

SUPPORTING INFORMATION

In-situ Growth of Porous Ultrathin Ni(OH)₂ Nanostructures On Nickel Foam: An Efficient and Durable Catalysts for Urea Electrolysis

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Section 1

1. Preparation of the Ni(OH)₂/NF catalysts

(1) Ni(OH)₂/NF-E: Ni(OH)₂ loaded on NF (0.5 cm×2.0 cm) was prepared using the reported electrodeposition methods (denoted as Ni(OH)₂/NF-E).^[1] A piece of NF was rinsed with ethanol and UP water, respectively. And then, the electrodeposition was carried out in a simple two-electrode cell by galvanostatic electrolysis. The NF was used as working electrode and a graphite electrode (spectral grade, 1.8 cm²) was used as the counter electrode. The Ni(OH)₂/NF-E was obtained by an electrodeposition with a current density of 0.5 mA cm⁻² for 30 min in a mixed solution of 9.0 mM Ni(NO₃)₂·6H₂O and 0.02 mM NH₄NO₃ at room temperature, and finally dried in the air.

(2) Ni(OH)₂/NF-H: Ni(OH)₂ nanosheet arrays were synthesized on NF (3.0 cm×2.0 cm) by a simple hydrothermal reaction (denoted as Ni(OH)₂/NF-H) according to Liu et al.^[2] In brief, the pre-cleaned NF was immersed into a 40 mL of HCl solution with pH = 3.0, and then transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was maintained at 180 °C for 6 h. After cooling naturally to room temperature, the sample was collected and washed for several times with deionized water, and further dried at 60 °C in vacuum for 12 h.

References

- [1] A.-L. Wang, H. Xu, G.-R. Li, *ACS Energy Lett.* **2016**, 1, 445.
- [2] G. Liu, Z. Sun, X. Zhang, H. Wang, G. Wang, X. Wu, H. Zhang, H. Zhao, *J. Mater. Chem. A* **2018**, 6, 19201.

Section 2

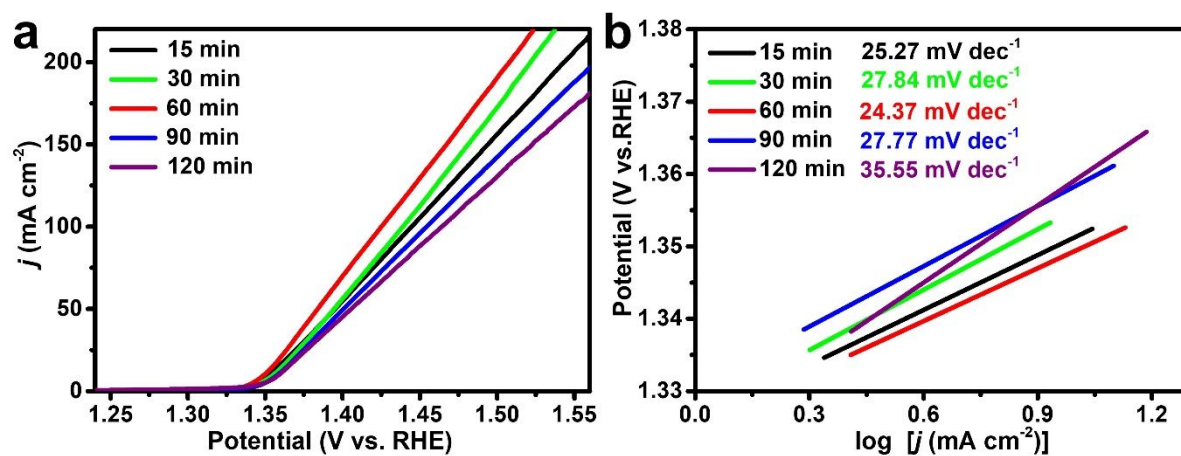


Figure S1. (a) LSV curves and (b) Tafel plots of Ni(OH)₂@NF with different activation time.

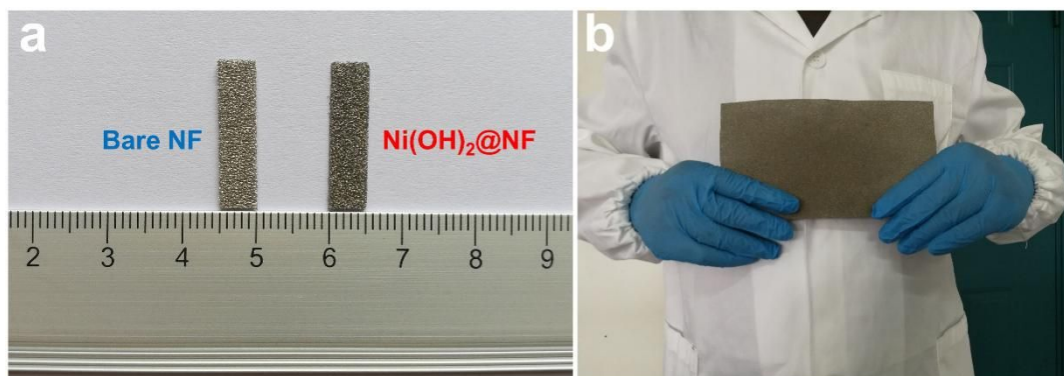


Figure S2. Optical images of bare NF and Ni(OH)₂@NF.

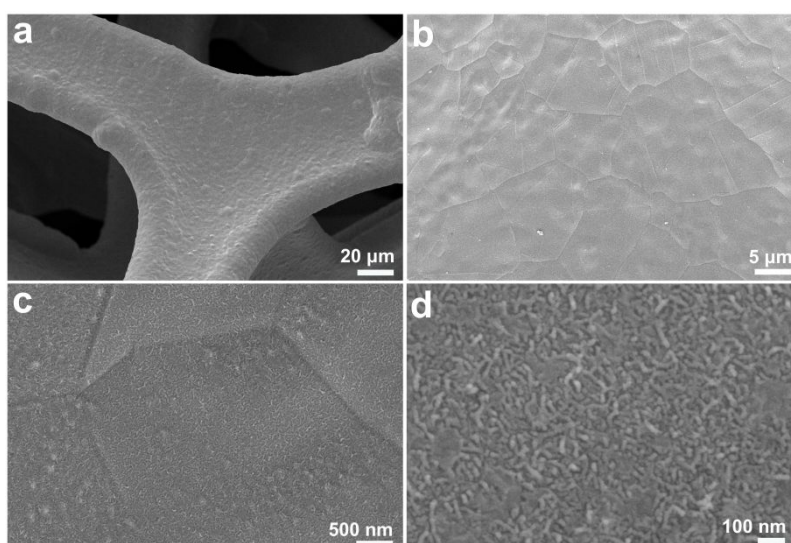


Figure S3. SEM images of bare NF.

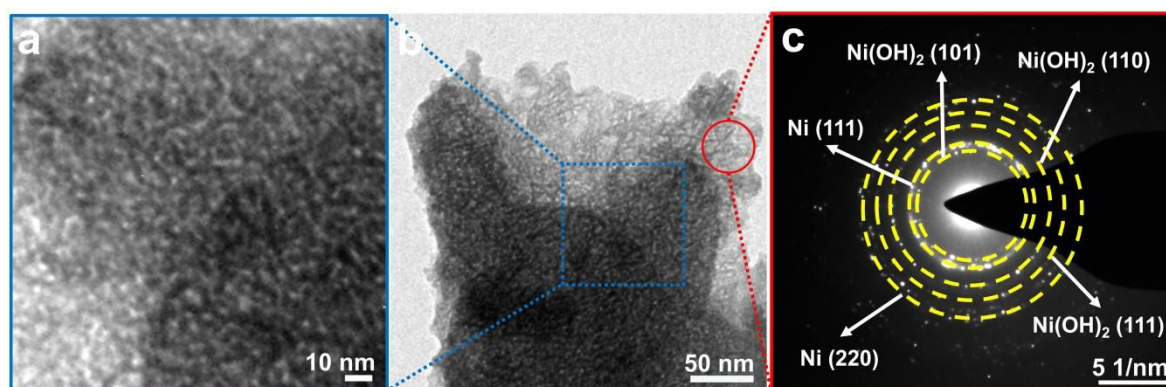


Figure S4. (a, b) TEM images of the Ni(OH)₂@NF; (c) Selected area electron diffraction pattern of the Ni(OH)₂@NF.

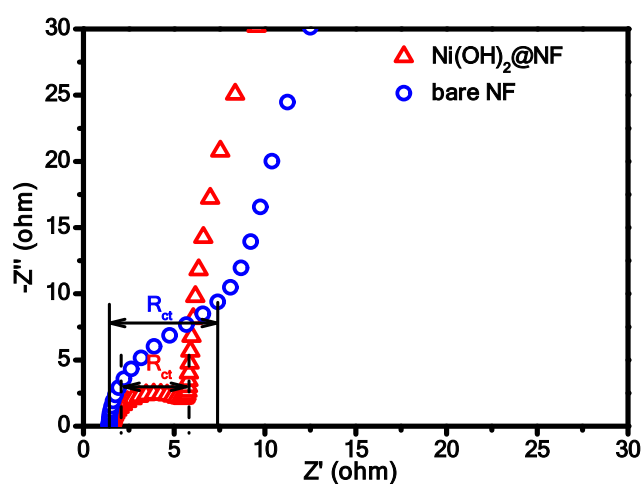


Figure S5. Nyquist plots of bare NF and Ni(OH)₂@NF samples.

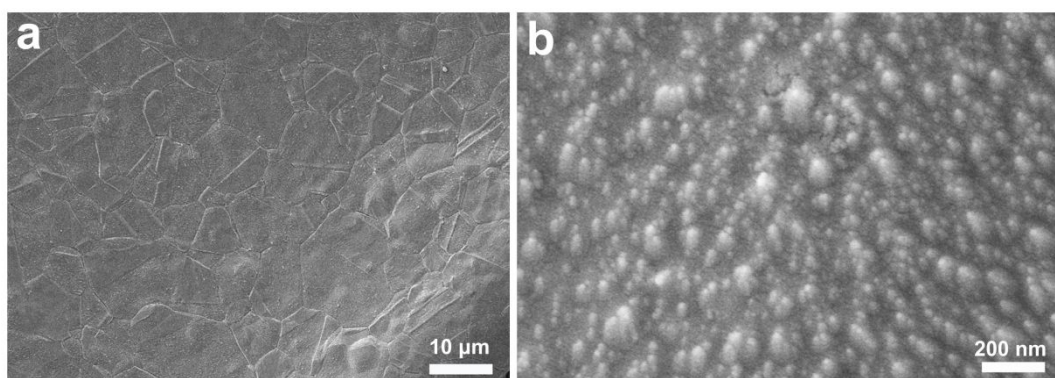


Figure S6. (a, b) SEM images of the Ni(OH)₂@NF after long-term electrolysis for UOR.

The SEM images with different magnification in Figure S6 reveal that the morphology and microstructure of Ni(OH)₂@NF not only remained unchanged after the UOR durability test.

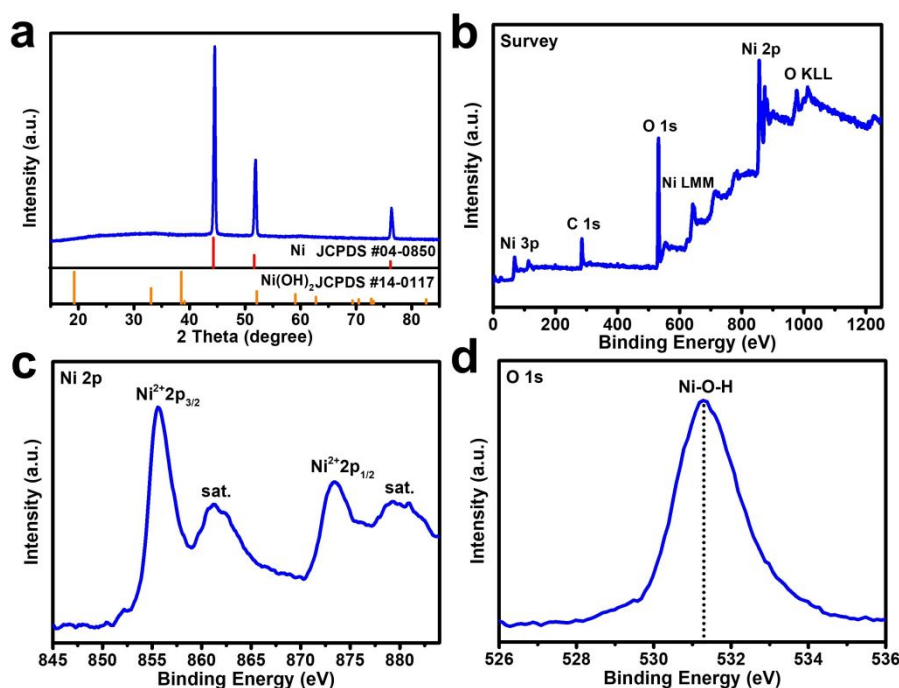


Figure S7. (a) XRD pattern of the $\text{Ni(OH)}_2\text{@NF}$ after long-term electrolysis for UOR; (b) Survey XPS spectra and high resolution XPS spectra of (c) Ni 2p, and (d) O 1s of the $\text{Ni(OH)}_2\text{@NF}$ after long-term electrolysis for UOR.

As shown in Figure S7, the XRD and XPS analysis results of the $\text{Ni(OH)}_2\text{@NF}$ catalyst show that its chemical composition and chemical state remain unchanged after a long-term stability test, which indicates that the $\text{Ni(OH)}_2\text{@NF}$ has a good stability. However, the peak of Ni^0 2p after UOR stability test was disappeared, its may due to a part of the surface metallic nickel of $\text{Ni(OH)}_2\text{@NF}$ was oxidized after continuous UOR test.

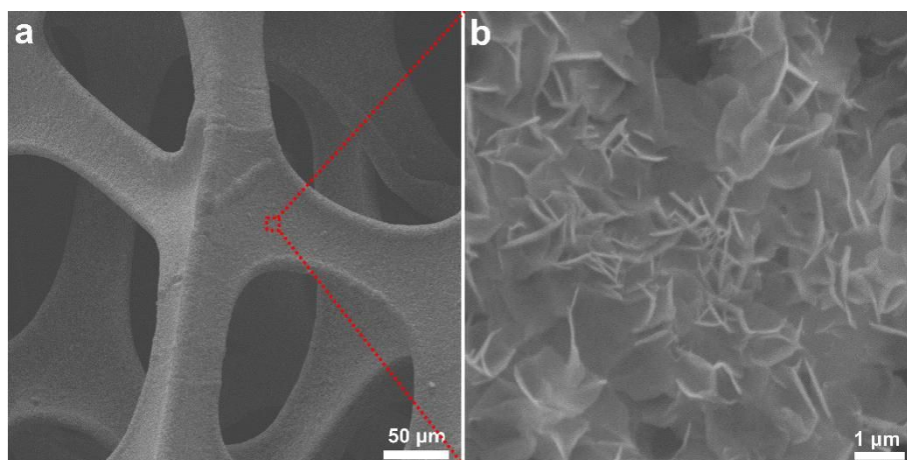


Figure S8. SEM images of the $\text{Ni(OH)}_2\text{/NF-E}$.

The low-magnification SEM image in (Figure S8a) displayed the surface of NF completely coverage by Ni(OH)₂ nanosheets, and the high-magnification SEM image (Figure S8b) further reveals that Ni(OH)₂ nanosheets are well-aligned and vertically grown on the NF surface.

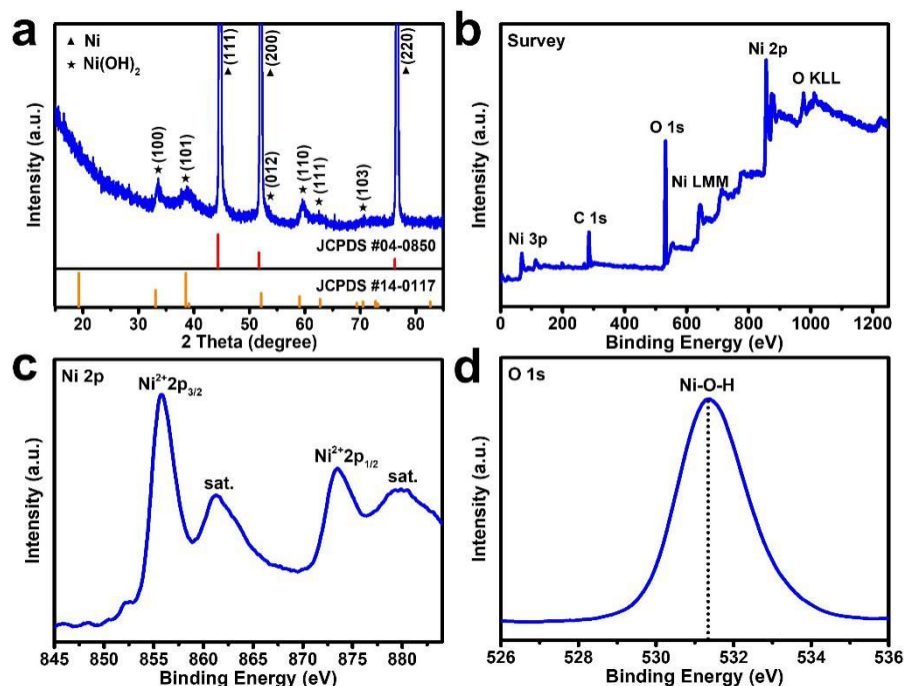


Figure S9. (a) XRD pattern of Ni(OH)₂/NF-E; (b) Survey XPS spectra of Ni(OH)₂/NF-E; high resolution XPS spectra of (c) Ni 2p, and (d) O 1s of Ni(OH)₂/NF-E.

As reflected in the XRD pattern (Figure S9a), except for the three typical peaks arise from the NF substrate (JCPDS No. 04-0850), other well-defined peaks corresponding to the composition Ni(OH)₂ (JCPDS No. 14-0117). The XPS survey spectra of the as prepared Ni(OH)₂/NF-E (shown in Figure S9b) indicated the presence of Ni and O, and the C 1s signal is due to the extraneous carbon contamination. The Ni 2p spectrum (Figure S9c) is divided into Ni 2p_{3/2} (855.8 eV) and its satellite (861.4 eV), and Ni 2p_{1/2} (873.4 eV) and its satellite (879.5 eV). In the O1s spectrum (Figure S9d), the peaks at 531.4 eV can be ascribed to the Ni-O-H bond. All these results fully confirming that the Ni(OH)₂ is uniformly grown upon the surface of NF.

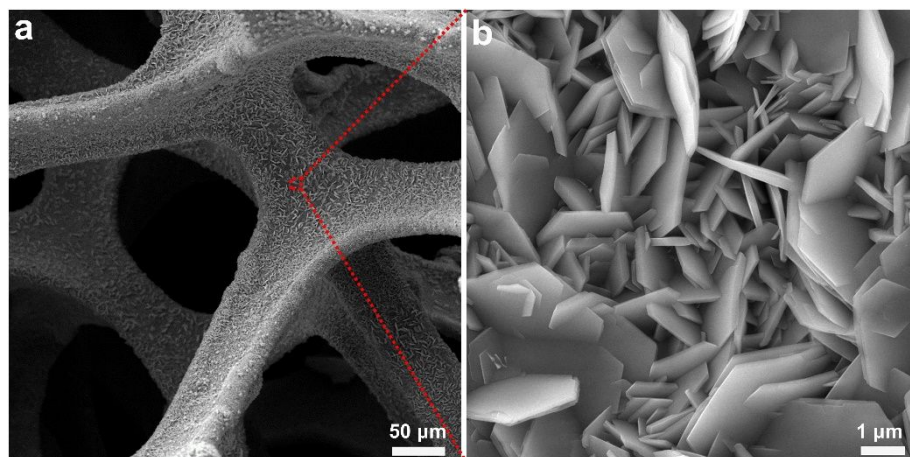


Figure S10. SEM images of the Ni(OH)₂/NF-H.

It can be seen that the surface of NF is completely covered by Ni(OH)₂ nanosheets (Figure S10a) after the hydrothermal reaction. The nanosheet is vertically grown and is interlinked from a perfect porous configuration with a network construction (Figure S10b).

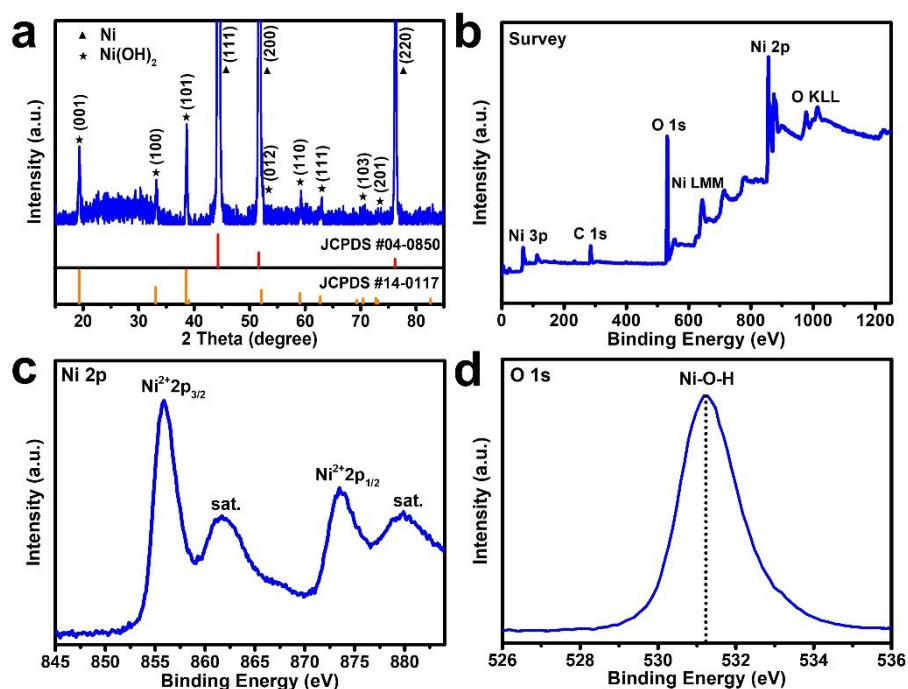


Figure S11. (a) XRD pattern of Ni(OH)₂/NF-H; (b) Survey XPS spectra of Ni(OH)₂/NF-H; high resolution XPS spectra of (c) Ni 2p, and (d) O 1s of Ni(OH)₂/NF-H.

As shown in Figure S11a, the XRD pattern of Ni(OH)₂/NF-H except for the three typical peaks of Ni (JCPDS No. 04-0850) arise from the NF substrate; other well-defined peaks are

assigned to the composition of Ni(OH)_2 (JCPDS No. 14-0117). The XPS survey spectra of the as prepared $\text{Ni(OH)}_2/\text{NF-H}$ (shown in Figure S11b) indicates the presence of Ni and O, and the C 1s signal is due to the extraneous carbon contamination. The Ni 2p spectrum (Figure S11c) is divided into Ni 2p_{3/2} (856.0 eV) and its satellite (861.7 eV), as well as Ni 2p_{1/2} (873.6 eV) and its satellite (879.6 eV). In the O1s spectrum (Figure S11d), the peaks at 531.2 eV are assigned to the Ni-O-H bond. All these results are in complete agreement with the fact that the Ni(OH)_2 is uniformly grown upon the surface of NF.

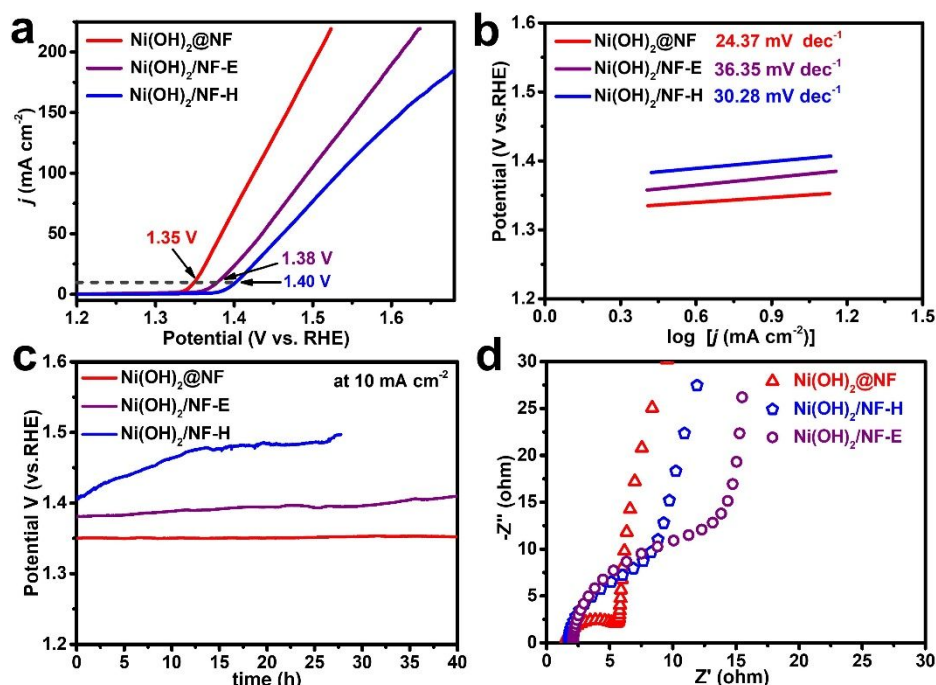


Figure S12. (a) Polarization curves of $\text{Ni(OH)}_2@\text{NF}$, $\text{Ni(OH)}_2/\text{NF-E}$ and $\text{Ni(OH)}_2/\text{NF-H}$ in 1.0 M KOH with 0.3 M urea at a scan rate of 5 mV s⁻¹; (b) Corresponding Tafel plots; (c) Chronopotentiometry plots of $\text{Ni(OH)}_2@\text{NF}$, $\text{Ni(OH)}_2/\text{NF-E}$ and $\text{Ni(OH)}_2/\text{NF-H}$ electrode obtained in constant current ($j = 10 \text{ mA cm}^{-2}$); (d) Nyquist plots of $\text{Ni(OH)}_2@\text{NF}$, $\text{Ni(OH)}_2/\text{NF-E}$ and $\text{Ni(OH)}_2/\text{NF-H}$ samples.

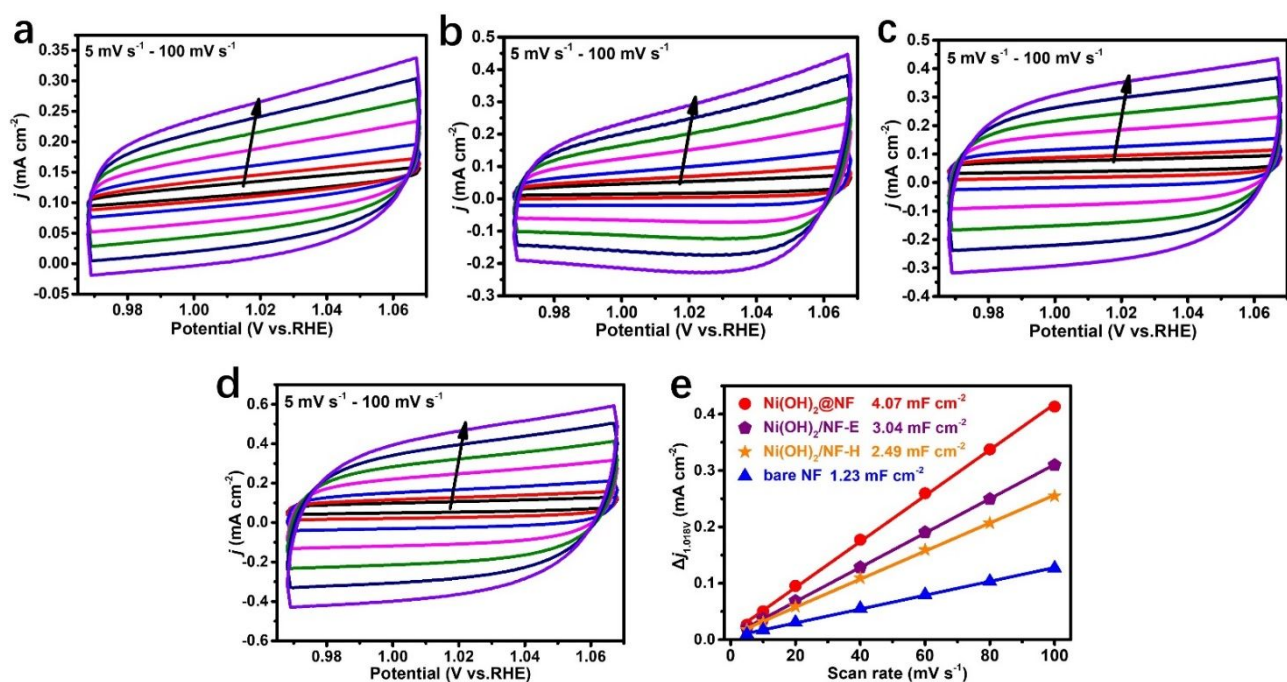


Figure S13. CVs of (a) bare NF, (b) Ni(OH)₂/NF-H, (c) Ni(OH)₂/NF-E and (d) Ni(OH)₂@NF at the different scan rates from 5~100 mV s⁻¹ in the potential rang of 0.968~1.068 V (vs. RHE); (e) Plots of capacitive currents at 1.018V (vs. RHE) as a function of scan rate for the bare NF, Ni(OH)₂/NF-H, Ni(OH)₂/NF-E and Ni(OH)₂@NF.

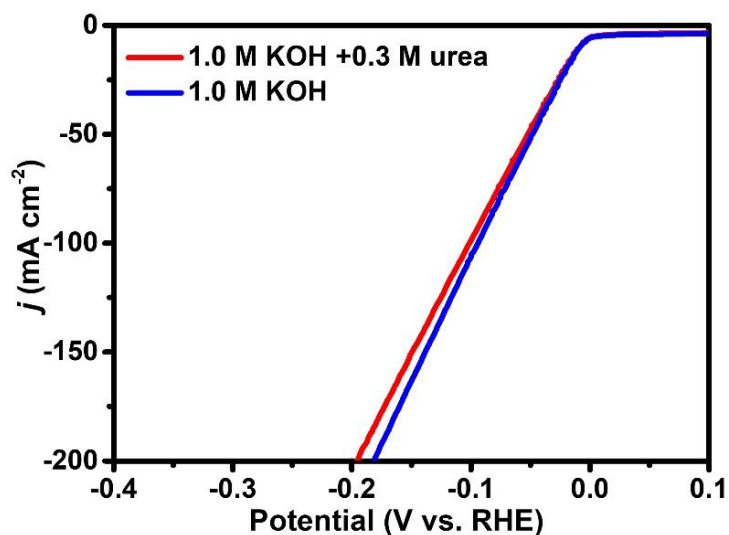


Figure S14. LSV curves of Pt/C-NF in 1.0 M KOH with and without 0.3 M urea.

Section 3

Table S1. Comparison of the values of required potential at 10 mA cm⁻² and Tafel slope of Ni(OH)₂@NF with other reported UOR electrocatalysts.

Catalytic material	Electrolyte	Potential @10 mA cm ⁻² (V vs. RHE)	Tafel slope (mV dec ⁻¹)	Reference
Ni(OH) ₂ @NF	1.0 M KOH 0.3 M urea	1.35	24.37	This Work
Pt/C-NF	1.0 M KOH 0.3 M urea	1.37	30.69	This Work
Ni(OH) ₂ -CFC	1.0 M KOH 0.33M urea	1.42	N.A.	<i>Electrochim. Acta</i> , 2017, 254 , 44-49.
Ni ₃ Se ₄ nanorod/NF	1.0 M KOH 0.5 M urea	1.38	N.A.	<i>J. Mater. Chem. A.</i> , 2018, 6 , 15653-15658.
Ni-Mo nanotube/NF	1.0 M KOH 0.1 M urea	1.36	55	<i>Nano Energy</i> , 2019, 60 , 894-902.
NiMoO-Ar/NF	1.0 M KOH 0.5 M urea	1.37	19	<i>Energy Environ. Sci.</i> , 2018, 11 , 1890-1897
Ni/C	1.0 M KOH 0.33 M urea	~1.38	N.A.	<i>ACS Appl. Mater. Interfaces</i> , 2018, 10 , 4750-4756
SL Ni(OH) ₂ NS/CC	1.0 M KOH 0.33M urea	~1.37	N.A.	<i>J. Mater. Chem. A.</i> , 2018, 6 , 13867-13873.
NF@p-Ni	1.0 M KOH 0.33M urea	~1.38	N.A.	<i>Electrochim. Acta</i> , 2019, 304 , 131-137.
Ni-MOF/NF	1.0 M KOH 0.5 M urea	1.37	N.A.	<i>Chem. Commun.</i> , 2017, 53 , 10906-10909.
Ni(OH) ₂ NS@NW/NF	1.0 M KOH 0.33 M urea	1.40	47	<i>Electrochim. Acta</i> , 2018, 268 , 211-217.

Table S2. The summary of the values of required potential at 10 mA cm⁻² and Tafel slope of Ni(OH)₂@NF with different activation time.

Time (min)	Potential @10 mA cm ⁻² (V vs. RHE)	Tafel slope (mV dec ⁻¹)
15	1.352	25.27
30	1.356	27.84
60	1.350	24.37
90	1.358	27.77
120	1.362	35.55