Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Engineering Nanostructured Spinel Ferrites by co-substitution for Total Water Electrolysis by Preferential Exposure of Metal Cations on the Surface

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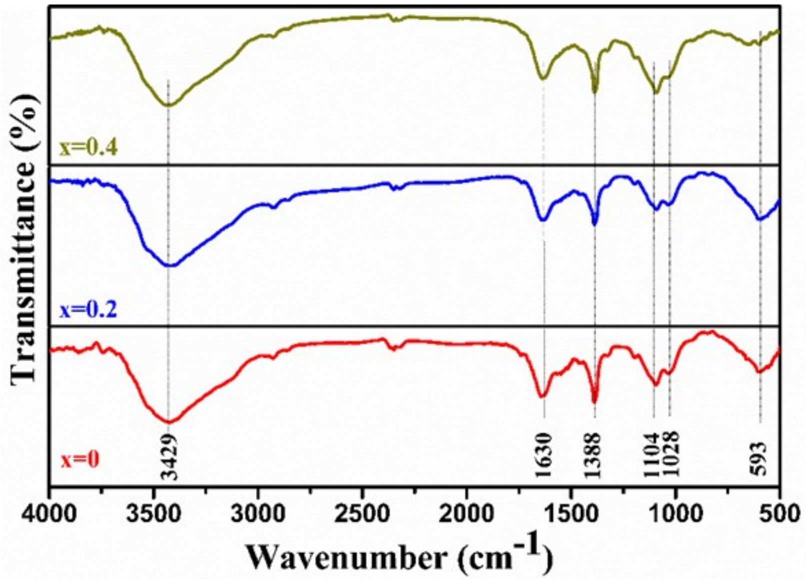

Figure S1. FTIR spectra of nanostructured $Co_xNi_{(0.4-x)}Fe_{0.6}^{II}Fe_2^{III}O_4$ (x=0, 0.2, and 0.4)

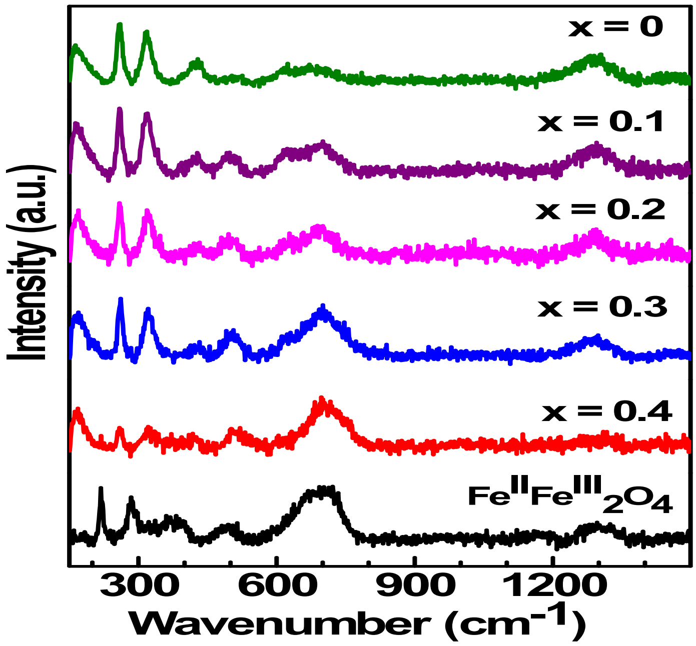

Figure S2: Raman spectra of the, Fe_3O_4 and Co and Ni co-substituted Fe_3O_4 described by the general formula $Co_xNi_{(0.4-x)}Fe_{0.6}^{II}Fe_2^{III}O_4$ (x=0, 0.1, 0.2, 0.3 and 0.4) respectively.

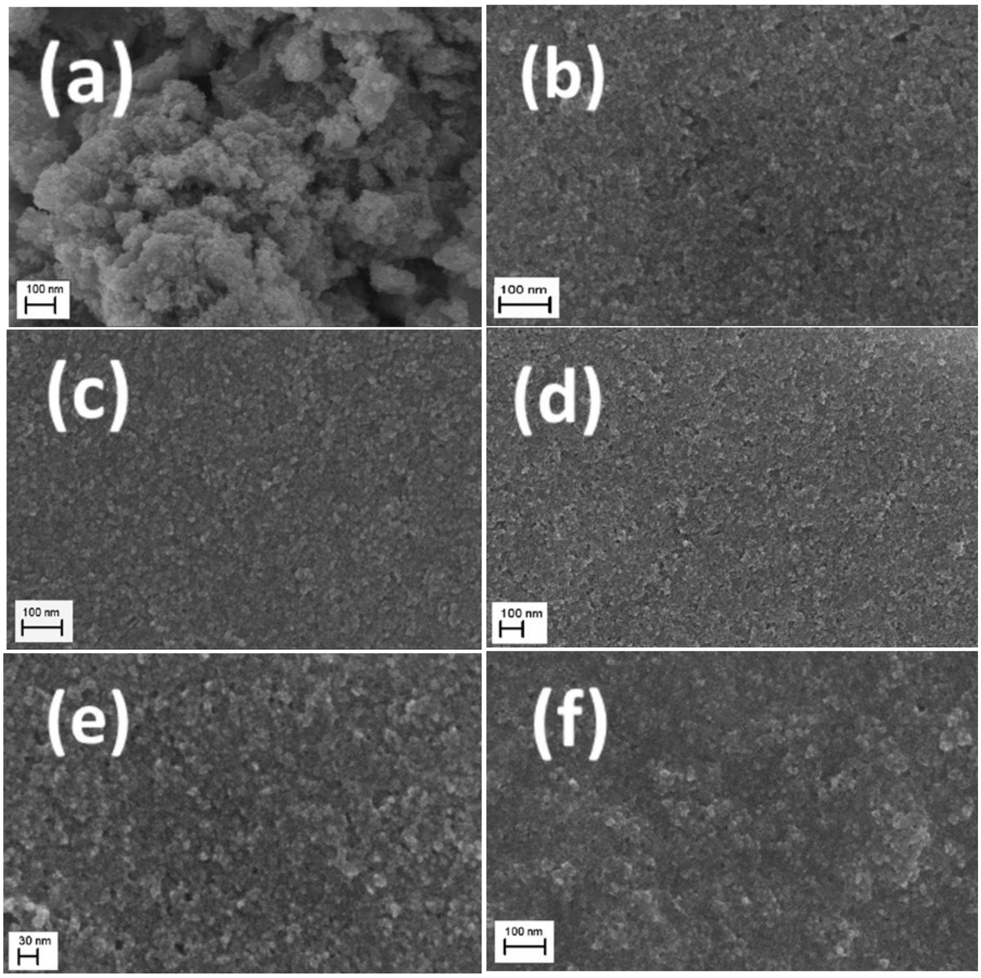

Figure S3: Scanning Electron Micrographs of (a) Fe_3O_4 and (b to f) Co and Ni co-substituted Fe_3O_4 described by the general formula $Co_xNi_{(0.4-x)}Fe_{0.6}^{II}Fe_2^{III}O_4$ (x=0, 0.1, 0.2, 0.3 and 0.4) NPs respectively.

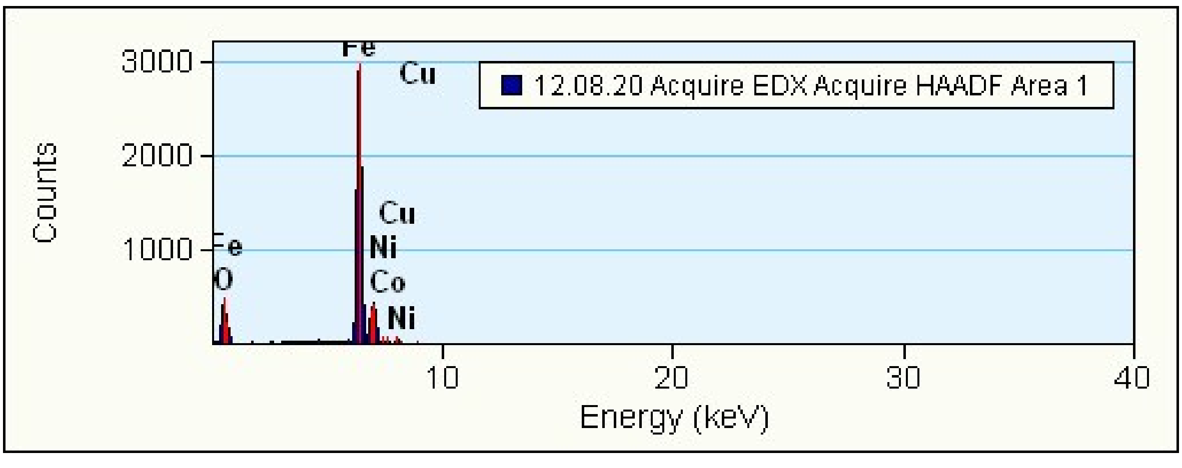

Figure S4: EDS spectra of $Co_{0.2}Ni_{0.2}Fe_{0.6}^{II}Fe_{2}^{III}O_{4}$ NPs

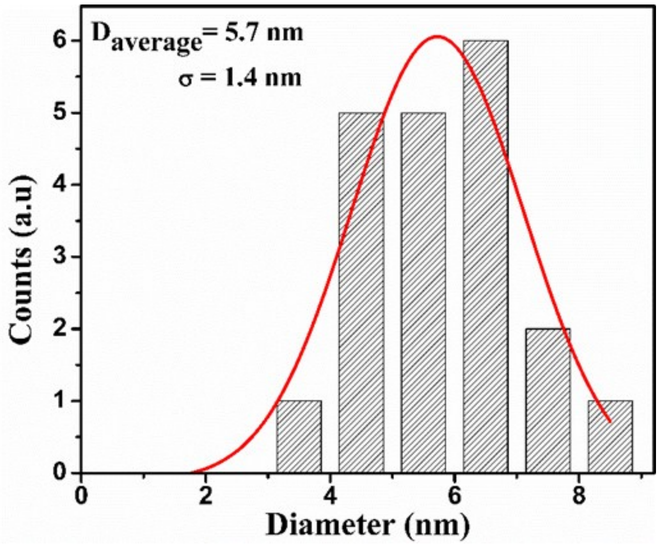

Figure S5: Particle size distribution of $Co_{0.2}Ni_{0.2}Fe_{0.6}^{II}Fe_{2}^{III}O_{4}$

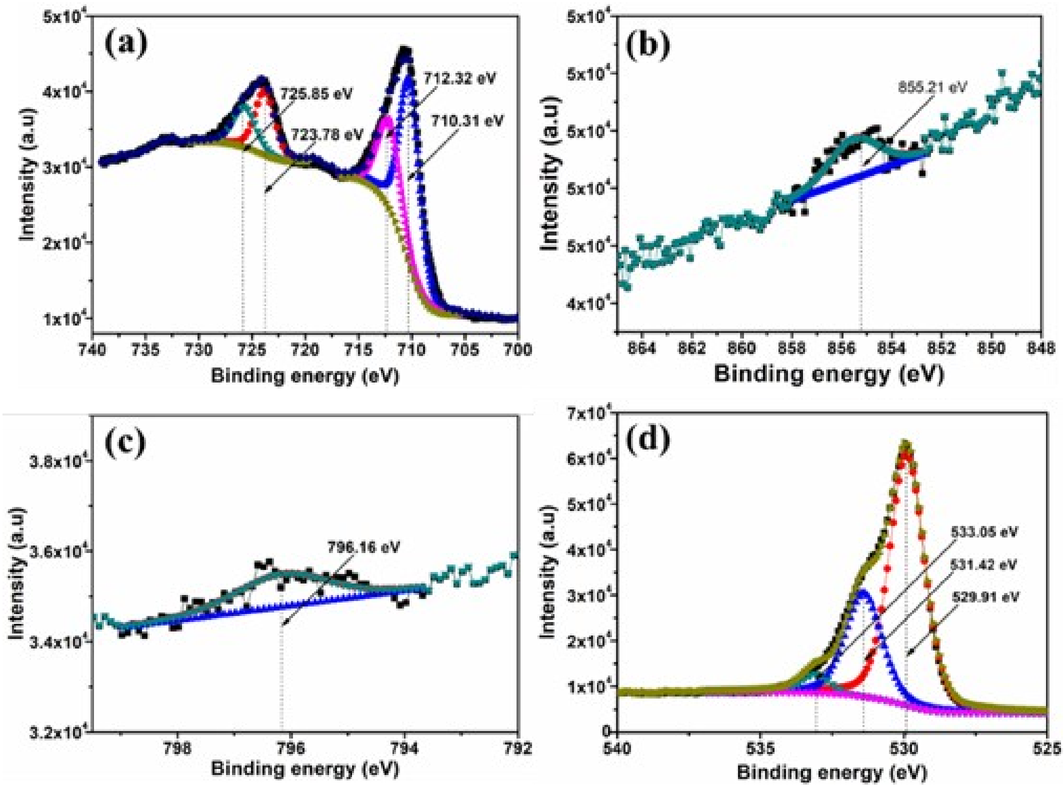

Figure S6: XPS fine spectra of (a) Fe (b) Ni2p (c) Co2p and (d) O1s

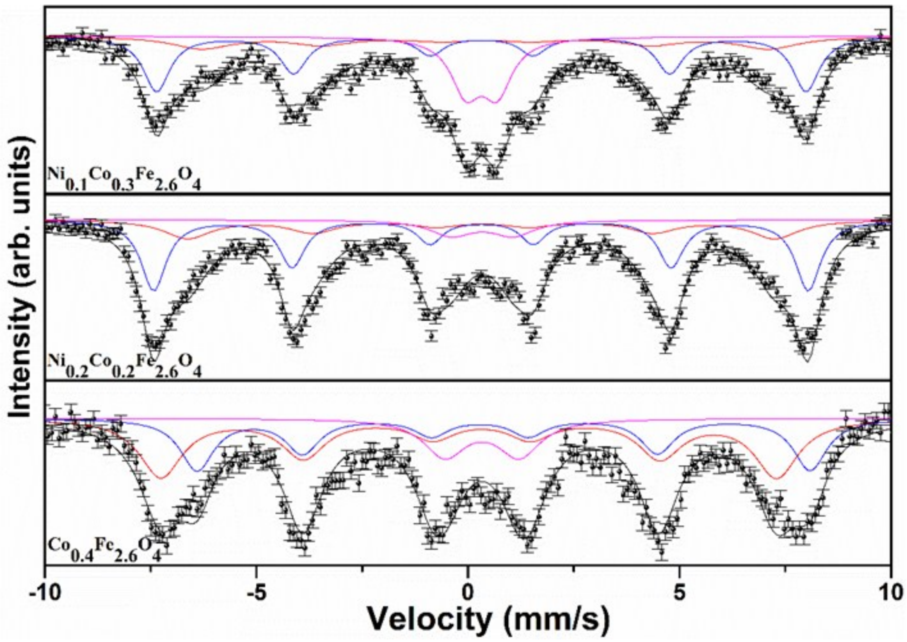

Figure S7: Mossbauer spectra of representative samples

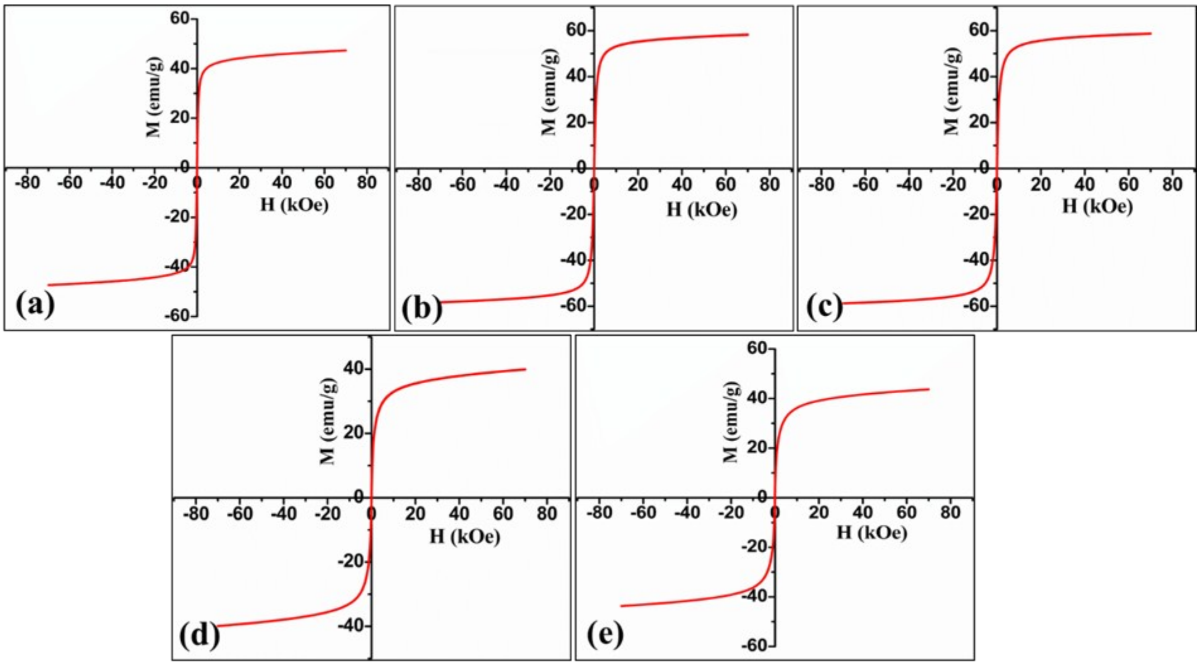

Figure S8. Magnetichysteresis loops of $Co_xNi_{(0.4-x)}Fe_{2.6}O_4$ (a) x=0 (b) x=0.1 (c) x=0.2 (d) x=0.3 (e) x=0.4

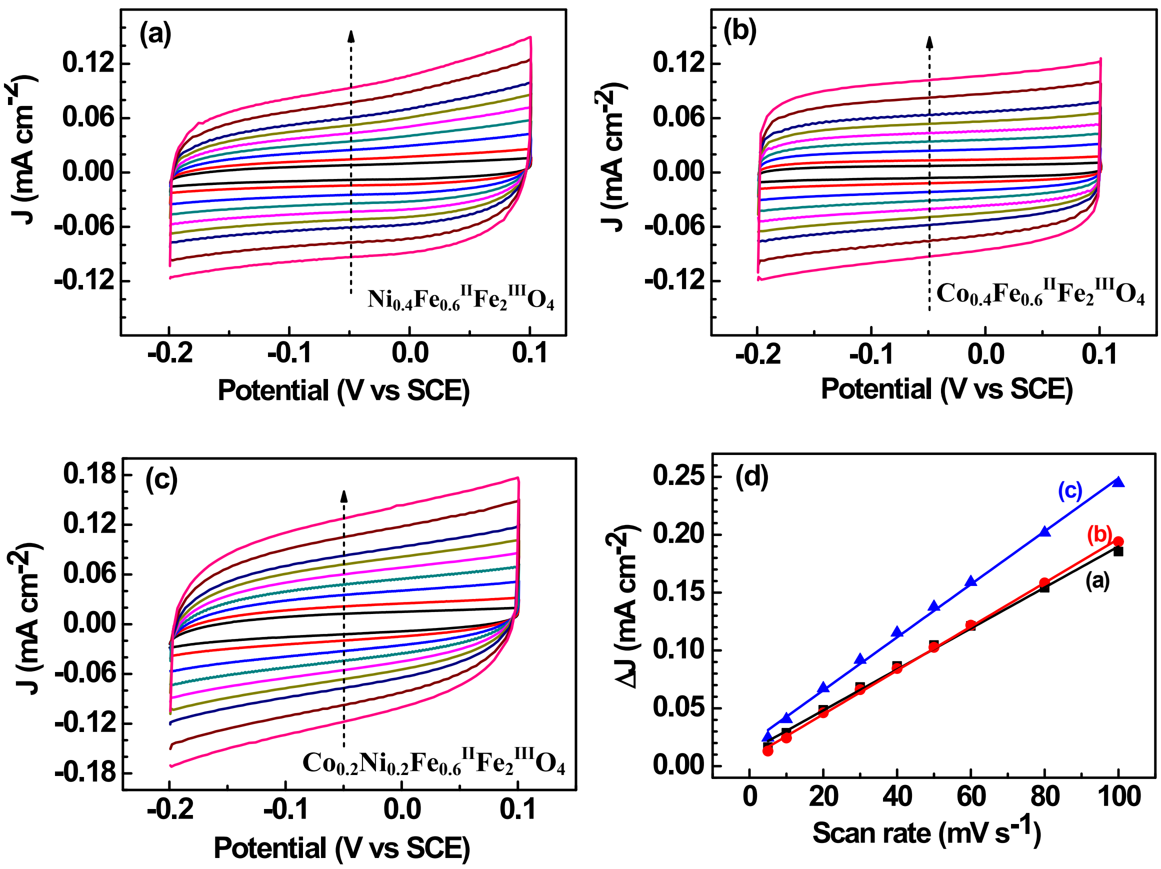

Figure S9: Double layer capacitance (C_{dl}) of different electrodes (Fig. a, b and c) is determined from cyclic voltammogram in the double layer region (without faradaic processes) at different scan rates. The C_{dl} values were calculated by plotting the change in current density $\Delta J = Ja - Jc$ (where Ja and Jc are the anodic and cathodic current densities measured at the same voltage from a CV loop) at -0.5 V vs SCE against the scan rate (Fig. d) and the linear slope was found to be twice that of C_{dl}.

Table S1: Variation of crystallite size with Co and Ni substitution

Sample	**Crystallite size (nm)**	**Lattice parameter (Å)**
Fe_3O_4	9.3	8.37
x= 0	7.3	8.34
x= 0.1	6.2	8.35
x= 0.2	6.4	8.36
x= 0.3	5.7	8.36
x= 0.4	5.4	8.370

Table S2: Hysteresis loop parameters of $Co_xNi_{(0.4-x)}Fe_{2.6}O_4$

Substitution concentration (x)	**Maximum magnetization (Mmax) emu/g**	**Coercivity (Hc) Oe**	**Remanence (Mr) emu/g**
x=0	47	31	2.36
x= 0.1	58	9	0.53
x= 0.2	59	8	0.44
x= 0.3	40	30	1.41
x= 0.4	44	31	1.46

Table S3: Comparison of OER, HER and overall water splitting performances of $Co_{0.2}Ni_{0.2}Fe_{0.6}^{II}Fe_2^{III}O_4$ with recently reported electrocatalysts in 1 M KOH.

Electrocatalysts	**OER η_{10} (mV)**	**HER η_{10} (mV)**	**OER,Tafel Slope (mV/dec)**	**HER, Tafel Slope (mV/dec)**	**Overall water splitting cell voltage (V, @10 mA cm^{-2})**	**References**
Hydrotalcite-like $Ni(OH)_2$/NF	170	127	150	140	1.68	ACS Appl. Mater. Interfaces **2016**, 8, 33601
Ni–Fe (hydr) oxide@NiCu	218	66	56.9	67.8	1.52	Adv. Mater. **2019**, 31, 1806769
NiFe Sponges	280	190	56	82	1.62	ChemistrySelect**2020**, 5, 1385
$NiFe_2O_4$/VACNT hybrid	240	155	77	88	1.72	Carbon, **2019**, 145, 201
S-$NiFe_2O_4$/NF	267	138	36.7	61.3	1.65	Nano Energy **2017**, 40, 264
$CoFe_2O_4$/SWNTs	310	263	85	46	~1.75	ACS Appl. Energy Mater. **2019**, 2, 1026
Fe-Co_3O_4/CNTs	290	120	64	54	---	Int. J. hydrogen Energ. 2018, 43, 5522
$Ni_{0.5}Co_{0.5}$/NC	300	176	62.9	132.1	1.75	Nanoscale **2016**, 8, 18507
$Co_{0.9}S_{0.58}P_{0.42}$	266	139	48	69	1.59	ACS Nano **2017**, 11, 11031
Ni-P/CF	325	98			1.68	J. Power Sources **2015**,299, 342
NSN/CFP	280	145	81	72	1.66	Electrochim. Acta **2019**, 305, 37
$Ni_xCo_{3-x}O_4$/NF	320	170	38	98	1.76@20 mA cm^{-2}	Chem. Asian J.**2019**, 14, 480
EG/$Co_{0.85}$Se/NiFe-LDH	--	260	57	160	1.67	Energy Environ. Sci., **2016**,9, 478
V/NF	292	176	68	82	1.74	Nanoscale, **2016**, 8, 10731
$Ni_xCo_{3-x}O_4$/NiCo/NiCoO_x	335	155	75	35	~1.75	Acs Appl. Mater. Inter., **2016**, 8, 3208
NiFe@NC	350	~240	56	--	1.81	Nano Energy **2016**, 30, 426
$Co_{0.2}Ni_{0.2}Fe_{0.6}^{II}Fe_2^{III}O_4$	**270**	**275**	**44**	**99**	**1.72**	**This work**