

Supporting Information

Ultrafast Preparation of Ruthenium Nanoparticle/Molybdenum Oxide/Nitrogen-Doped Carbon Nanocomposites by Magnetic Induction Heating for Efficient Hydrogen Evolution Reaction

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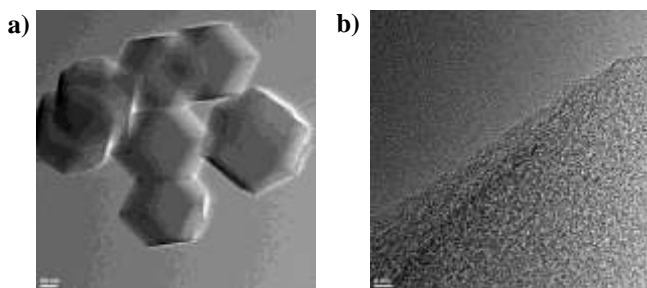


Figure S1. TEM images of MoO_x/NC. Scale bars are (a) 50 nm and (b) 5 nm.

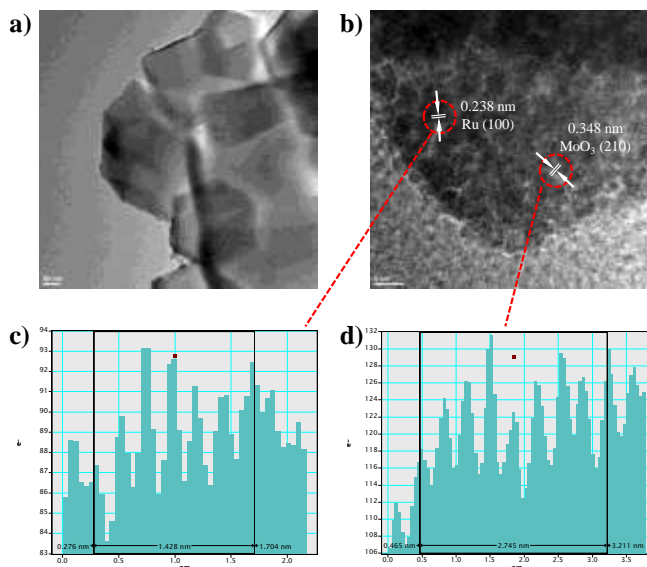


Figure S2. (a,b) TEM images of RuMoO_x/NC-1. Scale bars are (a) 50 nm and (b) 5 nm. The interplanar spacing of the lattice fringes for (c) Ru (100) and (d) MoO₃ (210) of the circled areas in panel (b).

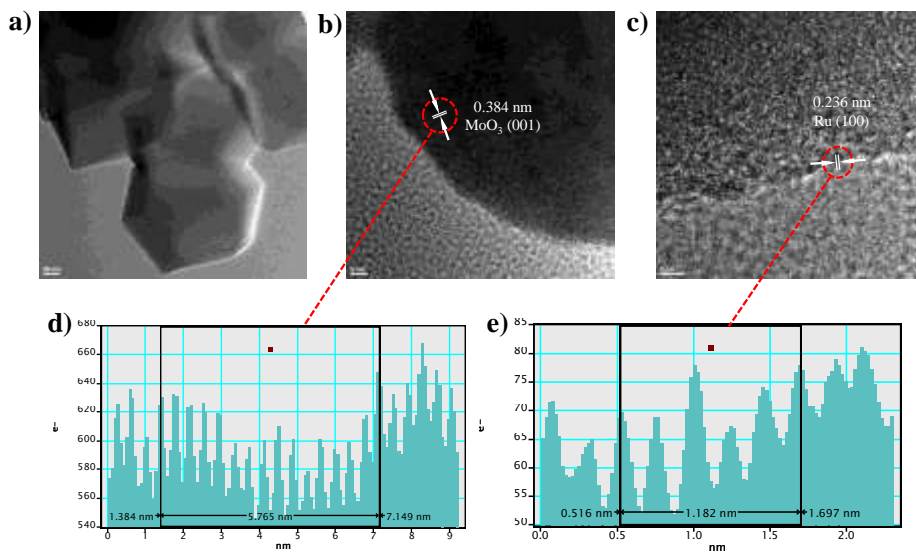


Figure S3. (a-c) TEM images of RuMoO_x/NC-2. Scale bars are (a) 50 nm, (b) 5 nm and (c) 2 nm. The interplanar spacing of the lattice fringes for (d) MoO₃ (001) and (e) Ru (100) of the circled areas in panel (b) and (c), respectively.

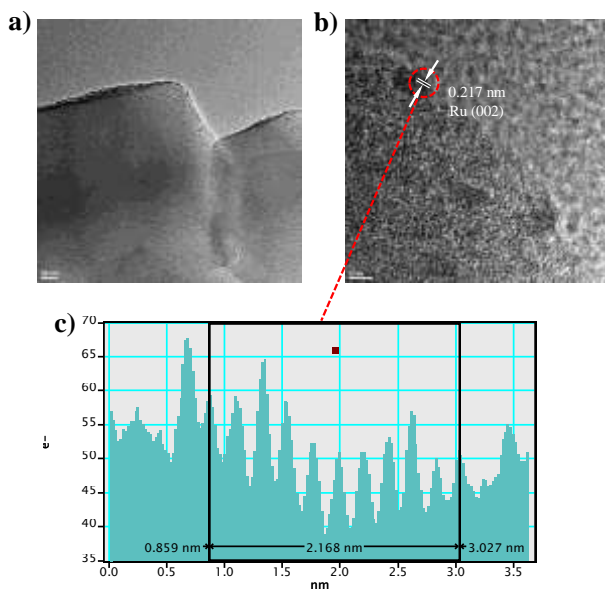


Figure S4. (a,b) TEM images of RuMoO_x/NC-3. Scale bars are (a) 20 nm and (b) 2 nm. The interplanar spacing of the lattice fringes for (c) Ru (002) of the circled area in panel (b).

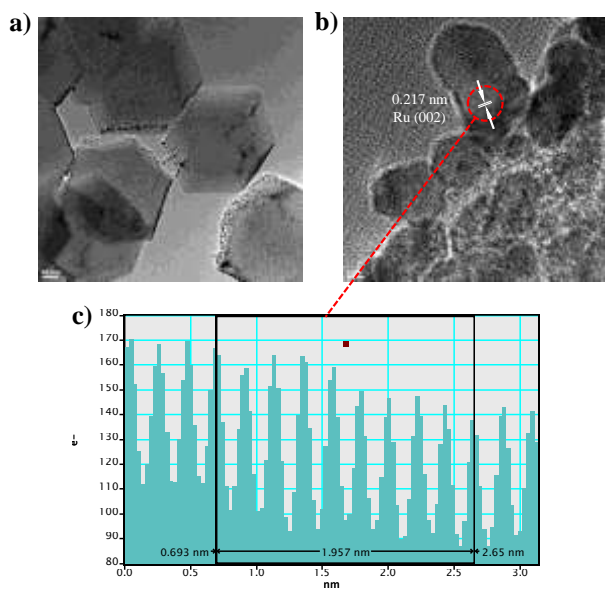


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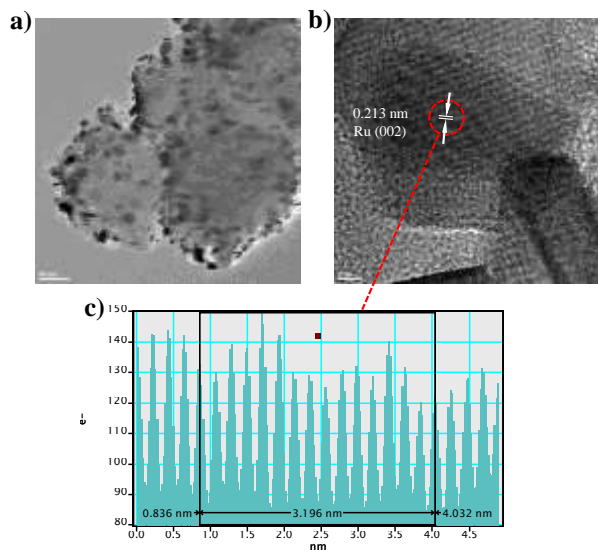


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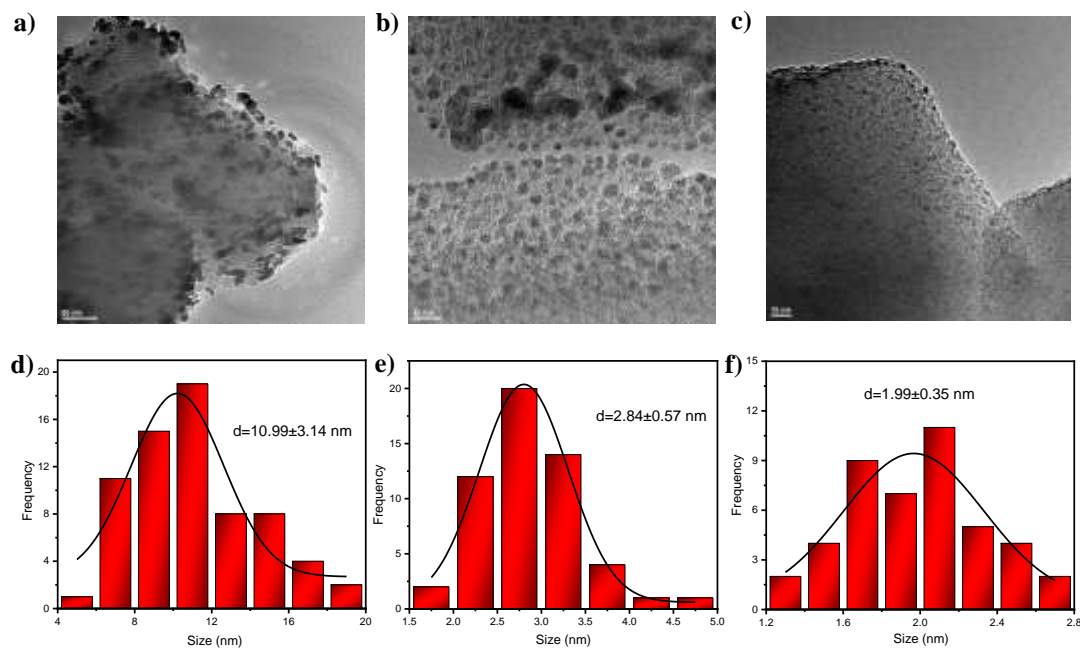


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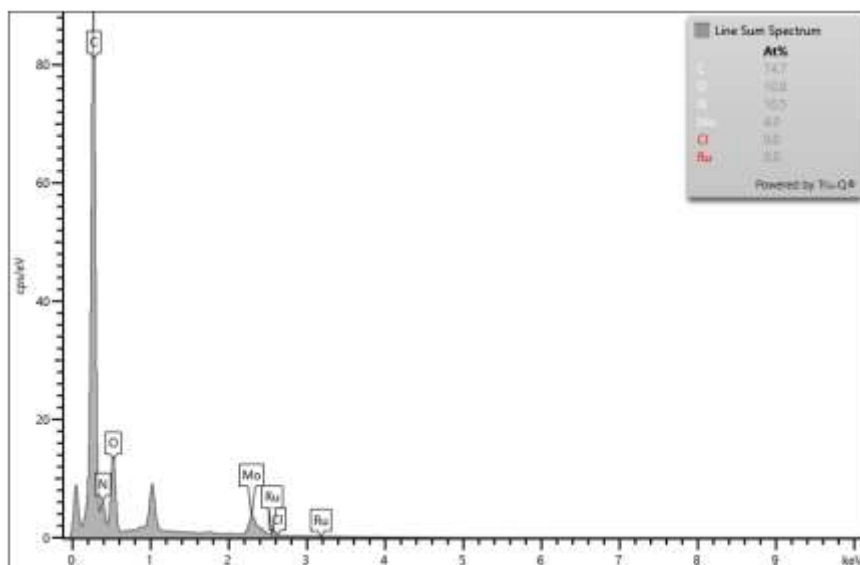


Figure S8. EDS plot of MoO_x/NC. Inset shows the elemental composition (at%).

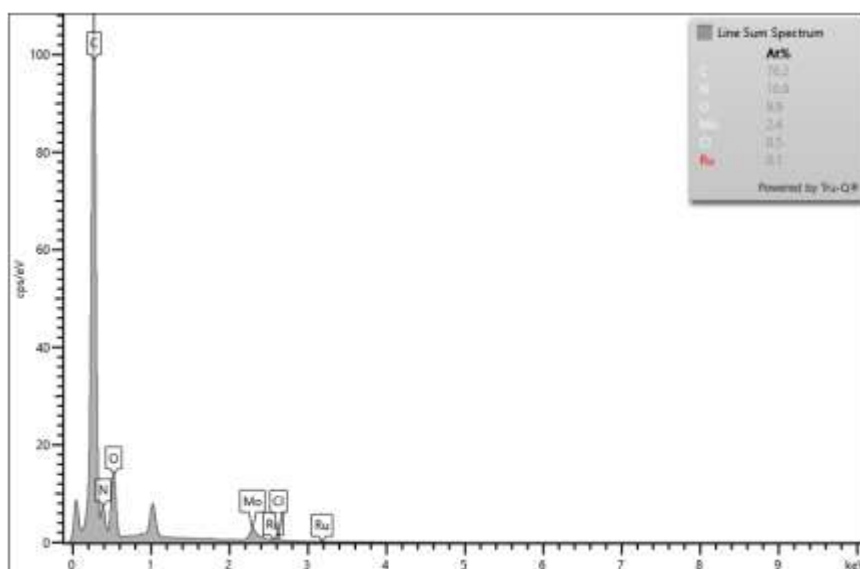


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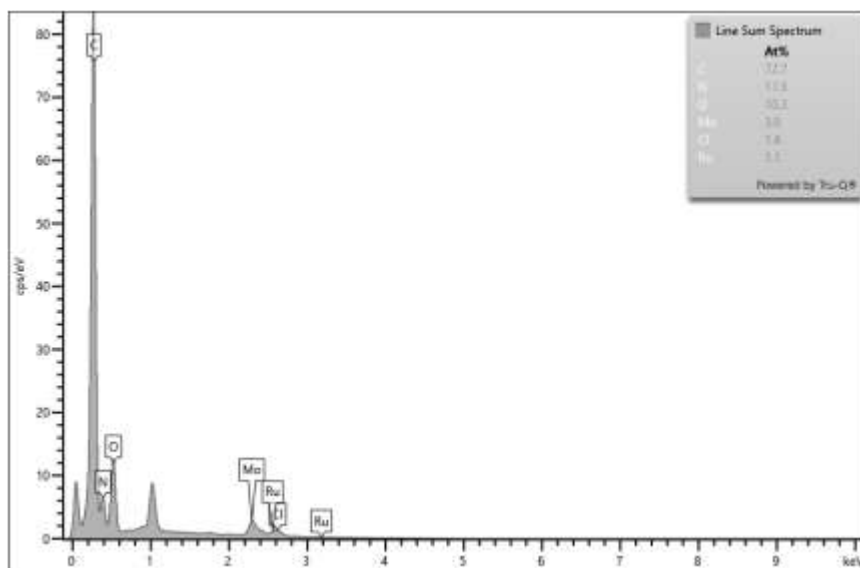


Figure S10. EDS plot of RuMoO_x/NC-2. Inset shows the elemental composition (at%).

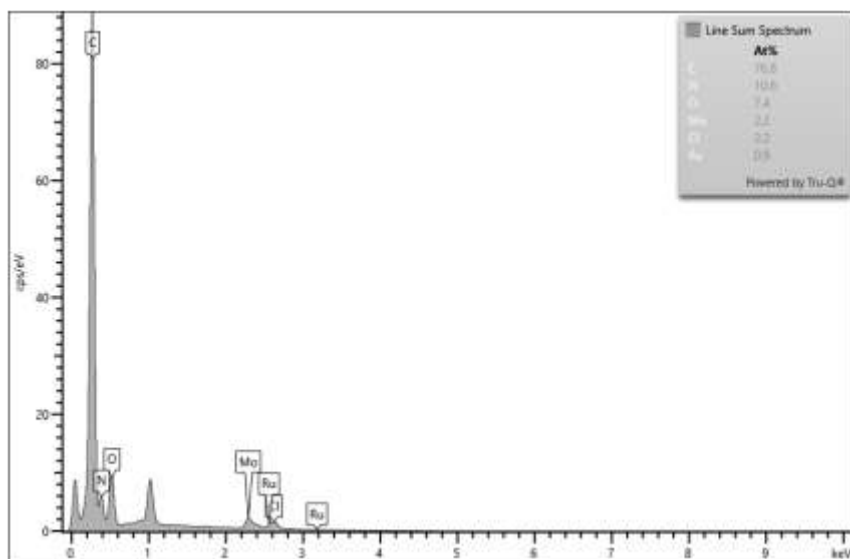


Figure S11. EDS plot of RuMoO_x/NC-3. Inset shows the elemental composition (at%).

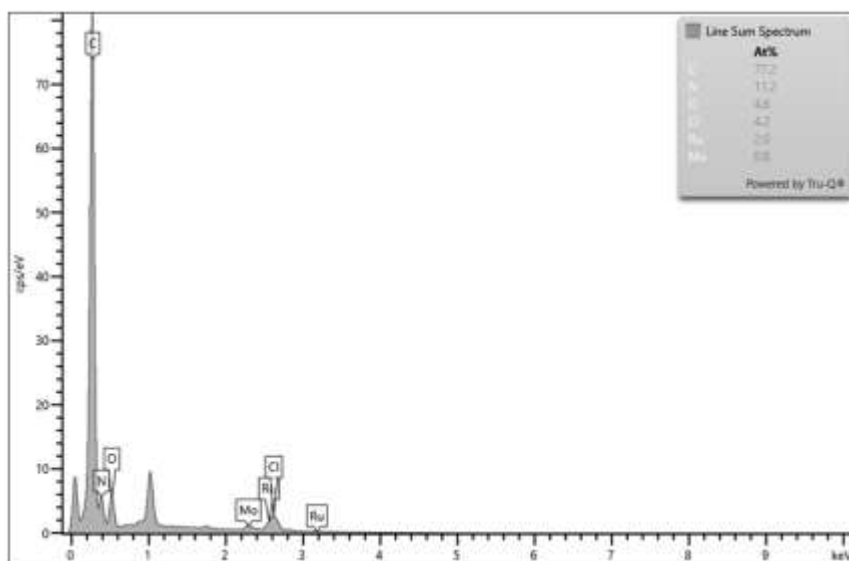


Figure S12. EDS plot of RuMoO_x/NC-4. Inset shows the elemental composition (at%).

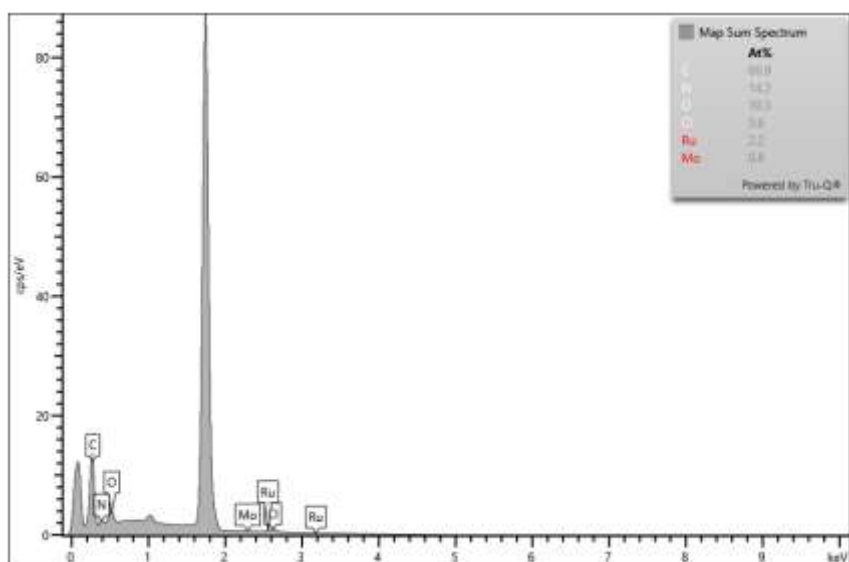


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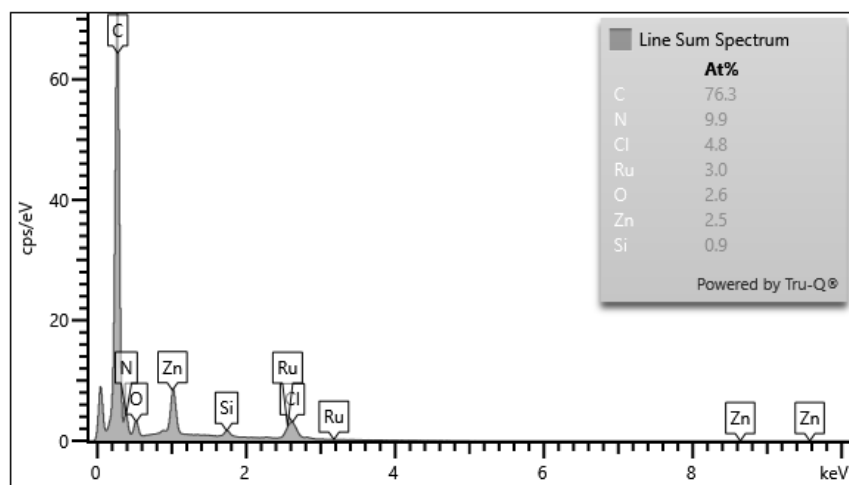


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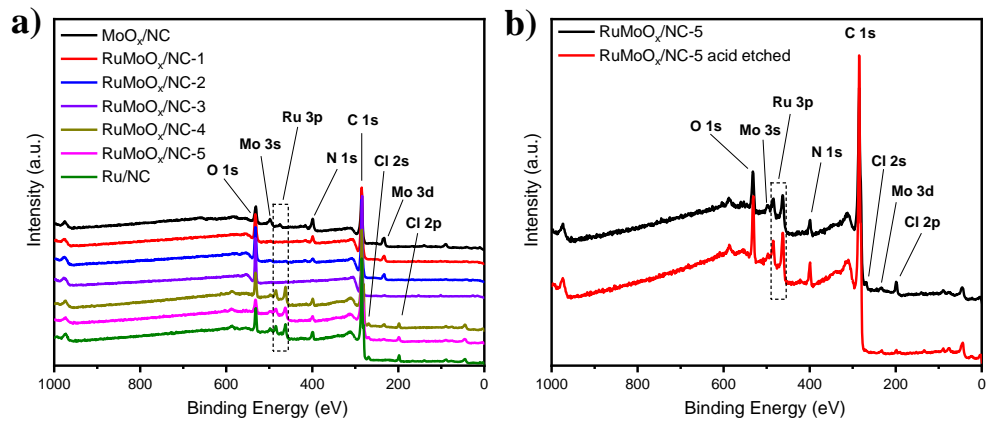


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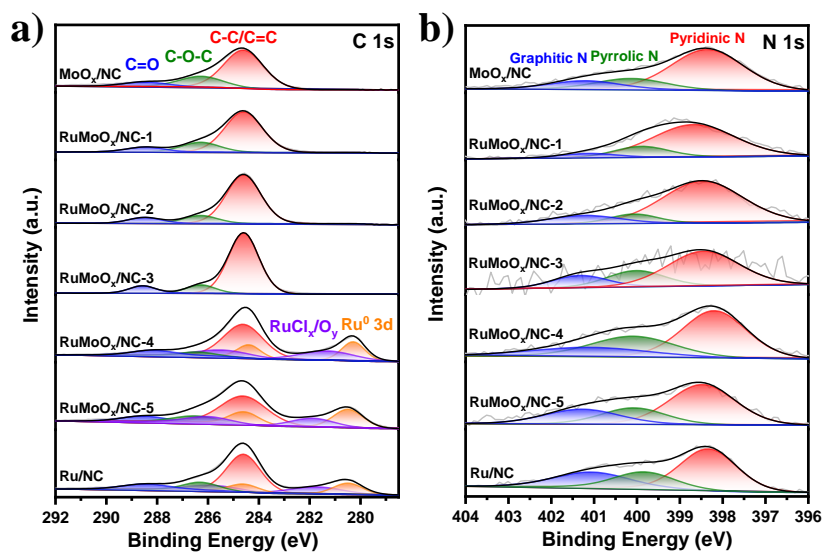


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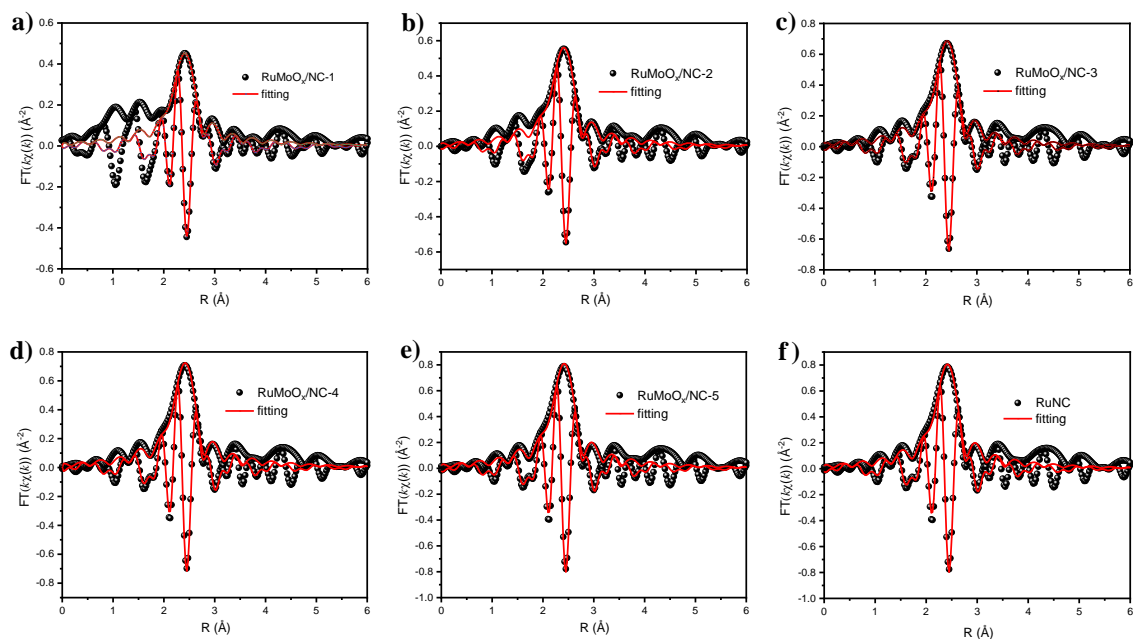


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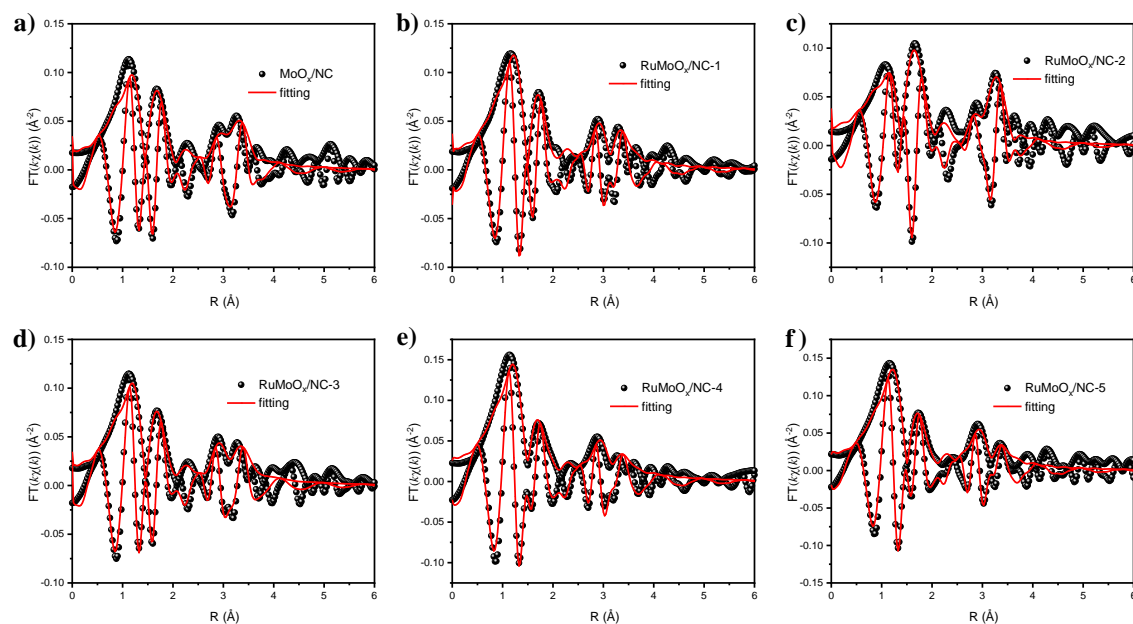


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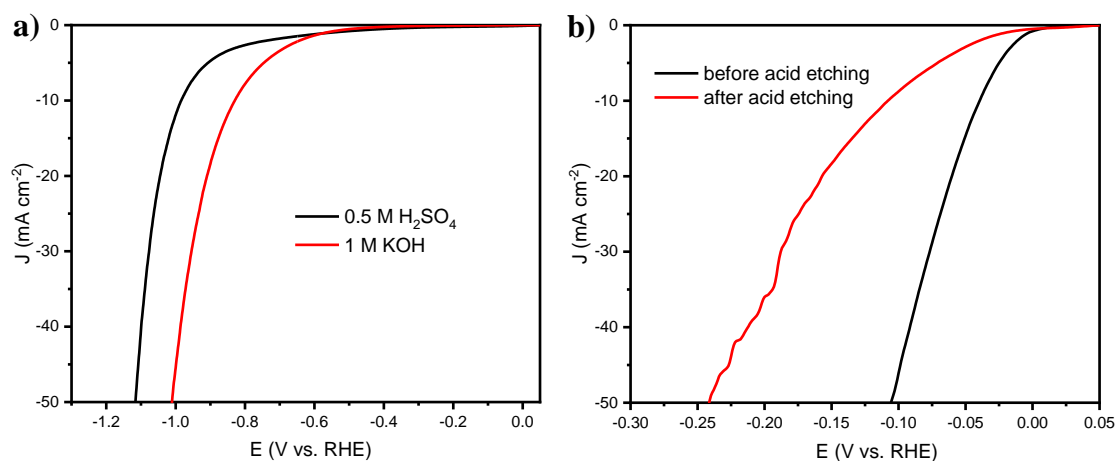


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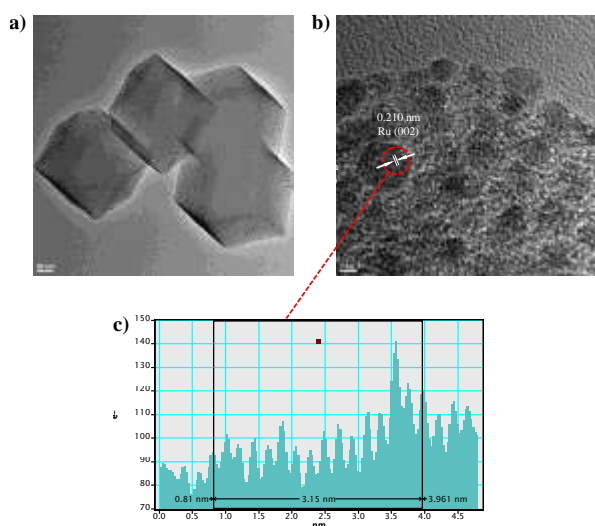


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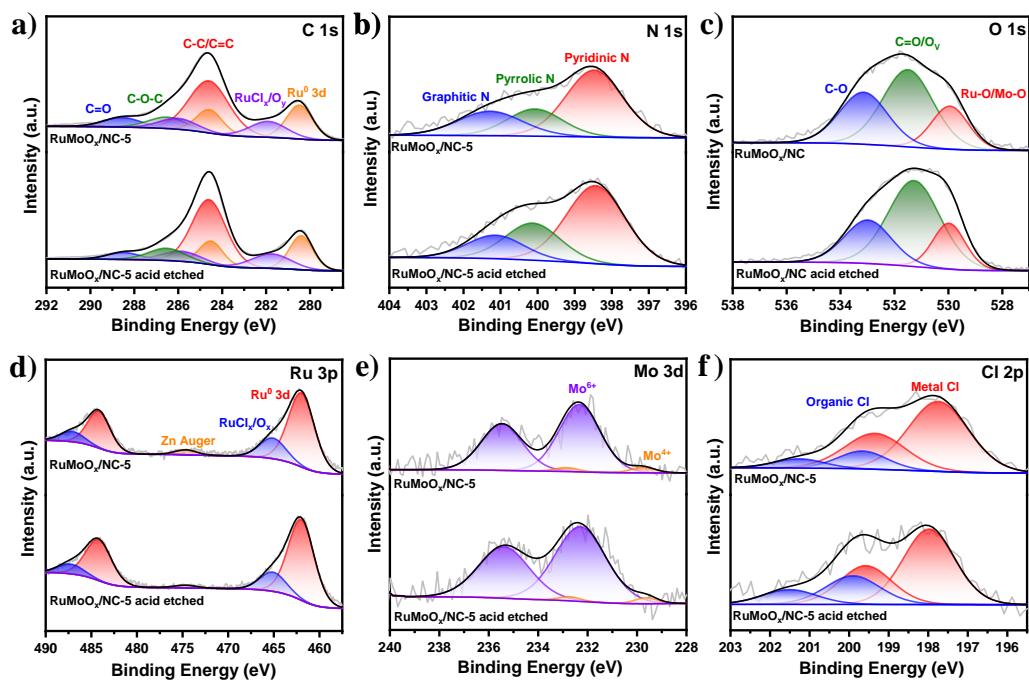


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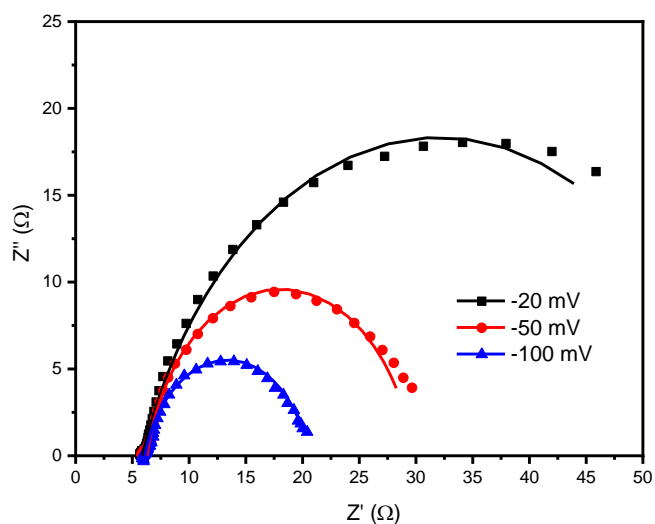


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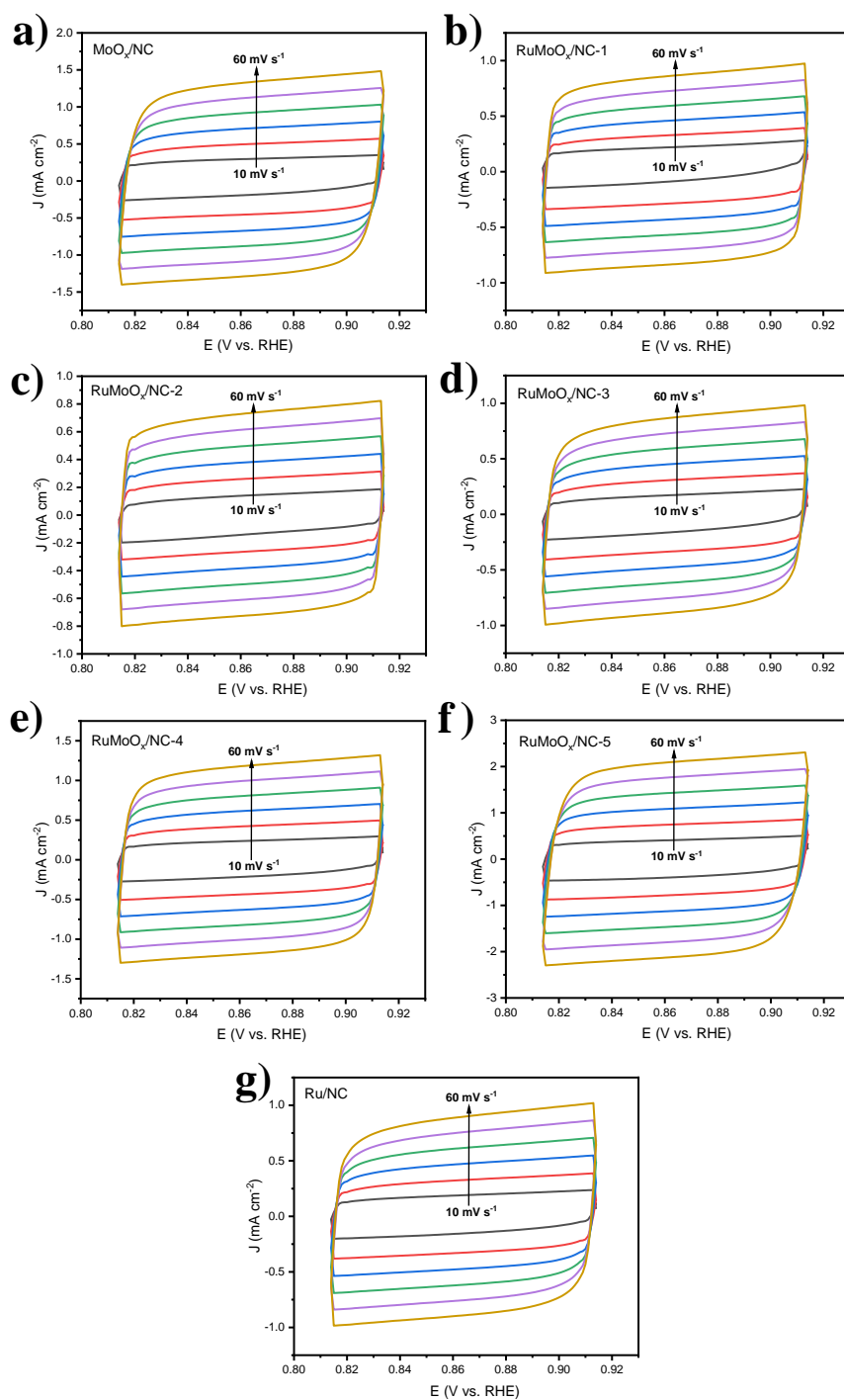


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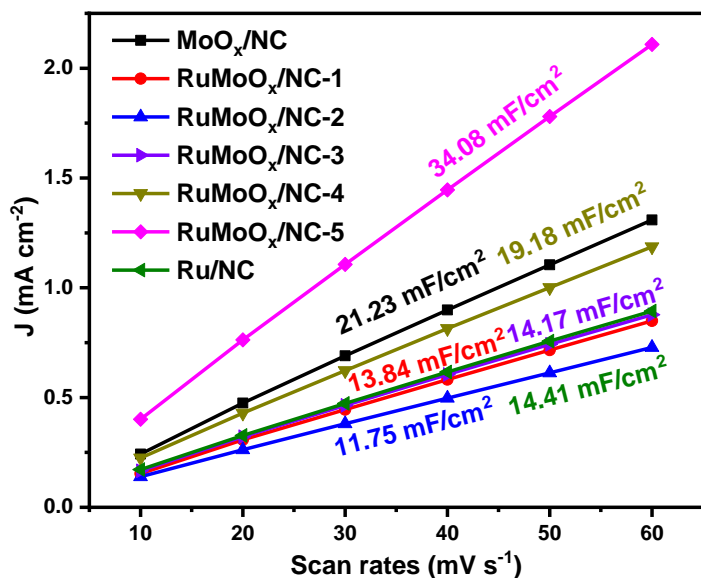


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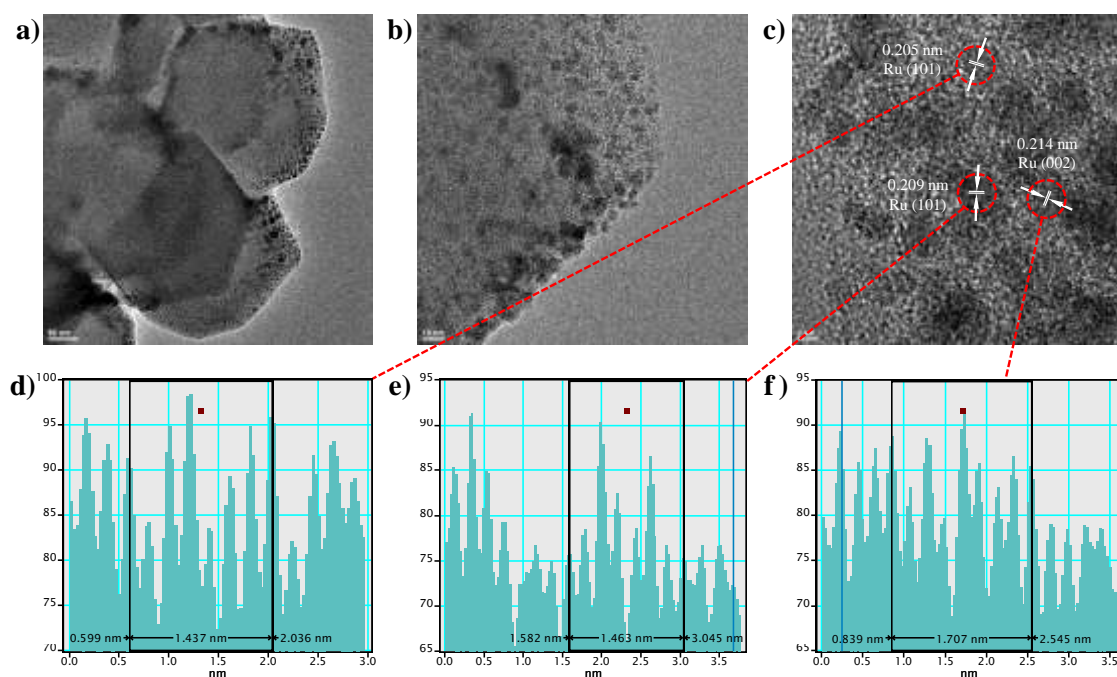


Figure S25. (a,b,c) TEM images of RuMoO_x/NC-5 after 5000 CV cycles. Scale bars are (a) 50 nm, (b) 10 nm and (c) 2 nm. The interplanar spacing of the lattice fringes of the circled areas in panel (c) are shown in panels (d,e) Ru (101) and (f) Ru (002).

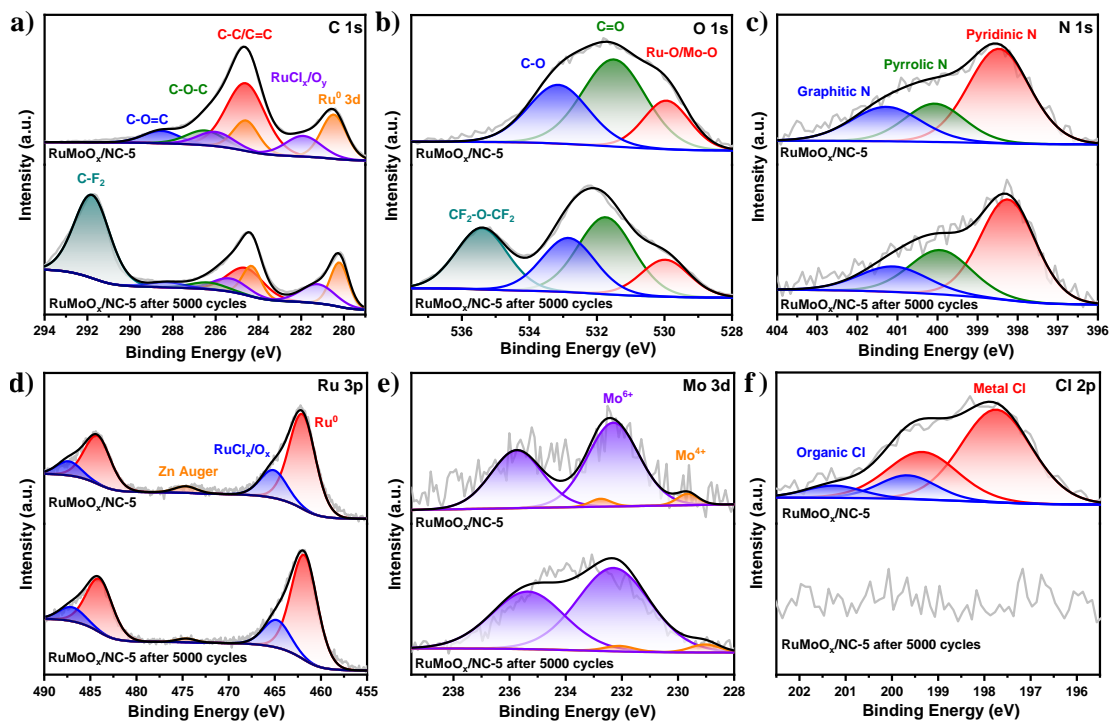


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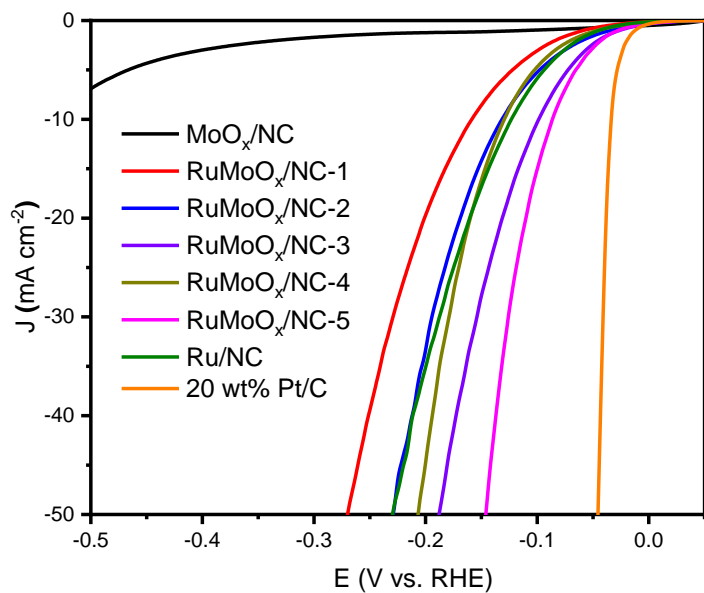


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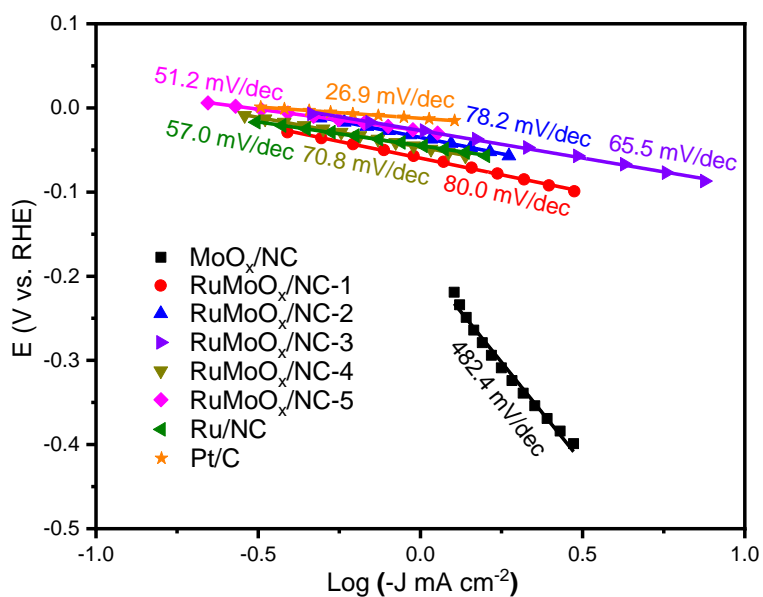


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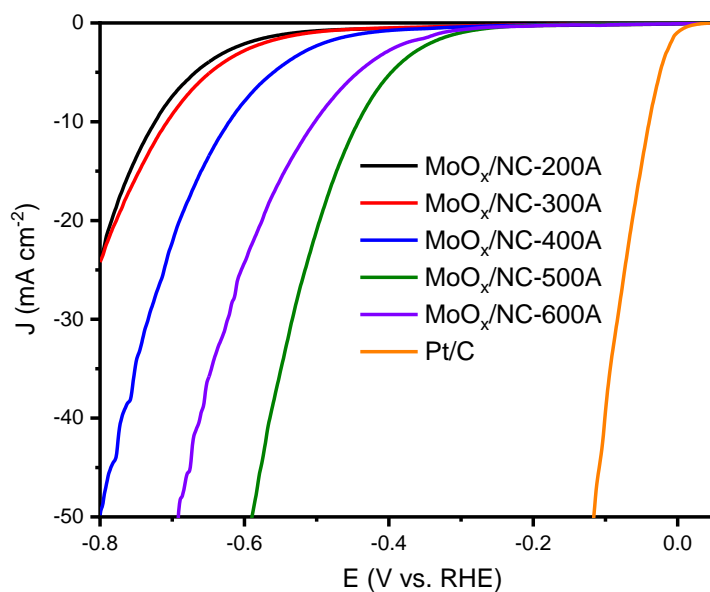


Figure S29. HER polarization curves of MoO_x/NC composites prepared by MIH at currents varied from 200 A to 600 A for 10 s (i.e., MoO_x/NC-200A, MoO_x/NC-300A, MoO_x/NC-400A, MoO_x/NC-500A, MoO_x/NC-600A) and 20 wt% Pt/C in 1 M KOH.

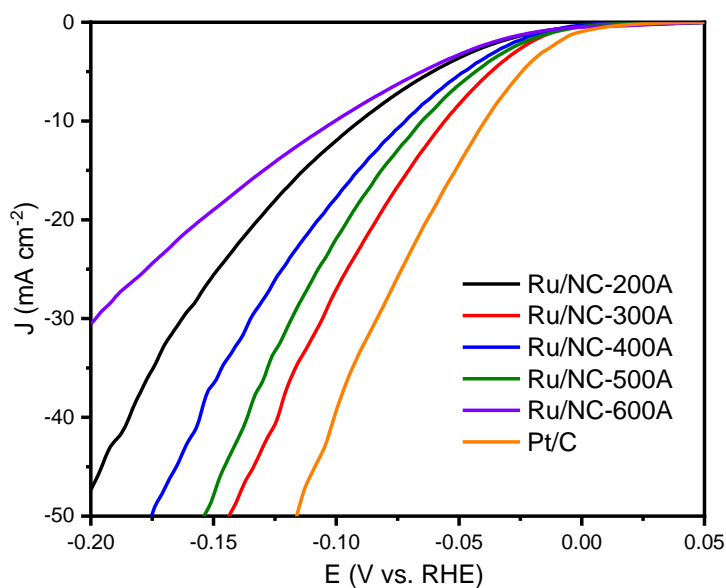


Figure S30. HER polarization curves of Ru/NC composites prepared by MIH at currents varied from 200 A to 600 A for 10 s (i.e., Ru/NC-200A, Ru/NC-300A, Ru/NC-400A, Ru/NC-500A, Ru/NC-600A) and 20 wt% Pt/C in 1 M KOH.

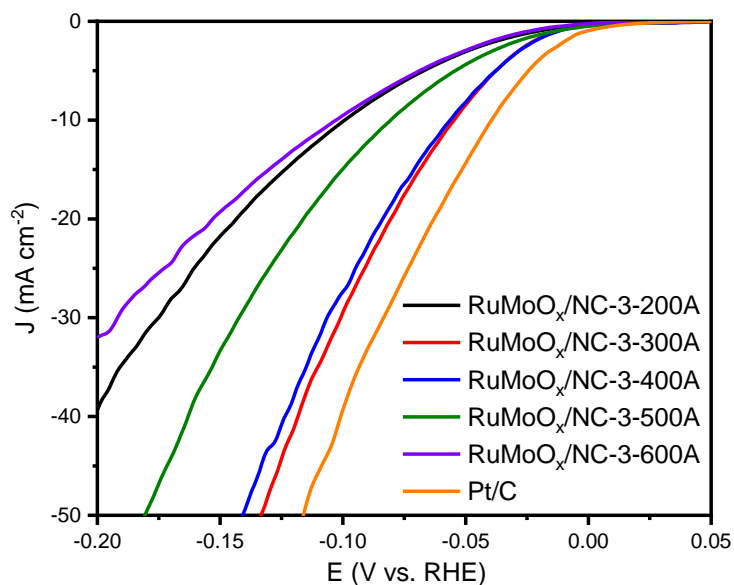


Figure S31. HER polarization curves of RuMoO_x/NC composites prepared by MIH at currents varied from 200 to 600 A for 10 s (i.e., RuMoO_x/NC-3-200A, RuMoO_x/NC-3-300A, RuMoO_x/NC-3-400A, RuMoO_x/NC-3-500A, RuMoO_x/NC-3-600A) and 20 wt% Pt/C in 1 M KOH.

Table S1. Elemental composition (at%) of various samples obtained from SEM elemental mapping.

Sample	C	O	N	Cl	Ru	Mo	Ru+Mo
MoO _x /NC	74.7	10.8	10.5	/	/	4.0	4.0
RuMoO _x /NC-1	76.2	9.9	10.9	0.5	0.1	2.4	2.5
RuMoO _x /NC-2	72.7	10.3	11.5	1.4	1.1	3.0	4.1
RuMoO _x /NC-3	76.8	7.4	10.6	2.2	0.9	2.2	3.1
RuMoO _x /NC-4	77.2	4.6	11.2	4.2	2.0	0.8	2.8
RuMoO _x /NC-5	66.9	10.3	14.2	5.6	2.2	0.8	3.0
Ru/NC	79.0	2.7	10.2	5.0	3.1	/	3.1

Table S2. Elemental composition (at%) of various samples obtained from XPS measurements.

Sample	C	O	N	Cl	Ru	Mo	Ru+Mo
MoO _x /NC	77.8	10.67	9.97	/	/	1.55	1.55
RuMoO _x /NC-1	81.81	13.15	4.07	/	0.21	0.76	0.97
RuMoO _x /NC-2	81.69	14.96	2.28	0.14	0.24	0.68	0.92
RuMoO _x /NC-3	83.75	15.23	0.65	0.10	0.15	0.12	0.27
RuMoO _x /NC-4	75.04	13.39	5.77	2.13	3.26	0.42	3.68
RuMoO _x /NC-5	76.45	11.31	5.67	2.92	3.31	0.34	3.65
RuMoO _x /NC-5 etched	77.83	11.98	6.22	0.63	3.18	0.17	3.35
RuMoO _x /NC-5 after CV cycles	73.02	21.63	2.45	/	2.45	0.45	2.90
Ru/NC	76.55	12.15	6.36	2.53	2.41	/	2.41

From Table S1, the N contents as evaluated by EDS are very consistent between 10-14 at% among the samples, while in Table S2 (by XPS measurements), the N contents are rather scattered. The discrepancy likely arises from their different probe depth. Results from EDS measurements mostly reflect the material bulk property, whereas XPS is in essence a surface analysis technique.

Table S3. Elemental composition (wt%) of various samples obtained from XPS measurements.

Sample	C	O	N	Cl	Ru	Mo
MoO _x /NC	67.05	12.25	10.02	/	/	10.67
RuMoO _x /NC-1	73.19	15.68	4.26	/	1.58	5.29
RuMoO _x /NC-2	72.74	17.75	2.37	0.37	1.65	5.12
RuMoO _x /NC-3	78.22	18.95	0.71	0.28	1.10	0.75
RuMoO _x /NC-4	54.90	13.05	4.92	4.60	20.08	2.46
RuMoO _x /NC-5	55.45	10.93	4.80	6.25	20.77	1.80
RuMoO _x /NC-5 etched	59.28	12.15	5.53	1.42	20.59	1.04
RuMoO _x /NC-5 after CV cycles	56.64	22.35	2.22	/	16.00	2.79
Ru/NC	59.40	12.55	5.76	5.80	16.48	/

Table S4. Ru 3p binding energies in the series of samples as determined by XPS measurements.

Sample	Ru ⁰ (eV)		Ru ^{δ+} (eV)		Zn Auger
RuMoO _x /NC-1	462.19	484.39	465.23	487.43	474.54
RuMoO _x /NC-2	462.16	484.36	465.21	487.41	474.91
RuMoO _x /NC-3	462.08	484.28	465.18	487.38	474.74
RuMoO _x /NC-4	462.04	484.24	465.16	487.36	474.56
RuMoO _x /NC-5	462.02	484.22	465.14	487.34	474.65
RuMoO _x /NC-5 etched	461.99	484.19	465.09	487.29	474.66
RuMoO _x /NC-5 after CV cycles	461.80	484.00	464.79	486.99	474.60
Ru/NC	462.01	484.21	465.12	487.32	474.75

Table S5. Mo 3d binding energies in the series of sample as determined by XPS measurements.

Sample	Mo⁴⁺ (eV)		Mo⁶⁺ (eV)	
MoO _x /NC	229.21	232.31	232.19	235.29
RuMoO _x /NC-1	229.50	232.60	232.21	235.31
RuMoO _x /NC-2	229.40	233.50	232.24	235.34
RuMoO _x /NC-3	229.56	232.66	232.25	235.35
RuMoO _x /NC-4	229.75	232.85	232.26	235.36
RuMoO _x /NC-5	229.56	232.66	232.33	235.43
RuMoO _x /NC-5 after CV cycles	229.03	232.08	232.31	235.35
RuMoO _x /NC-5 etched	229.63	232.73	232.29	235.39

Table S6. Fitting results of the EXAFS spectra for the series of samples.

Sample	Peak	σ^2 (Å ²)	Distance (Å)	Coordination number
MoO _x /NC (73.93% MoO ₃ , 26.07% MoO ₂)	Mo-O	0.0016	1.70	1.5
	Mo-O	0.0104	1.95	3.0
	Mo-O	0.0016	2.30	1.5
	Mo-Mo	0.0069	3.26	1.0
	Mo-Mo	0.0098	3.74	3.0
RuMoO _x /NC-1 (84.74% MoO ₃ , 15.26% MoO ₂)	Mo-O	0.0021	1.71	1.7
	Mo-O	0.0077	1.96	2.6
	Mo-O	0.0037	2.28	1.7
	Ru-Ru	0.0019	2.68	5.1
	Mo-Mo	0.0019	3.24	0.6
	Mo-Mo	0.0140	3.75	3.4
RuMoO _x /NC-2 (84.74% MoO ₃ , 15.26% MoO ₂)	Mo-O	0.0017	1.70	1.4
	Mo-O	0.0085	1.96	3.2
	Mo-O	0.0016	2.31	1.4
	Ru-Ru	0.0016	2.67	6.2
	Mo-Mo	0.0100	3.21	1.2
	Mo-Mo	0.0066	3.71	2.8
RuMoO _x /NC-3 (74.80% MoO ₃ , 25.20% MoO ₂)	Mo-O	0.0016	1.70	1.5
	Mo-O	0.0118	1.95	3.0
	Mo-O	0.0023	2.29	1.5
	Ru-Ru	0.0016	2.68	7.6
	Mo-Mo	0.0056	3.24	1.0
	Mo-Mo	0.0128	3.76	3.0
RuMoO _x /NC-4 (77.12% MoO ₃ , 22.88% MoO ₂)	Mo-O	0.0016	1.69	1.5
	Mo-O	0.0177	1.93	2.9
	Mo-O	0.0036	2.29	1.5
	Ru-Ru	0.0016	2.68	8.0
	Mo-Mo	0.0036	3.25	0.9
	Mo-Mo	0.0164	3.76	3.1
RuMoO _x /NC-5 (80.51% MoO ₃ , 19.49% MoO ₂)	Mo-O	0.0016	1.70	1.6
	Mo-O	0.0165	1.96	2.8
	Mo-O	0.0017	2.29	1.6
	Ru-Ru	0.0016:	2.68	8.9
	Mo-Mo	0.0026	3.25	0.8
	Mo-Mo	0.0167	3.76	3.2
Ru/NC	Ru-Ru	0.0016	2.68	8.9

Note: The minimum limit for σ is set at 0.04, as only strong bonds can exhibit values smaller than this threshold.

Table S7. Comparison of HER activity in 1M KOH between RuMoO_x/NC-5 and other Ru-based HER electrocatalysts.

Electrocatalyst	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Reference
RuMoO _x /NC-5	-39	28.3	This work
Ru/NC-400	-39	40	1
a-RuTe ₂ PNRs	-41	36	2
Ru-MoS ₂ /CC	-41	114	3
Pd ₃ Ru/C	-42	/	4
MoP-Ru ₂ P/NPC	-47	36.93	5
Ru ₂ P@PNC/CC-900	-50.7	28	6
Ru ₁ CoP/CDs-1000	-51	73.4	7
RuP ₂ @NPC	-52	69	8
Ru/C-H ₂ O/CH ₃ CH ₂ OH	-53	47	9
Ni ₅ P ₄ -Ru	-54	56.7	10
Sr ₂ RuO ₄	-61	51	11
Ru-Co ₂ P/N-C/NF	-65	65	12
RuNC-2	-81	88	13
S-RuP@NPSC	-92	90.23	14

Table S8. Comparison of charge transfer resistance (R_{ct} , Ω) for the catalysts at various overpotentials.

Sample	RuMoO _x /NC-1	RuMoO _x /NC-2	RuMoO _x /NC-3	RuMoO _x /NC-4	RuMoO _x /NC-5	Ru/NC
η_{20}	115.7	119.0	105.5	140.6	52.4	132.8
η_{50}	43.2	44.1	39.4	46.3	23.5	45.6
η_{100}	21.2	23.7	20.6	21.5	14.5	24.1

References

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