Supplementary information for:

Investigation of mixed-metal (oxy)fluorides as a new class of water oxidation electrocatalysts

Kévin Lemoine,[1] Jérôme Lhoste,[1] Annie Hémon-Ribaud,[1] Nina Heidary,[2] Vincent Maisonneuve,[1] Amandine Guiet,[1*] Nikolay Kornienko[2*]

[1]Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

[2]Department of Chemistry, Université de Montréal, Roger-Gaudry Building, Montreal, Quebec, H3C 3J7, Canada

* corresponding authors – amandine.guiet@univ-lemans.fr and nikolay.kornienko@umontreal.ca

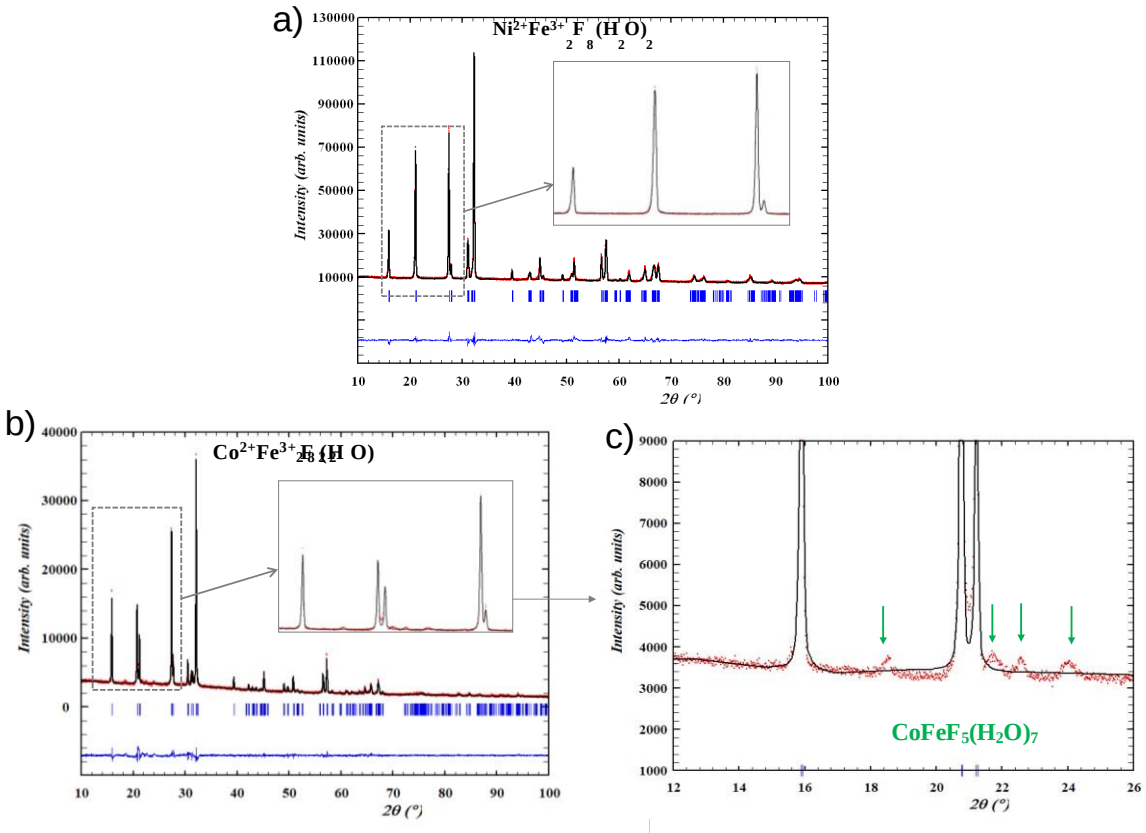

Figure S1: Rietveld refinement of the X-ray patterns of a) $NiFe_2F_8(H_2O)_2$, b) and c) $CoFe_2F_8(H_2O)_2$ using the structural model of $Fe_3F_8(H_2O)_2$ (ICSD-38366). Vertical markers give Bragg peak positions of the C2/m space group.

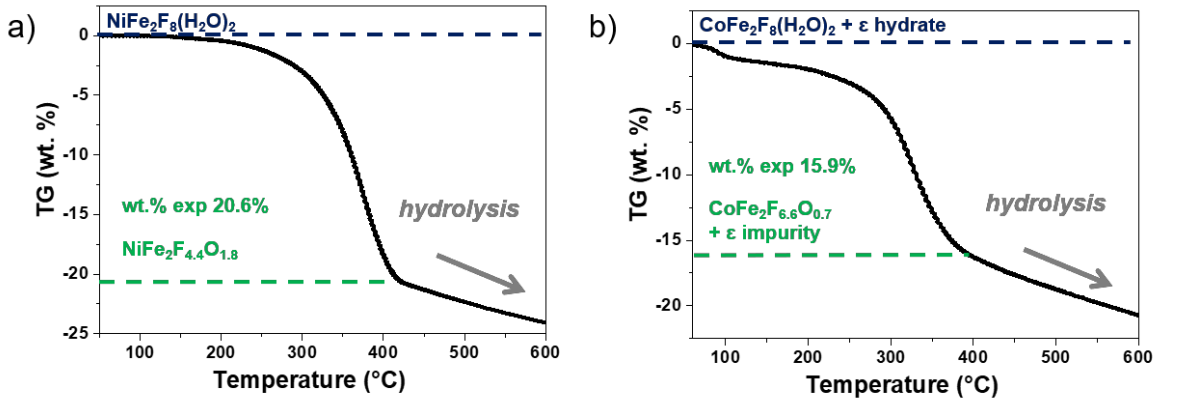

Figure S2: TGA analysis under dry air of a) $Ni^{2+}Fe^{3+}{}_2F_8(H_2O)_2$ and b) $Co^{2+}Fe^{3+}{}_2F_8(H_2O)_2$

Table S1: Summary of temperature domains for $M^{2+}M^{3+}{}_2F_8(H_2O)_2$ phases (M= Ni and Co).

Phases	Temperature domain		
	Crystallized phase	Amorphous phase	Oxide, *formula*
$NiFe_2F_8(H_2O)_2$	T < 340°C	340 ≤ T ≤ 380	380°C < T, $NiFe_2O_4$
$CoFe_2F_8(H_2O)_2$	T < 300°C	300 ≤ T ≤ 340	340°C < T, $CoFe_2O_4$

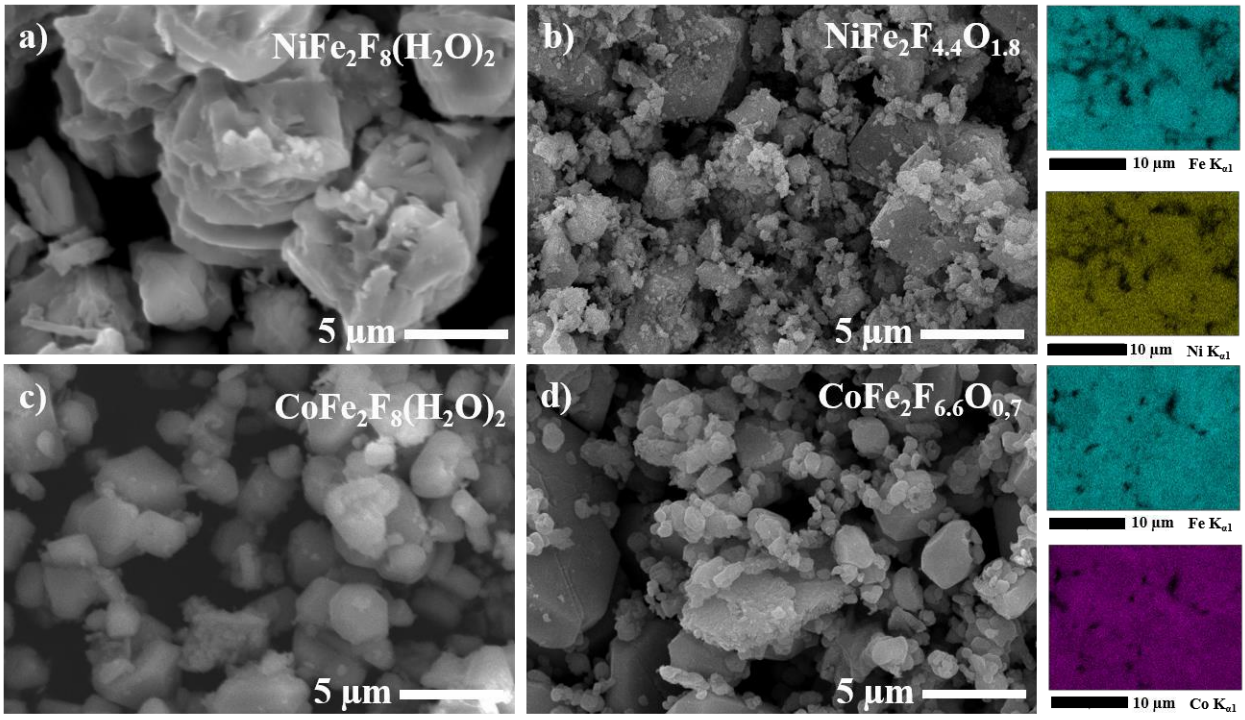

Figure S3: SEM images of a) $Ni^{2+}Fe^{3+}{}_2F_8(H_2O)_2$ and b) $Co^{2+}Fe^{3+}{}_2F_8(H_2O)_2$ powders before (a), c)) and after calcination (b), d)) under air. On the right: Corresponding EDS mapping on the calcined powders.

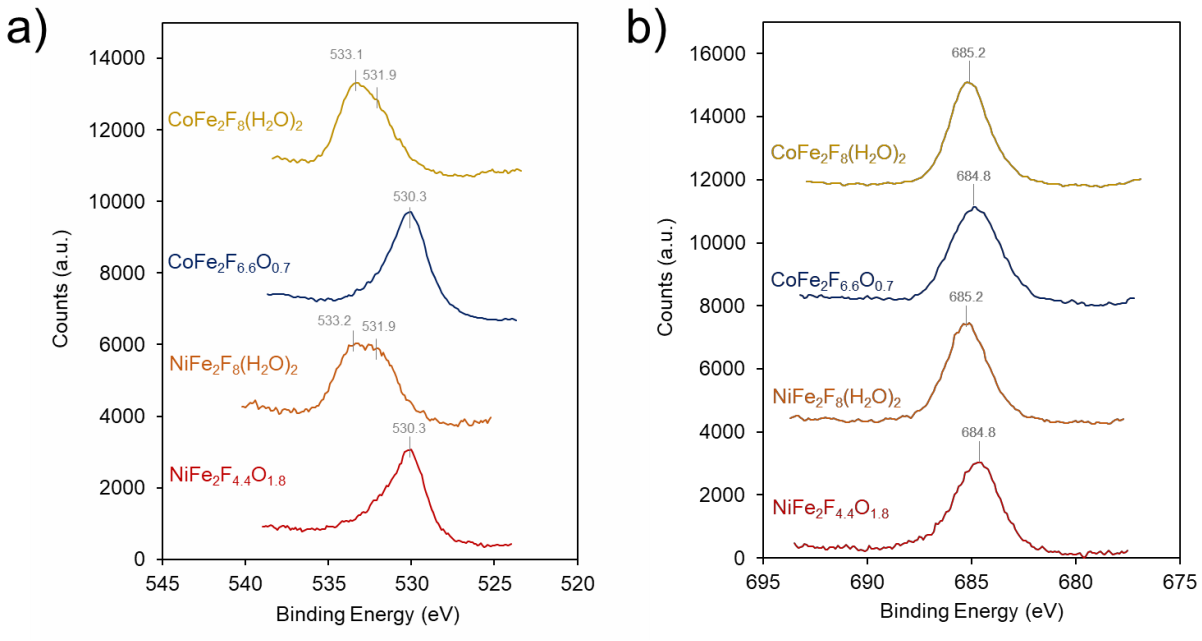

Figure S4: O1s a) and F1s b) XPS of the investigated (oxy)fluorides.

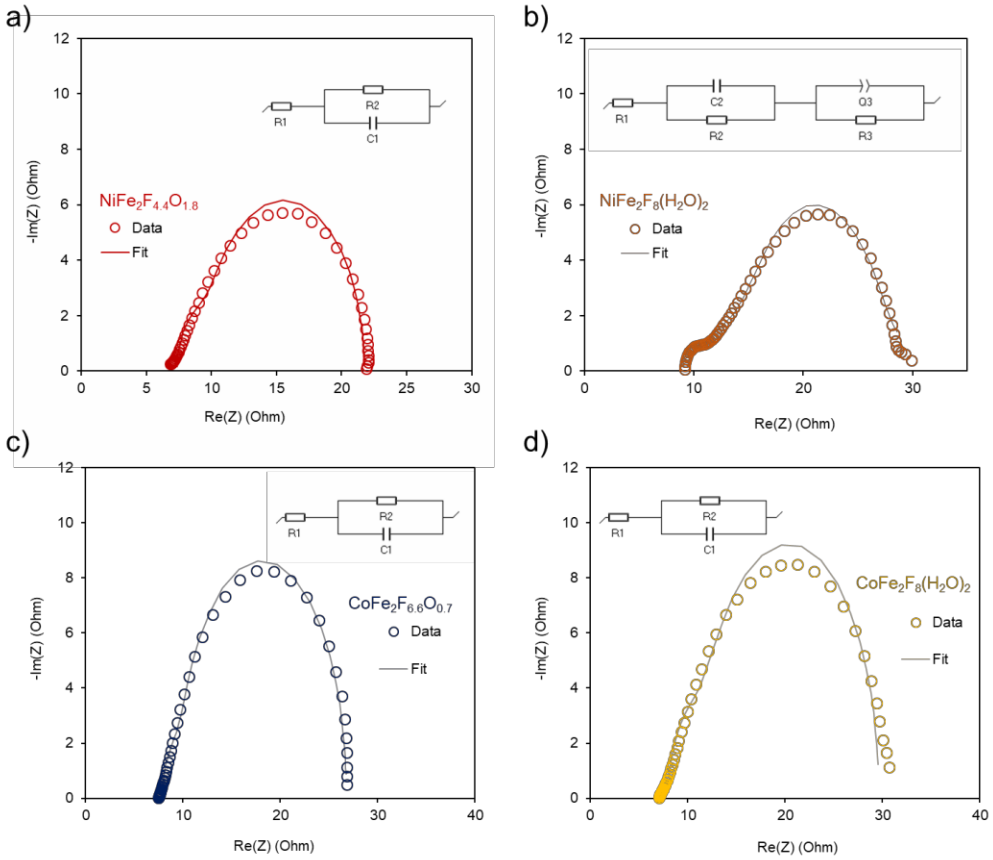

Figure S5: Example of EIS Fitting performed using a Randles circuit for (oxy)fluorides except for $NiFe_2F_8(H_2O)_2$, which needed an extra constant phase and resistive element, indicating that charge transfer through the material was, in part, limiting the system performance. R = resistive element, C = capacitive element, Q = constant phase element.

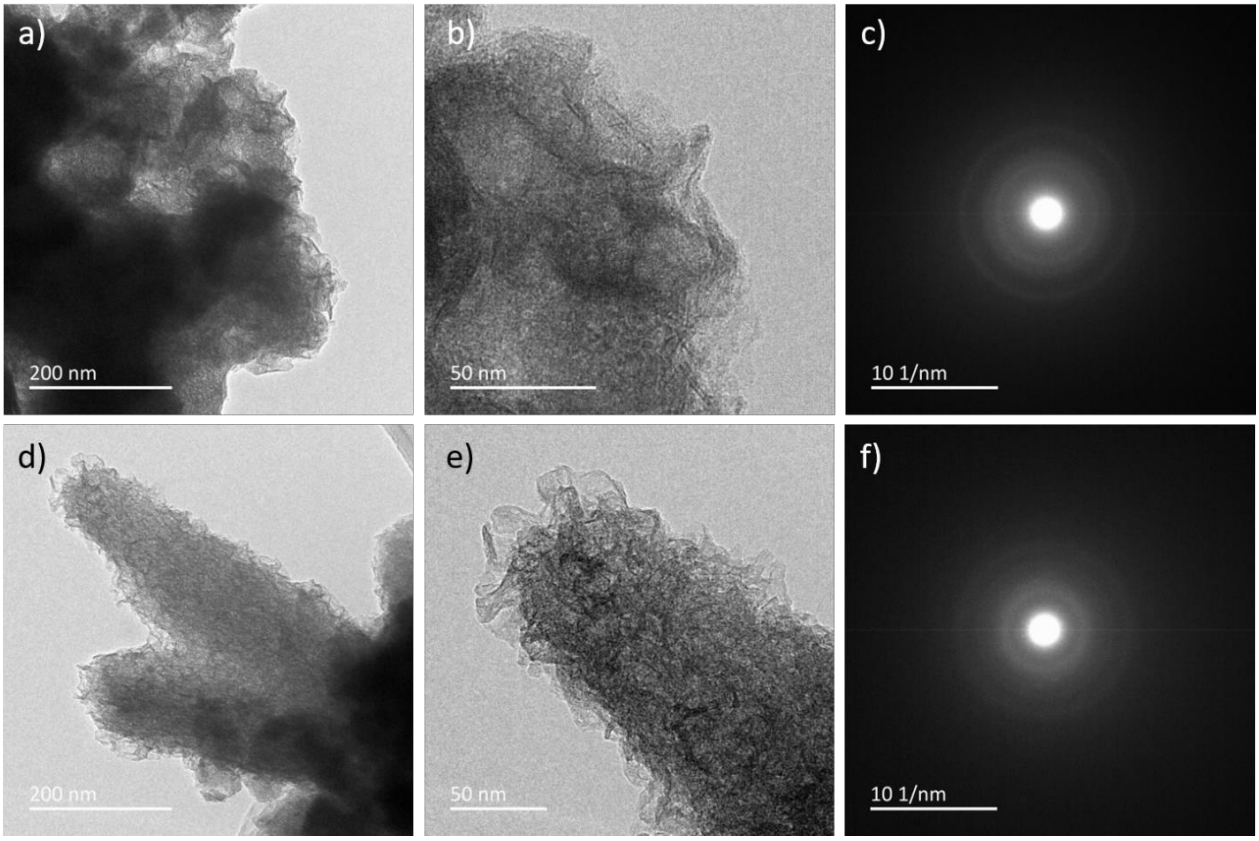

Figure S6: TEM micrographs of a), b) $NiFe_2F_{4.4}O_{1.8}$ and d), e) $CoFe_2F_{6.6}O_{0.7}$ after catalysis. c) and f) Corresponding SAED.

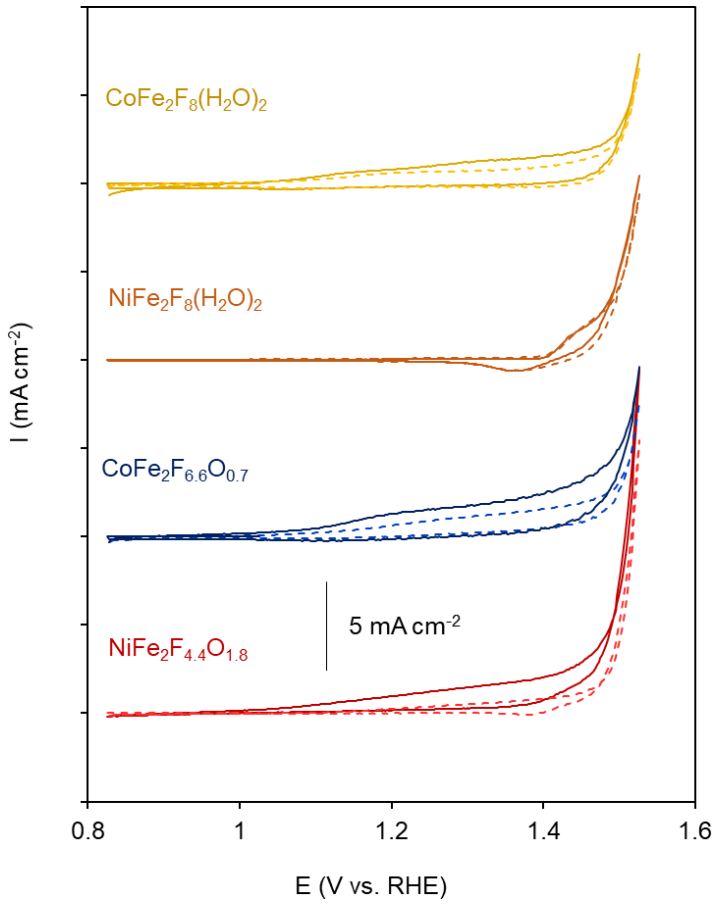

Figure S7: Cyclic voltammograms of (oxy)fluorides in 1.0 M KOH without (dotted lines) and with the addition of 10 mM methanol.

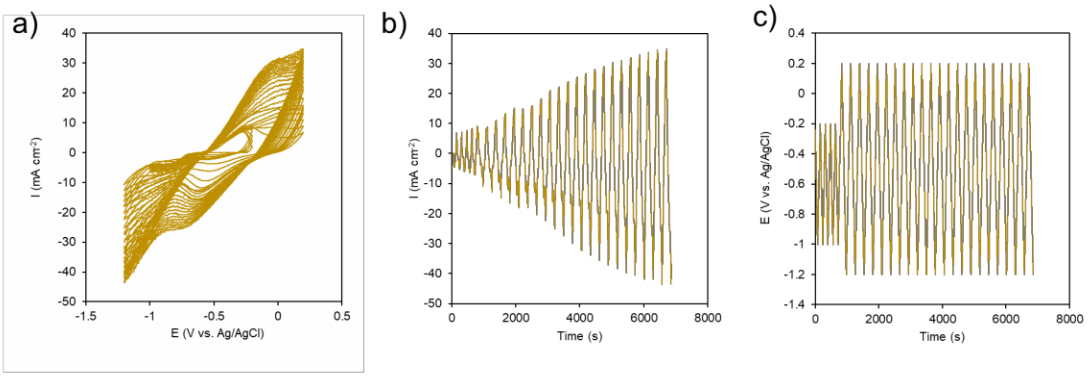

Figure S8: Electrodeposition of CoSx HER catalyst, depicted in current vs voltage a), current vs. time b) and voltage vs. time c).

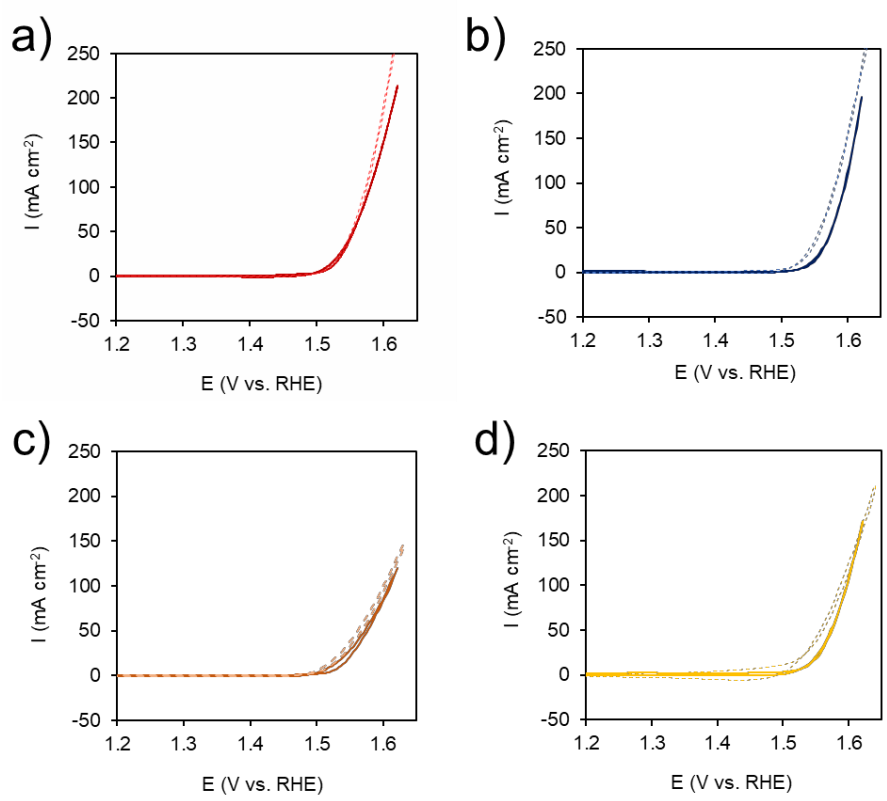

Figure S9: Cyclic voltammetry experiments were repeated without the use of a nafion binder (dotted line) and compared to those performed with nafion in the catalyst in (normal line) for $NiFe_2F_{4.4}O_{1.8}$ and a), $CoFe_2F_{6.6}O_{0.7}$ (b), $NiFe_2F_8(H_2O)_2$ (c) and $CoFe_2F_8(H_2O)_2$ (d)