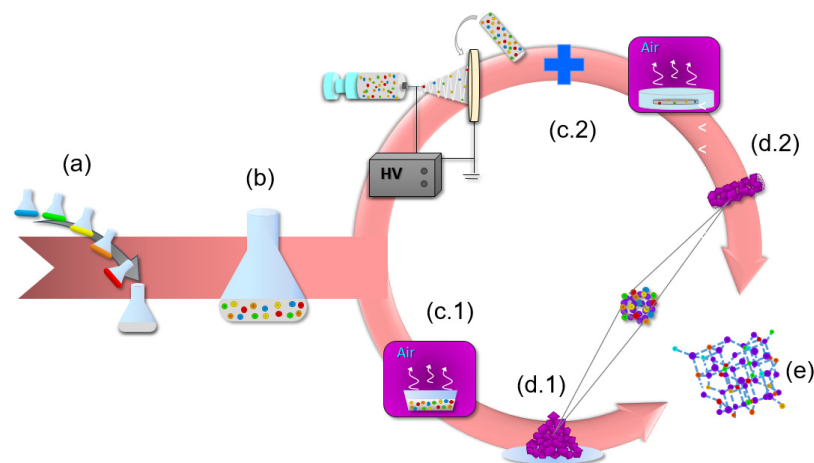


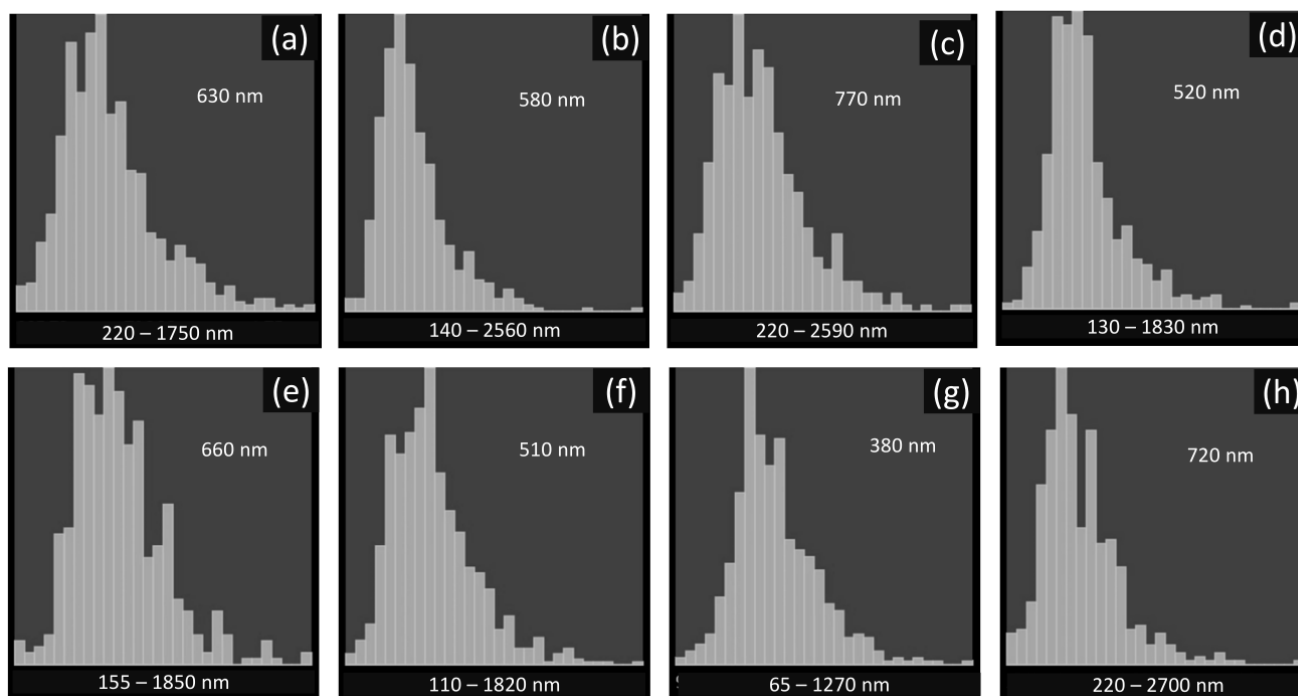
## Supplementary Materials

### Synthesis of the HESOs

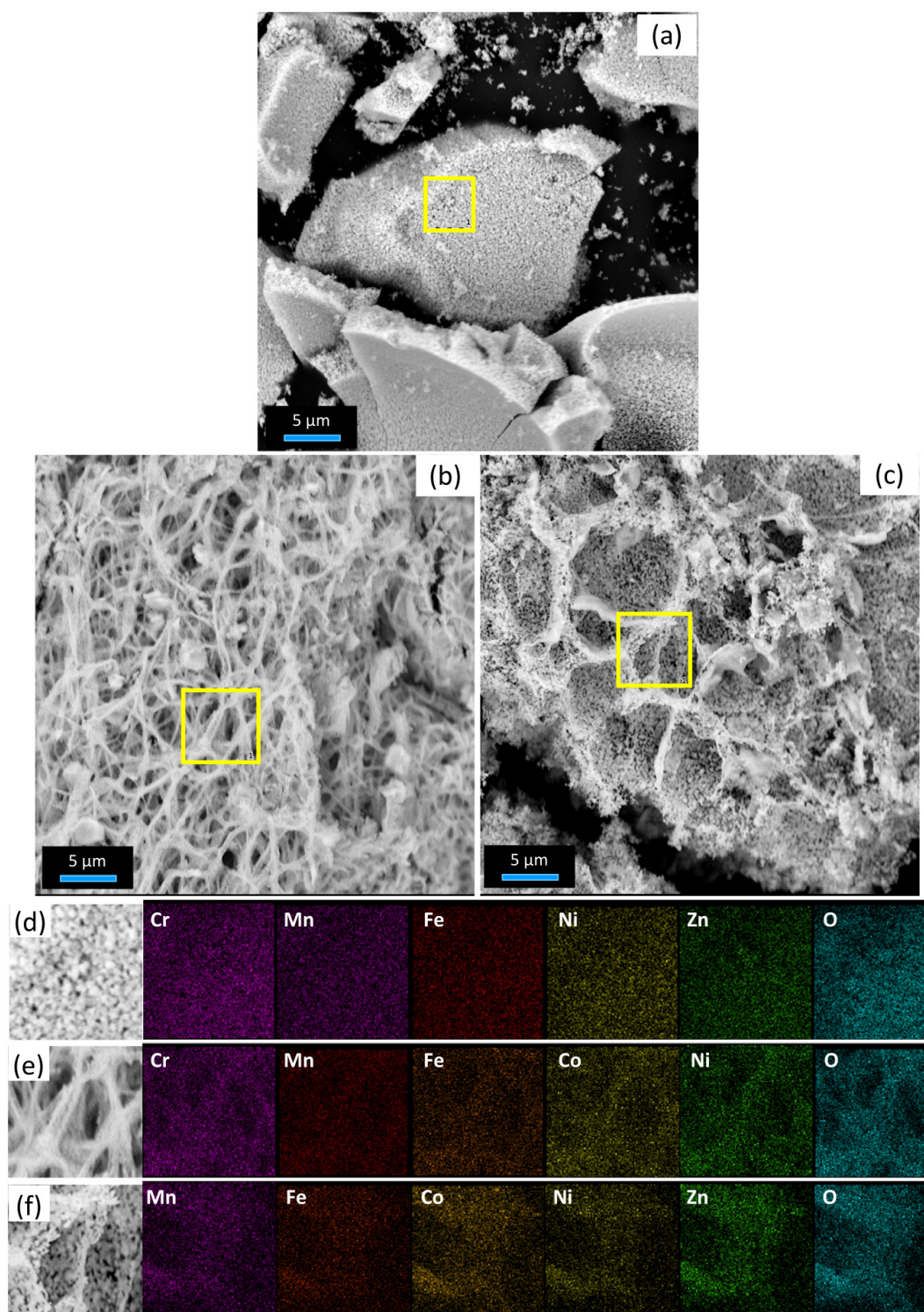


**Figure S1.** Schematic description of the experimental procedure followed to synthesize the HEO-samples: (a) addition of the selected reagents, one at a time, to the solvent(s) and (b) resulting solution containing an equimolar combination of five metals; (c.1) calcination and (d.1) HEO-nanoparticles obtained via sol-gel method; (c.2) electrospinning, followed by calcination, and (d.2) as-obtained HEO-nanofibers; (e) spinel structure of the HEO-grains constituting nanoparticles and nanofibers.

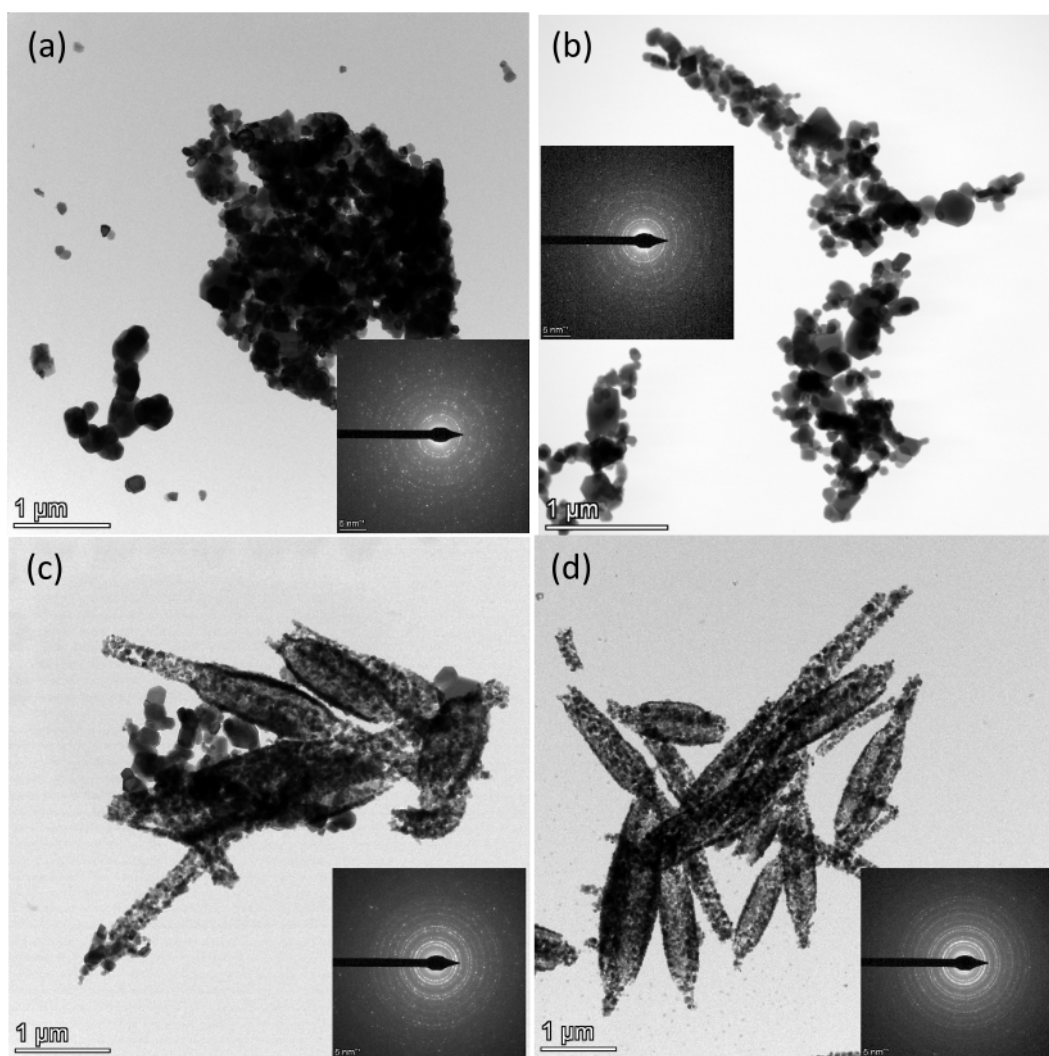
### Physicochemical properties of the produced HESOs



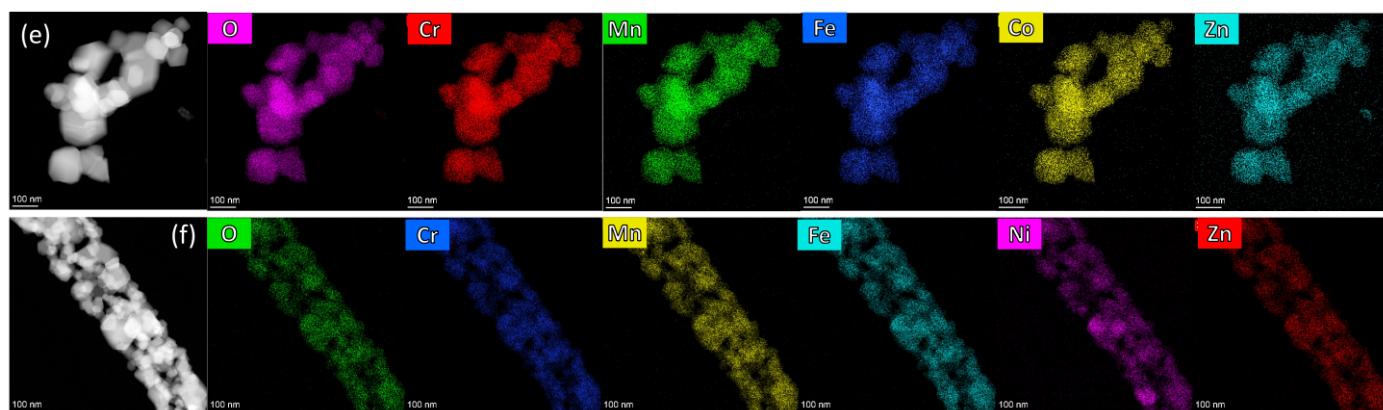
**Figure S2.** NF diameter distributions, as resulting from the automated measurement via the microscope software from their SEM images. The results shown refer to samples (a) 5ME-a, (b) 5MK-a, (c) 5ML-a, (d) 5MD-b, (e) 5ME-b, (f) 5MF-b, (g) 5MG-b and (h) 5ML-b.



**Figure S3.** Results of the SEM/EDX analysis on samples (a,d) 5MG-sg, (b,e) 5ME-a and (c,f) 5MD-a. (a–c) SEM images; (d–f) elemental maps.

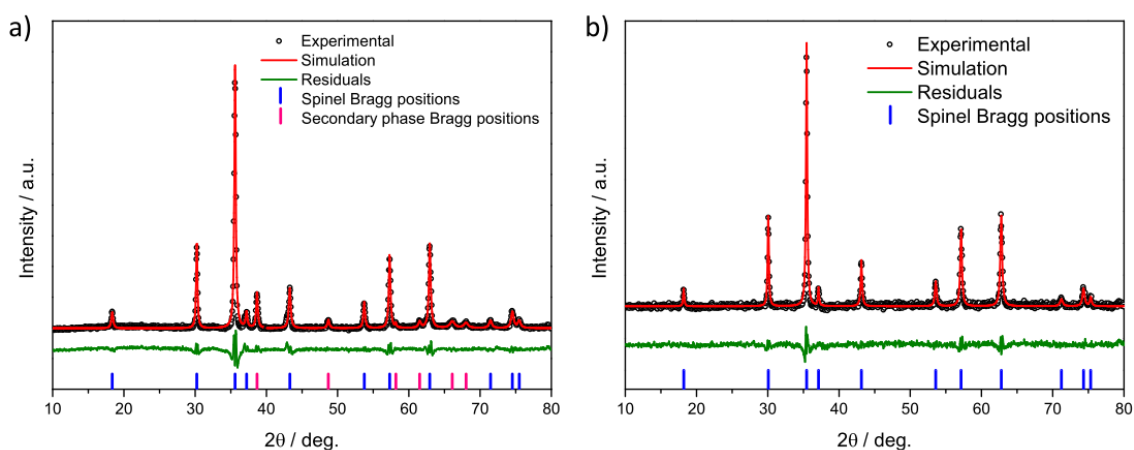


**Figure S4.** TEM images of samples (a) 5MF-sg, (b) 5ME-b, (c) 5MF-b and (d) 5MG-b. Insets: SAED patterns.



**Figure S5.** Results of the STEM/EDX analysis on samples (e) 5MF-sg and (d) 5MG-b.

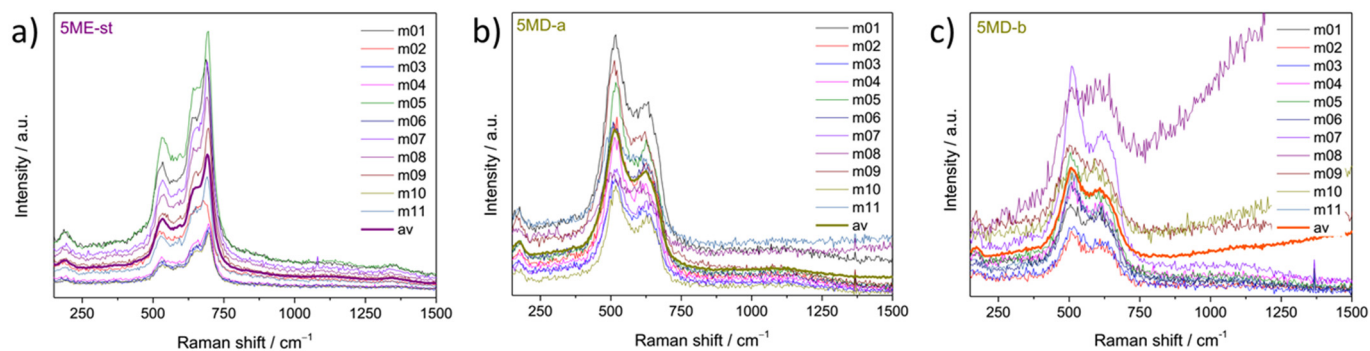




**Figure S6.** Rietveld refinements. The cases shown refer to samples (a) 5ML-sg and (b) 5MF-a.

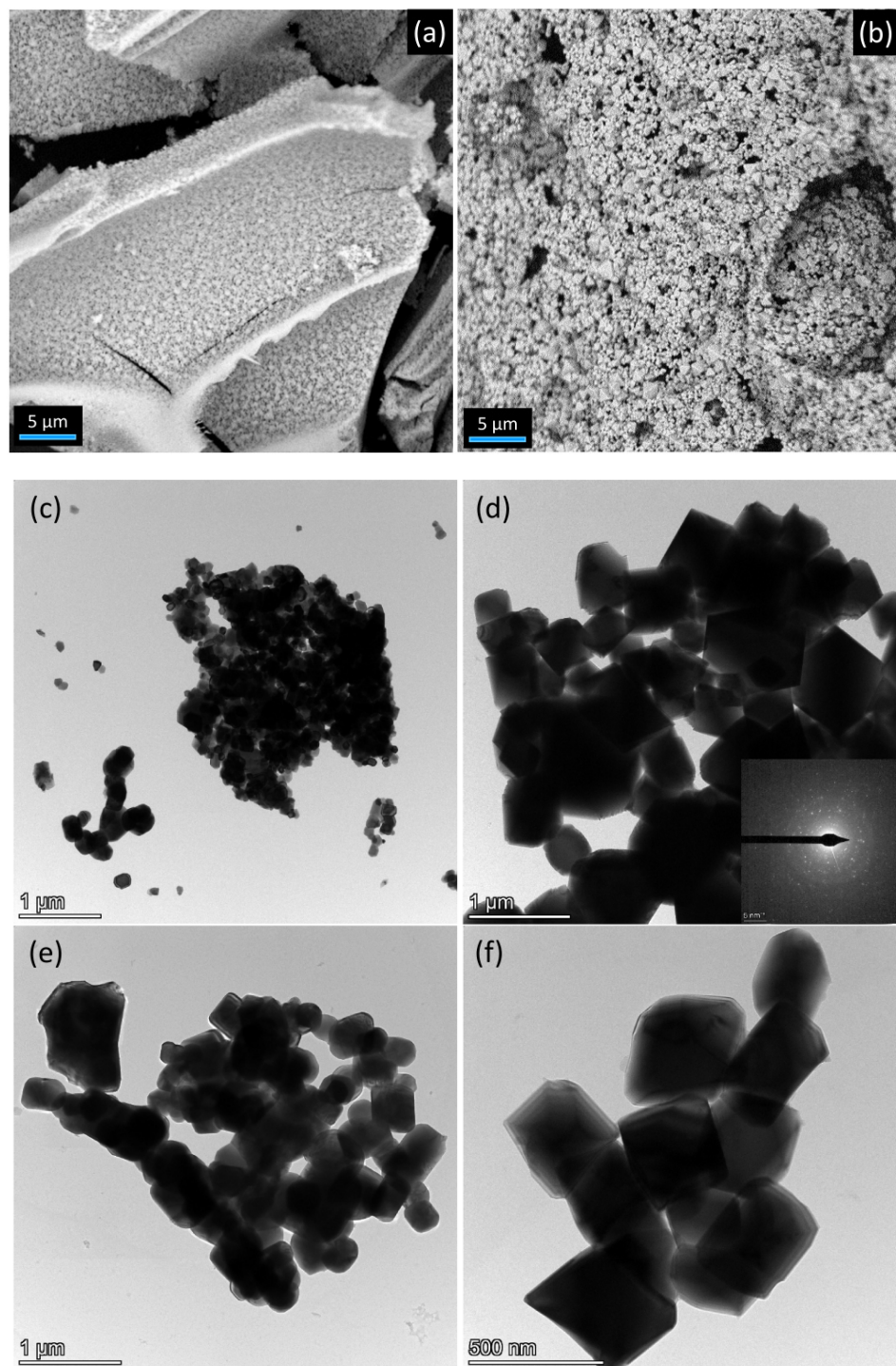
**Table S1.** Results of Rietveld refinements.

Sample	Secondary Phase(s)/%
5MA-sg	11.5
5MD-sg	0.0
5ME-sg	0.0
5MF-sg	0.0
5MG-sg	0.0
5MH-sg	1.6
5MI-sg	1.2
5MJ-sg	1.3
5MK-sg	3.1
5ML-sg	12.4
5MD-a	0.0
5ME-a	0.0
5MF-a	0.0
5MK-a	8.0
5ML-a	8.8
5MD-b	8.6
5ME-b	0.0
5MF-b	0.0
5MG-b	0.0
5ML-b	7.3

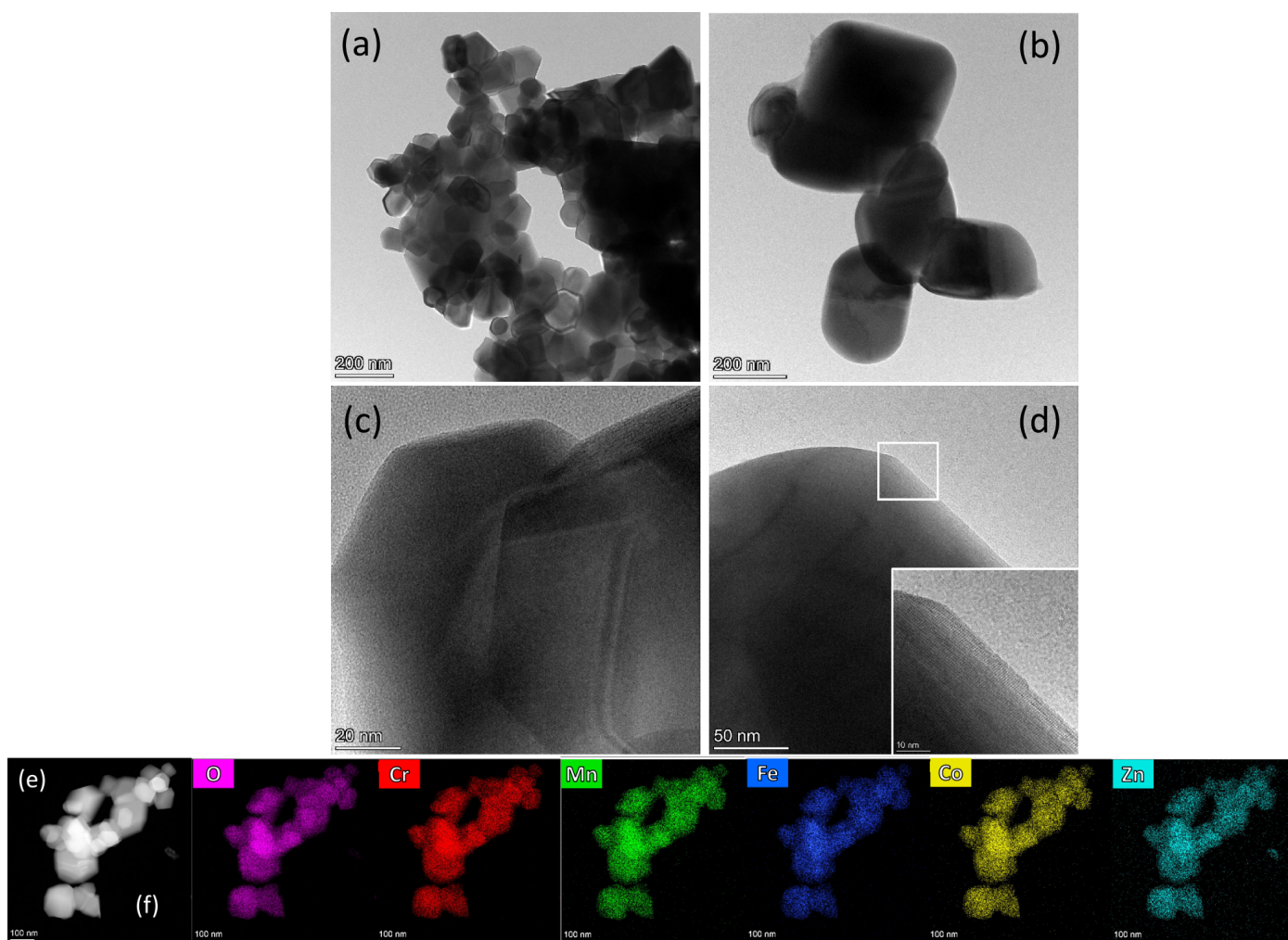


**Figure S7.** Micro-Raman spectra of representative samples (a) 5ME-sg, (b) 5MD-a and (c) 5MD-b, as measured at different random locations and relative averaged spectra (av), calculated for each sample.

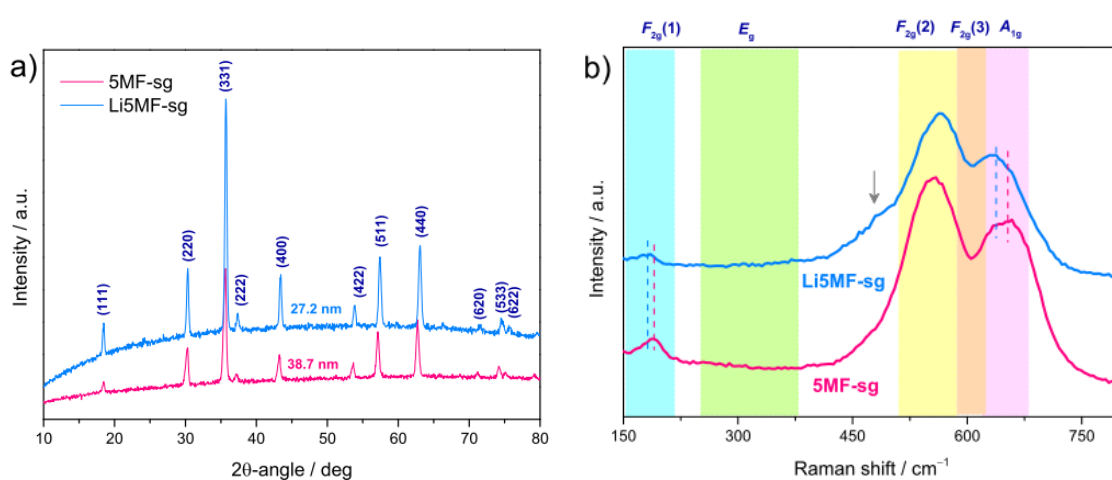
**Physicochemical properties of the (Li,Cr,Mn,Fe,Co,Zn) HESO NPs**



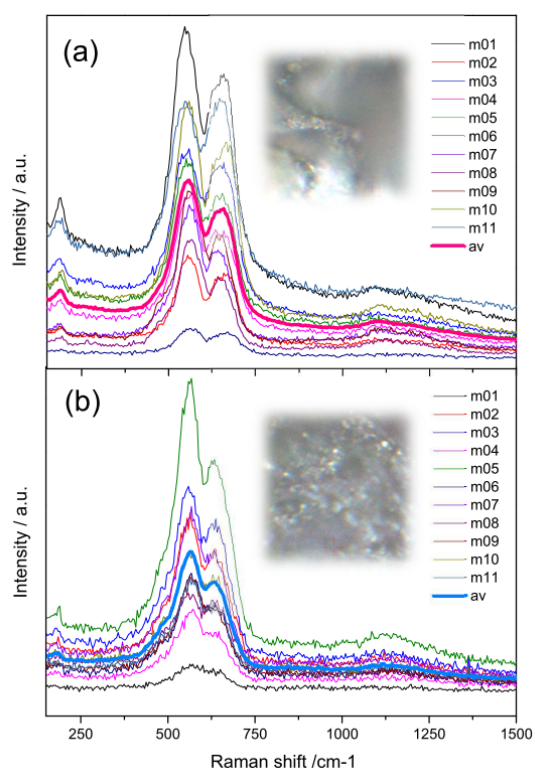
**Figure S8.** (a,b) SEM and (c–f) TEM images of samples (a,c) 5MF-sg and (b,d–f) Li5MF-sg.



**Figure S9.** HRTEM images of samples (a) 5MF-sg and (b-d) Li5MF-sg. (e) Results of the STEM/EDX analysis on sample Li5MF-sg.

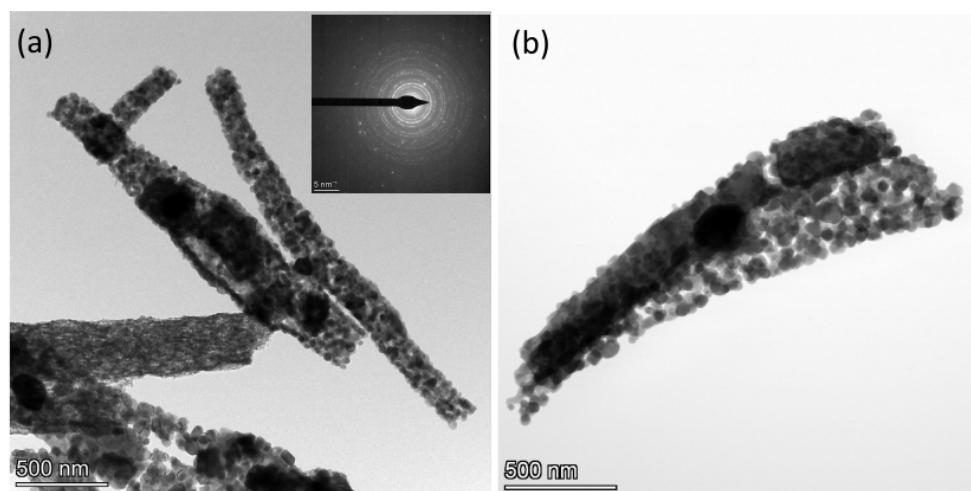


**Figure S10.** Results of (a) XRD and (b) MRS analyses on samples 5MF-sg and Li5MF-sg, evaluated as anode materials in LIBs.



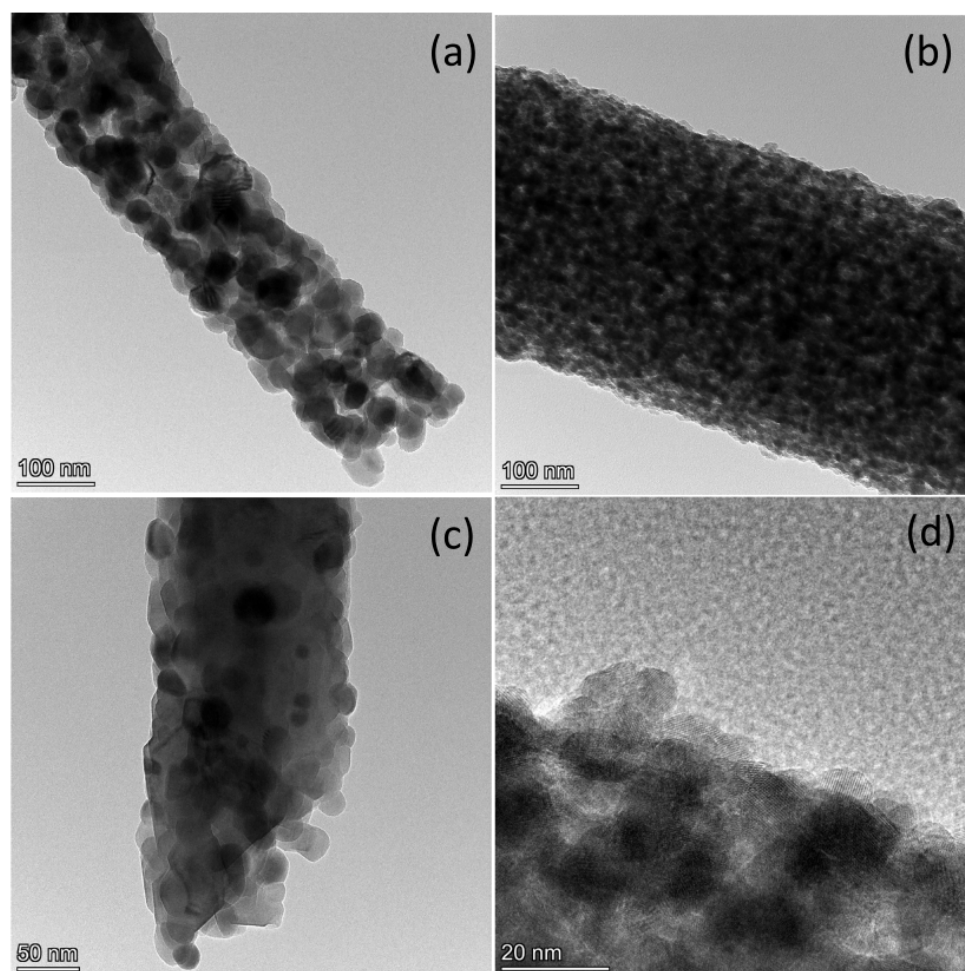
**Figure S11.** Micro-Raman spectra of samples (a) 5MF-sg and (b) Li5MF-sg, as measured at different random locations and relative averaged spectra (av), calculated for each sample.

#### Physicochemical properties of the C/(Cr,Mn,Fe,Co,Zn) HESO NFs



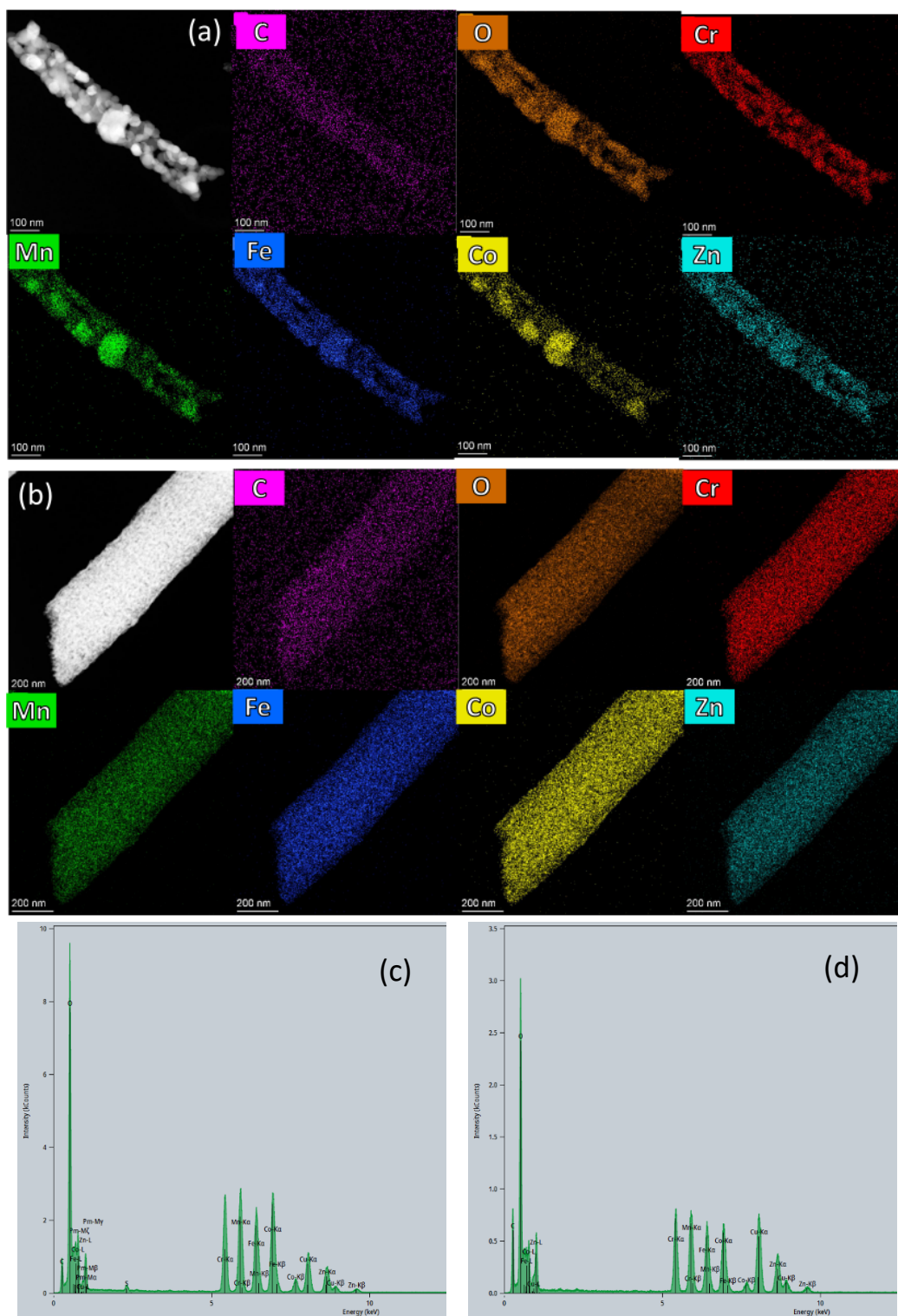
**Figure S12.** TEM images of sample C5MF-b. Inset: SAED pattern.



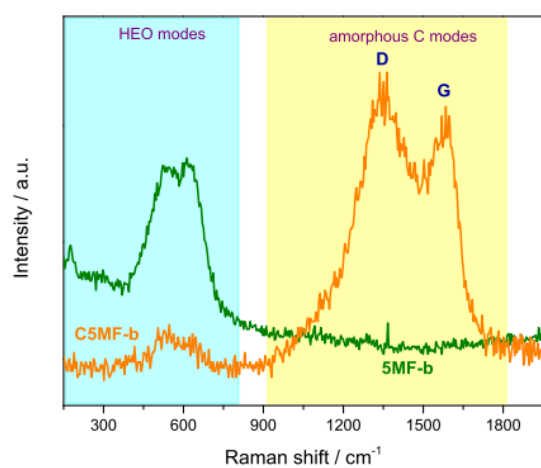


**Figure S13.** HRTEM images of sample C5MF-b. The shown results refer to (a) C-poorer and (b-d) C-richer NFs.





**Figure S14.** Results of the STEM/EDX analysis on sample C5MG-b. The shown results refer to (a,c) C-poorer and (b,d) C-richer NFs.



**Figure S15.** Micro-Raman spectra of samples 5MF-b and C5MF-b.