Supporting Information

Mechanochemical Synthesis of Novel Rutile-Type High Entropy Fluorides for Electrocatalysis

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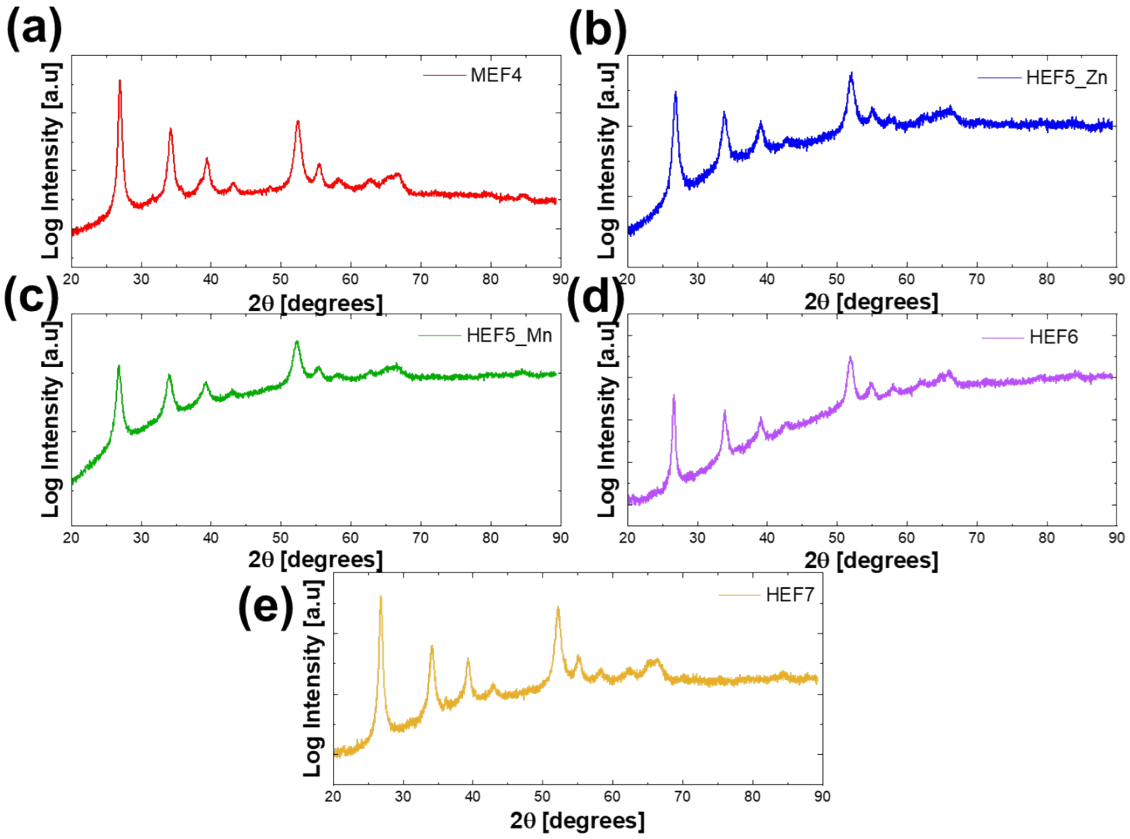

Figure S1. a) to e) XRD patterns of MEF and HEF based nanoparticles (MEF4, HEF5_Zn, HEF5_Mn, HEF6 and HEF7 respectively) in logarithmic intensity scale. The goodness of fit, Rp and Rwp values are detailed in **Table S3**. In general, all the samples predominantly show the rutile structure.

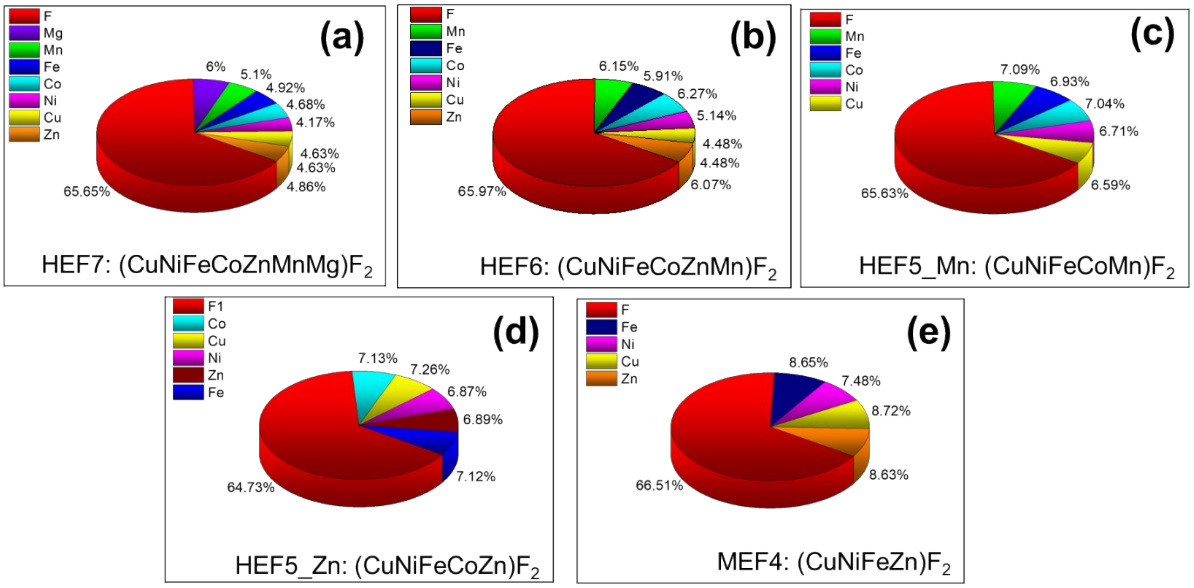

Figure S2. a) to **e)** Inductively coupled plasma-optical emission spectroscopy (ICP-OES) results of HEF based compounds with variant transition metal cations incorporation (MEF4, HEF5_Zn, HEF5_Mn, HEF6 and HEF7). All values are expressed in atomic %.

Configurational entropy values were calculated based on the following equation (S1)

$$S_{config} = -R\left[\left\{\sum_{i=1}^{N} x_i \ln x_i\right\}_{cation-site} + \left\{\sum_{j=1}^{M} x_j \ln x_j\right\}_{anion-site}\right] \quad \text{(S1)}$$

(where x_i,R, N and M are the mole fraction of the elements in cationic or anionic sites, Universal gas constant, number of cationic and anionic species respectively)

Table S1. Configurational entropy values (S_{config}) of the synthesized HEF

Fluoride type	**Compound**	**S_{config} value**
MEF4	$(Cu_{1/4}Ni_{1/4}Fe_{1/4}Zn_{1/4})F_2$	1.39R
HEF5_Zn	$(Cu_{1/5}Ni_{1/5}Fe_{1/5}Co_{1/5}Zn_{1/5})F_2$	1.61R
HEF5_Mn	$(Cu_{1/5}Ni_{1/5}Fe_{1/5}Co_{1/5}Mn_{1/5})F_2$	1.61R
HEF6	$(Cu_{1/6}Ni_{1/6}Fe_{1/6}Co_{1/6}Zn_{1/6}Mn_{1/6})F_2$	1.79R
HEF7	$(Cu_{1/7}Ni_{1/7}Fe_{1/7}Co_{1/7}Zn_{1/7}Mn_{1/7}Mg_{1/7})F_2$	1.95R

For every ion, the ionic radius in octahedral coordination (rutile) was taken. For calculating the average ionic radius of the incorporated ions, the ionic radii were simply added and then divided by the number of elements. e.g. Zn^{2+} / Ni^{2+} = (0.89Å + 0.84 Å)/2 = 0.87 Å. Hence for the case of MEF4, the average ionic radii (values in parenthesis indicate the metal ion) = [0.89 (Zn^{2+}) + 0.84 (Ni^{2+})+ 0.91 (Fe^{2+})+ 0.87 (Cu^{2+})]/4 = 0.88 Å.

Table S2. Crystal structure, lattice constants and expected cation radius of the precursor binary fluorides assuming octahedral coordination.

Binary Fluorides	**Crystal structure**	**Lattice constant (Å)**	**Ionic radius (Å)**	**References**
CuF_2	Monoclinic	a=3.2973; b=4.5624; c=4.6157	0.87	ICSD#71833
NiF_2	Rutile	a= b=4.6498 c=3.0838	0.84	ICSD#9168
FeF_2	Rutile	a= b=4.6945; c=3.3097	0.91(H)	ICSD#9166
CoF_2	Rutile	a= b=4.6941; c=3.1698	0.88 (H)	ICSD#9167
ZnF_2	Rutile	a= b=4.7048; c=3.1338	0.89	ICSD#9169
MnF_2	Rutile	a= b=4.877; c=3.311	0.96 (H)	ICSD#9165
MgF_2	Rutile	a= b=4.621; c=3.0519	0.86	ICSD#397
HEF7	Rutile	a= b=4.7134; c=3.1726	-	Calculated (TOPAS)

*H = high spin, adapted from[1]

Table S3. Refined structural parameters a, b, c, and V for MEF and HEF compounds from Rietveld analysis. The quality of refinements Rwp, Rp and GOF are also listed. Rietveld analysis was carried out using reference reflexes from ZnF_2 (ICSD#9169) thereby modifying the type of elements present in refined system and it indicated that all HEF samples possess rutile structure. This finding signified that the complex HEF system followed ideal rule of mixing, wherein equal probability of occupation was found in a random solid solution environment.

Parameters	HEF7	HEF6	HEF5_Mn	HEF5_Zn	MEF4
***a* [Å]**	4.71342	4.7288	4.6826	4.7173	4.6911
***b* [Å]**	4.71342	4.7288	4.6826	4.7173	4.6911
***c* [Å]**	3.17260	3.1823	3.1708	3.2089	3.1699
***V* [Å^3]**	70.4834	71.1571	69.5261	71.4082	69.7580
Rwp	0.78	1.10	0.73	0.79	1.19
Rp	0.73	0.87	0.63	0.63	0.92
GOF	1.25	1.23	1.14	1.14	1.59

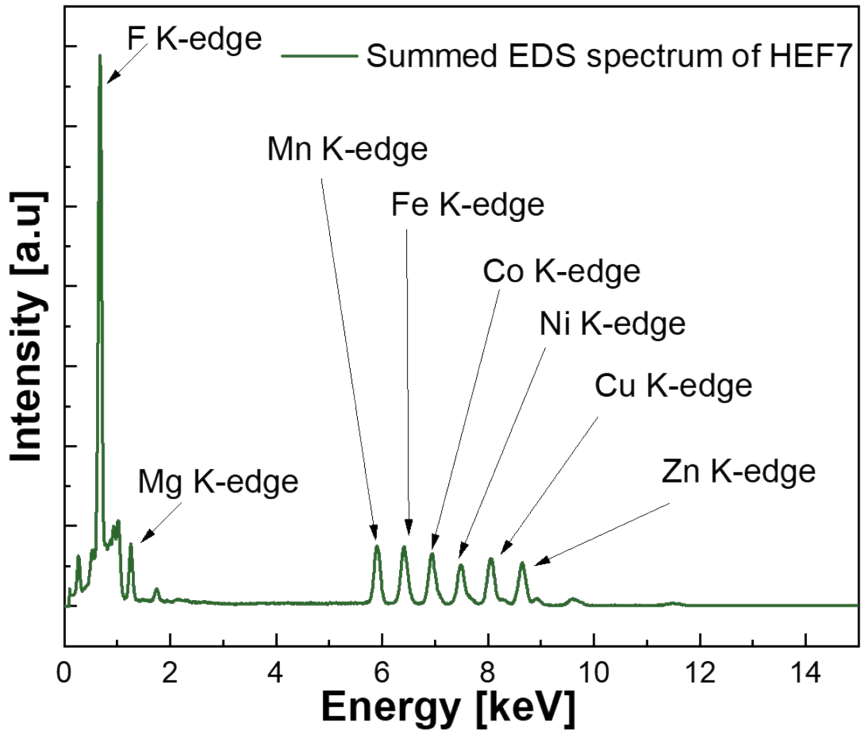

Figure S3. STEM based EDS spectrum of the as-prepared HEF7 sample. All the constituent elements in HEF7 sample are detected.

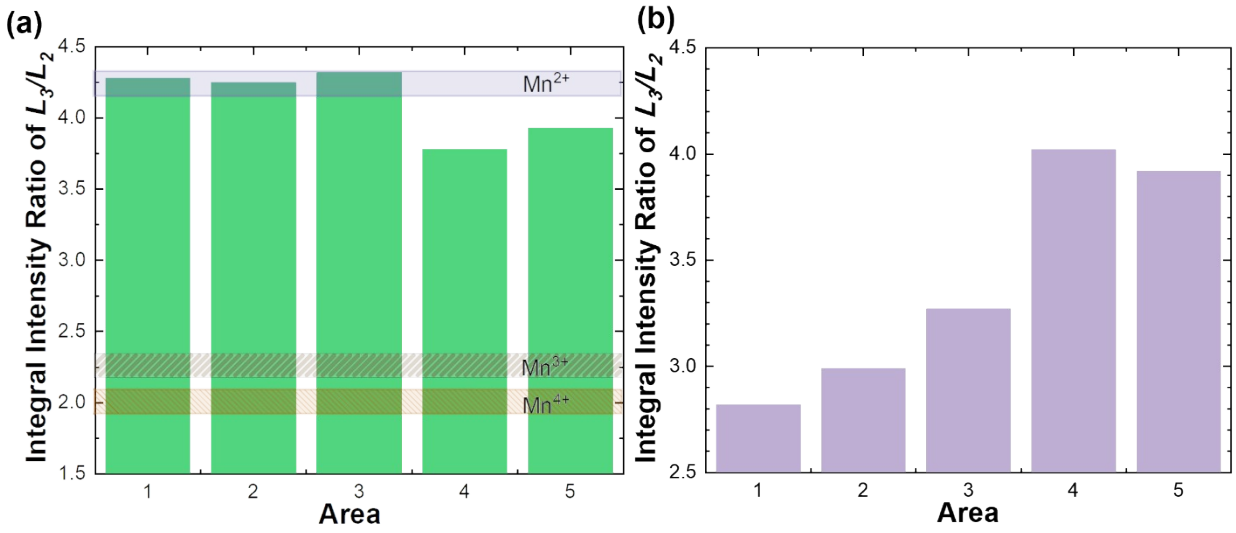

Figure S4. Plots of the intensity ratios of L_3/L_2 values of **a)** Mn (values in green colour) and **b)** Fe (values in purple colour) calculated from the spectra obtained from HEF7 nanoparticleas a function of the areal mapping values acquired at different points.

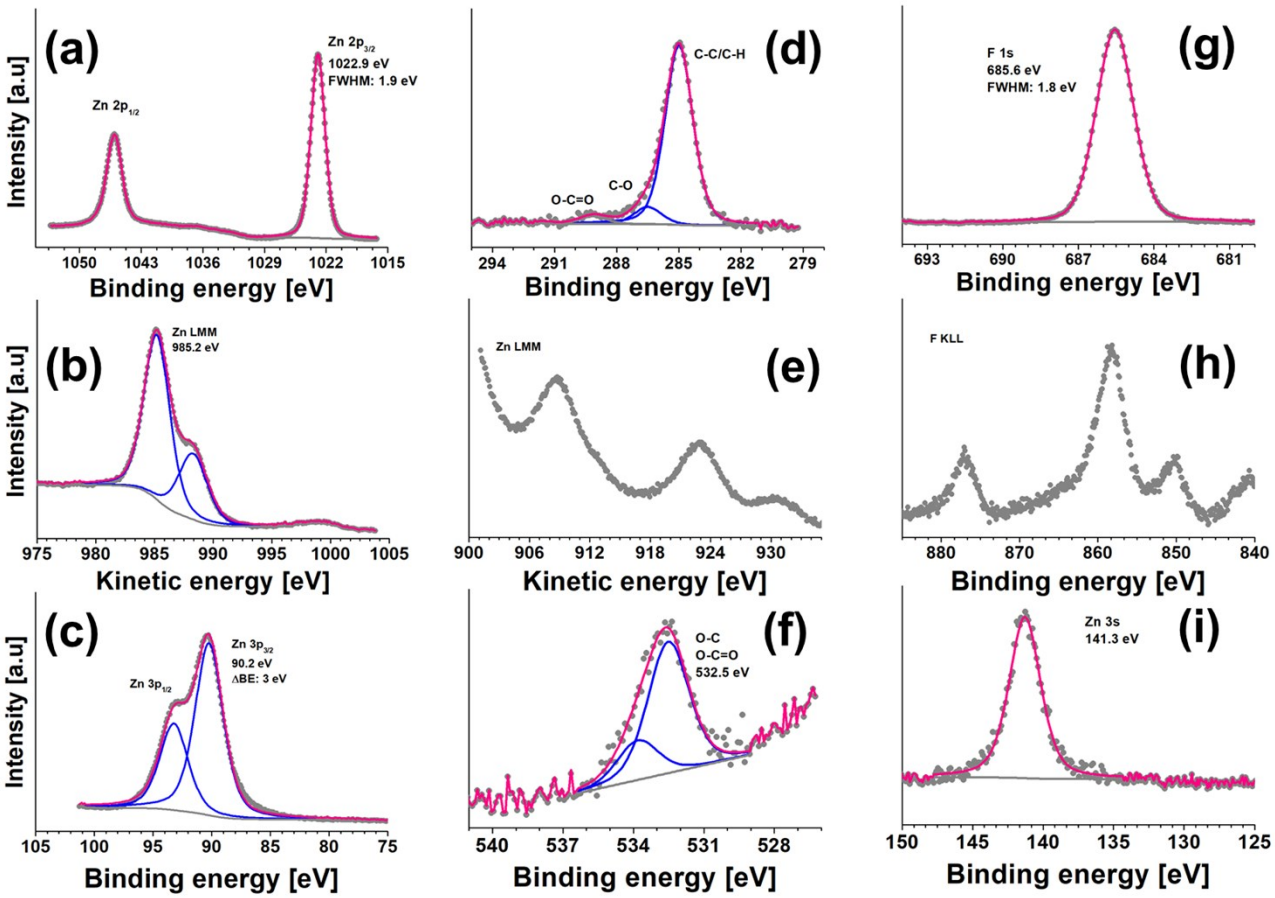

Figure S5. a) Zn 2p, **b)** Zn LMM, **c)** Zn 3p, **d)** C 1s, **e)** Zn LMM, **f)** O 1s, **g)** F 1s, **h)** F KLL, and **i)** Zn 3s XPS spectra of ZnF_2 powder.

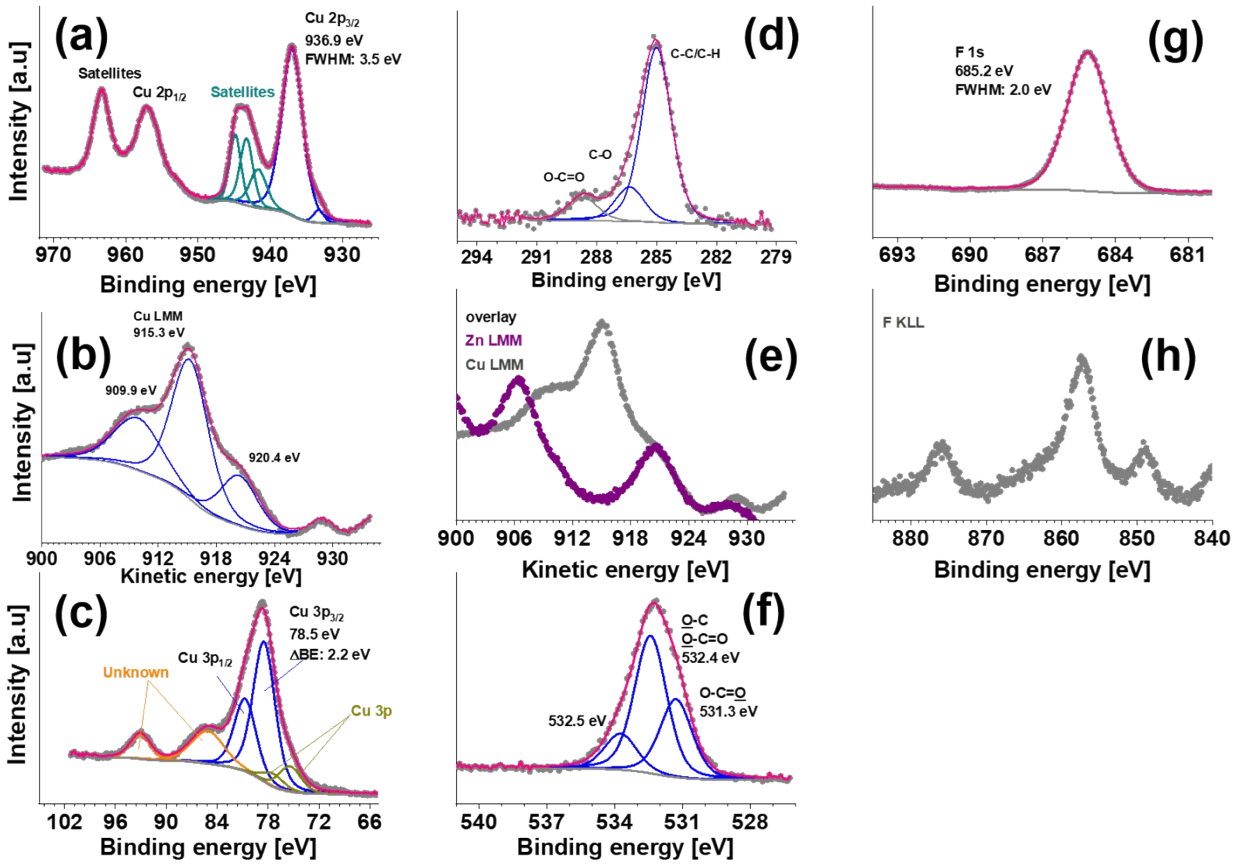

Figure S6. a) Cu 2p, **b)** Cu Auger LMM kinetic energy spectra, **c)** Cu 3p, **d)** C 1s, **e)** overlay plot of Zn LMM and Cu LMM kinetic energy spectra **f)** O 1s **g)** F 1s and **h)** F KLL, XPS spectra of CuF_2 powder (In pure CuF_2 powder, the Cu $2p_{3/2}$ spectrum has a pronounced peak at 936.9 eV with FWHM of 3.5 eV).

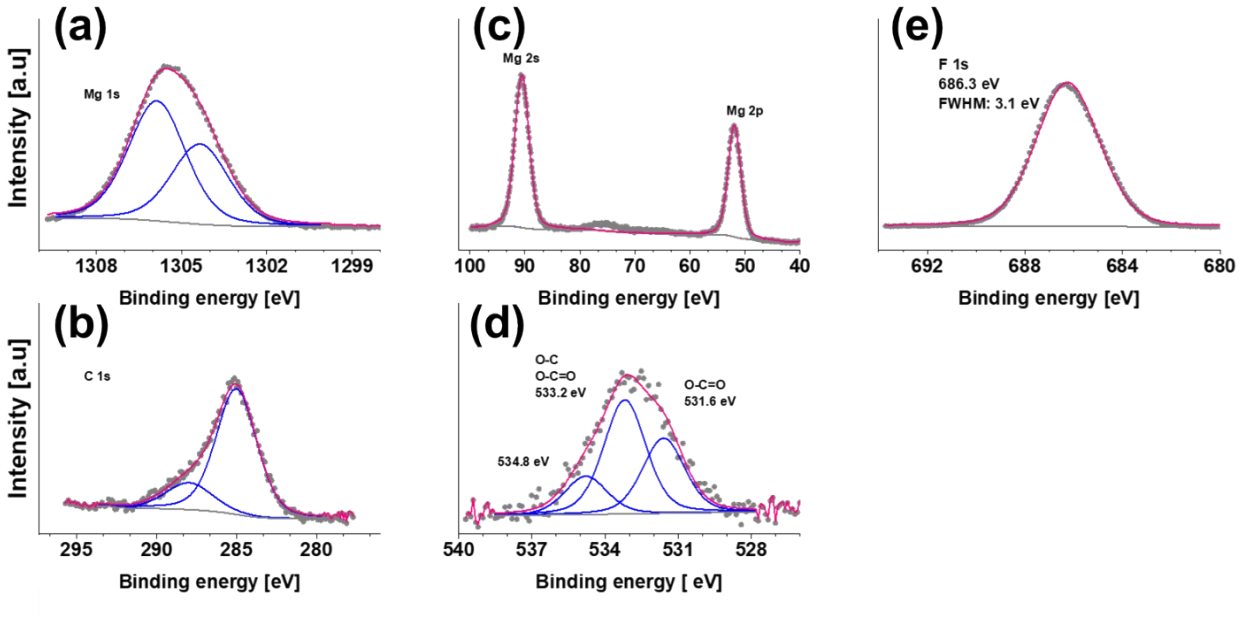

Figure S7. a) Mg 1s, **b)** C 1s, **c)** Mg 2p, Mg 2s, **d)** O 1s and **e)** F 1s, spectra of MgF_2. The broadening of C 1s and Mg 1s spectra is because of difficulties of charge compensation.

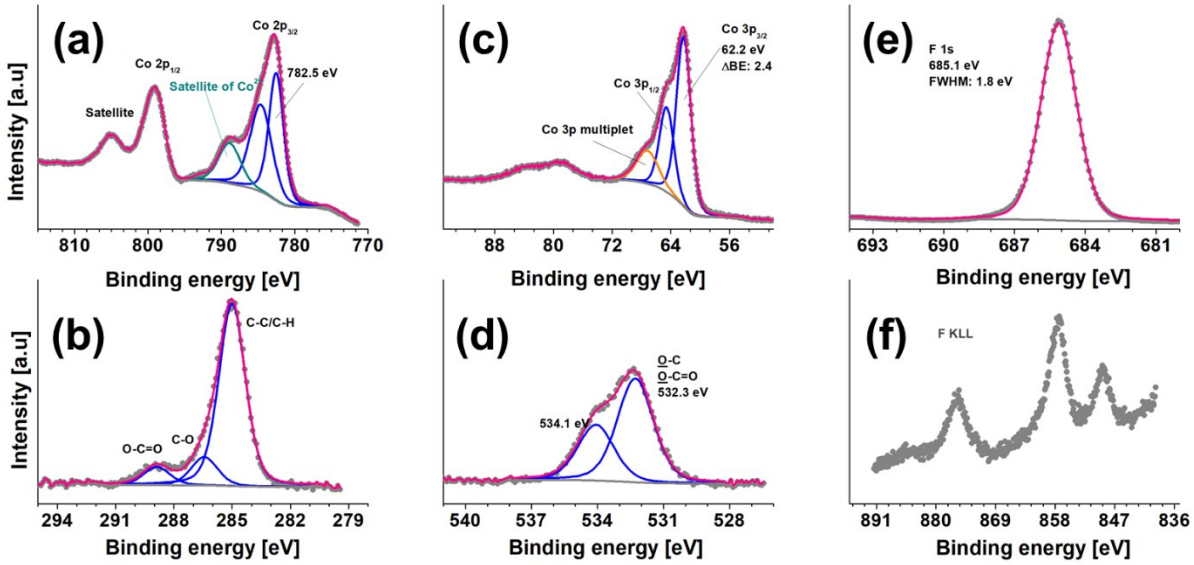

Figure S8. a) Co 2p, **b)** C 1s, **c)** Co 3p, **d)** O 1s **e)** F 1s, and **f)** F KLL XPS spectra of CoF_2 powder.

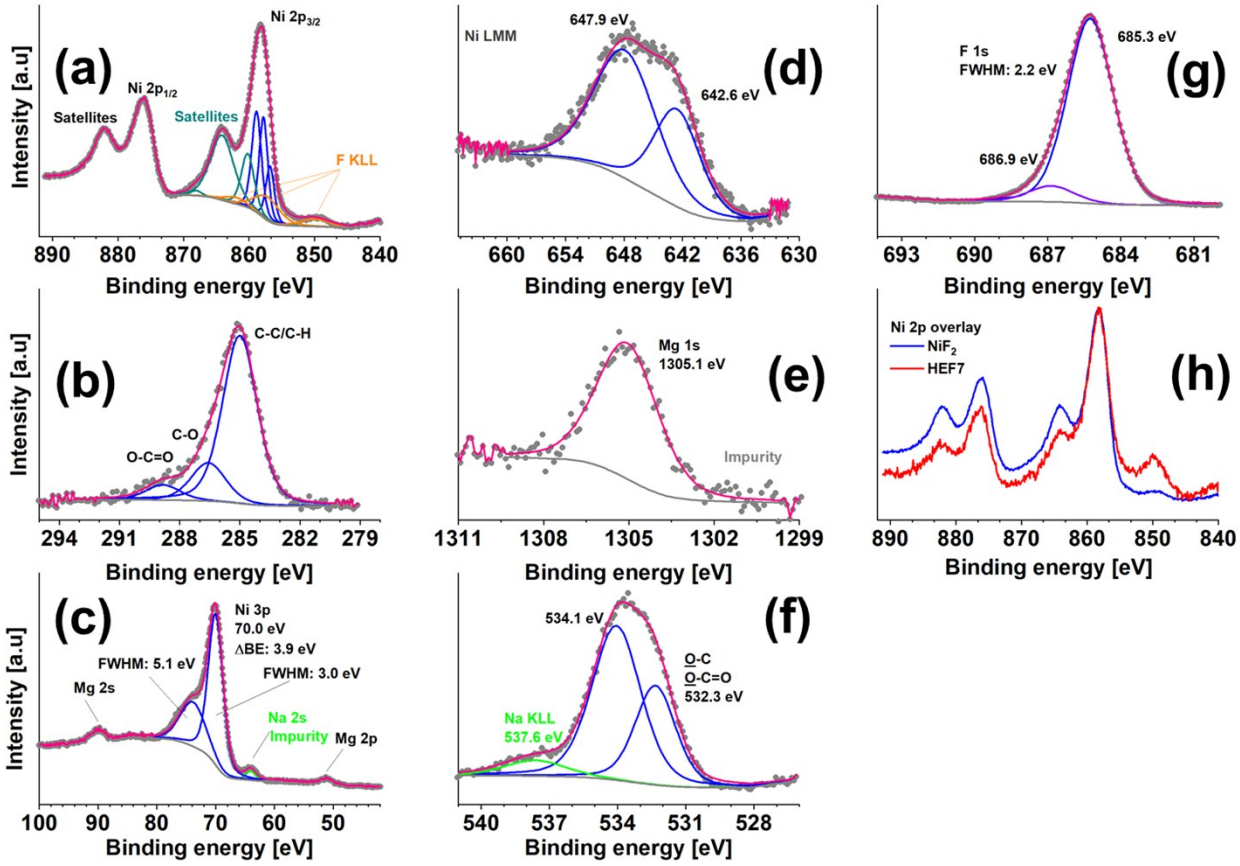

Figure S9. a) Ni 2p, **b)** C 1s, **c)** Ni 3p (Mg 1s, Na 2s as impurity), **d)** Ni LMM, **e)** Mg 1s, **f)** O 1s, **g)** F 1s XPS spectra of NiF_2 powder and **h)** overlay data of NiF_2 power (with HEF7)

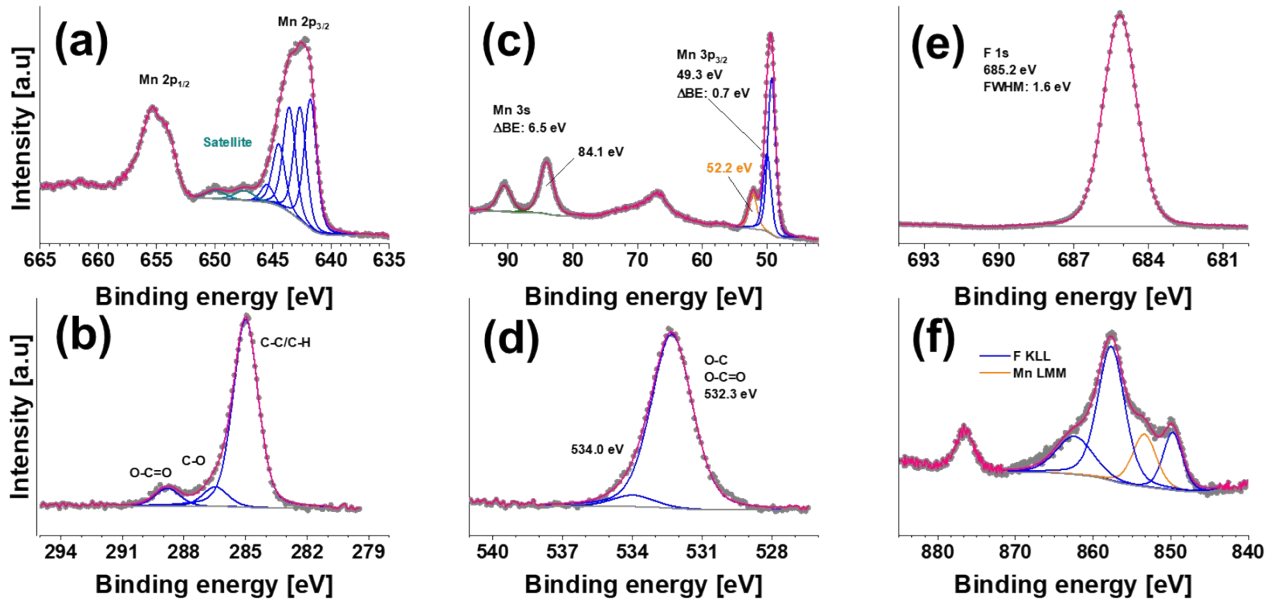

Figure S10. a) Mn 2p, **b)** C 1s **c)** Mn 3p, Mn 3s, **d)** O 1s **e)** F 1s and **f)** F KLL XPS spectra of MnF_2 powder.

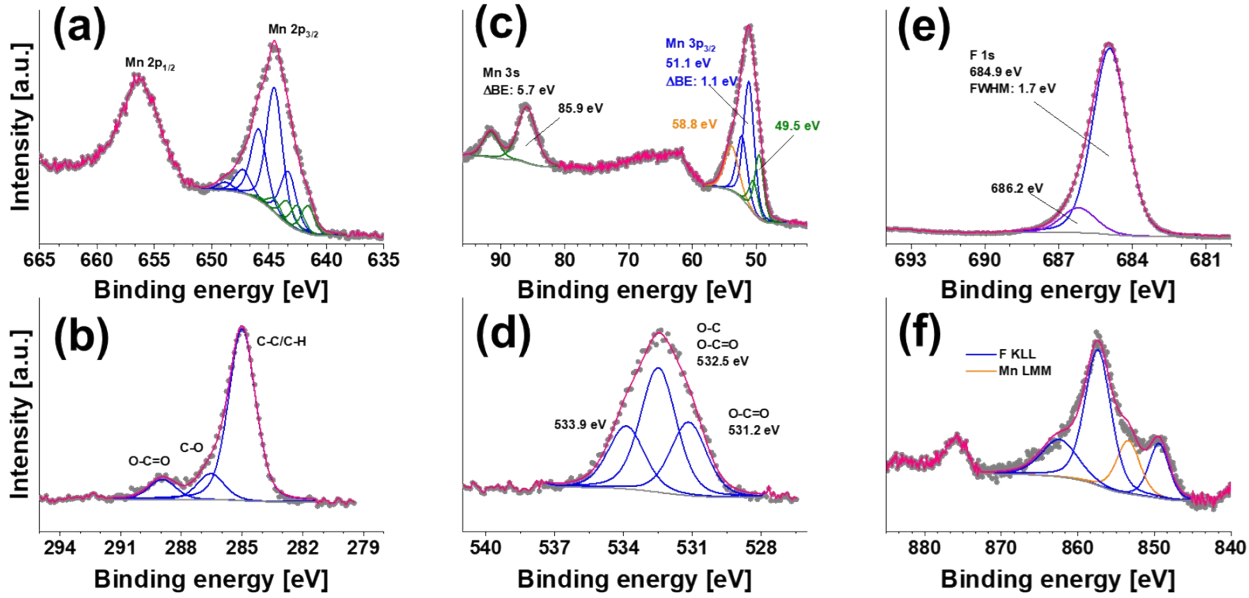

Figure S11. a) Mn 2p, **b)** C 1s **c)** Mn 3p, Mn 3s, **d)** O 1s **e)** F 1s and **f)** F KLL XPS spectra of MnF_3 powder.

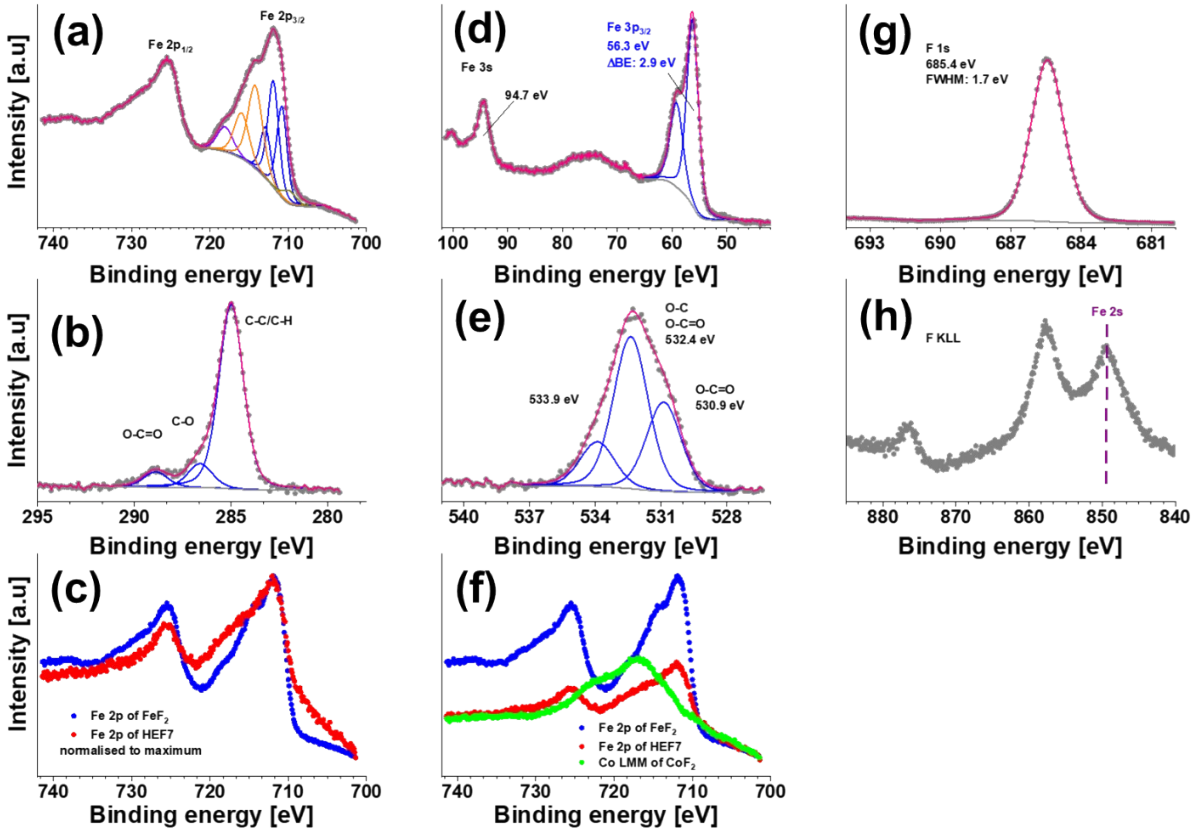

Figure S12. a) Fe 2p, **b)** C 1s, **c)** overlay comparison of FeF_2, HEF7 **d)** Fe 3p, Fe 3s **e)** O 1s, **f)** overlay comparison of FeF_2, HEF7, Co LMM of CoF_2 , **g)** F 1s and **h)** F KLL XPS spectra of FeF_2 powder.

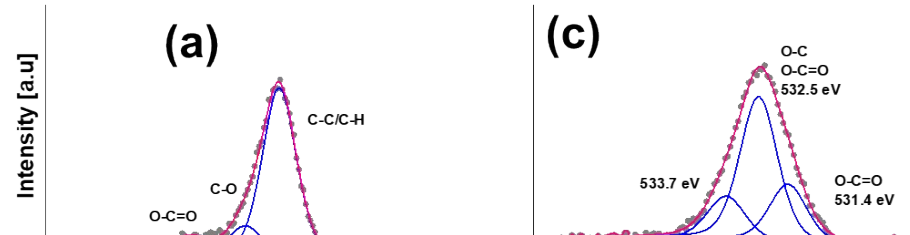

Figure S13. a) C 1s, **b)** overlapping spectra hamper evaluation of Mn 3p and Mn 3s for elucidation of Mn oxidation state **c)** O 1s and **d)** Cu LMM XPS spectra of HEF7 nanoparticles.

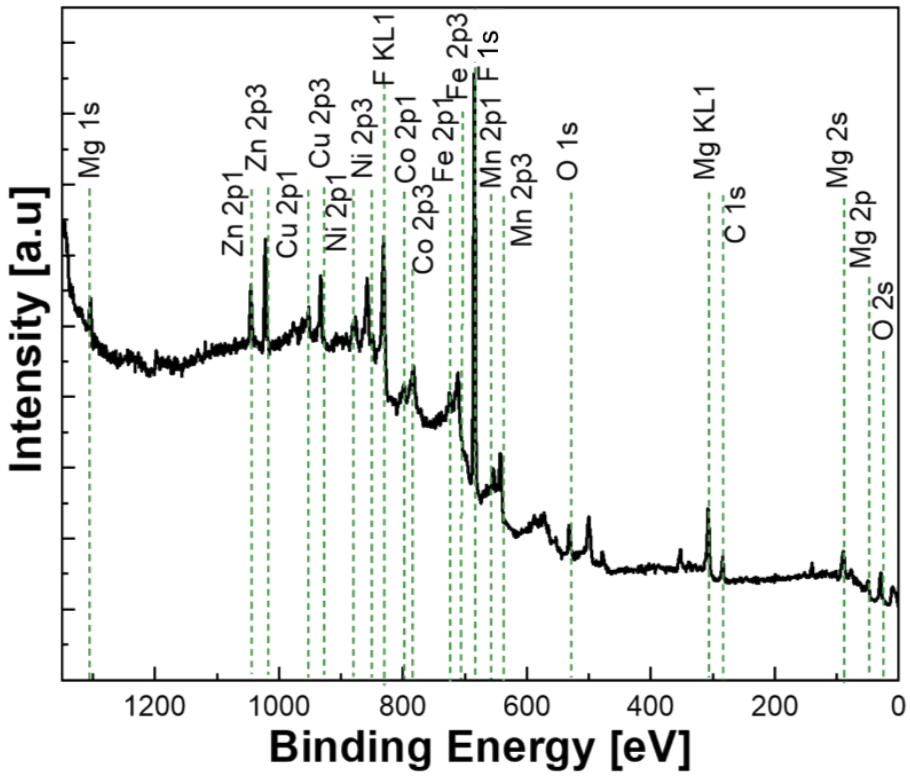

Figure S14. Survey scan spectrum of HEF7 nanoparticles.

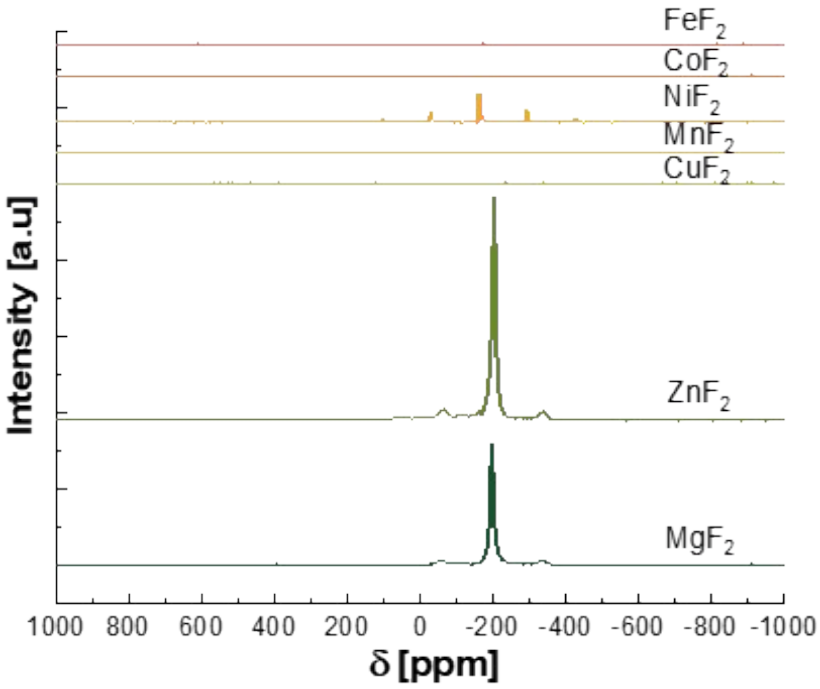

Figure S15. ^{19}F-NMR spectra of the reference binary fluorides used as the precursors for HEF based materials synthesis.

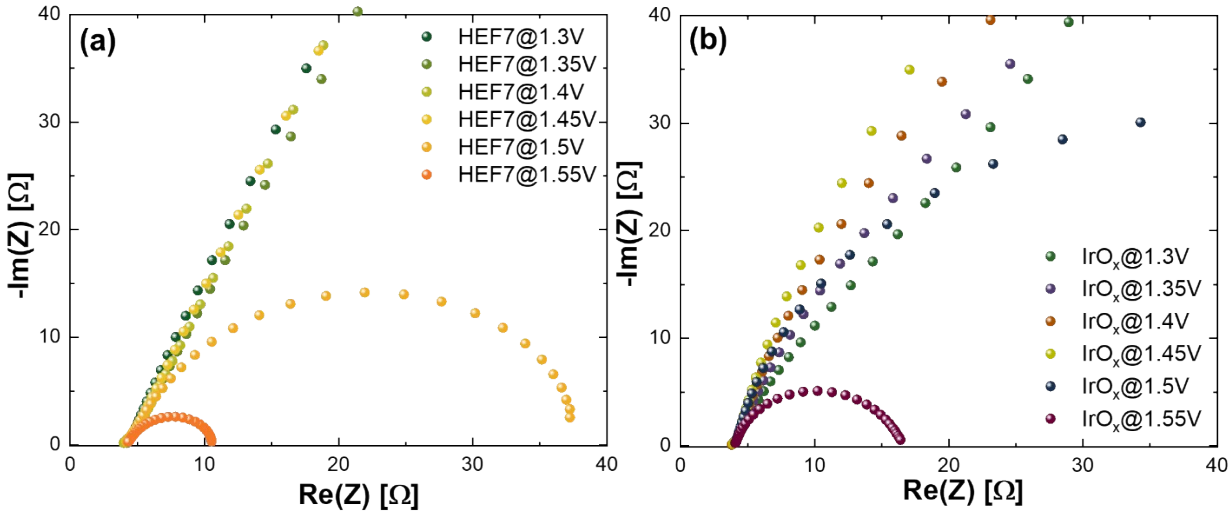

Figure S16. Nyquist plots of **a)** HEF7 and **b)** IrO_2 respectively in 1 M KOH. The EIS response was measured at different applied potentials from 1.3 V to 1.55 V to probe the electrochemical processes.

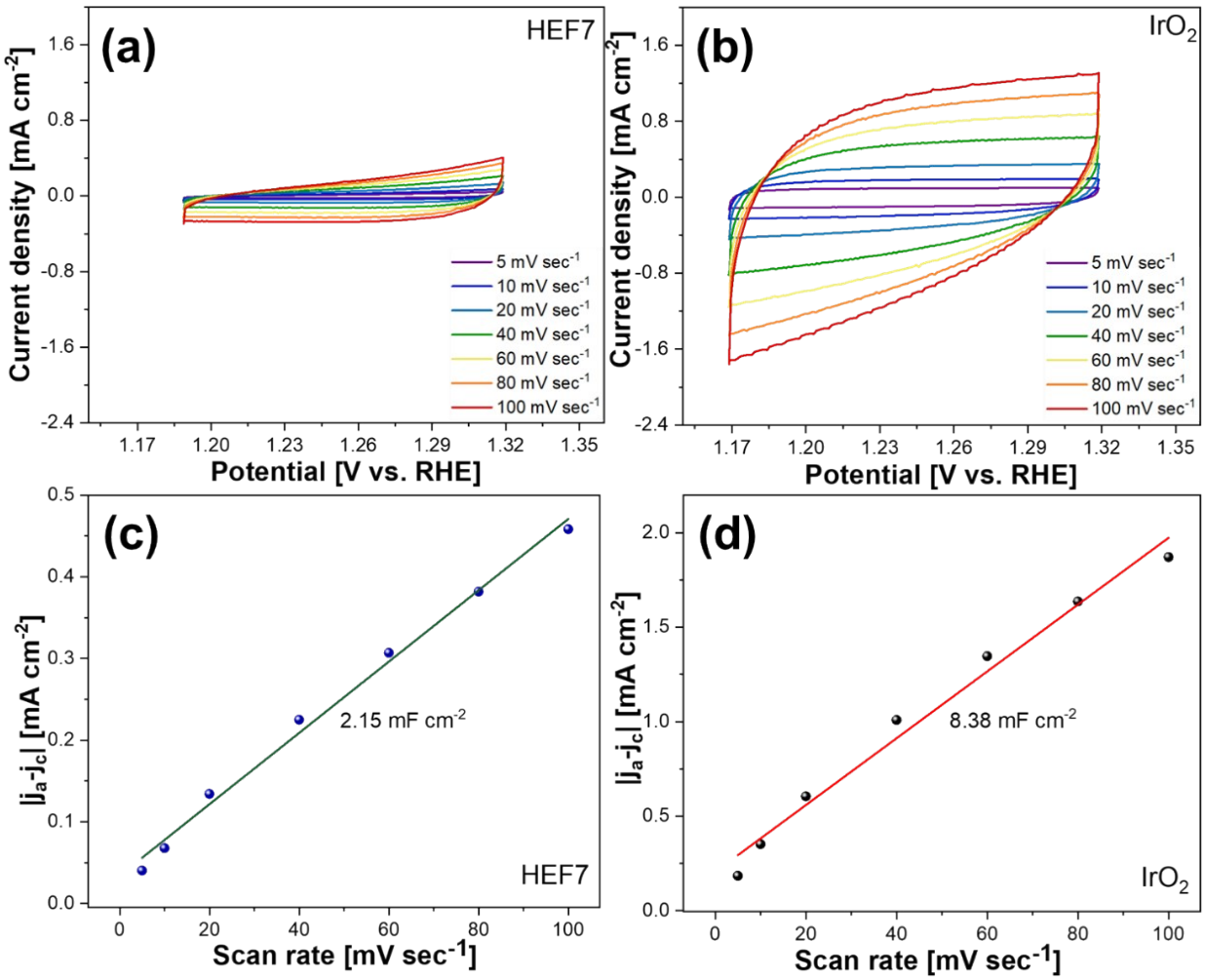

Figure S17. Cyclic voltammograms of **a)** HEF and **b)** IrO_2 measured in 1 M KOH at different scan rates (5, 10, 20, 40, 60, 80, 100 mV sec^{-1}) for the determination of the C_{dl}. Plots of **c)** HEF and **d)** IrO_2 in terms of the difference of the anodic and cathodic current densities, $\Delta J = |j_a - j_c|$, versus the scan rate.

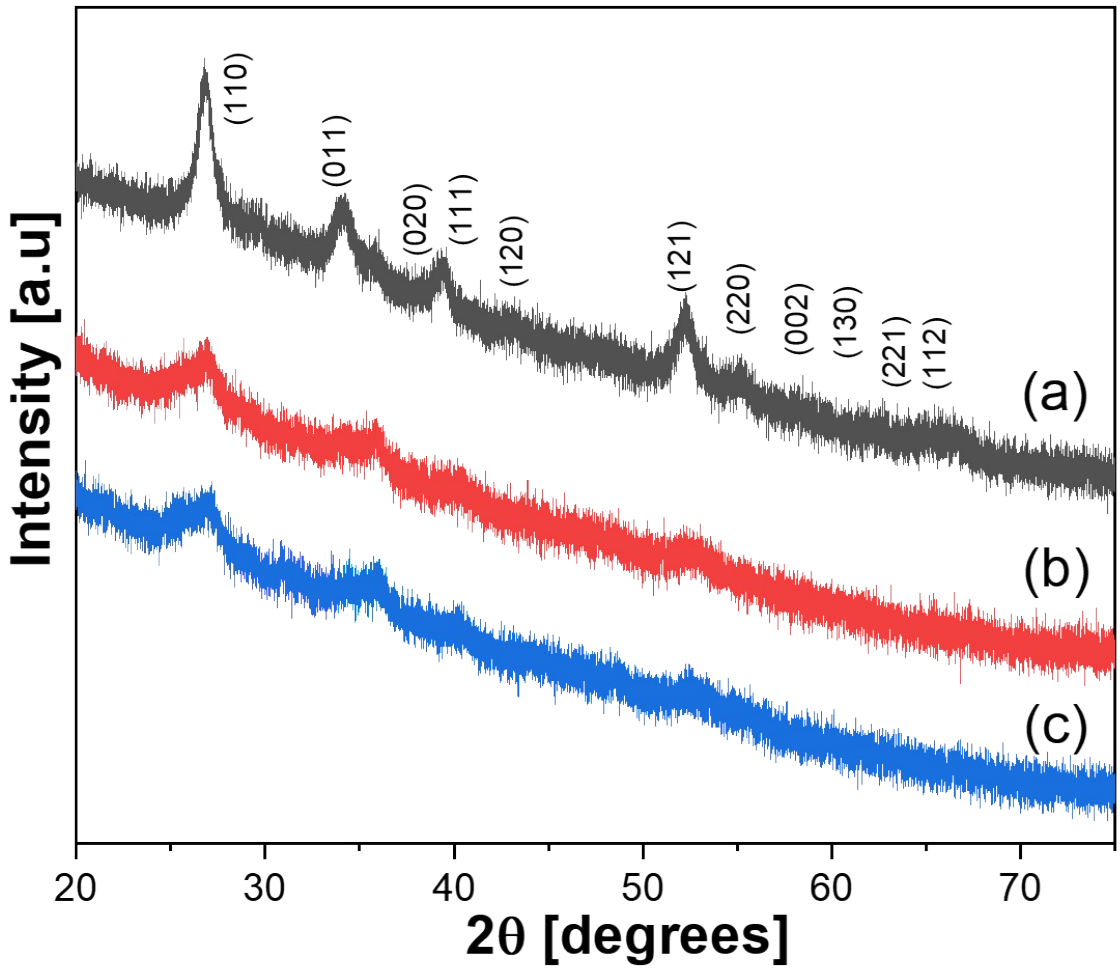

Figure S18. XRD patterns of **a)** catalyst ink containing HEF and HEF-deposited carbon cloth electrodes **b)** before and **c)** after 12 h of the electrolysis.

References

1 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.*, 1969, **25**, 925–946.