

Rational composition and structure design of the in-situ grown nickel-based electrocatalysts for efficient water electrolysis

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Experimental Section

Synthesis of the Ni/NiO array electrode. All chemicals used in this work were analytical reagent grade and commercially available, and used without further purification.

The Ni(OH)₂·0.75H₂O flake arrays were grown on nickel foams by a facile hydrothermal method according to the previous reported work¹. Briefly, 4 mmol Ni(NO₃)₂·6H₂O, 20 mmol urea and 8 mmol NH₄F were completely dissolved in 80 ml deionized water under magnetic stirring. A nickel foam substrate was vertically immersed in the solution after chemically cleaned with acetone, methanol, and deionized water. The resulting solution with nickel foams were then sealed in a 100-ml Teflon-lined stainless steel autoclave, and maintained at 120 °C for 6 h, followed by rinsing the nickel foams with deionized water and dried at 60 °C for 12 h. The loading mass of Ni(OH)₂·0.75H₂O on Ni foam is ~4 mg cm⁻². Powder products in the solution were collected by centrifugation. Secondly, the as-grown samples both on the nickel foams and powder from the solution were treated with a special Al reduction process to obtain the Ni/NiO electrode and Ni/NiO powder, according to the previous work

of our group². Specifically, the as-grown samples and aluminum were separately placed in a two zone tube furnace and then evacuated to a base pressure ~ 4 Pa, then the aluminum was heated at 850 °C and samples were heated at 300 °C, for 2h.

Synthesis of the NiO and Ni electrodes. The $\text{Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$ flake arrays were grown on nickel foams and $\text{Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$ powder was collected with the same method described above. Then they were annealed in Ar at 350 °C for 2h to obtain the NiO electrode and the NiO power. Similarly, the samples were annealed in H_2/Ar (H_2 10%) at 300 °C for 2h to obtain the Ni electrode and the Ni power.

Synthesis of the NiFe LDH array electrode. The NiFe LDH flake arrays were grown on nickel foams by a similar method for the preparation of $\text{Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}/\text{Ni}$ foam. Specifically, 4 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.45 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 20 mmol urea and 8 mmol NH_4F were completely dissolved in 80 ml deionized water under magnetic stirring. A nickel foam substrate was vertically immersed in the solution after chemically cleaned with acetone, methanol, and deionized water. The resulting solution with nickel foams were then sealed in a 100ml Teflon-lined stainless steel autoclave, and maintained at 120 °C for 6 h, followed by rinsing the nickel foams with deionized water and dried at 60 °C for 12 h. The loading mass of NiFe LDH on Ni foam is ~ 4 mg cm^{-2} . Powder products in the solution were collected by centrifugation.

Preparation of the NiFe LDH film electrode, RuO_2 film electrode and Pt/C electrode. Ethanol suspensions containing 900 μL ethanol, 4 mg of catalyst (NiFe LDH powder or RuO_2 powder or commercial 20 wt.% Pt/C powder), and 100 μL 5 wt % Nafion solutions were obtained by magnetic stirring overnight. Then the 1mL catalyst ink suspension was coated onto 1 cm^2 Ni foam and then it was left to dry in air.

Characterization. The samples were characterized by powder X-ray diffraction (XRD) using a Siemens D5000 X-ray diffract meter with nickel filtered Cu K α radiation ($k = 1.5418 \text{ \AA}$) at a scanning rate of $0.1^\circ \cdot \text{min}^{-1}$ in the 2θ range of 25° – 85° . The chemical compositions, the sizes and morphologies, and the microstructures of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR), and X-ray photoelectron spectroscopy (XPS, ESCALab250). Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020 analyzer at -196°C . The weight of the Ni/NiO powder used in the measurement was 100–200 mg.

Electrochemical measurements. The electrochemical tests were carried out in a conventional three electrode electrochemical cell by using a CHI660E. A Hg/HgO (1 M NaOH) and Pt wire were used as the reference electrode and the counter electrode, respectively. The as prepared samples on Ni foams were directly used as the working electrodes. All the electrochemical measurements of catalysts were measured in 1 M NaOH solution ($\text{pH} = 14$) after purging the electrolyte with N_2 gas for 30 min at 25°C . The potential, measured against a Hg/HgO (1 M NaOH) electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{vs \text{ RHE}} = E_{vs \text{ Hg/HgO}} + E_{\text{Hg/HgO}}^\theta + 0.059 \text{ pH} - iR$, and all the polarization curves were iR corrected using the data of the electrochemical impedance spectroscopy (EIS) measurements. Water-alkaline electrolysis measurement was carried out in a standard two-electrode system by using the Ni/NiO array/Ni foam ($1 \times 1 \text{ cm}$) as cathode and the single-crystalline NiFe LDH array/Ni foam ($1 \times 1 \text{ cm}$) were as anode. Linear sweep voltammetry was carried out at 1 mV s^{-1} for the polarization curves. Chronopotentiometry was measured under a constant current density of 20 mA cm^{-2} .

References

1. Wu, H.; Xu, M.; Wu, H.; Xu, J.; Wang, Y.; Peng, Z.; Zheng, G. Aligned NiO nanoflake arrays grown on copper as high capacity lithium-ion battery anodes. *J Mater Chem* 2012, 22, 19821.
2. Wang, Z.; Yang, C.; Lin, T.; Yin, H.; Chen, P.; Wan, D.; Xu, F.; Huang, F.; Lin, J.; Xie, X.; Jiang, M. Visible-light photocatalytic, solar thermal and photoelectrochemical properties of aluminium-reduced black titania. *Energy & Environmental Science* 2013, 6, 3007.

Supplementary data

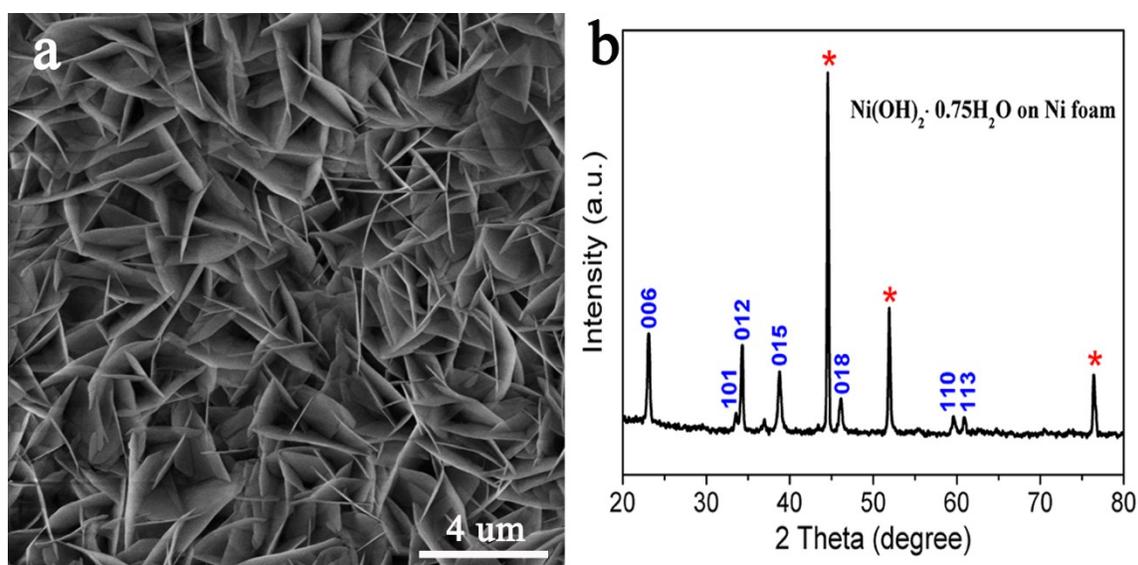


Figure S1. (a) SEM image and (b) XRD pattern of Ni(OH)₂·0.75H₂O nanoflake arrays on Ni foam. Diffraction peaks corresponding to the nickel foams substrate are marked with asterisks.

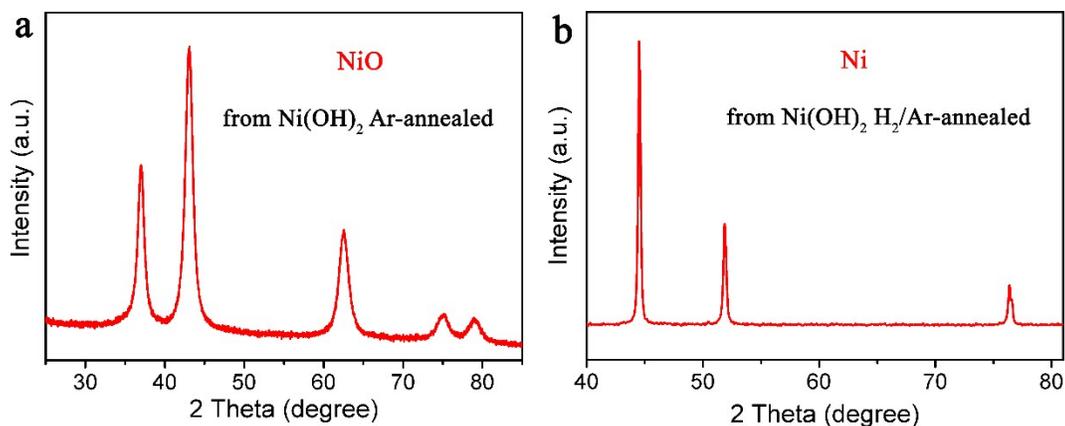


Figure S2. (a) XRD pattern of NiO powder which is obtained from Ni(OH)₂·0.75H₂O annealed in Ar at 350 °C for 2h. (b) XRD pattern of Ni powder which is obtained from Ni(OH)₂·0.75H₂O annealed in H₂/Ar at 300 °C for 2h.

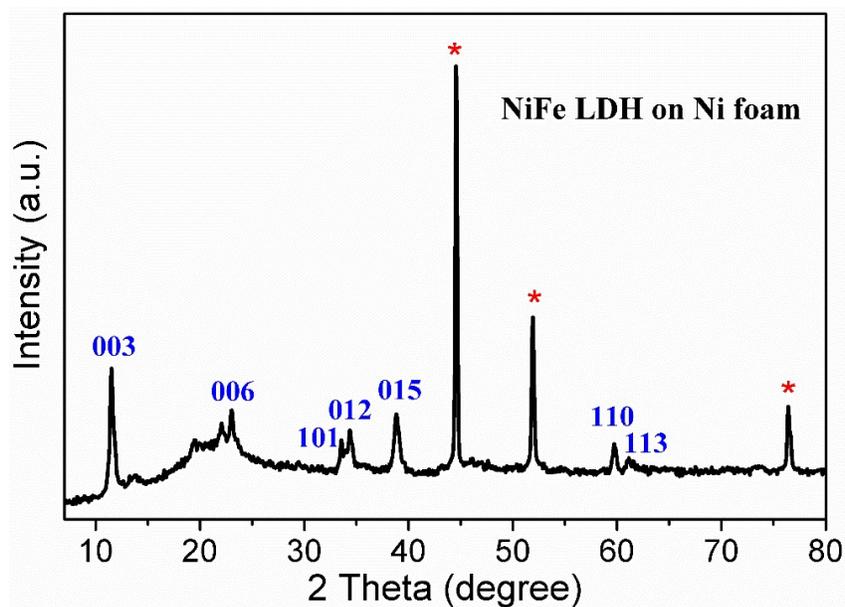


Figure S3. XRD pattern of the single-crystalline NiFe LDH flake arrays on Ni foam. Diffraction peaks corresponding to the nickel foams substrate are marked with asterisks.

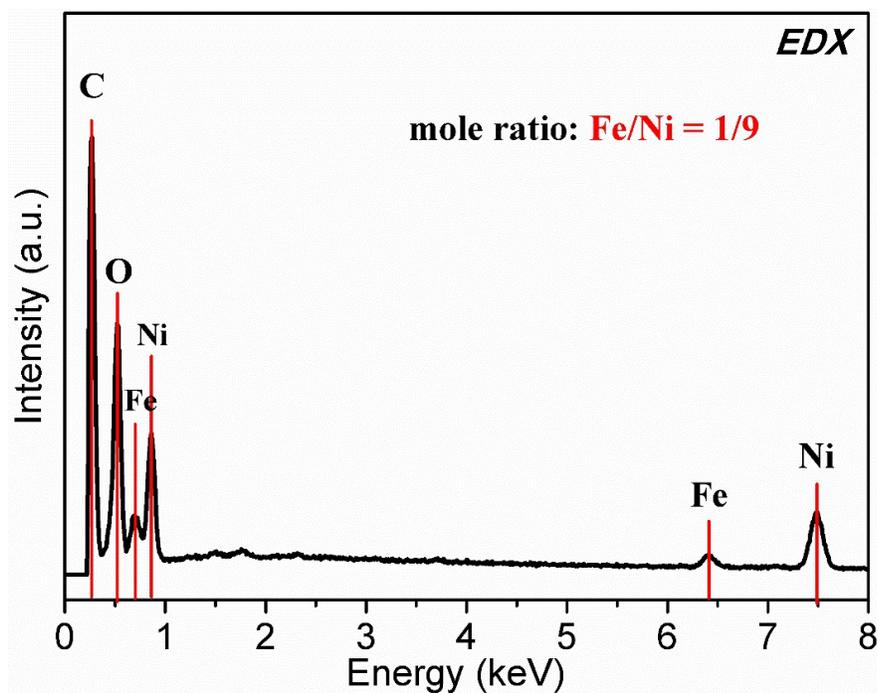


Figure S4. Energy dispersive X-ray spectrum of NiFe LDH powder.