

Supporting Information

Reagent-adaptive active site switching on IrO_x/Ni(OH)₂ catalyst

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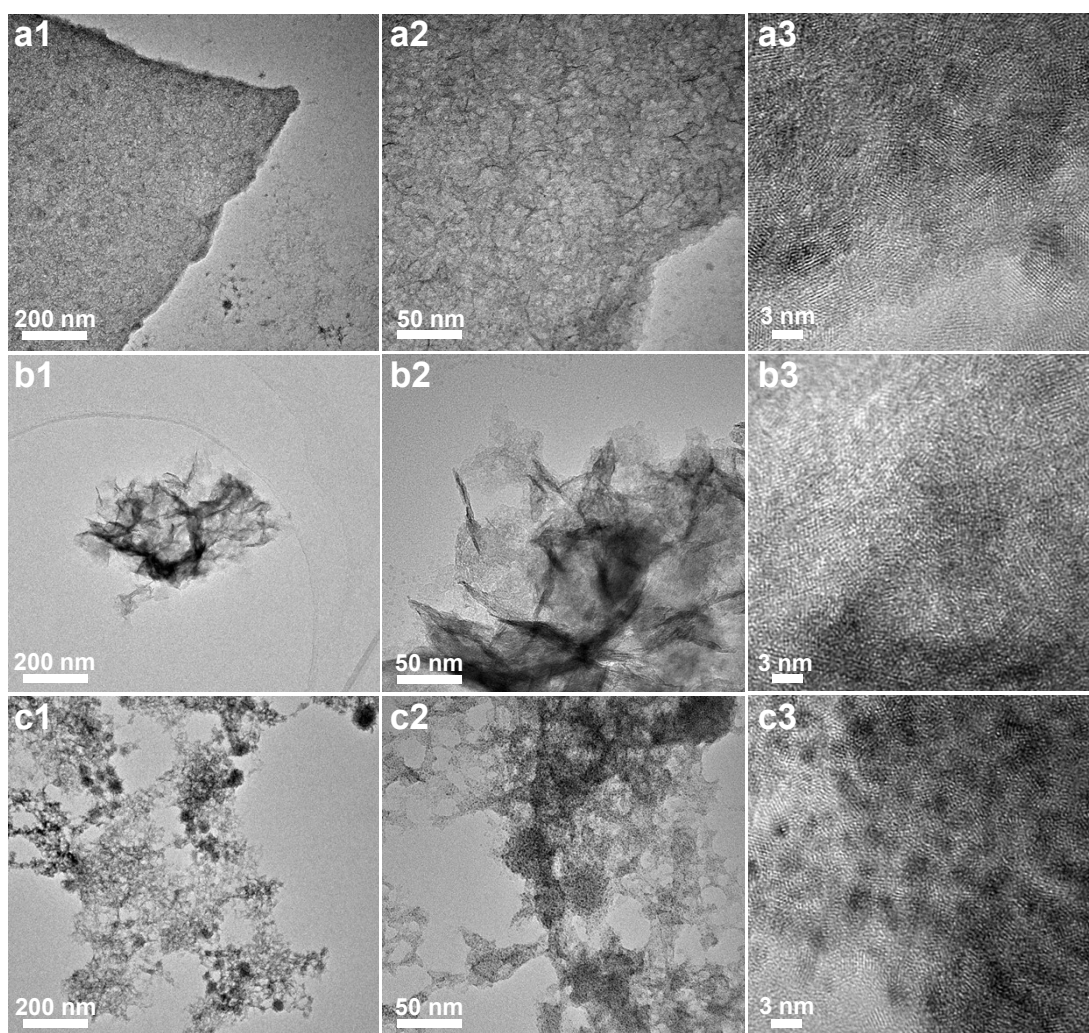


Fig.S1 The TEM images and high-resolution TEM lattice images of (a1-a3) Ni(OH)_2 , (b1-b3) $\text{Ni(OH)}_2\text{-CV}$, and (c1-c3) $\text{IrO}_x/\text{Ni(OH)}_2$.

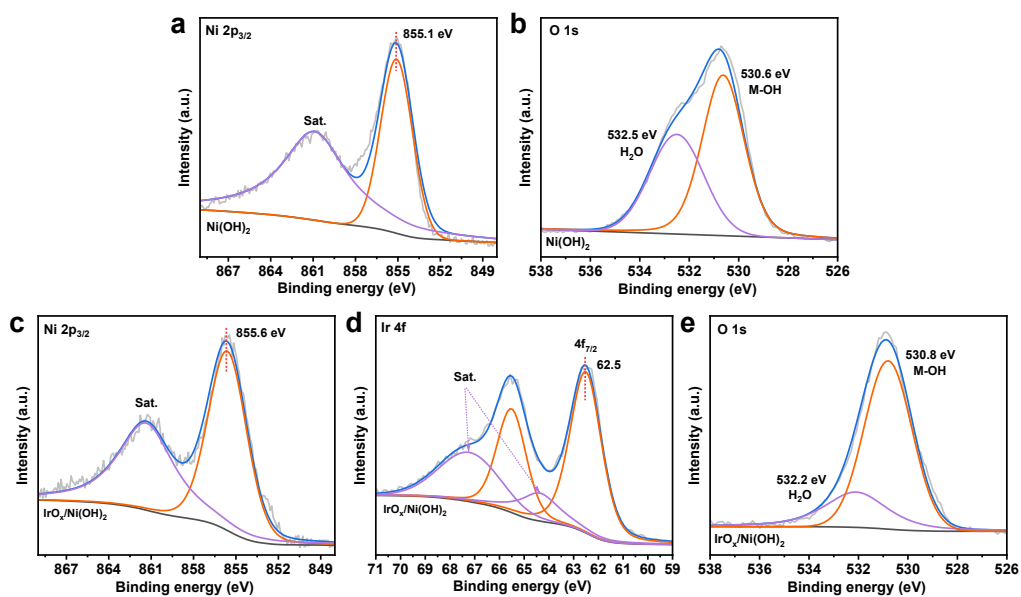


Fig. S2 (a) Ni 2p_{3/2} and (b) O 1s core-level XPS spectra of Ni(OH)₂. (c) Ni 2p_{3/2}, (d) Ir 4f, and (e) O 1s XPS core-level spectra of IrO_x/Ni(OH)₂.

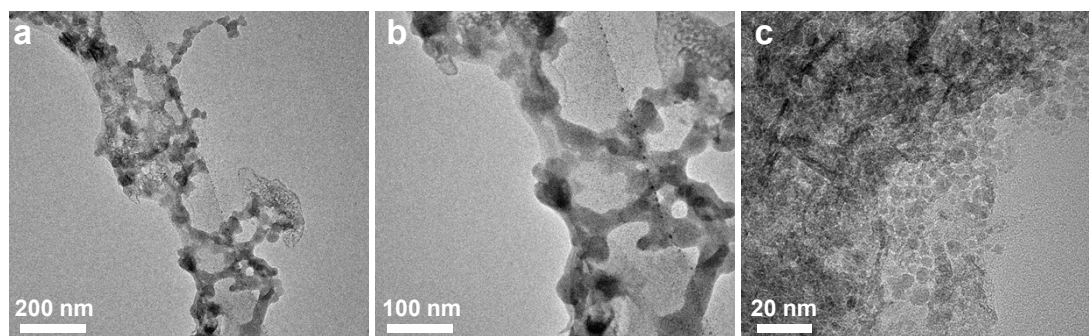


Fig. S3 The TEM images of electrodepositing IrO_x on carbon paper by 200 CV scans in 1 M KOH with Ir⁴⁺.

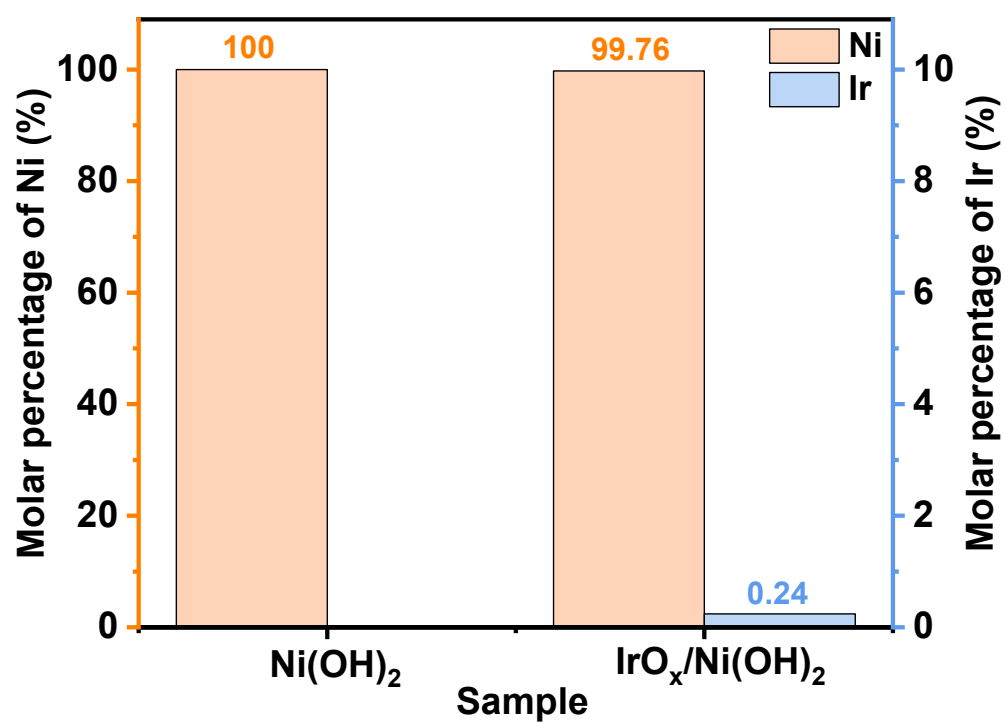


Fig. S4 ICP-AES analysis shows molar percentage of Ni and Ir in Ni(OH)_2 and $\text{IrO}_x/\text{Ni(OH)}_2$.

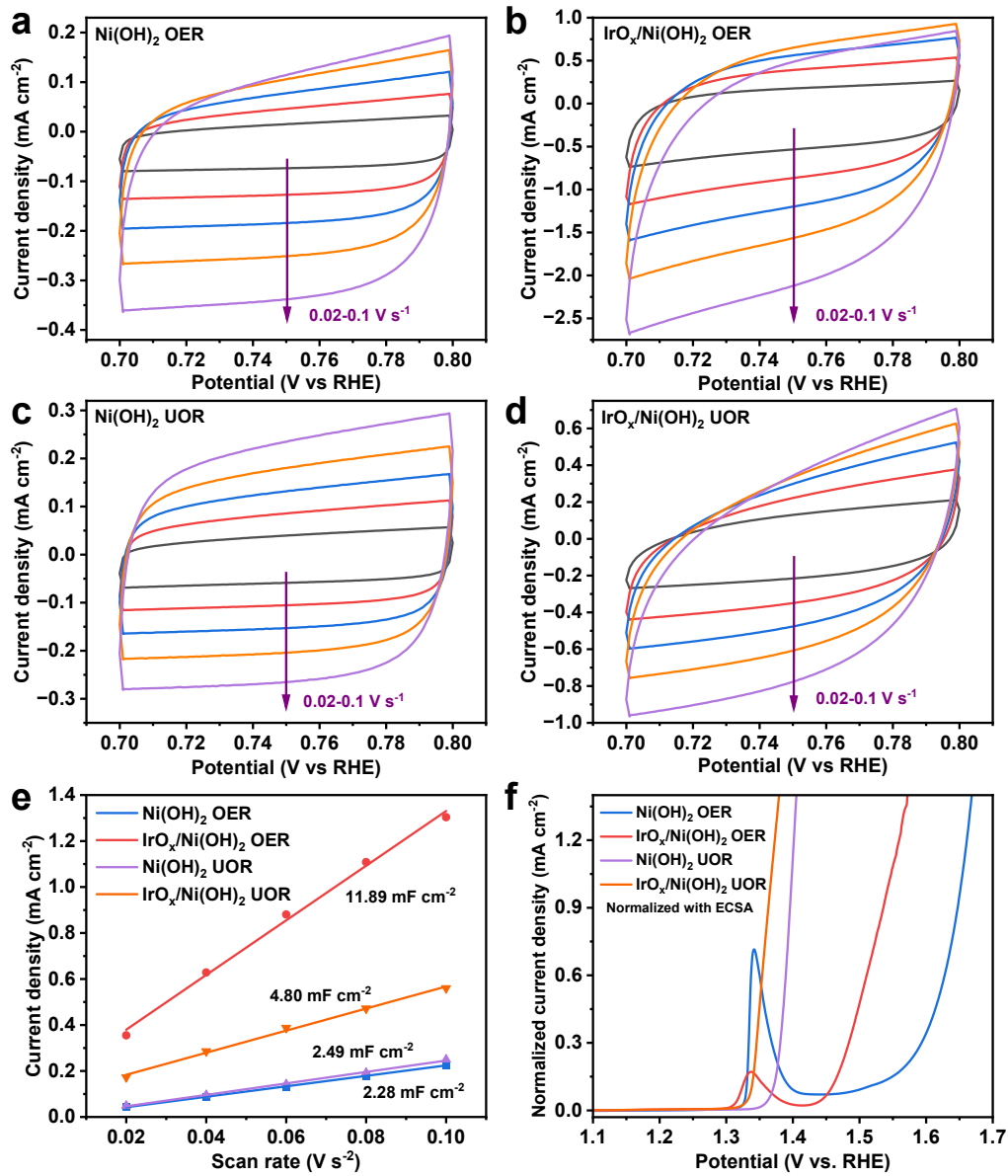


Fig. S5 CV scans for (a) Ni(OH)₂ and (b) IrO_x/Ni(OH)₂ in 1.0 M KOH, and (c) Ni(OH)₂ and (d) IrO_x/Ni(OH)₂ in 1.0 M KOH + 0.33 M urea. The CV scans were performed in a potential region from 0.7 to 0.8 V vs. RHE and the scan rates range from 0.02 to 0.1 V s⁻¹. (e) The linear relationship between the current density and scan rate of the studied electrodes, which is used to calculate the electrochemical active surface area (ECSA). The current density at 0.75 V was used for the calculation of the ECSA. The electrical double-layer capacitance (C_{dl}) was calculated by the equation $C_{dl} = (j_a - j_c)/2v$, where j_a and j_c are the anodic current density and cathodic current density, respectively, and v is the scan rate. Thus, C_{dl} is the slope of the linear relationship between $(j_a - j_c)/2$ and scan rates. The ECSA can be calculated by $ECSA = C_{dl}/C_{dl,Ref}$, where $C_{dl,Ref}$ is the specific capacitance of an ideal flat surface of the catalyst. Here, we use the average value of 0.04 mF cm⁻² for $C_{dl,Ref}$ in alkaline solutions without taking the used material and measurement conditions into account. (f) LSV curves in Fig.2a-b after normalized by ECSA.

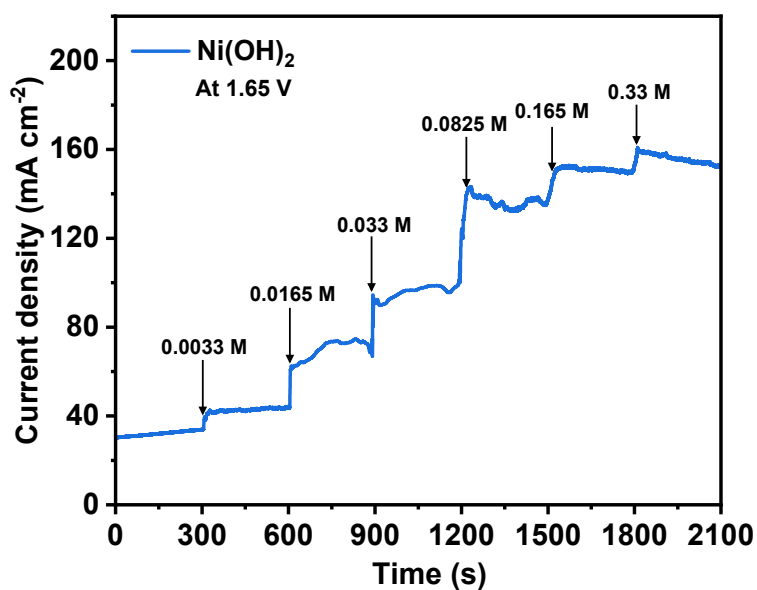


Fig. S6 The urea concentration-sensitive i-t curve for $\text{Ni}(\text{OH})_2$ electrode at 1.65 V.

The urea-concentration dependent i-t curve of $\text{Ni}(\text{OH})_2$ was recorded at 1.65 V in 1 M $\text{KOH} + x$ M urea ($0.0033 \leq x \leq 0.33$), as shown in **Fig. S6**. Obviously, the current density is closely dependent on the presence of urea, that is, the Ni^{3+} oxidizes the urea effectively. This result suggested that the $\text{Ni}(\text{OH})_2$ is an efficient UOR-active catalyst with inefficient water oxidation activity, thus the $\text{Ni}(\text{OH})_2$ electrode without IrO_x does not have the switching characteristic between UOR and OER.

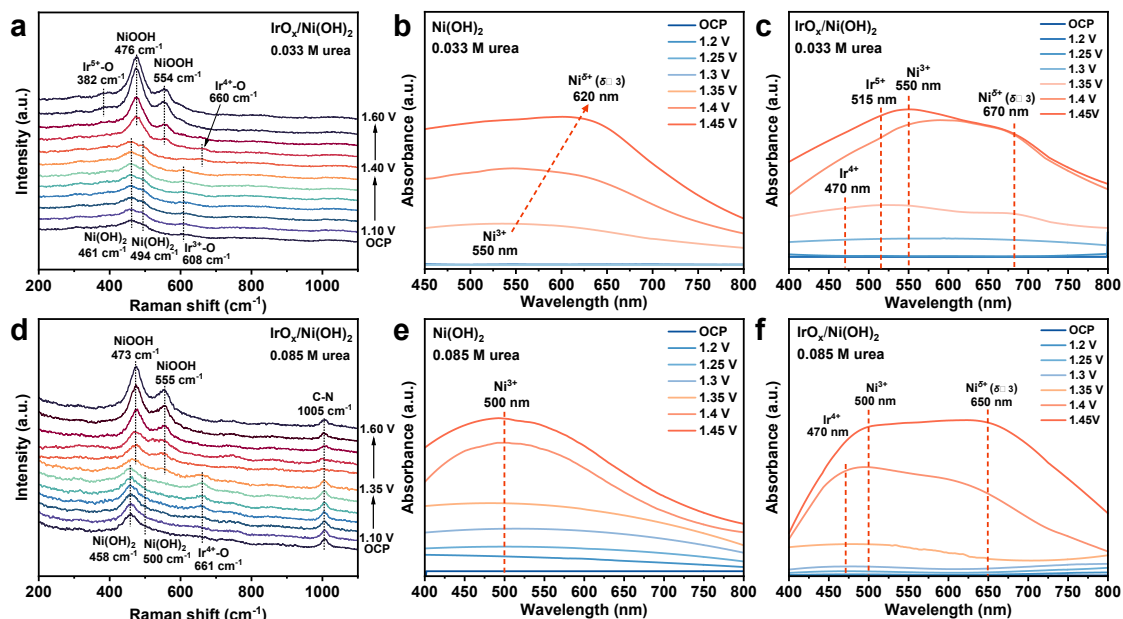


Fig. S7 Active species on IrO_x/Ni(OH)₂. (a) In situ Raman spectra of IrO_x/Ni(OH)₂ in 1 M KOH + 0.033 M urea. The potential increment is 0.05 V when varying potentials from open-circuit potential to 1.6 V. In situ UV-Vis absorption spectra for (b) Ni(OH)₂ and (c) IrO_x/Ni(OH)₂ in 1 M KOH + 0.033 M urea. The potential increment is 0.05 V when varying potentials from open-circuit potential to 1.45 V. (d) In situ Raman spectra of IrO_x/Ni(OH)₂ in 1 M KOH + 0.085 M urea. The potential increment is 0.05 V when varying potentials from open-circuit potential to 1.6 V. In situ UV-Vis absorption spectra for (e) Ni(OH)₂ and (f) IrO_x/Ni(OH)₂ in 1 M KOH + 0.085 M urea. The potential increment is 0.05 V when varying potentials from open-circuit potential to 1.45 V.

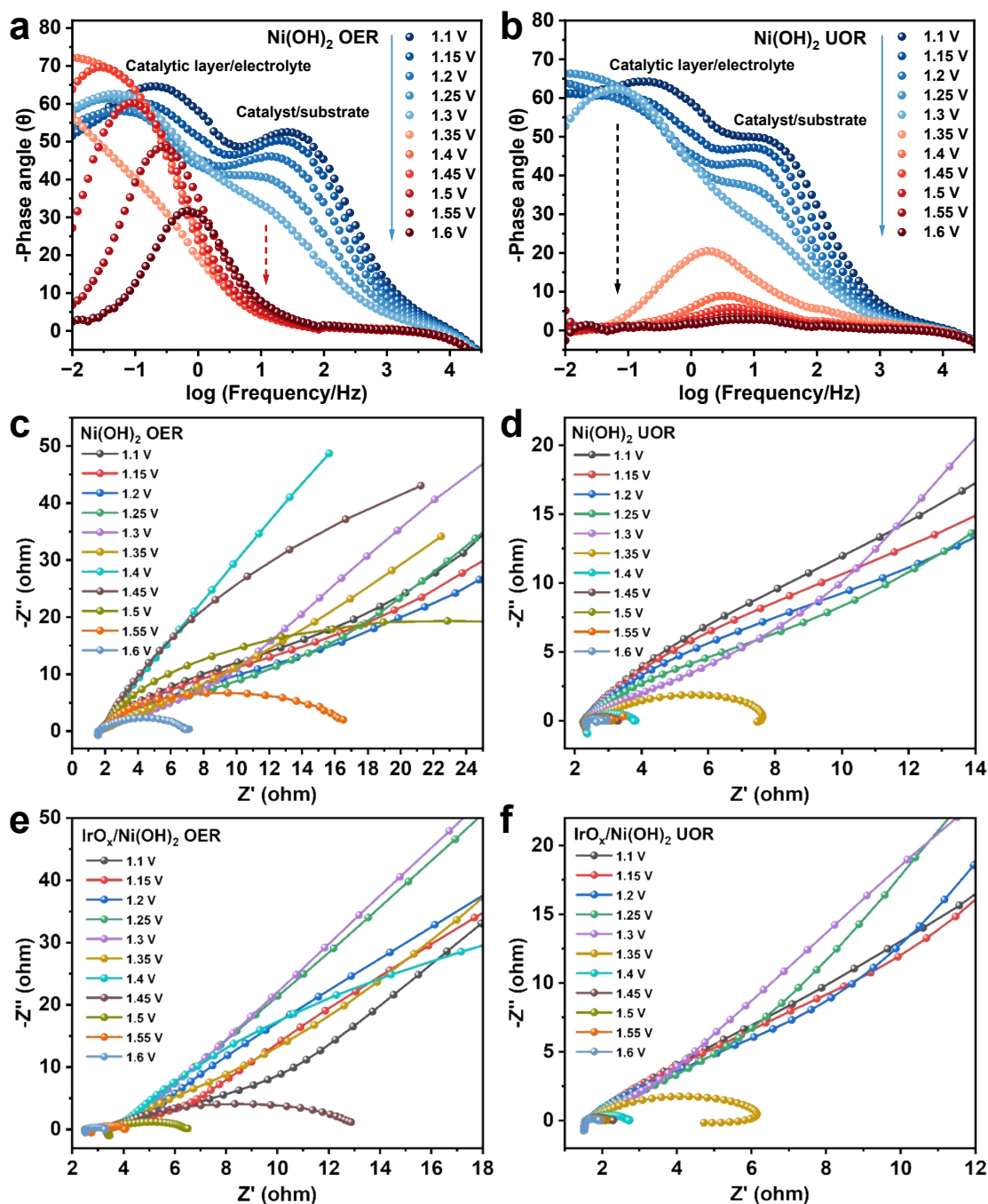


Fig. S8 Potential-dependent EIS Bode plots of $\text{Ni}(\text{OH})_2$ electrode when potentials varied from 1.1 to 1.6 V (a) in 1.0 M KOH and (b) in 1.0 M KOH + 0.33 M urea. Potential-dependent Nyquist plots of $\text{Ni}(\text{OH})_2$ electrode when potentials varied from 1.1 to 1.6 V (c) in 1.0 M KOH and (d) in 1.0 M KOH + 0.33 M urea. Potential-dependent Nyquist plots of $\text{IrO}_x/\text{Ni}(\text{OH})_2$ electrode when potentials varied from 1.1 to 1.6 V (e) in 1.0 M KOH and (f) in 1.0 M KOH + 0.33 M urea.

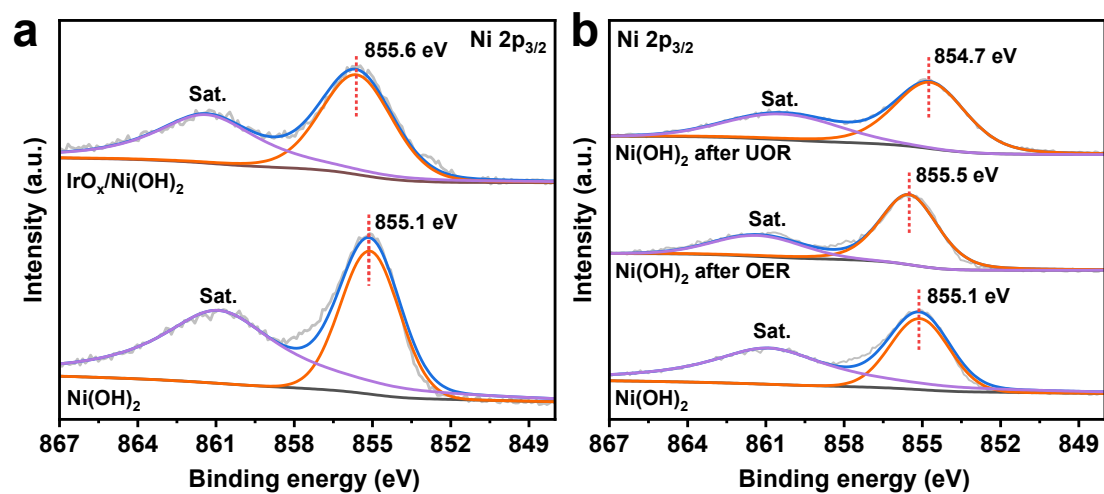


Fig. S9 (a) Ni 2p_{3/2} XPS spectra for Ni(OH)₂ and IrO_x/Ni(OH)₂. (b) Ni 2p_{3/2} XPS spectra for pristine Ni(OH)₂ and Ni(OH)₂ after OER and UOR.

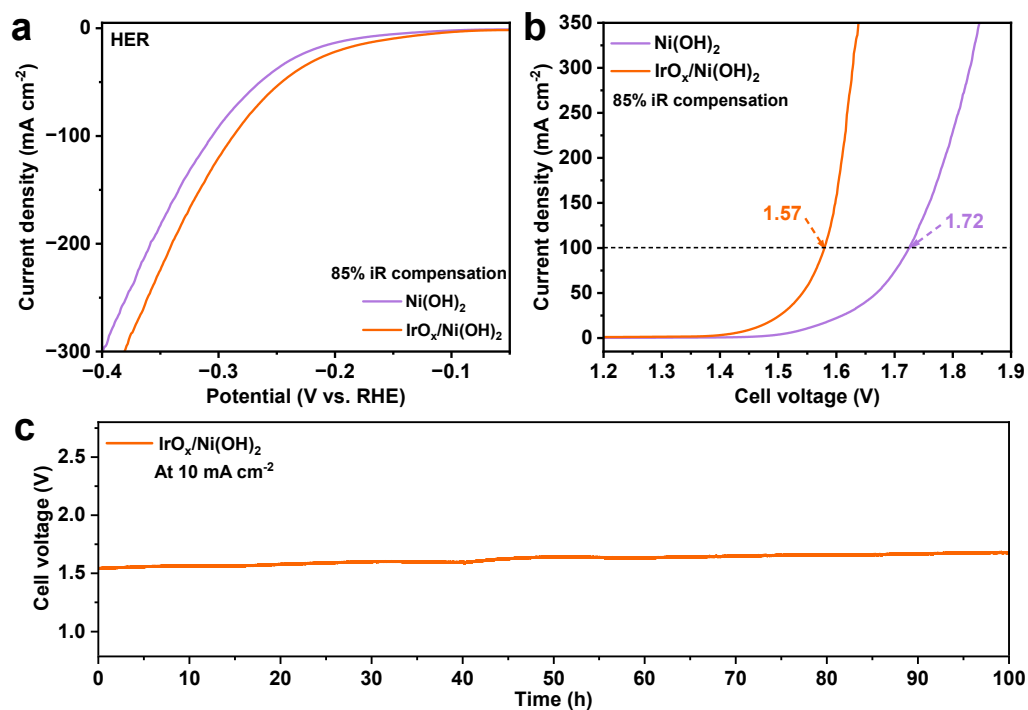


Fig. S10 (a) LSV curves for HER on Ni(OH)_2 and $\text{IrO}_x/\text{Ni(OH)}_2$ in 1 M KOH. (b) The cell voltage for Ni(OH)_2 electrolyzer and $\text{IrO}_x/\text{Ni(OH)}_2$ electrolyzer in 1 M KOH + 0.33 M urea. (c) The 100 h stability for the $\text{IrO}_x/\text{Ni(OH)}_2$ electrolyzer at 10 mA cm^{-2} in 1 M KOH + 0.33 M urea.

Table S1. The OER and UOR performances on the reported Ni/Ir-based catalysts

Electrocatalyst	Anodic reaction	Overpotential at 10 mA cm ⁻² (mV)	Electrolyte	References
IrO _x /Ni(OH) ₂	OER	206	1 M KOH	This work
Ir/Ni(OH) ₂	OER	224	1 M KOH	1
IrNiO _x /ATO	OER	340	0.05 M H ₂ SO ₄	2
Ir-Ni ₃ N	OER	273	1 M KOH	3
Mn-IrO ₂	OER	267	1 M KOH	4
Fe-IrO ₂	OER	300	1 M KOH	
Co-IrO ₂	OER	302	1 M KOH	
Cr-IrO ₂	OER	279	1 M KOH	
Electrocatalyst	Anodic reaction	Potential at 10 mA cm ⁻² (V vs. RHE)	Electrolyte	References
IrO _x /Ni(OH) ₂	UOR	1.337	1 M KOH+0.33 M urea	This work
NiIr	UOR	1.341	1 M KOH+0.5 M urea	5
Ni ₂ P	UOR	1.35	1 M KOH+0.5 M urea	6
Ni-Mo	UOR	1.36	1 M KOH+0.1 M urea	7
Ni ₂ P/Fe ₂ P	UOR	1.47	1 M KOH+0.5 M urea	8
Ni-WO _x	UOR	1.35	1 M KOH+0.33 M urea	9

Table S2. Fitting parameters of EIS data for Ni(OH)₂ and IrO_x/Ni(OH)₂ using the equivalent circuit proposed in Fig. 4d

	OER (1.55 V)		UOR (1.4 V)	
	Ni(OH) ₂	IrO _x /Ni(OH) ₂	Ni(OH) ₂	IrO _x /Ni(OH) ₂
R _s	1.401	1.675	1.675	1.31
^a R ₁	10.5	0.448	0.448	0.35
^a CPE ₁ -T	0.287	0.552	0.552	1.186
^a CPE ₁ -P	0.964	0.391	0.391	0.357
^b R ₂	2.465	1.111	1.111	0.526
^b CPE ₂ -T	0.427	0.083	0.083	0.104
^b CPE ₂ -P	0.643	0.823	0.823	0.897

Notes: ^a The subscript 1 stands for the electron transfer behavior at catalytic layer/electrolyte interface; ^b The subscript 2 indicates the electron transfer behavior at catalyst/substrate interface.

References

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