Ni_4N Interspersed Ru for Enhanced Hydrogen Oxidation Reaction in Alkaline Medium

Anagha Usha Vijayakumar#, Manoj Shanmugasundaram#, Vineesh Thazhe Veettil and David Zitoun*

Department of Chemistry, Bar-Ilan Institute of Nanotechnology and Advanced Materials (BINA), Israel National Institute for Energy Storage (INIES), Bar-Ilan University, Ramat Gan, 5290002, Israel

*Corresponding Author: E-mail address: david.zitoun@biu.ac.il

Experimental Section

2.1 Chemical and Materials

Vulcan carbon XC-72 (Cabot corporation). Ru/C (20 % Sigma Aldrich), $RuCl_3$ (AR Sigma Aldrich), $NiNO_3.6H_2O$ (AR Sigma Aldrich), $CuSO_4$. $6H_2O$ (AR Sigma Aldrich) and KOH (AR 99.998%), Isopropyl Alcohol (Sigma Aldrich), H_2SO_4 (Sigma Aldrich) Nafion (5 wt%, AR, Sigma Aldrich). Deionized water is used for synthesis and making electrolyte solutions.

2.2 Material Synthesis

Vulcan carbon (XC-72) was oxidized in the air at 400°C to make it more hydrophilic. To synthesize the catalysts, this oxidized Vulcan carbon was first dispersed in minimum amount of water and stirred continuously for 30 minutes. Subsequently, the ruthenium and nickel precursor salts (the carbon: metal loading was set to 80:20 at%) were added to this mixture and left for stirring until the formation of a thick slurry. The samples were then freeze-dried for 12 hrs to achieve uniform impregnation of the metal salts on the carbon. The fluffy freeze-dried powder was treated in an

Ar/H_2 (95:5) atmosphere at 350°C for 2 hrs, resulting in the reduction of the salts and formation of Ru-Ni nanoparticles dispersed on carbon. Two different compositions of the Ru-Ni (70:30, 85:15) alloy were synthesized by controlling the ratio of the metal precursors. These alloy samples were annealed under NH_3 at 350°C for 1 h, for nitridation and heterostructure formation. Under these conditions, Ru is unreactive to ammonia while Ni reacts and gets converted to Ni_4N. This selective reactivity of Ni to NH_3 enables dealloying and yields the heterostructure.

2.3 Particle Characterization

The morphology and elemental compositions of carbon supported electrocatalysts in this work were visualized using JEOL JEM-2100 (LaB6) at 200 kV for high resolution imaging). Fourier transform analysis (FFT) of high-resolution images technique was used for structural analysis. High Resolution Transmission Electron Microscopy (HRTEM) images together with energy dispersive X-ray spectroscopy (EDS) were obtained by a JEOL JEM-2100F Field Emission Electron Microscope operated at 200 kV. The crystalline phases and crystallinity of the prepared powders of final products were examined by a Rigaku Smartlab XRD in Bregg-Brentano (Theta-Two Theta) mode. The X-ray generator was operated at 40 kV and 30 mA with Cu-Ka radiation (0.154 nm). X-ray photoelectron spectra (XPS) were recorded using a Thermo Scientific Kα spectrometer with a monochromated Al X-ray source (hν = 1486.6 eV; spot size 400 μm). The survey spectra and core-level spectra were recorded with pass energies of 100 and 30 eV, respectively. All spectra were acquired using an electron flood gun to compensate for possible positive charge accumulation during the measurements. The obtained spectra were analyzed using CASA XPS software. HAADF-STEM was taken on a FEI TITAN transmission electron microscope operated at 300 kV. Ru k-edge

XAS spectra were recorded at Synchrotron- Light for Experimental Science and Applications in the Middle East (SESAME), Jordan.

2.4 Electrochemical Measurements

The electrochemical measurements were recorded in a Teflon cell in a three electrodes configuration, with a polished 0.196 cm^2 glassy carbon disk as working electrode, glassy carbon rod as counter electrode and Hg/HgO (1M KOH) as reference electrode. The glassy carbon electrode was polished with α-Al_2O_3 powder of 300 nm and 50 nm and then ultrasonically washed with deionized water and absolute ethanol. Typically, 2 mg of catalyst mixed with 10 µl of Nafion (5wt%) solution was dispersed in 0.9 ml of water-isopropanol solution and sonicated for 1 h to form homogeneous ink. A micropipette was used to drop 15 µl of the dispersion onto the Glassy carbon surface and then dried at ambient temperature with a rotation rate of 300 rpm for 10 minutes and 900 rpm for 30 minutes. The catalyst loading on the glassy electrode was maintained 15 μg_{Ru} cm^{-2} in all the measurements. The alkaline aqueous solution was prepared from KOH (Sigma–Aldrich, 99.998%) and ultrapure water. The glassy carbon was mounted on a rotating electrode (Pine instruments) and all the data was collected with a VMP3 potentiostat (Bio-Logic). The recorded potentials were referred to reversible hydrogen electrode (RHE) with iR correction. The RHE potential was determined by the equilibrium potential of HER/HOR zero-point current using Pt/C as a working electrode at 1600 rpm in H_2-saturated 0.1M KOH solution. Cu_{upd} stripping voltammetry was performed in N_2 saturated 0.5M H_2SO_4 solution containing 5mM $CuSO_4$ after Cu deposition at 0.276V for 100 s. The voltammogram of each catalyst in 0.5M H_2SO_4 solution is the baseline for the corresponding Cu_{upd} stripping voltammogram.

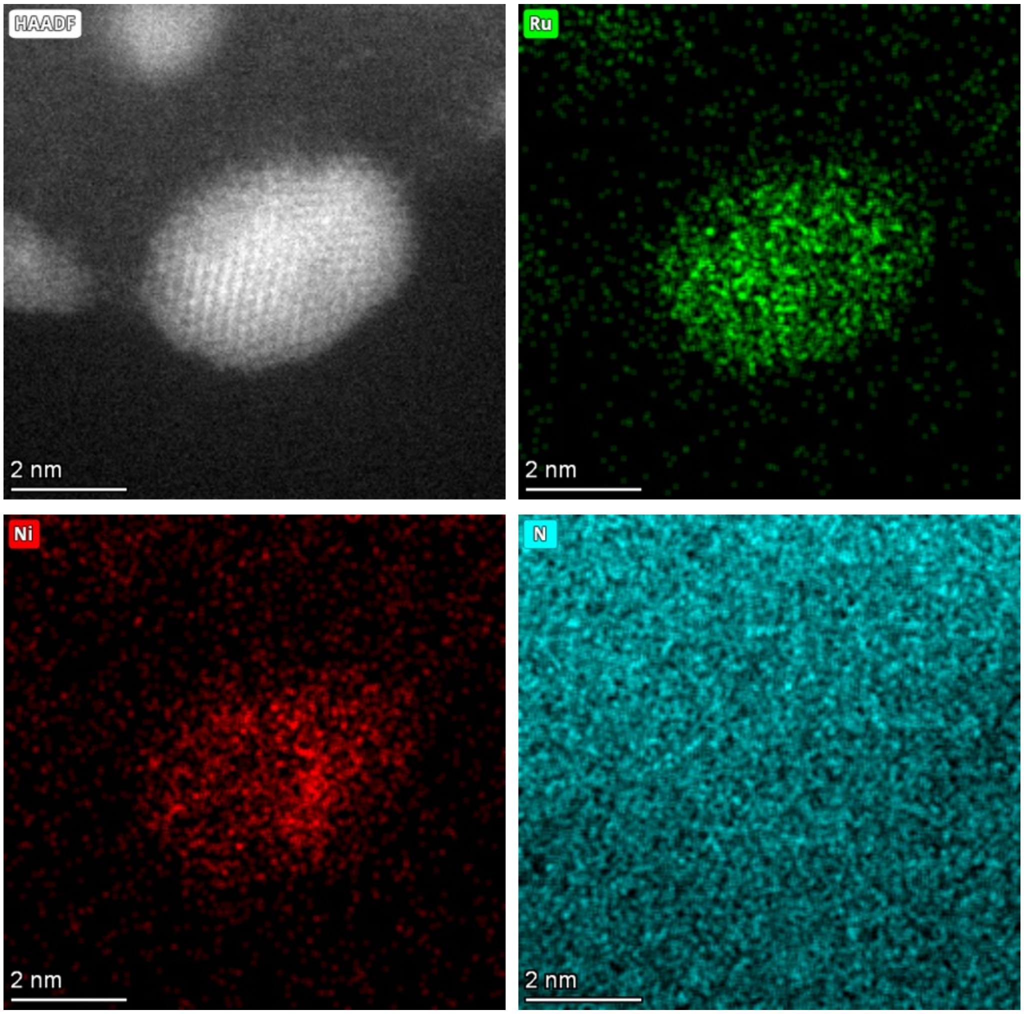

Figure S1. HAADF-STEM elemental mapping of $RuNi_4N$-7030

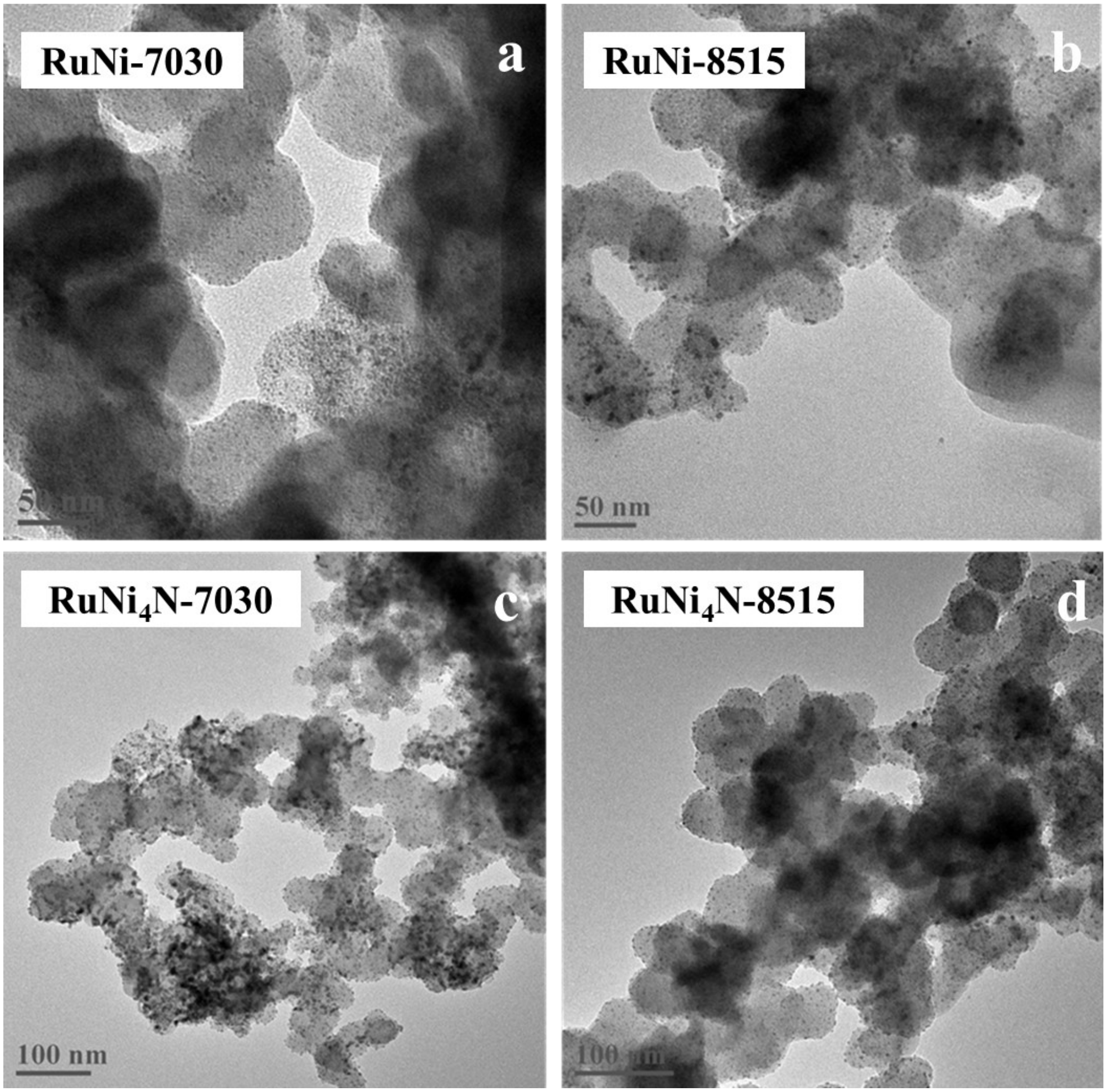

Figure S2. Transmission electron microscopy (TEM) images of the RuNi-7030, RuNi-8515, $RuNi_4N$-7030 and $RuNi_4N$-8515.

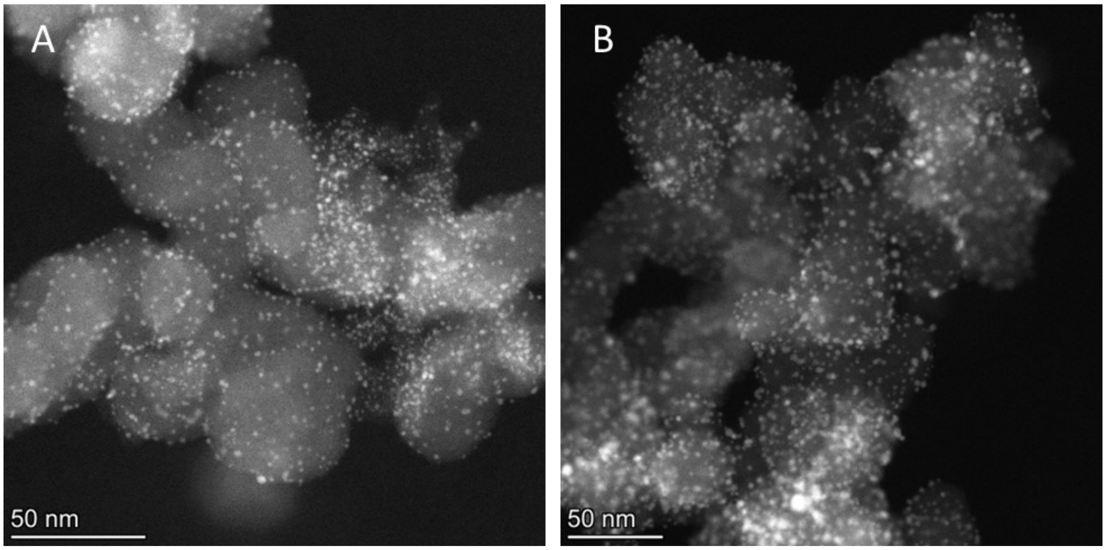

Figure S3. STEM images of the $RuNi_4N$-7030 and $RuNi_4N$-8515.

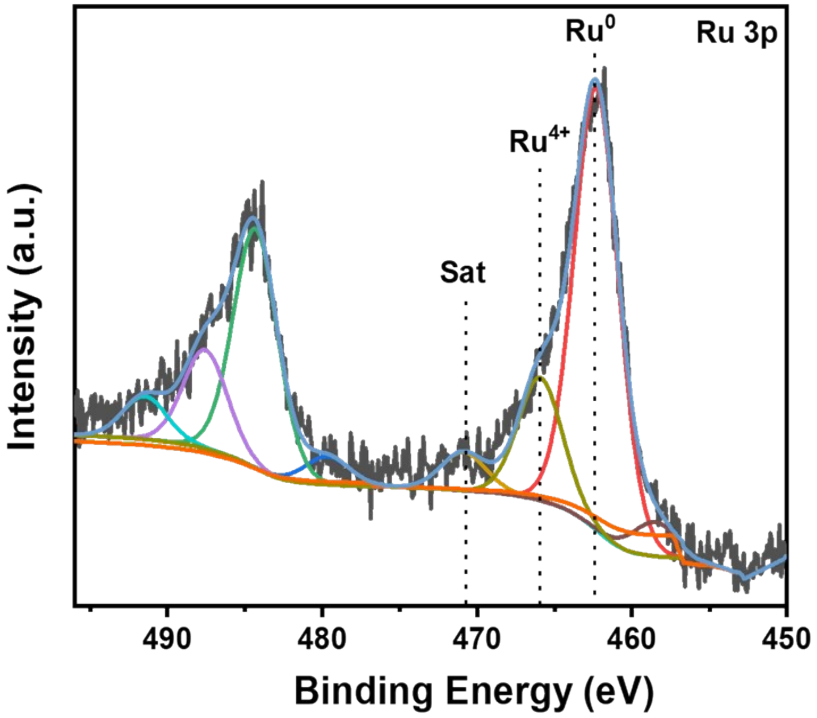

Figure S4. High resolution XPS spectra of Ru 3p of Ru/C

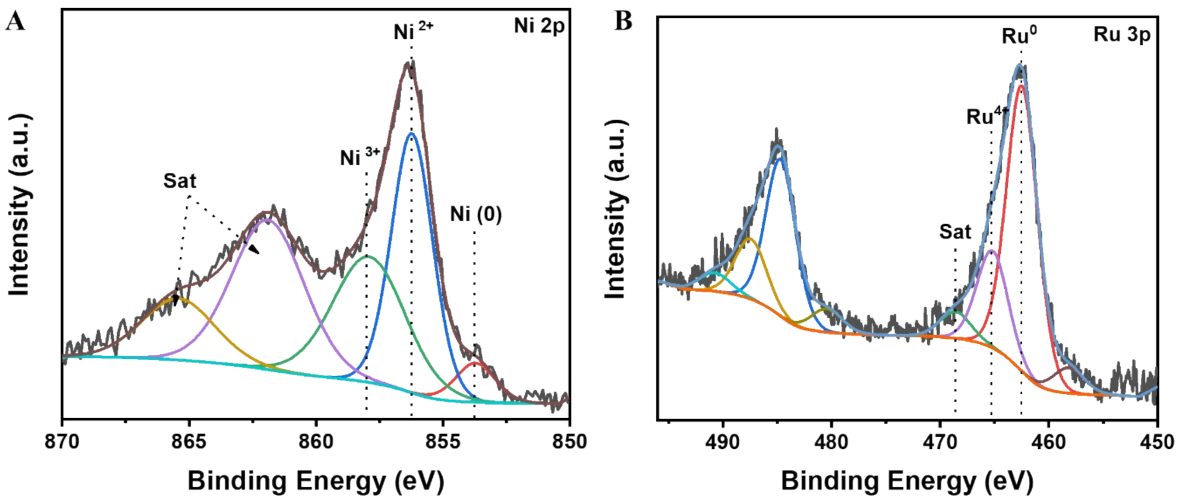

Figure S5. XPS of RuNi-8515

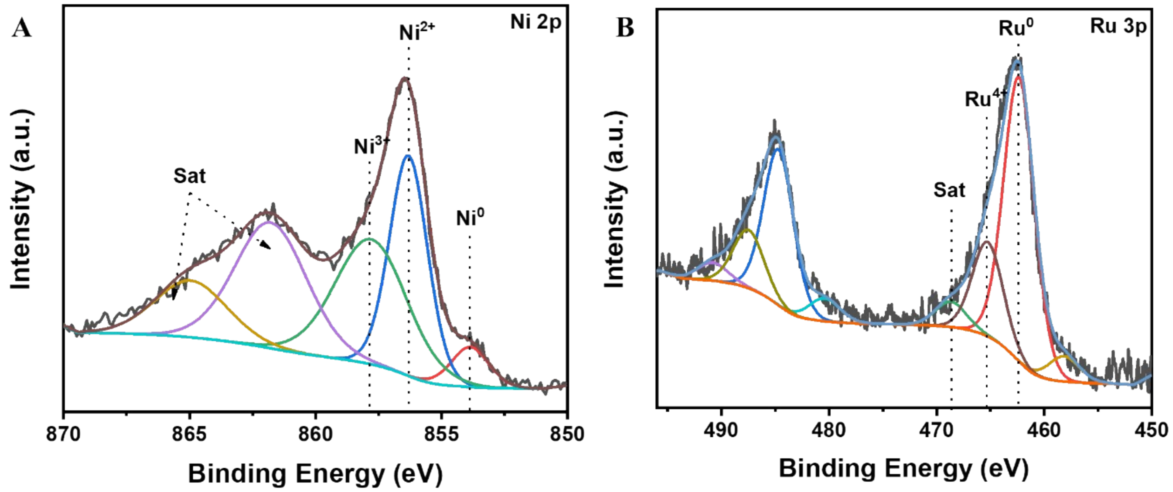

Figure S6. XPS of RuNi-7030

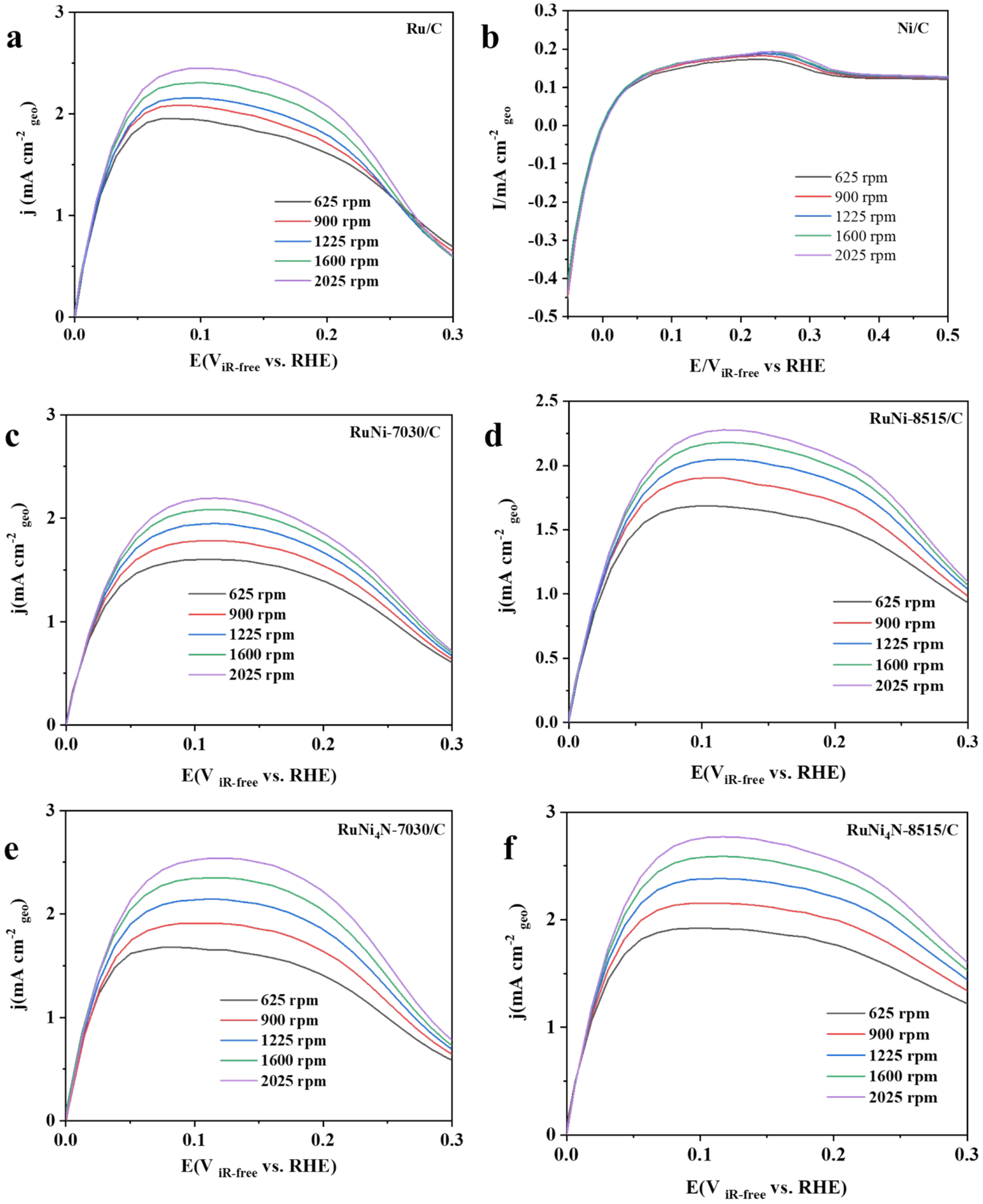

Figure S7. Linear sweep voltammetry at different rotation rates. (a) Ru/C, (b) Ni/C, (c) RuNi-7030/C, (d) RuNi-8515/C, (e) RuNi$_4$N-7030/C, and (f) RuNi$_4$N-8515/C.

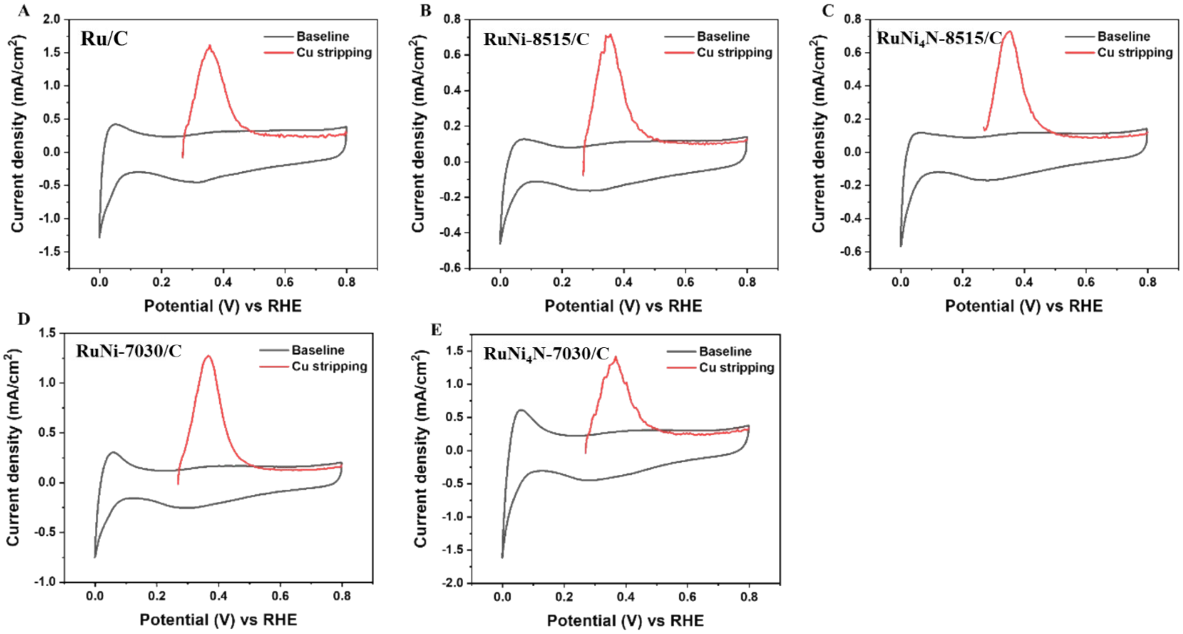

Figure S8. Cu stripping and ECSA calculations

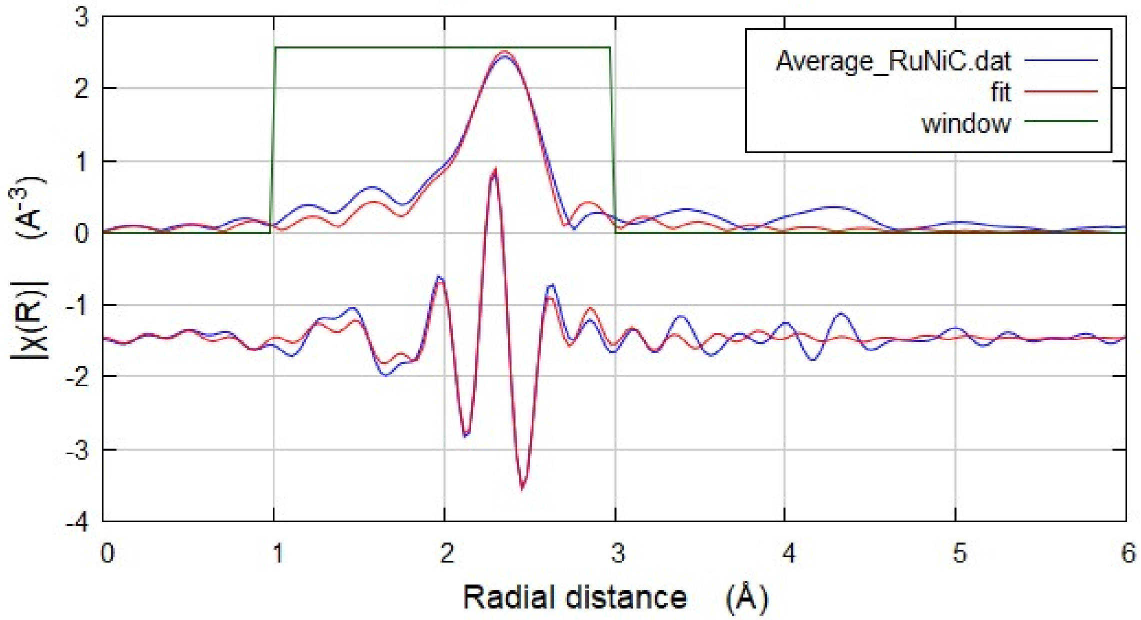

Figure S9. FT-EXAFS and fitting curves in the R space for the RuNi4N-8515/C

Table S1. Elemental compositions from HRSEM-EDX.

Sample Name	**Ni at %**	**Ru at %**
RuNi-8515	13.07	86.93
RuNi-7030	29.3	70.7
$RuNi_4N$-8515	15.7	84.3
$RuNi_4N$-7030	23.82	76.18

Table S2. Comparison table of HOR performance of the electrocatalysts (ECSA from Cu stripping, specific and mass activity from HOR activity at 0.1 V vs. RHE)

Electrocatalyst	Loadings [μg_{PGM} cm^{-2}]	ECSA [m^2 g_{metal}^{-1}]	Specific activity (mA cm^{-2} $_{ECSA}$)	Mass activity (A g^{-1})
Ru/C	20.4	225	0.20	112
RuNi-7030	16.3	121	0.30	125
RuNi-8515	18.4	109	0.30	131
$RuNi_4N$-7030	17.1	250	0.18	147
$RuNi_4N$-8515	18.4	108	0.45	156

References

1 C. P. Huang, M. C. Tsai, X. M. Wang, H. S. Cheng, Y. H. Mao, C. J. Pan, J. N. Lin, L. D. Tsai, T. S. Chan, W. N. Su and B. J. Hwang, *Catal. Sci. Technol.*, 2020, **10**, 893–903.

2 J. Liu, J. Wang, Y. Fo, B. Zhang, C. Molochas, J. Gao, W. Li, X. Cui, X. Zhou, L. Jiang and P. Tsiakaras, *Chem. Eng. J.*, 2023, **454**, 139959.

3 X. Fu, Z. Chen, S. Zhang, J. Wang, J. Ding and X. Han, *Small*, 2024, **20**, 1–7.

4 L. Han, P. Ou, W. Liu, X. Wang, H. T. Wang, R. Zhang, C. W. Pao, X. Liu, W. F. Pong, J. Song, Z. Zhuang, M. V. Mirkin, J. Luo and H. L. Xin, *Sci. Adv.*, 2022, **8**, 1–10.

5 Y. Xue, L. Shi, X. Liu, J. Fang, X. Wang, B. P. Setzler, W. Zhu, Y. Yan and Z. Zhuang, *Nat. Commun.*, 2020, **11**, 1–8.

6 X. Zhang, Z. Li, X. Sun, L. Wei, H. Niu, S. Chen, Q. Chen, C. Wang and F. Zheng, *ACS Mater. Lett.*, 2022, **4**, 2097–2105.