

Supplementary Information

Unraveling the Faradaic Electrochemical Efficiencies over Fe/Co Spinel Metal Oxides using Surface Spectroscopy and Microscopy Techniques.

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Calculation of Work function(ϕ_m):

$$\phi_m = h\nu - W$$

where, h = plank constant, ν = frequency of photon; here, $h\nu = 21.2$ eV; W = width of the emitted photoelectron's peak from the UPS spectrum.

Work function (ϕ_m) for Co_3O_4 (ϕ_1) = 5.6 eV; Fe_2O_3 (ϕ_2) = 6.1 eV; Co_2FeO_4 (ϕ_3) = 6.2 eV; CoFe_2O_4 (ϕ_4) = 6.3 eV.

Conduction Band (CB.) and Valence Band (VB): For the calculation of the conduction band (CB) and valence band (VB), the following formulae were used as reported previously in the literature ¹⁻⁴:

$$E_{CB} = \chi - E_c - \frac{1}{2}E_g$$

$$E_{VB} = E_{CB} + E_g$$

where, E_{CB} is the energy of CB, E_c is the energy of the free electron, E_g is the bandgap of the semiconductor and E_{VB} is the energy of VB. Also, χ represents the absolute electronegativity of the semiconducting material in the Mulliken electronegativity. The detailed calculations of the various nanocomposites are as follows:

First ionization energy of cobalt = 760.4 kJ/mol = 760.4/96.48 = 7.88 eV

First ionization energy of iron = 762.5 kJ/mol = 762.5/96.48 = 7.90 eV

Electron affinity of cobalt = 63.7 kJ/mol = 63.7/96.48 = 0.66 eV

Electron affinity of iron = 15.7 kJ/mol = 15.7/96.48 = 0.16 eV

$$\chi_{Co} = \frac{(EA + E_{ion})}{2} = \frac{(0.66 + 7.88)}{2} = 4.27 \text{ eV}$$

$$\chi_{Fe} = \frac{(EA + E_{ion})}{2} = \frac{(0.16 + 7.90)}{2} = 4.03 \text{ eV}$$

$\chi_0 = 7.49 \text{ eV}$; $\chi_{\text{Co}_3\text{O}_4} = 5.88 \text{ eV}$; $\chi_{\text{Co}_2\text{FeO}_4} = 5.83 \text{ eV}$; $\chi_{\text{CoFe}_2\text{O}_4} = 5.79 \text{ eV}$; $\chi_{\text{Fe}_2\text{O}_3} = 5.84 \text{ eV}$

Co₃O₄ $E_{CB} = \chi_{\text{Co}_3\text{O}_4} - E_c - \frac{1}{2}(E_{g,\text{Co}_3\text{O}_4}) = 5.88 - 4.5 - 1.15 = 0.23 \text{ eV}$

$$E_{VB} = E_{CB} + E_{g,\text{Co}_3\text{O}_4} = 0.23 + 2.3 = 2.53 \text{ eV}$$

$$\text{Co}_2\text{FeO}_4 \quad E_{CB} = \chi_{\text{Co}_2\text{FeO}_4} - E_c - \frac{1}{2}(E_{g,\text{Co}_2\text{FeO}_4}) = 5.83 - 4.5 - 1.25 = 0.08 \text{ eV}$$

$$E_{VB} = E_{CB} - E_{g,\text{Co}_2\text{FeO}_4} = 0.08 + 2.5 = 2.58 \text{ eV}$$

$$\text{CoFe}_2\text{O}_4 \quad E_{CB} = \chi_{\text{CoFe}_2\text{O}_4} - E_c - \frac{1}{2}(E_{g,\text{CoFe}_2\text{O}_4}) = 5.79 - 4.5 - 1.4 = -0.11 \text{ eV}$$

$$E_{VB} = E_{CB} - E_{g,\text{CoFe}_2\text{O}_4} = -0.11 + 2.8 = 2.69 \text{ eV}$$

$$\text{Fe}_2\text{O}_3 \quad E_{CB} = \chi_{\text{Fe}_2\text{O}_3} - E_c - \frac{1}{2}(E_{g,\text{Fe}_2\text{O}_3}) = 5.84 - 4.5 - 1.1 = 0.24 \text{ eV}$$

$$E_{VB} = E_{CB} - E_{g,\text{Fe}_2\text{O}_3} = 0.24 + 2.2 = 2.44 \text{ eV}$$

Catalyst Slurry Preparation:

Catalyst slurry for HER and OER: 2 mg of the catalyst was dispersed in 1 ml of 3:2 water:isopropyl solution. Subsequently, 40 µl of 5 wt. % Nafion solution was added as the binder. The dispersion was made feasible through ultra-sonication of the sample for 30 min. As such prepared catalyst slurry was drop coated on the glassy carbon electrode (geometrical surface area: 0.07 cm²), which was subsequently dried at room temperature.

Catalyst slurry for ORR: In a typical process, 2 mg of the catalyst along with 8 mg of Vulcan carbon and 40 µl of the 5 wt. % Nafion solution were dispersed in 1 ml of water:isopropyl alcohol (3:2 v/v) mixture by ultra-sonicating for 1 h. 10 µl of the catalyst slurry was coated over the surface of the glassy carbon electrode (geometrical surface area: 0.196 cm²). The electrode was dried at room temperature and subjected for the electrochemical studies.

Rotating Ring Disk Electrode Study:

The Rotating Ring Disc Electrode (RRDE) technique was used for estimating the percentage of H₂O₂ formed and the number of electrons transferred during the ORR process. A Pt ring (0.1866 cm²) surrounded glassy carbon disc electrode of an area of 0.2475 cm² was used as the working electrode by keeping the ring potential at 0.60 V (V vs Hg/HgO). Hg/HgO was used as the reference electrode and a graphite rod was used as the counter electrode in the studies. This analysis has been performed in O₂ saturated 0.1 M KOH solution.

The mathematical equations used for the RRDE analysis are given below:

$$H_2O_2(\%) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}}$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}$$

where,

I_r - Ring current

I_d - Disc current

N - Collection efficiency of the ring electrode (0.37)

n - No of electrons

Calculation of bandgap from UV-visible absorption spectra:

The band gap is calculated by UV- Visible spectroscopy using the Tauc plot. By plotting the graph between $(\alpha h\nu)^{\frac{1}{n}}$ vs. photon energy ($h\nu$).⁵

where,

α - optical absorption coefficient

h - Plank's constant

ν - Frequency

n - Power factor ($n= 0.5$ for direct transitions)

The energy band gap value is calculated by extrapolating the straight-line part of the curves to the zero-absorption coefficient value.

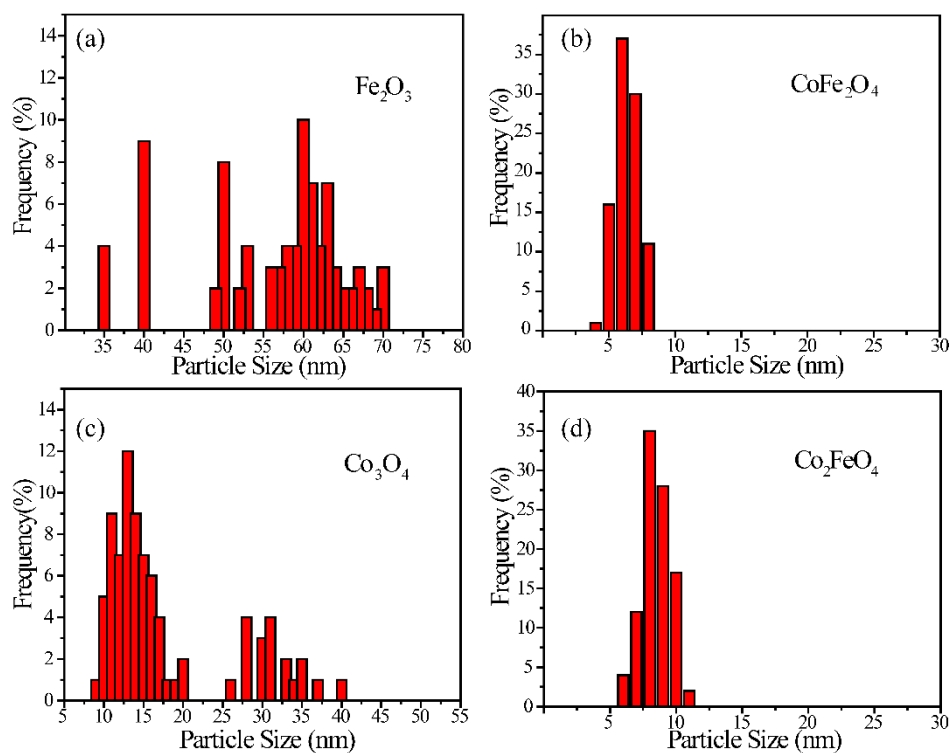


Fig. S1. The particle size distribution profiles of Fe_2O_3 (a), CoFe_2O_4 (b), Co_3O_4 (c), and Co_2FeO_4 (d) as calculated from the TEM analysis.

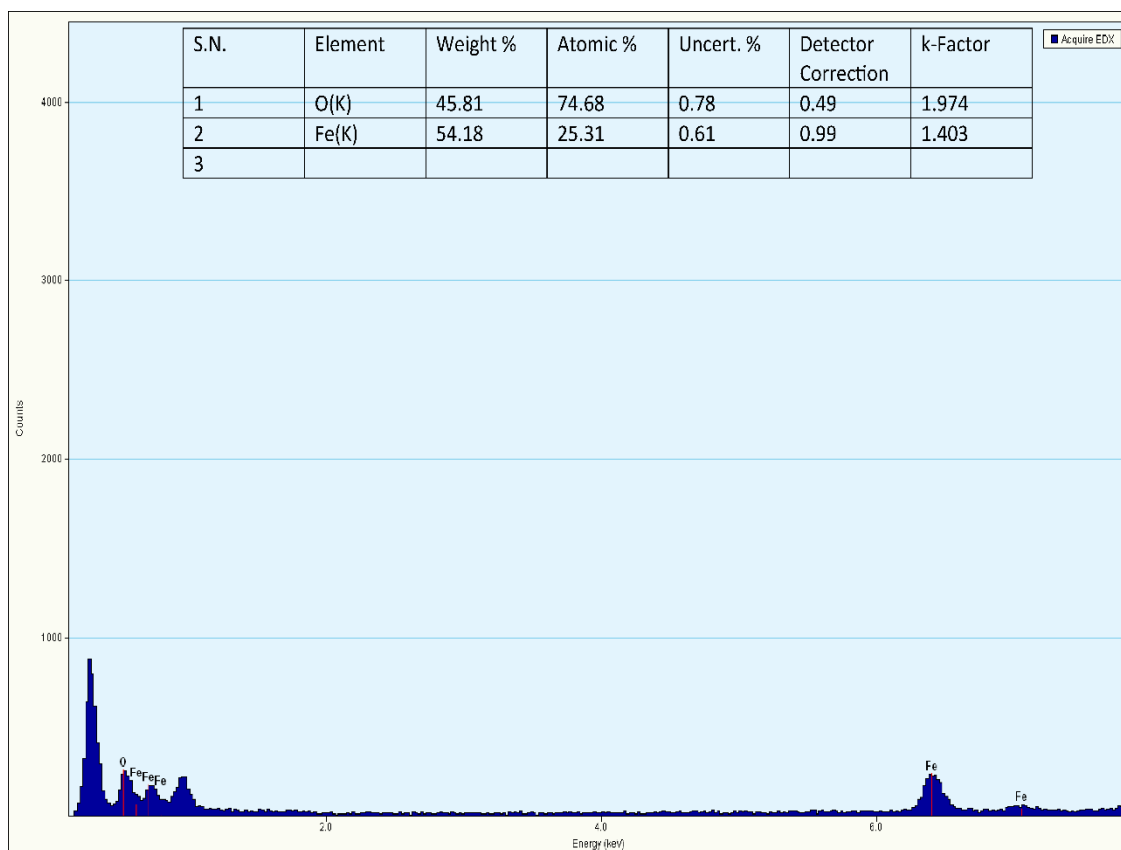


Fig. S2. EDAX of the Fe_2O_3 nanoparticles.

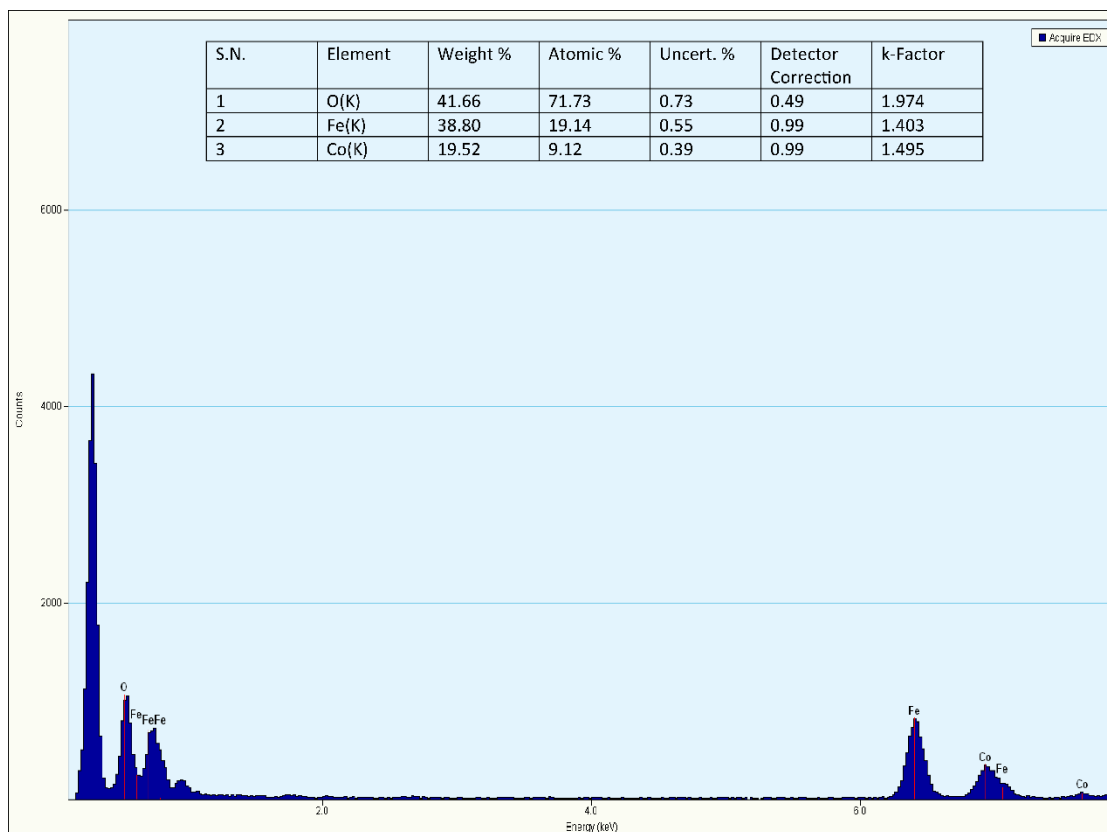


Fig. S3. EDAX of CoFe_2O_4 nanoparticles.

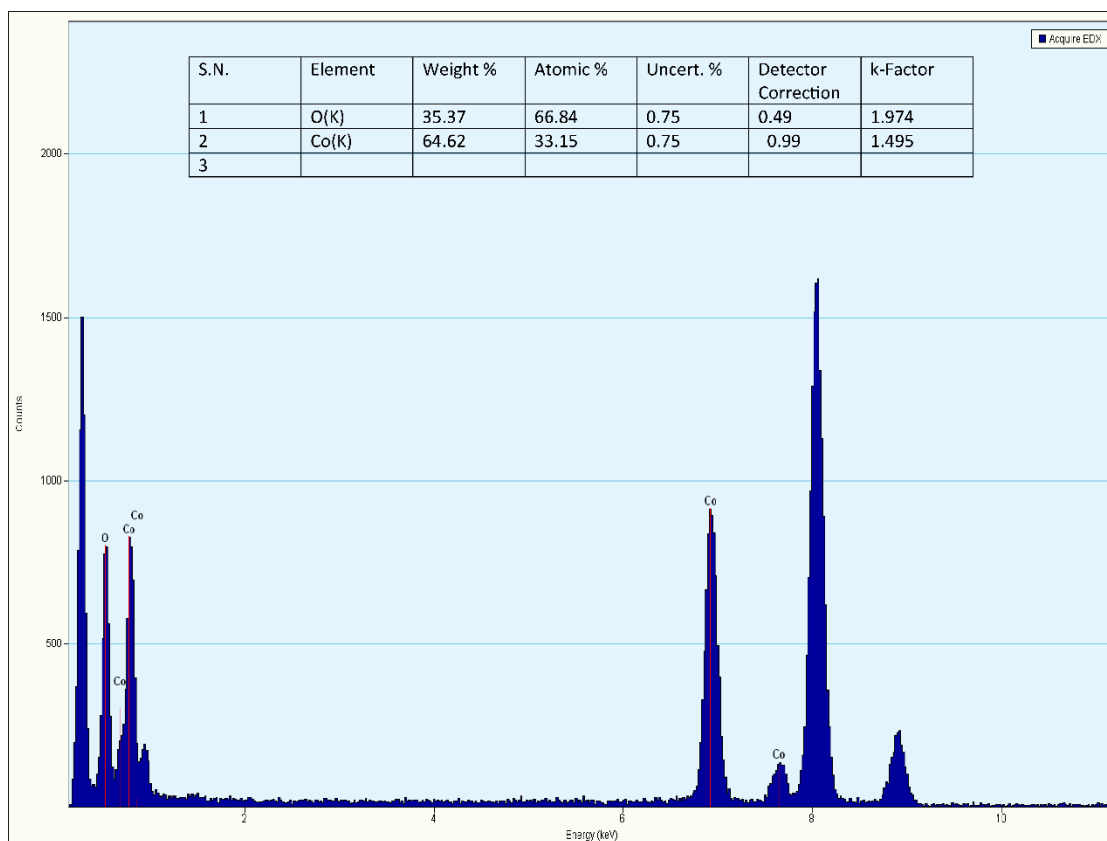


Fig. S4. EDAX of Co_3O_4 nanoparticles.

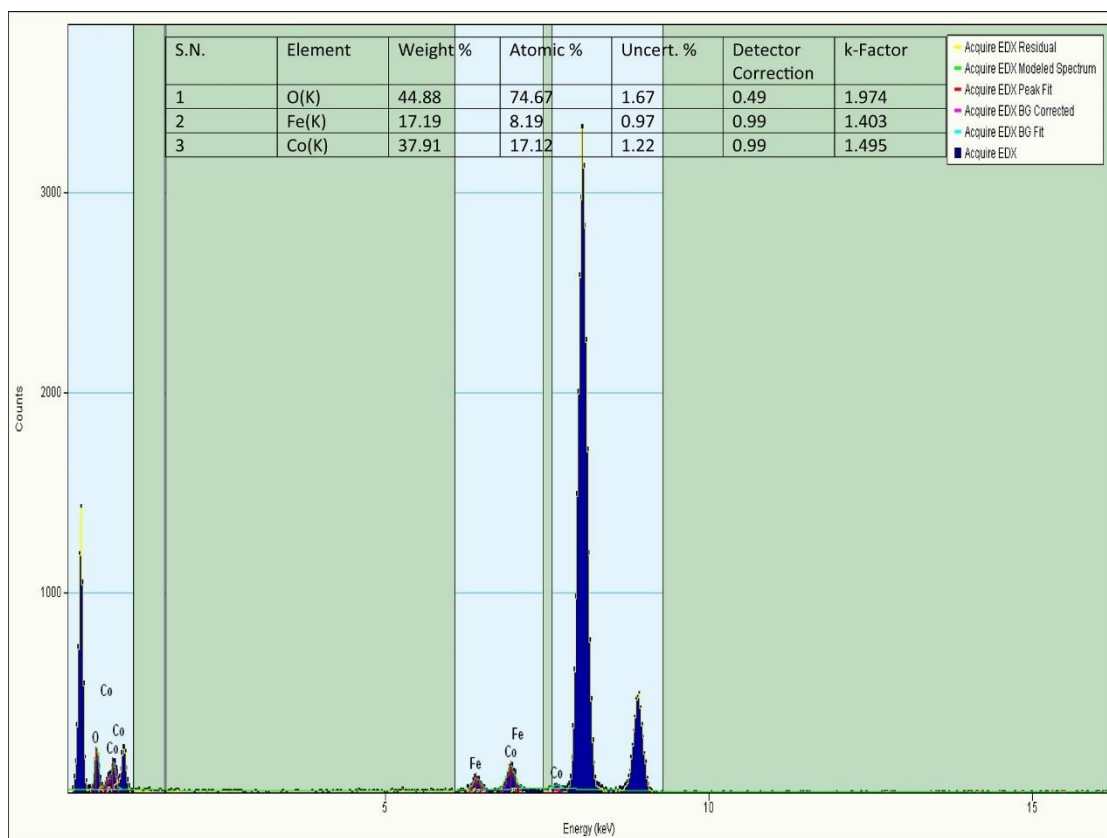


Fig. S5. EDAX of Co_2FeO_4 nanoparticles.

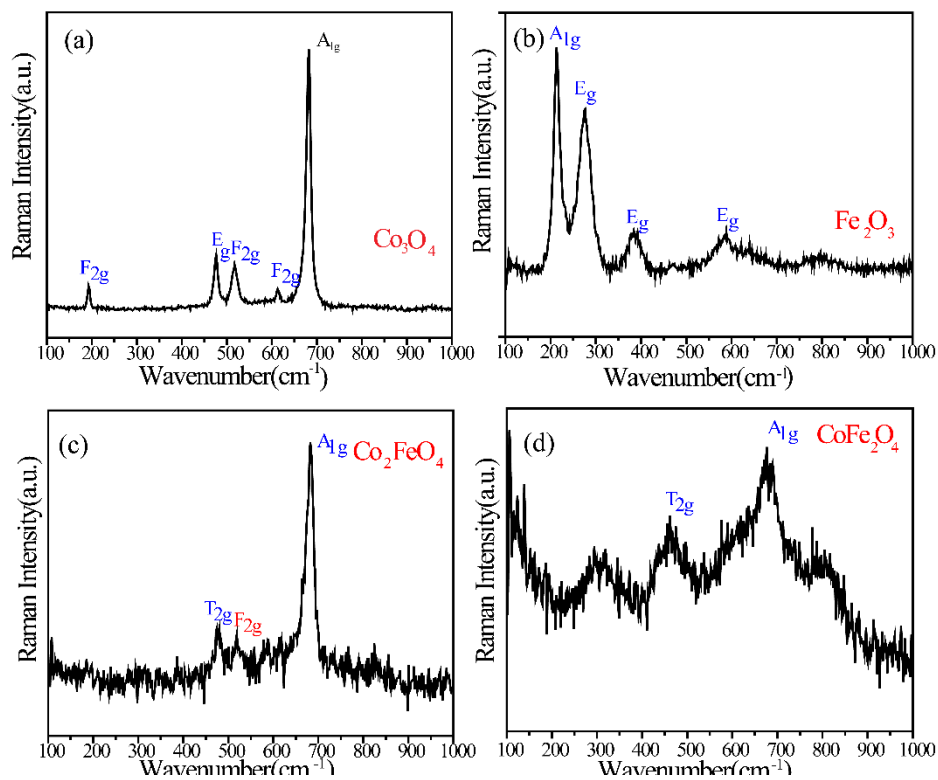


Fig. S6. Raman spectra of Co_3O_4 (a), Fe_2O_3 (b), Co_2FeO_4 (c), and CoFe_2O_4 (d).

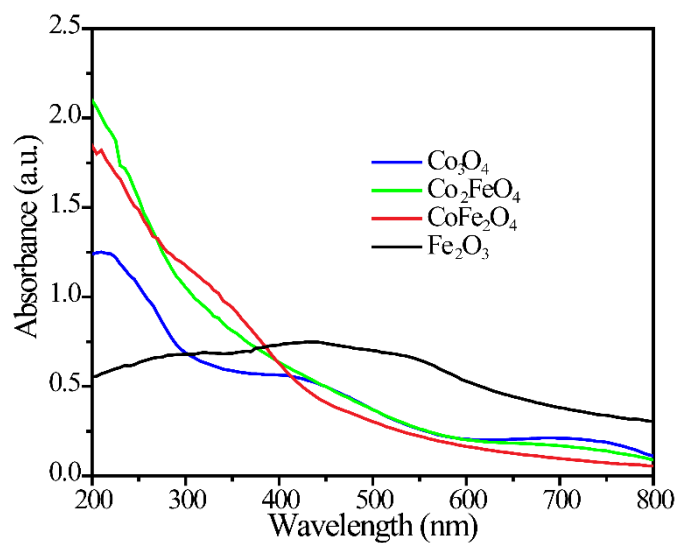


Fig. S7. UV-Visible spectra of the Fe_2O_3 , CoFe_2O_4 , Co_3O_4 and Co_2FeO_4 recorded using the water:ethanol solvent mixture.

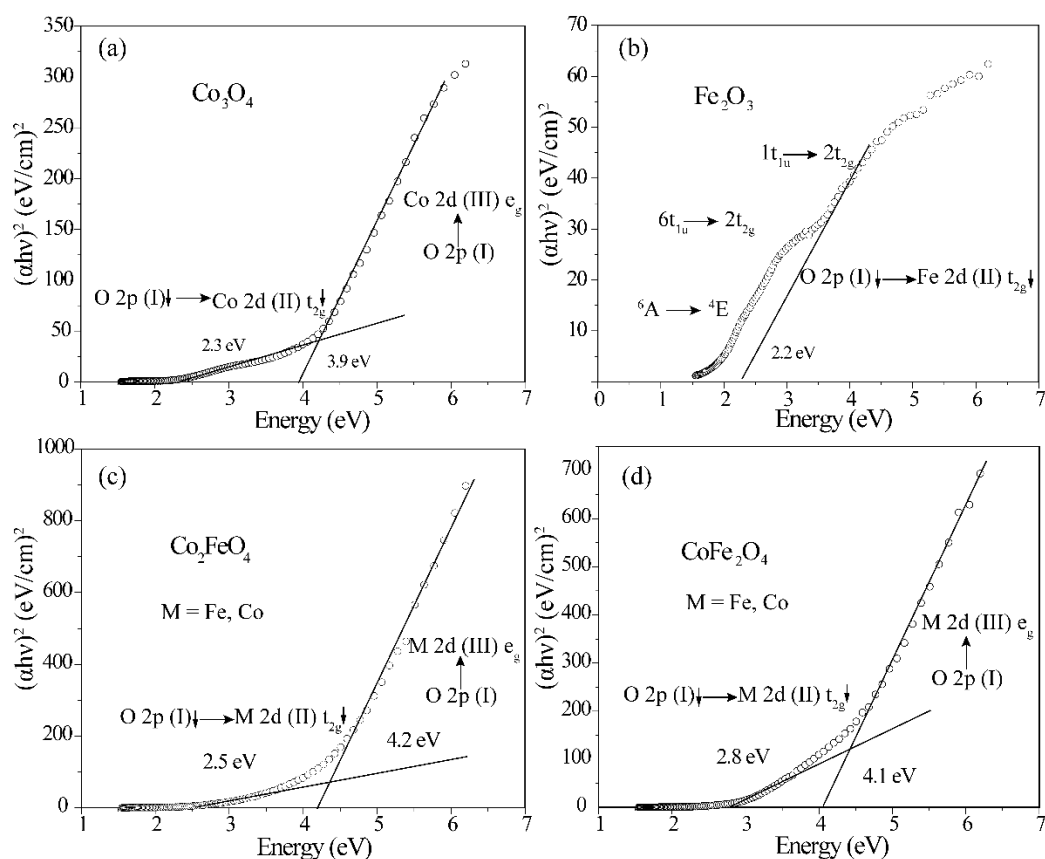


Fig. S8. Tauc plot of the Co_3O_4 , Fe_2O_3 , Co_2FeO_4 , and CoFe_2O_4 nanoparticles.⁶⁻⁹

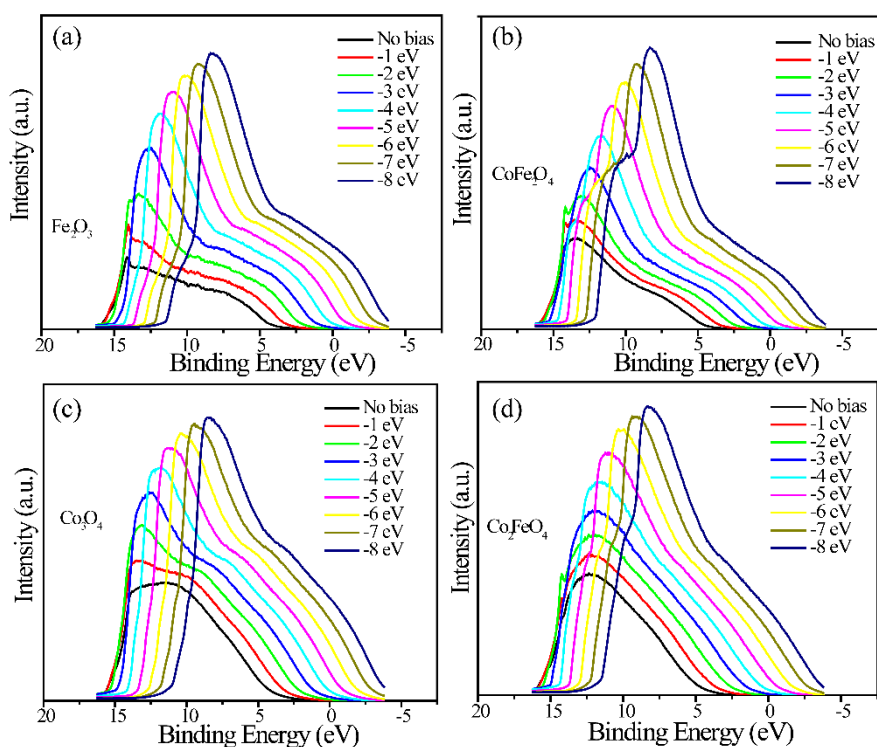


Fig. S9. Ultraviolet photoelectron spectra (UPS) of the Fe_2O_3 , CoFe_2O_4 , Co_2FeO_4 and Co_3O_4 nanoparticles.

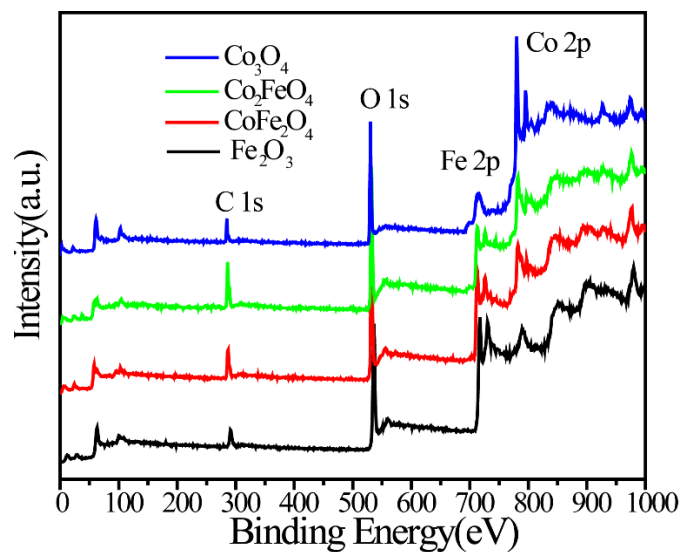


Fig. S10. Survey spectra of Co_3O_4 , Co_2FeO_4 , CoFe_2O_4 and Fe_2O_3 .

Table S1. Deconvoluted O 1s peak parameters of the Co_3O_4 , Co_2FeO_4 , CoFe_2O_4 and Fe_2O_3 nanoparticles.

S.N.	Nanoparticle	Peak	O_L	O_V	O_C
1	Co_3O_4	position	529.9	531.5	532.8
		height	145616.9	48842.8	10498.7
		width	1.1	1.5	1.2
		Area (%)	185701.4 (66.3 %)	78023.0 (27.8 %)	16050.3 (5.7 %)
2	Co_2FeO_4	position	530.8	532.3	533.0
		height	130563.5	80129.0	33767.8
		width	1.7	1.5	2.1
		area	242879.2 (54.2 %)	125254.9 (27.9 %)	79972.4 (17.8 %)
3	CoFe_2O_4	position	530.68	531.9	533.0
		height	119651.1	83609.2	29957.8
		width	1.7	2	2.5
		area	218238.6 (45.8 %)	179425.7 (37.7 %)	78060.6 (16.4 %)
4	Fe_2O_3	position	529.4	530.9	532.1
		height	229202.7	64652.0	22786.5
		width	1.2	1.4	2.0
		area	341243.8 (70.2 %)	96260.6 (19.8 %)	484899.4 (10.0 %)

Table S2. Deconvolute Co 2p and Fe 2p peak parameters of the Co_3O_4 , Co_2FeO_4 , CoFe_2O_4 and Fe_2O_3 nanoparticles.

S.N.	Metal Oxide	2p _{3/2} (eV)		2p _{1/2} (eV)		Satellite 1 (eV)	Satellite 2 (eV)
1	Co ₃ O ₄	Co ³⁺	779.8 (A=162432; W=1.6; H=94335.8)	Co ³⁺	794.8 (A=58622.2; W=1.6; H=36601.1)	786.5 (A=18545.3; W=2.5; H=5260.4)	803.6 (A=21249.3; W=2; H=7340.8)
		Co ²⁺	781.3 (A=296790.3; W=2.7; H=76977.4)	Co ²⁺	796.5 (A=83990.1; W=2.5; H=30701.8)	789.5 (A=17717.8; W=2.3; H=6642.3)	805.5 (A=6996.9; W=1.9; H=3517.2)
2	Co ₂ FeO ₄	Co ³⁺	780.0 (A=147928.7; W=2.5; H=50338.7)	Co ³⁺	795.8 (A=39840.6; W=2.5; H=14955.3)	784.7 (A=59912.2; W=3.7; H=15158.6)	802.1 (A=34540.3; W=3.2; H=7980.0)
		Co ²⁺	782.1 (A=65762.2; W=2.6; H=23860.3)	Co ²⁺	797.5 (A=35424.9; W=2.8; H=9496.3)	787.6 (A=67604.5; W=4.7; H=13521.2)	804.6 (A=19091.8; W=3.7; H=4250.5)
		Fe ²⁺	710.7 (A=135327.8; W=2.8; H=45106.4)	Fe ²⁺	723.8 (A=63302.9; W=3.2; H=14049.2)	718.2 (A=68578.4; W=5.1; H=12185.5)	733.0 (A=11242.4; W=2.5; H=3163.0)
		Fe ³⁺	713.2 (A=121275.1; W=3.7; H=26984.0)	Fe ³⁺	725.7 (A=48100.8; W=3.9; H=9787.6)		
3	CoFe ₂ O ₄	Co ³⁺	780.0 (A=128710.9; W=2.5; H=41233.0)	Co ³⁺	795.5 (A=41521.4; W=2.8; H=10600.5)	785.1 (A=70420.3; W=3.9; H=16997.7)	801.9 (A=28754.9; W=3.8; H=5522.7)
		Co ²⁺	782.1 (A=81191.2; W=3.0; H=25227.6)	Co ²⁺	796.7 (A=21976.7; W=2.5; H=8258.3)	788.0 (A=90033.4; W=5.2; H=15395.7)	803.4 (A=19170.9; W=3.4; H=4106.1)
		Fe ²⁺	710.7 (A=224118.9; W=2.9; H=71866.5)	Fe ²⁺	724.0 (A=126612.9; W=3.5; H=28959.8)	718.4 (A=105608.0; W=5.2; H=19325.6)	732.7 (A=20947.2; W=3.8; H=4672.3)
		Fe ³⁺	713.5 (A=133193.4; W=3.4; H=33981.2)	Fe ³⁺	726.5 (A=66133.7; W=3.9; H=12939.2)		
4	Fe ₂ O ₃	Fe ²⁺	709.1 (A=243638.9; W=2.5; H=91565.8)	Fe ²⁺	722.7 (A=146835.2; W=3.0; H=38769.2)	716.9 (A=161404.6; W=6.6; H=22815.4)	731.1 (A=40813.6; W=4.5; H=8498.8)

		Fe ³⁺	711.4 (A=174102.9; W=3.2; H=49390.3)	Fe ³⁺	725.0 (A=104031.7; W=4; H=21140.7)		
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Table S3. Bandgap (E_g), conduction band (CB), valence band (VB) and work function (ϕ) values of the Co₃O₄, Co₂FeO₄, CoFe₂O₄ and Fe₂O₃ nanoparticles. (Diff. OER: Potential difference from oxygen electrode potential; Diff. ORR: Potential difference from oxygen reduction electrode potential).

S.N.	Metal Oxide	Band Gap (eV)	C B (V vs NHE)	VB (V vs NHE)	Work function (ϕ) (eV)
1	Co ₃ O ₄	2.3	0.23 (Diff. OER*: ~ 1.0 eV)	2.53 (Diff. ORR*: ~ 1.3 eV)	5.6
2	Co ₂ FeO ₄	2.6	0.08 (Diff. OER*: ~ 1.15 eV)	2.58 (Diff. ORR*: ~ 1.35 eV)	6.2
3	CoFe ₂ O ₄	2.8	-0.11 (Diff. OER*: ~ 1.34 eV)	2.69 (Diff. ORR*: ~ 1.46 eV)	6.3
4	Fe ₂ O ₃	2.2	0.24 (Diff. OER*: ~ 0.9 eV)	2.44 (Diff. ORR*: ~ 1.21 eV)	6.1

DFT Method:

Plane-wave density functional theory (DFT) calculations as implemented in Vienna ab initio simulation package (VASP-5.3.5 version) were performed to calculate the oxygen vacancy formation energy for the Co₃O₄ and CoFe₂O₄ catalysts.¹⁰ Projector augmented wave method (PAW) was used for describing the interactions between the electrons and ions.¹¹ An energy cut-off of 396 eV was applied for truncating the plane-wave basis set. Perdew-Burke-Ernzerhof (PBE) exchange-correlation function developed by Perdew *et al.*, was used for all the DFT calculations.¹² Spin-polarized set-up was used, along with Hubbard U_{eff} parameters for Co and Fe of value 3.32 eV and 5.3 eV, respectively.¹³⁻¹⁴ The CoFe₂O₄ crystal geometry was obtained from the materials project database, whereas the Co₃O₄ crystal was obtained by replacing the

Fe with Co and performing lattice parameter optimization.¹⁵ Subsequently, the Co_3O_4 and CoFe_2O_4 bulk crystals were cleaved along the (001) direction to obtain the $\text{Co}_3\text{O}_4(001)$ and $\text{CoFe}_2\text{O}_4(001)$ surfaces. The $\text{Co}_3\text{O}_4(001)$ and $\text{CoFe}_2\text{O}_4(001)$ surface 3x3 supercell slabs were modelled using a slab of four Co(III)/Fe(III) atomic layers and three Co(II) atomic layers, having chemical formula $\text{Co(II)}_6\text{Co(III)}_{16}\text{O}_{32}$ and $\text{Co(II)}_6\text{Fe(III)}_{16}\text{O}_{32}$, as shown in Fig. S6. Both the bare $\text{Co(II)}_6\text{Co(III)}_{16}\text{O}_{32}$ and $\text{Co(II)}_6\text{Fe(III)}_{16}\text{O}_{32}$ (001) surface slabs have an overall formula charge of - 4. In order to balance the formal charge and to mimic the experimental OER condition, both the top and bottom surfaces of the $\text{Co}_3\text{O}_4(001)$ and $\text{CoFe}_2\text{O}_4(001)$ surface slabs were modified with 4H^+ , 2OH^- and $2\text{H}_2\text{O}$, as has been suggested by Plaisance *et al.*¹⁶ The $\text{Co}_3\text{O}_4(001)$ and $\text{CoFe}_2\text{O}_4(001)$ surfaces have been shown in Fig. 9(a) and 9(b). Monkhorst-Pack k-point mesh of $2 \times 2 \times 1$ and Gaussian smearing of 0.01 eV was used.¹⁷ For all the geometry optimization calculations, the bottom four atomic layers were kept fixed to their bulk configurations.

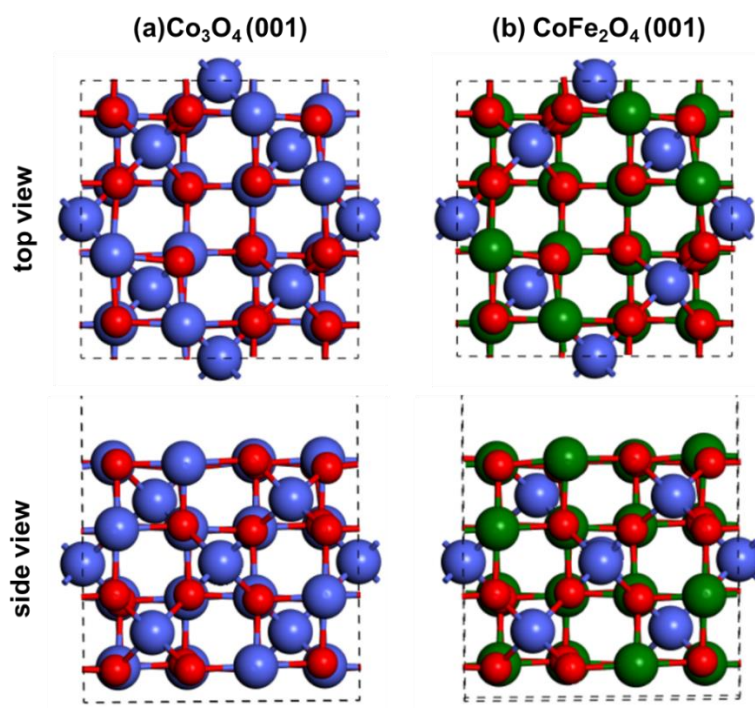


Fig. S11. $\text{Co}_3\text{O}_4(001)$ and $\text{CoFe}_2\text{O}_4(001)$ surfaces as cleaved from bulk geometry. Color code: Co (blue), Fe (green), O (red) and H (white).

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