

Supporting Information

Microwave Initiated Facile Formation of Ni₃Se₄ Nanoassemblies for Enhanced and Stable Water Splitting in Neutral and Alkaline Media

Sengeni Anantharaj^{1,2}, Jeevarathinam Kennedy⁴ and Subrata Kundu^{1,2,3*}

¹Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Electrochemical Research Institute (CSIR-CECRI) Campus, New Delhi, India

²Electrochemical Materials Science (ECMS) Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006, Tamil Nadu, India

³Department of Materials Science and Mechanical Engineering, Texas A&M University, College Station, Texas, TX-77843, USA

⁴Central Instrumentation Facility (CIF), CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006, Tamil Nadu, India

* To whom correspondence should be addressed, *E-mail:* kundu.subrata@gmail.com; skundu@cecri.res.in, Phone: (+ 91) 4565-241486 and (+ 91) 4565-241487.

Reagents and Instruments

Selenium metal powder and sodium borohydride were procured from Sigma-Aldrich. Commercial RuO₂ catalyst was obtained from Alfa Aesar. Hg/HgO reference electrode, Pt-foil counter electrodes were purchased from CH Instruments Pvt. Ltd. Ni foam was also purchased from Sigma Aldrich and used after surface treatment (see experimental section in main text). Deionized water (18.2 MΩcm⁻²) was used for the entire nanoassemblies fabrication and electrocatalysis processes. The fabricated Ni₃Se₄ nanoassemblies was characterized with HR-TEM, (TecnaiTM G² TF20) working at an accelerating voltage of 200 kV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the FE-SEM instrument (Oxford) with a separate EDS detector connected to that instrument. The XRD analysis was done with a scanning rate of 5° min⁻¹ in the 2θ range 10-90° using a Bruker X-ray powder diffractometer (XRD) with Cu K_α radiation (λ = 0.154 nm). X-ray photoelectron spectroscopic (XPS) analysis was performed using a Theta Probe AR-XPS system (Thermo Fisher Scientific, UK). Electrochemical analyzer CHI6084c version 12.13 was used for the entire water splitting and related studies. The Ni₃Se₄ nanoassemblies grown Ni foam 3D electrode was used as working electrode.

Sample preparation for various characterizations

The fabricated Ni₃Se₄ nanoassemblies on Ni foam was directly taken for XRD and XPS analyses. TEM samples were prepared by subjecting the fabricated Ni₃Se₄ nanoassemblies to ultra-sonication for 10 min in 5 mL of Milli pore water during which the Ni₃Se₄ nanoassemblies water became blackish turbid solution. The solution was then drop casted on carbon coated copper TEM grid after dilution with appropriate amount of Milli pore water and dried at RT in dark and vacuum.

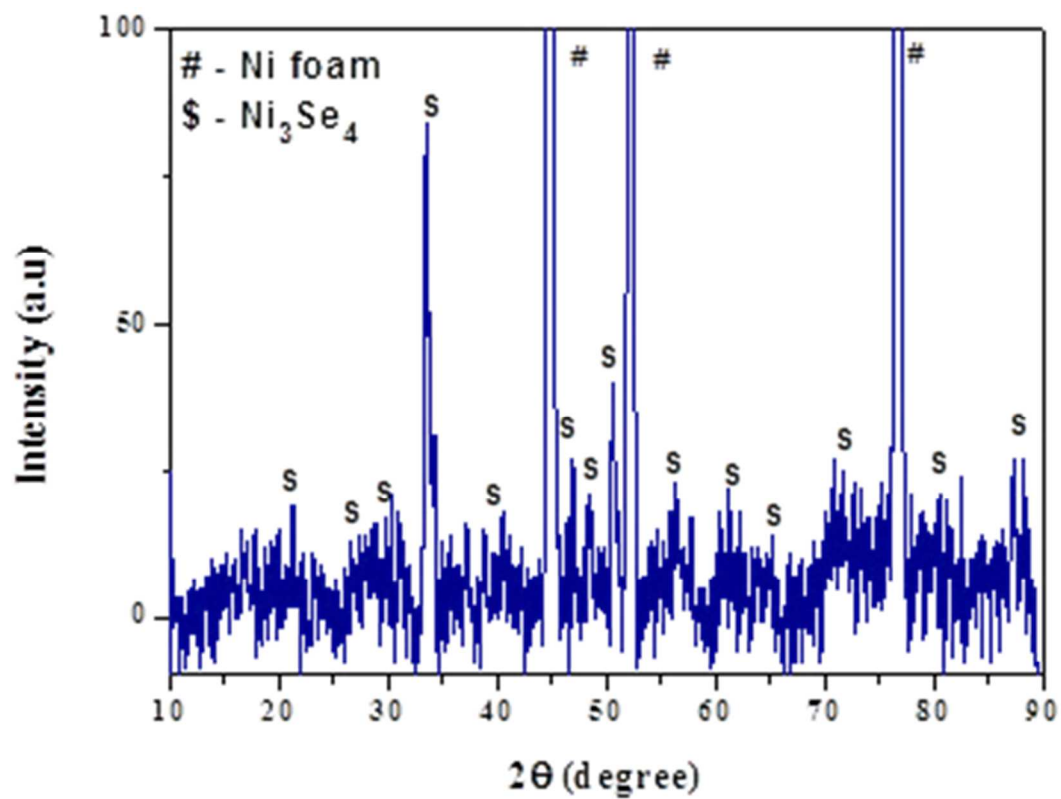


Figure S1: XRD pattern of Ni_3Se_4 nanoassemblies on Ni foam with decreased Y scale.

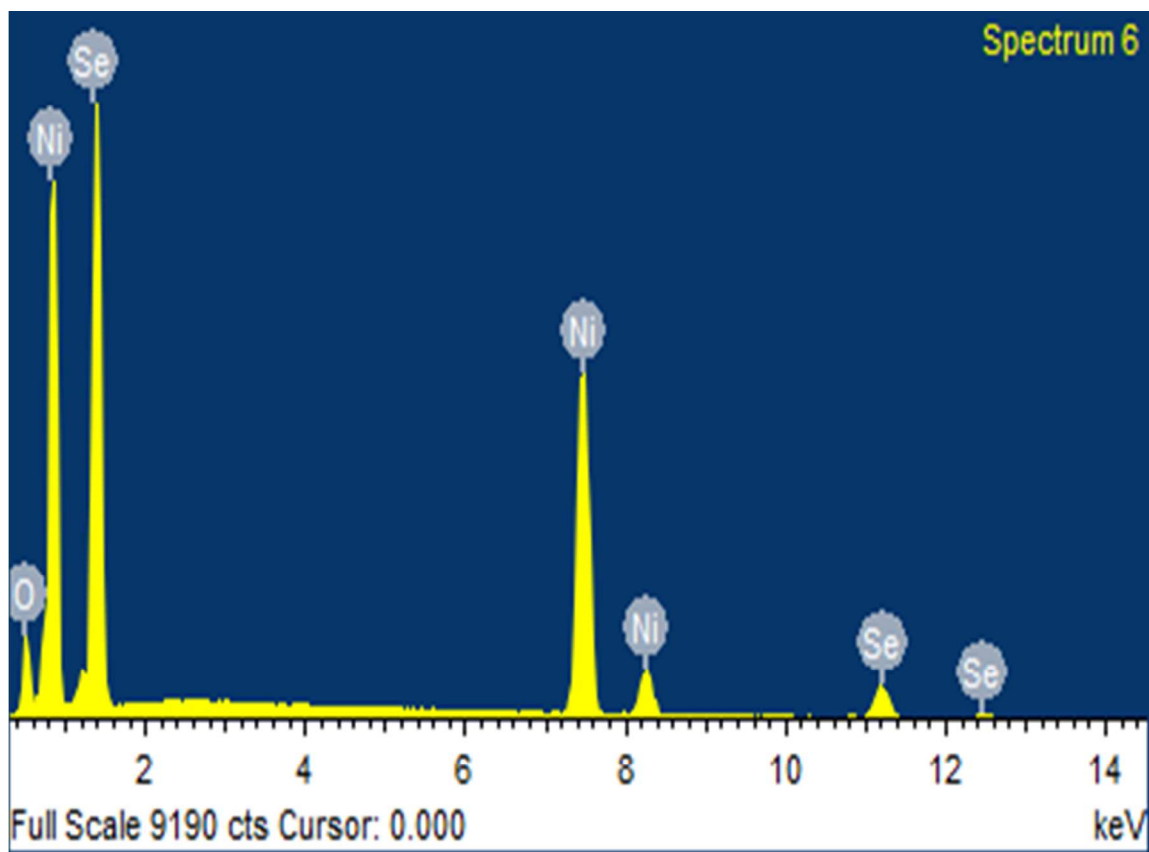


Figure S2: EDS spectrum of Ni_3Se_4 nanoassemblies on Ni foam.

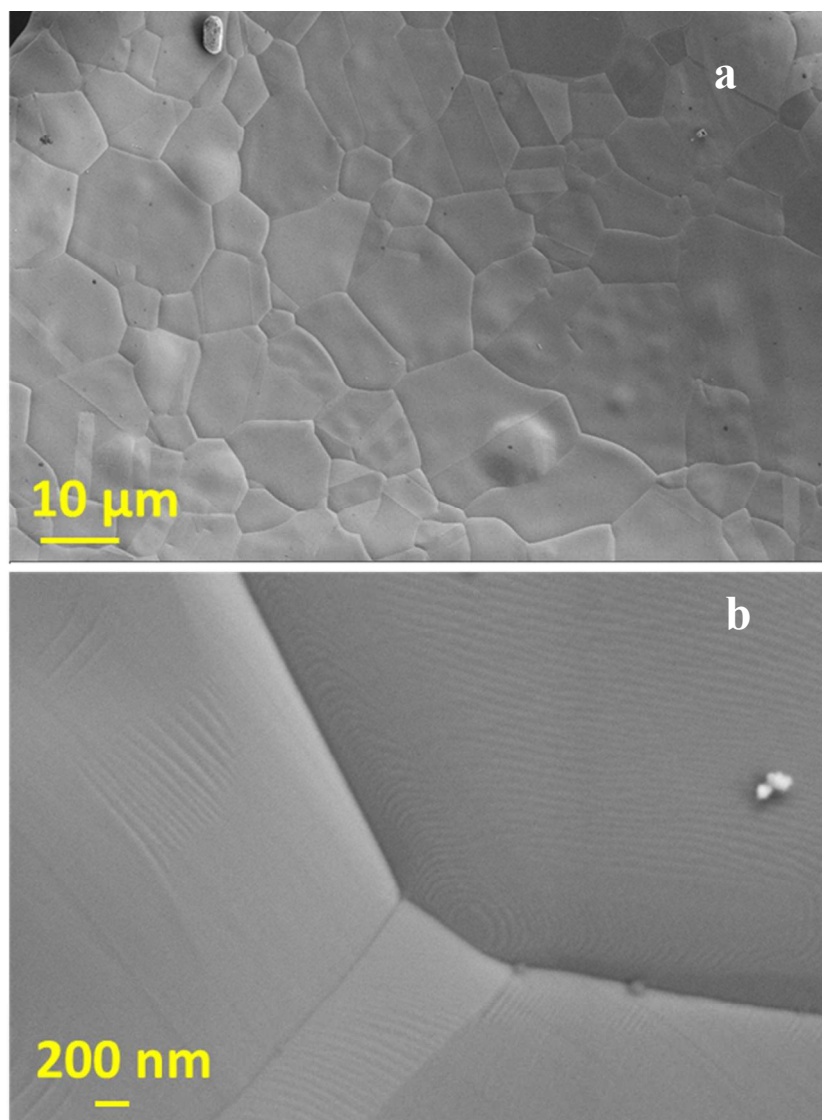


Figure S3: (a-b) FESEM micrographs of Ni foam.

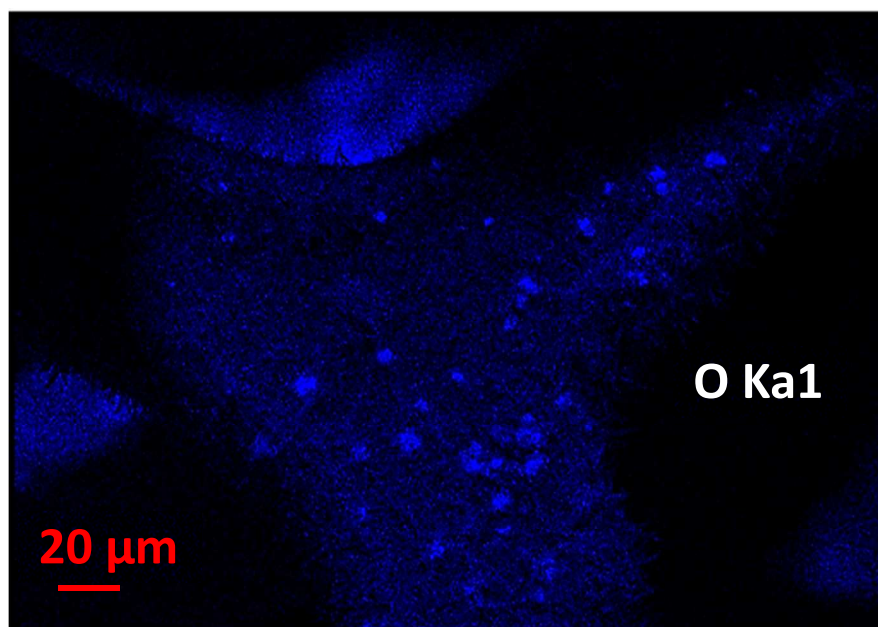


Figure S4: EDS color mapping of Ni_3Se_4 nanoassemblies on Ni foam that shows the presence of O on the surfaces.

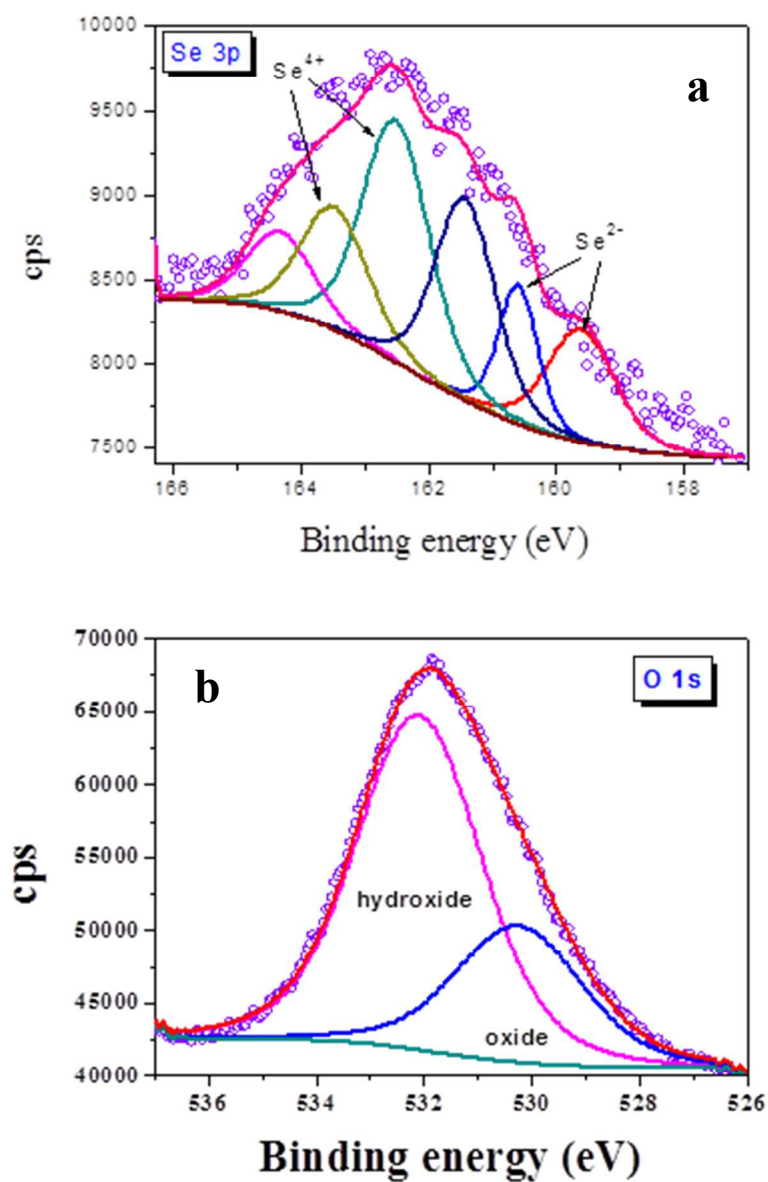


Figure S5: (a-b) XPS high resolution spectra of Se 3p and O 1s state from Ni_3Se_4 nanoassemblies on Ni foam.

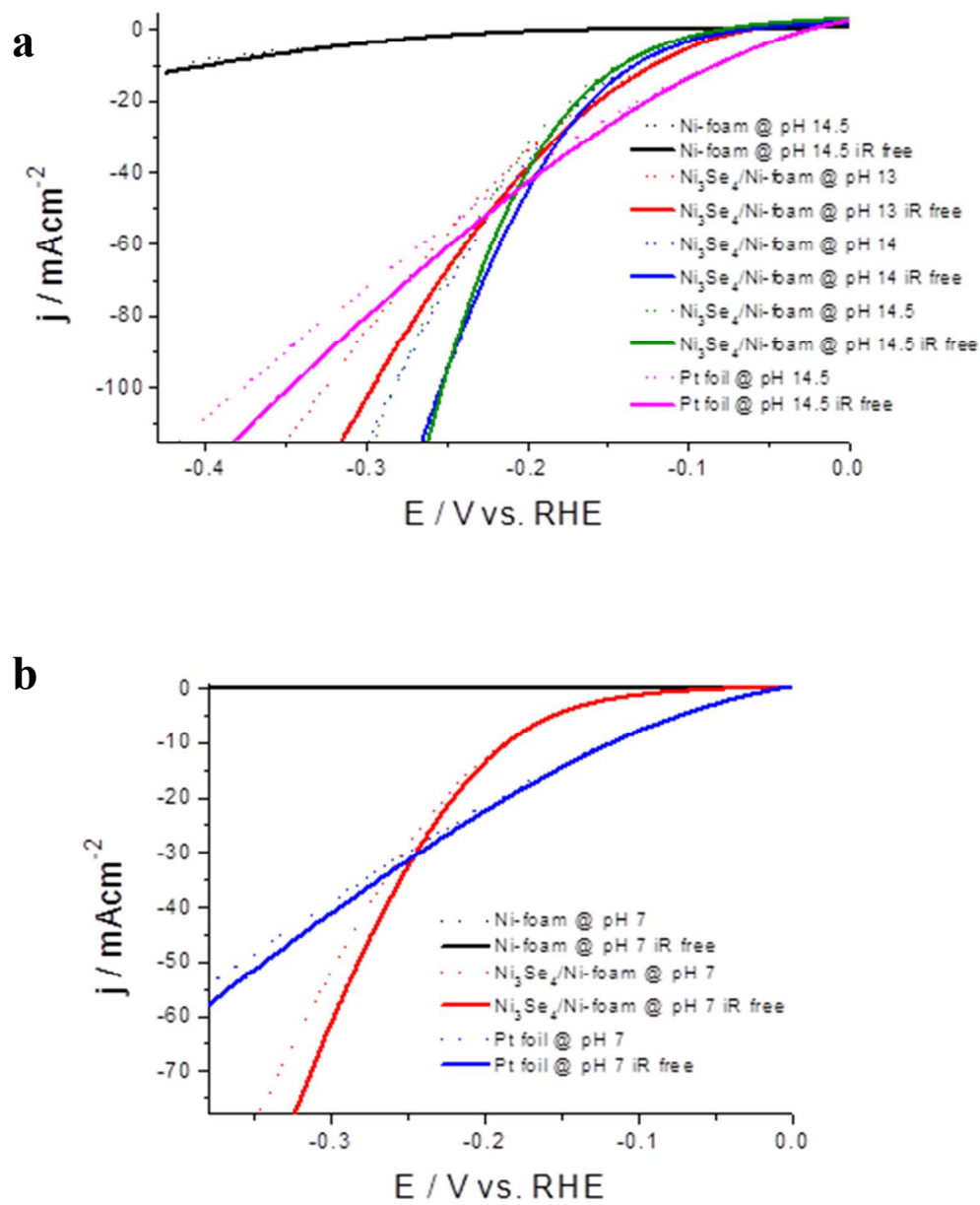


Figure S6: (a-b) the iR free and iR uncompensated HER polarization curves acquired at 5 mVs⁻¹ of $\text{Ni}_3\text{Se}_4/\text{Ni}$ in alkaline and neutral conditions in comparison with Pt.

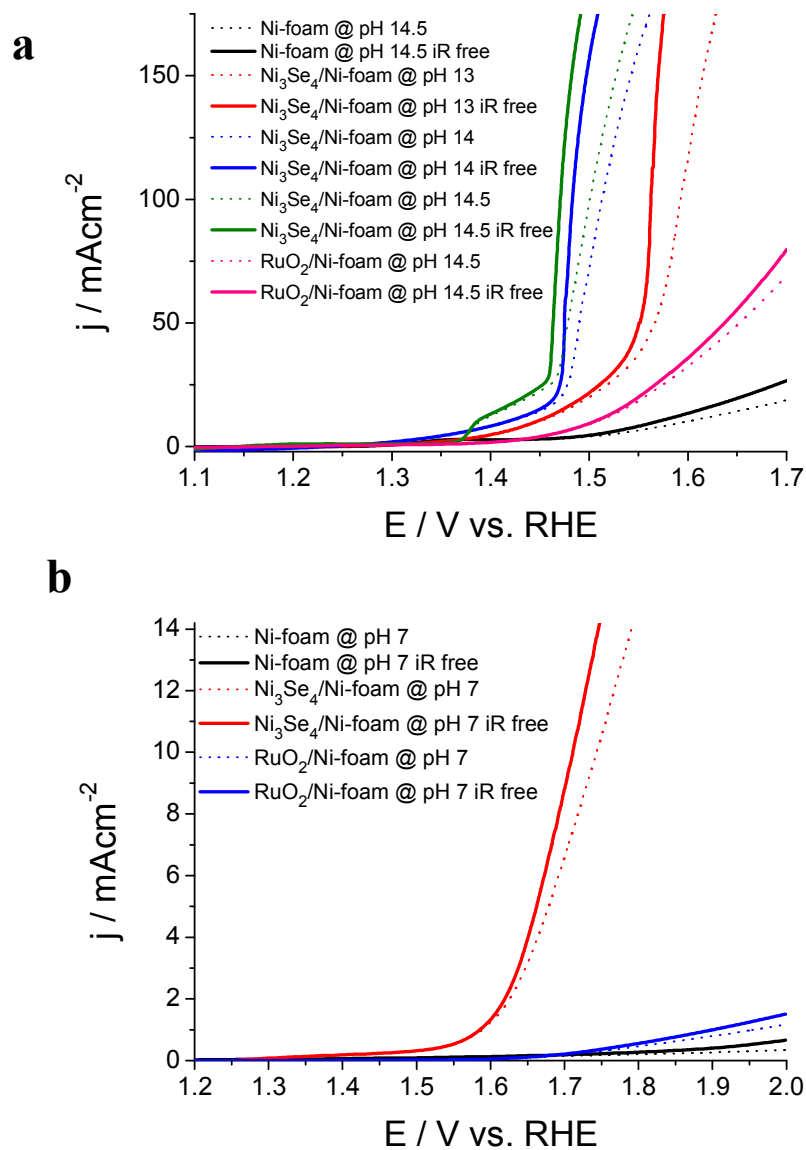


Figure S7: (a-b) the iR free and iR uncompensated OER polarization curves acquired at 5 mVs⁻¹ of $\text{Ni}_3\text{Se}_4/\text{Ni}$ in alkaline and neutral conditions in comparison with RuO_2/Ni foam.

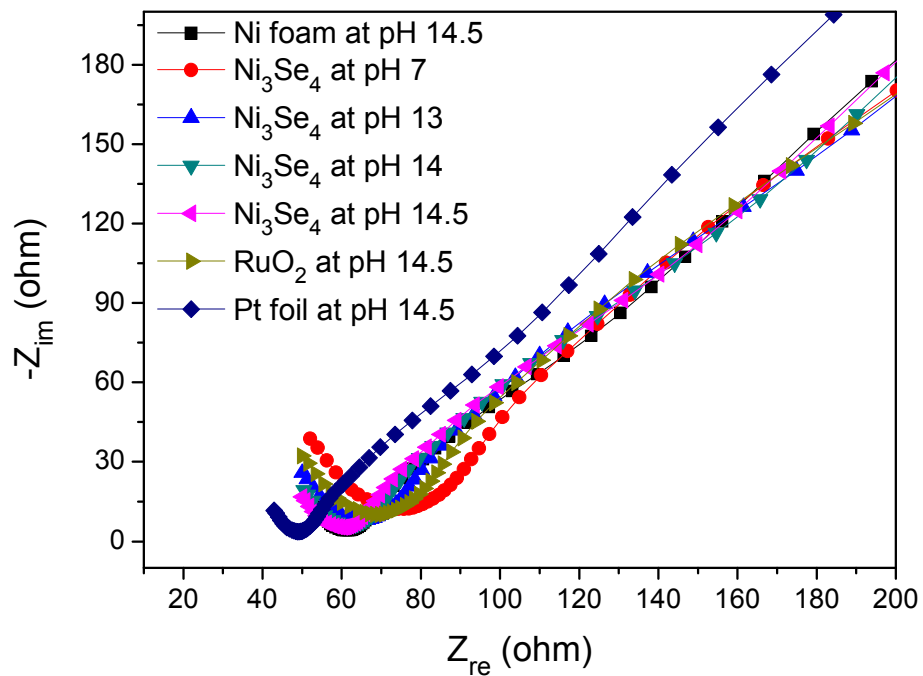


Figure S8: The Nyquist plots of $\text{Ni}_3\text{Se}_4/\text{Ni}$, RuO_2/Ni foam and Pt foil electrode interfaces in alkaline and neutral conditions.

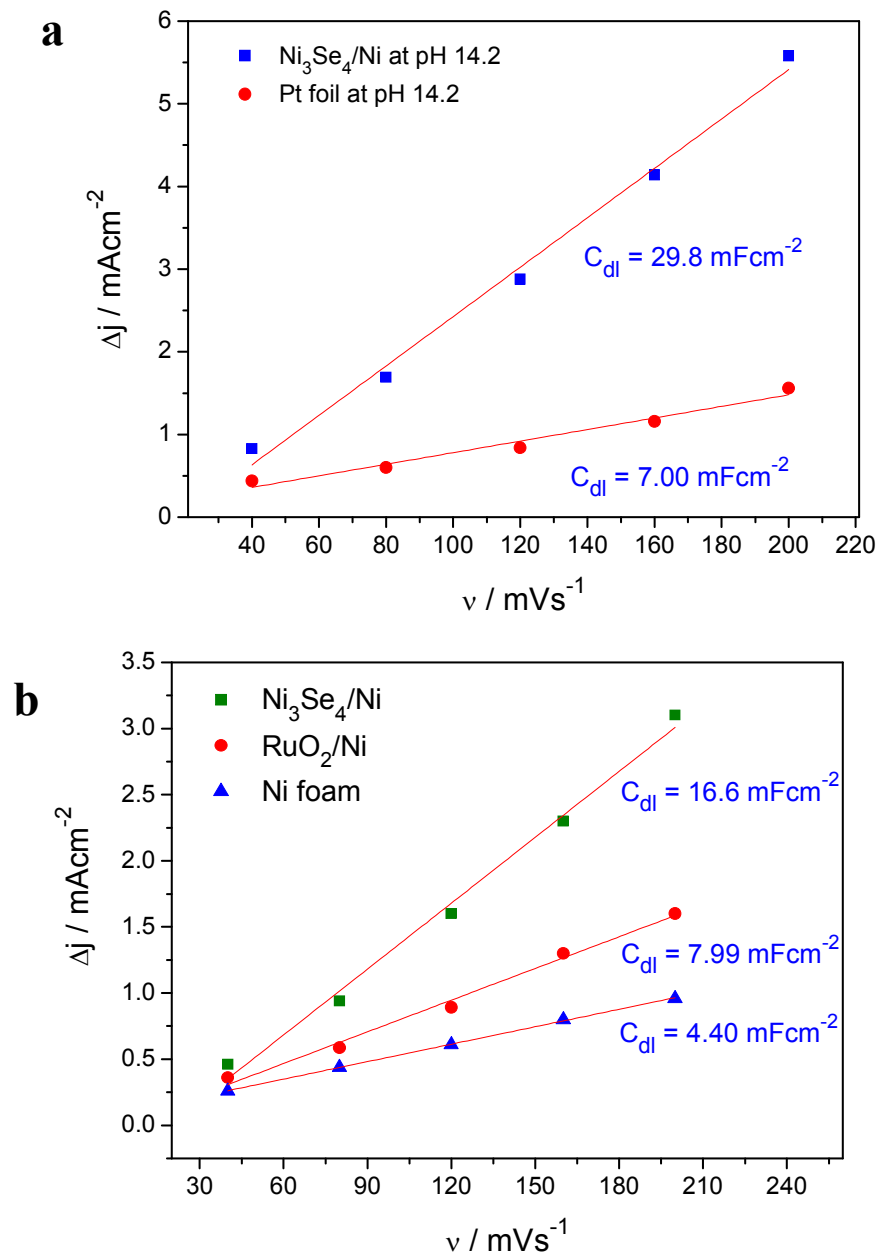


Figure S9: (a-b) The plot of the difference in double layer charging currents vs. scan rate at 0.12 V vs. RHE and 1.12 V vs. RHE respectively.

Region	Catalyst	2Cdl (mFcm ⁻²)	Relative active area (cm ²)
(1.12 V vs. RHE)	Ni ₃ Se ₄ /Ni	16.6	3.772
	RuO ₂ /Ni	7.99	1.815
	Ni foam	4.40	1
(0.15 V vs. RHE)	Ni ₃ Se ₄ /Ni	29.8	4.257
	Pt foil	7.00	1

Table S1: The double layer charging currents and the corresponding relative ECSA of Ni₃Se₄/Ni, RuO₂/Ni and Pt foil electrodes.

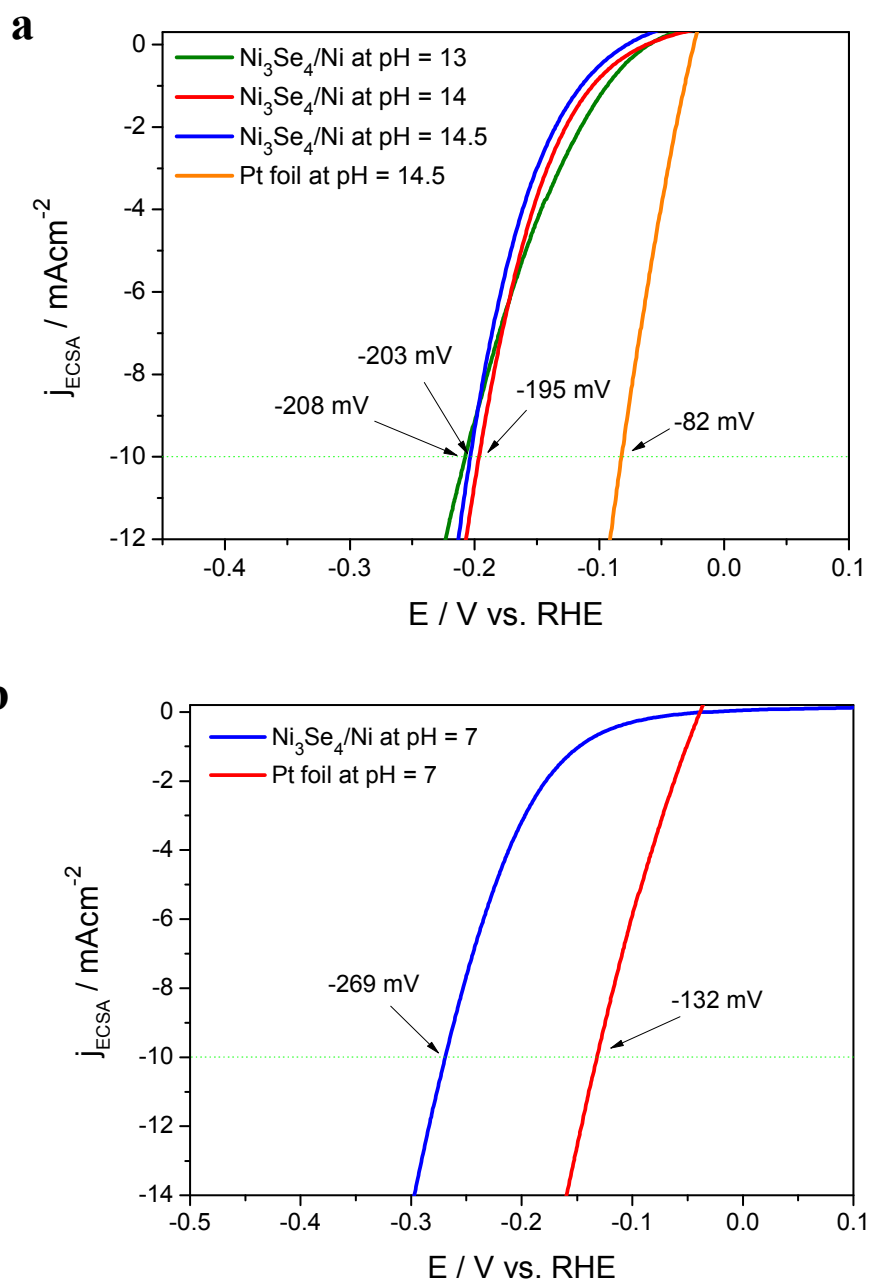


Figure S10: (a-b) The ECSA normalized HER polarization curves of $\text{Ni}_3\text{Se}_4/\text{Ni}$ and Pt in alkaline and neutral electrolytes.

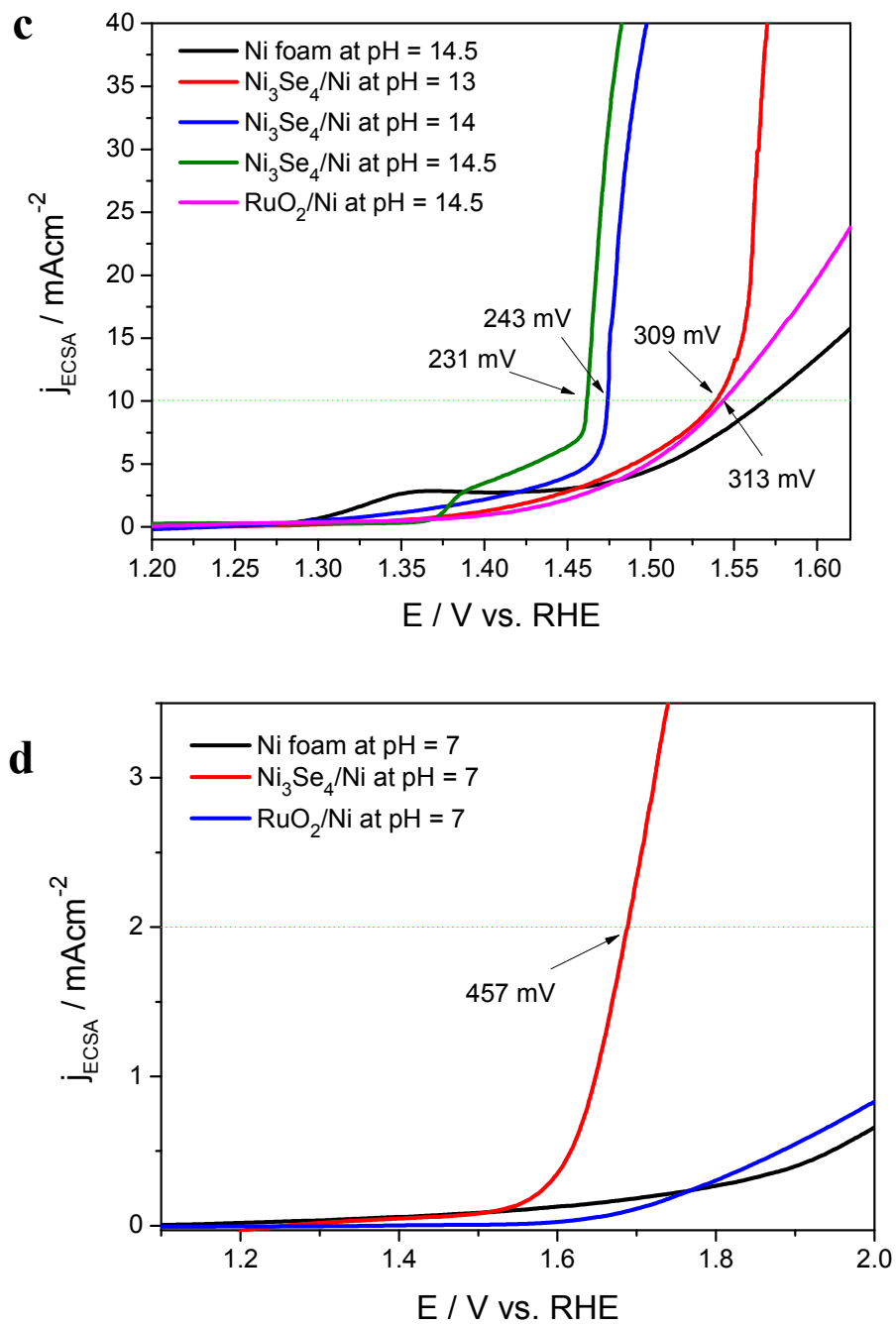


Figure S10: (c-d) The ECSA normalized OER polarization curves of $\text{Ni}_3\text{Se}_4/\text{Ni}$ and RuO_2/Ni in alkaline and neutral electrolytes.



Figure S11: A snapshot taken the during operation of two electrode water electrolyser that consists the Ni_3Se_4 nanoassemblies on Ni foam as both anode and cathode while powered with an AAA alkaline battery of optimum voltage output of 1.5 V.

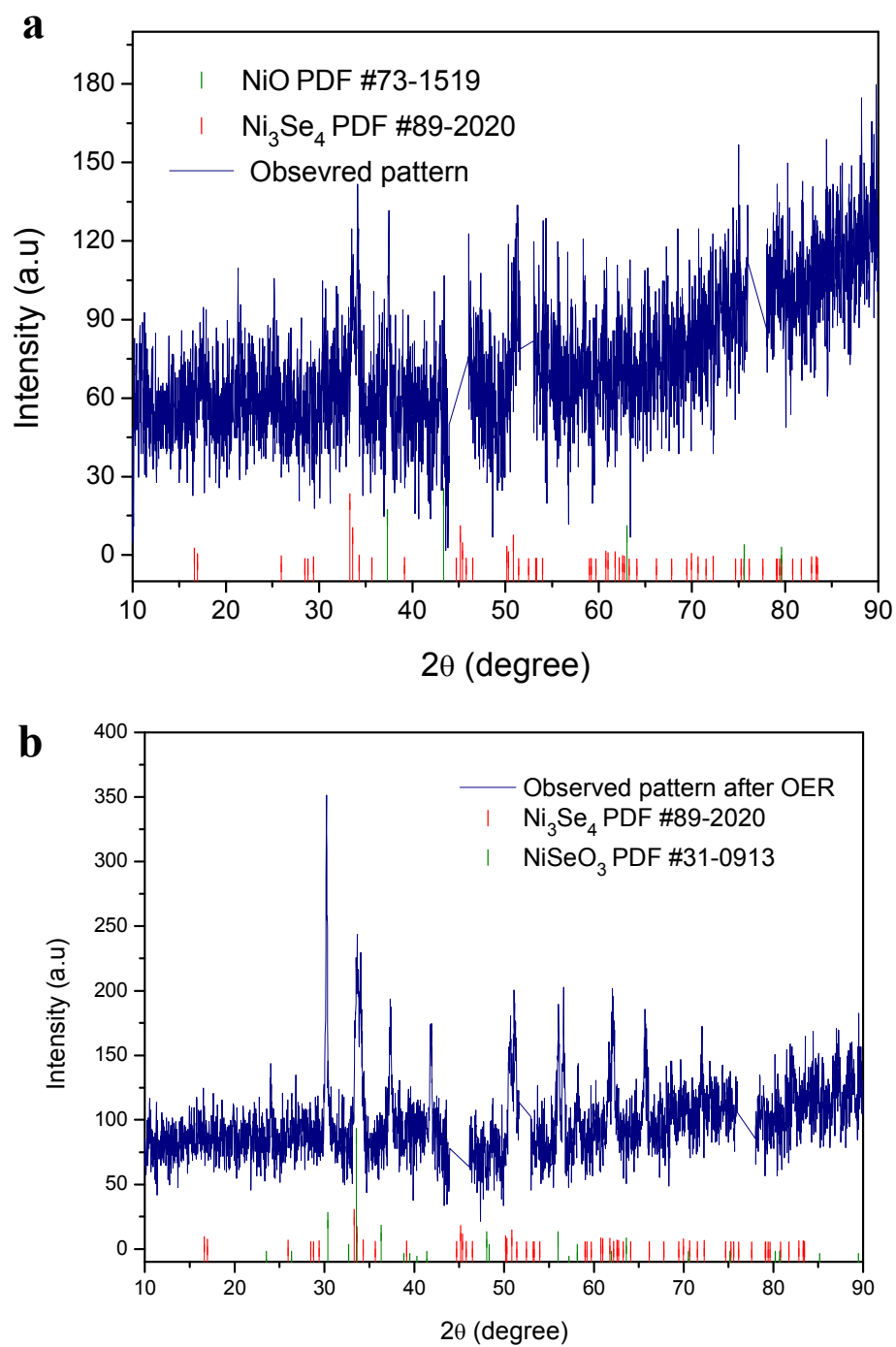


Figure S12: (a-b) XRD patterns of Ni₃Se₄/Ni after cathodic and anodic polarizations.

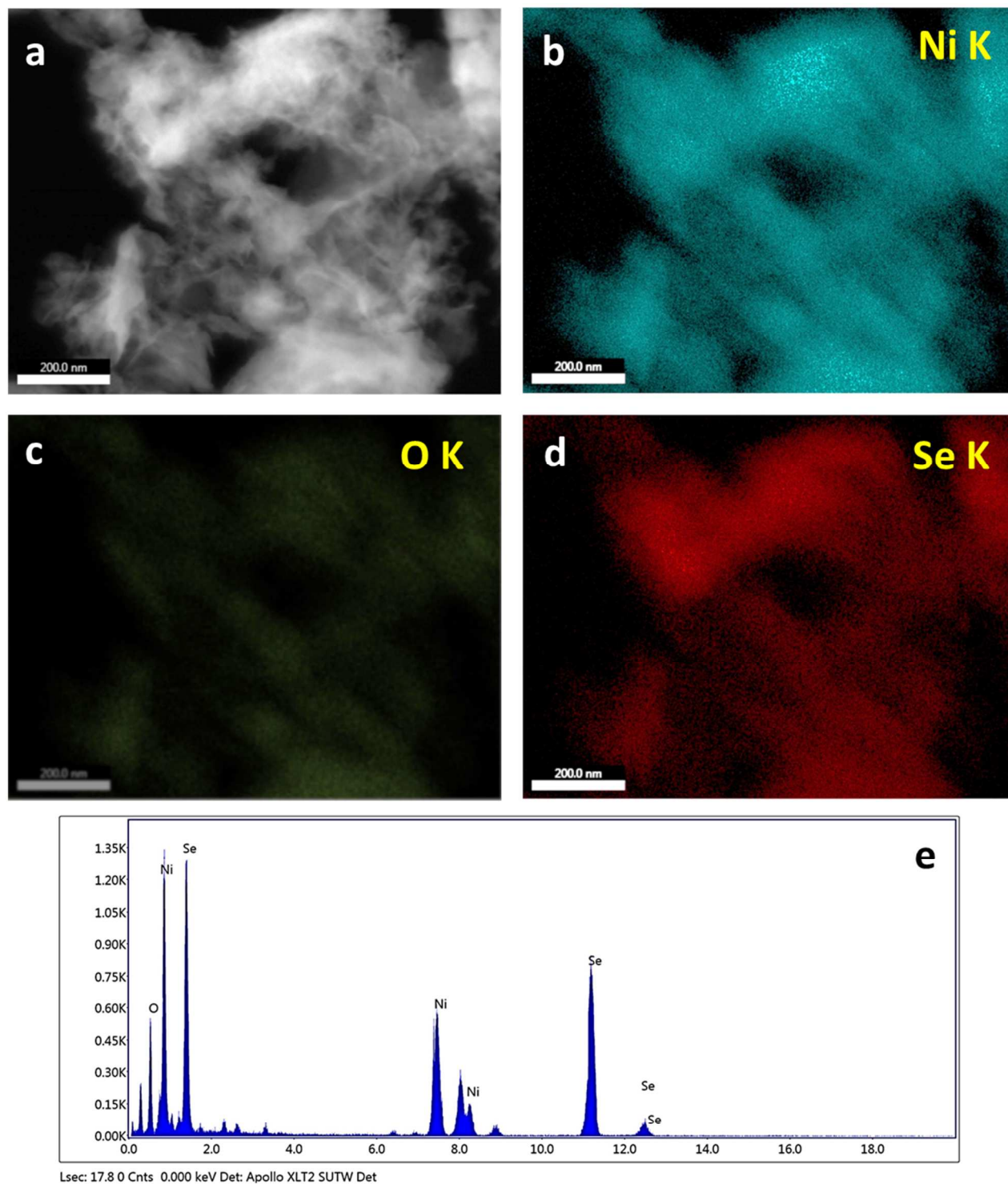


Figure S13: (a) HAADF micrograph of Ni_3Se_4 after OER characterizations that shows the area chosen for the elemental mapping. (b-d) color maps of Ni K, O K and Se K respectively in EDAX mode. (e) the corresponding EDAX spectrum.

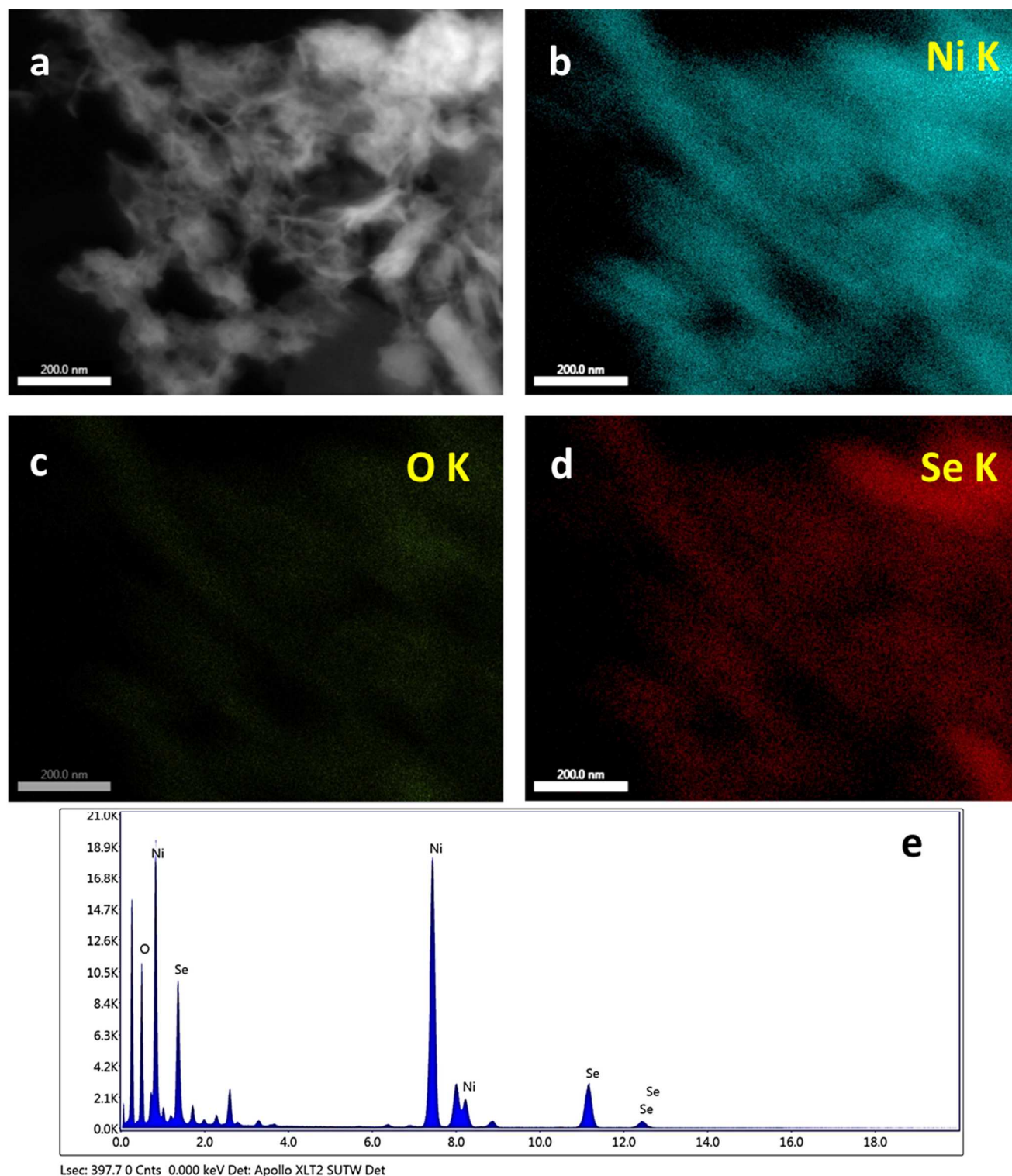


Figure S14: (a) HAADF micrograph of Ni_3Se_4 after HER characterizations that shows the area chosen for the elemental mapping. (b-d) color maps of Ni K, O K and Se K respectively in EDAX mode. (e) the corresponding EDAX spectrum.