

Supporting Information

for

Boosting OER via Metal-Support Interaction and H-Bond Network: Amorphous RuO_x on Fluorinated Ruddlesden-Popper Perovskite

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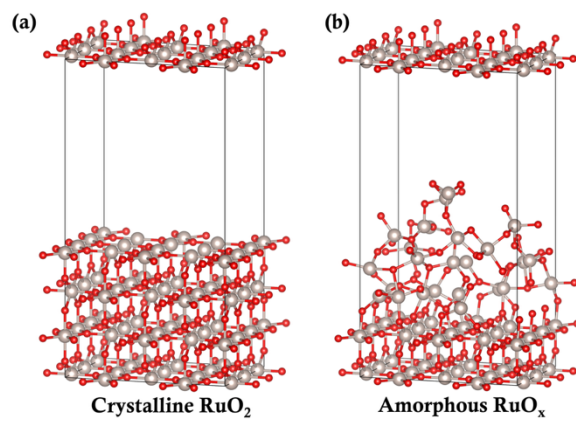


Figure S1. Optimized atomic models of (a) crystalline RuO_2 and (b) amorphous RuO_x ; gray spheres denote Ru atoms, and red spheres denote O atoms.

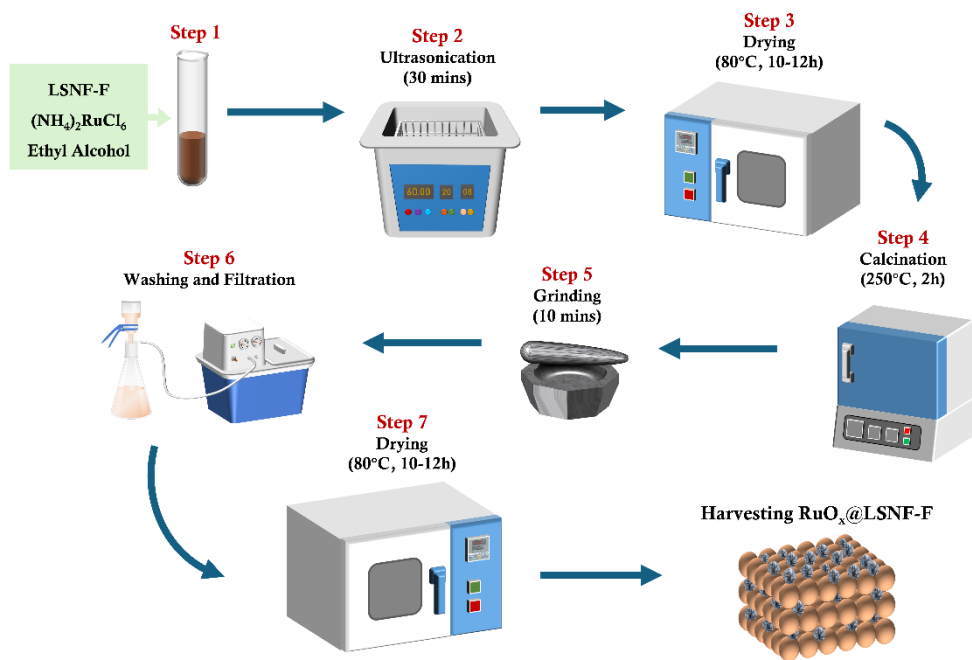


Figure S2. Schematic diagram of the synthesis process of RuO_x@LSNF-F.

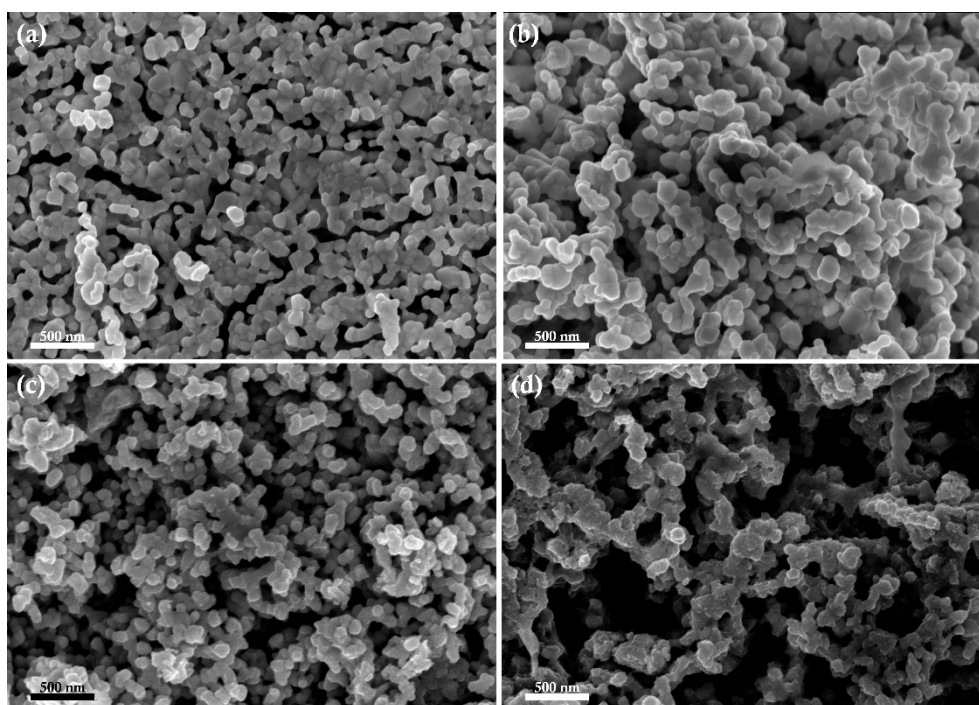


Figure S3. SEM image of (a) LSNF; (b) LSNF-F; (c) RuO_x@LSNF; (d) RuO_x@LSNF-F.

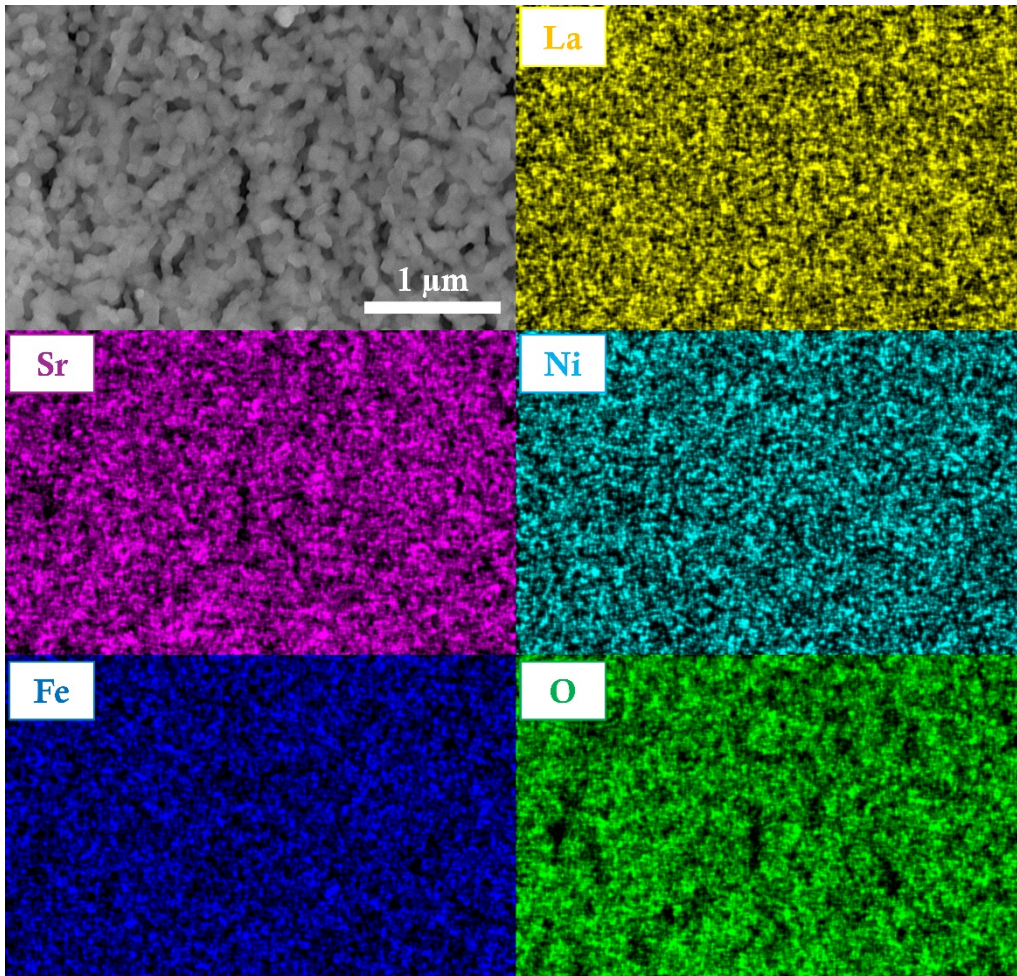


Figure S4. SEM-EDS mapping of LSNF.

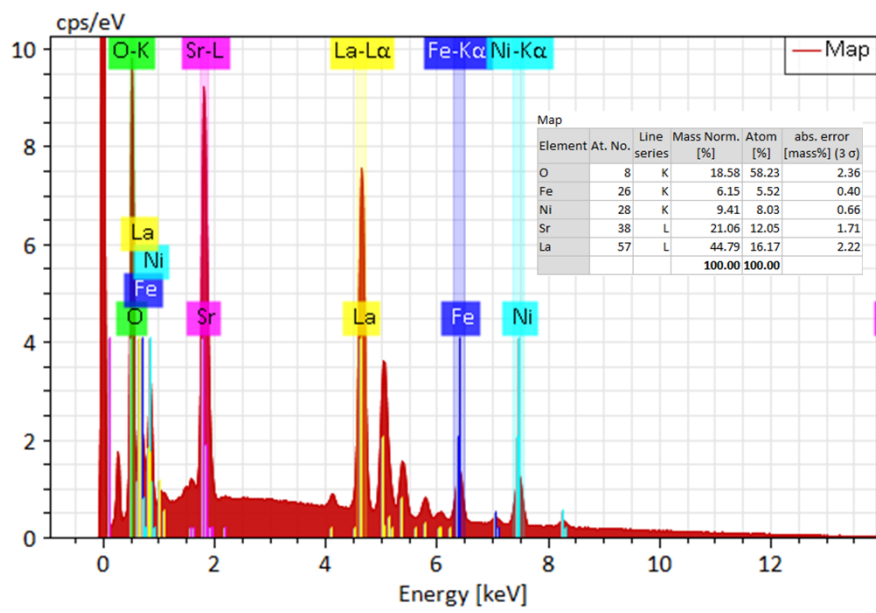


Figure S5. Proportion of each element in LSNF.

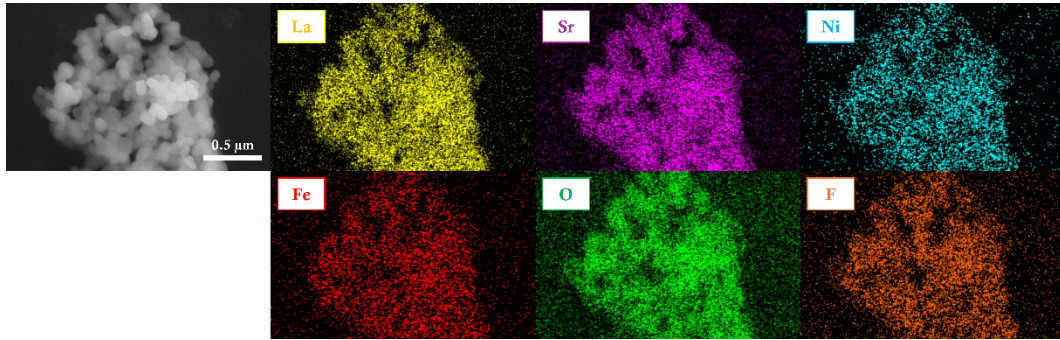


Figure S6. SEM-EDS mapping of LSNF-F.

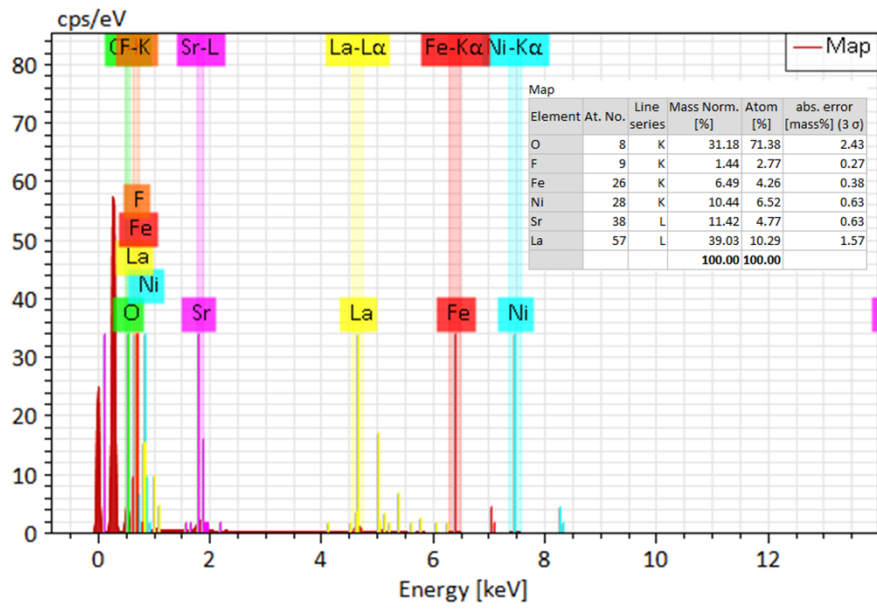


Figure S7. Proportion of each element in LSNF-F.

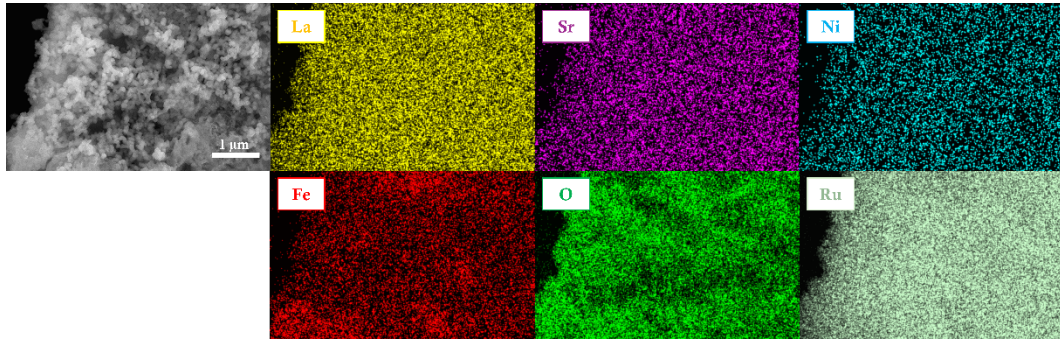


Figure S8. SEM-EDS mapping of RuO_x@LSNF.

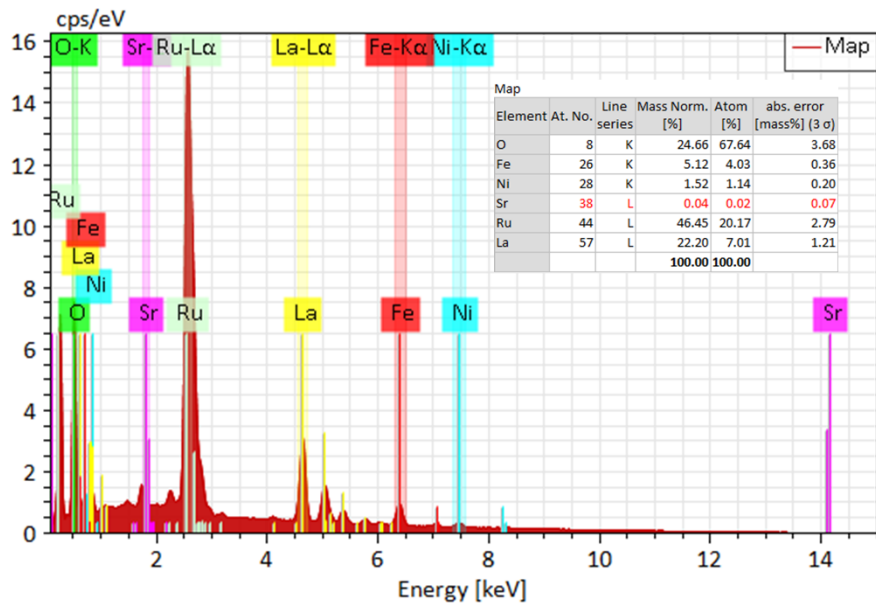


Figure S9. Proportion of each element in RuO_x@LSNF.

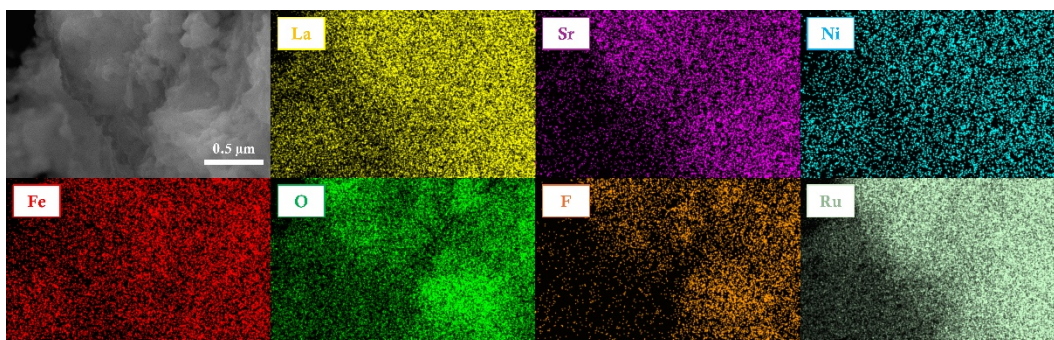


Figure S10. SEM-EDS mapping of RuO_x@LSNF-F.

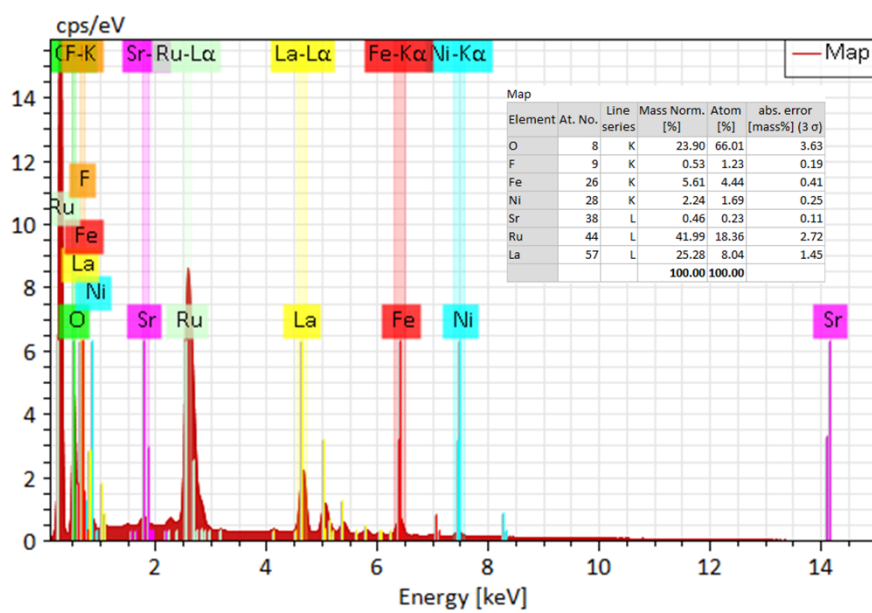


Figure S11. Proportion of each element in RuO_x@LSNF-F.

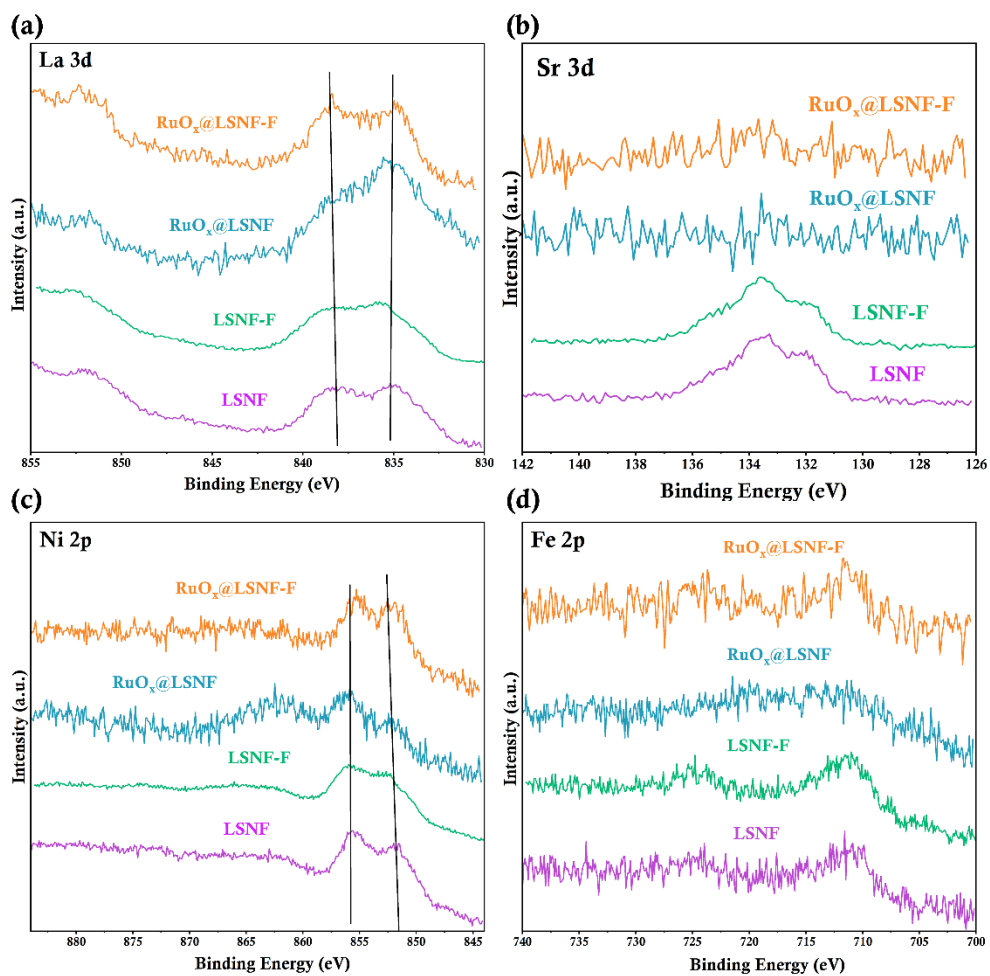


Figure S12. (a) La 3d; (b) Sr 3d; (c) Ni 2p; (d) Fe 2p XPS survey spectra of LSNF, LSNF-F, RuO_x@LSNF, RuO_x@LSNF-F.

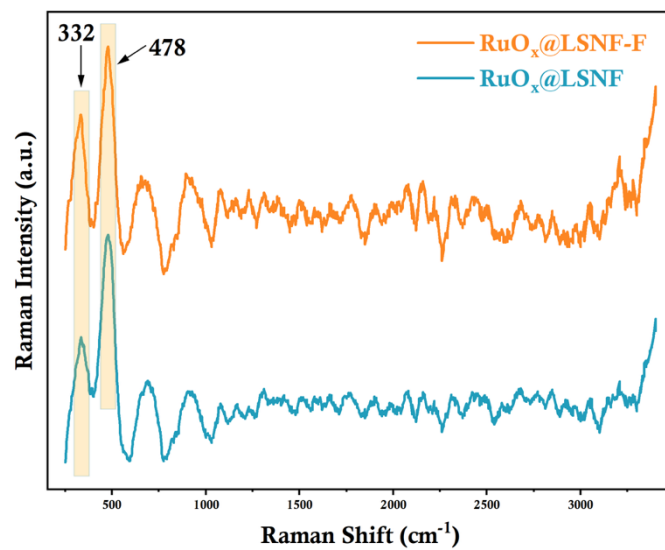


Figure S13. Raman shifts of RuO_x@LSNF-F and RuO_x@LSNF.

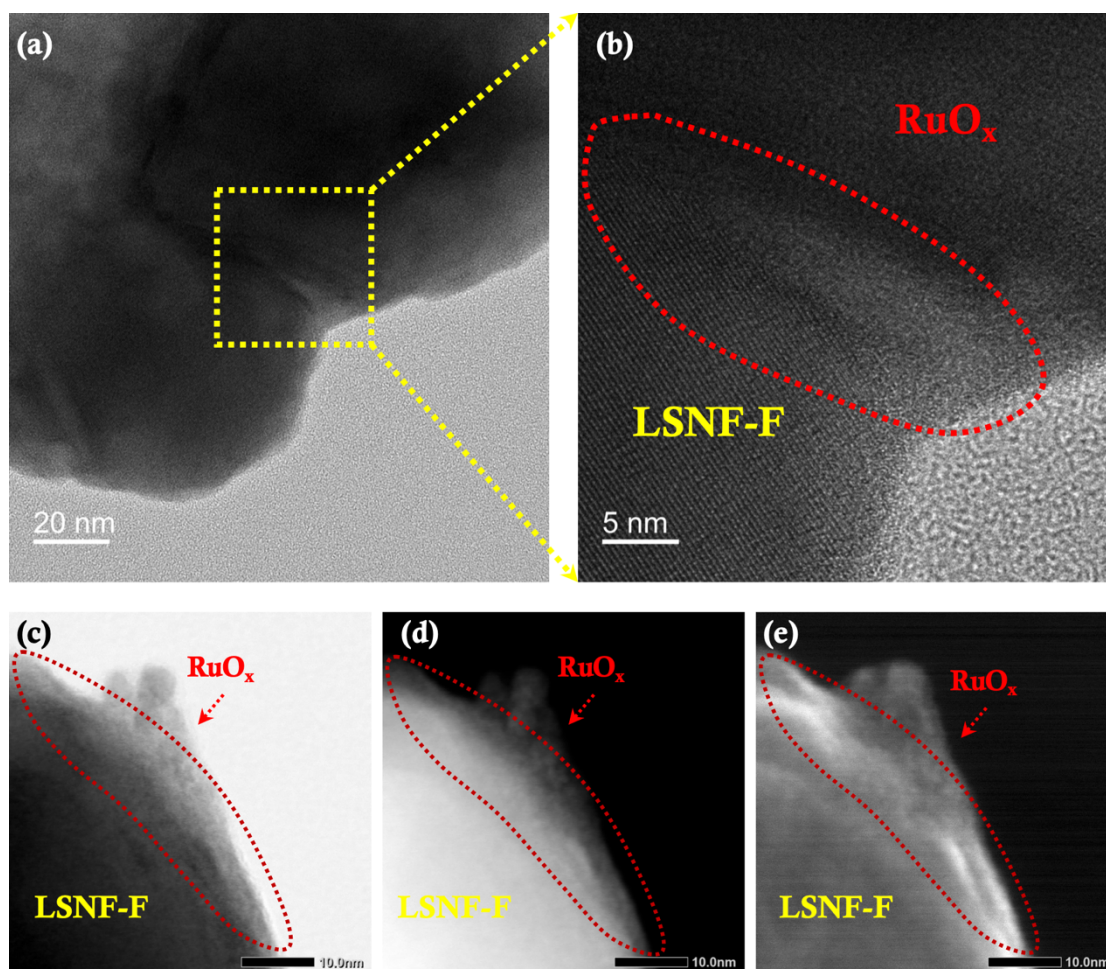


Figure S14. Structural characterization of $\text{RuO}_x@$ LSNF-F. (a) Low-magnification HRTEM image of $\text{RuO}_x@$ LSNF-F, showing the overall morphology of the catalyst with a uniform particle size. (b) High-magnification HRTEM image of the region marked by the yellow dashed box in (a), clearly revealing a distinct core-shell structure: the inner crystalline LSNF-F support with well-ordered lattice fringes, and the outer amorphous RuO_x layer with no observable lattice fringes, confirming the successful loading of amorphous RuO_x on the perovskite support. (c)-(e) HAADF-STEM images of $\text{RuO}_x@$ LSNF-F at different magnifications, further verifying the uniform distribution of the amorphous RuO_x overlayer on the surface of the crystalline LSNF-F support.

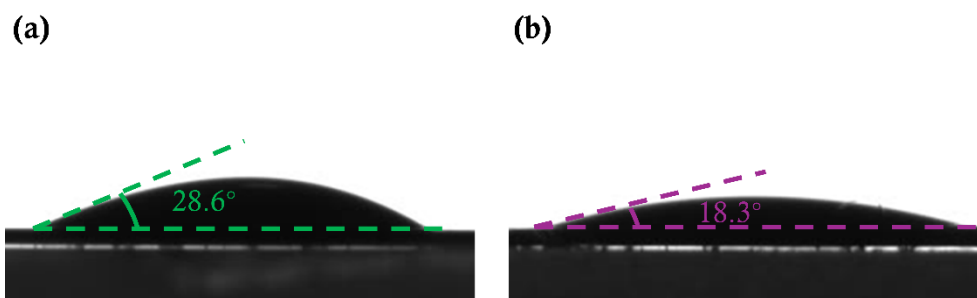


Figure S15. Water contact angle of (a) LSNF-F; (b) LSNF.

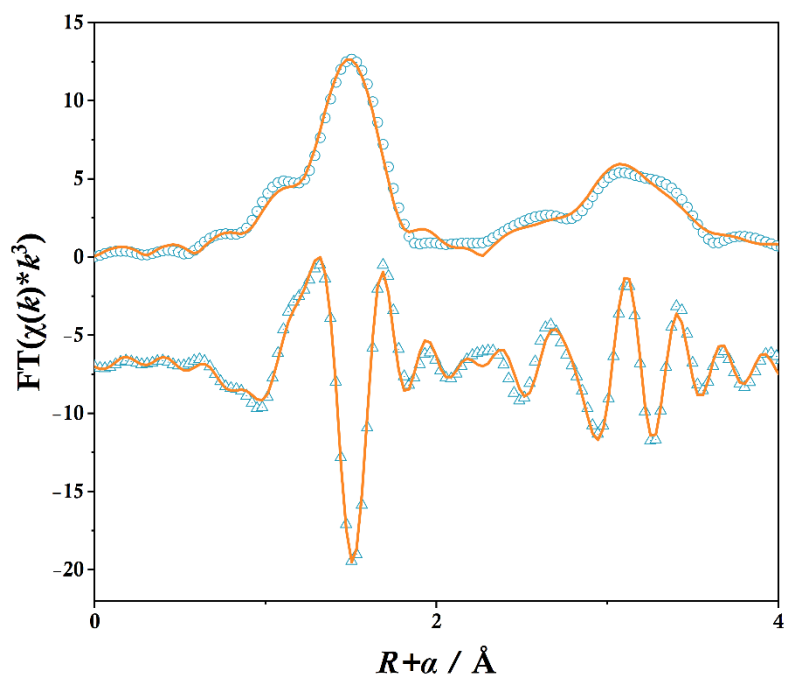


Figure S16. Ru K-edge EXAFS (points) and curvefit (line) for RuO_x@LSNF-F, shown in R-space (FT magnitude and imaginary component). The data are k^3 -weighted and not phase-corrected.

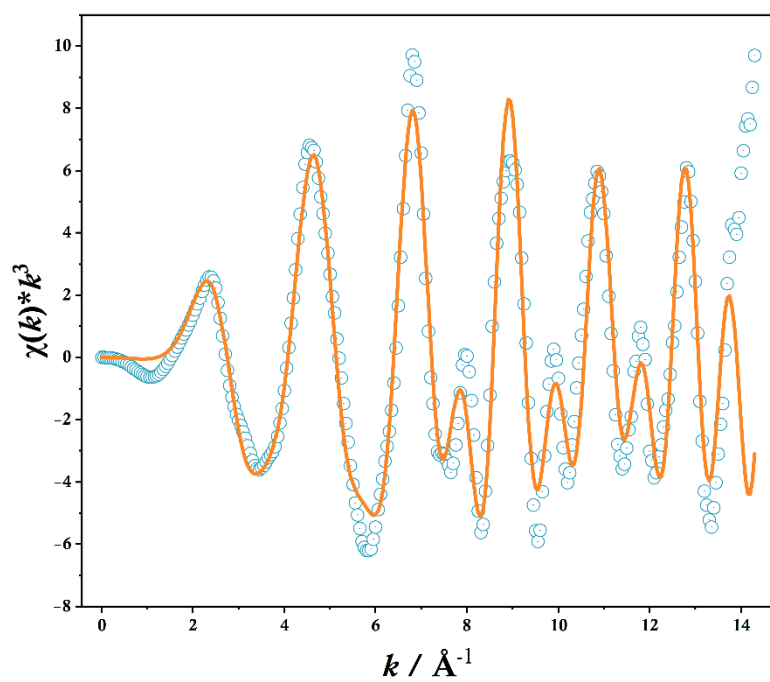


Figure S17. Ru K-edge EXAFS (points) and the curvefit (line) for RuO_x@LSNF-F, shown in k^3 -weighted K-space.

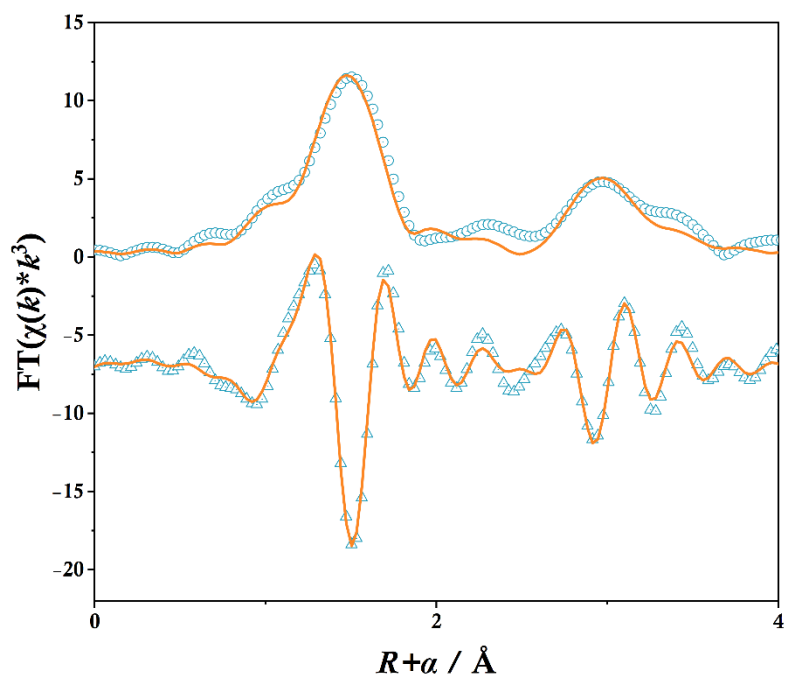


Figure S18. Ru K-edge EXAFS (points) and curvefit (line) for RuO_x@LSNF, shown in R-space (FT magnitude and imaginary component). The data are k^3 -weighted and not phase-corrected.

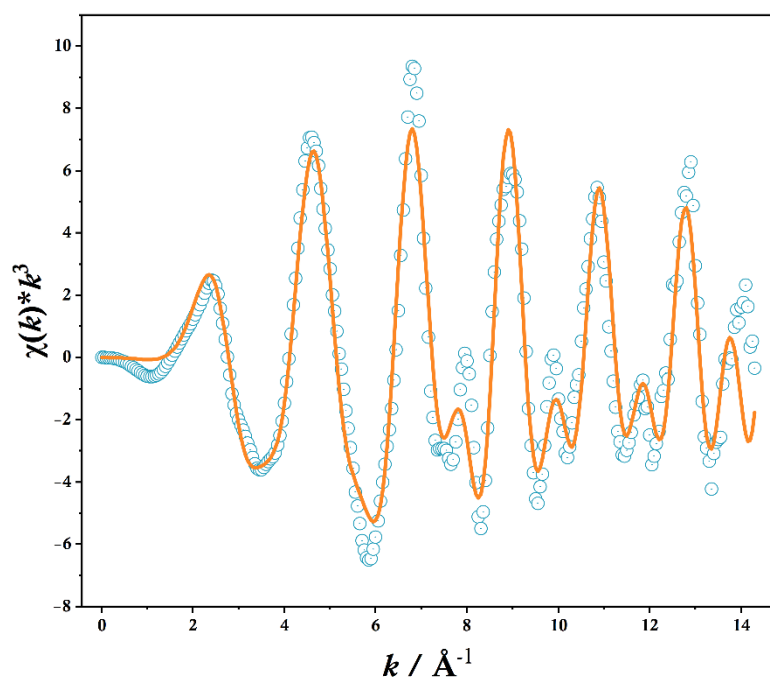


Figure S19. Ru K-edge EXAFS (points) and the curvefit (line) for RuO_x@LSNF, shown in k^3 -weighted K-space.

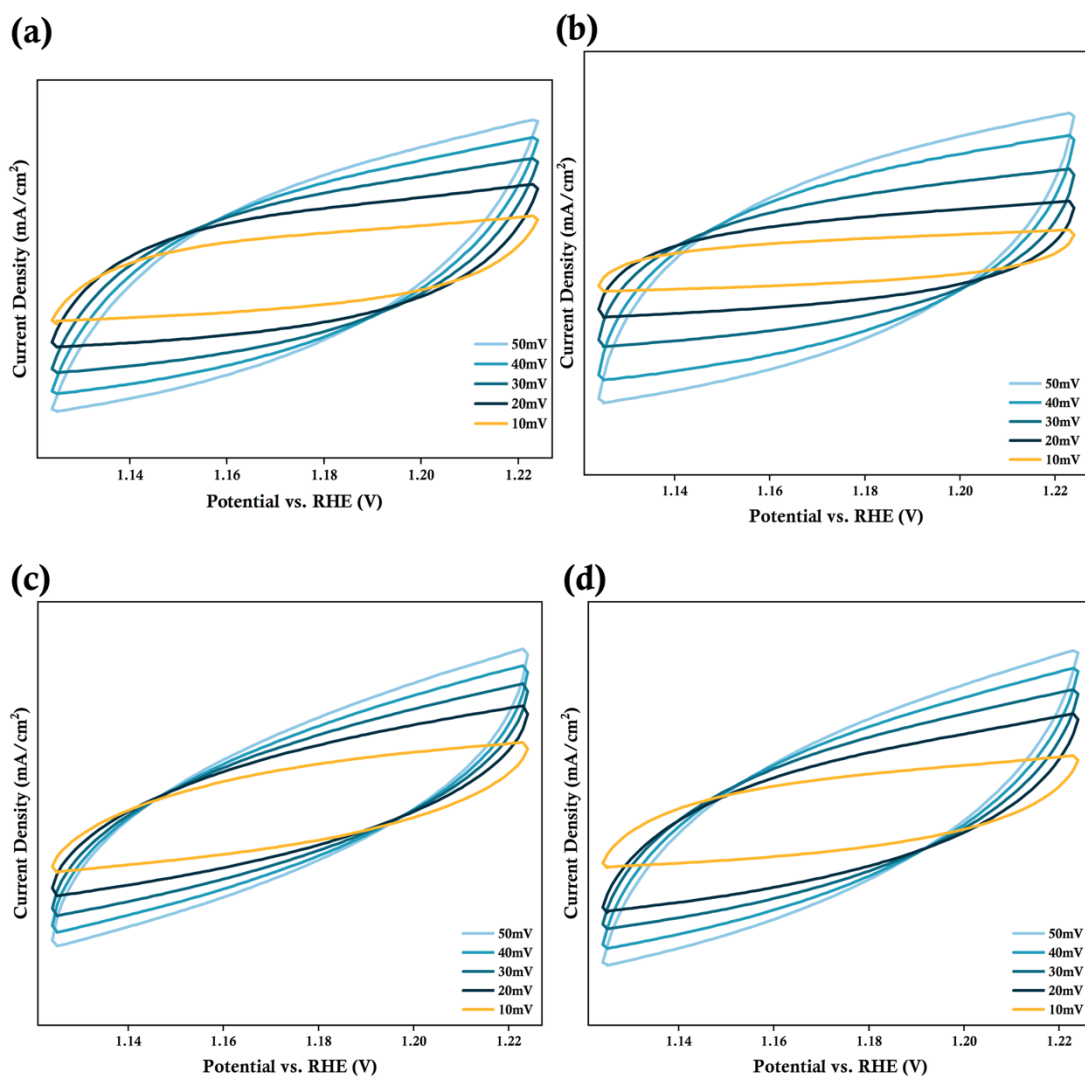


Figure S20. CV curves at different scan rates of (a) RuO_x@LSNF-F; (b) RuO_x@LSNF; (c) LSNF-F; (d) LSNF.

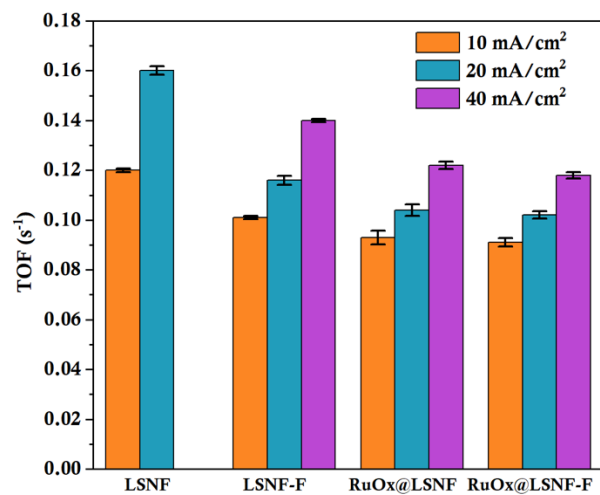


Figure S21. TOF values of the catalysts calculated at a fixed current density of 10/20/40 mA/cm² based on the Ru molar amount quantified by ICP-MS. The error bars represent the standard deviation (SD) from three independent measurements.

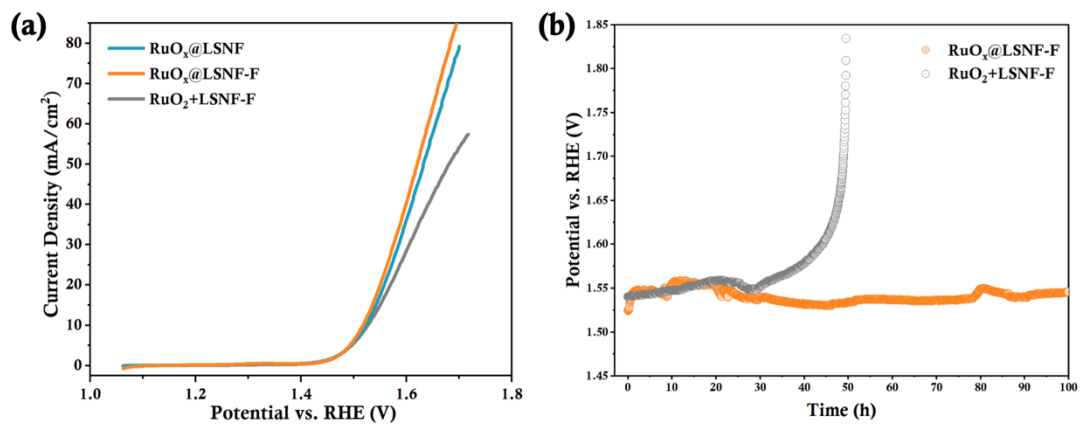


Figure S22. Comparison (a) LSV activity and (b) CP time of RuO_x@LSNF-F, RuO_x@LSNF and RuO₂+LSNF-F.

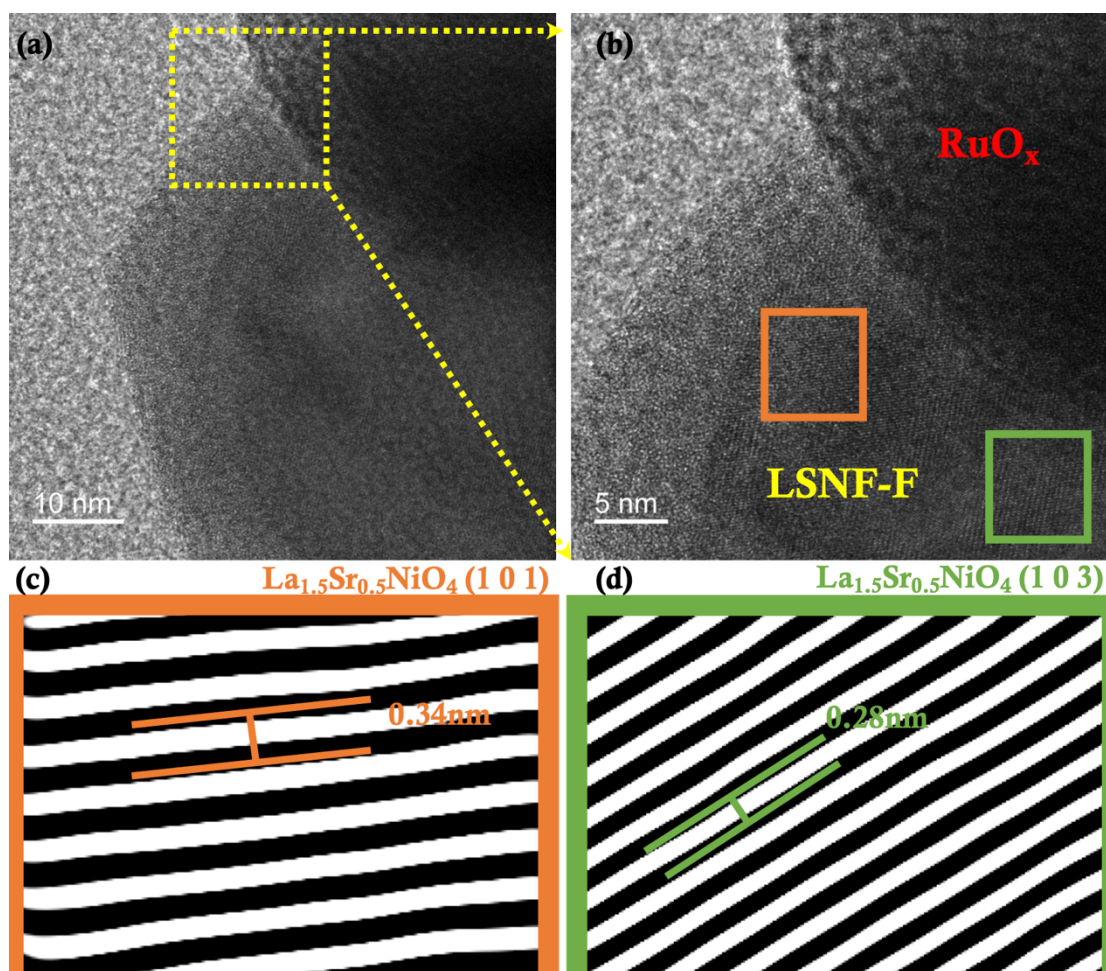


Figure S23. Post-93h-durability (a), (b) HRTEM images and (c), (d) local inverse FFT images of RuO_x@LSNF-F.

Table S1**ICP-MS test result of RuO_x@LSNF-F.**

Ru (wt%)	La (wt%)	Sr (wt%)	Ni (wt%)	Fe (wt%)
31.420	27.585	13.058	10.063	8.596

Table S2**Curvefit parameters^a for Ru K-edge EXAFS for RuO_x@LSNF-F standard**

Path	$d^b/\text{Å}$	N	$R/\text{Å}$	$\sigma^2/\text{Å}^2$	$\Delta E/\text{eV}$	R-factor
Ru – O	1.986	5.3±0.4	1.96±0.01	0.003±0.001	-3.09±0.86	0.017
Ru – Ru1	3.105	6.3±0.8	3.17±0.02	0.002 ^c		
Ru – Ru2	3.539	1.1±0.1	3.55±0.01	0.000 ^c		

^a S_0^2 was fixed as 1.0. Data ranges: $2.25 \leq k \leq 13 \text{ Å}^{-1}$, $1.0 \leq R \leq 3.5 \text{ Å}$. The number of variable parameters is 8, out of a total of 16.9 independent data points. ^b The distances for Ru – O and Ru – Ru are from the crystal structure of RuO₂. ^c These Debye-Waller factors were constrained as $\sigma^2(\text{Ru} - \text{Ru1}) = 0.002$ and $\sigma^2(\text{Ru} - \text{Ru2}) = 0.000$ for reducing the number of variables.

Table S3**Curvefit parameters^a for Ru K-edge EXAFS for RuO_x@LSNF standard**

Path	$d^b / \text{\AA}$	N	$R / \text{\AA}$	$\sigma^2 / \text{\AA}^2$	$\Delta E / \text{eV}$	R-factor
Ru – O	1.986	5.2±0.5	1.96±0.01	0.003±0.001	-1.97±0.8	0.017
Ru – Ru1	3.105	7.9±0.8	3.19±0.02	0.004 ^c		
Ru – Ru2	3.539	1.3±0.2	3.55±0.03	0.000 ^c		

^a S_0^2 was fixed as 1.0. Data ranges: $2.25 \leq k \leq 12 \text{\AA}^{-1}$, $1.0 \leq R \leq 3.2 \text{\AA}$. The number of variable parameters is 8, out of a total of 13.45 independent data points. ^b The distances for Ru – O and Ru – Ru are from the crystal structure of RuO₂. ^c These Debye-Waller factors were constrained as σ^2 (Ru – Ru1) = 0.004 and σ^2 (Ru – Ru2) = 0.000 for reducing the number of variables

Table S4**Dissolution of RuO_x@LSNF-F in 1M KOH after 100 h CP test (results from ICP-MS test for 80ml sample used for CP test) and the percentage of dissolved fraction to its original mass (fresh 1M KOH electrolyte has been confirmed by ICP-MS test to be free of La, Sr, Ni, Fe and Ru).**

	La	Sr	Ni	Fe	Ru
Concentration of metal elements in the electrolyte (mg/L)	0.001	0.002	0.033	0.002	0.003
Percentage of dissolved fraction	0.58%	2.45%	52.41%	3.72%	1.52%

Table S5**Comparison of overpotentials and CP test hours @ 10mA/cm² of reported Ru-based and perovskite-based catalysts in alkaline media.**

	Electrolyte	Overpotential @ 10mA/cm ² (mV)	CP test hours (h)	Reference
RuO _x @LSNF-F	1M KOH	287	100	This work
RuO _x @LSNF	1M KOH	292	33	This work
LSNF-F	1M KOH	317	15	This work
Mn/Ru DSA	1M NaOH	300	14.5	(1)
RuO ₂ com.	1M KOH	366	10	(2)
Ru ₂ Ni ₂ SNs/C	1M KOH	310	40	(3)
SFR30	1M KOH	334	96	(4)
Ni _{1.25} Ru _{0.75} P	1M KOH	340	20	(5)
PSCR0.05	0.1M KOH	321	10	(6)
SNCF-NR	0.1M KOH	390	10	(7)
LSCF-30	1M KOH	360	56	(8)

r-LSCN-P	0.1M KOH	410	14	(9)
SCFM10	1M KOH	310	100	(10)

References

- (1) Browne, M. P.; Nolan, H.; Duesberg, G. S.; Colavita, P. E.; Lyons, M. E. G. Low-Overpotential High-Activity Mixed Manganese and Ruthenium Oxide Electrocatalysts for Oxygen Evolution Reaction in Alkaline Media. *ACS Catalysis* **2016**, *6* (4), 2408–2415. <https://doi.org/10.1021/acscatal.5b02069>.
- (2) Gao, M.-R.; Cao, X.; Gao, Q.; Xu, Y.-F.; Zheng, Y.-R.; Jiang, J.; Yu, S.-H. Nitrogen-Doped Graphene Supported CoSe₂ Nanobelt Composite Catalyst for Efficient Water Oxidation. *ACS Nano* **2014**, *8* (4), 3970–3978. <https://doi.org/10.1021/nn500880v>.
- (3) Ding, J.; Shao, Q.; Feng, Y.; Huang, X. Ruthenium-Nickel Sandwiched Nanoplates for Efficient Water Splitting Electrocatalysis. *Nano Energy* **2018**, *47*, 1–7. <https://doi.org/10.1016/j.nanoen.2018.02.017>.
- (4) Zhang, W.; Xue, M.; Zhang, X.; Si, C.; Tai, C.; Lu, Q.; Wei, M.; Han, X.; Ma, J.; Chen, S.; Guo, E. Boosting Oxygen/Hydrogen Evolution Catalysis via Ruthenium Doping in Perovskite Oxide for Efficient Alkaline Water Splitting. *Applied Surface Science* **2024**, *664*, 160278. <https://doi.org/10.1016/j.apsusc.2024.160278>.
- (5) Liyanage, D. R.; Li, D.; Cheek, Q. B.; Baydoun, H.; Brock, S. L. Synthesis and Oxygen Evolution Reaction (OER) Catalytic Performance of Ni_{2-x}Ru_xP Nanocrystals: Enhancing Activity by Dilution of the Noble Metal. *Journal of Materials Chemistry A* **2017**, *5* (33), 17609–17618. <https://doi.org/10.1039/c7ta05353c>.
- (6) Zhao, Y.-N.; Liu, C.; Xu, S.; Min, S.; Wang, W.; Mitsuzaki, N.; Chen, Z. A/B-Site Management Strategy to Boost Electrocatalytic Overall Water Splitting on Perovskite Oxides in an Alkaline Medium. *Inorganic Chemistry* **2023**, *62* (31), 12590–12599. <https://doi.org/10.1021/acs.inorgchem.3c01965>.
- (7) Zhu, Y.; Zhou, W.; Zhong, Y.; Zhong, Q.; Chen, X.; Liu, M.; Zhou, W. A Perovskite Nanorod as Bifunctional Electrocatalyst for Overall Water Splitting. *Advanced Energy Materials* **2017**, *7* (8), 1602122–1602122. <https://doi.org/10.1002/aenm.201602122>.
- (8) Zong, R.; Fang, Y.; Zhu, C.; Zhang, X.; Wu, L.; Hou, X.; Tao, Y.; Shao, J. Surface Defect Engineering on Perovskite Oxides as Efficient Bifunctional Electrocatalysts for Water Splitting. *ACS Applied Materials & Interfaces* **2021**, *13* (36), 42852–42860. <https://doi.org/10.1021/acsami.1c11895>.
- (9) Wang, Y.; Wang, Z.; Jin, C.; Li, C.; Li, X.; Li, Y.; Yang, R.; Liu, M. Enhanced Overall Water Electrolysis on a Bifunctional Perovskite Oxide through Interfacial Engineering. *Electrochimica Acta* **2019**, *318*, 120–129. <https://doi.org/10.1016/j.electacta.2019.06.073>.
- (10) Zhang, W.; Si, C.; Lu, Q.; Wei, M.; Han, X.; Chen, S.; Guo, E. Mo-Doped SrCo_{0.5}Fe_{0.5}O_{3-δ} Perovskite Oxides as Bifunctional Electrocatalysts for Highly Efficient Overall Water Splitting. *Electrochimica Acta* **2024**, *491*, 144323. <https://doi.org/10.1016/j.electacta.2024.144323>.