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

Electronic Supplementary Information

Cobalt (II) ions and Cobalt Nanoparticle Embedded Porous Organic Polymers: An Efficient Electrocatalyst for Water-splitting Reactions

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Experimental Section

Materials and methods

All reagents and solvents were purchased from Sigma-Aldrich/Alfa Aesar and used without further purification.

The morphological structures of the prepared samples were captured using Scanning Electron Microscope (SEM) of TESCAN, VEGA 3 with Bruker Detecter. FTIR analysis was carried out on a BRUKER - TENSOR 27 (Optik GmbH) using RT DLaTGS (Varian) Detector. Raman spectra were recorded using a high resolution Renishaw Raman microscope employing a He-Ne laser of 18 mW at 633 nm.

Cyclic voltammetry was carried on an autolab PGSTAT 302N workstation at room temperature in a standard three-electrode cell. The working electrode was a carbon paper with (area = 1 cm^2, mass loading of 2 mg cm^{-2}) and modified GC and the counter electrode was a Pt wire. The reference electrode was Ag/AgCl/KCl (3 M) electrode. Oxygen evolution reaction was studied by using linear sweep voltammetry carried out at room temperature using 1 M KOH as the electrolyte at a scan rate of 1 mV/s. For the ease of comparison of results, the potentials were converted to RHE scale.

Electrode preparation

The tory carbon paper was used as working electrode by equimolar preparation 1:1:1 (Water: IPA: Nafion) and the solution was sonicated for 3 hr. 100 µml of this solution was added to 5 mg of the catalyst to prepare slurry and was sonicated for 30 mins. The catalyst ink was coated on the surface of tory carbon by manual brush coating. The modified tory carbon was allowed to dry at room temperature.

Synthesis of EPOP and Cobalt composite

Under inert conditions, ethylene diamine (1.4 g, 24.4 mmol) was dissolved in anhydrous 1,4-dioxane (100 mL) under constant stirring at RT. To this solution, K_2CO_3 (4.5 g, 32.5 mmol) was added and stirred for 30 mins. Then the solution was cooled to 10 °C, and cyanuric chloride (3 g, 16.27 mmol) dissolved in 100 mL anhydrous 1,4-dioxane was added dropwise over 8 h. The mixture was allowed to warm to RT and refluxed for 3 days (during the course of the reaction, color changed from dark brown to pale brown). The solution was cooled to RT, the mixture was filtered, washed with 1,4-dioxane and methanol to remove unreacted SM and dried under vacuum to yield **EPOP** (yield = 90%).[1]

Preparation of Co-EPOP catalyst

EPOP (1g) was soaked in 20 mL of water and then 10% of Cobalt nitrate was added in same solution, these solution was kept in 60 °C for overnight. The solution was cool down, resulting Co-EPOP washed with water.

Preparation of Co-EPOP-300 & Co-EPOP-500 catalysts

The 1 g of resulting EPOP material grind with Cobalt nitrate $Co(NO_3)_2$ and added 5ml of hydrazine hydrate dropwise. Then the samples were heated to 300 °C and 500 °C in tubular furnace, to obtain Co-EPOP-300 and Co-EPOP-500 respectively.

Preparation of Co-EPOP-HT

A mixture of finely ground EPOP, $Co(NO_3)_2$ and hydrazine hydrate (5 mL) were suspended in water and heated to 180 °C in a stainless steel autoclave for 8 h under inert atmosphere to obtain **Co-EPOP-HT**.

Preparation of Co-NP

Cobalt nanoparticle was synthesized by simple reduction method. 0.4 M hydrazine hydride aqueous solution was slowly added to 0.2 M aqueous cobalt nitrate solution. The pH of the solution was maintained at pH > 10 by adding aqueous ammonia solution. The solution was stirred for 4 h at 80 °C temperature. After the completion of reaction, the obtained Co-NP was filtered, washed with distilled water and ethanol several times and dried.[2]

FT-IR

The resulting Co modified polymer samples were characterized by Fourier-transform infrared (FT-IR). Figure 1 shows the FT-IR spectrum of Co-EPOP-HT, Co-EPOP-300, Co-EPOP-500, Co-EPOP samples. The characteristic stretching and bending vibration of triazine moieties were observed at 1539-1570 and 1342-1370 cm^{-1}. The broad peak at 3273-3300 cm^{-1} corresponds to NH stretching vibration and peak at 2937-2950 cm^{-1}, 1430-1448 cm^{-1} corresponding to sp^3-CH_2- moiety. Slight shift in the NH stretching vibration is observed compared to pure EPOP sample due to the metal ion/metal nanoparticle interaction with these organic groups. Finally synthesized cobalt nanoparticle was characterized by FT-IR (dark yellow), the peak at 561 and 659 cm^{-1} is a characteristic fingerprint region for Co-O stretching vibration, 561 cm^{-1} is assigned to the Co-O vibrations in the octahedral site, whereas 659 cm^{-1} is related to the Co-O vibrations of Co_3O_4.[3]

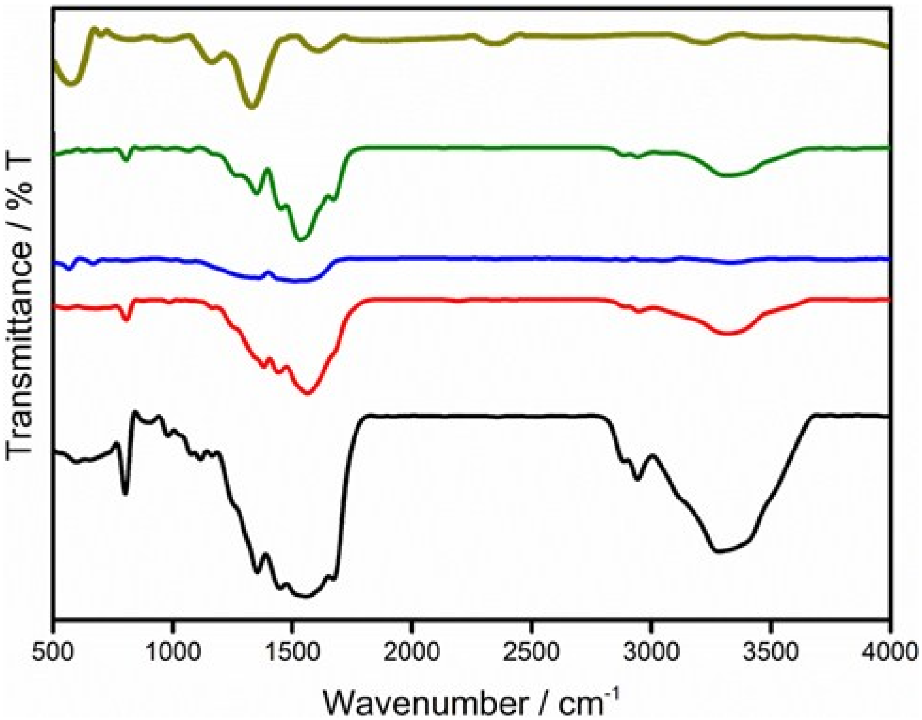


Figure S1. FT-IR spectrum of Co-EPOP-HT (black), Co-EPOP-300 (red), Co-EPOP-500 (blue), Co-EPOP (green) and Co-NP (dark yellow)

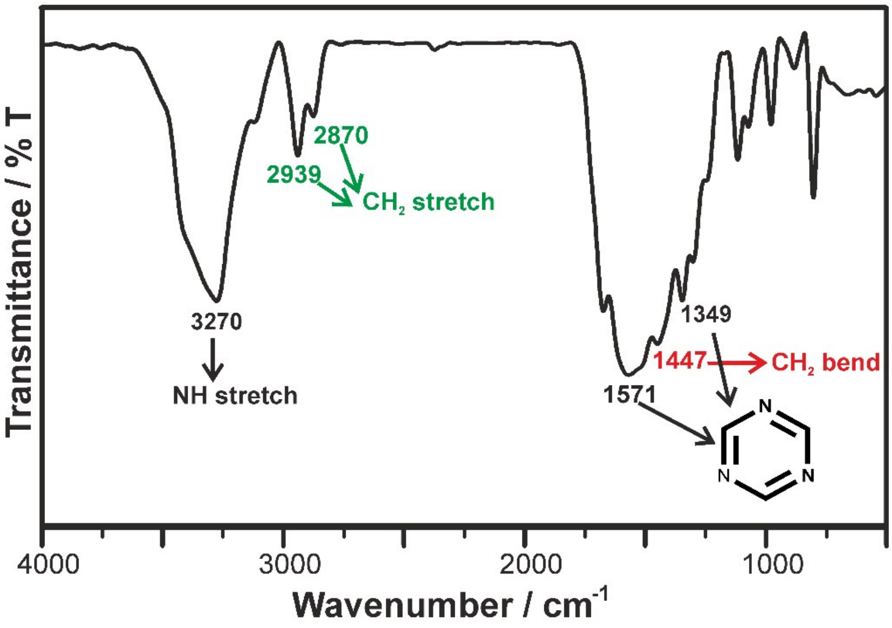


Figure S2. FT-IR spectrum of EPOP.

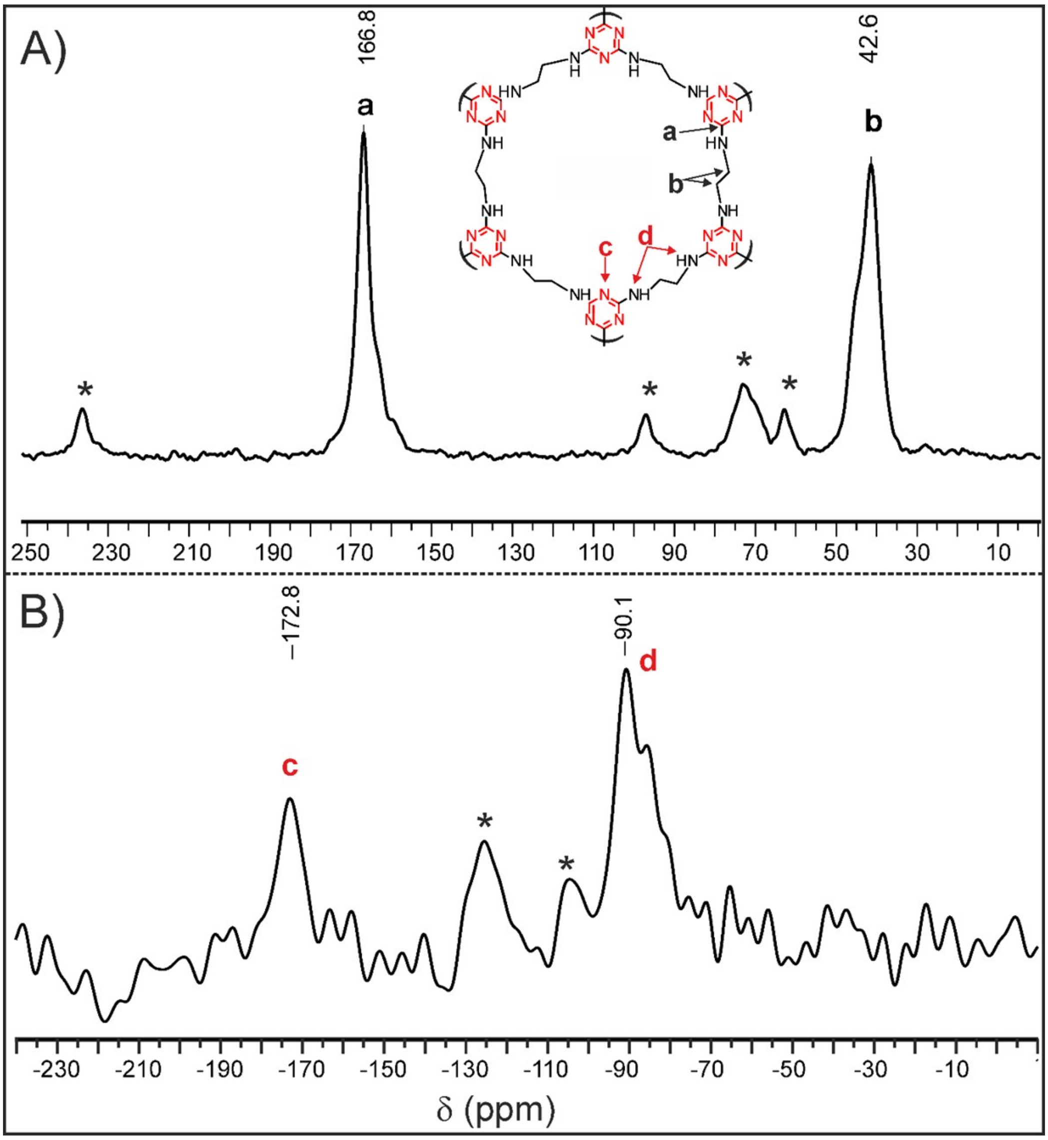


Figure S3. A) ^{13}C CP-MAS solid state NMR and B) ^{15}N CP-MAS solid state NMR of EPOP, *denotes side bands

FESEM images of the catalysts

Before recording the FESEM, the samples were sputtered.

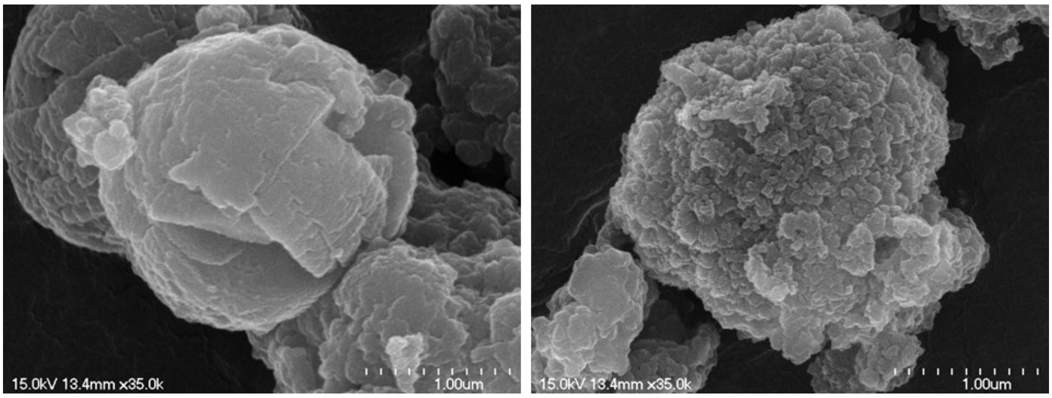


Figure S4. FE-SEM image of Co-EPOP-HT

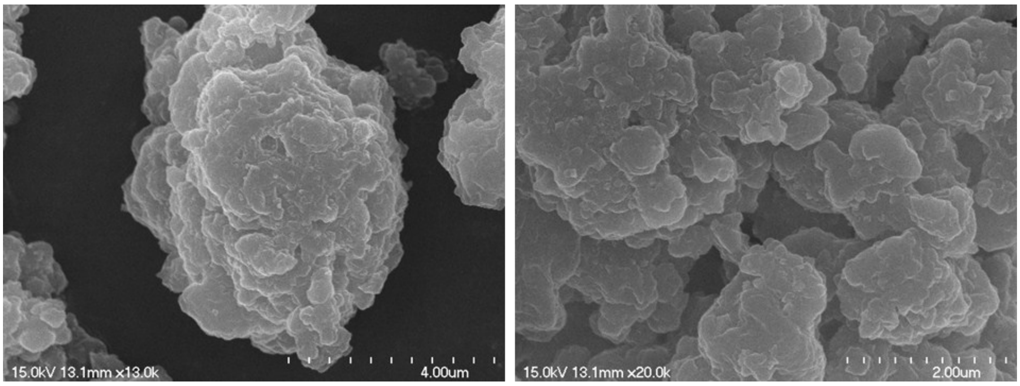


Figure S5. FE-SEM image of Co-EPOP-300

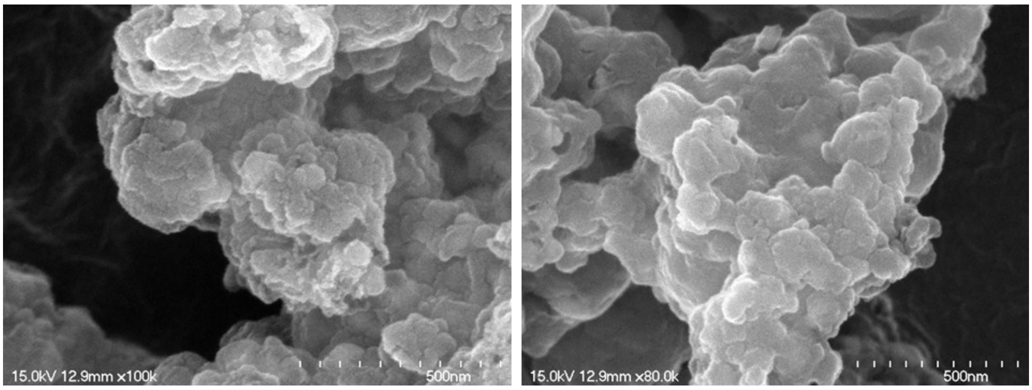


Figure S6. FE-SEM image of Co-EPOP-500

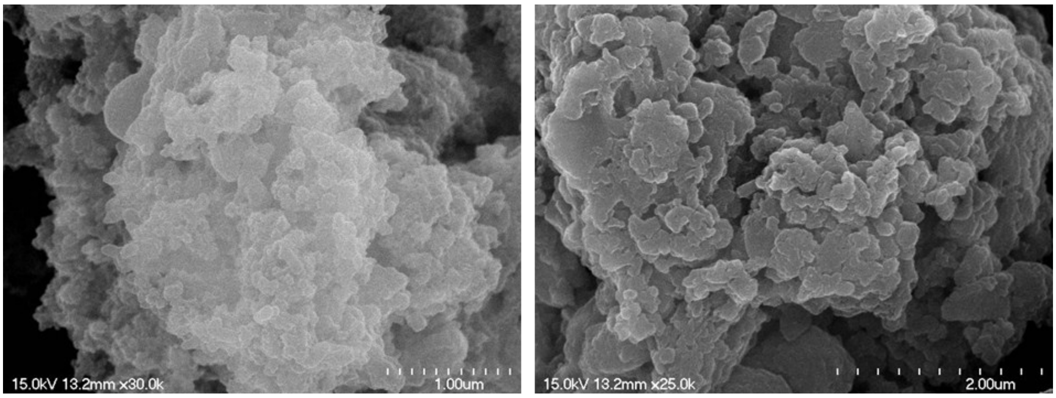


Figure S7. FE-SEM image of Co-EPOP

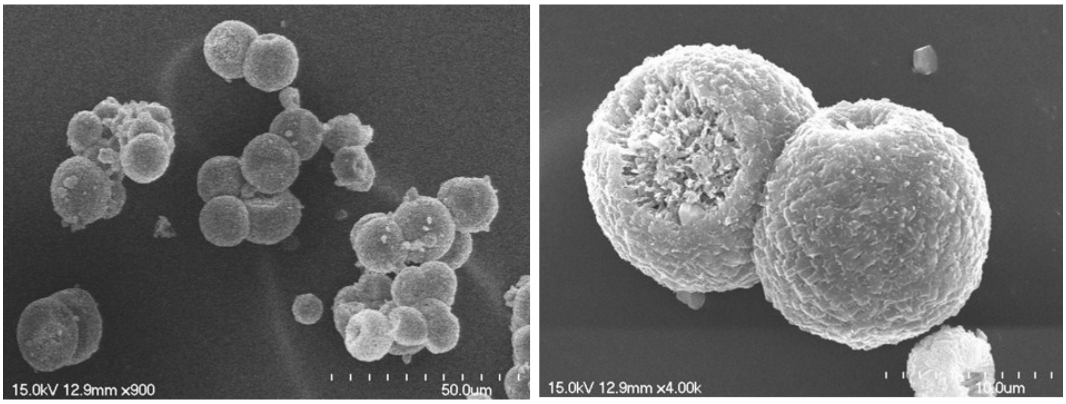


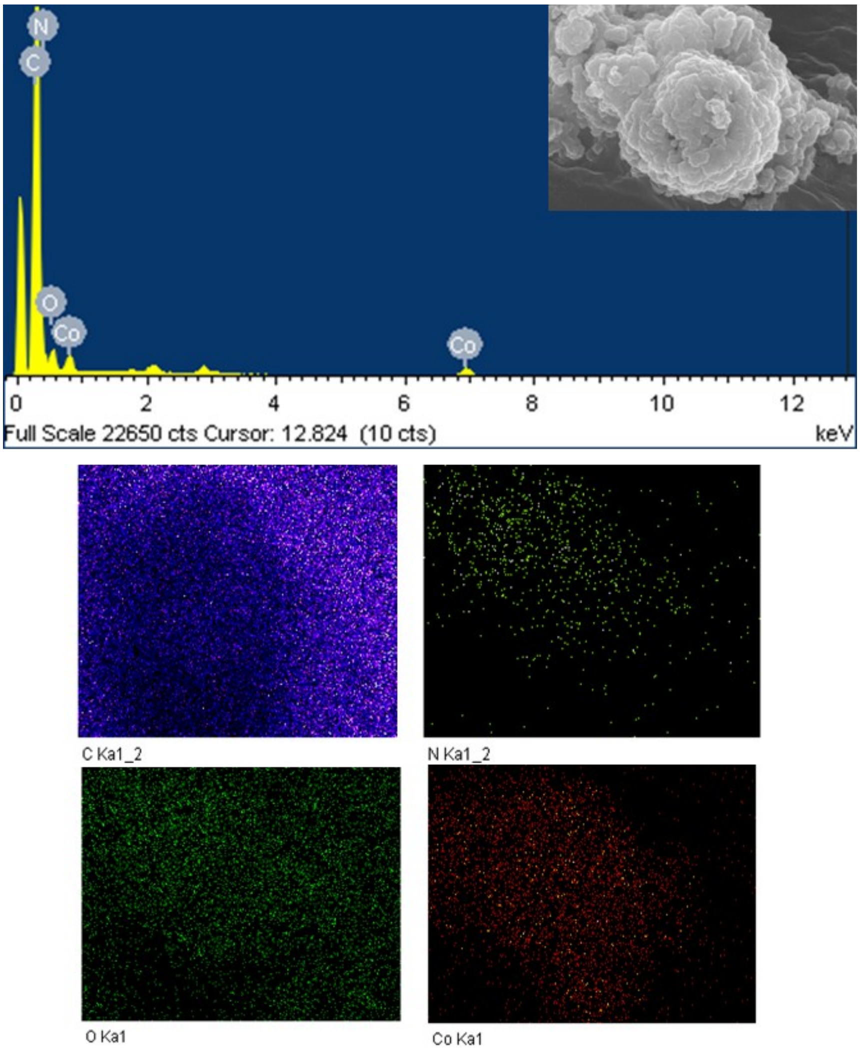
Figure S8. FE-SEM image of Co-NP

EDX spectrum of samples

Samples	C %	N %	O %	Co %	C/N ratio
Co-EPOP-HT	57.29	25.99	12.01	4.72	2.2
Co-EPOP-300	56.53	27.33	13.37	2.77	2.06
Co-EPOP-500	54.83	23.80	13.06	8.31	2.30
Co-EPOP	51.32	36.36	11.13	1.19	1.41
Co-NP	-	-	79.50	20.50	
EPOP*	54.75	28.02	-	-	1.95

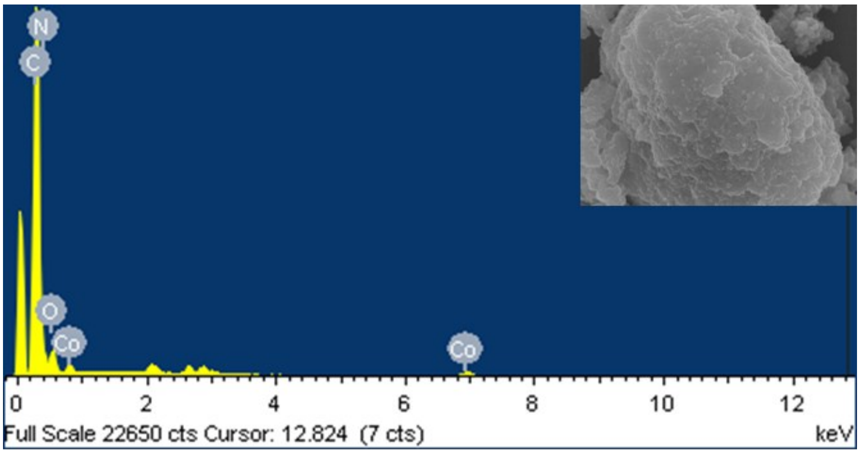
* Obtained from elemental analysis

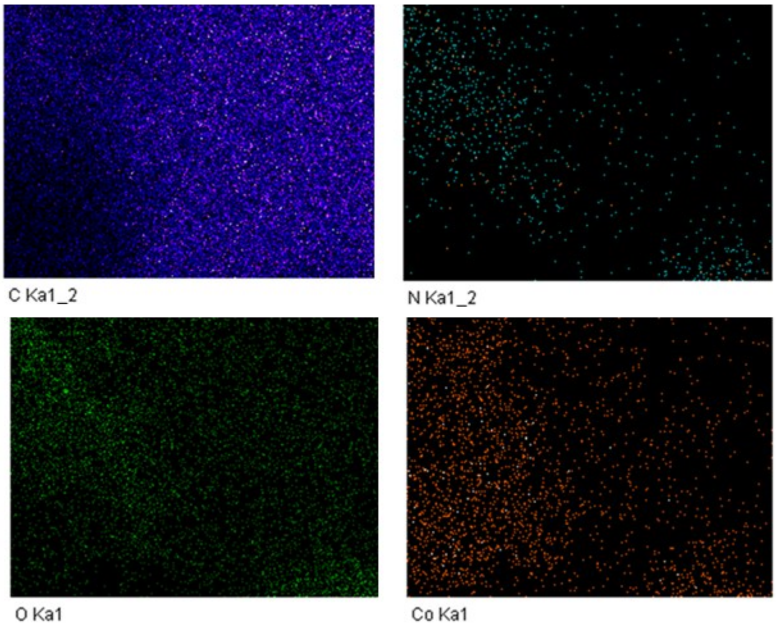
Elemental mapping



Element	Weight%	Atomic%
C K	57.29	63.98
N K	25.99	24.89
O K	12.01	10.06
Co K	4.72	1.07
Totals	100.00	

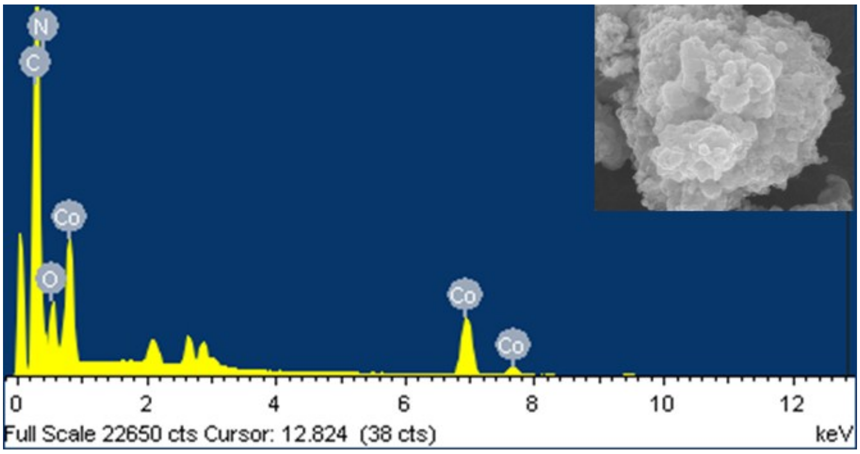
Co-EPOP-HT

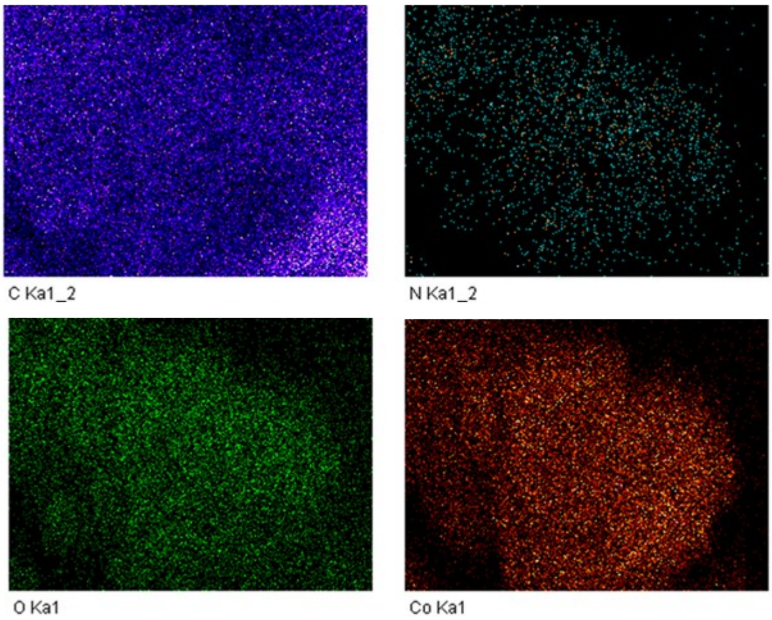




Element	Weight%	Atomic%
C K	56.53	62.42
N K	27.36	25.90
O K	13.34	11.06
Co K	2.77	0.62
Totals	100.00	

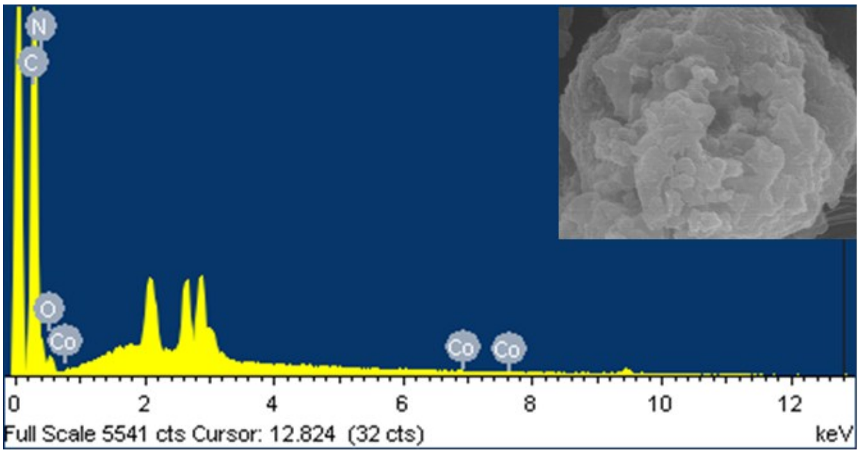
Co-EPOP-300

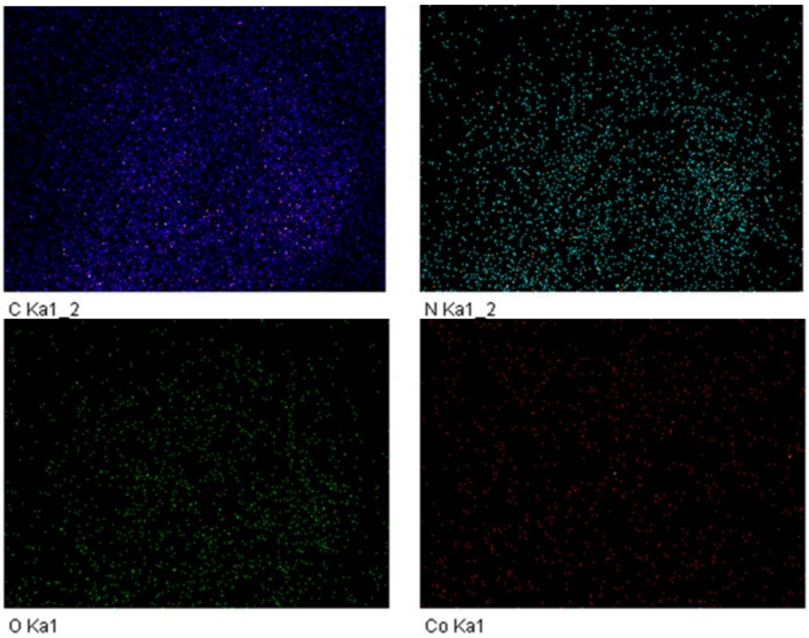




Element	Weight%	Atomic%
C K	54.83	62.69
N K	23.80	20.28
O K	13.06	12.34
Co K	8.31	4.69
Totals	100.00	

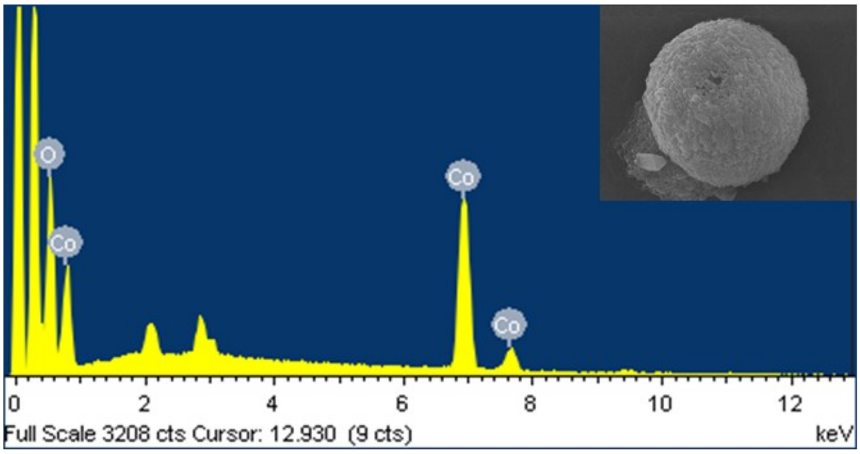
Co-EPOP-500

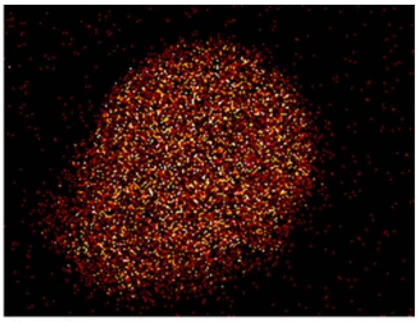




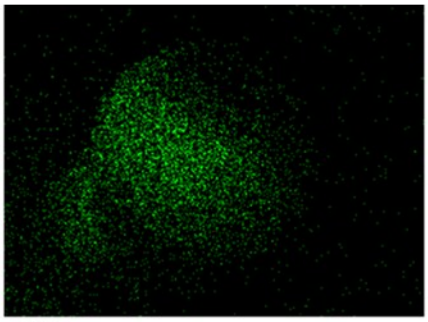
Element	Weight%	Atomic%
C K	51.32	55.93
N K	36.36	34.52
O K	11.13	9.11
Co K	1.19	0.44
Totals	100.00	

Co-EPOP





Co Ka1



O Ka1

Element	Weight%	Atomic%
Co K	79.50	51.28
O K	20.50	48.72
Totals	100.00	

Co-NP

Calculation of Electrochemical Active Surface Area

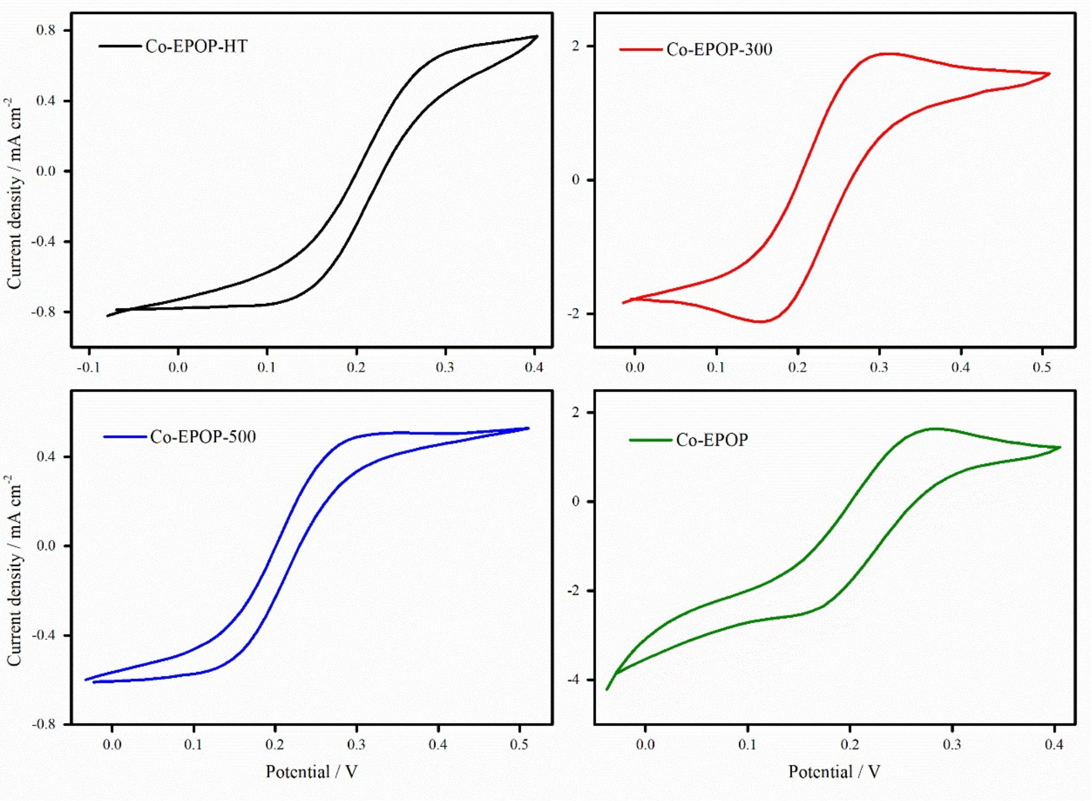


Figure S9. Ferro-Ferri response of modified electrode for active surface area calculations.

Table S1. Electrochemical active surface area of the electrocatalysts

S.No	Catalyst	Active surface area ECSA (cm^{-2})
1	Co-EPOP-HT	0.00409
2	Co-EPOP-300	0.01085
3	Co-EPOP-500	0.00409
4	Co-EPOP	0.00293

XPS (X-ray Photoelectron spectroscopy)

XPS Co-EPOP

From the figure S. core level indicates the presence of C1s, N1s, O1s and Co2p spectrum of Co-EPOP sample. The C1s core level spectra shows three peaks at 284.6, 286.23 and 287.89 eV for corresponds to sp^2 carbon, C-O and carbonyl group C=O.[4] The N1s spectra shows three peaks at 397.9 eV for triazine N, 399.4 eV for amine N and 400.1 eV assigned to the oxidation of amine bond.[5] O1s peaks at 530.8 eV, 531.7, and 532.9 eV corresponds to the metal oxygen bond, OH- ion, adsorbed oxygen respectively.[6] Co2p peaks with very less intensity are due to the low concentration of Co metal (EDX, elemental analysis) in the sample Co-EPOP. Co2p1/2 peak is observed at 787.73 eV and Co2p3/2 peak at 795.55 eV.

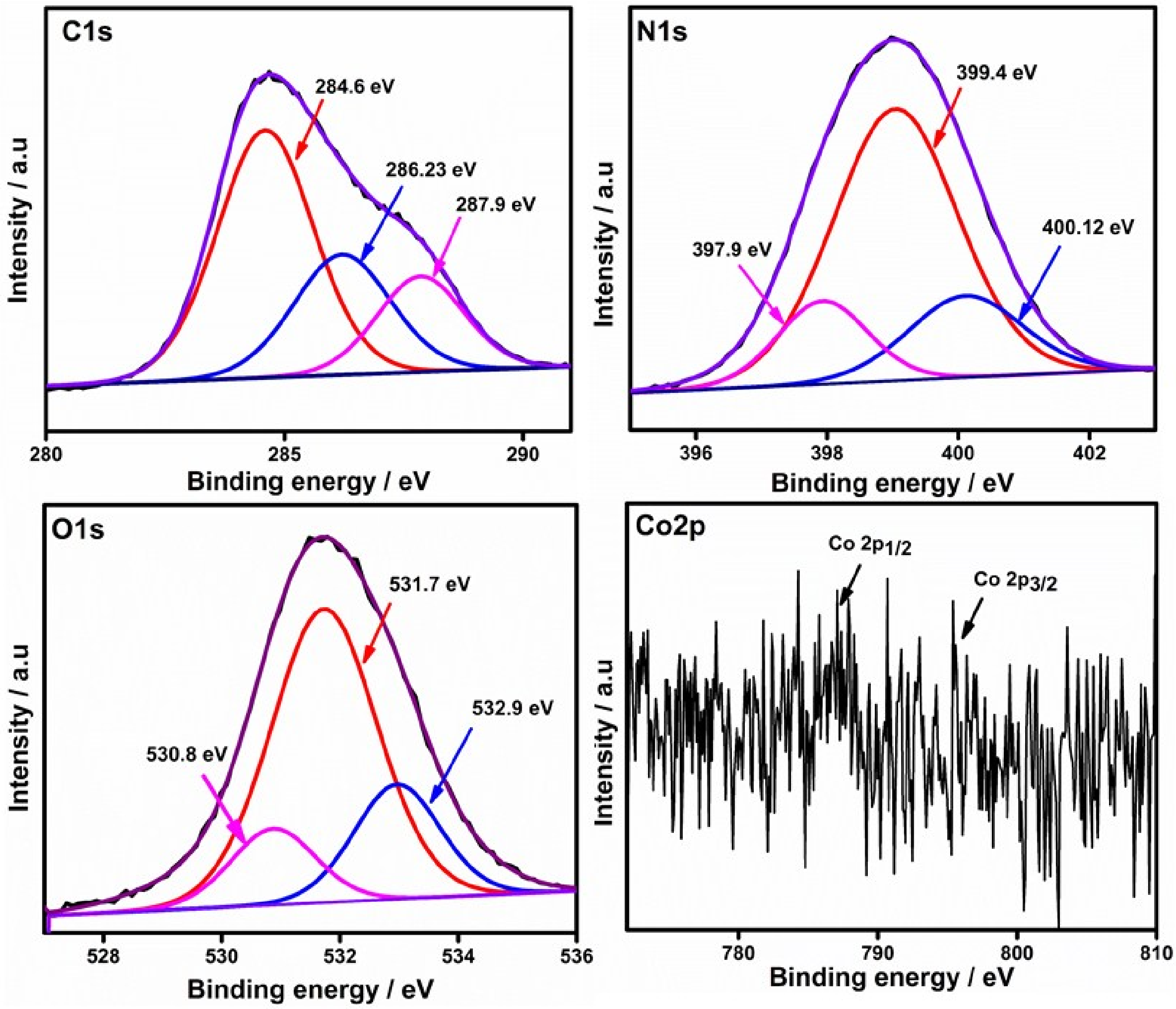


Figure S10. X-ray photoelectron spectra of C1s core level, O 1s core level, N 1s core level Co 2p core level of Co-EPOP.

The surface elemental and bonding configuration of Co-EPOP nanocomposites were investigated by X-ray photoelectron spectroscopy (XPS). The element survey demonstrated the presence of C, N, O and Co in Co-EPOP-HT, Co-EPOP-300, Co-EPOP-500 samples (Figure 4). The corresponding deconvoluted spectra are shown below.

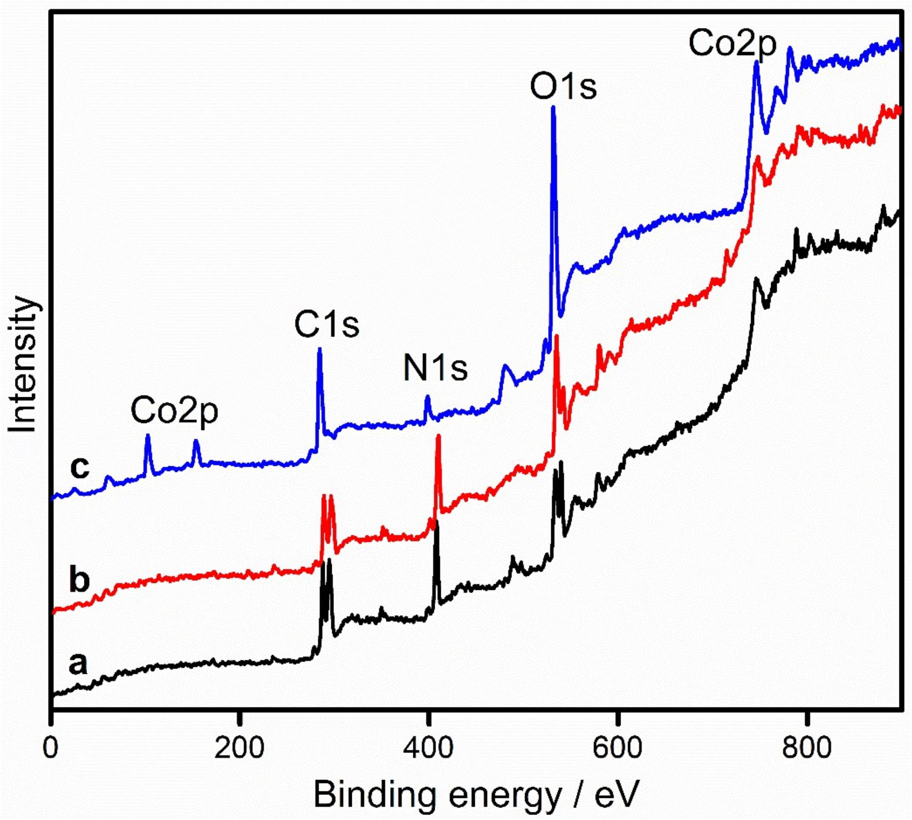


Figure S11. Element surveys by XPS of a) Co-EPOP-HT, b) Co-EPOP-300, c) Co-EPOP-500

The XPS spectra of Co-EPOP-HT, Co-EPOP-300, Co-EPOP-500 confirms the presence of C, N, O, and Co metal in all the above catalyst. Element survey demonstrated the presence of C, O, and Co in all the catalyst (Figure S11).

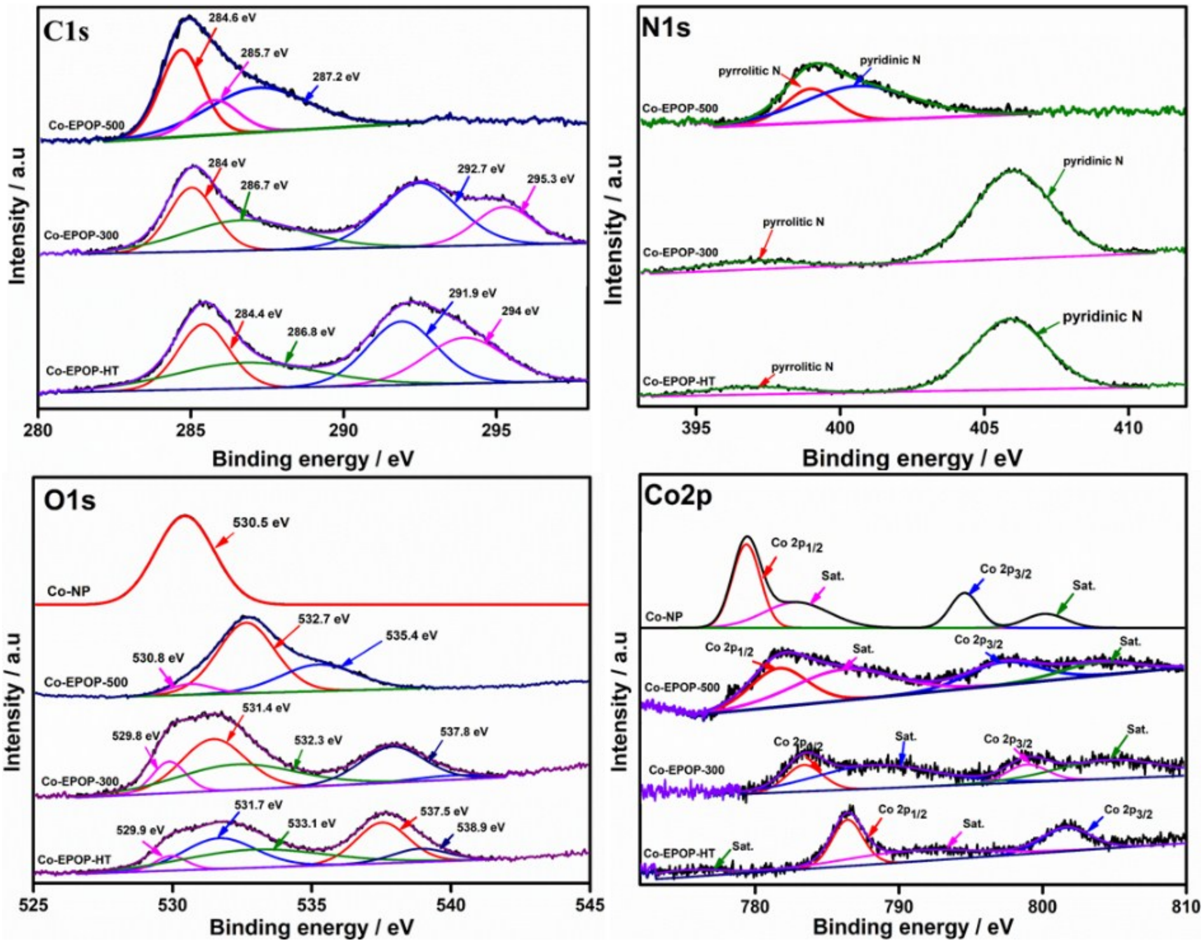


Figure S12. X-ray photoelectron spectra of C1s core level, O 1s core level, N 1s core level Co 2p core level of synthesised material.

After Catalytic activity

To understand the long-term stability of the catalysts under OER conditions, the catalysts were subjected to SEM analysis after stability tests to understand the change in morphology (Figure S12). We did not observe any difference in the morphology after long-term OER stability test indicating the excellent stability of the catalysts under OER conditions.

Similarly, the catalysts were subjected to FT-IR analysis after the OER long-term stability tests. From the FT-IR spectra, one could infer the following information.

The triazine bond was obtained at 1505 to 1575 cm^{-1} and corresponding NH stretching vibration at 3187 to 3334 cm^{-1}. The band between 2318 to 2417 cm^{-1} correspond sp^3 –CH$_2$– moiety. These results clearly indicate that the carbon functionalities does not undergo any significant changes after cycling.

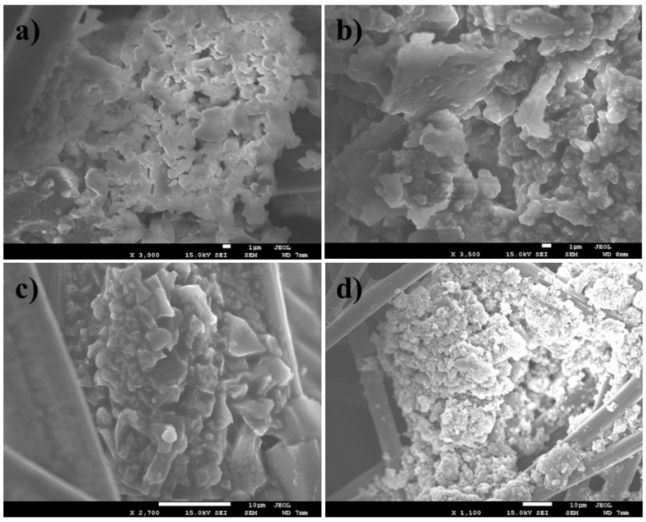


Figure S13. SEM image of the modified carbon electrode with synthesized a) Co-EPOP-HT, b) Co-EPOP-300, c) Co-EPOP-500, and d) Co-EPOP samples after OER long-term stability test.

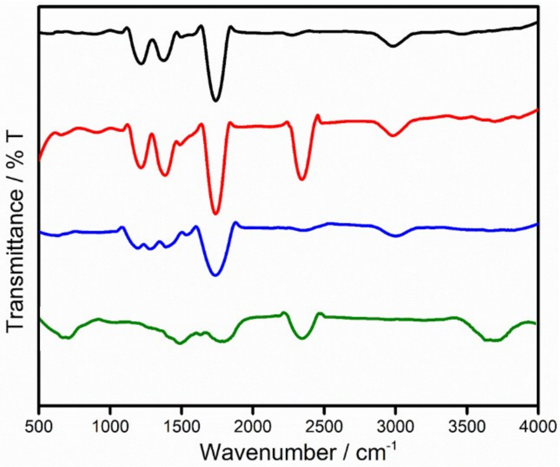


Figure S14. FT-IR spectrum of Co-EPOP-HT (black), Co-EPOP-300 (red), Co-EPOP-500 (blue) and Co-EPOP (green) after OER long-term stability test.

LSV curves

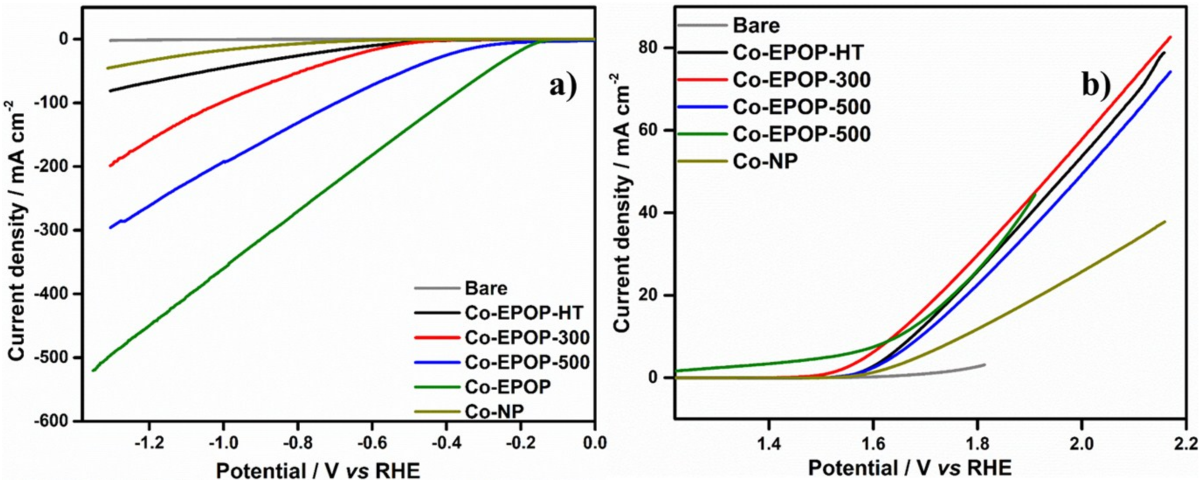


Figure S15. LSV curves a) HER, b) OER

Supporting References

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