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Electronic Supplementary Information

Inlay Ultrafine Ru Nanoparticles into Self-supported $Ni(OH)_2$ Nanoarray for Hydrogen Evolution with Low Overpotential and Enhanced Kinetics

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Experimental Section

Materials: All chemicals and solvents were obtained commercially and used without further purification.

Synthesis of the NiFe LDH/NF: NiFe LDH/NF was prepared as reported with urea as precipitant. In detail, 0.4 mmol $Ni(OH)_2 \cdot 6H_2O$, 0.4 mmol $Fe(OH)_3 \cdot 9H_2O$ and 120 mg urea were dissolved into 15 mL water. Then the solution was transferred to a 25 mL Teflon-lined stainless-steel autoclave with a cleaned Ni foam (1 cm × 3 cm), which was sealed and maintained at 120 °C for 12 h in an electric oven, and then allowed to cool to room temperature to obtain NiFe LDH/NF.

Synthesis of the $Ni(OH)_2$/NF: A piece of Ni foam (1 cm × 3 cm) was immersed into a 15 mL solution containing 1 mM $Ni(OH)_2 \cdot 6H_2O$ and 10 mM urea. Then the above solution was transferred to a 25 mL Teflon-lined stainless-steel autoclave, which was sealed and maintained at 120 °C for 12 h in an electric oven, and then allowed to cool to room temperature to obtain $Ni(OH)_2$/NF.

Synthesis of Ru NPs: 100 mg $RuCl_3 \cdot xH_2O$ was dissolved in 5 mL H_2O which was recorded as solution A. Then, 10 mL $NaBH_4$ aqueous solution (containing 200 mg $NaBH_4$) was dropped into solution A slowly. The mixed solution was maintained at 100 ^oC for 2 h to obtain Ru NPs.

The preparation of Pt/C, Ru NPs and RuO_2 electrode: Typically, 25 mg commercial 10% Pt/C, Ru NPs or RuO_2 was dispersed in 1 mL mixture containing 500 μL water, 440 μL ethanol, 60 μL Nafion solution, and then the mixture was sonicated for more than 1 h to generate an uniform catalyst ink. Next, 16 μL of the dispersion was dropped onto 0.5 × 0.5 cm^{-2} Ni foam (1.6 mg cm^{-2}) carefully and dried at room temperature overnight to obtain Pt/C and RuO_2 electrode.

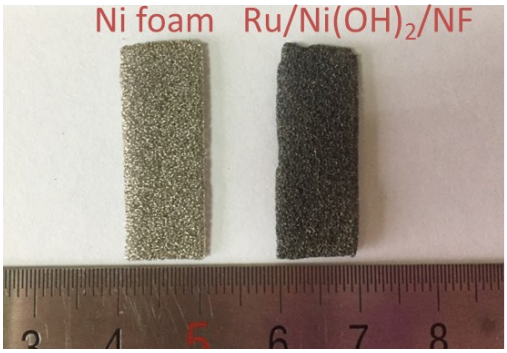

Fig. S1. Ni foam (left) and $Ru/Ni(OH)_2/NF$ (right).

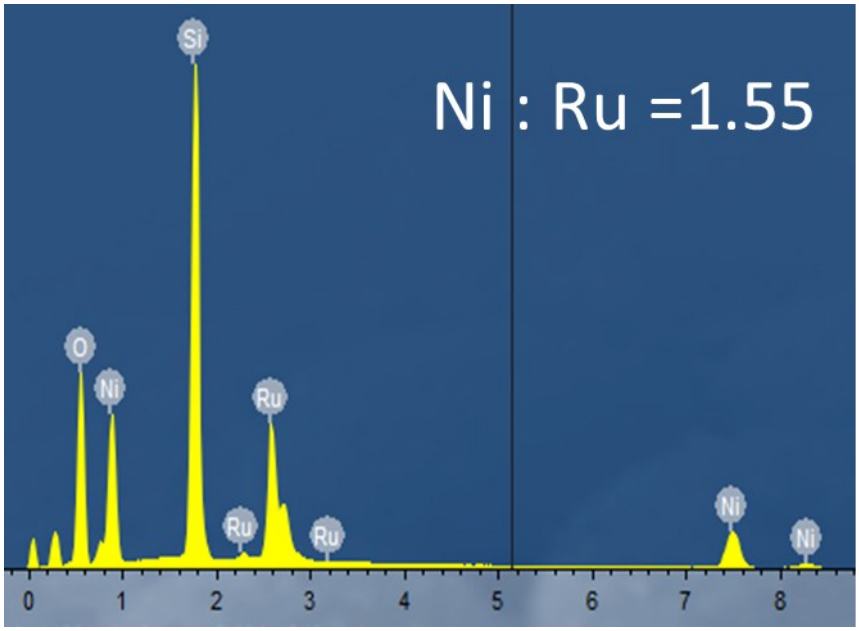

Fig. S2. EDS spectrum of $Ru/Ni(OH)_2$ scratched from the $Ru/Ni(OH)_2/NF$. Si peak is originated from Si substrate.

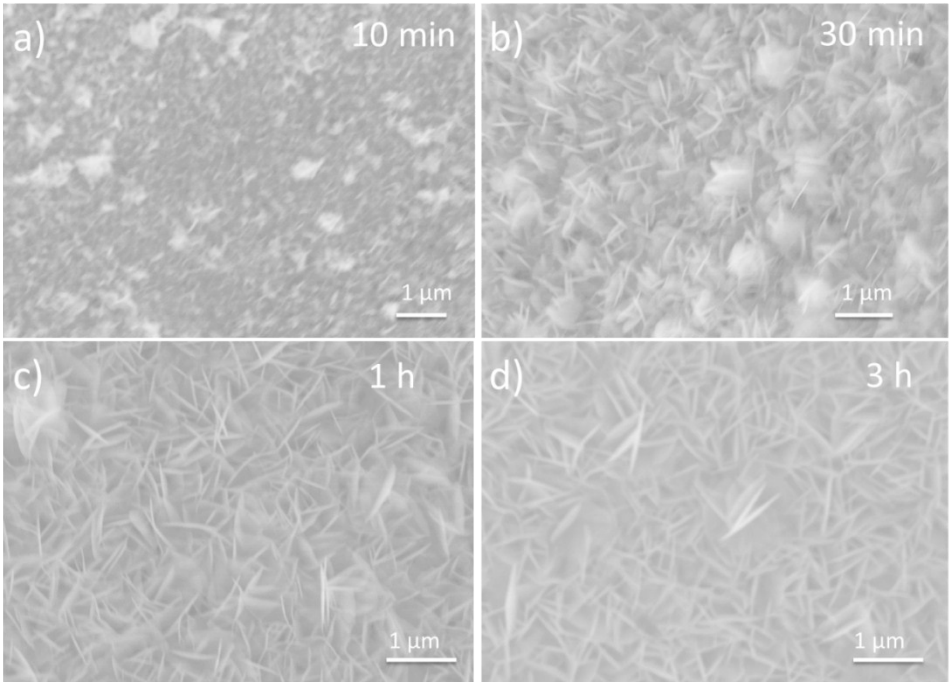

Fig. S3. Samples synthesized at different time scales. 10 min (a), 30 min (b), 1 h (c) and 3 h (d).

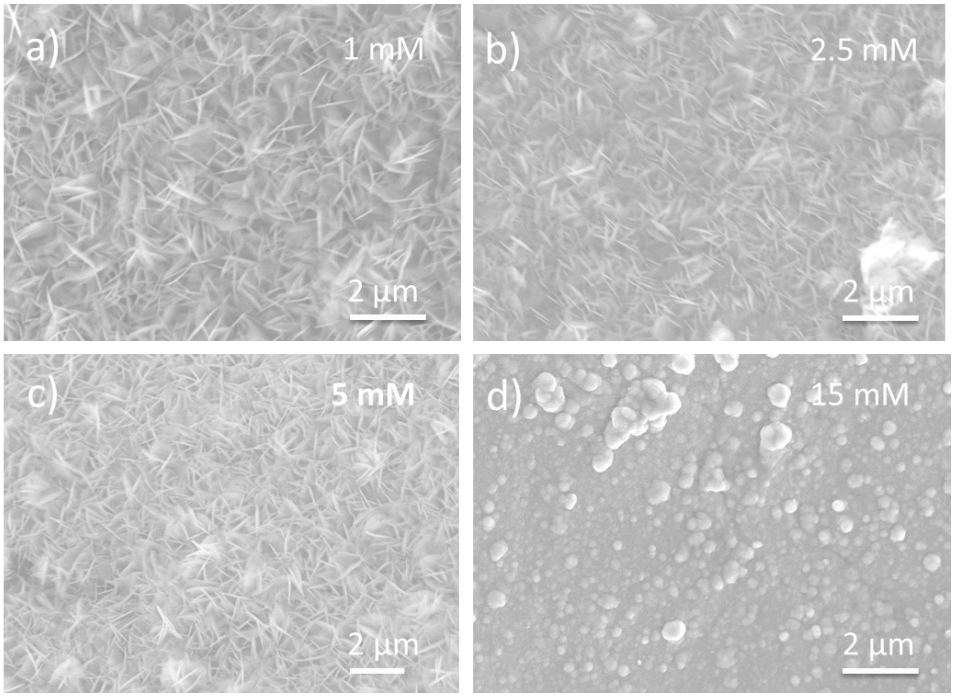

Fig. S4. Samples synthesized at different concentrations of $RuCl_3$ solution. 1.0 mM (a), 2.5 mM (b), 5.0 mM (c), 15.0 mM (d).

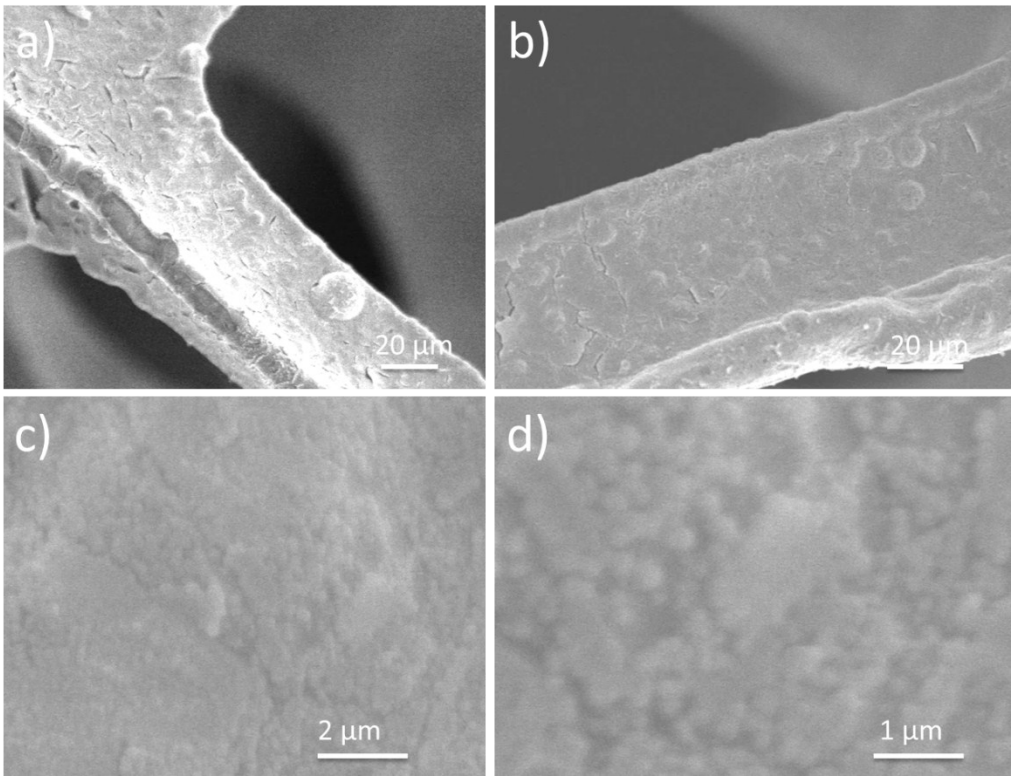

Fig. S5. Samples synthesized under Ar atmosphere.

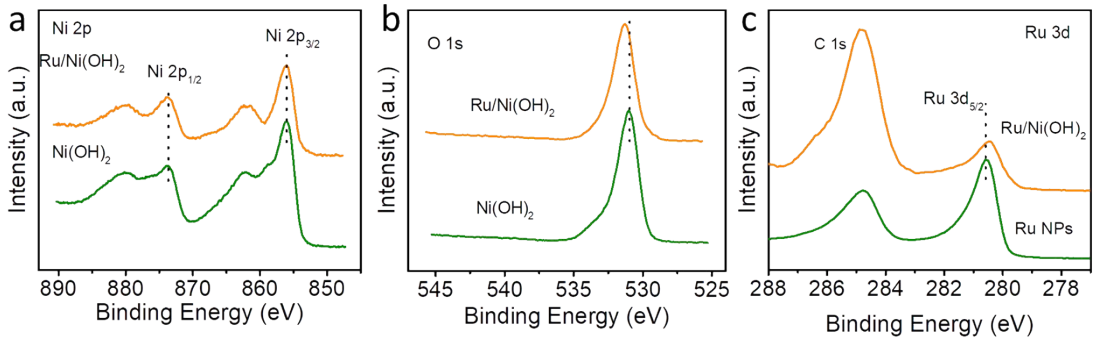

Fig. S6. High resolution XPS of $Ru/Ni(OH)_2$, $Ni(OH)_2$ and Ru NPs. (a) Ni 2p, (b) O 1s, (c) Ru 3d.

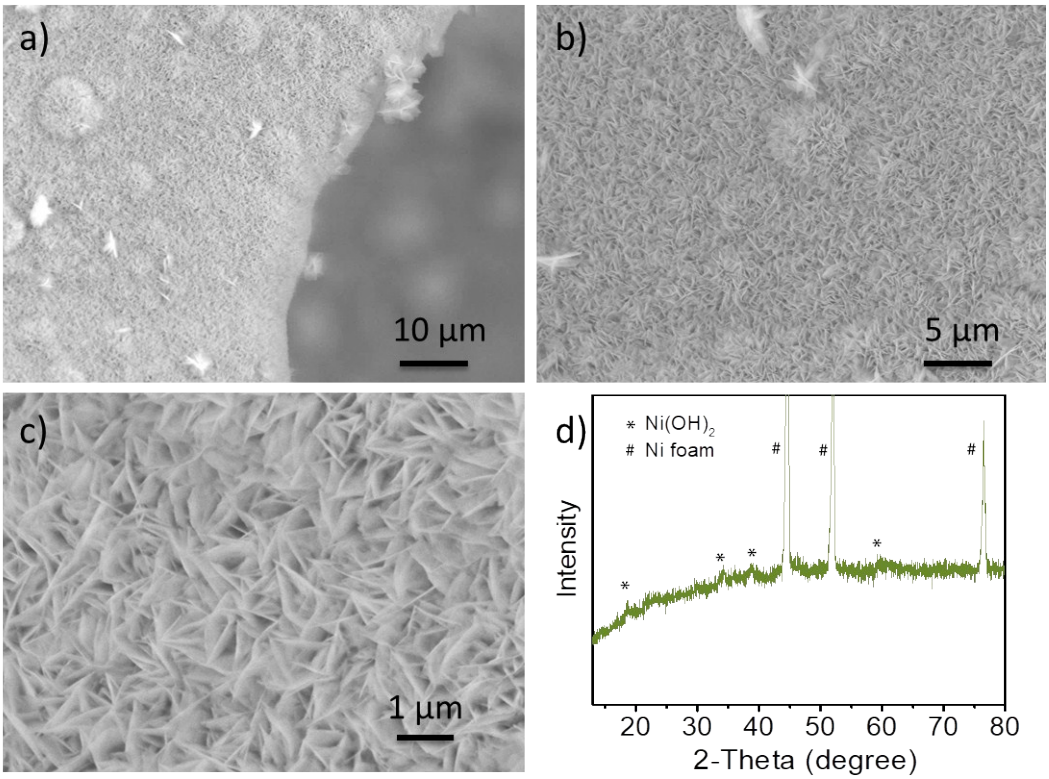

Fig. S7. (a-c) SEM images and (d) XRD pattern of $Ni(OH)_2$/NF.

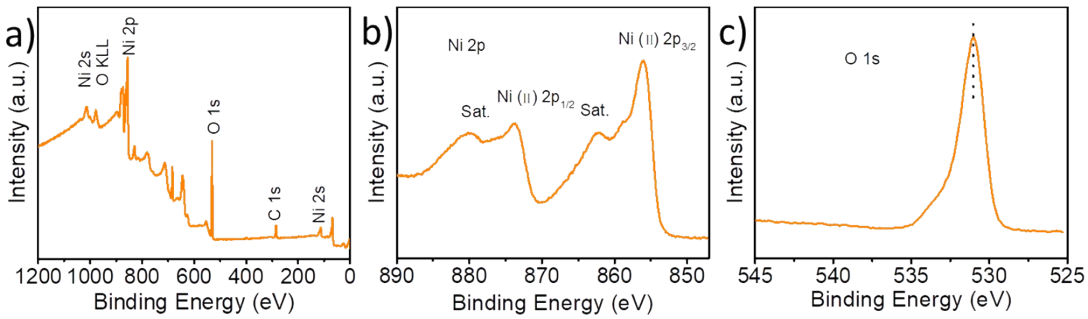

Fig. S8. XPS spectra of $Ni(OH)_2$.

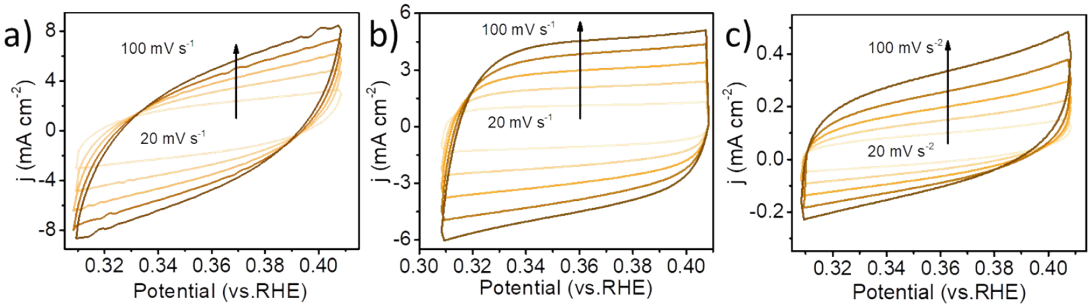

Fig. S9. CV curves for the as-prepared $Ru/Ni(OH)_2$/NF (a), Ru NPs/NF (b) and $Ni(OH)_2$/NF (c).

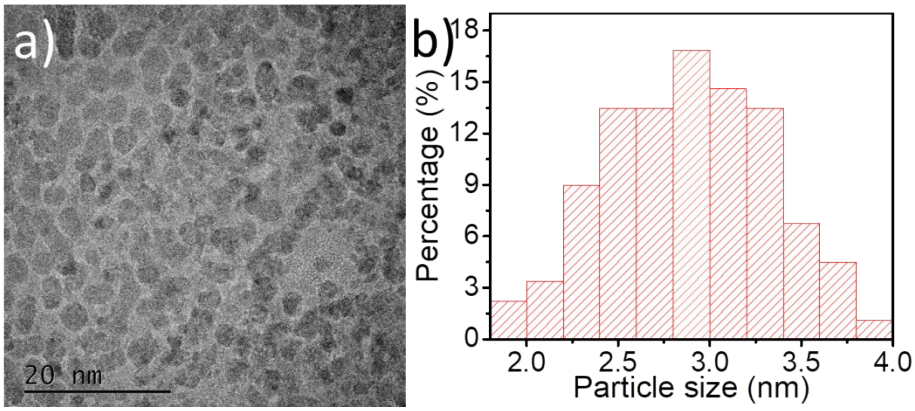

Fig. S10. (a) TEM image of Ru/Ni(OH)$_2$ after 20 h HER at 20 mA cm^{-2}, (b) the size distribution of Ru NPs in (a).

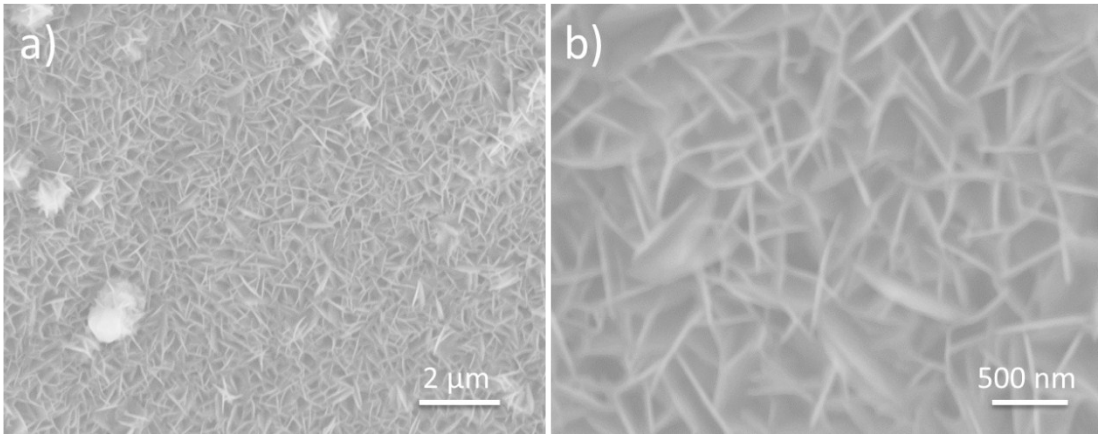

Fig. S11. SEM images of Ru/Ni(OH)$_2$/NF after HER at 20 mA cm^{-2} for 20 h.

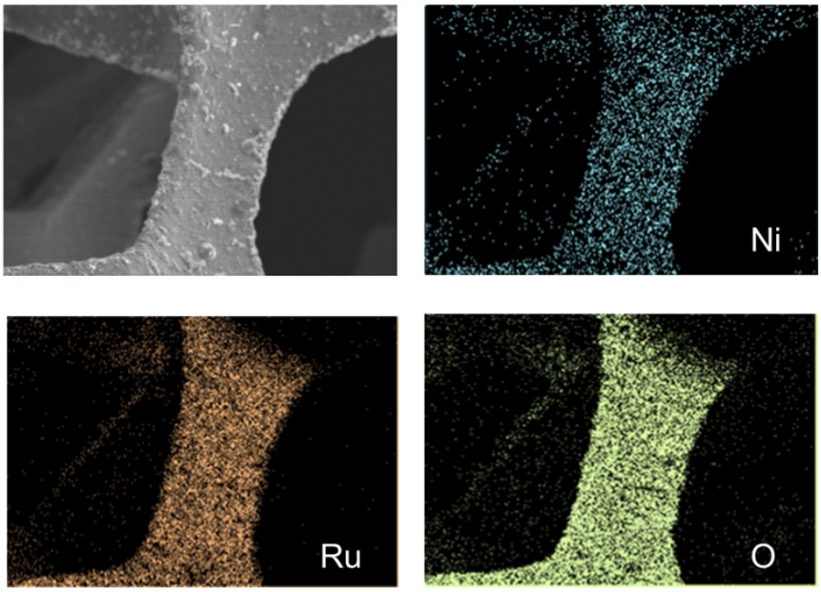

Fig. S12. SEM-mapping of Ru/Ni(OH)$_2$/NF after HER at 20 mA cm^{-2} for 20 h.

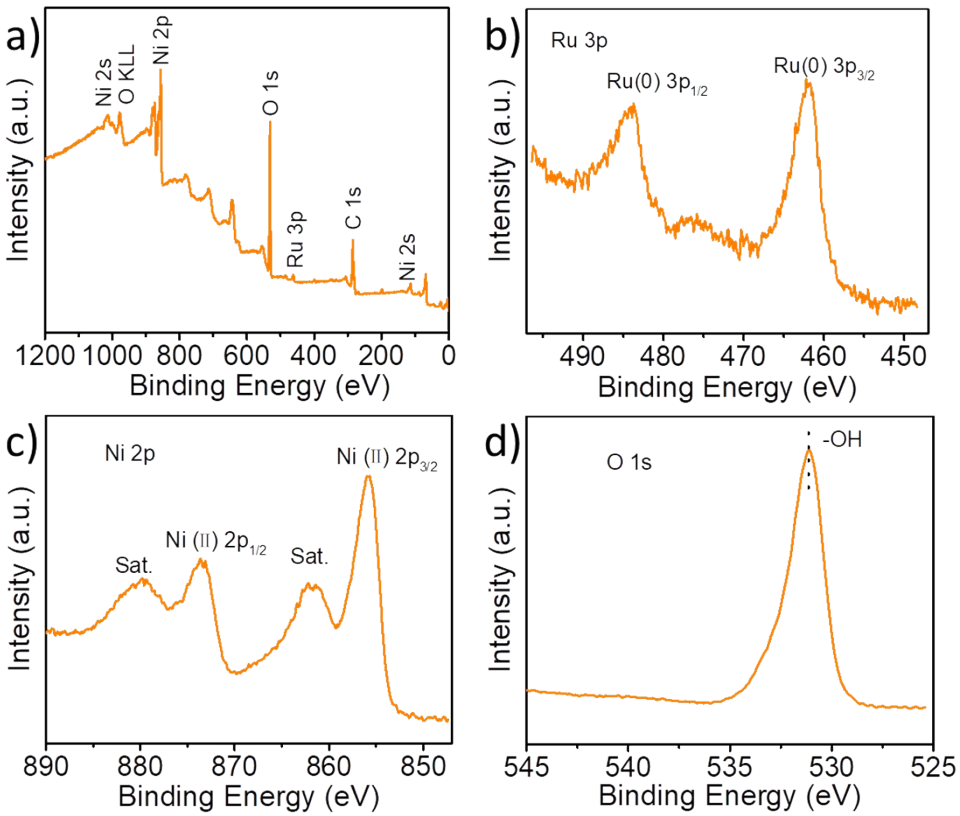

Fig. S13. XPS spectra of Ru/Ni(OH)$_2$ after HER at 20 mA cm^{-2} for 20 h.

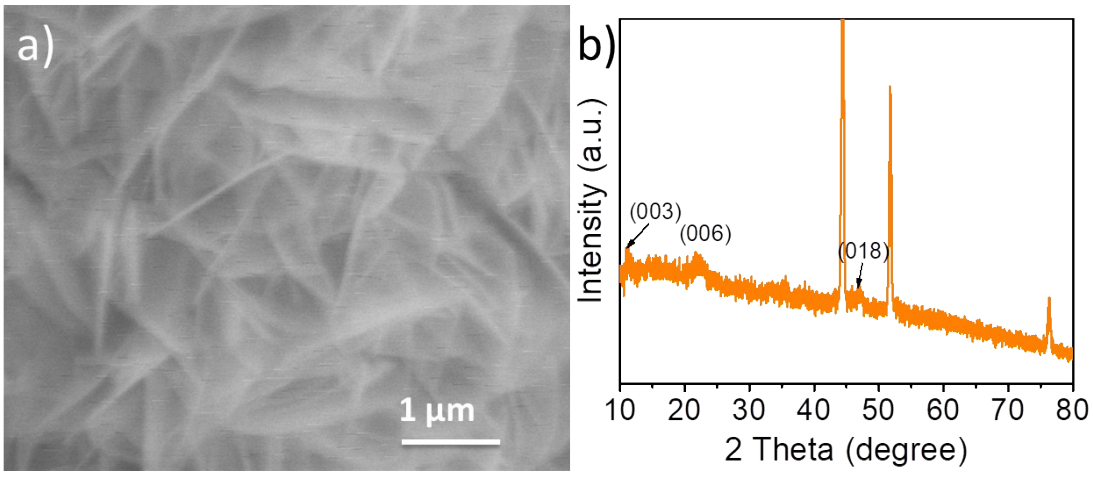

Fig. S14. SEM image (a) and XRD pattern (b) for NiFe LDH/NF.

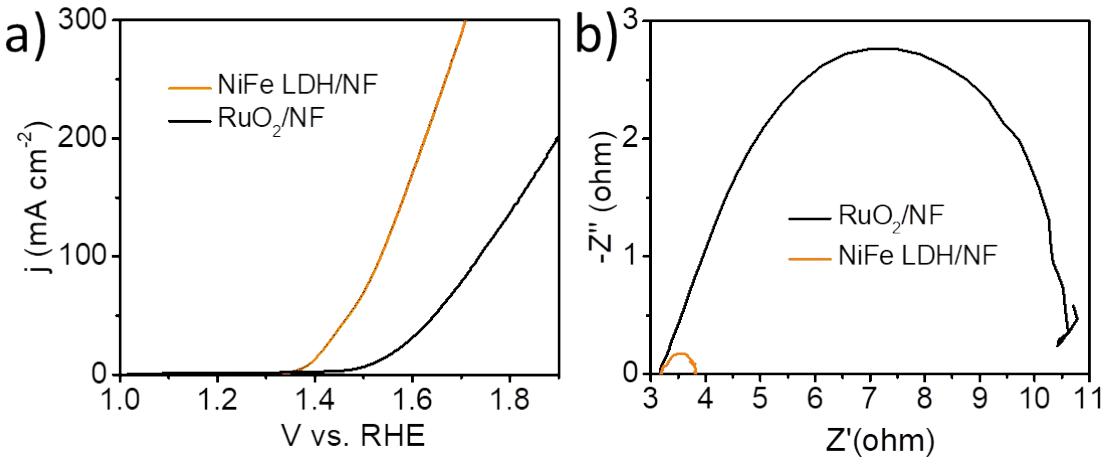

Fig. S15. LSV curves (a) and EIS spectra (b) for NiFe LDH/NF and RuO_2/NF.

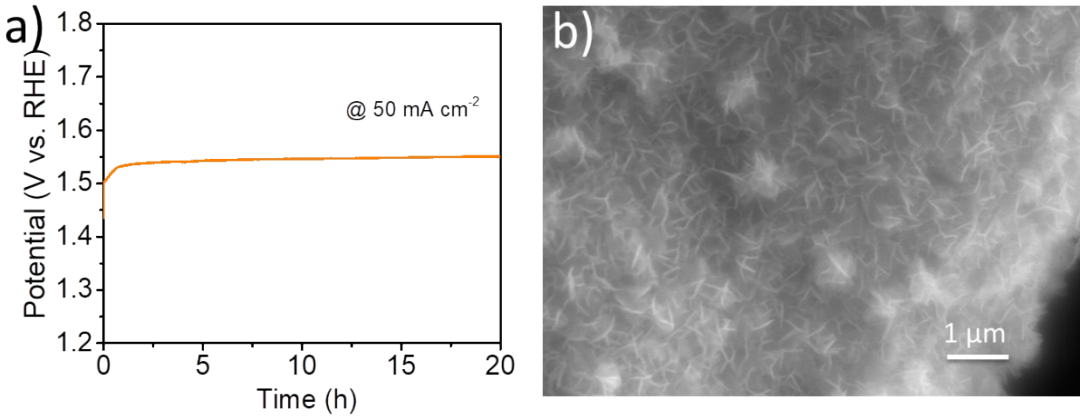

Fig. S16. (a) Chronopotentionmetry test at 50 mA cm^{-2} for NiFe LDH/NF. (b) SEM image of NiFe LDH/NF after OER at 50 mA cm^{-2} for 20 h.

Table S1. pH values of solutions with different $RuCl_3$ concertrations.

Concentration of $RuCl_3$ solution	pH value
1.0 mM	4.00
2.5 mM	2.29
5.0 mM	2.09
15.0 mM	1.76