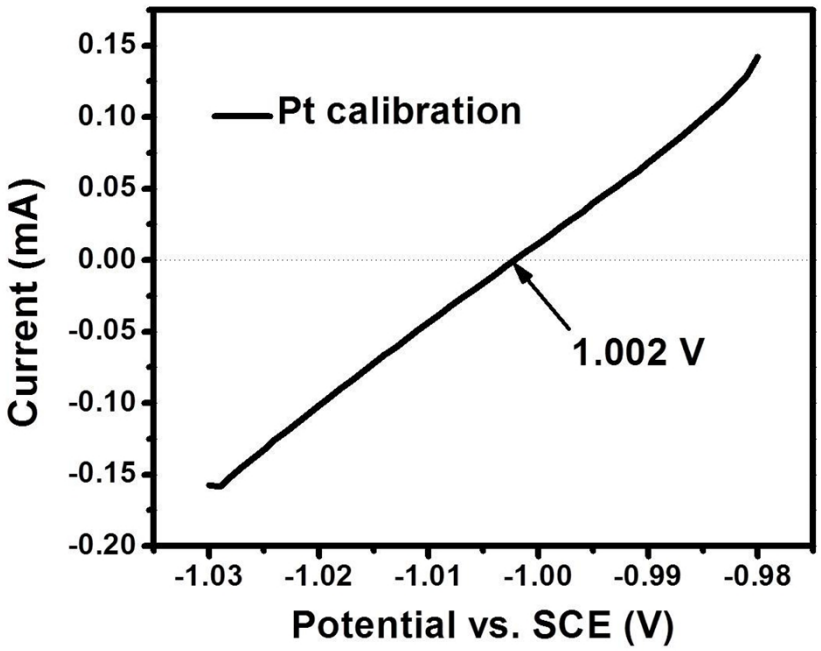

Figure S3. Potential calibration of the reference electrode in 0.1 M KOH solution. In this case, the potentials showed were calculated by the following equation:

$$V_{RHE} = V_{SCE} + 1.002\ V$$

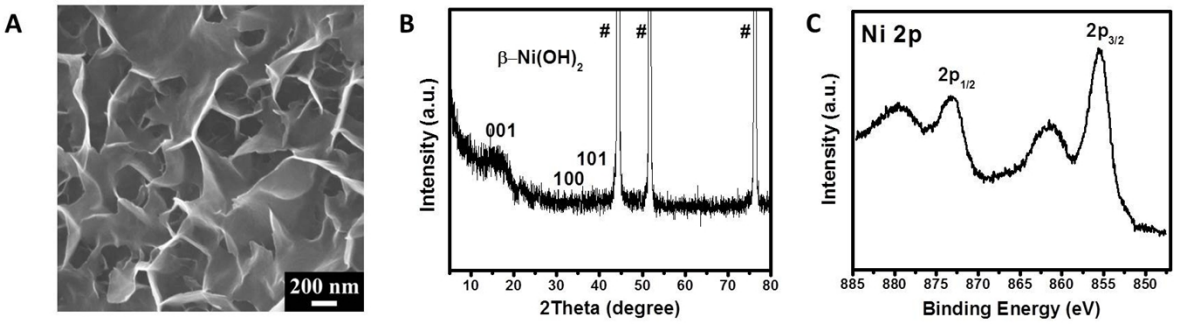

Figure S4. (A), (B) and (C), SEM image, XRD spectra and XPS data of $Ni(OH)_2$ NP film.

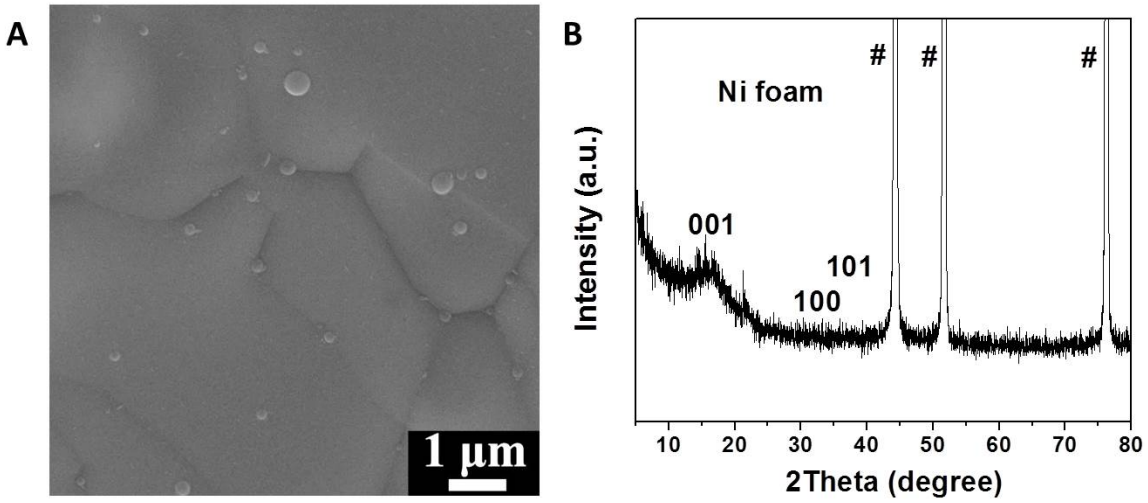

Figure S5. (A) and (B), SEM image and XRD pattern of pure nickel foam. The nickel foam exhibits a flat surface with inevitably formed $Ni(OH)_2$, which results in the reasonable OER activity.

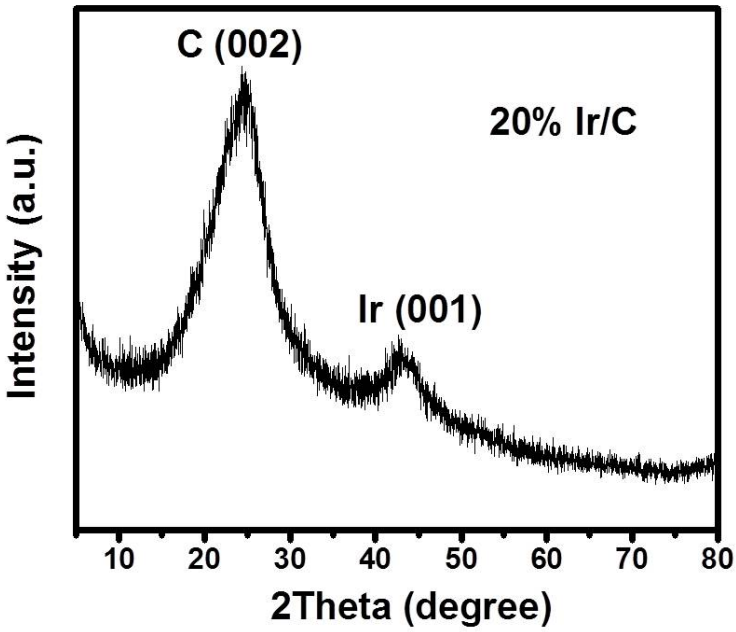

Figure S6. XRD pattern of 20 wt% Ir/C catalyst.

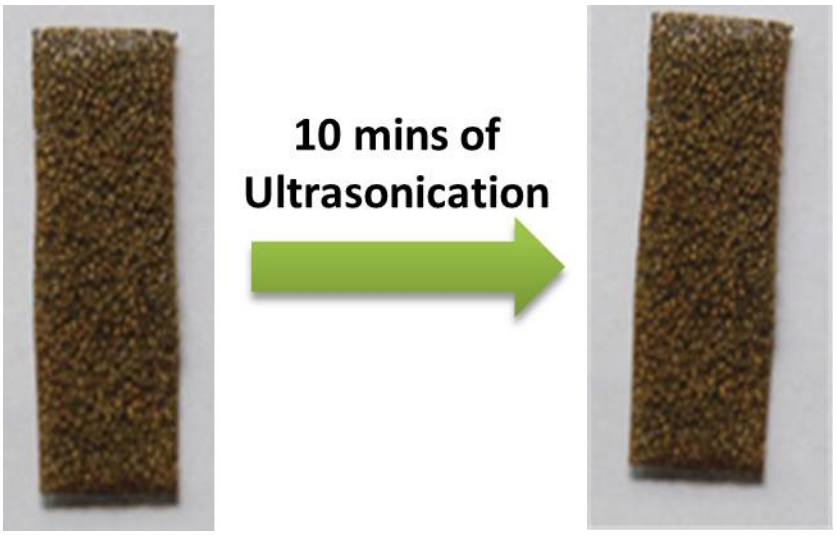

Figure S7. Optical images of NiFe-LDH NP film before (left) and after (right) ultrasonication treatment for 10 minutes. Long time ultrasonication cannot dislodge the surface color of the NiFe-LDH NP film, indicating the strong binding between the NiFe-LDH layer and the underlying substrate.

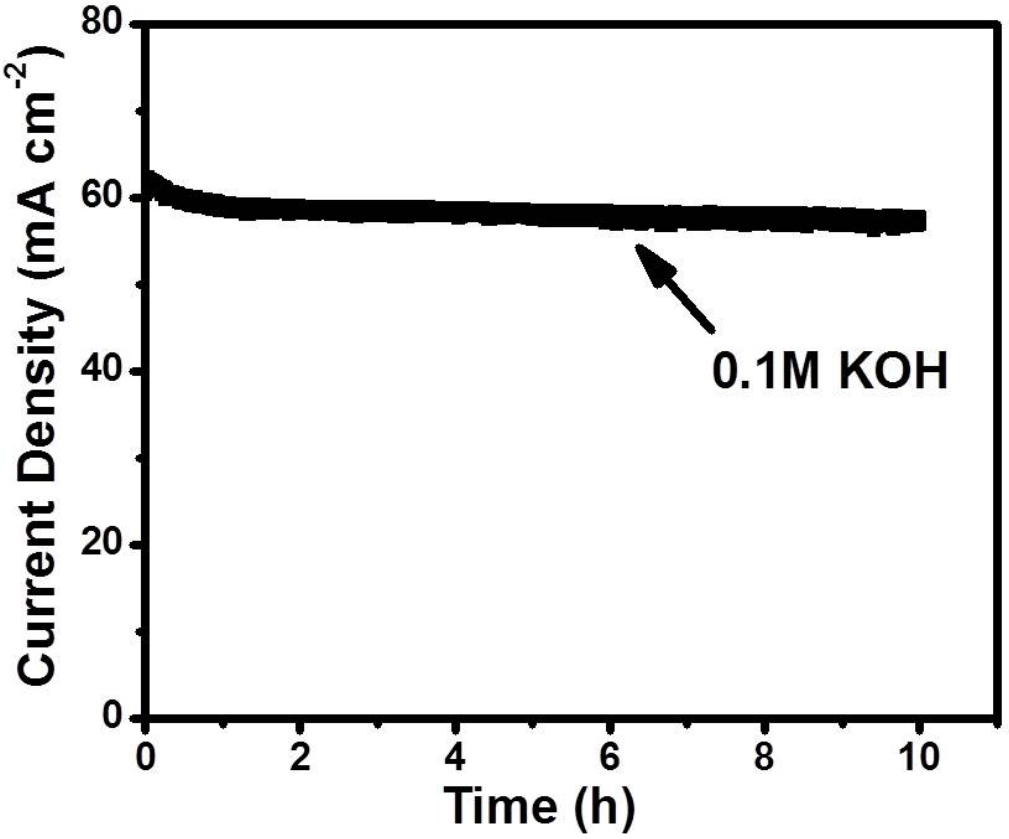

Figure S8. Stability testing of $Ni(OH)_2$ NP film for OER. The $Ni(OH)_2$ NP film showed a good stability, further demonstrating the advantage of the 3D structure design.

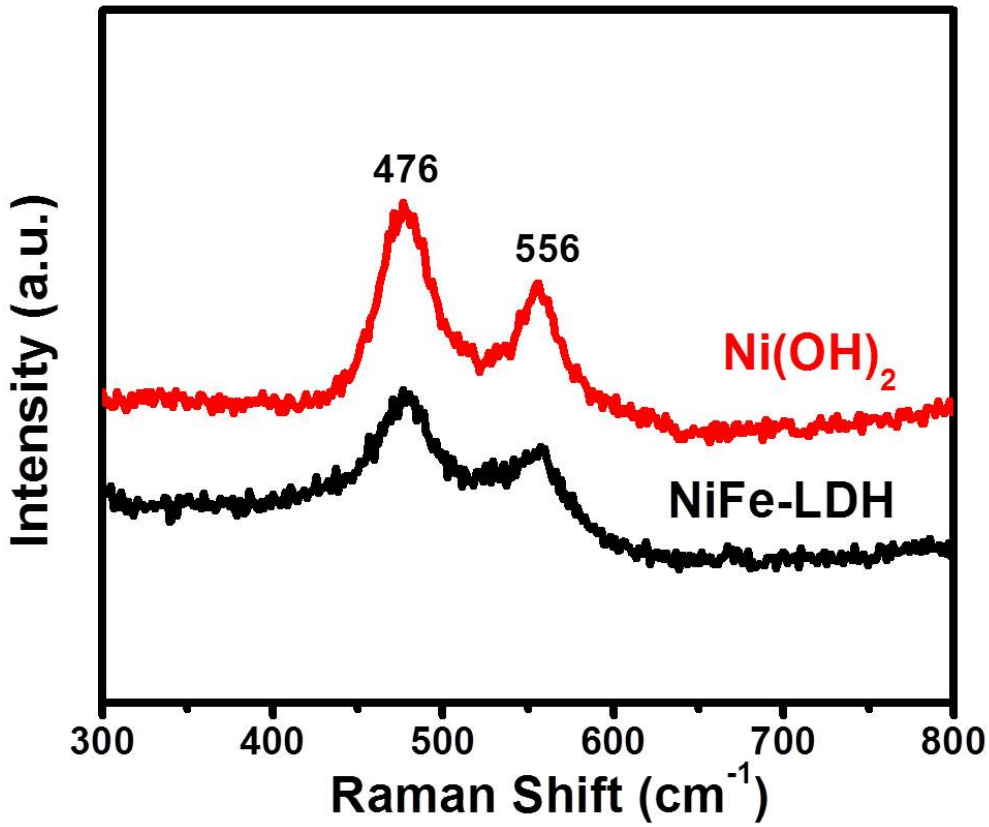

Figure S9. *In-situ* Raman spectroscopy of NiFe-LDH and $Ni(OH)_2$ NP film under OER operation. The intensity ratios of the two bands (I_{476}/I_{556}) of NiFe-LDH was lower than that of $Ni(OH)_2$, indicating a more disorder structure with higher defects.

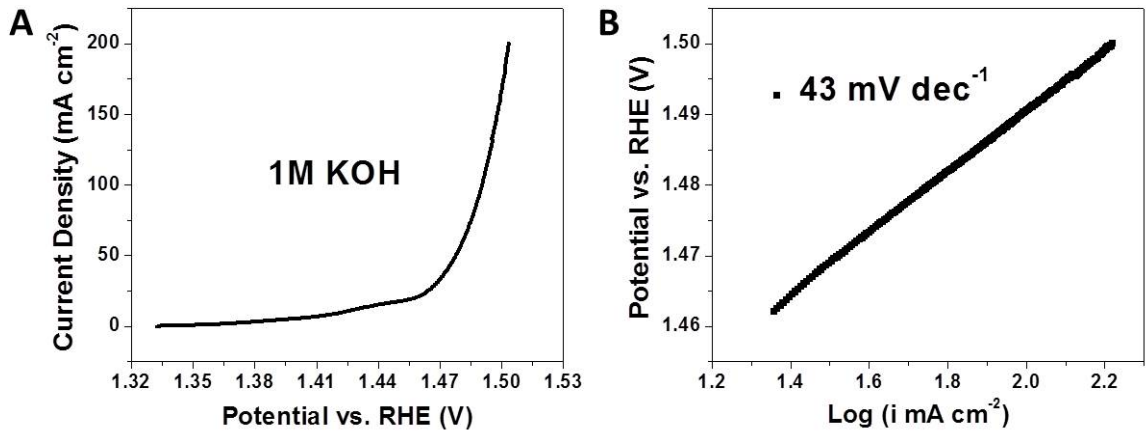

Figure S10. OER activity of NiFe-LDH NP film in 1 M KOH solution.

Samples	Onset Potential (V vs. RHE)	Tafel slope ($mV \cdot dec^{-1}$)	Stability
NiFe-LDH NP film (this work)	1.46	50	~200 $mA \cdot cm^{-2}$ for 10 h
Ni_3S_2 nanorods array on nickel foam (ref 35)	1.39	159	~10 $mA \cdot cm^{-2}$ for 10 h
"inverse opal" Fe_2O_3 film (ref 33)	1.5	64	NA
3D Ni/carbon on Nickel foam (ref 32)	1.5	NA	800 cycles
$Ni_xCo_{3-x}O_4$ nanowires arrays (ref 29)	1.5	59	NA

Table S1. Comparisons of our 3D NiFe-LDH NP electrodes with previous reports. Among these 3D electrodes for OER, our sample showed the lowest Tafel slope, reasonable onset potential and the most stable performance.

Samples	Specific Surface Area
Pure Ni foam	0.06 m^2/cm^2
NiFe-LDH NPs on Ni foam	0.24 m^2/cm^2

Table S2. Specific surface areas of pure Ni foam and NiFe-LDH NPs grown on Ni foam. The specific surface area of the NiFe-LDH NP film is ~4 times that of pure Ni foam.