

Tuning of Cationic Distribution in “Partially Inversed” Cobalt Ferrite Spinel Nanocubes via Nitrogen-doped Graphene Oxide Support for Enhanced Bifunctional Oxygen Electrocatalysis

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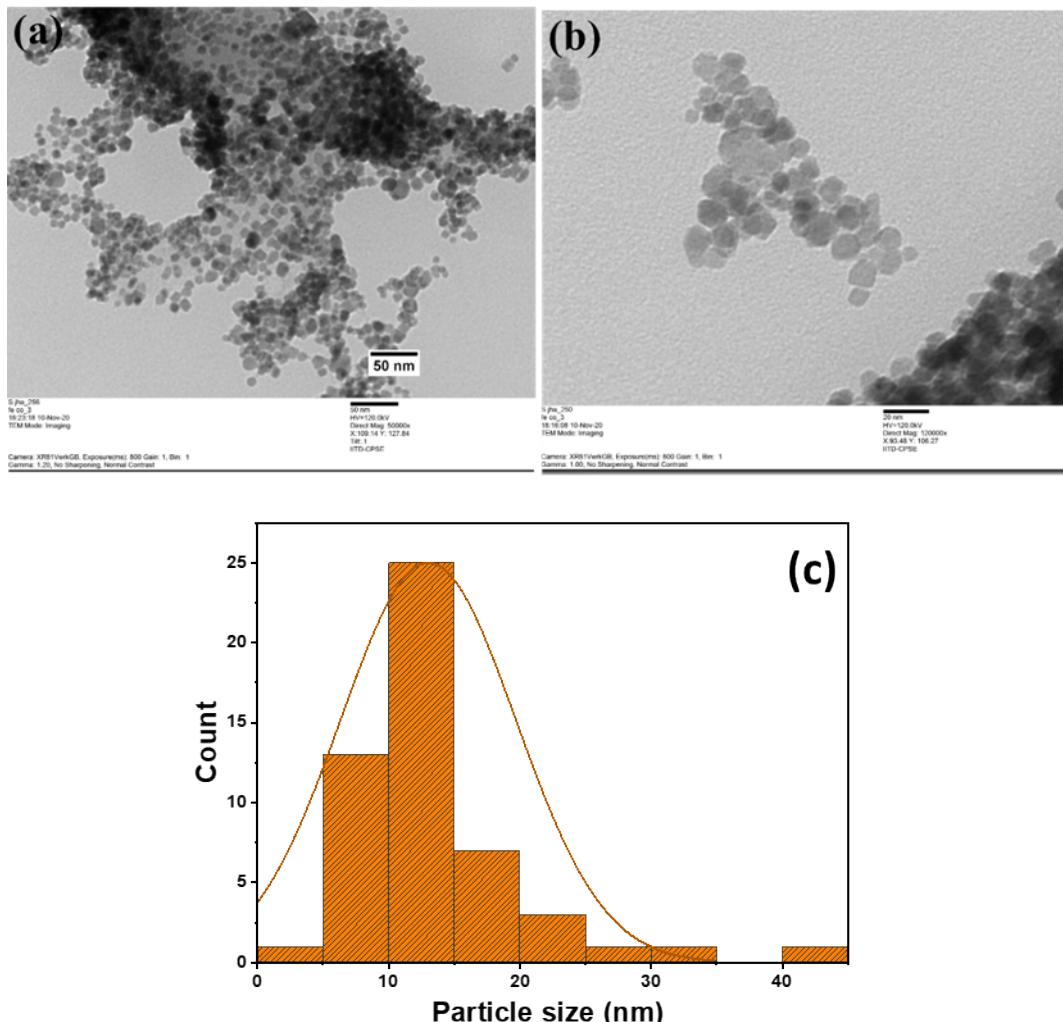


Fig. SI-1. TEM images for CoFe_2O_4 with scale bar (a) 50 nm and (b) 20 nm and (c) size distribution histogram of CoFe_2O_4 .

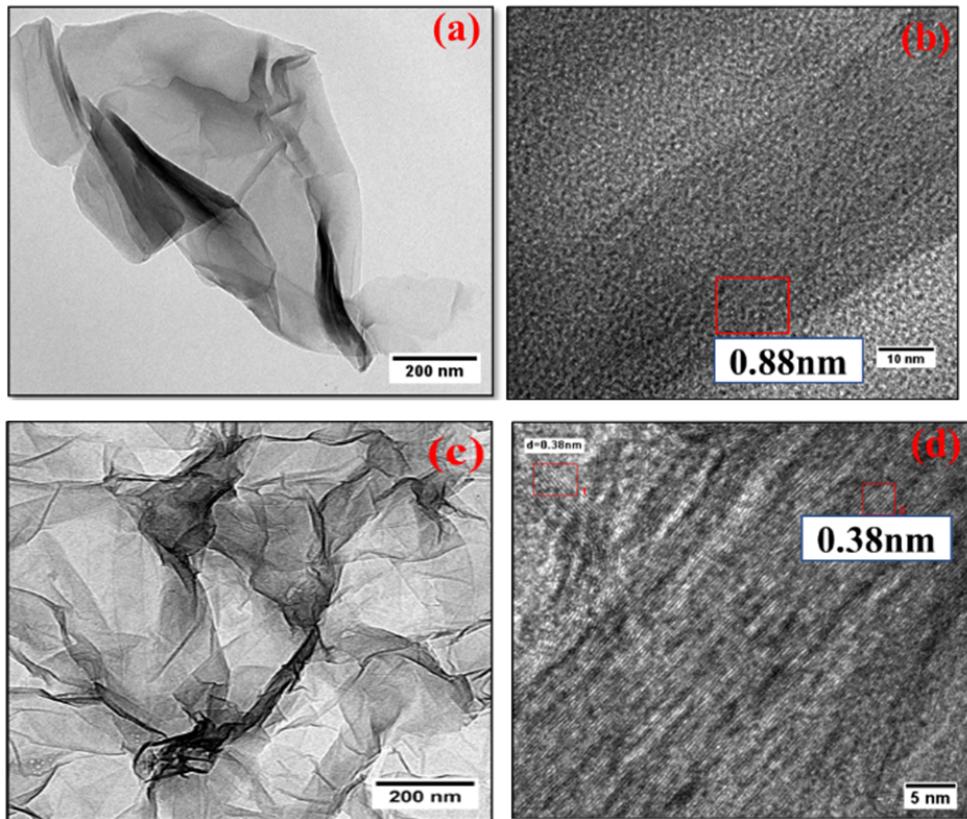


Fig. SI-2. TEM and HRTEM images of (a, b) GO, and (c, d) NGO. The number in the white background depicts the fringe spacings.

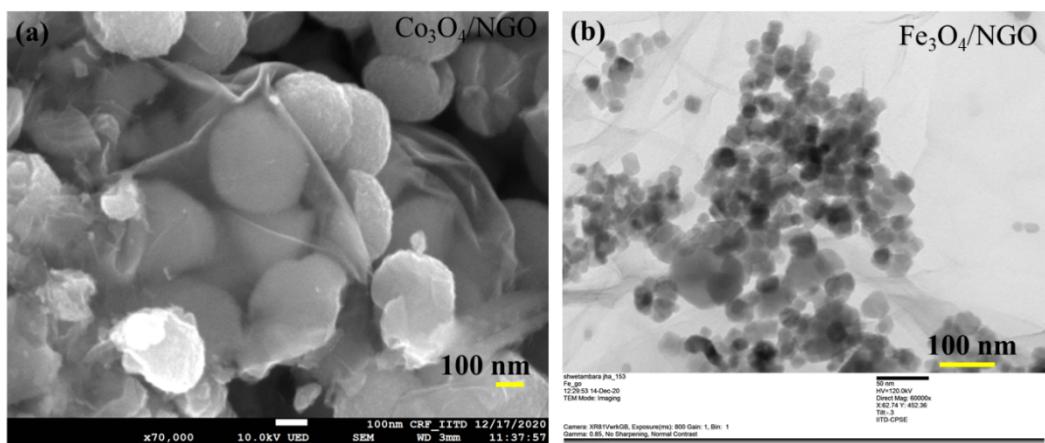


Fig. SI-3. TEM Images for (a) $\text{Co}_3\text{O}_4/\text{NGO}$ and (b) $\text{Fe}_3\text{O}_4/\text{NGO}$.

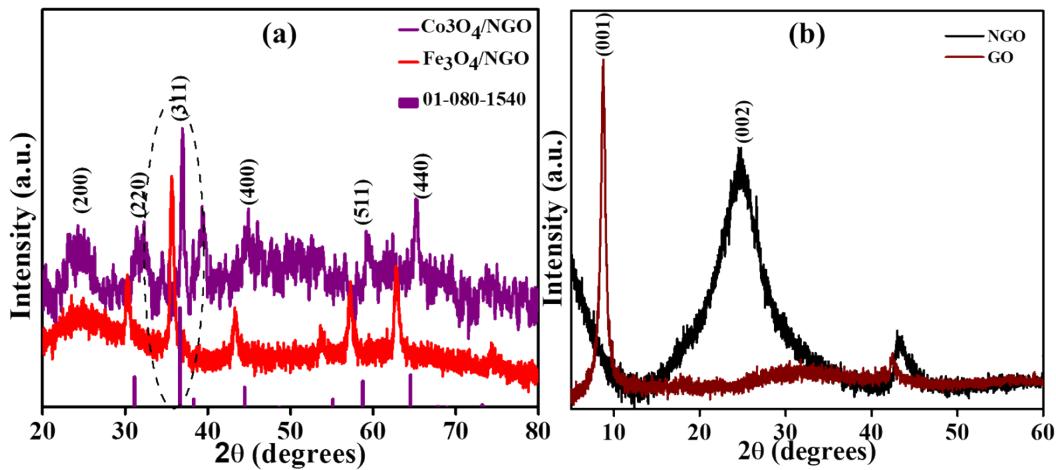


Fig. SI-4. (a) Overlay of XRD patterns of as-synthesized $\text{Co}_3\text{O}_4/\text{NGO}$, $\text{Fe}_3\text{O}_4/\text{NGO}$ and NGO and (b) the XRD pattern of GO and NGO.

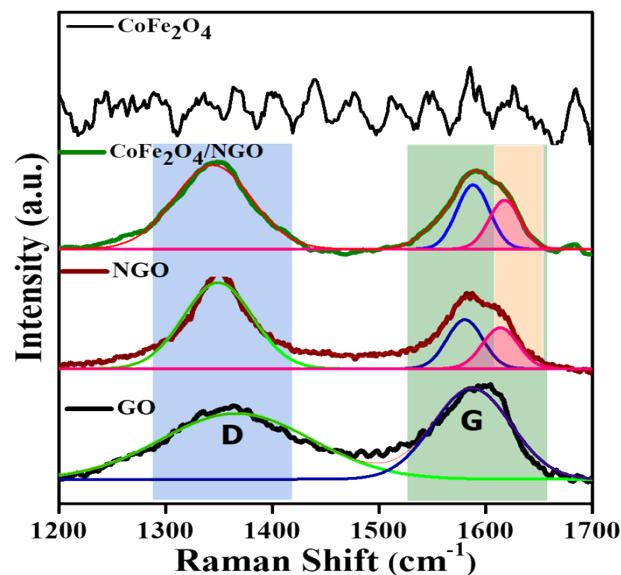


Fig. SI-5. Zoomed and deconvoluted view of Raman spectra of as synthesized CoFe_2O_4 , $\text{CoFe}_2\text{O}_4/\text{NGO}$, NGO and GO .

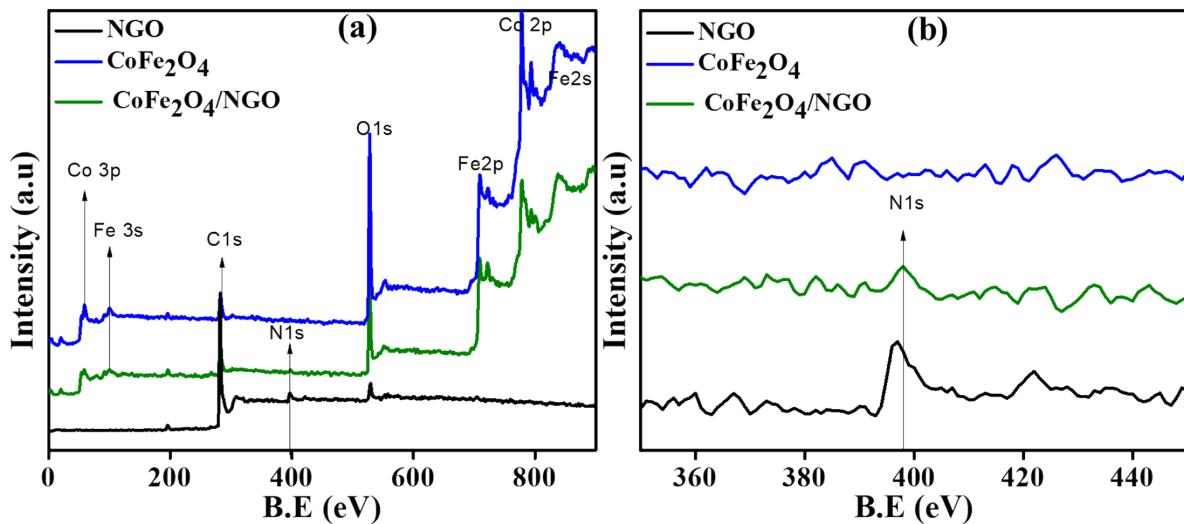


Fig. SI-6. (a) Survey XPS spectra of the samples showing the presence of Co, Fe, N, O, and C, (b) and (b) zoom view of image (a) in the range of (350 eV -450 eV).

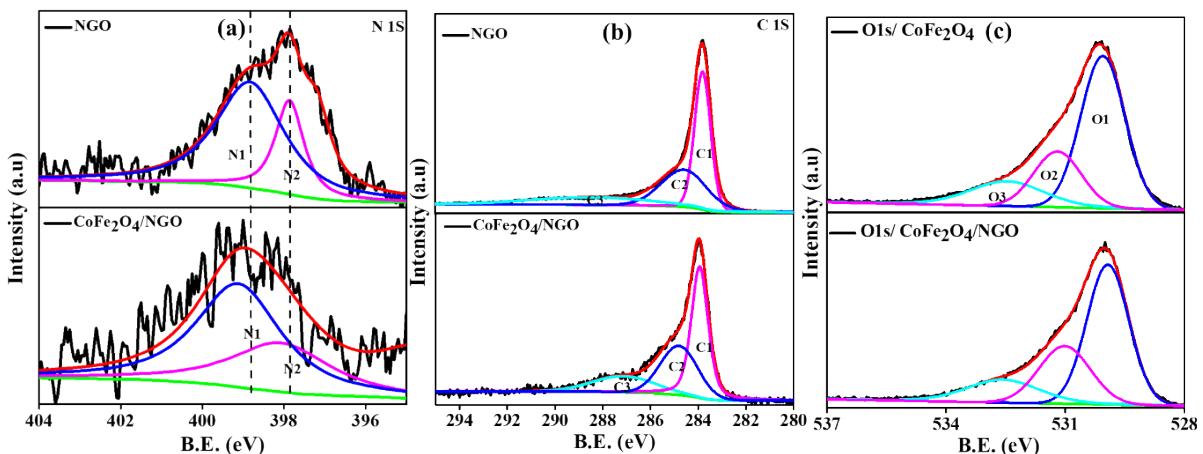


Fig. SI-7. XPS spectra of (a) N 1s, (b) C 1s, and (c) O 1s for CoF₂O₄ and CoFe₂O₄/NGO.

Table SI-1. Summary of the composition data for the catalysts on the basis of XPS analysis.

XPS peak/Sample	CoFe ₂ O ₄		CoFe ₂ O ₄ /NGO	
	O _h	T _h	O _h	T _h
Co 2p _{3/2} (eV)	779.84	781.1	777.62	779.4
Co 2p _{1/2} (eV)	796.8	794.95	793	794.42
Occupancy (%)	59	41	71	29
Fe 2p _{3/2} (eV)	708.94	711.41	707.85	709.79
Fe 2p _{1/2} (eV)	722.24	723.74	718.16	722.96
Occupancy (%)	49	51	45	55

N 1s (eV)	-	-	398.13	399.17
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Table SI-2. Composition data for the catalysts based on XANES analysis.

Samples	Co K edge	Fe K edge	Fe K edge	Reduced X^2	% Occupancy of Fe	
	E_0 (eV)	E_0 (eV)	Centroid (eV)		Oh	Th
CoFe ₂ O ₄	7709	7120	7114.65	0.0006	47	53
CoFe ₂ O ₄ /NGO	7714	7122	7117.97	0.0008	41	59

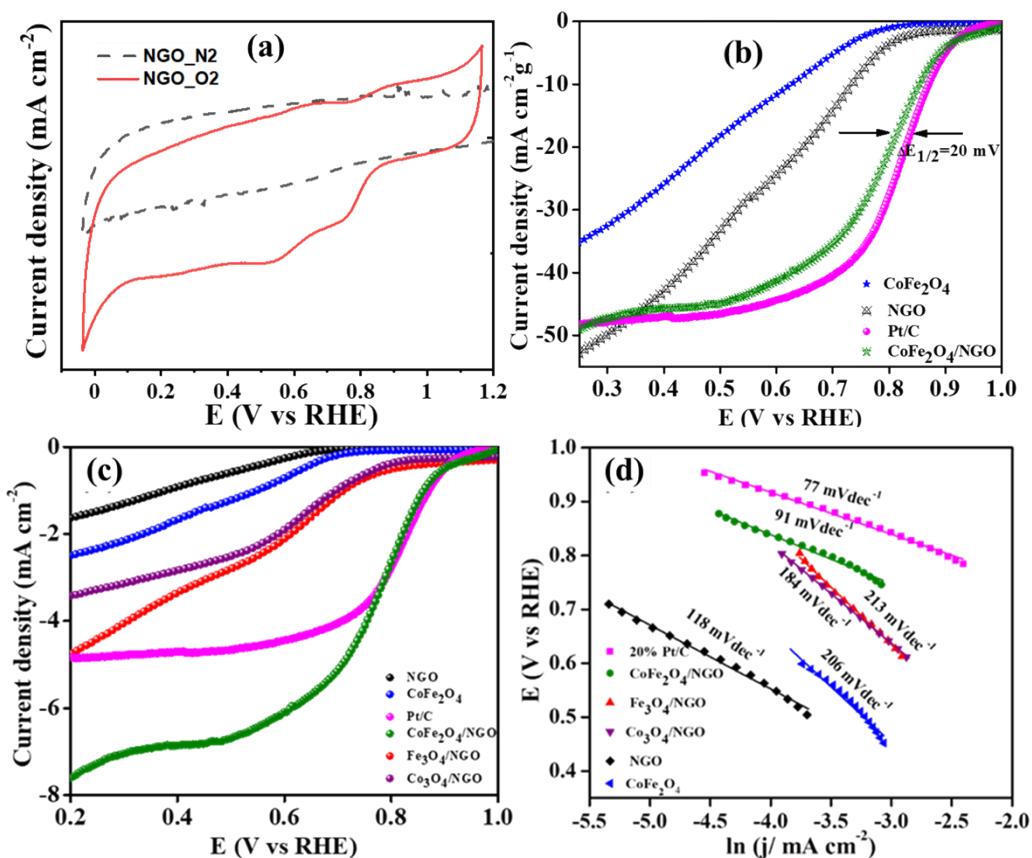


Fig. SI-8. (a) CV curve in N₂ and O₂ saturated 0.1 M KOH for NGO (b) comparison of mass normalized LSV at 1600 rpm for as synthesized materials. (c) LSV comparison of the crafted samples at 1600 rpm in O₂ saturated 0.1 M KOH and (d) Mass transfer corrected Tafel slopes for as synthesized materials.

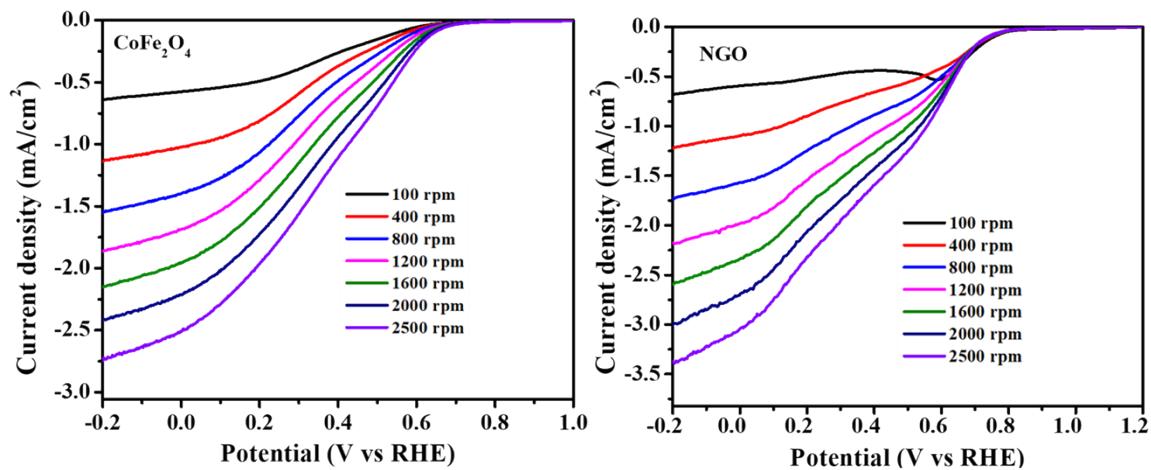


Fig. SI-9. LSV curves at different rotation rates for a) CoFe_2O_4 and b) NGO.

Fig. SI-10. LSV of $\text{CoFe}_2\text{O}_4/\text{NGO}$ in O_2 saturated 0.1 M KOH from 100 to 1600 rpm disk current and ring current.

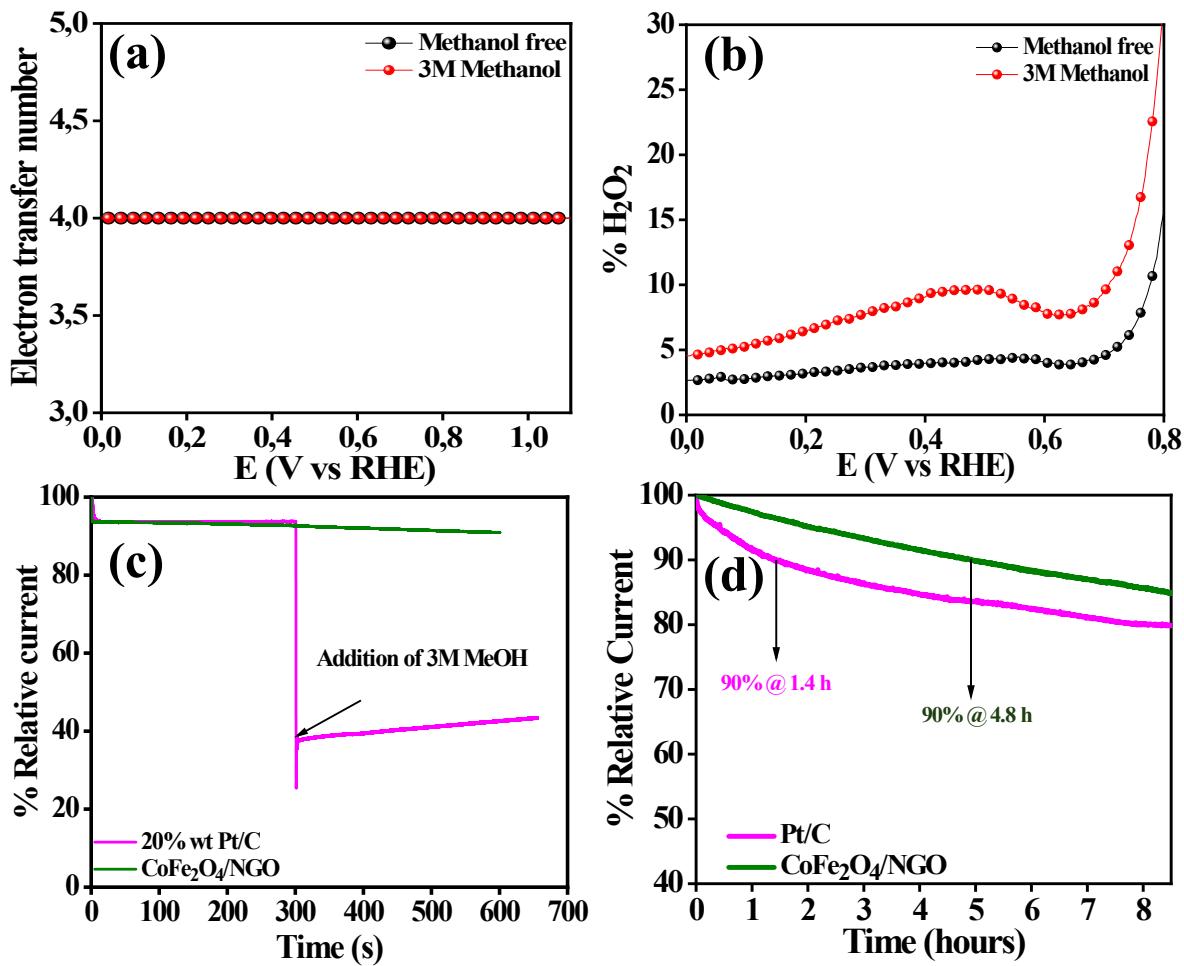


Fig. SI-11. Effect of methanol addition on (a) ' n ' and (b) '% H_2O_2 ' generated during ORR for $CoFe_2O_4/NGO$ in O_2 saturated 0.1 M KOH. (c) Methanol tolerance tests via i - t curve, and (d) ORR stability test for 8 h via chronoamperometry at 0.82 V vs RHE.

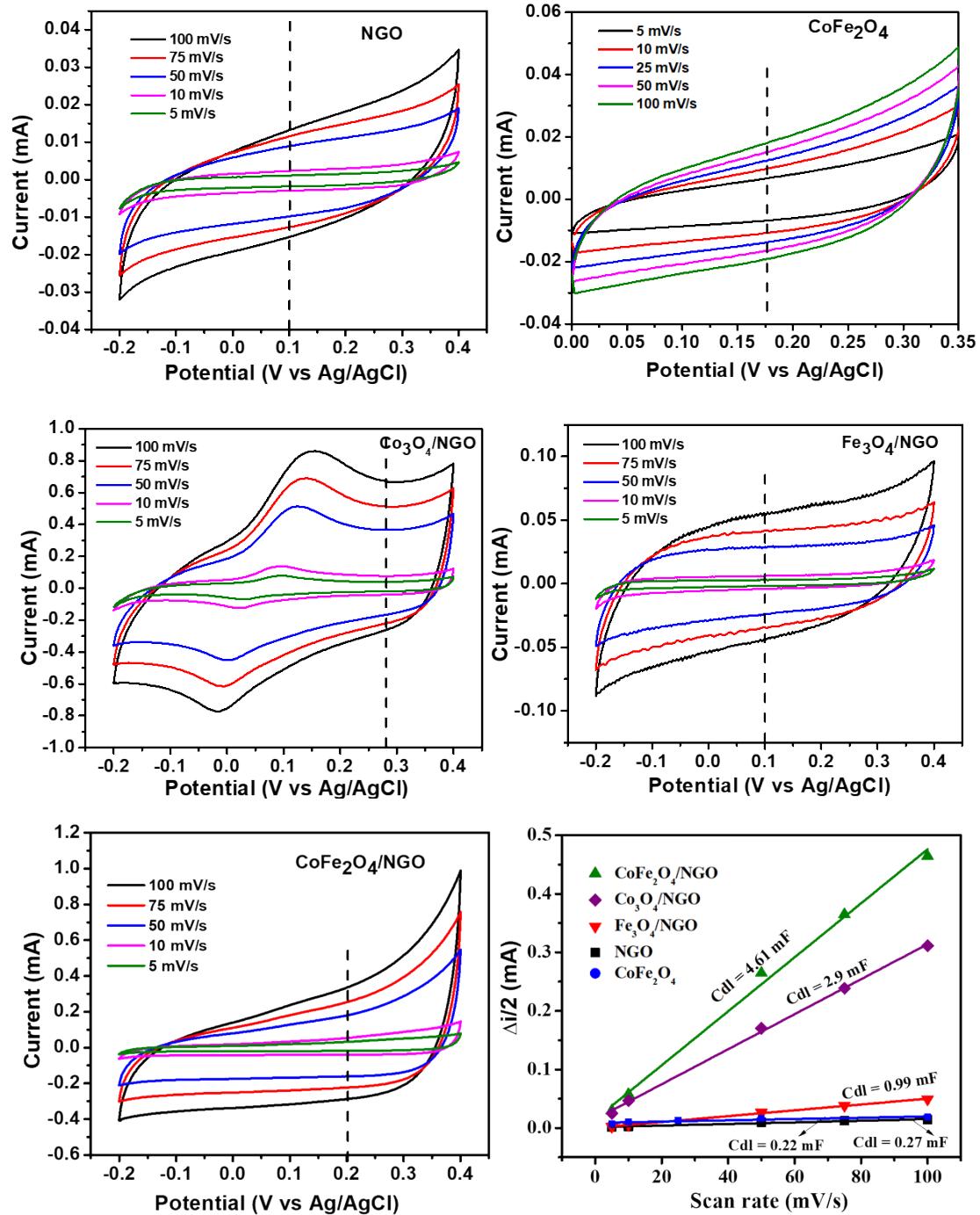


Fig. SI-12. The CVs at different scan rates for the calculation of C_{dl} and comparison of C_{dl} for the crafted materials.

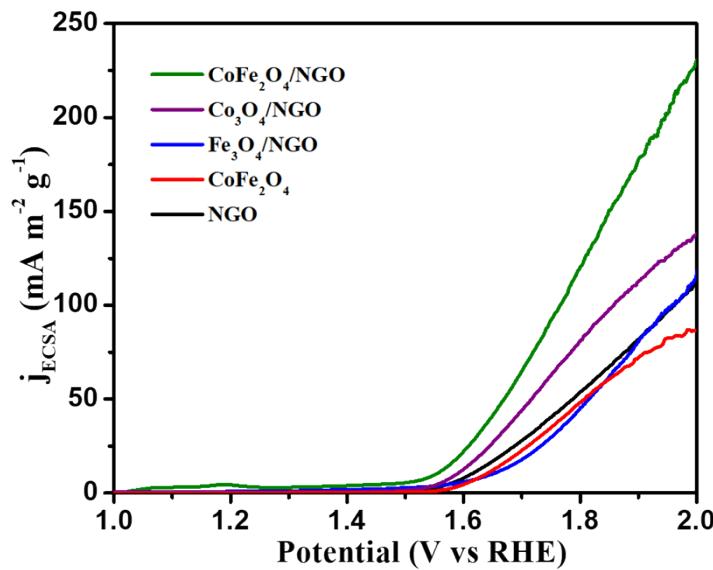


Fig. SI-13. The comparison of ECSA normalized LSV for the as synthesized materials for OER activity comparison in 1 M KOH at 10 mV/s.

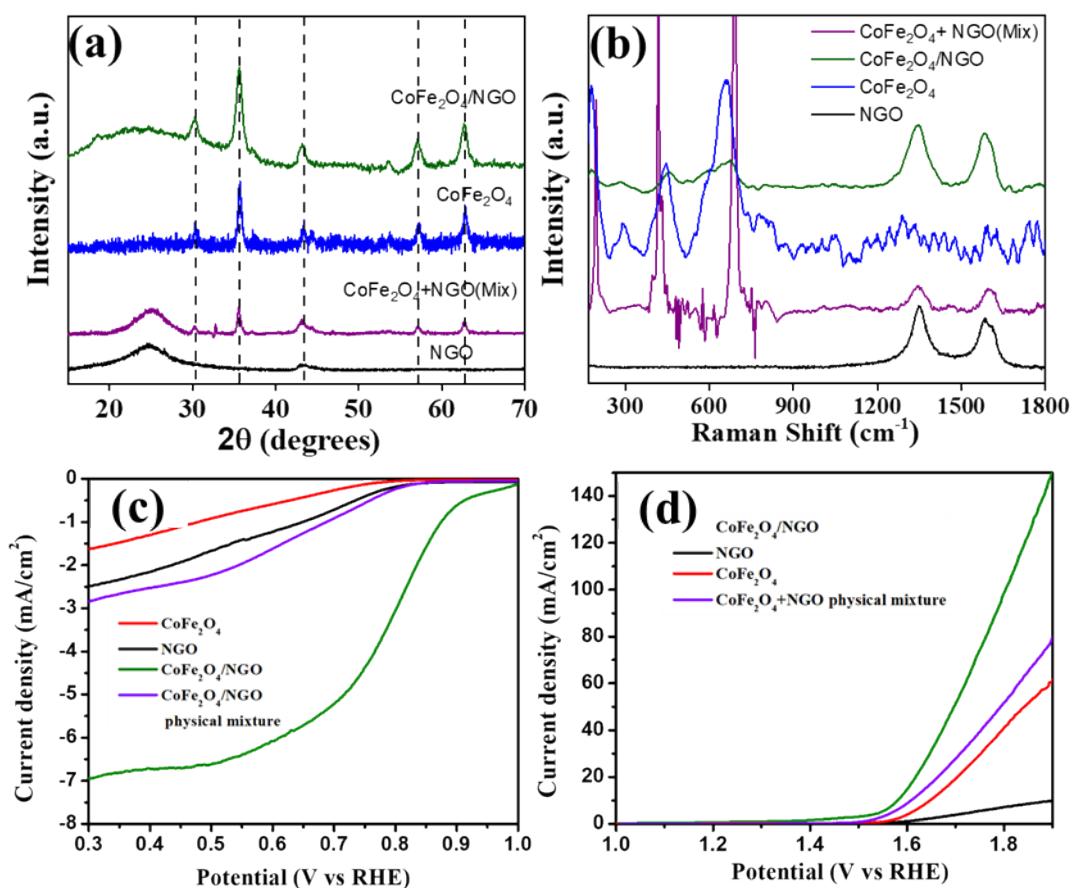


Fig. SI-14. The comparison of a) PXRD pattern, b) Raman spectra, c) RDE polarization curves for ORR in 0.1 M KOH, and d) LSV curves for OER in 1 M KOH for individual components as well as physical mixture of CoFe_2O_4 and NGO with $\text{CoFe}_2\text{O}_4/\text{NGO}$.

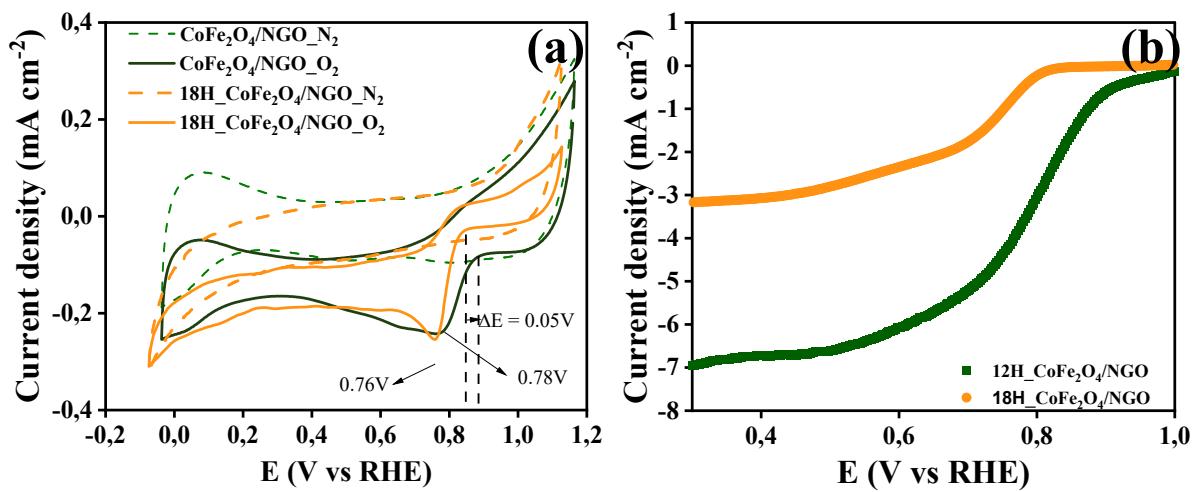


Fig. SI-15: Comparison of catalytic performance of materials synthesized in 12- and 18-hours hydrothermal treatment (a) cyclic voltammetry experiment in O_2 (solid line) N_2 (dotted line) and (b) LSV of as-synthesized catalyst.

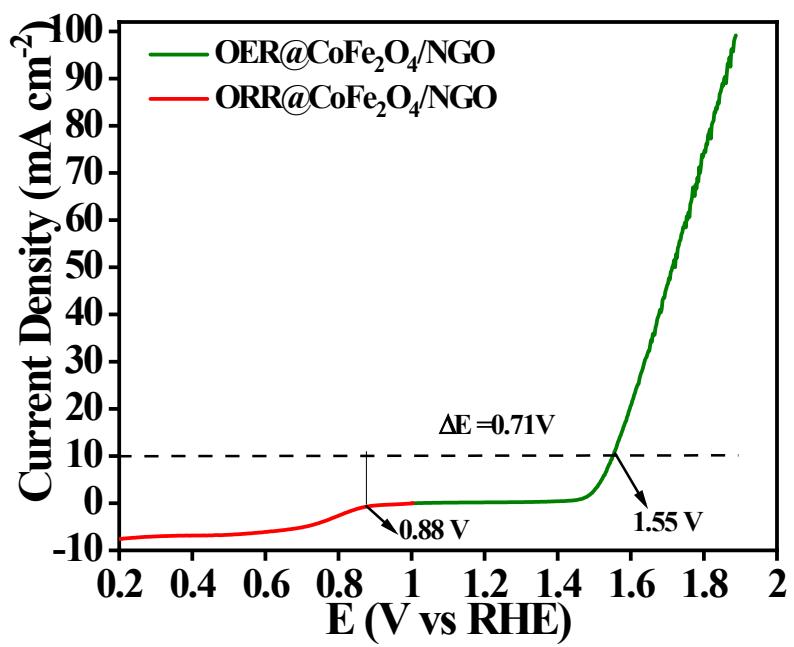


Fig. SI-16. The bifunctional oxygen electrocatalytic activity in terms of ΔE for $\text{CoFe}_2\text{O}_4/\text{NGO}$.

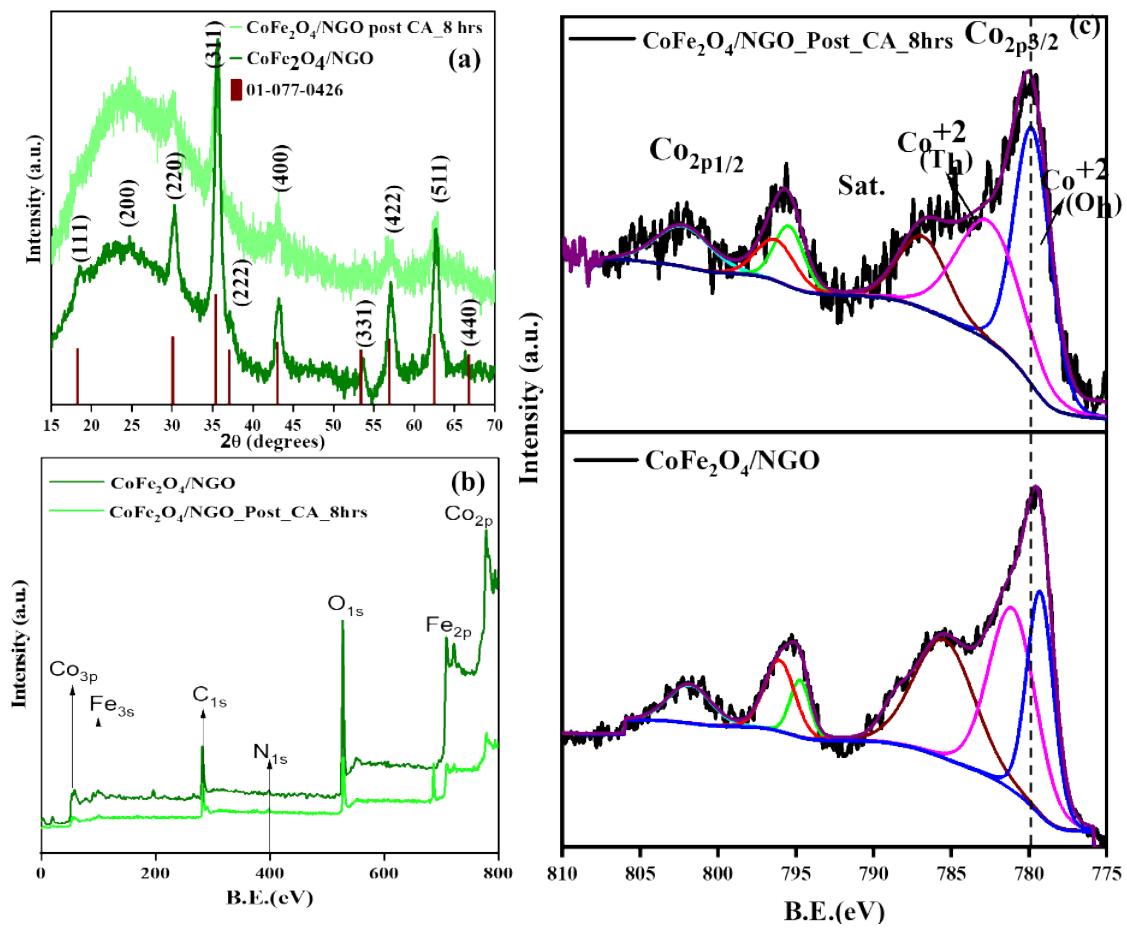


Fig. SI-17. Analysis of catalyst $\text{CoFe}_2\text{O}_4/\text{NGO}$ in O_2 saturated 0.1M KOH before and after 8 hours chrono-amperometry runs (a) XRD, (b) XPS survey spectra and (c) deconvoluted spectra of Co 2p.

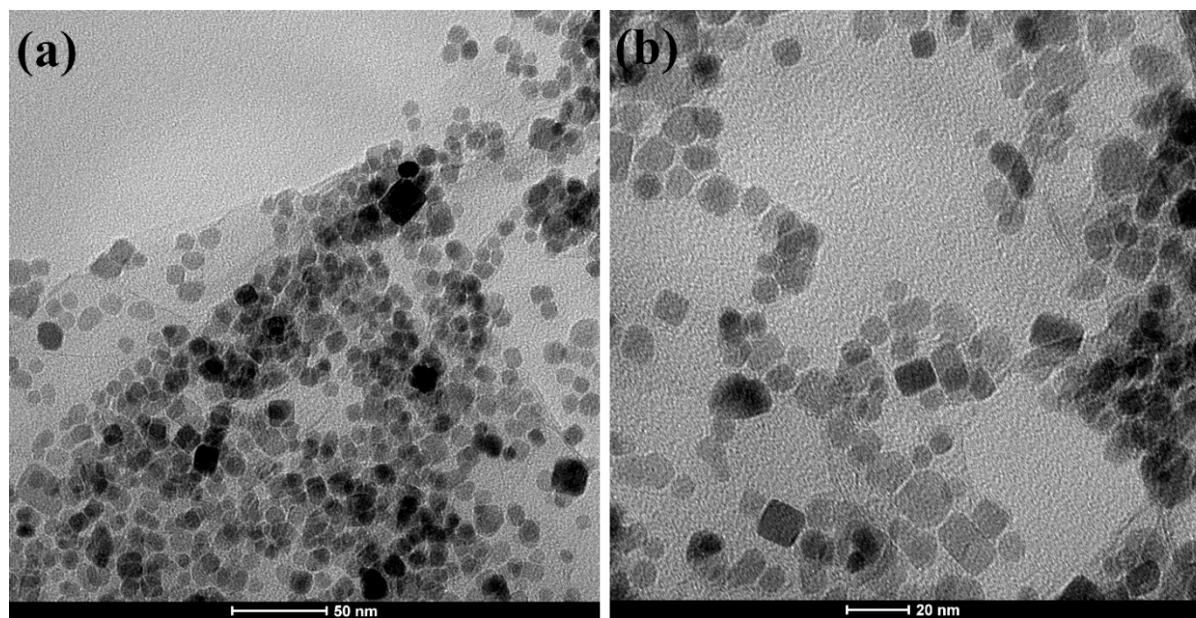


Fig. SI-18. HR TEM images at scale bar (a) 50 nm and (b) 20 nm) for $\text{CoFe}_2\text{O}_4/\text{NGO}$ after 8 hours chrono-amperometry runs in O_2 saturated 0.1 M KOH electrolyte.

