Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Accelerating the reaction kinetics of $Ni_{1-x}O/Ni(OH)_2/NF$ by defect engineering for urea-assisted water splitting

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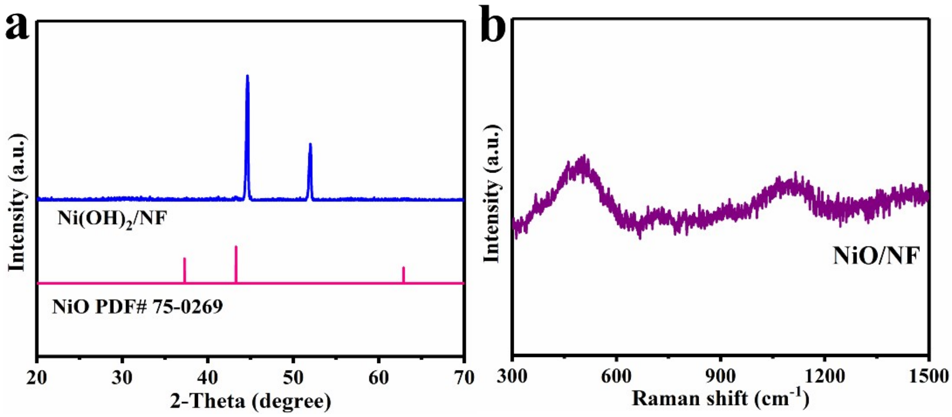

Fig. S1 (a) The XRD pattern of $Ni(OH)_2$/NF. (b) The Raman spectrum of NiO/NF.

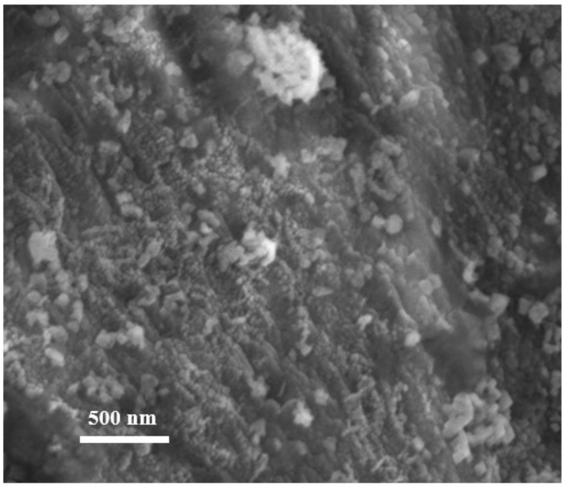

Fig. S2 The SEM image of $Ni(OH)_2$/NF.

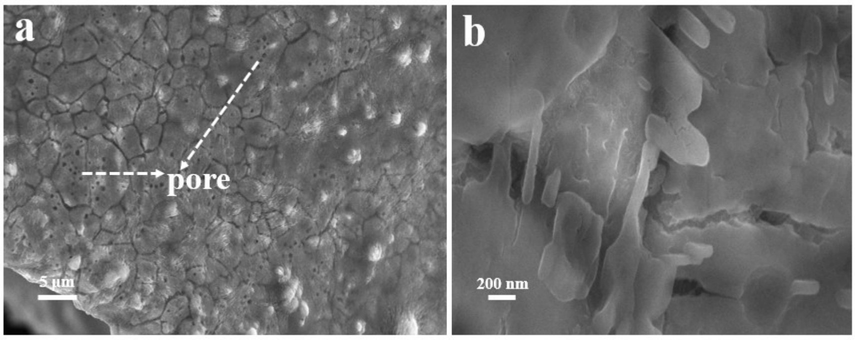

Fig. S3 SEM images at different magnifications of treated nickel foam (a, b).

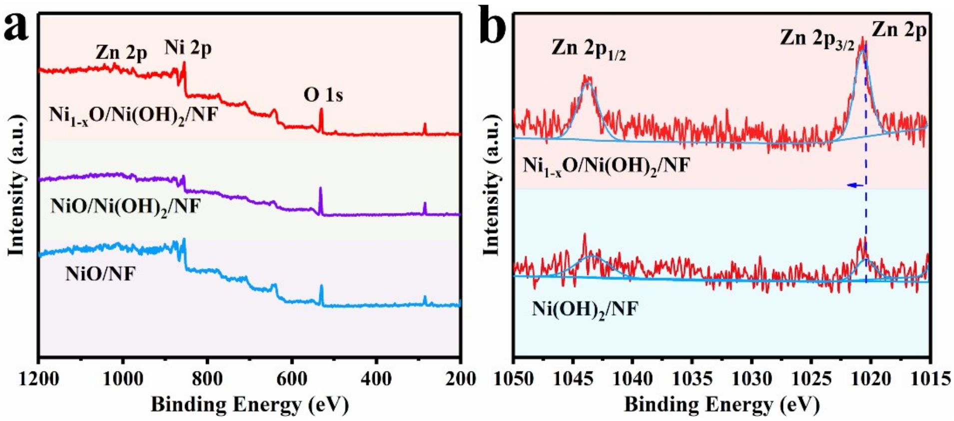

Fig. S4 (a) XPS survey spectra of NiO/NF, NiO/Ni(OH)$_2$/NF and Ni$_{1\text{-}x}$O/Ni(OH)$_2$/NF. (b) High-resolution Zn 2p XPS spectra of Ni$_{1\text{-}x}$O/Ni(OH)$_2$/NF and Ni(OH)$_2$/NF.

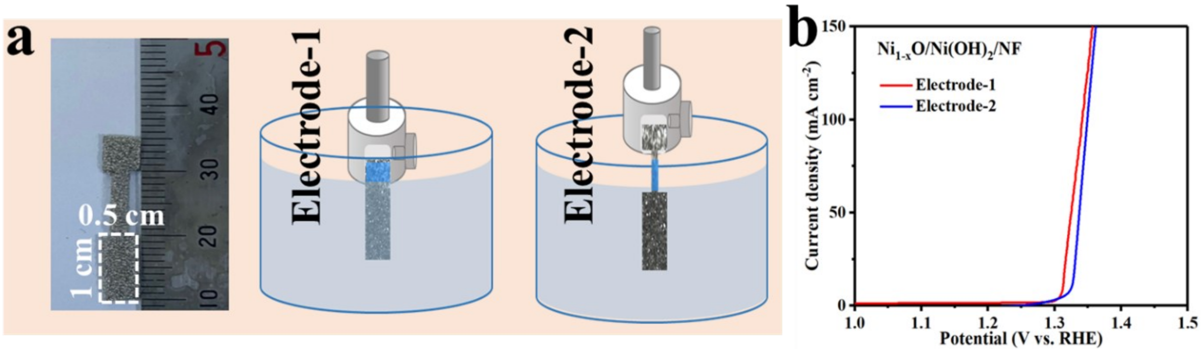

Fig. S5 (a) A representative digital photograph of the working electrode with a specifically designed shape. The schematic diagram illustrates the application of the working electrode in UOR performance measurement without (electrode-1) and with (electrode-2) the special shape. (b) LSV curves acquired with electrode-1 and electrode-2 loading with Ni$_{1\text{-}x}$O/Ni(OH)$_2$/NF.

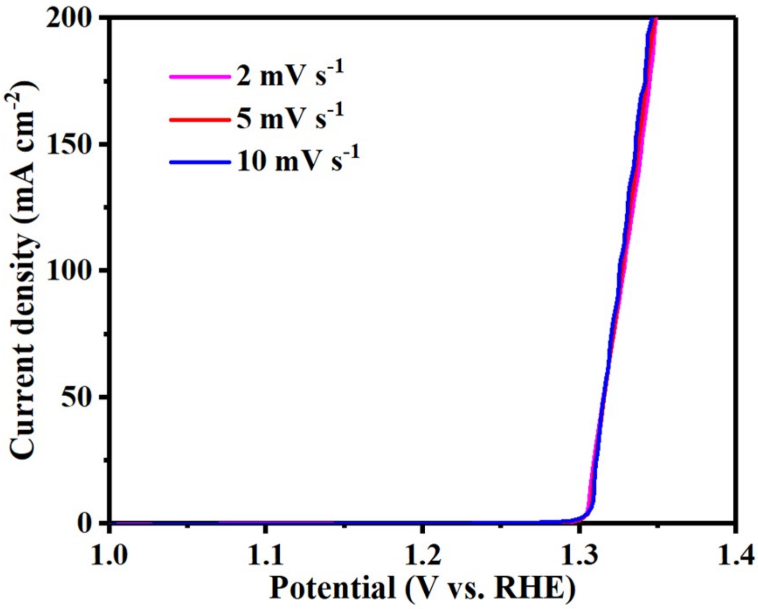

Fig. S6 UOR polarization curves of $Ni_{1-x}O/Ni(OH)_2/NF$ in 1 M KOH with 0.33 M urea at scanning rates of 10 mV s^{-1}, 5 mV s^{-1} and 2 mV s^{-1}, respectively.

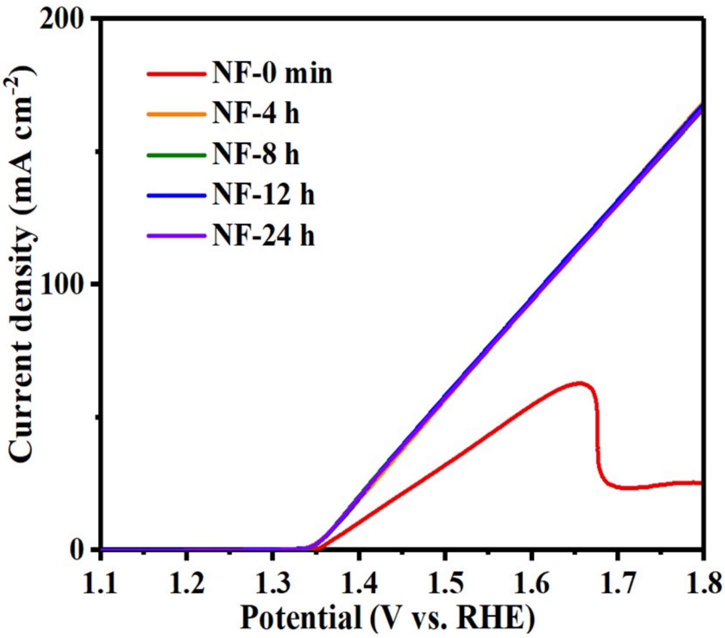

Fig. S7 LSV curves of NF with different acid etching time durations.

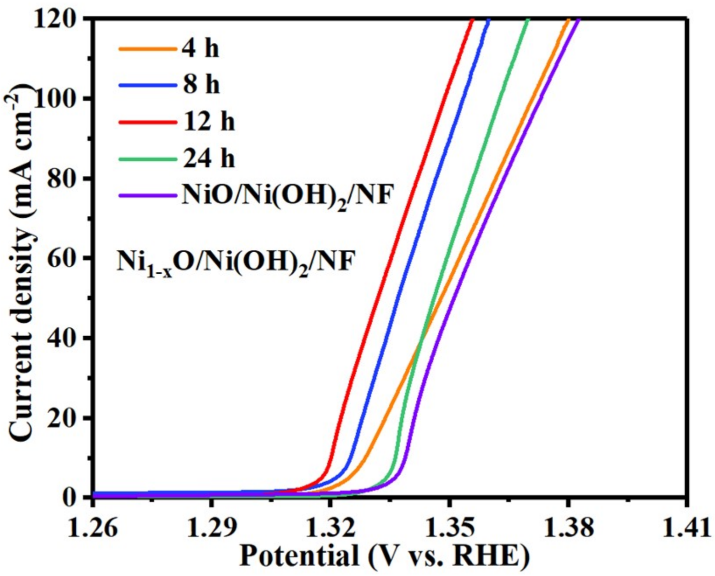

Fig. S8 LSV curves of $Ni_{1-x}O/Ni(OH)_2/NF$ with different acid etching times and $NiO/Ni(OH)_2/NF$.

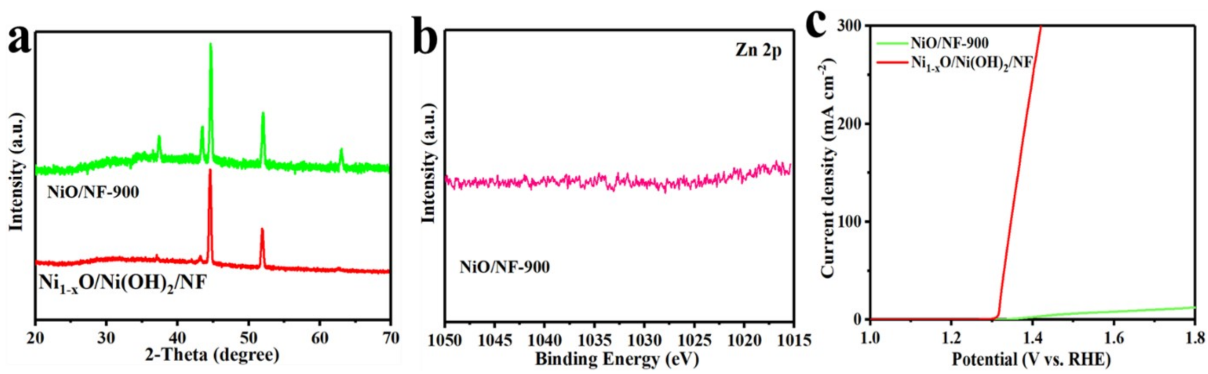

Fig. S9 (a) XRD patterns of NiO/NF-900 and $Ni_{1-x}O/Ni(OH)_2/NF$. (b) The high-resolution Zn 2p XPS spectrum of NiO/NF-900. (c) LSV curves of NiO/NF-900 and $Ni_{1-x}O/Ni(OH)_2/NF$.

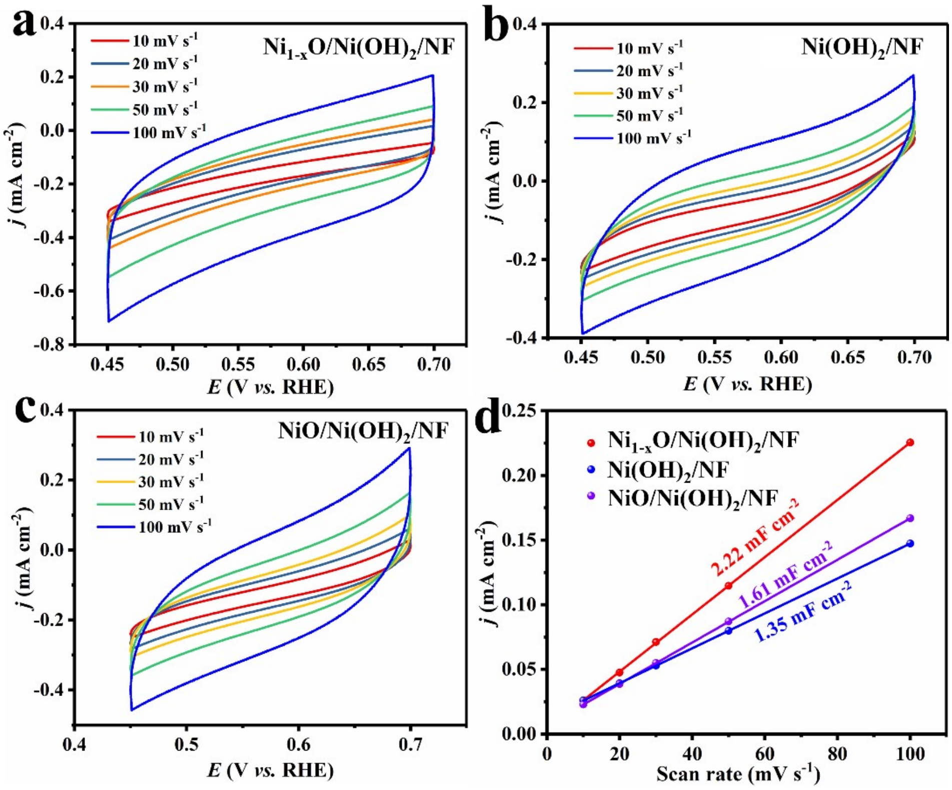

Fig. S10 CV curves for (a) $Ni_{1-x}O/Ni(OH)_2/NF$, (b) $Ni(OH)_2/NF$, and (c) $NiO/Ni(OH)_2/NF$ at different scan rates in the non-faradaic potential region. (d) Linear relationships between the capacitive current and the scan rate of catalysts.

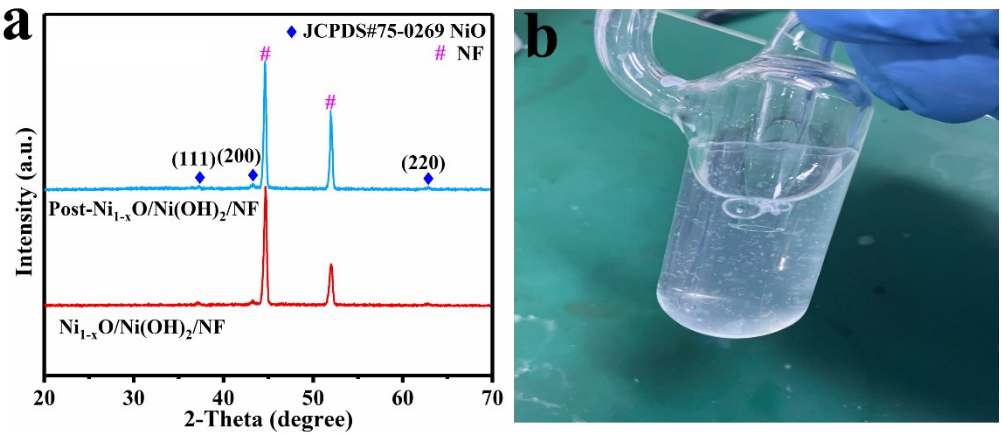

Fig. S11 XRD patterns of the Post-$Ni_{1-x}O/Ni(OH)_2/NF$ and $Ni_{1-x}O/Ni(OH)_2/NF$. (b) The digital photograph during the chronopotentiometry test of $Ni_{1-x}O/Ni(OH)_2/NF$, in which the saturated $Ca(OH)_2$ solution became turbid, signifying the production of CO_2.[1]

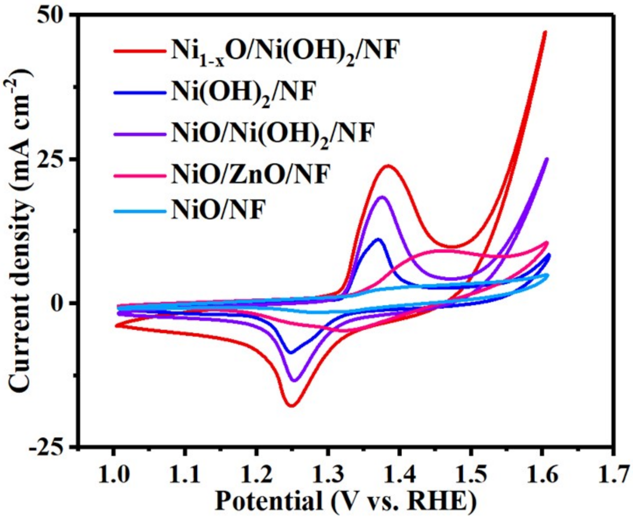

Fig. S12 CV curves of $Ni_{1-x}O/Ni(OH)_2/NF$, $Ni(OH)_2/NF$, $NiO/Ni(OH)_2/NF$, NiO/ZnO/NF and NiO/NF in 1 M KOH with 10 mV s^{-1}.

Ni^{2+} sites are firstly electrochemically oxidized to high-valent Ni^{3+} species in the forward scanning, and Ni^{3+} species then chemically oxidize urea molecules with themselves being reduced back to Ni^{2+}. As shown in Fig. S12, the CV curve of $Ni_{1-x}O/Ni(OH)_2/NF$ exhibits the largest oxidation peak, suggesting most Ni^{3+} sites are generated in $Ni_{1-x}O/Ni(OH)_2/NF$ and conducive to a great UOR performance.

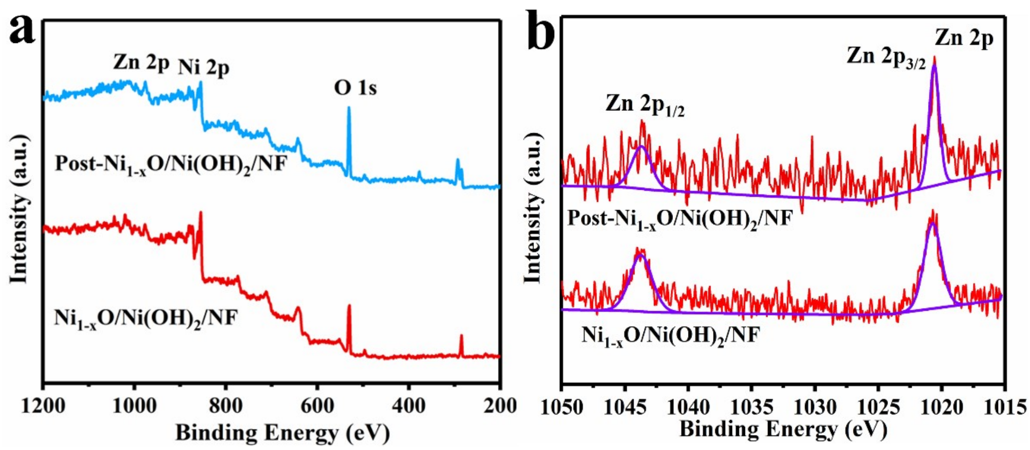

Fig. S13 (a) XPS survey spectra and (b) high-resolution XPS spectra of Zn 2p for $Ni_{1-x}O/Ni(OH)_2/NF$ and Post-$Ni_{1-x}O/Ni(OH)_2/NF$.

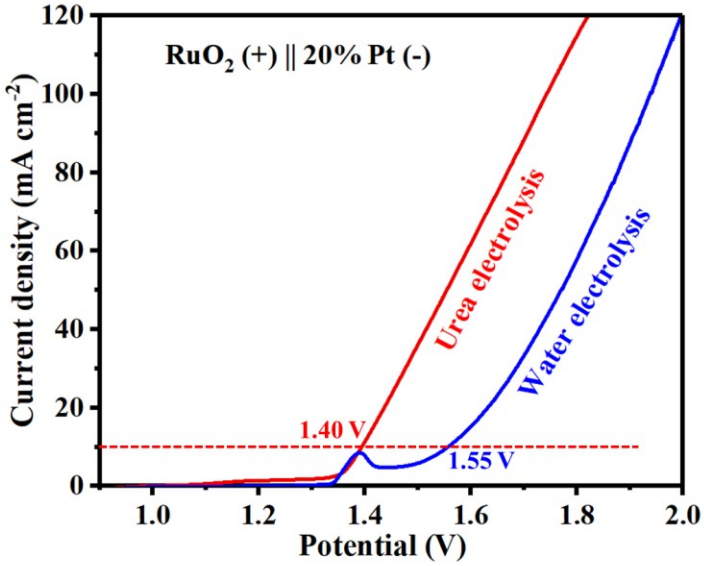

Fig. S14 Two-electrode polarization curves for water splitting and urea splitting of commercial RuO_2 (+) || 20% Pt/C (-).

Table S1. Element Zn, Ni and O contents of $Ni_{1-x}O/Ni(OH)_2/NF$ with different acid etching times.

Catalysts	Element	Atomic%*
4 h	Ni	28.36
	Zn	4.94
	O	66.70
8 h	Ni	28.32
	Zn	3.51
	O	68.17
12 h	Ni	25.44
	Zn	2.88
	O	71.68
24 h	Ni	26.92
	Zn	1.55
	O	71.53
Post-$Ni_{1-x}O/Ni(OH)_2/NF$	Ni	21.90
	Zn	2.72
	O	75.38

*These values were estimated by XPS.

Table S2. Comparison of UOR performances of $Ni_{1-x}O/Ni(OH)_2/NF$ with recent reported electrocatalysts.

Catalysts	Potential (vs. RHE)	Tafel slope (mV dec^{-1})	Reference
$Ni_{1-x}O/Ni(OH)_2/NF$	**1.317@10** **1.346@100**	**18.7**	***This work***
$Ir/NiPS_3$	1.36@10	21.1	*Nat. Commut.**2024**,15,*2851.
$Ni(OH)_2/g\text{-}C_3C_4$	1.361@10	/	*Small* **2024**, 2401053.
$LaNiO_3$–NiO	1.34@10	39.87	*ACS Materials Lett.* **2024**, *6,* 1029-1041.
Pt–$Ni(OH)_2$@Ni-CNFs-2	1.363@10	13.4	*Energy Environ. Sci.,* **2024**. *17,*1984-1996.
pt-NFS	1.37@10	49.87	*Small Methods* **2024**, 2301434.
V-$Co_2P_4O_{12}$/CC	1.33@10	50	*Adv. Funct. Mater.***2024**, 2313974.
CF@CoOS-2	1.36@10	155	*Small* **2024**, 2310112.
a-RuO_2/NiO	1.334@10	34.8	*ACS Nano* **2024**, *18,* 1214-1225.
NiB_x	1.40@100	22.8	*Adv. Funct. Mater.* **2024**, *2411011.*
Ni SAs-NC	1.39@10	42	*Appl. Catal. B. Environ* **2022**, *310,* 121352.
NiO/CuO@CuM	1.35@10	32.2	*Nano Energy* **2023**, *115,* 108714.
$Cu_{0.5}Ni_{0.5}$/NF	1.33@10	22.77	*Small* **2023**, *19,* 2300959.
Co/$CoSe_2$@CNx	1.34@10	-	*J. Mater. Chem. A,* **2023**,*11,* 5179-5187.
WM-$Ni_{0.99}Co_{0.01}(OH)_2$	1.37@10	31	*Energy Environ. Mater.***2023**,*0,* e1257.
Ni/W_5N_4/NF	1.34@10	35.8	*Appl. Catal. B. Environ.* **2023**,*323,* 122168.
$Ni_{0.05}$/CW	1.36@10	20.93	*J. Energy Chem.* **2023**, *76,*566-575.
Cu-NiFe LDH	1.35@onset	26	*Adv. Energy Mater.* **2024**, *2403004.*
Ni(OH)S/NF	1.34@10	-	*Appl. Catal. B. Environ.* **2022**, *312,* 121389.
Rh/NiV-LDH	1.33@10	36	*Sci. Bulletin* **2022**, *67,*1763-1775.

Table S3. Comparison of urea electrolysis performances of $Ni_{1-x}O/Ni(OH)_2$/NF||20% Pt/C with that of previously reported catalysts.

Catalysts	Current density (mA/cm^{-2})	Potential(V)	Reference
$Ni_{1-x}O/Ni(OH)_2$/NF||20% Pt/C	**10**	**1.379**	**This work**
YNi-10|| Pt/C	10	1.47	ACS Appl. Mater. Interfaces **2024**, 16, 50937−50947.
V-$Ni(OH)_2$|| Pt foil	10	1.50	*Adv. Funct. Mater.* **2022**, 2209698
WN/Ni_3N|| Pt/C	10	1.38	*Adv. Energy Mater*. **2023**, *13*, 2302452.
NiFe-F-4|| Pt/C	50	1.65	*J. Colloid Interf. Sci.* **2022**,*615*, 309-317.
CrCoNiFe || Pt/C	10	1.485	*J. Mater. Sci. Technol.* **2024**,*203*, 97-107.
aNi-cys (+) || Pt/C (-)	10	1.41	*J. Colloid Interf. Sci.* **2025**,*679*, 1141-1149.
CoS-2 || Pt/C	10	1.56	*Small* **2024**, *20*,2310112.
Mo-FeNi LDH || Pt/C	10	1.38	*Small* **2024**, *20*,2305877.
Ni/MNO-10 || Pt/C	10	1.45	*Small Struct.* **2023**, *4*, 2300212.
FeNi-OH/$Co(OH)_2$/NF|| Pt/C	10	1.44	*Appl. Surf. Sci.* **2024**,*670,*160649.

REFERENCE

1 Z. Ji, Y. Song, S. Zhao, Y. Li, J. Liu and W. Hu, ACS Catal., 2021, **12**, 569-579.