Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Mechanistic role of support-catalyst interface in electrocatalytic water reduction by Co_3O_4 supported nanocarbon florets

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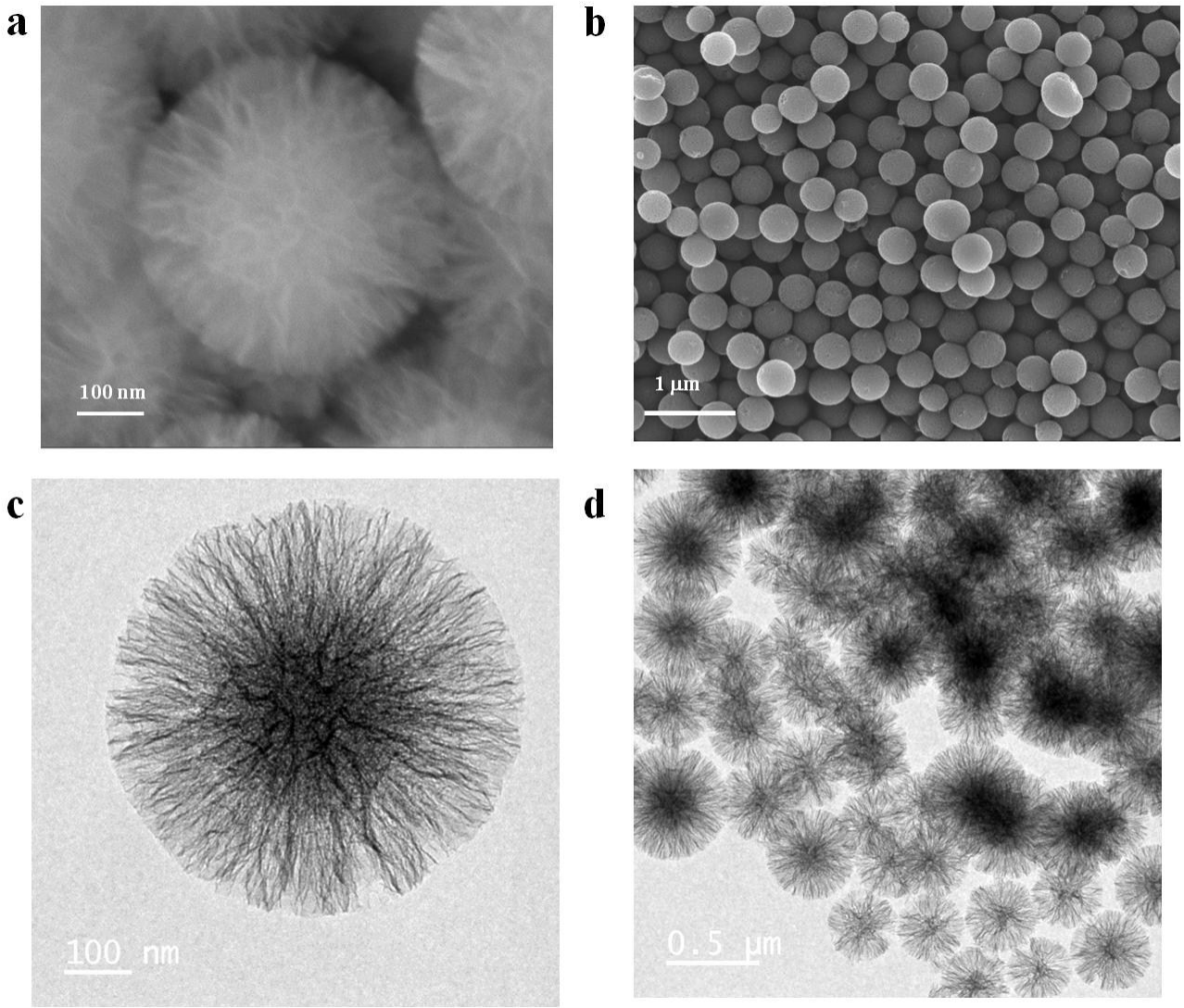


Figure S1. (a,b) SEM images and (c,d) TEM image of DFNS.

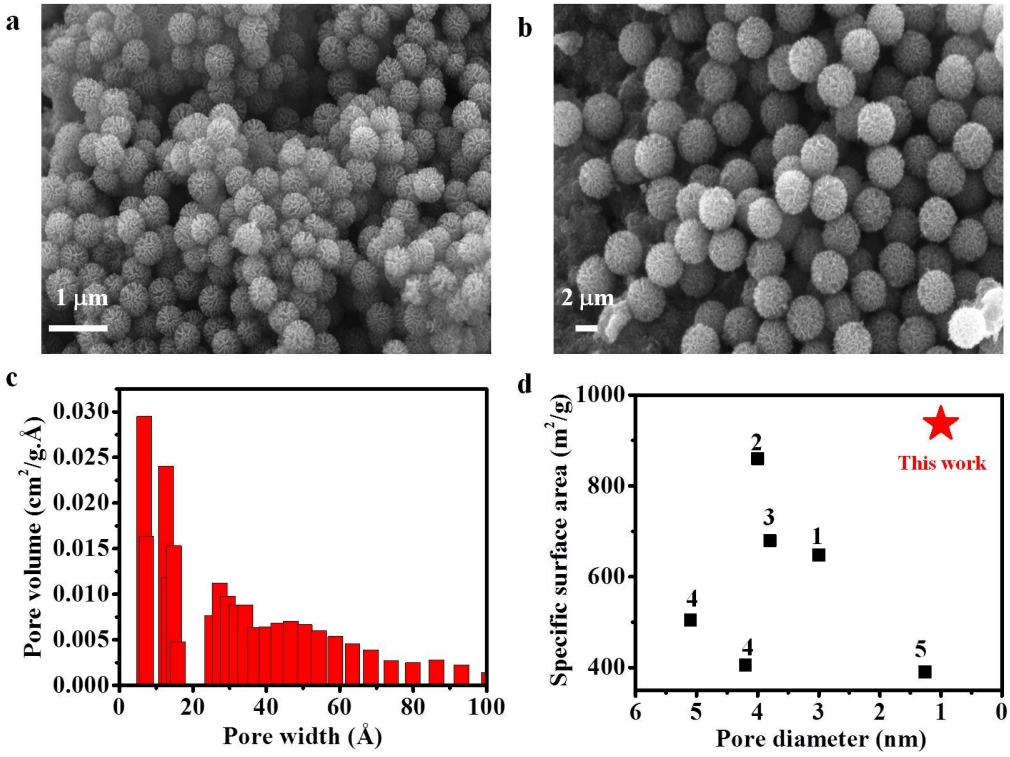


Figure S2. (a, b) SEM images of NCF. (c) Pore-width distribution of NCF. (d) Ashby plot of SSA with pore diameter with different material.[1–5]

Table S1. Summary of specific surface area and pore diameter of various carbon materials

Serial No.	Material	Specific surface area (m^2/g)	Pore diameter (nm)	References
1	Nanocarbon floret (NCF)	936	< 1	This work
2	Carbon hollow spheres	648	3	[1]
3	HMCSs	769.5	3.8	[3]
4	HCSs	88	-	[6]
5	Annealed HCSs	328	-	
6	Hollow carbon nanospheres	42	-	[7]
7	Mesoporous Carbons	200	20-50	[8]
8	Hollow carbon sphere	860	2-4	[2]
9	N-doped hollow mesoporous carbon	504	5.1	[4]
10	Hollow carbon sphere	390	1.26	[5]
11	Activated porous carbon	405	4.2	[9]
12	Co-m-NC	342	4.7	[10]
13	MCN	596	-	[11]
14	HMC	340	-	[12]

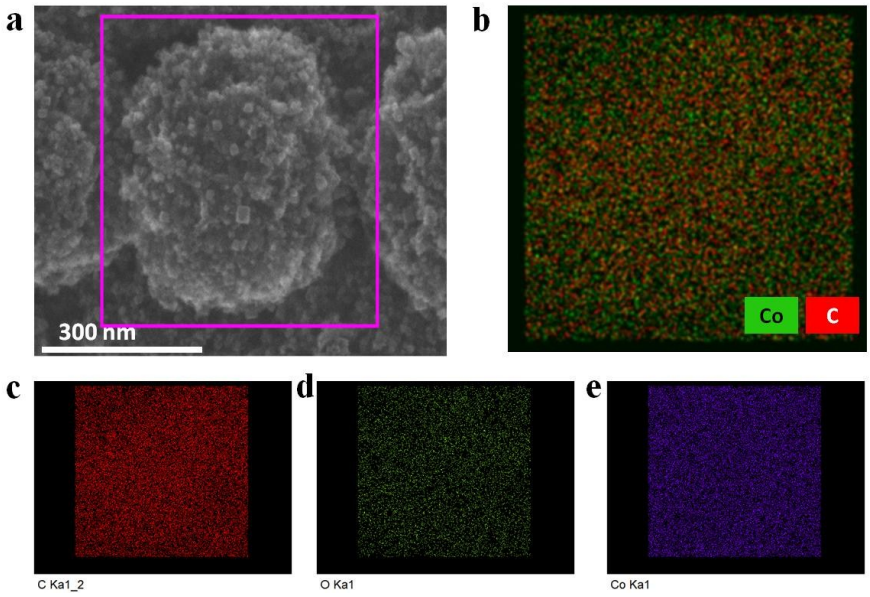


Figure S3. (a) SEM image and (b) composite mapping of Co (green) and C (red) of Co_3O_4-NCF. Individual mapping of (c) C, (d) O and (e) C.

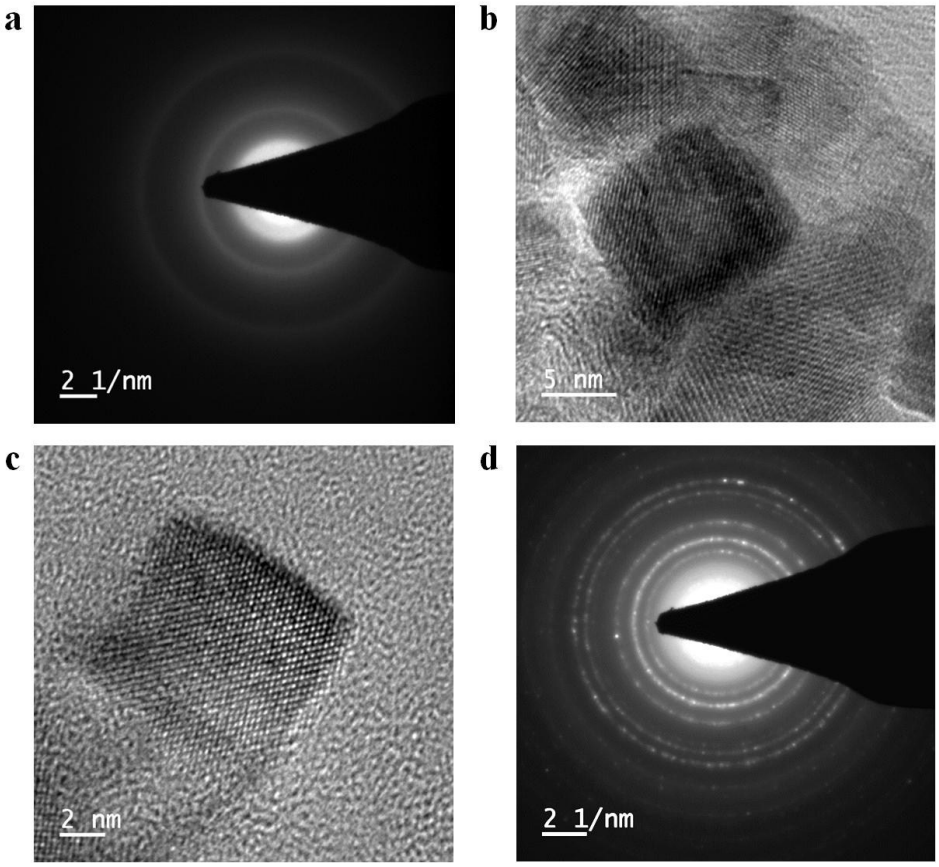


Figure S4. SAED pattern of (a) pristine NCF and (b, c) HRTEM and (d) SAED pattern of Co_3O_4-NCF.

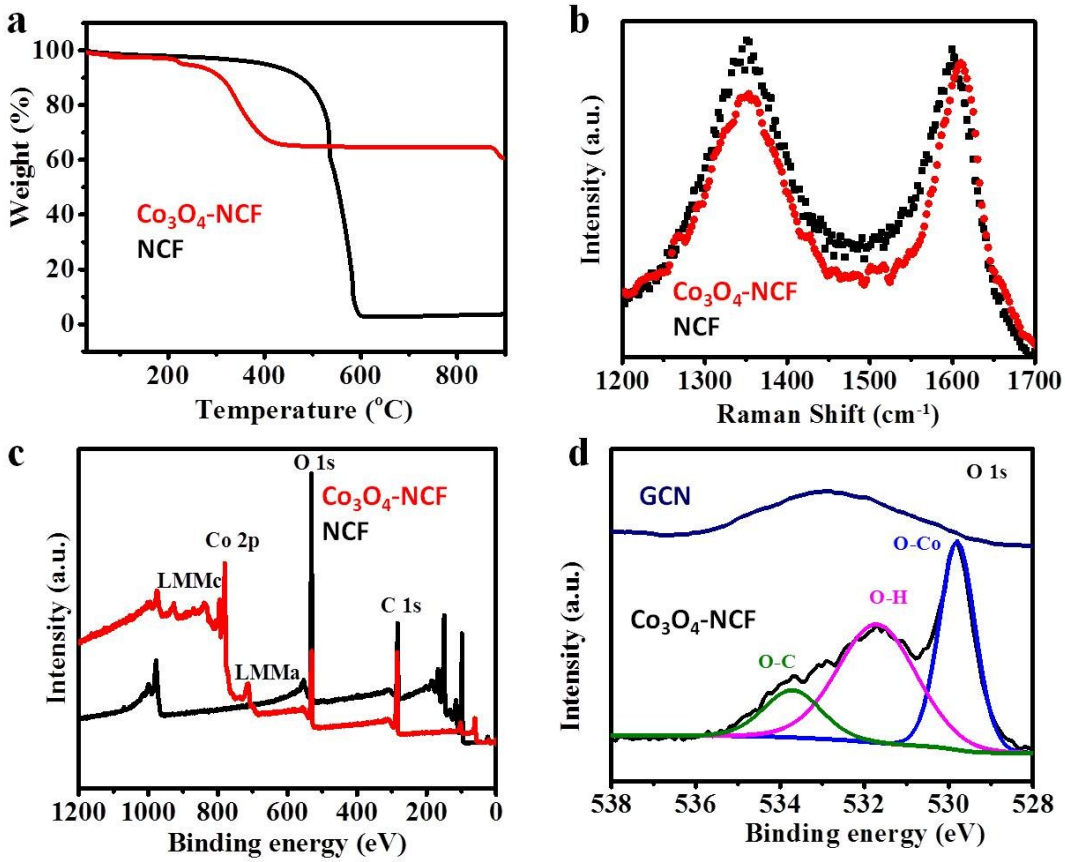


Figure S5. (a) Thermo-gravimetric analysis (TGA) of pristine NCF and Co_3O_4-NCF. (b) Raman spectra of pristine NCF and Co_3O_4-NCF (c) XPS of pristine NCF and Co_3O_4-NCF. (d) O 1s XPS of NCF and deconvolution of O 1s XPS of Co_3O_4-NCF.

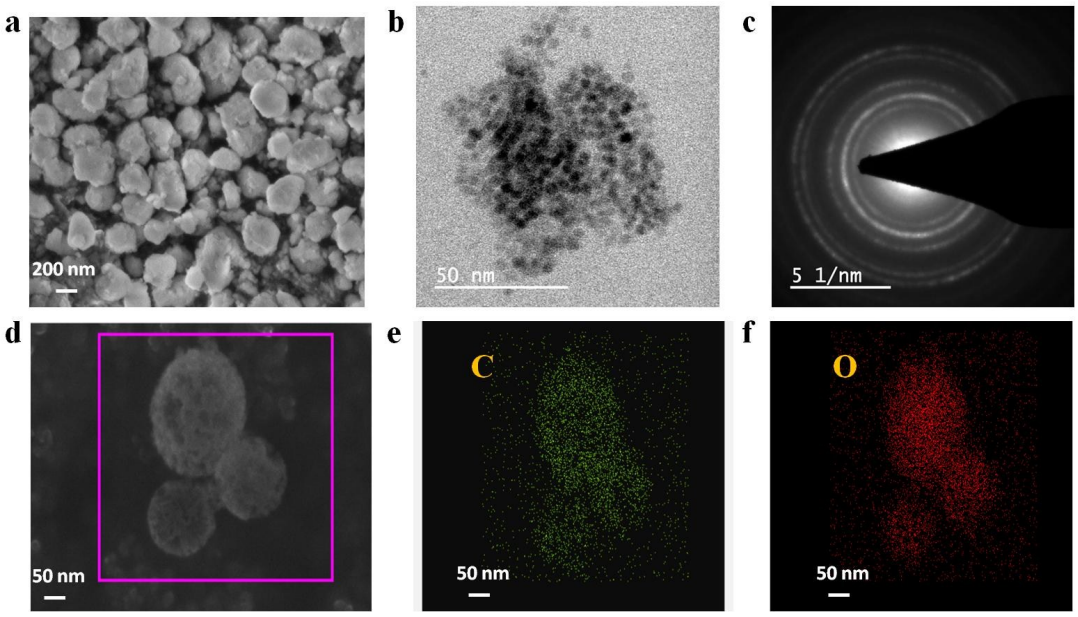


Figure S6. (a) SEM and (b) TEM image of pure Co_3O_4 prepared without NCF. (c) SAED pattern of pure Co_3O_4. (d) EDS mapping of pure Co_3O_4, (e) Carbon mapping and (f) Oxygen mapping.

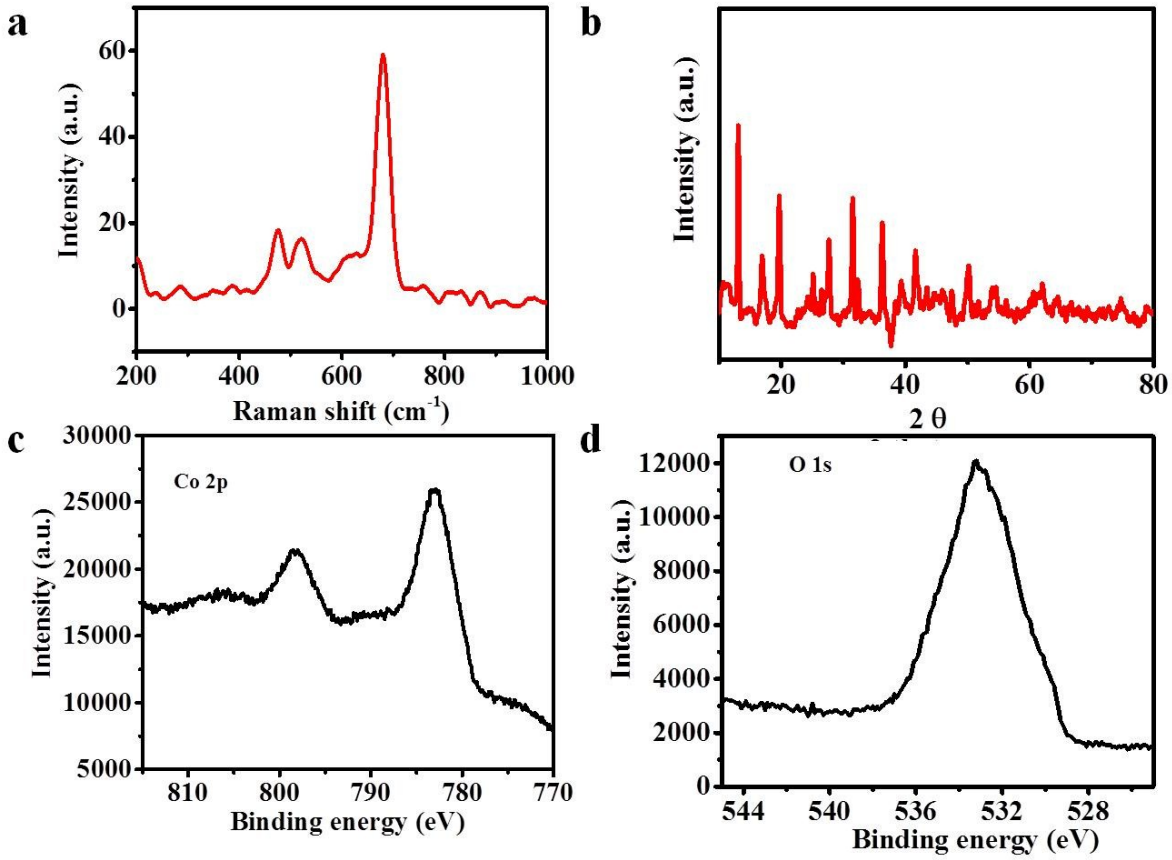


Figure S7. (a) Raman spectra, (b) XRD, (c) Co 2p XPS and (d) O1s XPS of pure Co_3O_4.

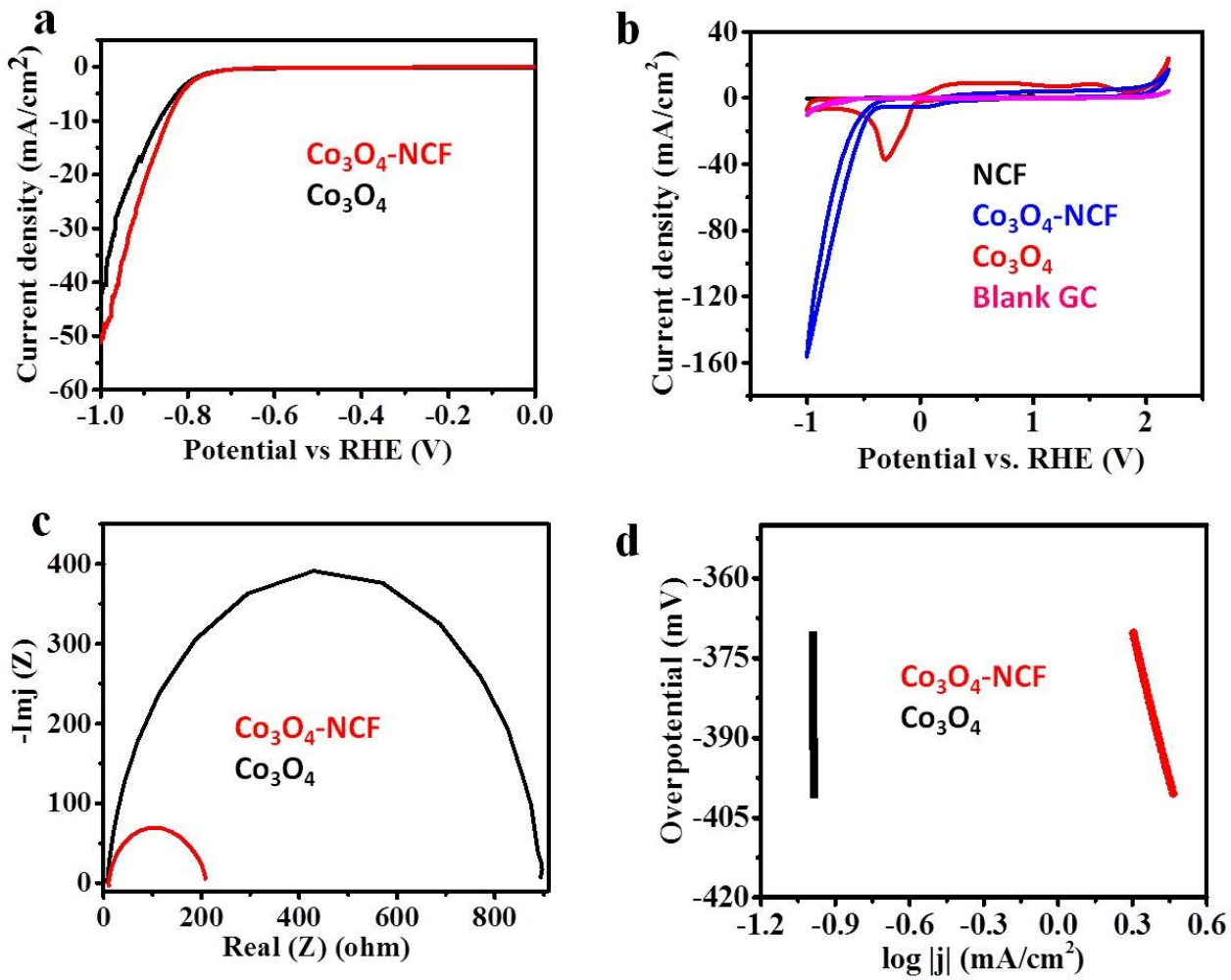
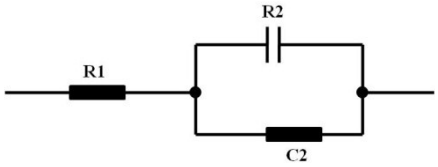


Figure S8. (a) Linear sweep voltammetry in 0.5 M H_2SO_4 (pH=0.5) of pure Co_3O_4 and Co_3O_4-NCF (scan rate= 2 mV/s). (b) Cyclic voltammetry in 0.5 M H_2SO_4 (pH=0.5) of blank glassy carbon (GC), pristine NCF, pure Co_3O_4 and Co_3O_4-NCF (scan rate= 100 mV/s). (c) Nyquist plots of pure Co_3O_4 and Co_3O_4-NCF. (d) Tafel plots of pure Co_3O_4 and Co_3O_4-NCF.

Tafel slope calculation

The current density (j) vs overpotential (t) data obtained from LSV (2 mV/s) were transformed into overpotential (t) vs log(|j|). Further, the overpotential varied linearly as a function of log(|j|) from log(|j|)=0 to 1 (1 corresponds to j=10 mA/cm^2). The slope of the function was obtained using linear fit having R^2=0.998, which gives the Tafel slope (mV/dec) for HER in alkaline and acidic medium.

Table S2. Equivalent circuit extracted circuit parameters for different systems investigated.



Catalyst	Medium	R1 Electrolyte Resistance (ohm)	R2 Charge transfer resistance (ohm)	C_{dl} double layer capacitance (mF/cm^2)
Pure Co_3O_4	0.5 M H_2SO_4	7.887	846.4	42
Co_3O_4-NCF	0.5 M H_2SO_4	10.74	170.5	190
Pure Co_3O_4	1 M KOH	14.04	350.9	36.5
Co_3O_4-NCF	1 M KOH	16.39	35.8	410
Pure Co_3O_4	0.5 M $HClO_4$	37.98	1986	31
Co_3O_4-NCF	0.5 M $HClO_4$	57.27	80	75

Table S3. Summary of electrochemical parameters of some reported catalysts

Serial No.	Catalyst	Medium	Overpotential (mV)	Current density (mA/cm^2)	Tafel slope (mV/dec)	Reference (SI)
1	Co_3O_4-NCF	1 M KOH	460	10	119	This work
2	Co_3O_4-NCNT	1 M KOH	350	10	-	[13]
3	Co_3O_4-carbon paper	1 M KOH	350	16.5	115	[14]
4	Co_3O_4-calcinated carbon	1 M KOH	350	8.5	198	[14]
5	CoOx-CC	1 M KOH	193	20	-	[15]
6	U-CNT-900	1 M KOH	240	10	-	[16]
7	Co_3O_4-Ni foam	1 M KOH	50	1	-	[17]

Table S4. Summary of SSA and C_{dl} of recently reported materials

Serial No.	Materials	SSA (m^2/g)	Cdl (mF/cm^2)	Reference
1	Metal-N-C (M=W, Mo, Cr, Mn, Fe, Co, Ni, Cu, Zn)	712-382	-	[18]
2	Co_3O_4-NCNT	37	-	[13]
3	CoO_x-CNT-CC	88	1155	[15]
4	Co_3O_4-NCF	646	410	This work

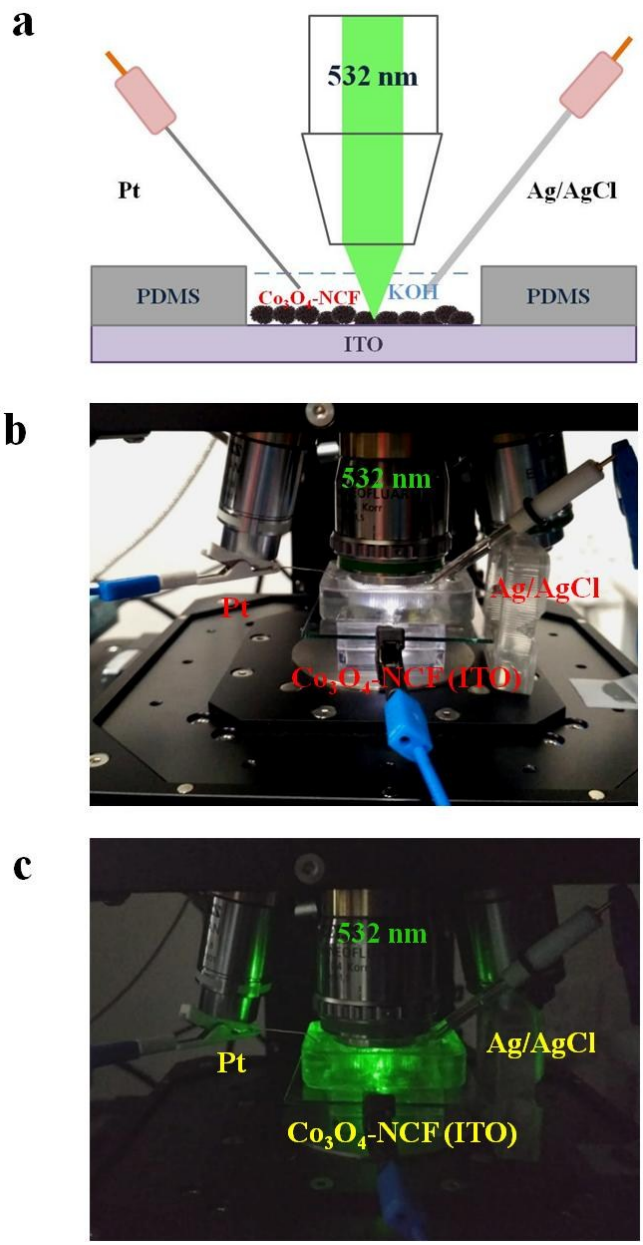


Figure S9. (a) Schematic representation of the operando Raman setup. Photograph of customized operando Raman setup with laser on (b) and laser off (c).

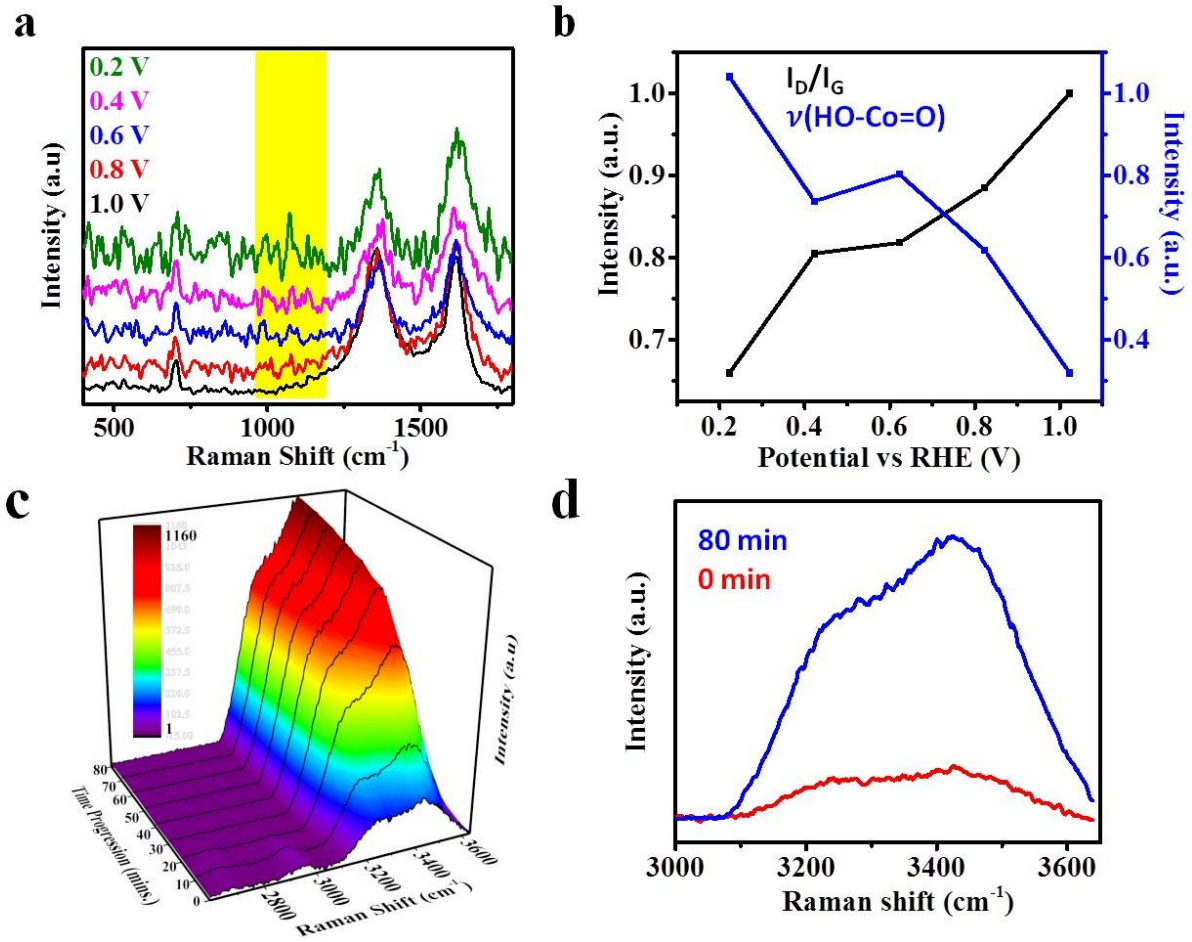


Figure S10. (a) Operando Raman spectra of Co_3O_4-NCF in 1 M KOH with different applied potential. (b) Evolution of of I_D/I_G (blue) and HO-Co=O (black) in 1 M KOH.[2] (c) Operando Raman spectroscopy of HER at 0.8 V (vs RHE) in 1 M KOH using Co_3O_4-NCF catalyst (region 2600-3600 cm^{-1}). (d) Raman spectroscopy of HER at 0.8 V (vs RHE) in 1 M KOH using Co_3O_4-NCF catalyst (region 2600-3600 cm^{-1}) at 0 min (red) and 80 min (blue).

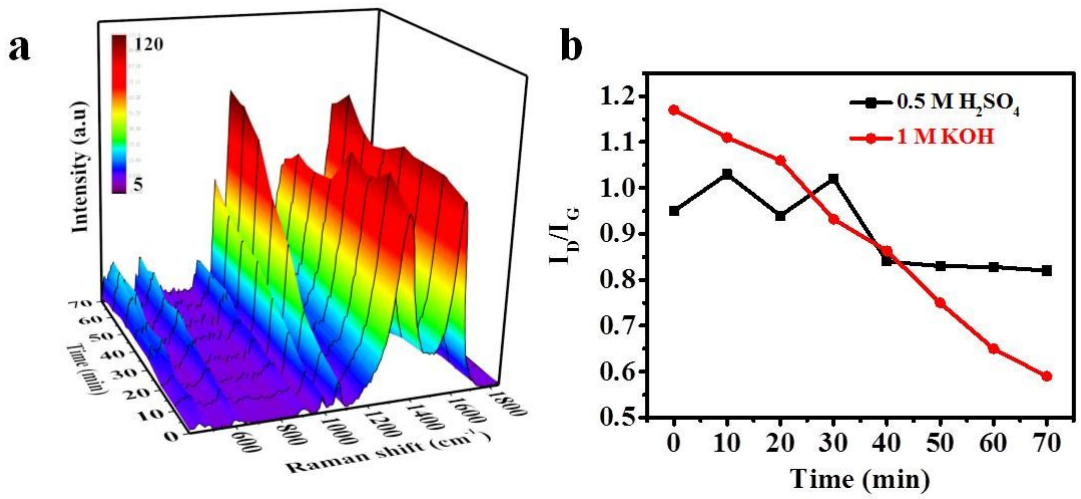


Figure S11. (a) Operando Raman spectroscopy of HER at 0.2 V (vs RHE) in 0.5 M H_2SO_4 using Co_3O_4-NCF catalyst. (b) Spectral evolution of of I_D/I_G with time in 0.5 M H_2SO_4 (black) and 1 M KOH (red).

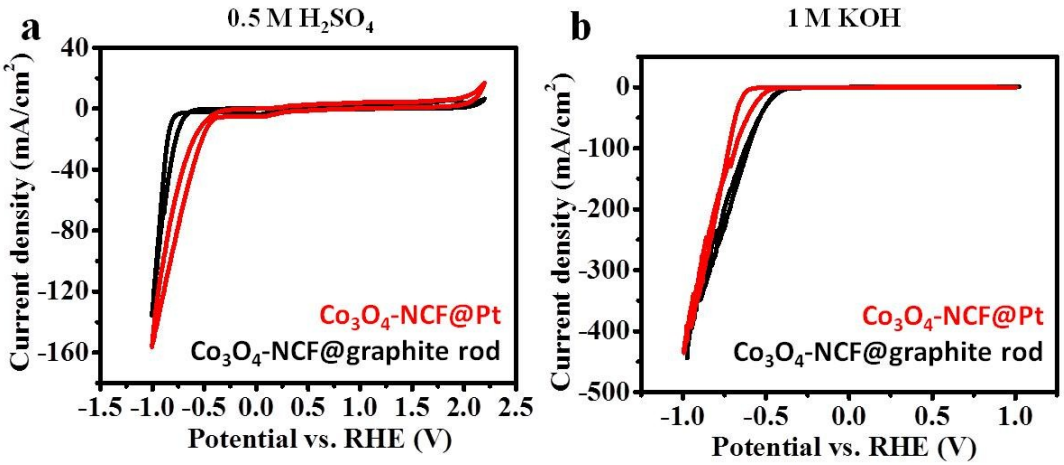


Figure S12. Comparison CV of Co_3O_4-NCF with different counter electrodes (graphite rod and Pt) in both (a) acidic and (b) alkaline pH.

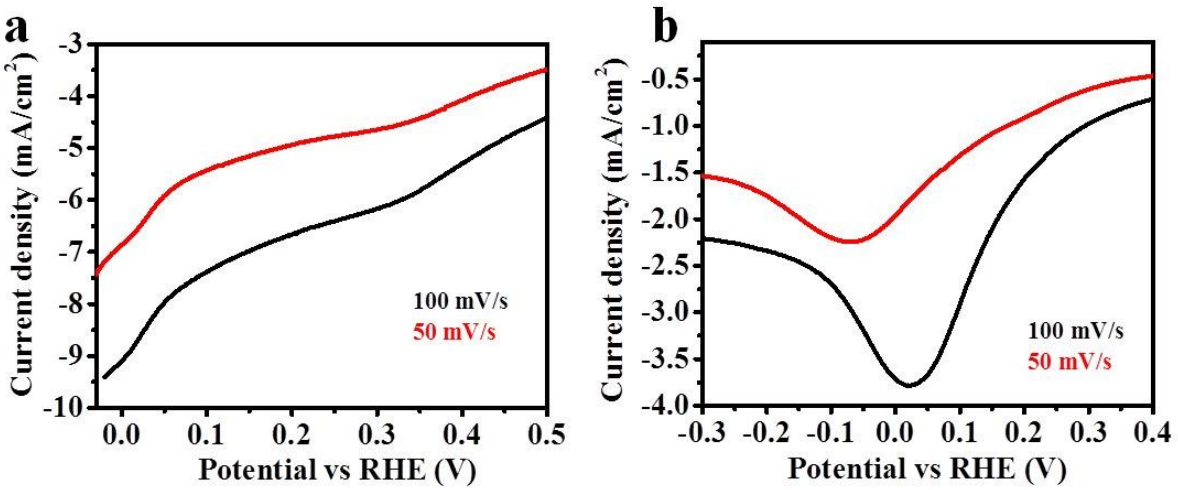


Figure S13. Cyclic voltammogram (CV) of Co_3O_4-NCF in (a) basic medium and (b) acidic medium.

Table S5. ICP-AES analysis of acid treated Co_3O_4-NCF

Sample	Concentration of Cobalt (ppm)
Co_3O_4-NCF in H_2SO_4	> 140

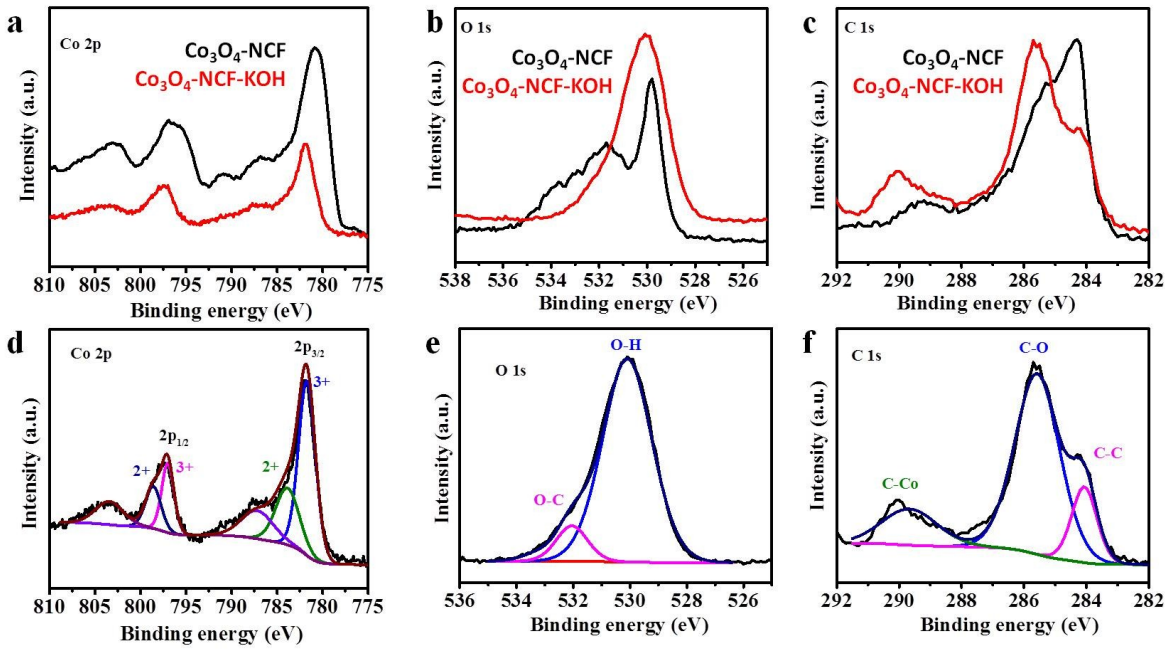


Figure S14. Comparison of (a) Co 2p, (b) O 1s and (c) C 1s XPS of Co_3O_4-NCF before and after HER in 1 M KOH. Decovoluted (d) Co 2p, (e) O 1s and (f) C 1s XPS of Co_3O_4-NCF after HER in 1 M KOH.

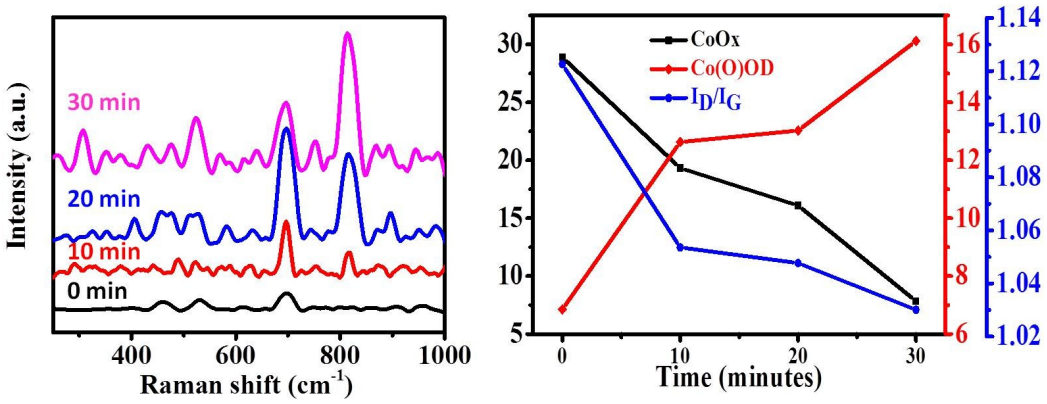


Figure S15. a) Time resolved in-situ Raman spectro-electrochemical study of Co_3O_4-NCF in heavy water (D_2O) for alHER and b) Intensity of Co-OOD peak (815 cm^{-1}), Co-O_x (699 cm^{-1}) and I_D/I_G at -0.4V (vs RHE) with time under in-situ conditions.

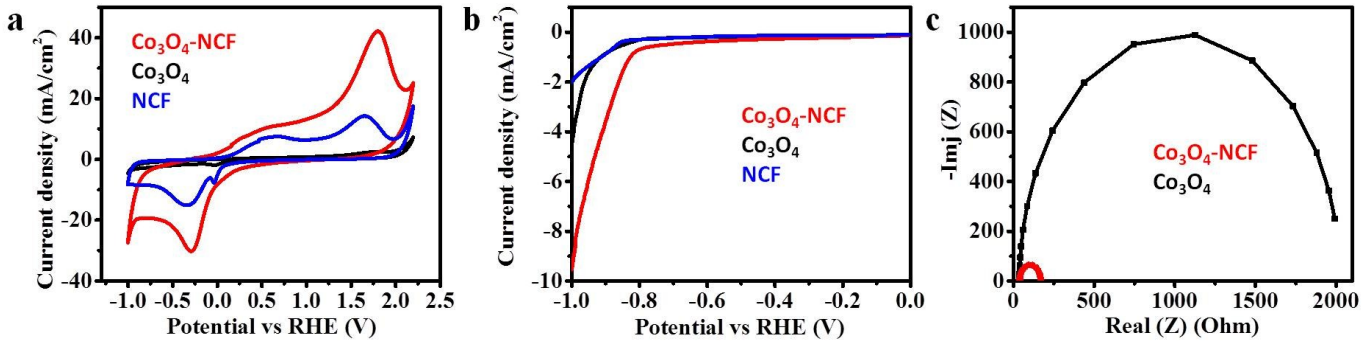
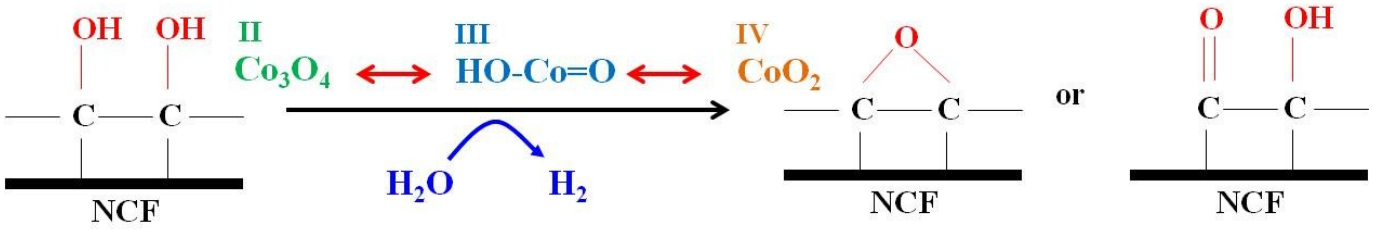


Figure S16. a) Cyclic voltammetry in 0.5 M $HClO_4$ of pristine NCF, pure Co_3O_4 and Co_3O_4-NCF (scan rate= 100 mV/s). (b) Linear sweep voltammetry in 0.5 M $HClO_4$ pristine NCF, pure Co_3O_4 and Co_3O_4-NCF (scan rate= 2 mV/s). (c) Nyquist plots of pure Co_3O_4 and Co_3O_4-NCF.



Scheme S1. Proposed mechanism of HER at Co_3O_4-NCF surface.

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