

Supporting Information

Scalable synthesis of hetero-structured Ni/NiO@RE₂O₃/C for high-performance industrial-scale HER catalysis by AEMWE

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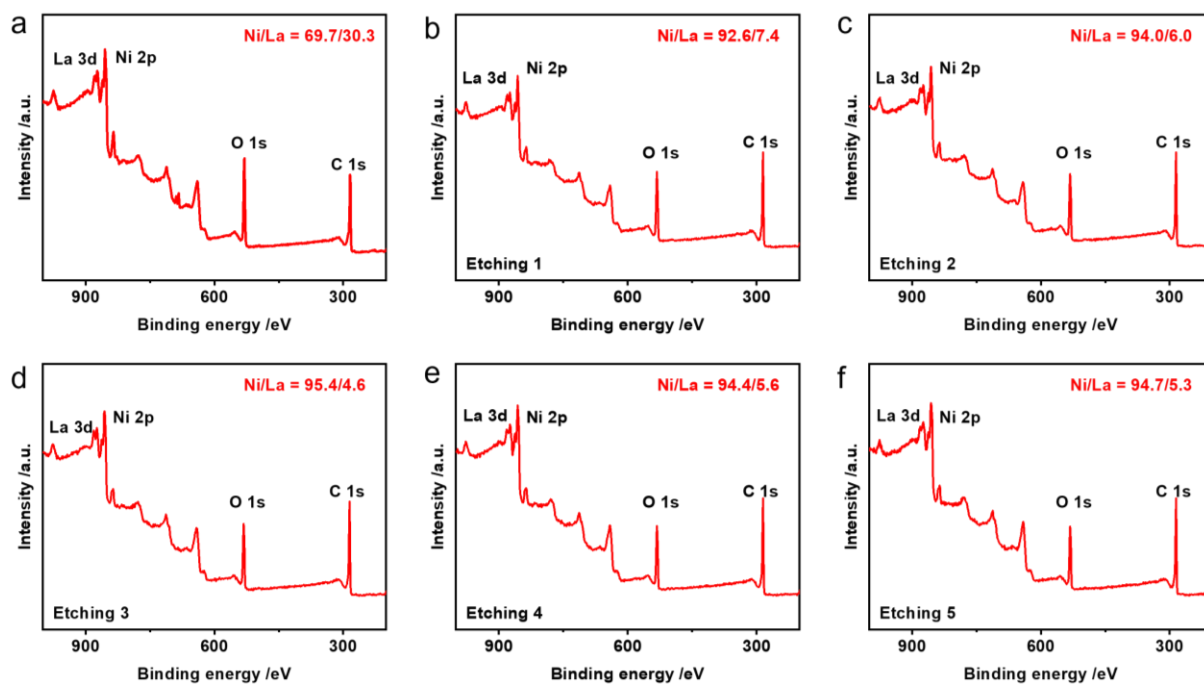
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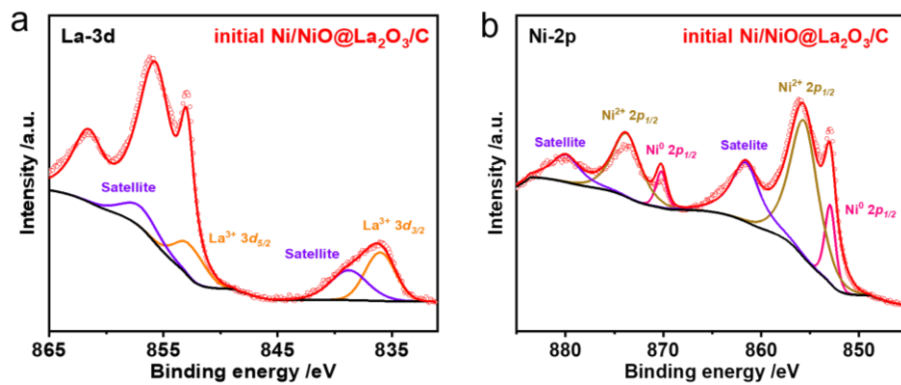
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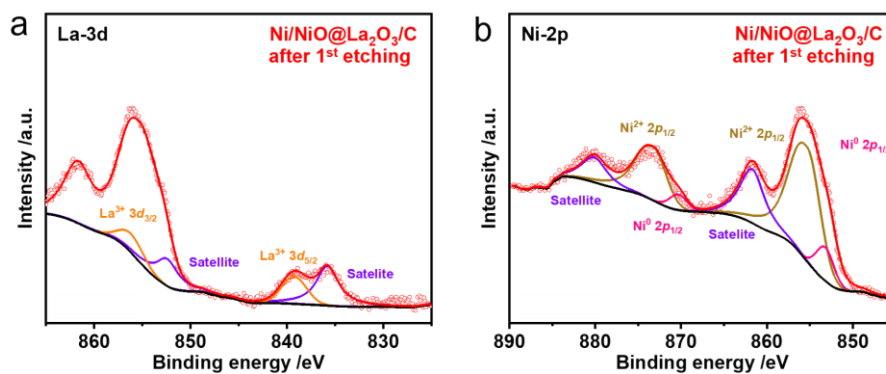
Supplementary Figures and Tables:



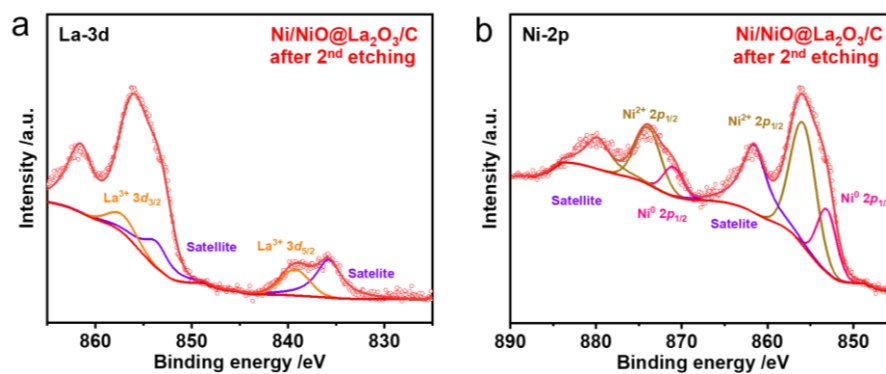
Supplementary Figure 1. XPS survey spectra of Ni/NiO@La₂O₃/C (a) before and (b-f) after the (b) 1st, (c) 2nd, (d) 3rd, (e) 4th and (f) 5th etching. The initial Ni/NiO@La₂O₃/C without etching was defined as the sample of (a) S₀. The Ni/NiO@La₂O₃/C after different etching degrees were defined as samples of (b) S₁, (c) S₂, (d) S₃, (e) S₄ and (f) S₅.



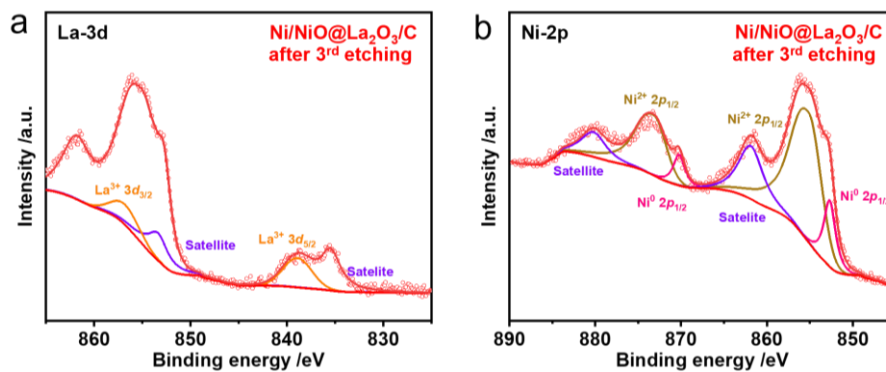
Supplementary Figure 2. XPS spectra of (a) La 3d and (b) Ni 2p for initial Ni/NiO@La₂O₃/C (S₀).



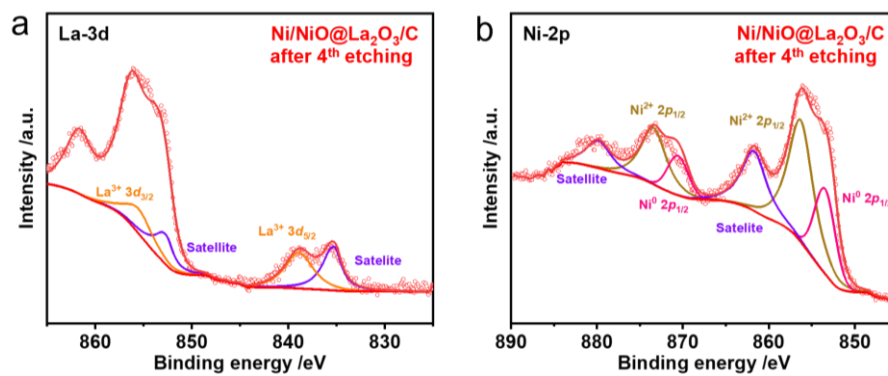
Supplementary Figure 3. XPS spectra of (a) La 3d and (b) Ni 2p for Ni/NiO@La₂O₃/C after the 1st etching (S₁).



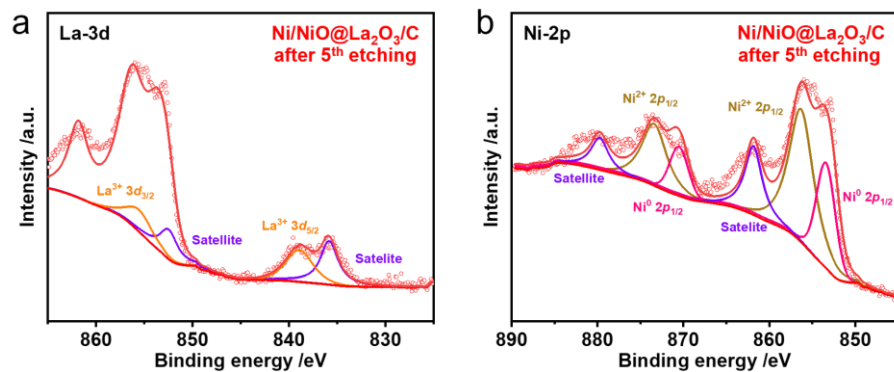
Supplementary Figure 4. XPS spectra of (a) La 3d and (b) Ni 2p for Ni/NiO@La₂O₃/C after the 2nd etching (S₂).



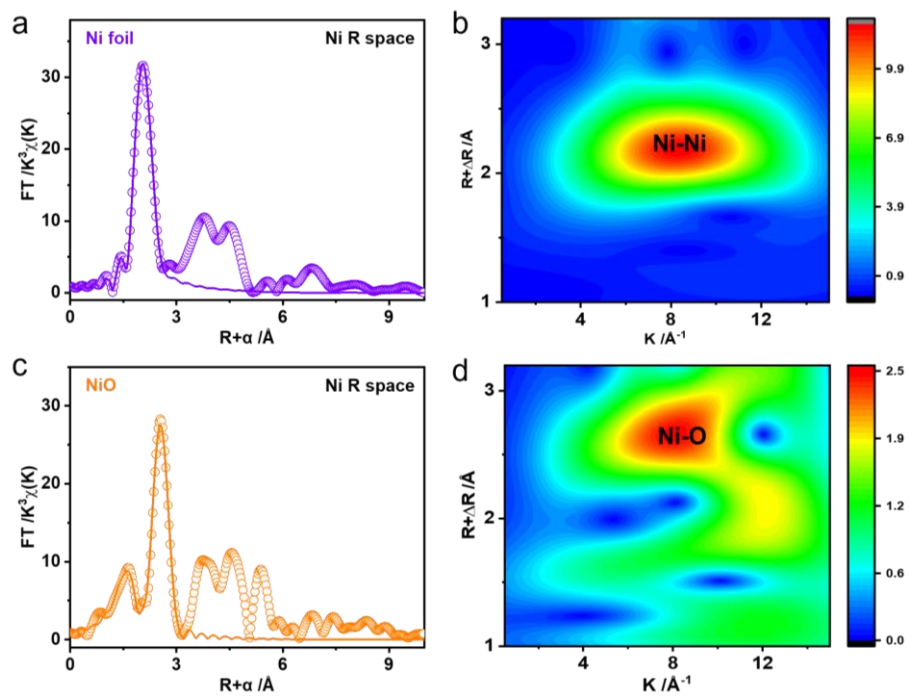
Supplementary Figure 5. XPS spectra of (a) La 3d and (b) Ni 2p for Ni/NiO@La₂O₃/C after the 3rd etching (S₃).



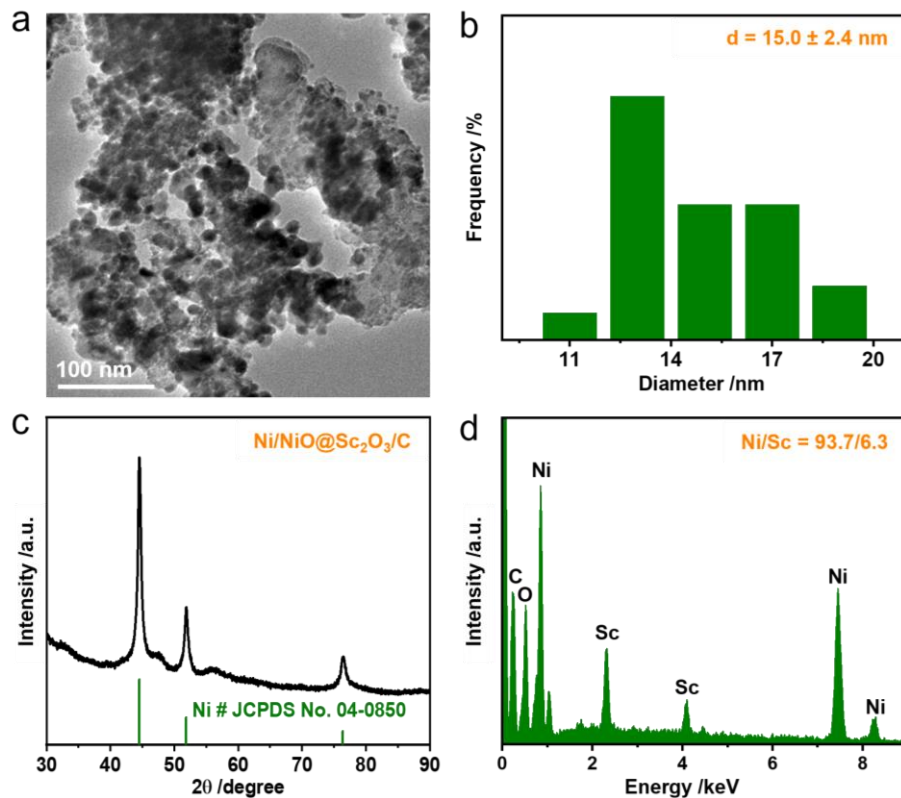
Supplementary Figure 6. XPS spectra of (a) La 3d and (b) Ni 2p for Ni/NiO@La₂O₃/C after the 4th etching (S4).



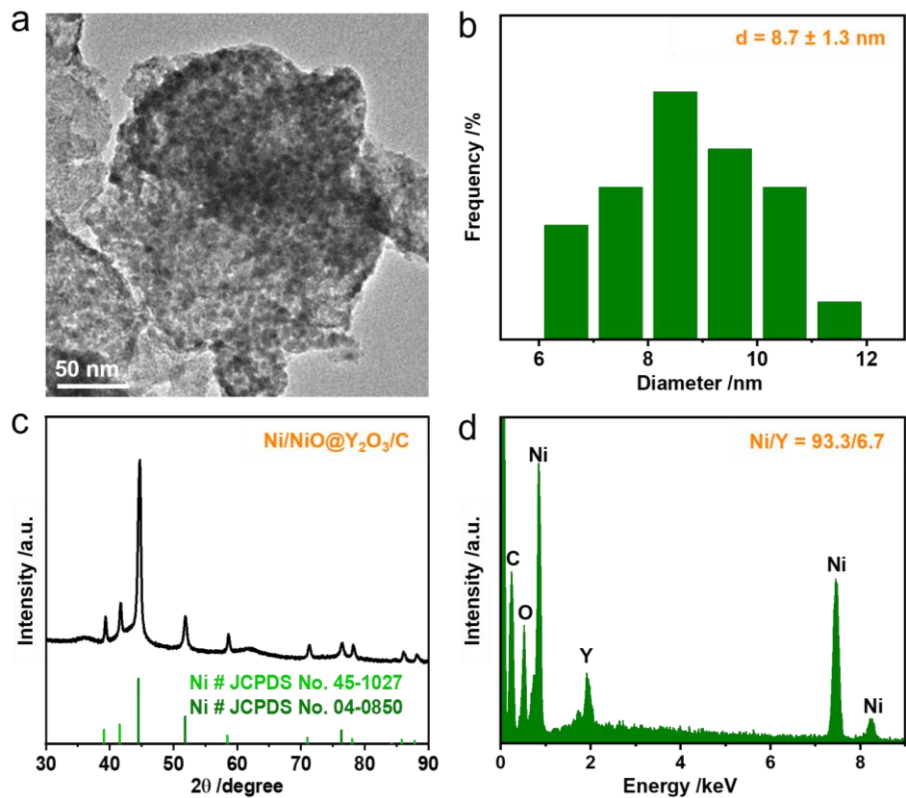
Supplementary Figure 7. XPS spectra of (a) La 3d and (b) Ni 2p for Ni/NiO@La₂O₃/C after the 5th etching (S₅).



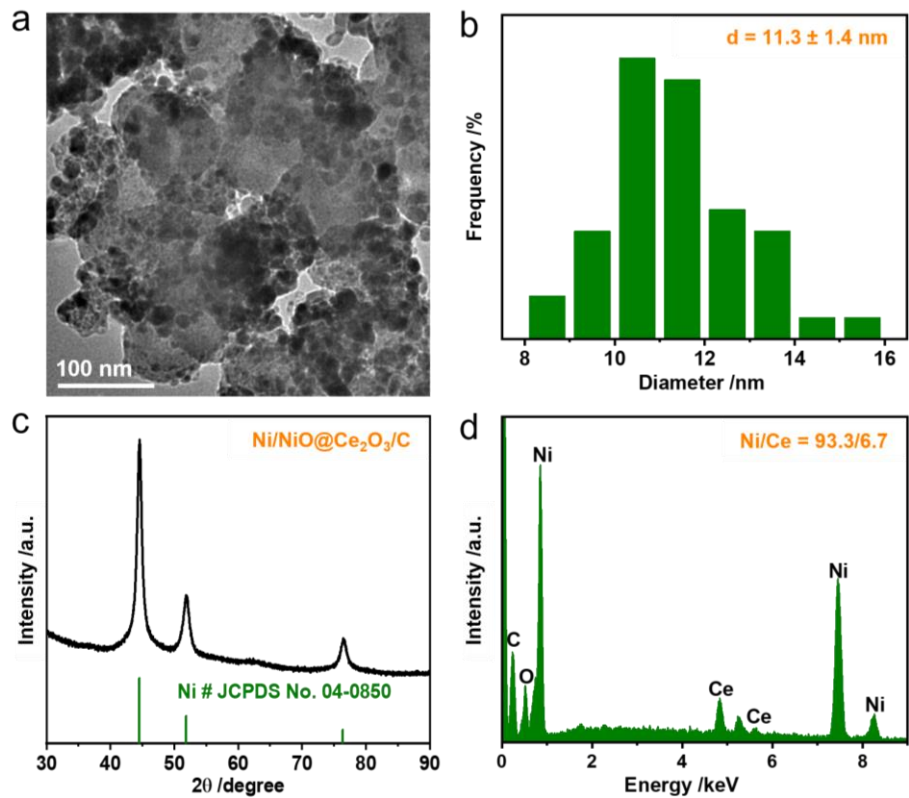
Supplementary Figure 8. (a, c) Ni K-edge EXAFS analyses in R and k spaces for (a) Ni foil and (c) NiO. (b, d) WT analyses of Ni K-edge FT-EXAFS data for (b) Ni foil and (d) NiO.



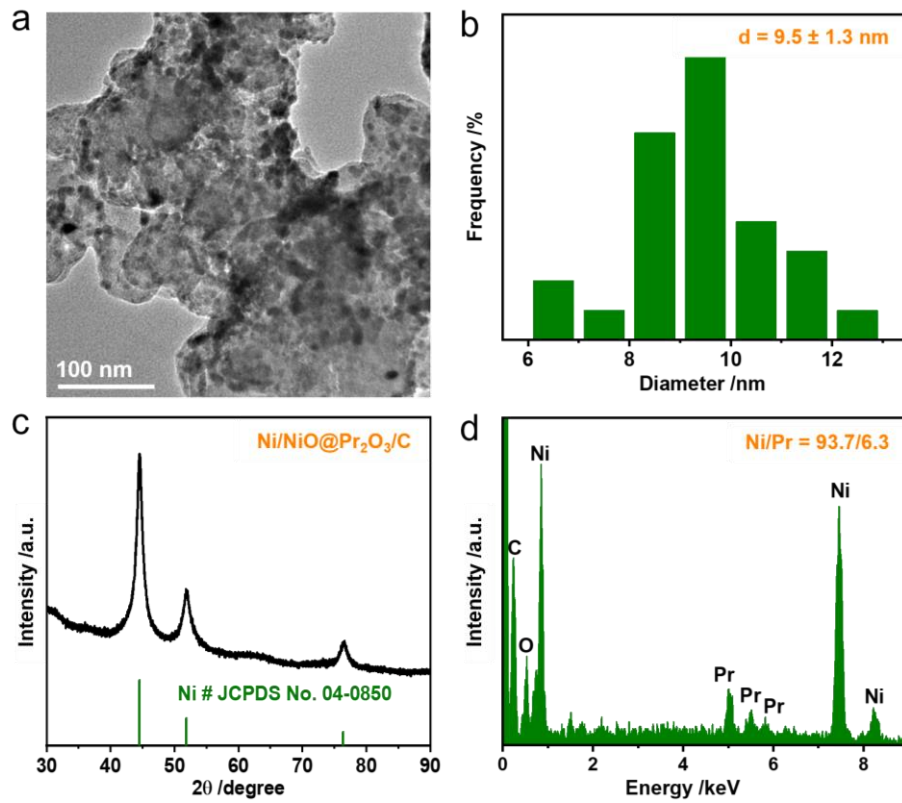
Supplementary Figure 9. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Sc₂O₃/C.



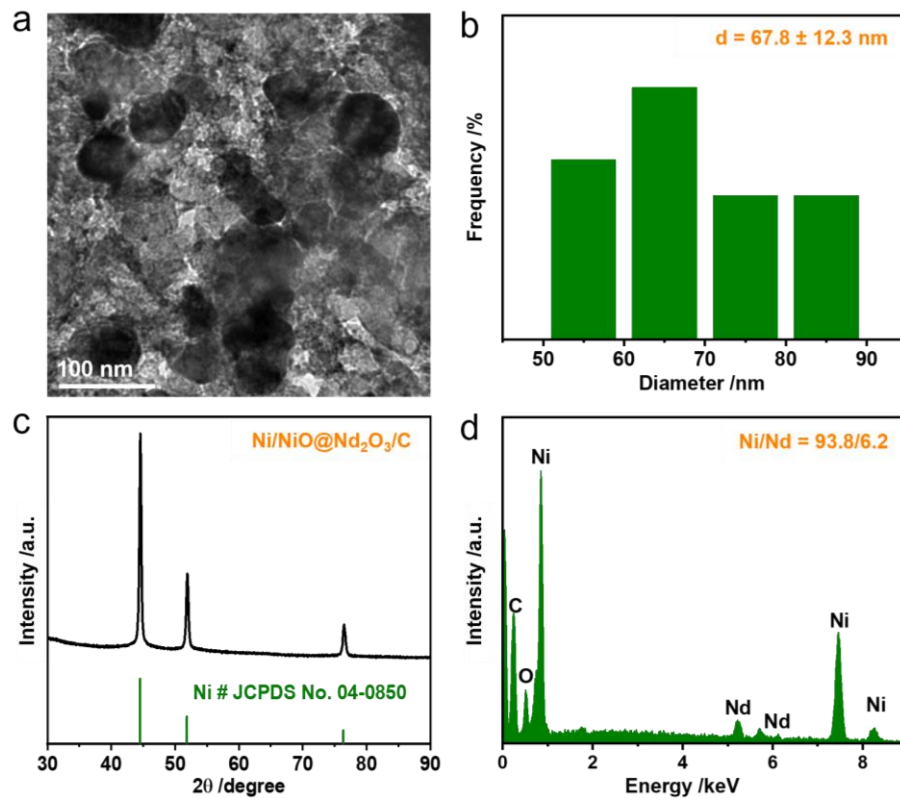
Supplementary Figure 10. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Y₂O₃/C.



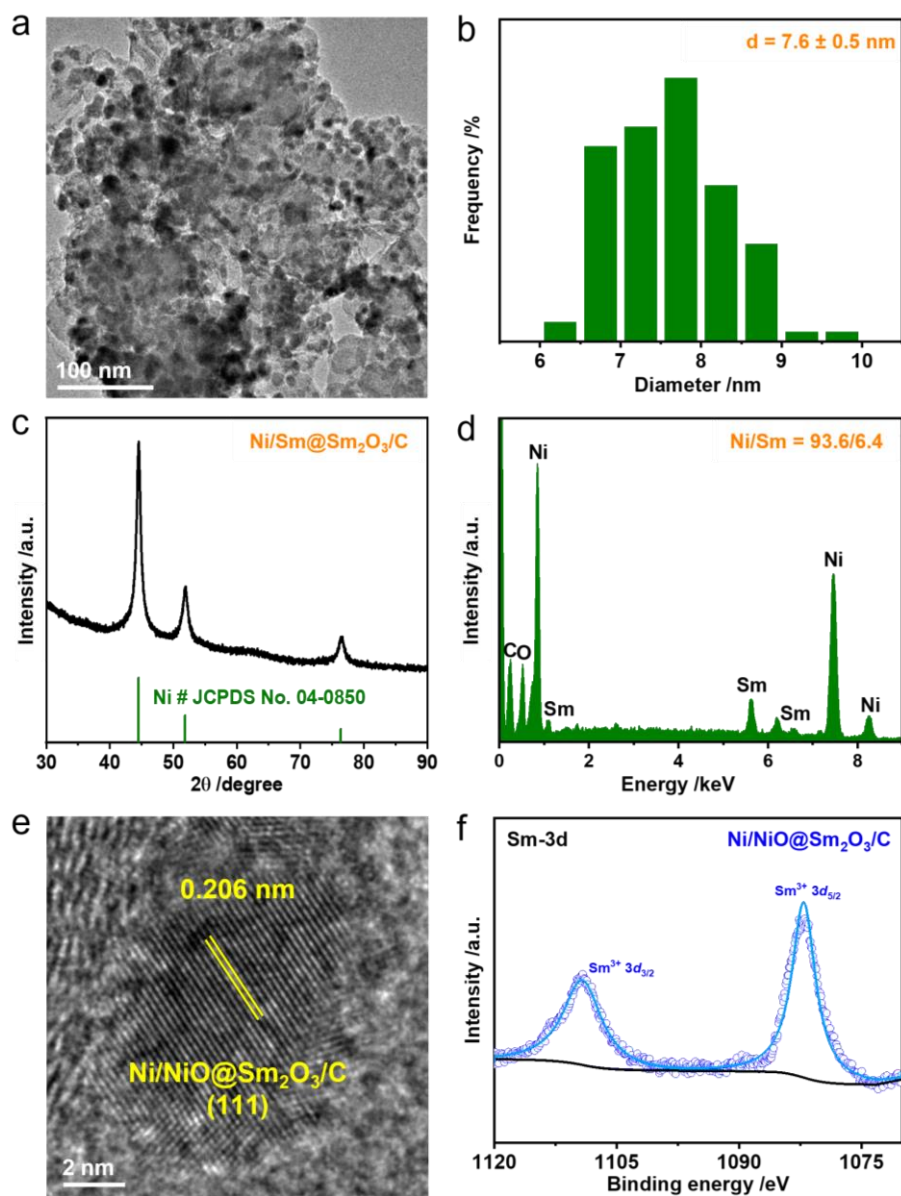
Supplementary Figure 11. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Ce₂O₃/C.



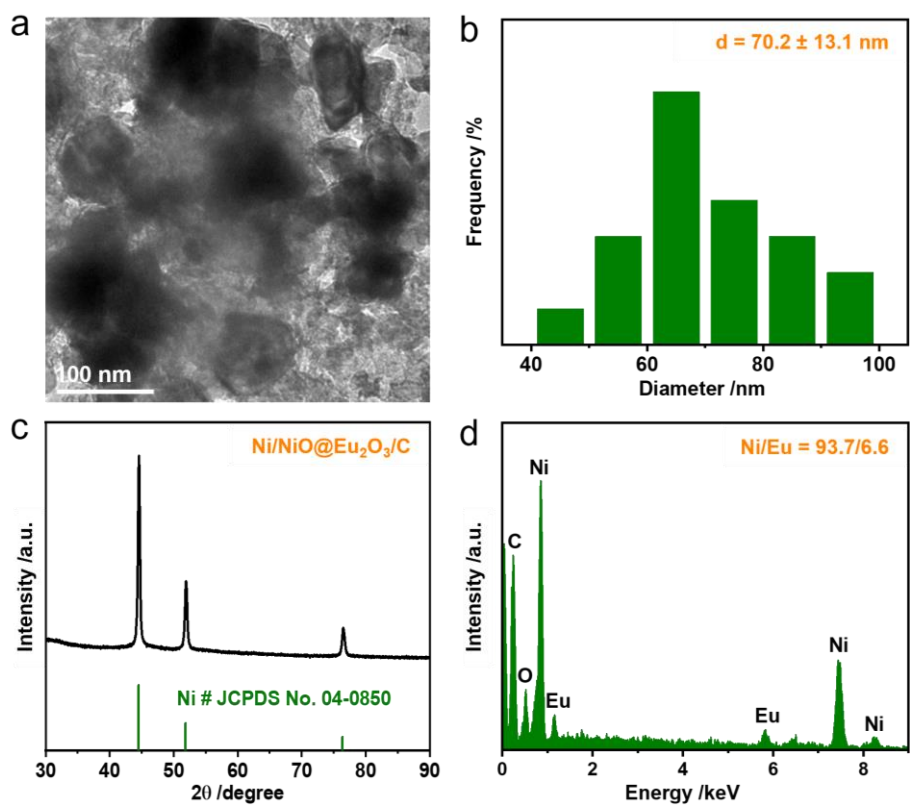
Supplementary Figure 12. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Pr₂O₃/C.



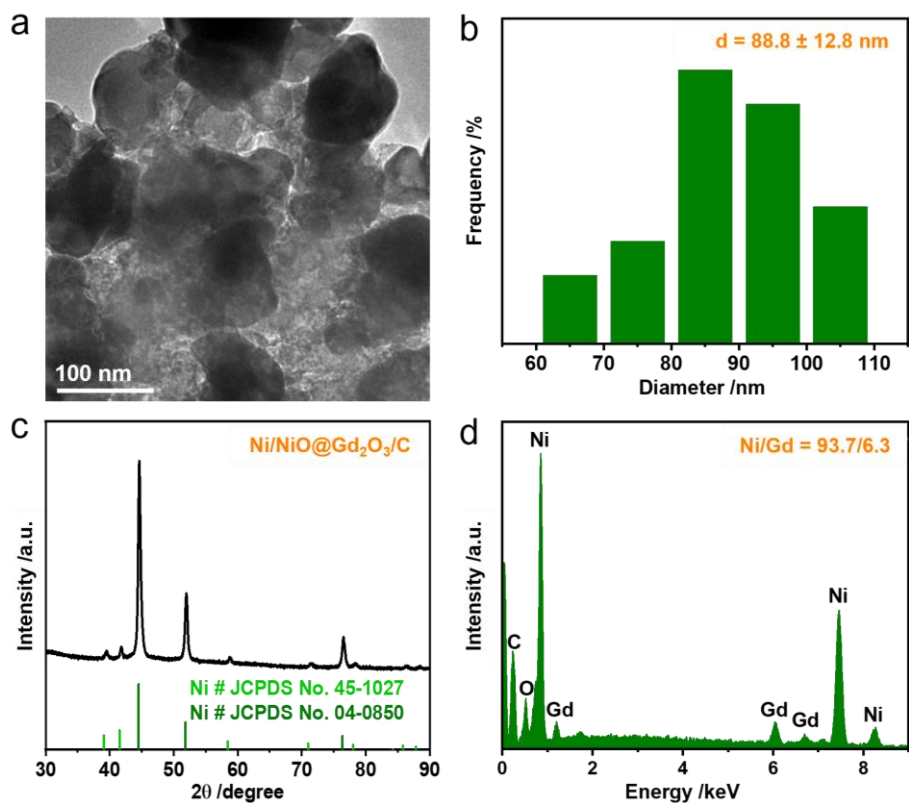
Supplementary Figure 13. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Nd₂O₃/C.



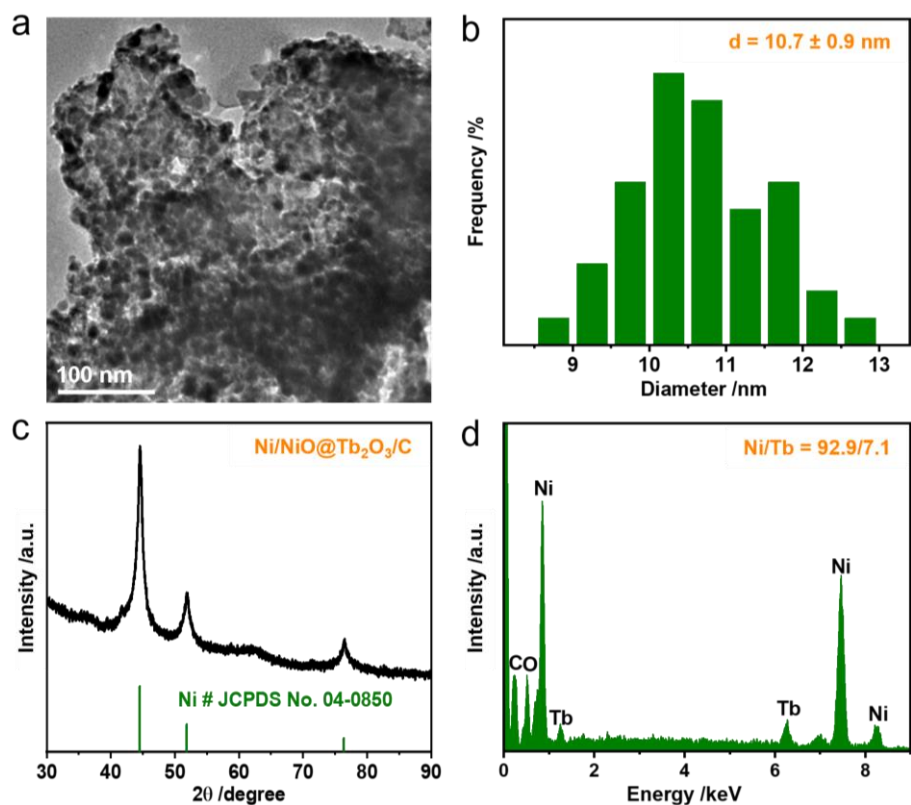
Supplementary Figure 14. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS, (e) HRTEM image and (f) 3d XPS spectrum of Sm of Ni/NiO@Sm₂O₃/C.



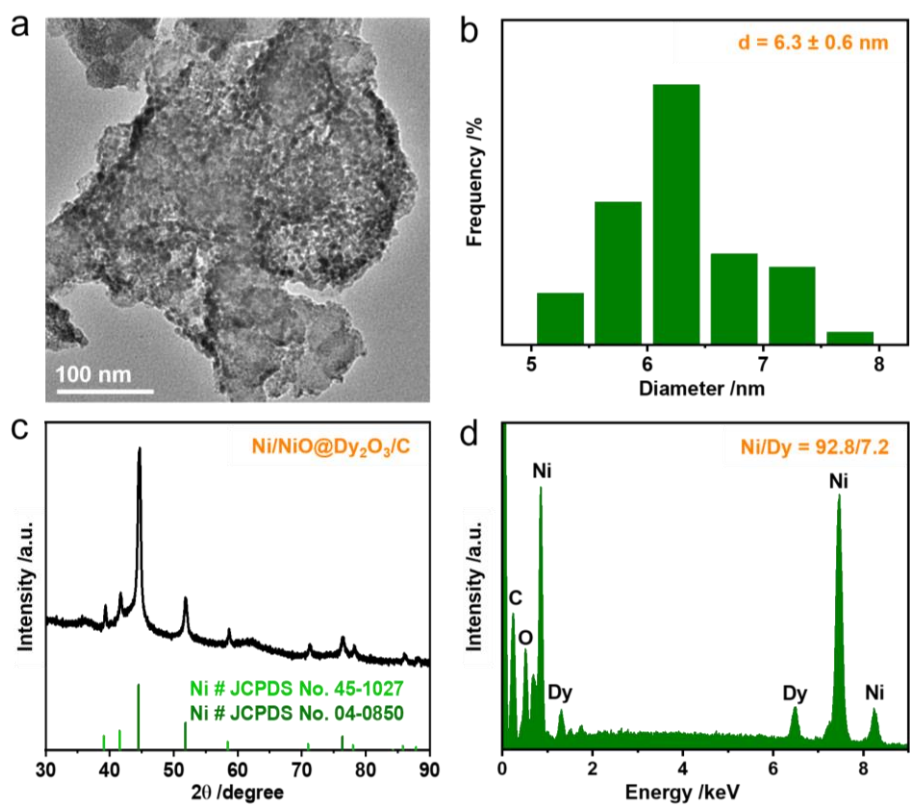
Supplementary Figure 15. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Eu₂O₃/C.



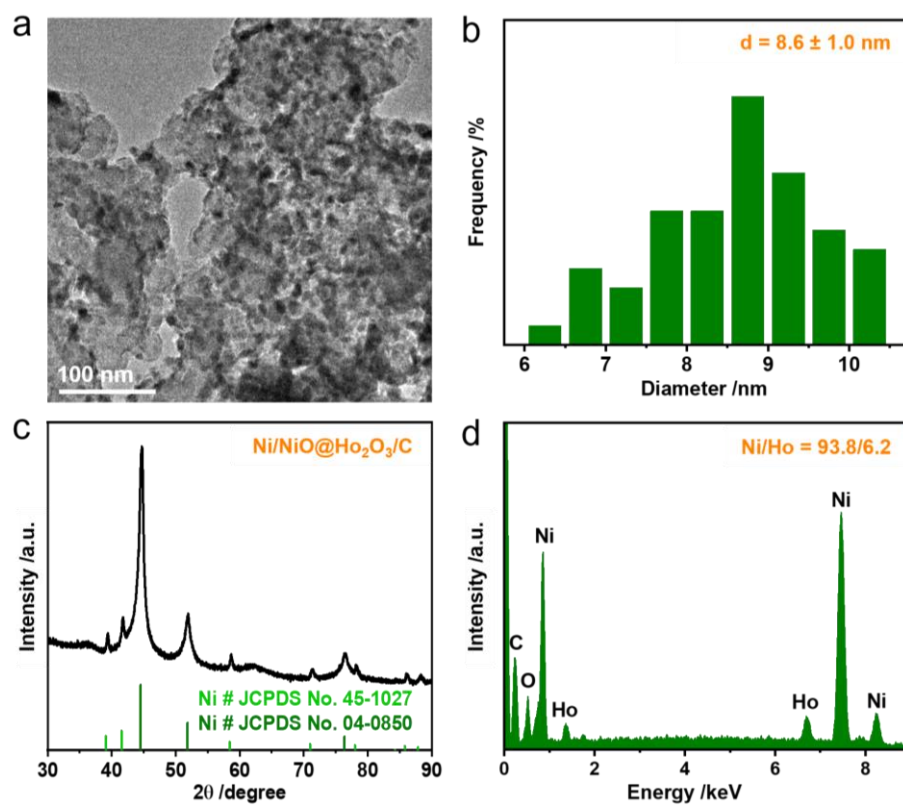
Supplementary Figure 16. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Gd₂O₃/C.



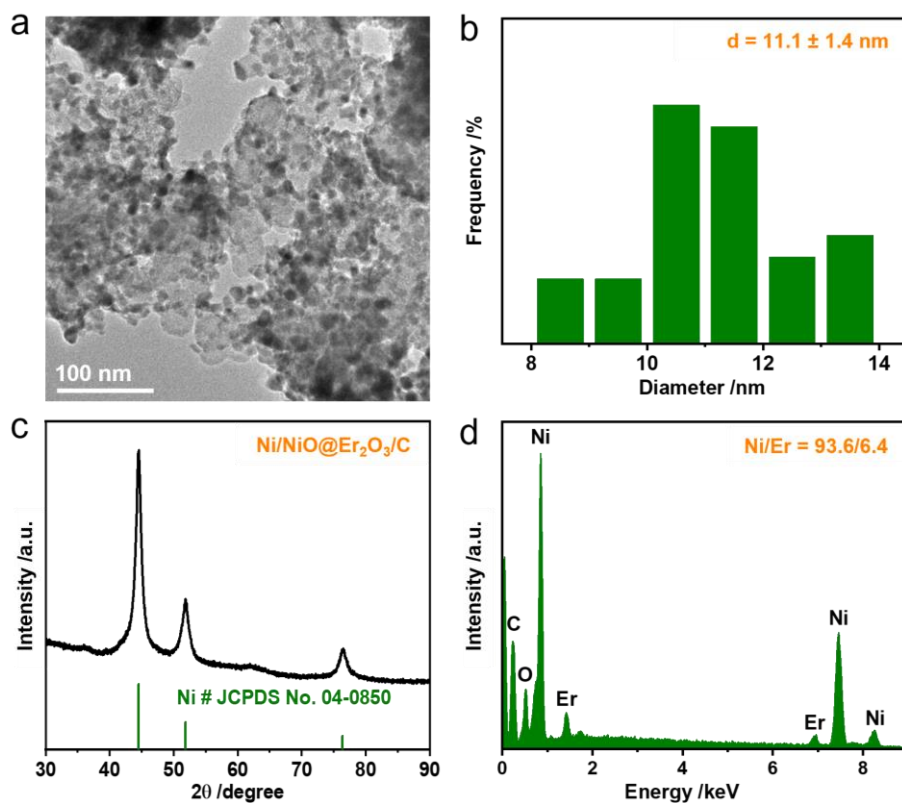
Supplementary Figure 17. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Tb₂O₃/C.



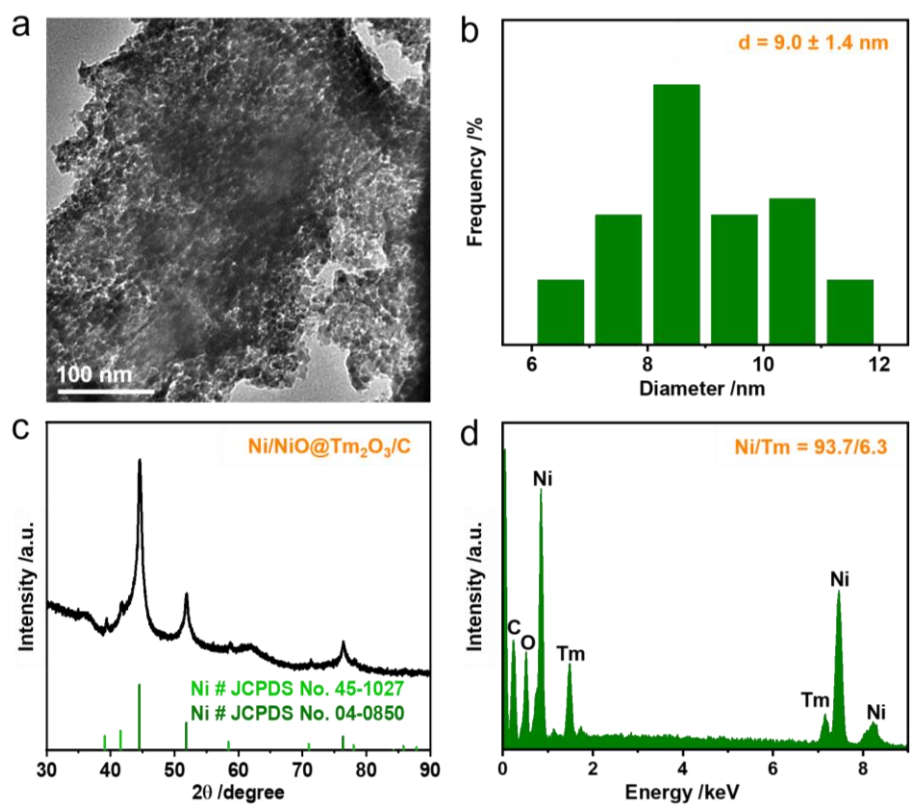
Supplementary Figure 18. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Dy₂O₃/C.



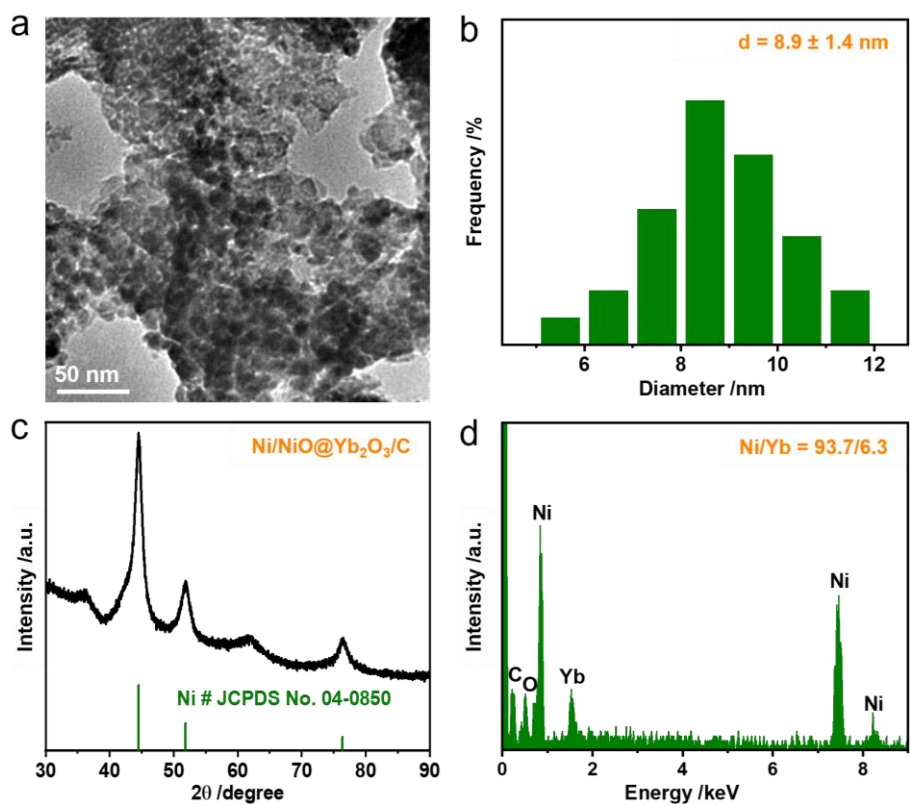
Supplementary Figure 19. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Ho₂O₃/C.



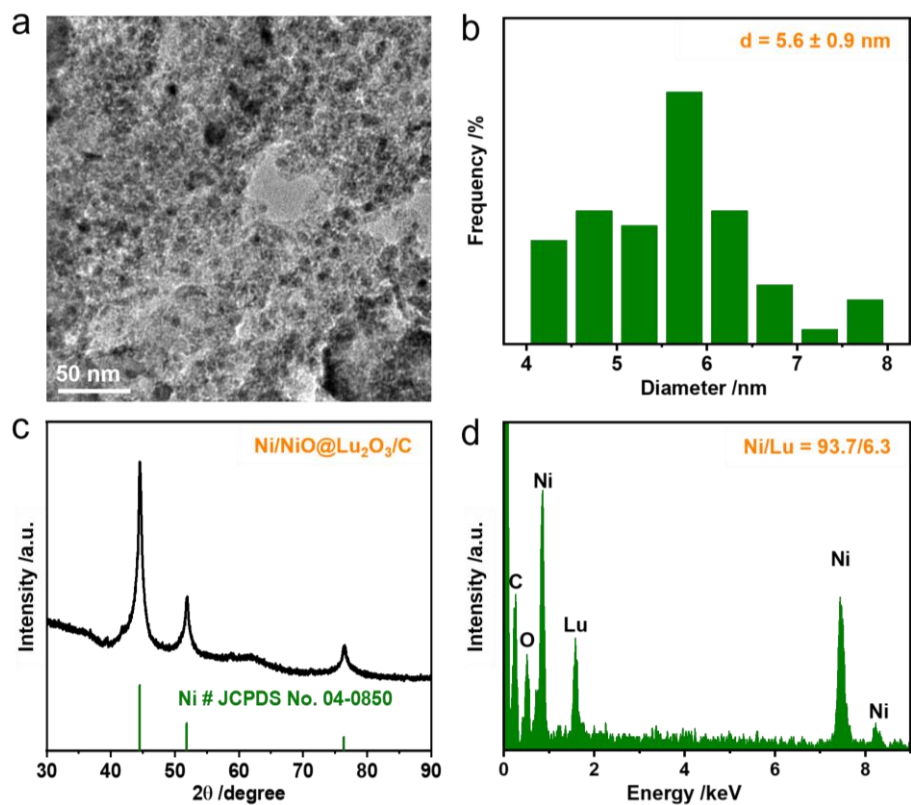
Supplementary Figure 20. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Er₂O₃/C.



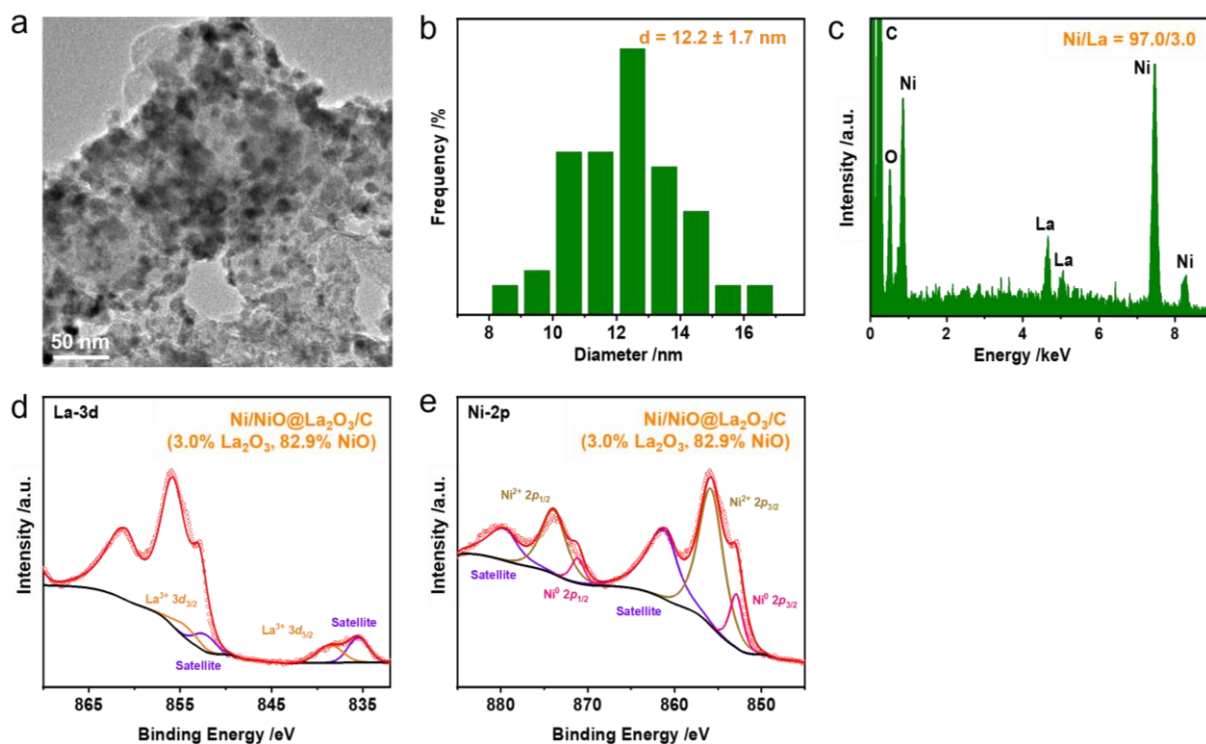
Supplementary Figure 21. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Tm₂O₃/C.



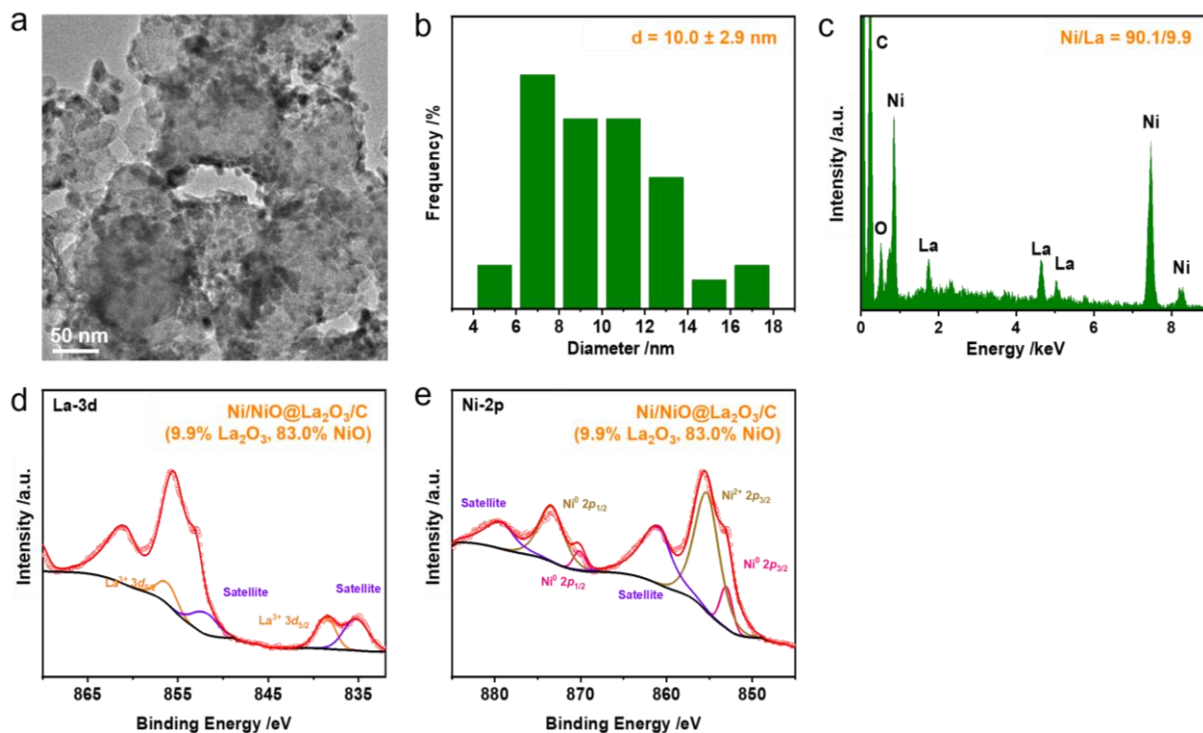
Supplementary Figure 22. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Yb₂O₃/C.



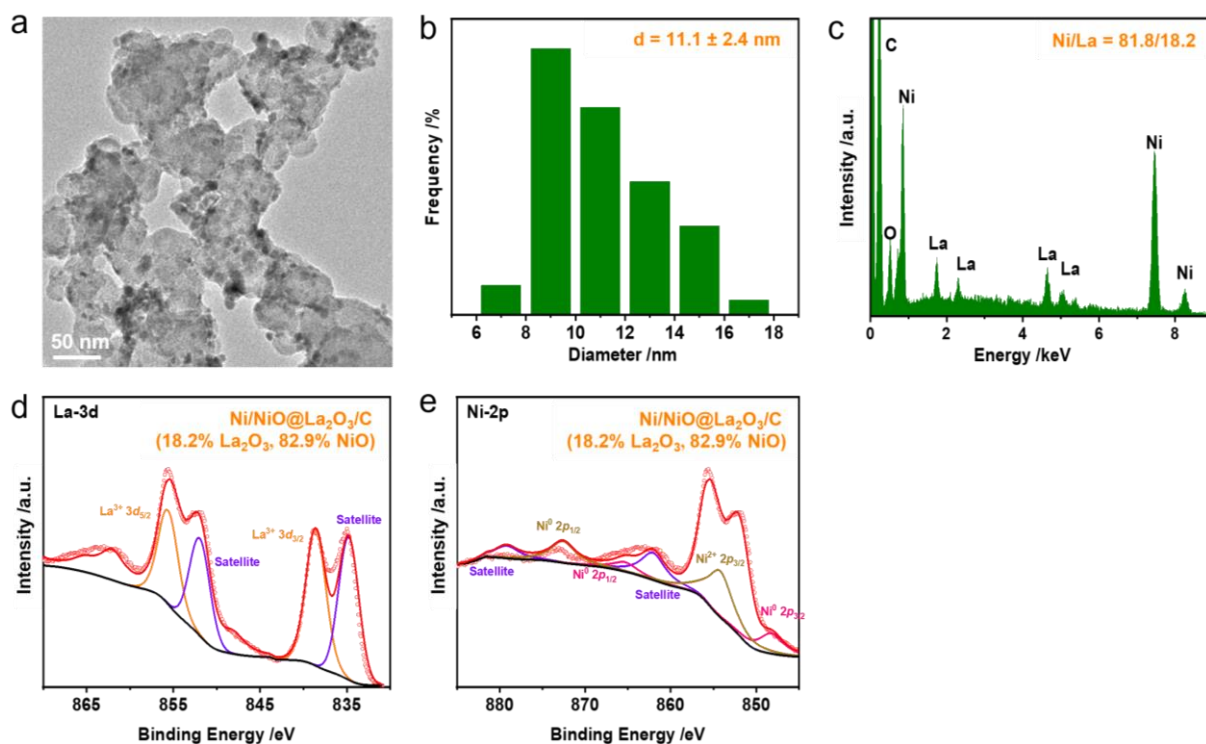
Supplementary Figure 23. (a) TEM image, (b) diameter distribution, (c) XRD pattern and (d) SEM-EDS of Ni/NiO@Lu₂O₃/C.



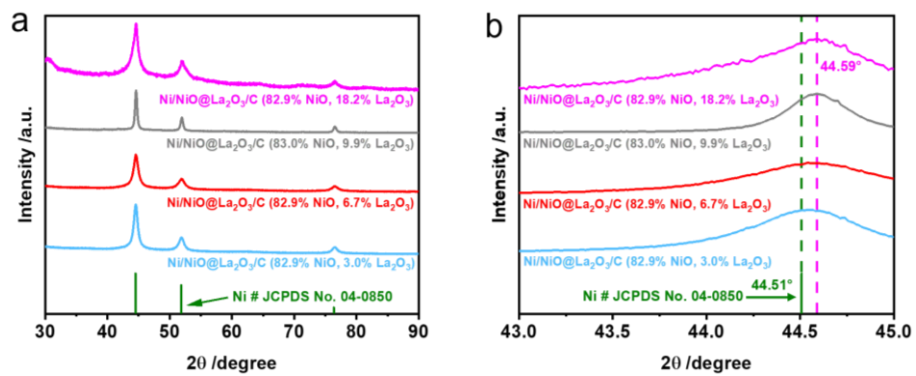
Supplementary Figure 24. (a) TEM image, (b) diameter distribution, (c) SEM-EDS, (d) La 3d XPS spectrum and (f) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (3.0% La₂O₃, 82.9% NiO).



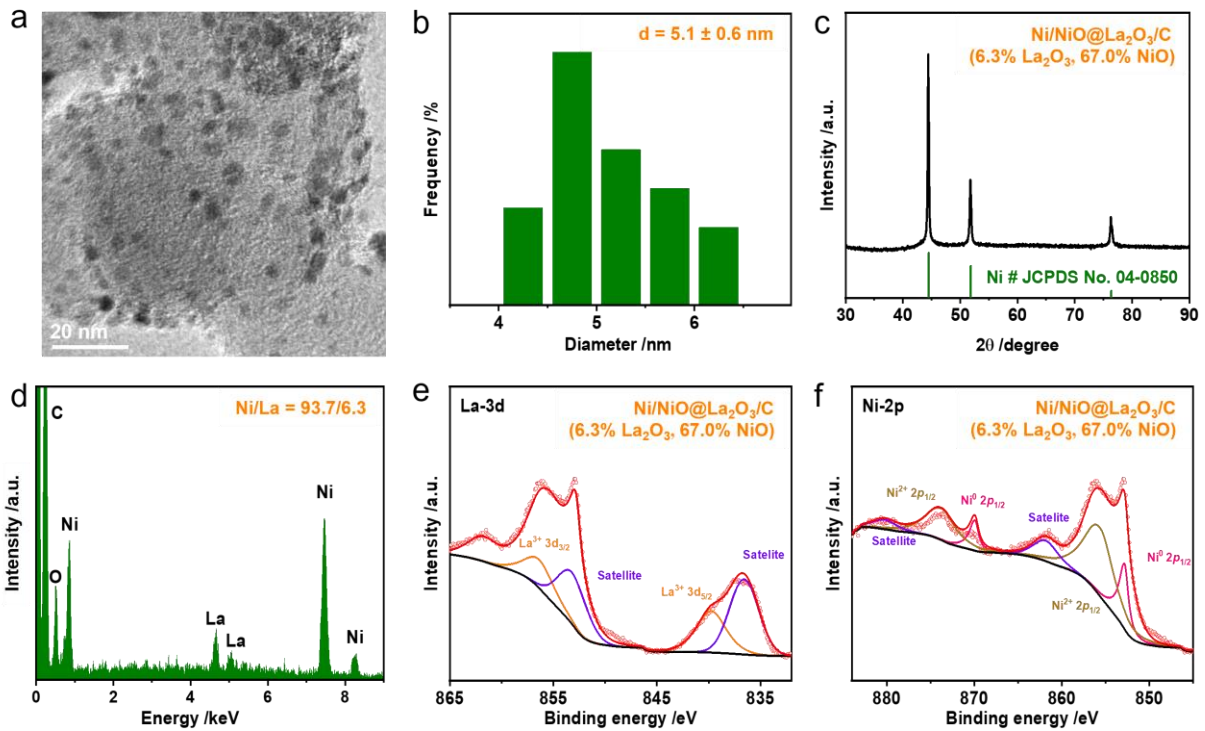
Supplementary Figure 25. (a) TEM image, (b) diameter distribution, (c) SEM-EDS, (d) La 3d XPS spectrum and (e) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (9.9% La₂O₃, 83.0% NiO).



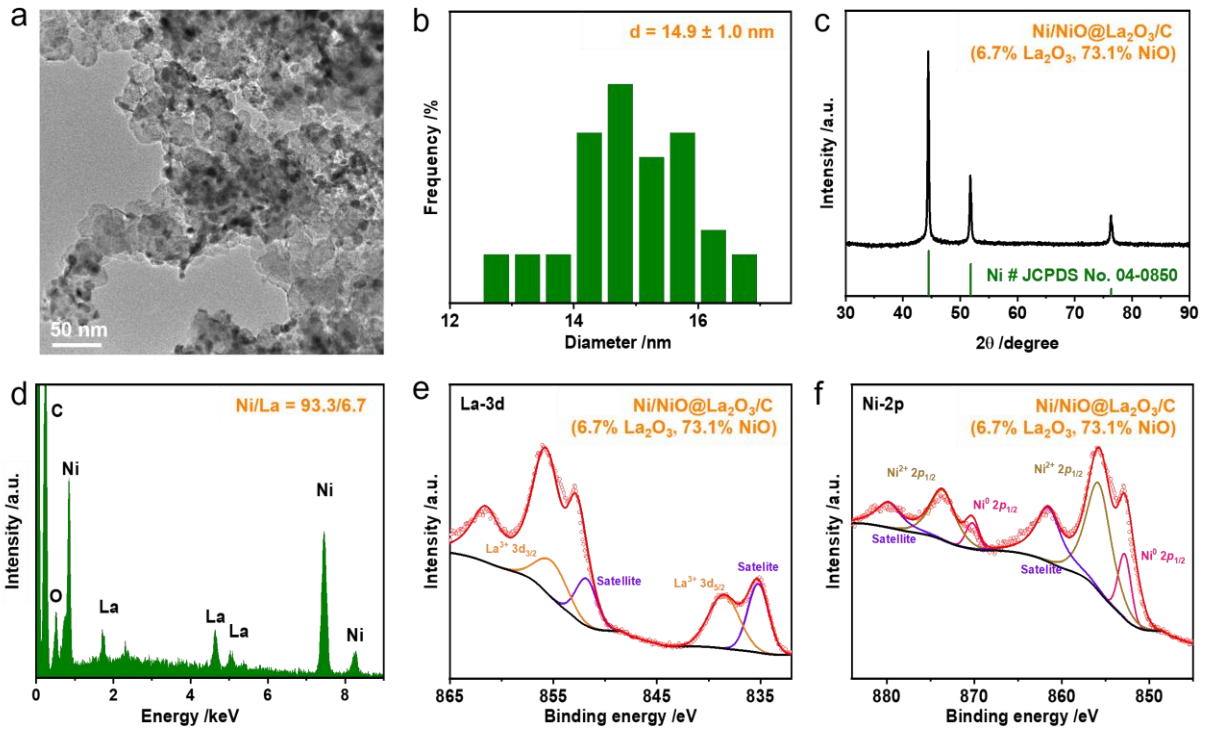
Supplementary Figure 26. (a) TEM image, (b) diameter distribution, (c) SEM-EDS, (d) La 3d XPS spectrum and (e) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (18.2% La₂O₃, 82.9% NiO).



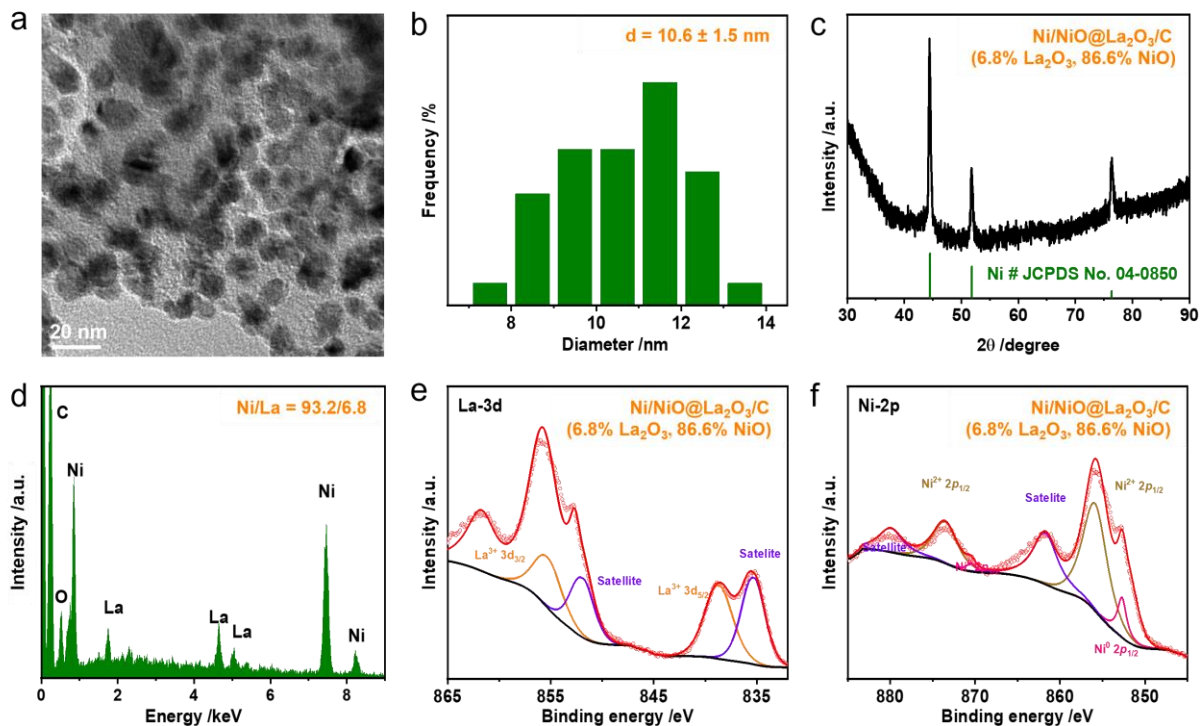
Supplementary Figure 27. (a) XRD patterns and (b) enlarged XRD patterns of Ni/NiO@La₂O₃/C (82.9% NiO) with different amounts of La₂O₃ (3.0%, 6.7%, 9.9% and 18.2%).



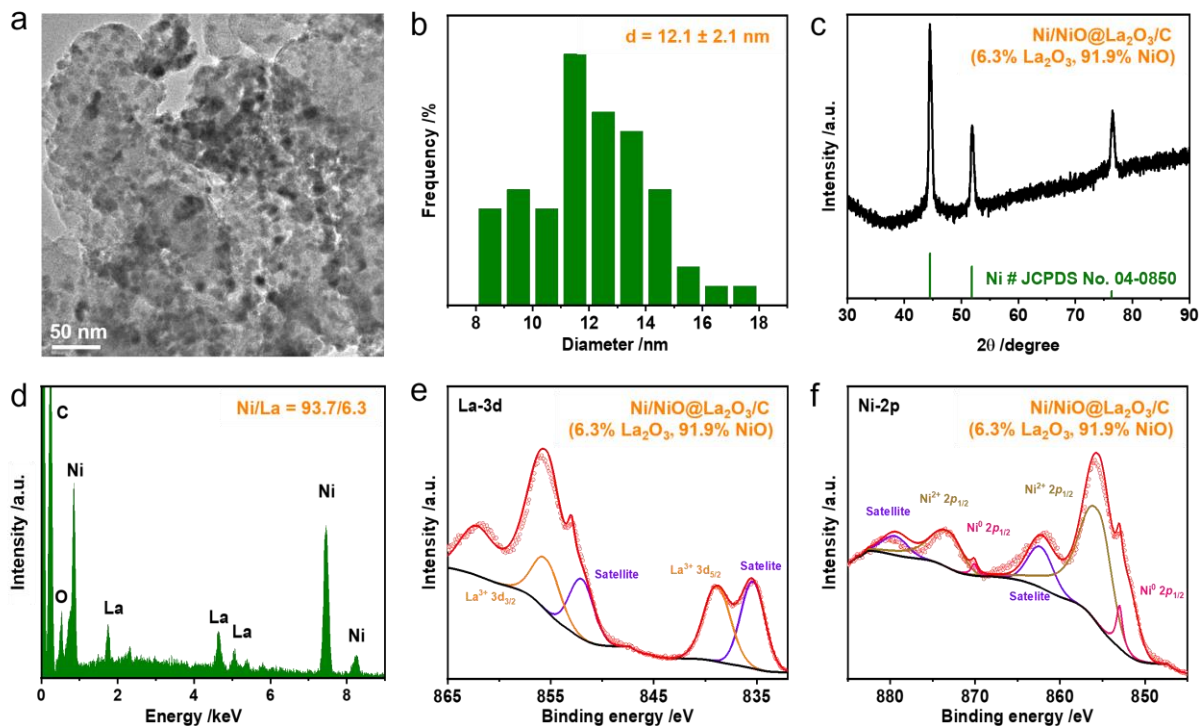
Supplementary Figure 28. (a) TEM image, (b) diameter distribution, (c) XRD pattern, (d) SEM-EDS, (e) La 3d XPS spectrum and (f) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (6.3% La₂O₃, 67.0% NiO).



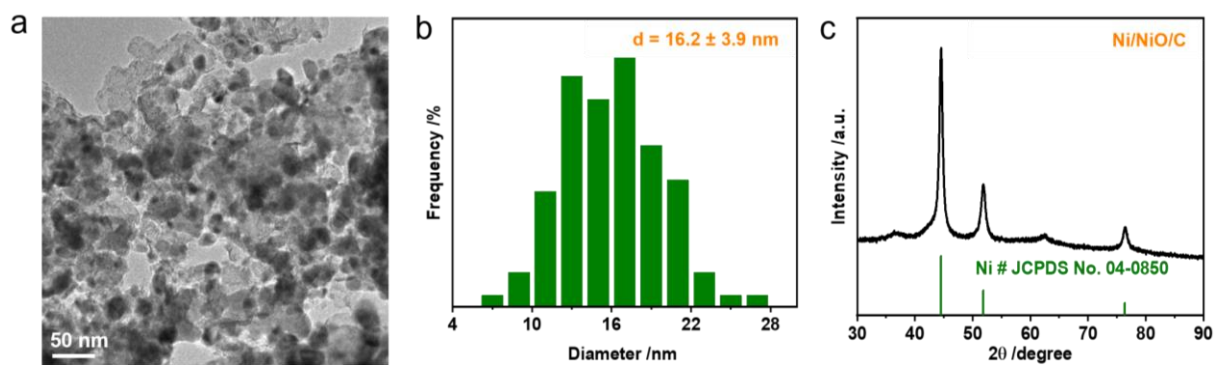
Supplementary Figure 29. (a) TEM image, (b) diameter distribution, (c) XRD pattern, (d) SEM-EDS, (e) La 3d XPS spectrum and (f) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (6.7% La₂O₃, 73.1% NiO).



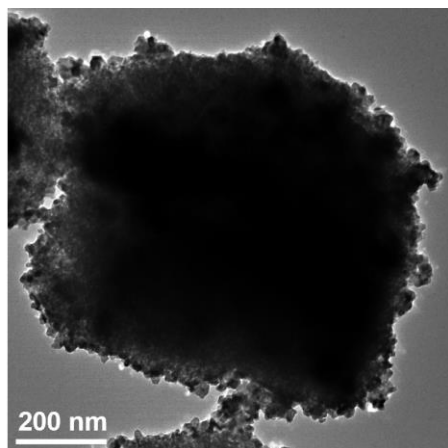
Supplementary Figure 30. (a) TEM image, (b) diameter distribution, (c) XRD pattern, (d) SEM-EDS, (e) La 3d XPS spectrum and (f) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (6.8% La₂O₃, 86.6% NiO).



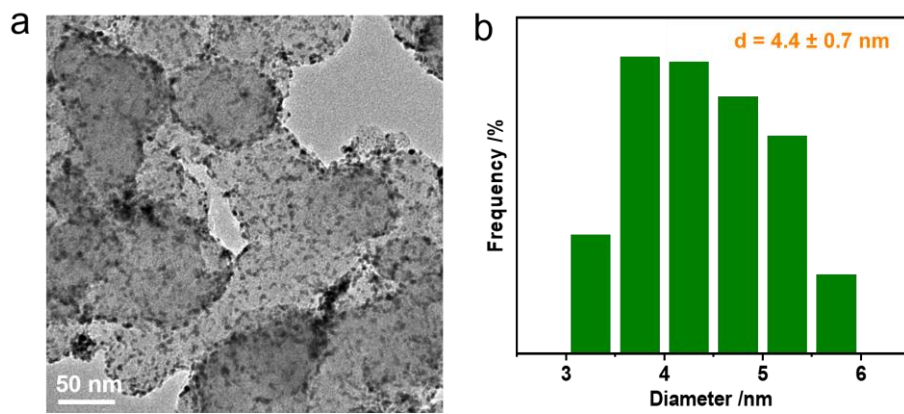
Supplementary Figure 31. (a) TEM image, (b) diameter distribution, (c) XRD pattern, (d) SEM-EDS, (e) La 3d XPS spectrum and (f) Ni 2p XPS spectrum of Ni/NiO@La₂O₃/C (6.3% La₂O₃, 91.9% NiO).



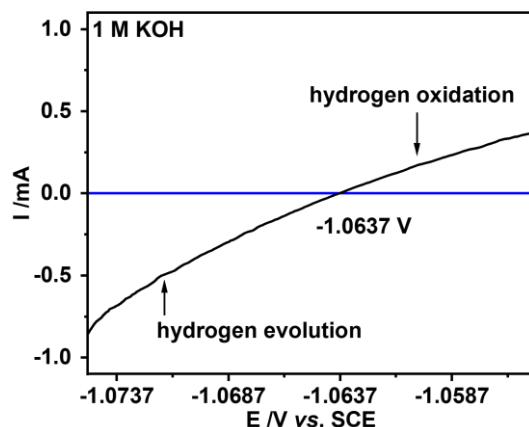
Supplementary Figure 32. (a) TEM image, (b) diameter distribution and (c) XRD pattern of Ni/NiO/C.



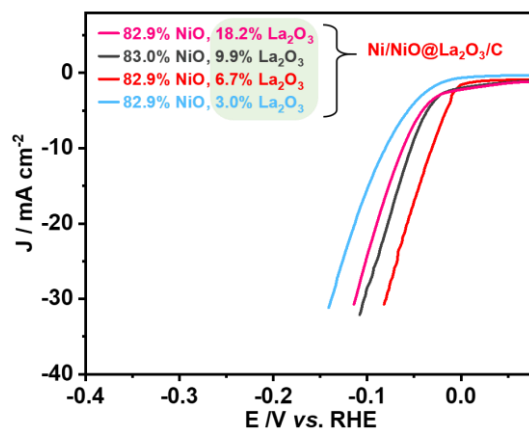
Supplementary Figure 33. TEM image of Raney Ni.



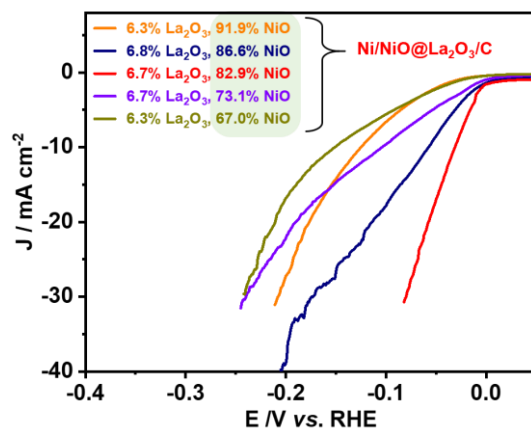
Supplementary Figure 34. (a) TEM image and (b) diameter distribution of commercial Pt/C.



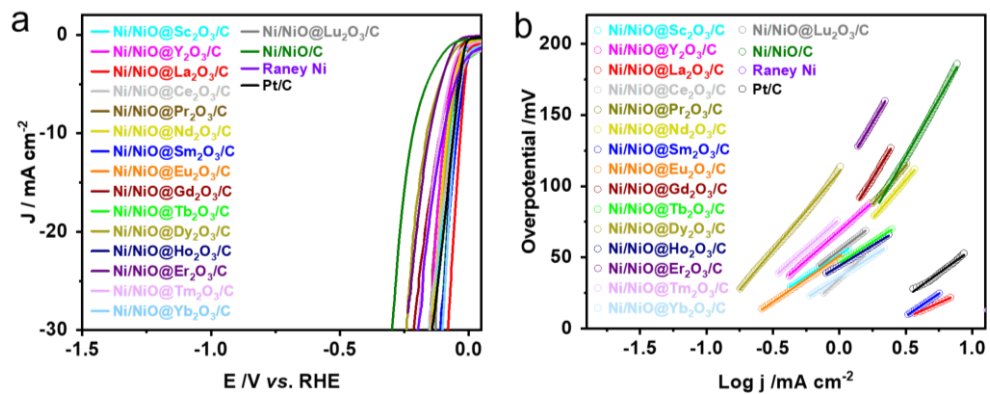
Supplementary Figure 35. Calibration of SCE and conversion to RHE. The calibration of saturated calomel electrode (SCE) reference electrode was performed in a standard three-electrode system with polished platinum electrodes as the working and counter electrodes, and the SCE as the reference electrode. Electrolyte was pre-purged and saturated with high purity H_2 . Linear scanning voltammetry (LSV) was then run at a scan rate of 0.1 mV s^{-1} , and the potential at which the current crossed zero was taken to be the thermodynamic potential (vs. SCE) for the hydrogen electrode reaction. In 1 M KOH solution, the zero current point was at -1.0637 V , so $E(\text{RHE}) = E(\text{SCE}) + 1.0637 \text{ V}$.



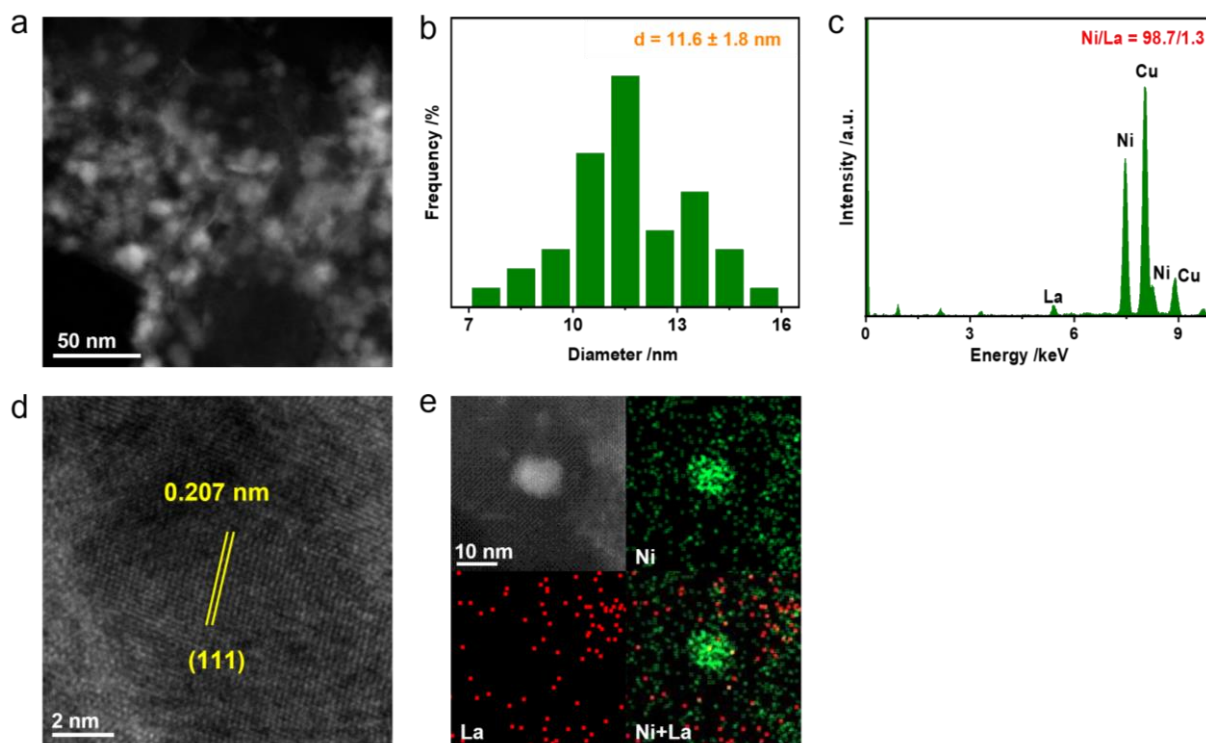
Supplementary Figure 36. LSV curves of Ni/NiO@La₂O₃/C (82.9% NiO, 18.2% La₂O₃), Ni/NiO@La₂O₃/C (83.0% NiO, 9.9% La₂O₃), Ni/NiO@La₂O₃/C (82.9% NiO, 6.7% La₂O₃) and Ni/NiO@La₂O₃/C (82.9% NiO, 3.0% La₂O₃) measured in 1 M KOH. The different contents of La₂O₃ are based on the SEM-EDS measurements.



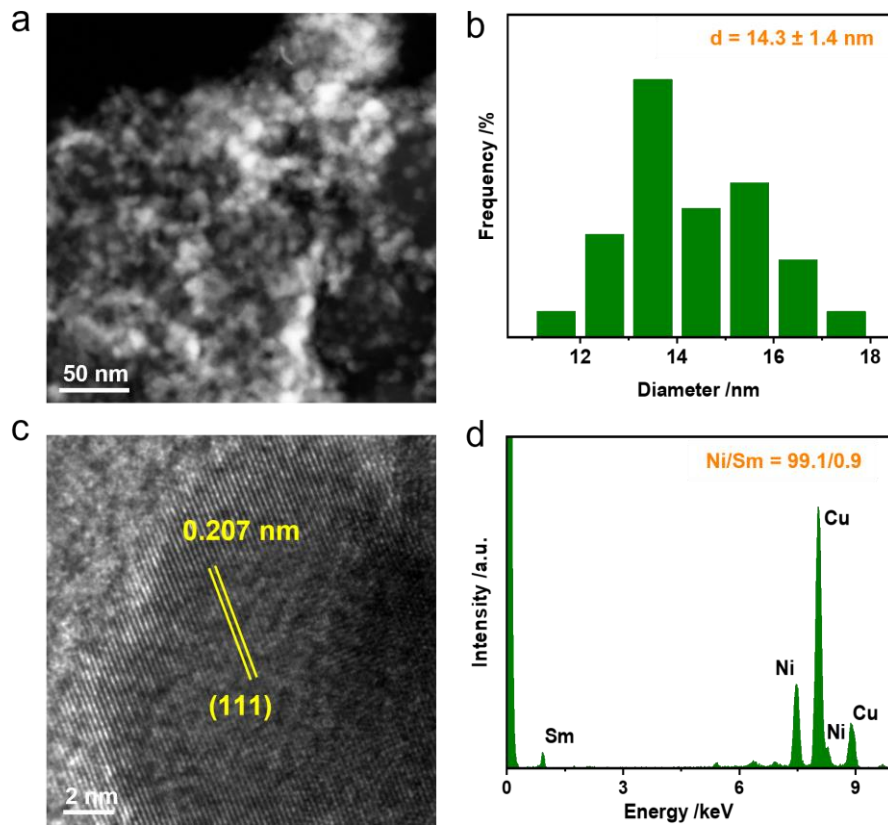
Supplementary Figure 37. LSV curves of Ni/NiO@La₂O₃/C (6.3% La₂O₃, 91.9% NiO), Ni/NiO@La₂O₃/C (6.8% La₂O₃, 86.6% NiO), Ni/NiO@La₂O₃/C (6.7% La₂O₃, 82.9% NiO), Ni/NiO@La₂O₃/C (6.7% La₂O₃, 73.1% NiO) and Ni/NiO@La₂O₃/C (6.3% La₂O₃, 67.0% NiO) measured in 1 M KOH. The different contents of NiO are based on the XPS measurements.



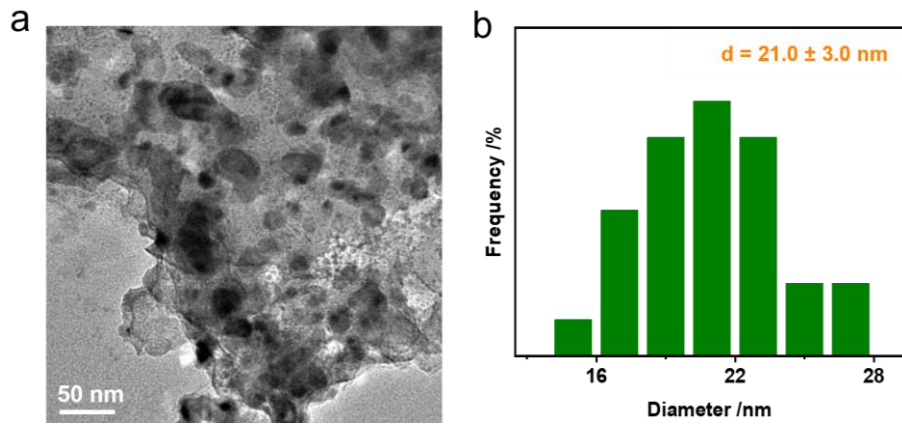
Supplementary Figure 38. (a) LSV curves and (b) corresponding Tafel slopes of 16 kinds of Ni/NiO@RE₂O₃/C, Ni/NiO/C, Raney Ni and commercial Pt/C measured in 1 M KOH.



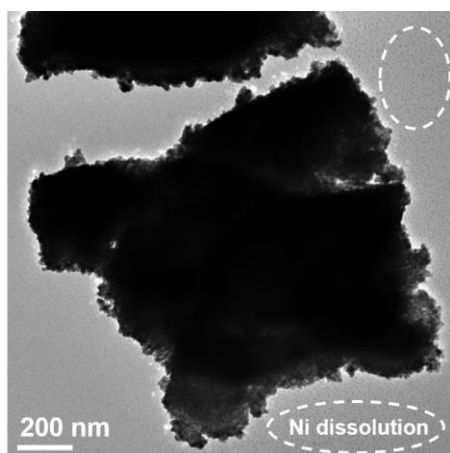
Supplementary Figure 39. (a) HAADF-STEM image, (b) diameter distribution, (c) TEM-EDS, (d) HRTEM image and (e) HAADF-STEM image with elemental mappings of Ni/NiO@La₂O₃/C after the HER durability test for 130 h.



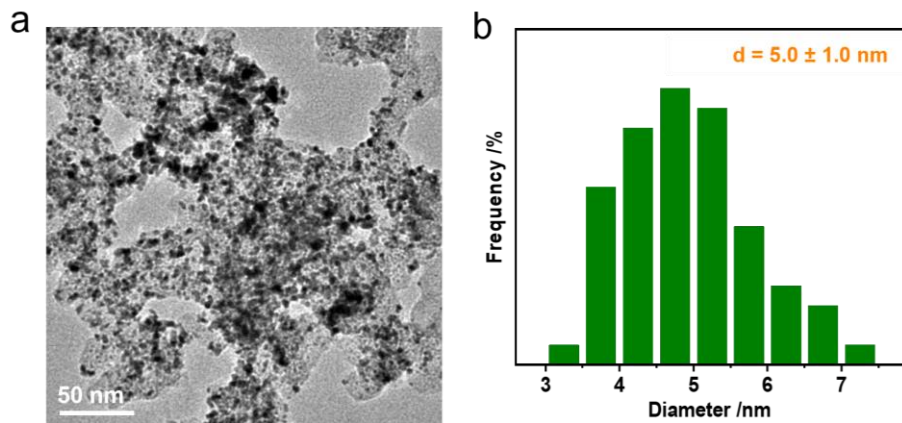
Supplementary Figure 40. (a) HAADF-STEM image, (b) diameter distribution, (c) SEM-EDS and (d) HRTEM image of Ni/NiO@Sm₂O₃/C after the HER durability test for 130 h.



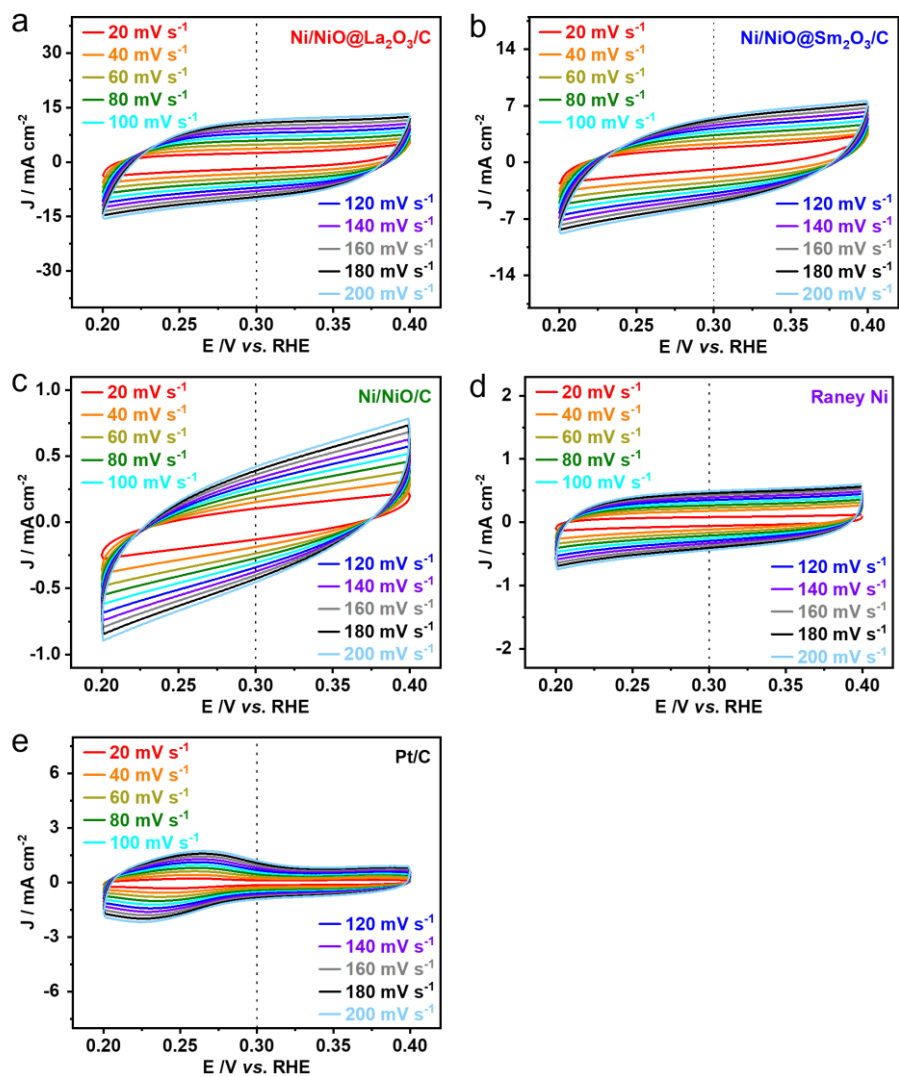
Supplementary Figure 41. (a) TEM image and (b) diameter distribution of Ni/NiO/C after the HER durability test for 130 h.



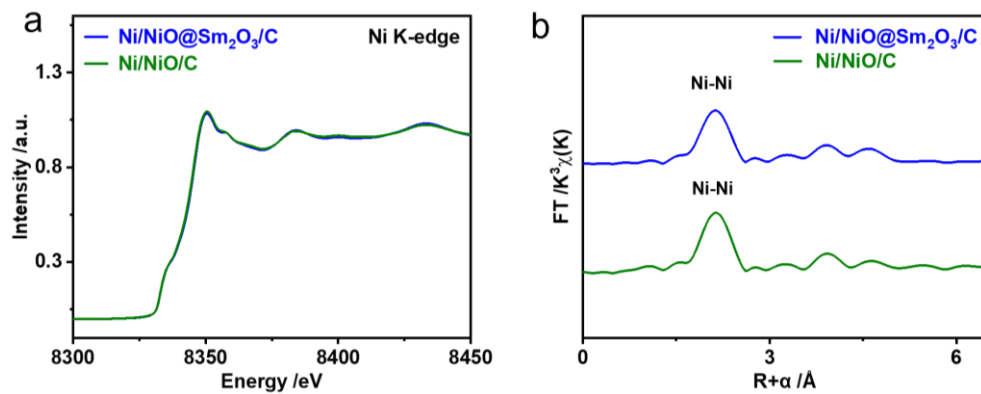
Supplementary Figure 42. TEM image of Raney Ni after the HER durability test for 24 h. The white dotted circles display the Ni dissolution.



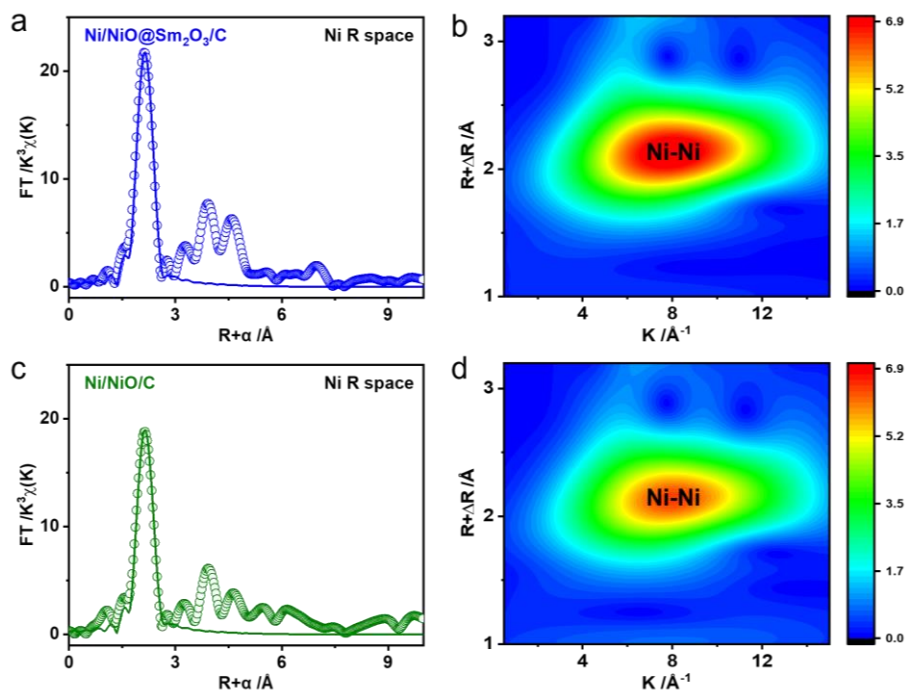
Supplementary Figure 43. (a) TEM image and (b) diameter distribution of commercial Pt/C after the HER durability test for 24 h.



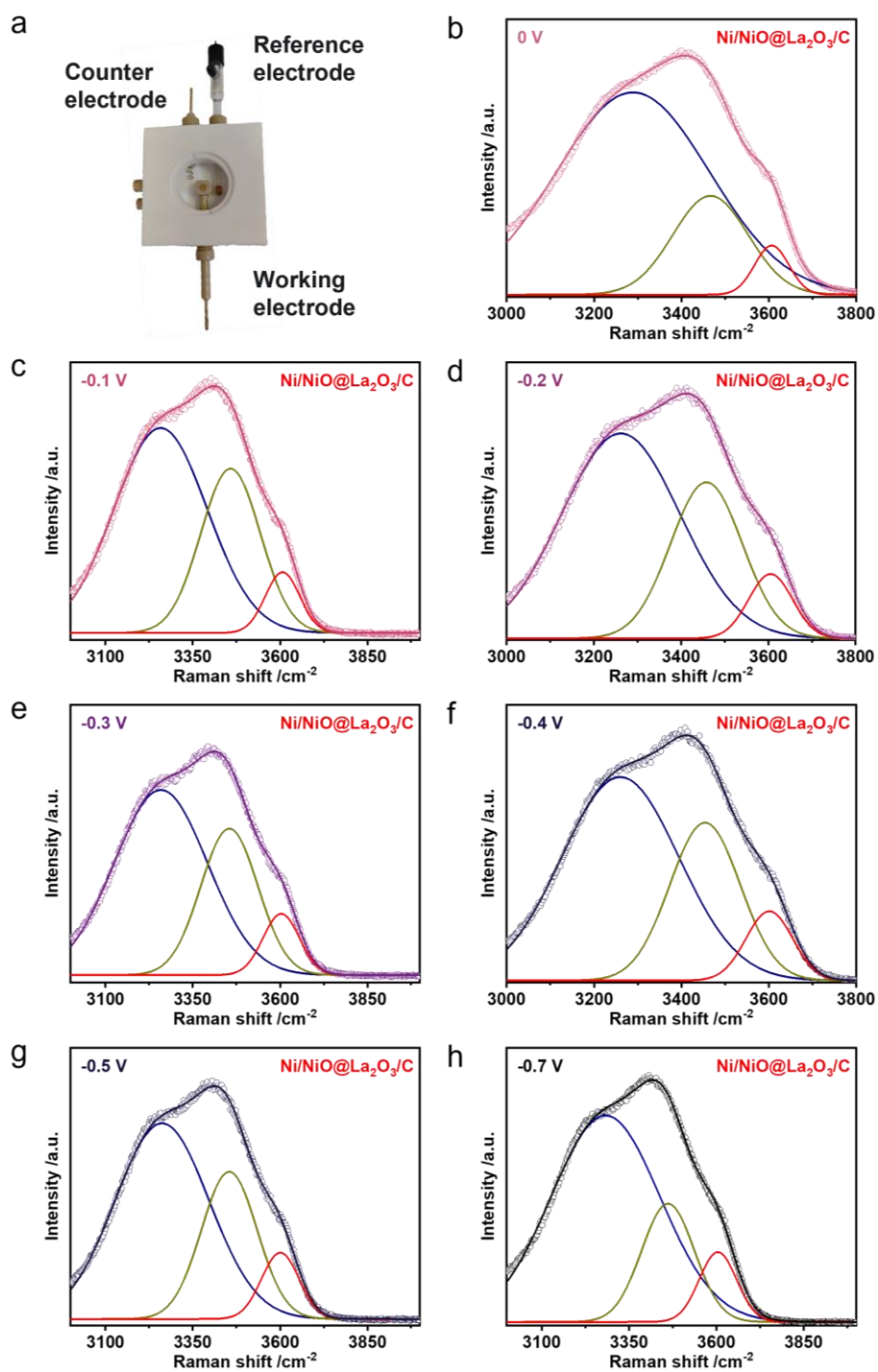
Supplementary Figure 44. CV curves of (a) Ni/NiO@La₂O₃/C, (b) Ni/NiO@Sm₂O₃/C, (c) Ni/NiO/C, (d) Raney Ni and (e) commercial Pt/C with different scan rates from 20 to 200 mV s⁻¹ in 1 M KOH.



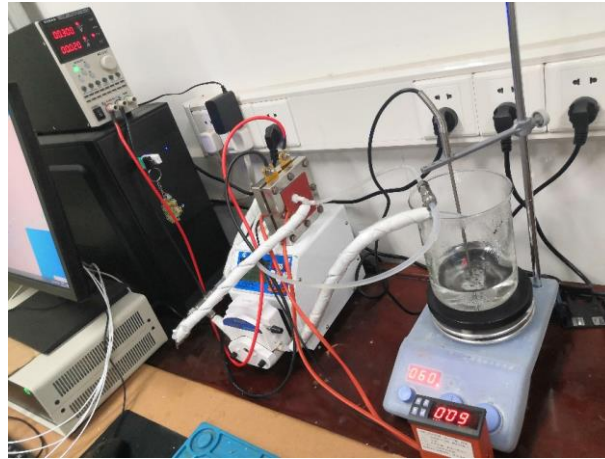
Supplementary Figure 45. (a) Ni K-edge XANES spectra and (b) corresponding FT-EXAFS spectra of Ni/NiO@Sm₂O₃/C and Ni/NiO/C.



Supplementary Figure 46. (a, c) Ni K-edge EXAFS analyses in R and k spaces for (a) Ni/NiO@Sm₂O₃/C and (c) Ni/NiO/C. (b, d) WT analyses of Ni K-edge FT-EXAFS data for (b) Ni/NiO@Sm₂O₃/C and (d) Ni/NiO/C.



Supplementary Figure 47. (a) Electrolytic cell used for *in-situ* Raman spectrum testing. (b-h) Enlarged *in-situ* Raman spectra (with peak fitting) of Ni/NiO@La₂O₃/C for alkaline HER at (b) 0 V, (c) -0.1 V, (d) -0.2 V, (e) -0.3 V, (f) -0.4 V, (g) -0.5 V and (h) -0.7 V vs. RHE.



Supplementary Figure 48. The whole MEA test system of AEMWE used in this work.

Supplementary Table 1. Ni 3*d* binding energy and Ni²⁺/Ni⁰ ratio results for Ni/NiO@La₂O₃/C with different etching degrees in this work, as revealed by XPS.

Sample	Ni ²⁺		Ni ⁰		Ni ²⁺ /Ni ⁰	La ³⁺	
	Ni 2 <i>p</i> _{3/2}	Ni 2 <i>p</i> _{1/2}	Ni 2 <i>p</i> _{3/2}	Ni 2 <i>p</i> _{1/2}	ratio	La 3 <i>d</i> _{5/2}	La 3 <i>d</i> _{3/2}
initial Ni/NiO@La₂O₃/C (S₀)	855.78	873.88	852.98	870.18	82.9/17.1	838.83	856.73
Ni/NiO@La ₂ O ₃ /C after the 1 st etching (S ₁)	855.33	873.26	853.22	870.33	86.5/13.5	839.27	856.16
Ni/NiO@La ₂ O ₃ /C after the 2 nd etching (S ₂)	855.86	873.94	853.08	871.02	71.6/28.4	839.27	857.17
Ni/NiO@La ₂ O ₃ /C after the 3 rd etching (S ₃)	855.14	873.21	852.68	870.22	66.4/33.6	838.91	856.81
Ni/NiO@La ₂ O ₃ /C after the 4 th etching (S ₄)	855.45	873.44	853.51	870.62	64.8/35.2	838.85	856.45
Ni/NiO@La ₂ O ₃ /C after the 5 th etching (S ₅)	856.3	873.41	853.4	870.51	62.2/37.8	838.93	855.53

Supplementary Table 2. Ni K-edge FT-EXAFS parameters of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C, Ni foil and NiO.

Sample	bond type	CN	R (Å)	σ^2 (Å ²)	R-factor (%)
Ni/NiO@La ₂ O ₃ /C	Ni-Ni	7.4 ± 1.1	2.49 ± 0.01	0.006 ± 0.001	0.023
Ni/NiO@Sm ₂ O ₃ /C	Ni-Ni	6.9 ± 1.3	2.49 ± 0.01	0.006 ± 0.001	0.017
Ni/NiO/C	Ni-Ni	9.8 ± 1.0	2.49 ± 0.01	0.006 ± 0.001	0.032
Ni foil	Ni-Ni	12	2.95	6.5	0.004
NiO	Ni-O	6	2.08	5.6	0.001

R, radial distance between absorber and backscatter atoms.

CN, coordination number.

σ^2 , Debye-Waller factor value.

The passive electron reduction factor (S_0^2) was fixed to 1.00, as determined from Pt foil fitting.

R-factor (%) indicates the goodness of the fit.

Supplementary Table 3. Overpotentials at 10 mA cm⁻² of different Ni/NiO@La₂O₃/C catalysts with different contents of La₂O₃ and NiO. The different contents of La₂O₃ are based on the SEM-EDS measurements, while the different contents of NiO are based on the XPS measurements.

Sample	Overpotential (mV)
Ni/NiO@La ₂ O ₃ /C (18.2% La ₂ O ₃ , 82.9% NiO)	62
Ni/NiO@La ₂ O ₃ /C (9.9% La ₂ O ₃ , 83.0% NiO)	54
Ni/NiO@La₂O₃/C (6.7% La₂O₃, 82.9% NiO)	32
Ni/NiO@La ₂ O ₃ /C (3.0% La ₂ O ₃ , 82.9% NiO)	81
Ni/NiO@La ₂ O ₃ /C (6.3% La ₂ O ₃ , 91.9% NiO)	125
Ni/NiO@La ₂ O ₃ /C (6.8% La ₂ O ₃ , 86.6% NiO)	58
Ni/NiO@La₂O₃/C (6.7% La₂O₃, 82.9% NiO)	32
Ni/NiO@La ₂ O ₃ /C (6.7% La ₂ O ₃ , 73.1% NiO)	105
Ni/NiO@La ₂ O ₃ /C (6.3% La ₂ O ₃ , 67.0% NiO)	152

Supplementary Table 4. Overpotentials at 10 mA cm⁻² and Tafel slopes of 16 kinds of Ni/NiO@RE₂O₃/C, Ni/NiO/C, Raney Ni and commercial Pt/C.

Sample	Overpotential (mV)	Tafel slope (mV dec ⁻¹)
Ni/NiO@La₂O₃/C	32	29.2
Ni/NiO@Sc ₂ O ₃ /C	73	60.3
Ni/NiO@Y ₂ O ₃ /C	93	81.8
Ni/NiO@Ce ₂ O ₃ /C	63	85.6
Ni/NiO@Pr ₂ O ₃ /C	93	108.5
Ni/NiO@Nd ₂ O ₃ /C	83	108.3
Ni/NiO@Sm ₂ O ₃ /C	45	63.4
Ni/NiO@Eu ₂ O ₃ /C	78	64.5
Ni/NiO@Gd ₂ O ₃ /C	112	151.0
Ni/NiO@Tb ₂ O ₃ /C	62	59.0
Ni/NiO@Dy ₂ O ₃ /C	163	110.2
Ni/NiO@Ho ₂ O ₃ /C	60	57.0
Ni/NiO@Er ₂ O ₃ /C	152	157.4
Ni/NiO@Tm ₂ O ₃ /C	112	81.9
Ni/NiO@Yb ₂ O ₃ /C	54	59.5
Ni/NiO@Lu ₂ O ₃ /C	77	70.9
Ni/NiO/C	216	162.8
Raney Ni	99	139.3
commercial Pt/C	59	67.3

Supplementary Table 5. Overpotentials at 10 mA cm⁻² and Tafel slopes of Ni/NiO@La₂O₃/C and non-noble metal-based catalysts reported in recent five years for alkaline HER measured in 1.0 M KOH.

Sample	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Ref.
Ni/NiO@La ₂ O ₃ /C	32	29.2	This work
Hom-NiO/Cu	33	51	<i>ACS Nano</i> 2021 , <i>15</i> , 15017-15026.
NiCo ₂ S ₄ /ReS ₂	85	78.3	<i>Adv. Funct. Mater.</i> 2023 , <i>33</i> , 2210072
I-Ni@C	78	60	<i>J. Am. Chem. Soc.</i> 2024 , <i>146</i> , 26844-26854
NiS ₂ -Vs 5.9%	108	82	<i>Nano-Micro Lett.</i> 2024 , <i>16</i> , 63
W/WO ₂	35	34	<i>Nat. Commun.</i> 2023 , <i>14</i> , 5363
P-NiMoO ₄	45	65	<i>ACS Nano</i> 2024 , <i>18</i> , 3791-3800
Mn _{0.25} Ni _{0.75} O	266	46.15	<i>J. Energy Chem.</i> 2023 , <i>86</i> , 167-179
PS-C	261	143.58	<i>Adv. Funct. Mater.</i> 2022 , <i>32</i> , 2112367
NiCo DASs/N-C	189	72.5	<i>Adv. Funct. Mater.</i> 2023 , <i>33</i> , 2210867
Ni ₃ N@W ₅ N ₄	60	56	<i>Angew. Chem. Int. Ed.</i> 2025 , <i>64</i> , e202414647
MoS ₂ /NiPS ₃	112	64	<i>Adv. Mater.</i> 2022 , <i>34</i> , 2203615
Ni _{0.2} Fe _{0.8} S ₂	121	55	<i>Energy Environ. Sci.</i> 2022 , <i>15</i> , 633-644
Ni ₃ S ₂ /Cr ₂ S ₃ @NF	55	87	<i>J. Am. Chem. Soc.</i> 2022 , <i>144</i> , 6028-6039
[Fe ₂ L ₂ (H ₂ O) ₂ -(SO ₄) ₂](CH ₄ O)	62	45.7	<i>Angew. Chem. Int. Ed.</i> 2023 , <i>62</i> , e202307832

WN-Ni@N,P-CNT	70	59.8	<i>Appl. Catal. B</i> 2021 , 298, 120511
Ni@NCW-2.0	158	36	<i>Adv. Mater.</i> 2024 , 36, 2304917
Ni _{SA} -O/Mo ₂ C	133	83.6	<i>Nat. Commun.</i> 2024 , 15, 1342
Fe-Ni ₂ P@C/NF	75	45	<i>Appl. Catal. B</i> 2022 , 307, 121170
NiCo@C-NiCoMoO/NF	39	63.5	<i>Nano-Micro Lett.</i> 2021 , 13, 77
Cr-Ni NHs	75	124	<i>J. Am. Chem. Soc.</i> 2021 , 143, 1399-1408
Ni-GF/VC	128	80	<i>Adv. Energy Mater.</i> 2020 , 10, 2002260
B-Fe ₇ S ₈ /FeS ₂	113	57.4	<i>Adv. Funct. Mater.</i> 2022 , 32, 2107802
W-ACs	53	38	<i>Nat. Commun.</i> 2022 , 13, 763
CoSe ₂ @NC	98	63.4	<i>Angew. Chem. Int. Ed.</i> 2021 , 60, 21575-21582
(MoVNb)Se ₂	80	55	<i>Adv. Mater.</i> 2022 , 34, 2205524
NiCoP	56	88.9	<i>Adv. Energy Mater.</i> 2023 , 13, 2300499
CoSe ₂ /a-CoP	151	80	<i>Adv. Mater.</i> 2022 , 34, 2110631
In5	67	107	<i>Angew. Chem. Int. Ed.</i> 2023 , 62, e202301269
S-NiBDC	100	75	<i>Nat. Commun.</i> 2022 , 13, 6486
CoPGT	103	66.1	<i>Nat. Commun.</i> 2023 , 14, 7708
Fe-Ni ₅ P ₄ /NiFeOH	197	94	<i>Appl. Catal. B</i> 2021 , 291, 119987
Ni ₂ P-NiSe ₂	66	72.6	<i>Appl. Catal. B</i> 2020 , 262,

			118245
MCu _{0.10} -BNiMo	156	40.4	<i>Adv. Mater.</i> 2024 , <i>36</i> , 2313156
Fe(OH) _x @CuMOF	112	76	<i>Sci. Adv.</i> 2021 , <i>7</i> , eabg2580
MoC-Mo ₂ C-790	98.2	62	<i>Nat. Commun.</i> 2021 , <i>12</i> , 6776
Cr-Ni film	75	72	<i>J. Am. Chem. Soc.</i> 2021 , <i>143</i> , 1399
Cu ₁ Co ₂ -Ni ₂ P/NF	61	14.4	<i>Adv. Mater.</i> 2023 , <i>35</i> , 2305598
CoFe-P NAs/IF	40	62	<i>J. Mater. Chem. A</i> 2024 , <i>12</i> , 5331-5339
AlPMoO ₂ @Mo ₂ C	40	45	<i>Nat Commun.</i> 2025 , <i>16</i> , 418
GDY/MoO ₃	170	70	<i>J. Am. Chem. Soc.</i> 2021 , <i>143</i> , 8720-8730
AlO@Mo ₂ N-NrGO	111	64	<i>Adv. Sci.</i> 2022 , <i>9</i> , 2204949
Ni ₃ S ₂ @BLMoS ₂	78	54	<i>Adv. Mater.</i> 2022 , <i>34</i> , 2202195
Co-MoS ₂ @CoS ₂	76	73	<i>Angew. Chem. Int. Ed.</i> 2022 , <i>61</i> , e202114899
Mo ₂ C/MoC/CNT	82	42	<i>Nat. Commun.</i> 2022 , <i>13</i> , 3338
Zn-MoC/Mo ₂ C-0.2	139	49.8	<i>Nano Energy</i> , 2022 , <i>98</i> , 107232
MoO ₂ /MoS ₂ /C	77	41	<i>Adv. Funct. Mater.</i> 2021 , <i>31</i> , 2101715
Co ₂ Mo ₃ O ₈ /MoO ₂ /NF	23	20	<i>Appl. Catal. B: Environ.</i> 2023 , <i>338</i> , 123015
Mo ₂ C@NG	135	41	<i>Adv. Funct. Mater.</i> 2022 , <i>32</i> , 2108167
Fe-NiS ₂ @NaBH ₄	114	65	<i>ACS Catal.</i> 2025 , <i>15</i> , 13948-13957

V-NiS/NiS ₂	220	72	<i>Adv. Energy Mater.</i> 2023 , 13, 2300978
NiMoCu	49	46	<i>Adv. Energy Mater.</i> 2025 , 15, 2501852
N-NiMo	95	63	<i>Chem. Mater.</i> 2024 , 36, 4164
Ni ₄ Mo/N-NiMoO ₄	35	68	<i>Appl. Catal. B</i> 2025 , 361, 124660
NiMoFe HI	73	121	<i>ACS Catal.</i> 2024 , 14, 18003
d-MoNi	121	27	<i>Adv. Mater.</i> 2024 , 36, 2402156
NiCoCu-Mo _{0.078} /CF	35	50.12	<i>Adv. Funct. Mater.</i> 2024 , 34, 2404055
Ni/Y ₂ O ₃	61.1	52.8	<i>Adv. Energy Mater.</i> 2024 , 14, 2303563
Co _{0.59} Ni _{0.41} C ₂ O ₄ @PANI/ NF	43	36.41	<i>Adv. Funct. Mater.</i> 2023 , 33, 2211576
Co ₅₀ Ni-C/NF	30	45.1	<i>J. Colloid Interface Sci.</i> 2026 , 707, 139746
Fe ₂ O ₃ /CuO	70	97.9	<i>Adv. Energy Mater.</i> 2022 , 12, 2200067
Ni _{SA} Fe _{SA} -Ni _X Fe/CNT	64	53.1	<i>ACS Catal.</i> 2022 , 12, 1167-1179
Co/CoMoN	61	50.2	<i>Adv. Sci.</i> 2022 , 9, e2105313
Ni/MoN/rNS	67	52	<i>Adv. Sci.</i> 2022 , 9, e2105869

Supplementary Table 6. Ni 2*p* and La/Sm 3*d* binding energies as well as Ni²⁺/Ni⁰ ratios for Ni/NiO@La₂O₃/C with different contents of NiO, Ni/NiO@Sm₂O₃/C (6.4% Sm₂O₃, 83.2% NiO) and Ni/NiO/C in this work, as revealed by XPS.

Sample	Ni ²⁺		Ni ⁰		Ni ²⁺ /Ni ⁰	RE ³⁺	
	Ni 2 <i>p</i> _{3/2}	Ni 2 <i>p</i> _{1/2}	Ni 2 <i>p</i> _{3/2}	Ni 2 <i>p</i> _{1/2}	ratio	RE 3 <i>d</i> _{5/2}	RE 3 <i>d</i> _{3/2}
Ni/NiO@La ₂ O ₃ /C (6.3% La ₂ O ₃ , 91.9% NiO)	855.50	873.10	853.00	870.11	91.9/8.1	838.83	855.43
Ni/NiO@La ₂ O ₃ /C (6.8% La ₂ O ₃ , 86.6% NiO)	855.89	873.53	852.70	870.48	86.6/13.4	838.66	855.26
Ni/NiO@La₂O₃/C (6.7% La₂O₃, 82.9% NiO)	855.78	873.88	852.98	870.18	82.9/17.1	838.83	856.73
Ni/NiO@La ₂ O ₃ /C (6.7% La ₂ O ₃ , 73.1% NiO)	855.79	873.64	852.82	870.23	73.1/26.9	838.52	855.12
Ni/NiO@La ₂ O ₃ /C (6.3% La ₂ O ₃ , 67.0% NiO)	855.58	873.70	852.81	869.92	67.0/33.0	836.58	853.18
Ni/NiO@Sm ₂ O ₃ /C (6.4% Sm ₂ O ₃ , 83.2% NiO)	855.78	873.88	852.88	870.28	93.2/16.8	1082.09	1109.22
Ni/NiO/C	856.08	874.18	852.88	872.58	68.4/31.6	/	/

Supplementary Table 7. MEA voltages and current densities as well as cathode and anode catalysts used in this work and other works reported in recent five years for AEMWE.

Cathode catalyst	Anode catalyst	Voltage @ Current density	Ref.
Ni/NiO@La ₂ O ₃ /C	NiFe-LDH@NF	1.5 V @ 0.5 A cm ⁻² 1.6 V @ 1 A cm ⁻² 1.7 V @ 2 A cm ⁻²	This work
Ni ₃ N@W ₅ N ₄	NFP	2.01 V @ 1 A cm ⁻²	<i>Angew. Chem. Int. Ed.</i> 2025 , 64, e202414647
NiFeCr-LDH@NF	Ni ₃ S ₂ /Cr ₂ S ₃ @NF	2.04 V @ 0.75 A cm ⁻²	<i>J. Am. Chem. Soc.</i> 2022 , 144, 6028-6039
Co-1T MoS ₂	NiFe LDH	2.55 V @ 0.5 A cm ⁻²	<i>Angew. Chem. Int. Ed.</i> 2023 , 62, e202313845
FeP-CoP/NC	FeP-CoP/NC	2.10 V @ 0.75 A cm ⁻²	<i>Nat. Commun.</i> 2021 , 12, 4143
VCoP-2/Ni	VCoP-2/Ni	1.90 V @ 1 A cm ⁻²	<i>Energy Environ. Sci.</i> 2022 , 15, 1882-1892
Acta 4030	Acta 3030	1.90 V @ 0.5 A cm ⁻²	<i>Joule.</i> 2021 , 5, 1776-1799
NiCoP@NiFeP	NiCoP@NiFeP	1.93 V @ 1 A cm ⁻²	<i>J. Mater. Chem. A.</i> 2022 , 10, 10209-10218
CoNi-Ti ₃ C ₂ T _x	CoNi-Ti ₃ C ₂ T _x	1.87 V @ 0.5 A cm ⁻²	<i>ACS Nano</i> 2024 , 18, 4256-4268
Ni ₄ Mo-MoO _x	NiFe	1.75 V @ 1 A cm ⁻²	<i>Energy Environ. Sci.</i> 2025 , 18, 1533-1543
NiFeP _x	NiFe LDH	1.98 V @ 0.15 A cm ⁻²	<i>J. Mater. Chem. A.</i> 2023 , 11, 9682-9690
Mil53-HE	Mil53-HE	1.9 V @ 0.52 A cm ⁻²	<i>Nano Energy.</i> 2025 , 134, 110529
Etched-NiPB@MS	Etched-NiPB@MS	1.98 V @ 1 A cm ⁻²	<i>Nano Energy.</i> 2024 , 128, 109923
FeCoNiCuMo/NM	NiFe-LDH	1.777 V @ 2 A cm ⁻²	<i>Nano Energy.</i> 2024 , 126, 109703
Mn-NiFe@WO _x	Mn-NiFe@WO _x	1.91 V @ 2 A cm ⁻²	<i>Chem. Eng. J.</i> 2024 , 500, 157106
3D-O ₂ -Cat	PCMO	1.63 V @ 1 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 ,

			35, 2423537
NA-LT-CA	NA-LT-CA	1.975 V @ 0.8 A cm ⁻²	<i>Chem. Eng. J.</i> 2024 , 486, 150180
NiMo	NiFeOOH	1.91 V @ 2 A cm ⁻²	<i>ACS Energy Lett.</i> 2023 , 8, 5018-5024
MoNi ₄ /MoO ₂	Ni ₂ P@FePO _x Hy	1.715 V @ 1 A cm ⁻²	<i>Appl. Catal. B: Environ.</i> 2022 , 306, 121127
NiMoCo	NiFeCr-LDH	2.11 V @ 1 A cm ⁻²	<i>Small.</i> 2022 , 18, 2200303
Ni-Mo	Ni-Fe	2 V @ 0.68 A cm ⁻²	<i>Angew. Chem. Int. Ed.</i> 2025 , 64, e202514264
P-Co/Co(OH) ₂	NiFe-LDH	2.03 V @ 0.2 A cm ⁻²	<i>Adv. Energy Mater.</i> 2025 , 15, e03695.
Mn _{0.15} -CoP/CC	Mn _{0.15} -CoP/CC	1.45 V @ 0.14 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , https://doi.org/10.1002/adfm.202514250
NiMo/NiMoP-C	IrO ₂	1.8 V @ 1 A cm ⁻²	<i>Energy Environ. Sci.</i> , 2025 , 18, 4811-4820
Ce _{0.1} -CoP/Ni ₃ P@NF	Ce _{0.1} -CoP/Ni ₃ P@NF	1.81 V @ 1 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , 35, 2500861
NMF	S-NiFeZn LDH/NF	1.96 V @ 1 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , 35, 2501070
R-NiFe LDH	R-NiFe LDH	2.19 @ 1 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , 35, 2505763
NiCoPi-NiS/NF	FePi-NiS/NF	2.1 @ 1 A cm ⁻²	<i>Appl. Catal. B Environ.</i> 2024 , 340, 123252
Cu ₂ S@Ni	NiFeP@Ag	1.88 V @ 0.4 A cm ⁻²	<i>Adv. Mater.</i> 2023 , 36, 2306062
Ni/CeO _x	Ni-Fe-Zn	1.981 V @ 2 A cm ⁻²	<i>Energy Environ. Sci.</i> 2025 , 18, 6248-6259
Ni ₃ N/Ni/Ti mesh	NiFe ₂ O ₄	1.88 V @ 0.5 A cm ⁻²	<i>Energy Environ. Sci.</i> 2022 , 15, 185-195
NiMoN	d-(Fe,Ni)OOH	1.795 V @ 0.5 A cm ⁻²	<i>Adv. Mater.</i> 2023 , 35, 2306097
NiMoCu	NiFe LDH	1.56 V @ 0.2 A cm ⁻²	<i>Adv. Energy Mater.</i> 2025 , 15, 2501852

O-NiMoP/NF	O-NiMoP/NF	1.85 V @ 0.05 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2021 , 31, 2104951
NiMoFe HI	NiMoFe HI	1.68 V @ 0.1 A cm ⁻²	<i>ACS Catal.</i> 2024 , 14, 18003
NiMoN/Ni ₃ S ₂	NiMoN/Ni ₃ S ₂	1.63 V @ 0.1 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , 35, 2409924
Co(OH) ₂ /NiMo CA@CC	Co(OH) ₂ /NiMo CA@CC	1.65 V @ 0.15 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2021 , 31, 2102117
NiMPL-PTL	NiMPL-PTL	2.1 V @ 0.5 A cm ⁻²	<i>Joule</i> 2021 , 5, 1776-1799
NiCoO-NiCo/C	CuCoO/NF	1.85 V @ 0.504 A cm ⁻²	<i>Appl. Catal. B Environ.</i> 2021 , 292, 120170
catalyst slurry	NiFeOOH	1.9 V @ 3.6 A cm ⁻²	<i>ACS Catal.</i> 2022 , 12, 135- 145
NiTe/Ni ₂ FeP/NF	NiTe/Ni ₂ FeP/NF	2.49 V @ 1.5 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , https://doi.org/10.1002/adfm.202528467
Ni-Fe	Ni-Fe	2 V @ 1.6 A cm ⁻²	<i>Energy Environ. Sci.</i> 2021 , 14, 6338-6348
Ni@NCW	NF	2.15 V @ 1.6 A cm ⁻²	<i>Adv. Mater.</i> 2024 , 36, 2304917
S-Co ₃ O ₄ /CC	S-Co ₃ O ₄ /CC	1.9 V @ 1 A cm ⁻²	<i>Adv. Energy Mater.</i> 2024 , 14, 2400052
LFA	LFA	2 V @ 2.1 A cm ⁻²	<i>Adv. Mater.</i> 2024 , 36, 2307925
NiFeO _x	HTS-Ru-NCs/TiN	1.83 V @ 2 A cm ⁻²	<i>Adv. Mater.</i> 2024 , 36, 2403525
Co ₅₀ Ni-C/NF	RuO ₂ /NF	1.93 V @ 0.5 A cm ⁻²	<i>J. Colloid Interface Sci.</i> 2026 , 707, 139746
NiMo-H ₂ @NF	NiFe-LDH	1.61 V @ 0.5 A cm ⁻²	<i>Nano Res.</i> 2024 , 17, 3769-3776
Noble metal-based	/	/	/
NA-Ru ₃ Ni/C	NA-Ru ₃ Ni/C	2.05 V @ 1 A cm ⁻²	<i>Energy Environ. Sci.</i> 2023 , 16, 285-294
Pt black	IrO ₂	1.75 V @ 0.5 A cm ⁻²	<i>Joule.</i> 2021 , 13, 51917-

			51924
MOC-Ru	RuO ₂	1.97 V @ 0.25 A cm ⁻²	<i>Adv. Mater.</i> 2023 , <i>35</i> , 2303331
Pt/C	Co, Mo-NiFe LDH	1.94 V @ 2 A cm ⁻²	<i>Adv. Energy Mater.</i> 2023 , <i>15</i> , 2203595
IE 20 wt%	IE 20 wt%	1.75 V @ 1 A cm ⁻²	<i>Small</i> , 2022 , <i>18</i> , 2200380
Pt/C	CCO*	1.9 V @ 1 A cm ⁻²	<i>ACS Sustainable Chem. Eng.</i> 2020 , <i>8</i> , 2344-2349
HfOx-in-Ir SSC/CP	RuO ₂ /CP	1.98 V @ 1 A cm ⁻²	<i>Adv. Mater.</i> 2025 , <i>37</i> , 2507080
us-HEA/CFP	NiFeOx	1.94 V @ 1 A cm ⁻²	<i>Adv. Mater.</i> 2025 , <i>37</i> , e08975
Pt-HEA-cluster/CeO ₂ /C	NiFe/NF	1.95 V @ 2 A cm ⁻²	<i>Adv. Mater.</i> 2025 , https://doi.org/10.1002/adma.202514269
RuVCoCuZnW	RuVCoCuZnW	1.66 V @ 0.5 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2025 , https://doi.org/10.1002/adfm.202517292
PtRu/C	LDH-Ti _{9 wt%} /HCC	2 V @ 8.5 A cm ⁻²	<i>Nat. Commun.</i> 2025 , <i>16</i> , 11090
PtRu/C	FNC/HCC	2 V @ 10.29 A cm ⁻²	<i>Energy Environ. Sci.</i> 2023 , <i>16</i> , 5019-5028
Pt/C	CoFeP@NiFe LDH	1.67 V @ 1 A cm ⁻²	<i>J. Colloid Interface Sci.</i> 2026 , <i>706</i> , 139632
Pt/C	Co _{2.8} ,W _{3.8} -NiFe LDH	1.86 V @ 1 A cm ⁻²	<i>Adv. Energy Mater.</i> 2024 , <i>14</i> , 2402046
Pt/C	Ru-S-NiFe LDH	1.92 V @ 1 A cm ⁻²	<i>Adv. Energy Mater.</i> 2025 , <i>15</i> , 2500554
Pt/C	RT-NiFe-LDH	1.69 V @ 1 A cm ⁻²	<i>Nat. Commun.</i> 2025 , <i>16</i> , 6138
Ru-Fe ₇ C ₃ @CNF	NiFe LDH	1.67 V @ 0.5 A cm ⁻²	<i>Angew. Chem. Int. Ed.</i> 2025 , https://doi.org/10.1002/anie.202517861

Pt@S-NiFe LDH	S-NiFe LDH	1.74 V @ 0.2 A cm ⁻²	<i>Adv. Mater.</i> 2023 , <i>35</i> , 2208209
Pt/C	CF-FeSO	1.61 V @ 0.1 A cm ⁻²	<i>Nat Commun.</i> 2022 , <i>13</i> , 605
PtNi-octa	Pt black	1.98 V @ 0.5 A cm ⁻²	<i>Adv. Energy Mater.</i> 2024 , <i>14</i> , 2302971
Pt/C	2D-FGT _v	2.51 V @ 1 A cm ⁻²	<i>Adv. Sci.</i> 2024 , <i>11</i> , 2310115
Pt/C	(NiCo) ₃ Se ₄	2 V @ 2 A cm ⁻²	<i>Adv. Mater.</i> 2021 , <i>33</i> , 2103812
PtNi/LDH	PtNi/LDH	2.20 V @ 0.8 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2024 , <i>34</i> , 2308575
Pt/C	PiperION-A60-HCO ₃	1.92 V @ 1 A cm ⁻²	<i>Nat. Commun.</i> 2024 , <i>15</i> , 3416
Pt/C	AF2-HLF825X	1.90 V @ 1 A cm ⁻²	<i>Nat. Catal.</i> , 2024 , <i>7</i> , 546
Turing Pt	Sustainion X37-50	2.40 V @ 0.8 A cm ⁻²	<i>J. Am. Chem. Soc.</i> 2024 , <i>146</i> , 5355
Pt/C	d-NiOOH/NDL	1.79 V @ 1 A cm ⁻²	<i>Adv. Mater.</i> 2025 , https://doi.org/10.1002/adma.202512188
Pt/C	NDCO	1.8 V @ 1 A cm ⁻²	<i>J. Am. Chem. Soc.</i> 2024 , <i>146</i> , 20379-20390
Pt/C	GCB-NiFe	1.68 V @ 1 A cm ⁻²	<i>Adv. Mater.</i> 2025 , https://doi.org/10.1002/adma.202509805
Pt/C	Bi/BiCeO _{1.8}	1.79 V @ 1 A cm ⁻²	<i>Adv. Mater.</i> 2024 , <i>36</i> , 2314211
Pt/C	NiFeO	1.71 V @ 1 A cm ⁻²	<i>Energy Environ. Sci.</i> 2024 , <i>17</i> , 3347-3357
IrO ₂	EE.300s	2 V @ 0.1 A cm ⁻²	<i>Energy Environ. Sci.</i> 2024 , <i>17</i> , 5854-5865
UP-RuNiSAs/C	NiFeO _x	1.95 V @ 1 A cm ⁻²	<i>Nat. Commun.</i> 2024 , <i>15</i> , 2218
CoCrOx	Pt/C	2.1 V @ 1.5 A cm ⁻²	<i>Nat. Commun.</i> 2024 , <i>15</i> , 3416

Ru-NiCr LDH-r	NiFe LDH	1.8 V @ 1.8 A cm ⁻²	<i>ACS Catal.</i> 2024 , <i>14</i> , 3466-3474
Pt/C	Ti-NFO	1.73 V @ 1 A cm ⁻²	<i>ACS Catal.</i> 2024 , <i>14</i> , 4453-4462
Pt/C	FCO 1.5	1.85 V @ 1.59 A cm ⁻²	<i>Adv. Funct. Mater.</i> 2024 , <i>34</i> , 2314573
Pt/C	NiFeCo-OOH	1.809 V @ 2 A cm ⁻²	<i>Adv. Sci.</i> 2024 , <i>11</i> , 2401782
Pt/C	Co _{0.15} -NiNH	1.99 V @ 1 A cm ⁻²	<i>Energy Environ. Sci.</i> 2024 , <i>17</i> , 1468-1481
Pt/C	NiCoFe-NDA	1.8 V @ 0.325 A cm ⁻²	<i>Energy Environ. Sci.</i> 2021 , <i>14</i> , 6546-6553