

Supporting Information

In-situ self-organization of uniformly dispersed Co-N-C centers at moderate temperature without sacrificial subsidiary metal

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Experimental section

Preparation of Co-N-C@T (380, 600, 750, 900)

Co-N-C catalyst were prepared by the pyrolysis of the mixture of 200 mg dicyandiamide (DCDA) as a nitrogen and carbon source and macrocyclic compound cobalt phthalocyanine (CoPc) as a cobalt source at different temperature (T: 380, 600, 750, 900°C) and denoted as Co-N-C@T (T=380, 600, 750, 900), where T is the pyrolysis temperature. The mixture of DCDA and CoPc was ground using mortar and pestle until it get homogeneously mixed and loaded in quartz tube (diameter= 11mm and length=60cm with one end closed) which introduced at the middle of furnace (Lenton LTF 14/-/180). The temperature of furnace raised for respective samples at the rate of 10°C per minute and maintained for 3 hours followed by cooling to room temperature by natural convection. The present work elucidates the role of pyrolysis temperature during synthesis on the ORR performance.

Characterizations

High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF STEM) imaging and X-ray Energy Dispersive Spectroscopy (EDS) were performed on a Cs aberration corrected FEI Titan® Themis 60-300 kV and TEM-TITAN operated at an accelerating voltage of 300 kV. The TEM sample was prepared by dispersing the as synthesized catalyst in ethanol solution, followed by 30 minutes ultrasonication and drop-casted on carbon coated copper grid and then dried at room temperature. XRD analysis was performed by PANalytical X'Pert Pro equipped with Cu K α radiation of wavelength

1.5406 Å at the scan rate of 0.05 s⁻¹ and 2θ range applied was 5-90°. Raman spectroscopy of as-synthesized samples were carried out using a WITec Alpha 300 (Nd:YAG laser source, excitation wavelength 532 nm). The chemical composition and elemental oxidation state of the samples were investigated by XPS spectroscopy (XPS, AXIS ULTRA DLD from kratos monochromatic Al Kα 1486.6 eV excitation source). The XAS measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. X-ray Absorption Spectroscopy (XAS) measurements, comprising of both X-ray Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) techniques, have been carried out on at Co K edge to understand the local structure around the Co atoms. The sample has been prepared and measured in transmission mode at room temperature. The oscillations in the absorption spectra $\mu(E)$ has been converted to absorption function $\chi(E)$ defined as follows :¹

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)}$$

Where, E_0 is absorption edge energy, $\mu_0(E_0)$ is the bare atom background and $\Delta\mu_0(E_0)$ is the step in $\mu(E)$ value at the absorption edge. The energy dependent absorption coefficient $\chi(E)$ has been converted to the wave number dependent absorption coefficient $\chi(k)$ using the relation,

$$K = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

where, m is the electron mass. $\chi(k)$ is weighted by k^2 to amplify the oscillation at high k and the $\chi(k)k^2$ functions are fourier transformed in R space to generate the $\chi(R)$ versus R spectra in terms of the real distances from the center of the absorbing atom. The Demeter software package have been used for EXAFS data analysis.[4]With the help of ATHENA software background reduction and Fourier

transform to derive the $\chi(R)$ vs R spectra from the absorption spectra has been analysed. The generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of experimental data with the theoretical spectra using ARTEMIS software.

Electrochemical measurements

All of the electrochemical measurements were carried out at room temperature using a CHI7052E electrochemical workstation with standard three electrode cell, where Pt-ring served as counter, KCl saturated Ag/AgCl as reference and as synthesized electrocatalysts decorated glassy carbon (GCE, active geometrical area of $\sim 0.07 \text{ cm}^2$ for the RDE and 0.196 cm^2 for the RRDE) as working electrode. The electrochemical characterizations were carried out in a rotating disc electrode (RDE) and rotating ring disc electrode (RRDE) system. 7 mg of as prepared catalyst or state-of-art catalyst (Pt/C) was dispersed in the 1 ml mixture of solution (Milli-Q water: ethanol= 1:1 (v/v)) followed by 30 min sonication to form homogeneous ink. 60 μl of ink mixed with 10 μl Nafion (14.29 wt%) solution as a binder followed by sonication of 30 min. The fabrication of working electrode was done by loading 0.37 mg/cm^2 (i.e. optimised loading) of ink onto glassy carbon electrode and dried at room temperature. All electrochemical measured potential was carried out against Ag/AgCl are converted with respected to reversible hydrogen electrode (RHE) using equation $E_{\text{RHE}} = E_{\text{O Ag/AgCl}} + (0.059 \cdot \text{pH}) + E_{\text{Ag/AgCl}}$, where $E_{\text{O Ag/AgCl}}$ is 0.197 V vs. SHE.²

The double layer capacitance (C_{dl}) was carried out by performing the cyclic voltammogram in O_2 saturated alkaline 0.1 M NaOH solution at the scan rate of 10-100 mV/s in non-faradaic region. The electrochemically active surface area (ECSA) and roughness factor were calculate by the following equations (1) and (2), respectively.³

$$\text{ECSA (in cm}^2\text{)} = \frac{C_{\text{dl}}}{C_{\text{s}}} \quad (\text{S1})$$

$$R_f = \frac{ECSA}{A_g} \quad (S2)$$

where C_{dl} is the double layer capacitance and C_s is the capacitance of atomically smooth, flat surface of catalyst material per unit area under similar experimental condition, i.e. 0.040 mF cm^{-2} (in alkaline solution).^{4,5} A_g represents the geometric area of the working electrode ($A_g = 0.07 \text{ cm}^2$ for RDE).

The ORR LSV-RRDE polarization curves were carried out in O_2 saturated 0.1 M NaOH solution at the scan rate of 10 mV/s at various rotating speed ($2400, 2000, 1600, 1200 \text{ rpm}$) within the potential window of 0.164 V to 1.0 V (vs. RHE). Furthermore, an in-depth understanding of the ORR process, the electron transfer number (n) and hydrogen peroxide formation ($\% HO_2^-$) were deduced from RRDE-LSV polarization curve, calculated by the following equations:

$$n = 4 \times \frac{I_D}{\frac{I_R}{N} + I_D} \quad (S3)$$

$$\%HO_2^- = 200 \times \frac{I_R/N}{I_R/N + I_D} \quad (S4)$$

where I_D and I_R represent the disc and ring currents, respectively and $N=0.3$ is the collection efficiency of the Pt ring.^{2,3}

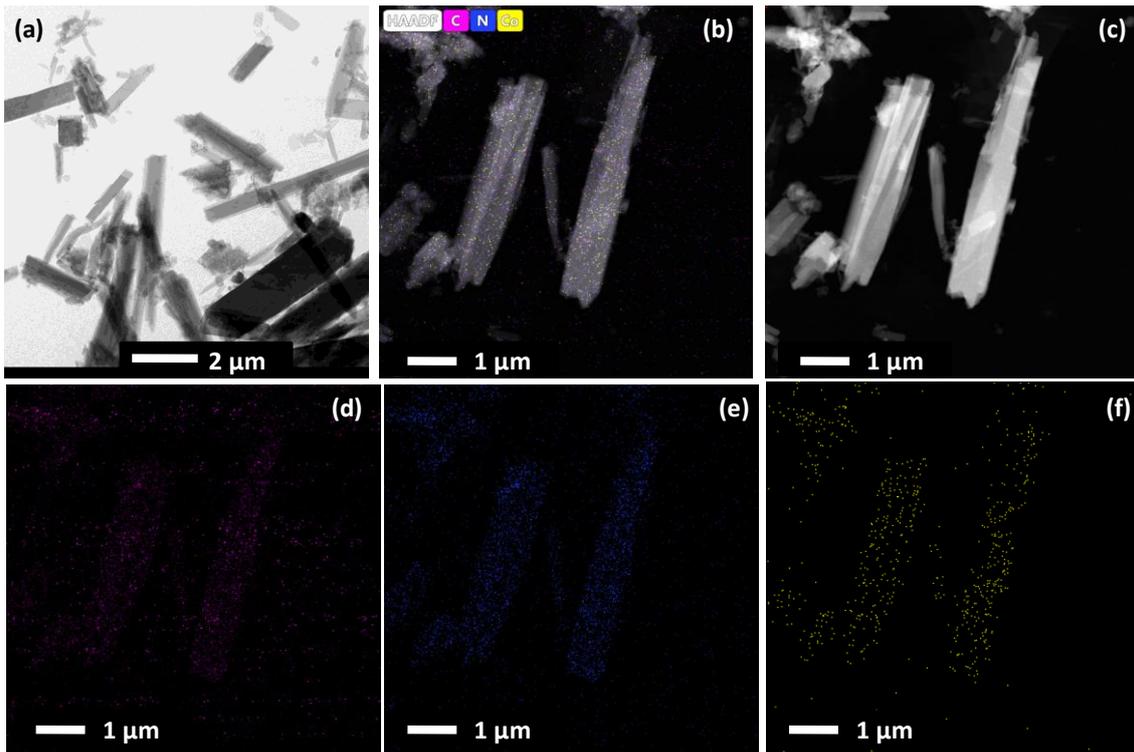


Fig S1: (a) Bright field TEM image of CoPc, (b,c) HAADF-STEM image and (d-f) corresponding EDS mapping of C, N, Co elements, respectively for CoPc.

TGA of CoPc

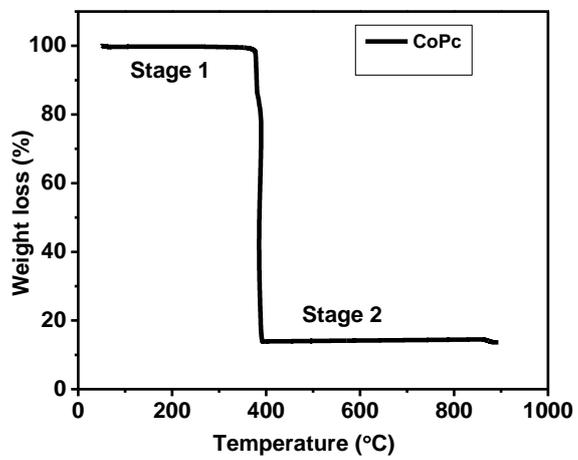


Fig S2: Thermo gravimetric analysis (TGA) of CoPc.

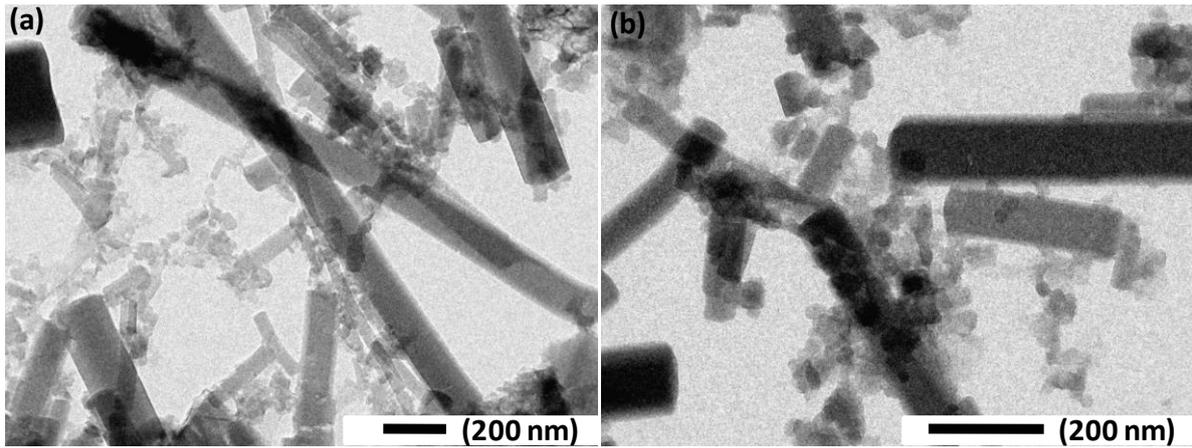


Fig S3:(a,b) Bright field TEM image of Co-N-C@380.

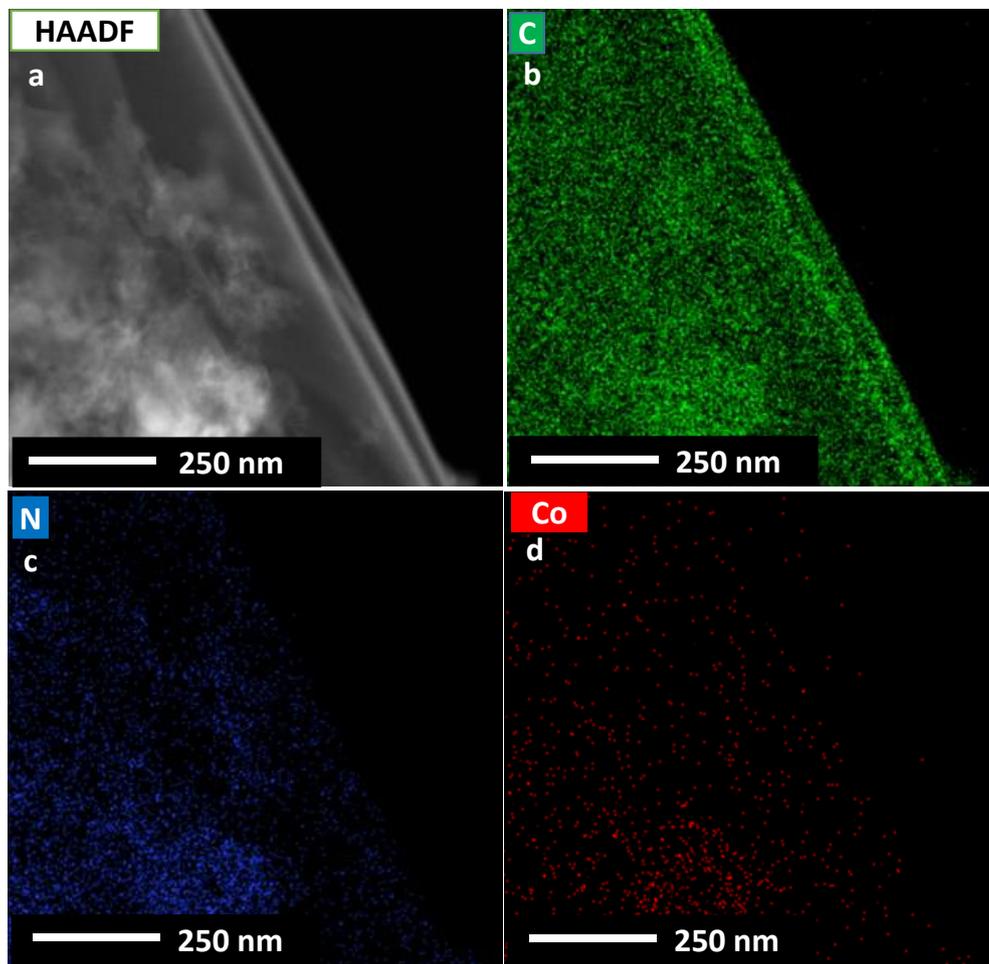


Fig S4: (a) HAADF-STEM image of Co-N-C@600, (b-d) corresponding EDS mapping of C, N, Co elements, respectively for Co-N-C@600.

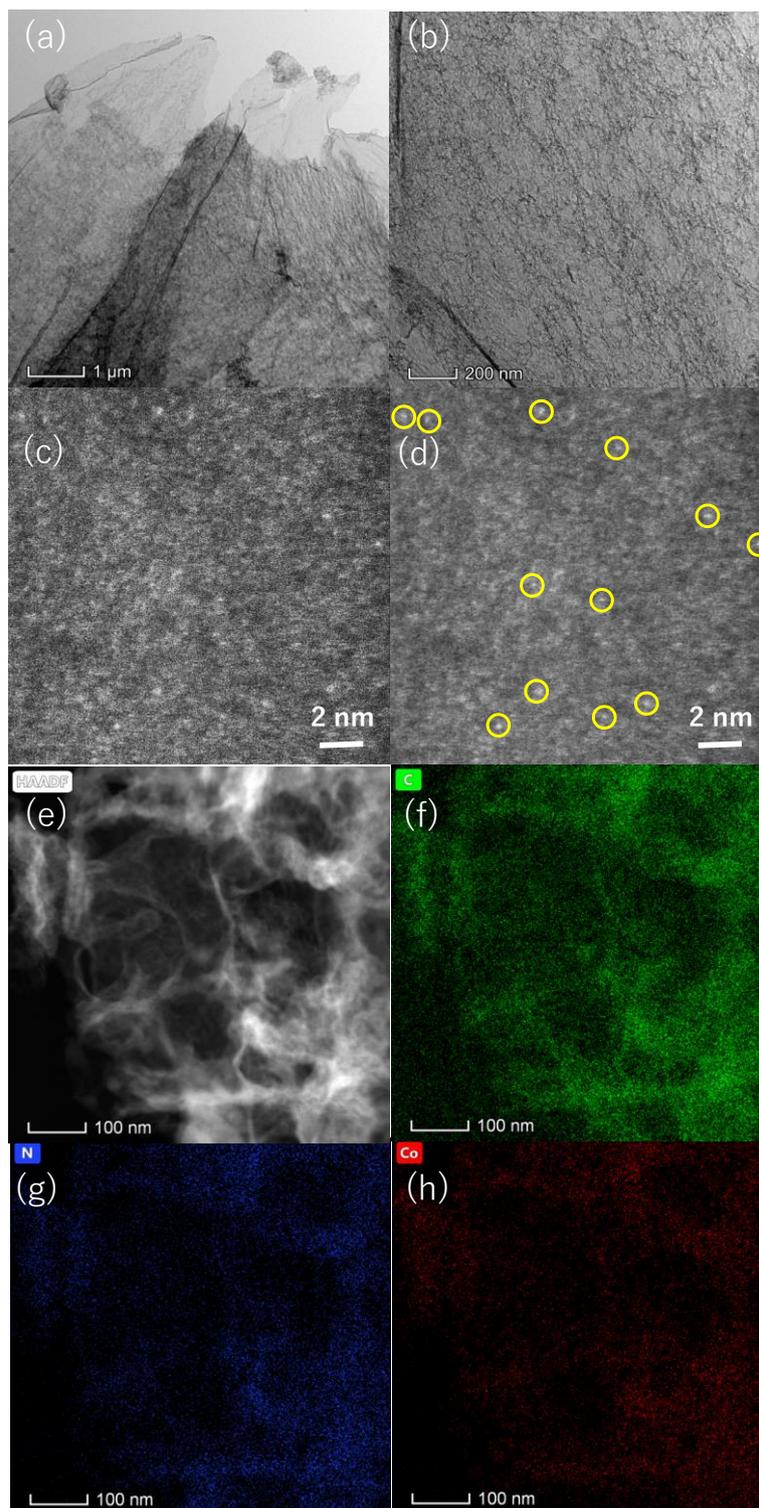


Fig S5:(a,b)Bright field TEM images of Co-N-C@750 at different magnification, (c-e) HAADF-STEM image of Co-N-C@750, (f-h) corresponding EDS mapping of C, N, Co elements, respectively for Co-N-C@750.

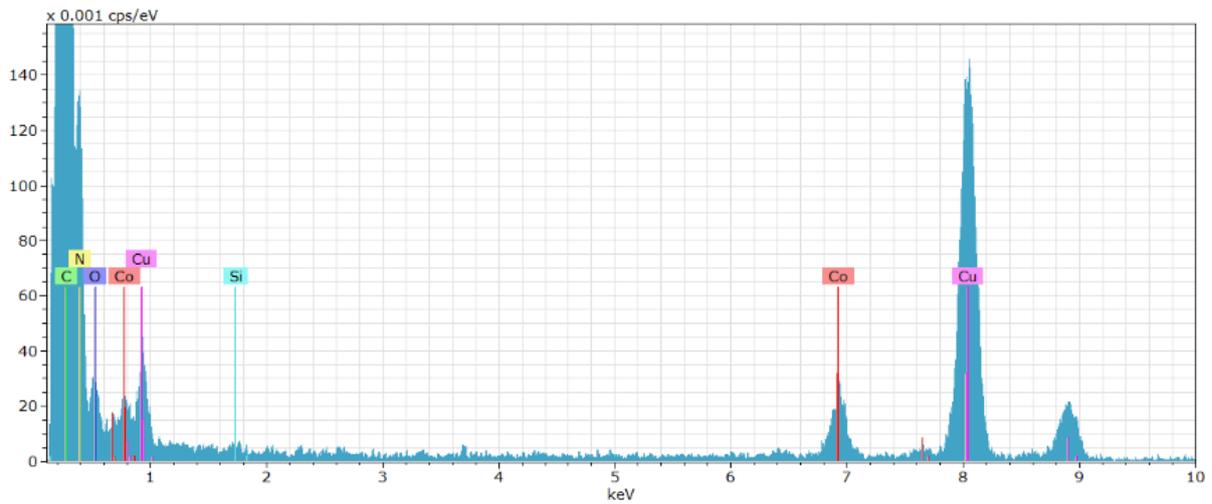


Fig S6: EDS spectra corresponding to elemental mapping fig 3 (d-f).

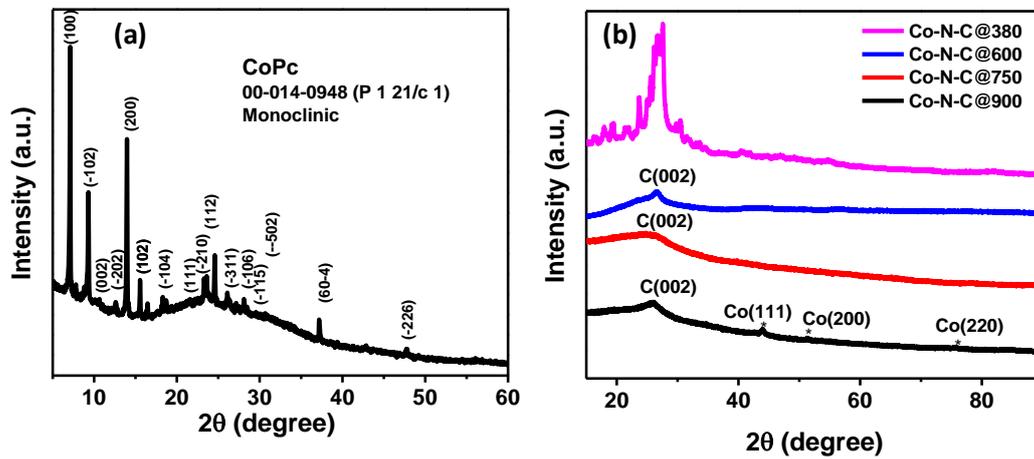


Fig S7: XRD patterns of (a) CoPc, (b) Co-N-C@T (T= 380, 600, 750, 900).

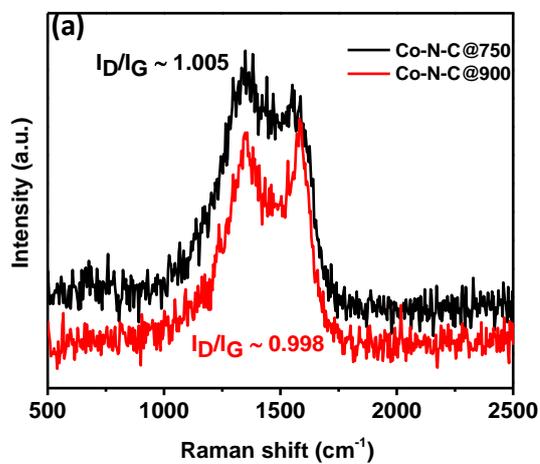


Fig S8: (a) Raman spectra of Co-N-C@750 and Co-N-C@900.

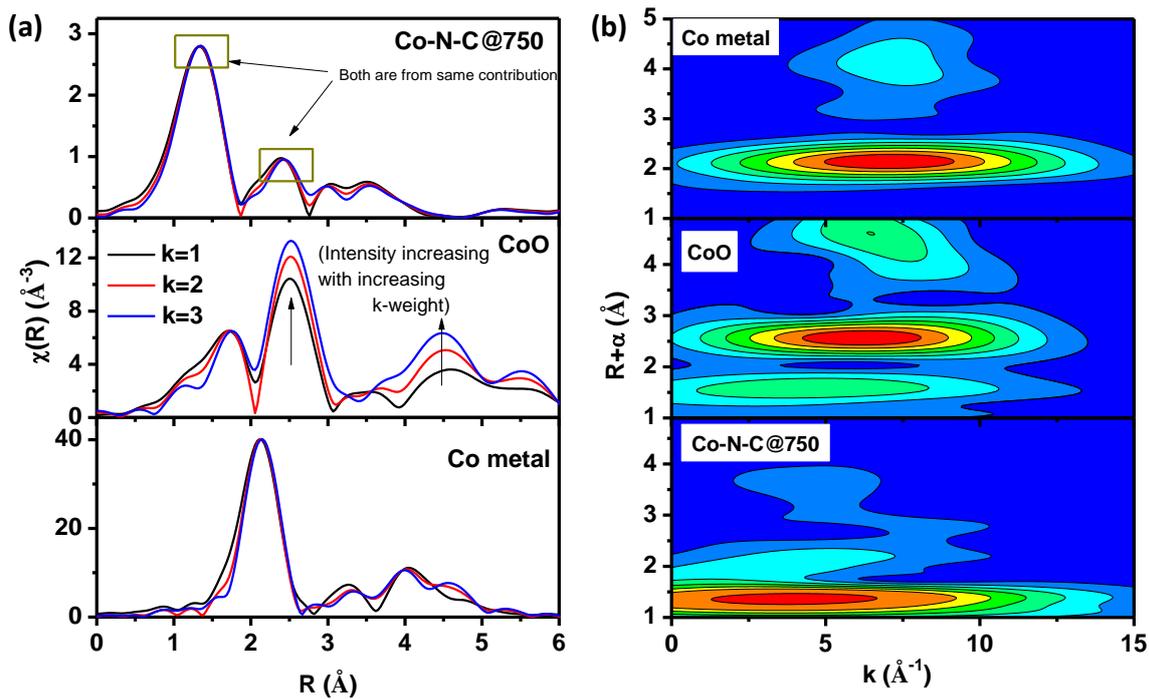


Fig S9:(a) The Fourier transform with different k weighted test on Co-N-C@750, CoO and Co metal, (b) Wavelet transforms EXAFS spectra at Co K edge of Co metal, CoO and Co-N-C@750.

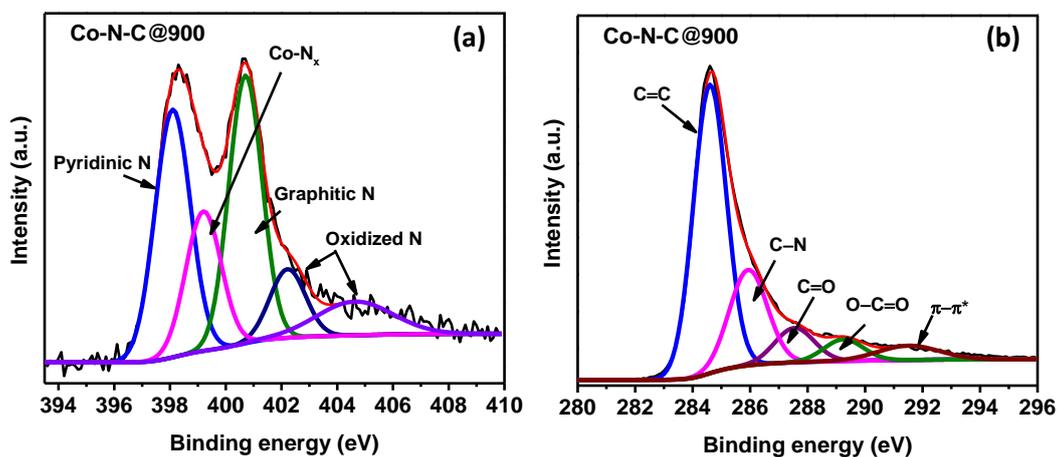


Fig S10: High resolution (a) N 1s XPS spectra and (b) C 1s XPS spectra of Co-N-C@900.

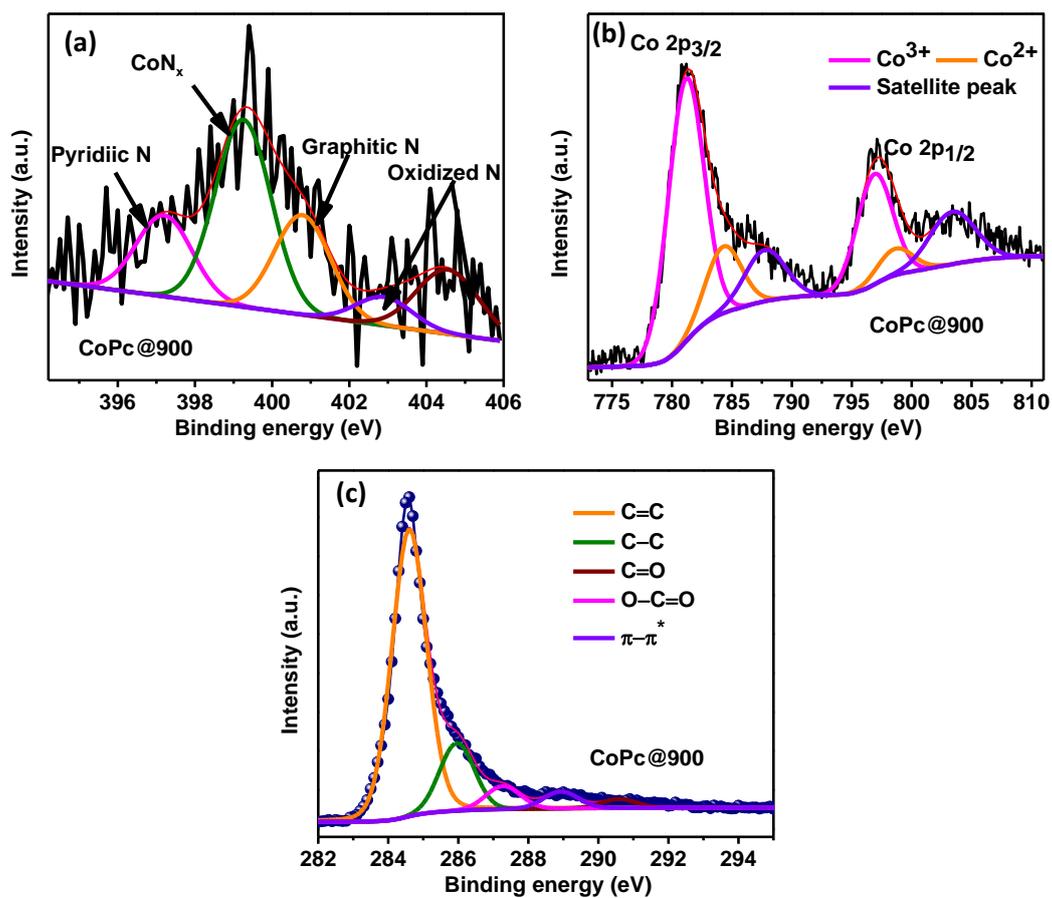


Fig S11: High resolution (a) N 1s XPS spectra, (b) Co 2p XPS spectra and (c) C 1s XPS spectra of CoPc@900.

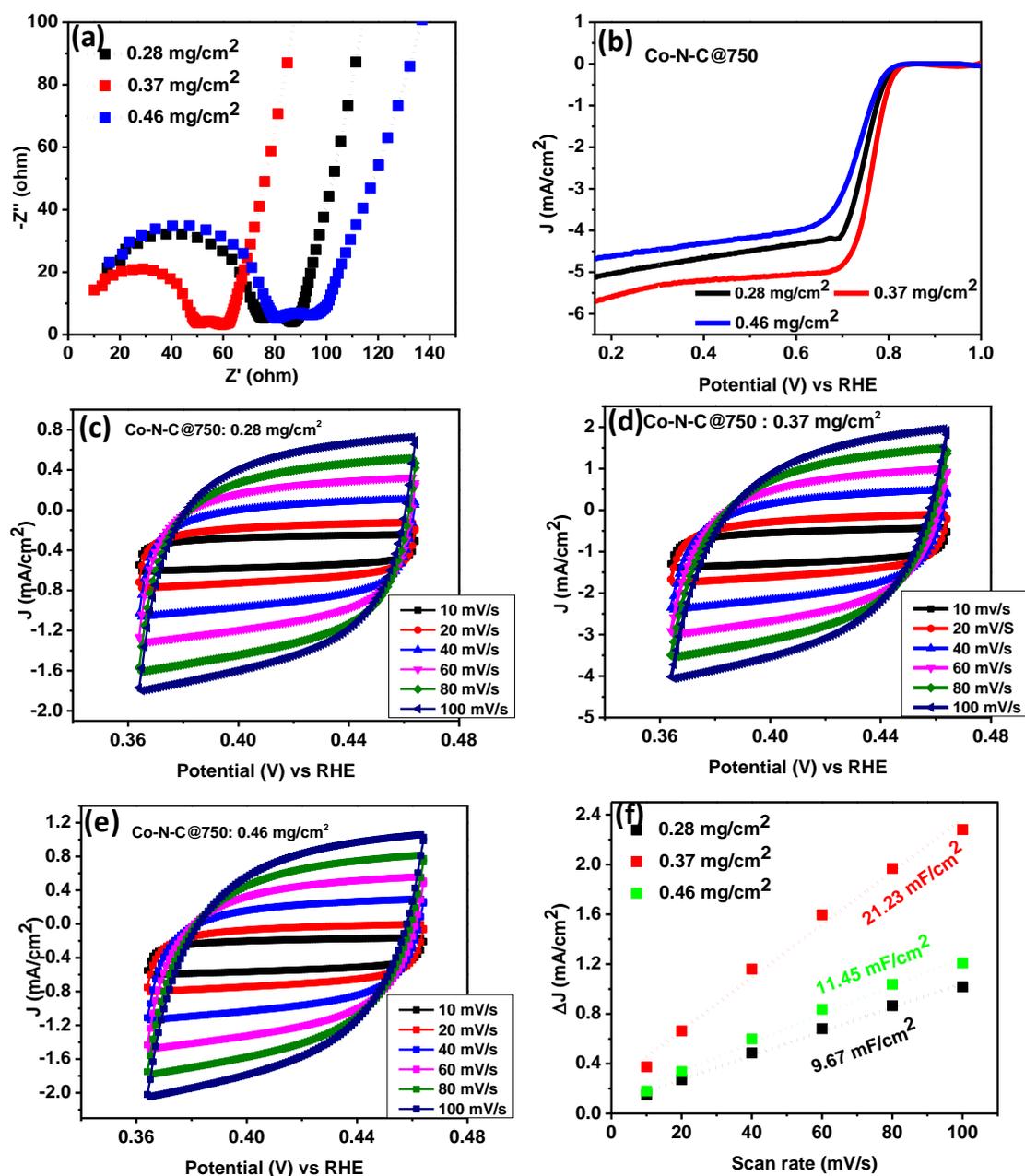


Fig S12:(a) Nyquist plot of Co-N-C@750 at various loading of 0.28 mg/cm², 0.37mg/cm², 0.46 mg/cm², (b)ORR LSV-RDE polarization curve of as prepared Co-N-C@750 at different loading (in O₂ saturated 0.1 M NaOH solution at scan rate 10 mV/s @2400 rpm), (c-e)Cyclic voltammograms in oxygen saturated alkaline 0.1 M NaOH electrolyte at the scan rate of 10-100 mV/s in non-faradaic region for 0.28 mg/cm², 0.37mg/cm², 0.46 mg/cm², respectively, (f)Double layer capacitance measurement of Co-N-C@750 for different loading.

Table S1: C_{dl} , ECSA, R_f of Co-N-C@750 at different catalyst loading.

| Electrocatalysts loading(mg/cm ²) | C_{dl} (mF /cm ²) | ECSA (cm ²) | R_f |
|---|----------------------------------|--------------------------|--------|
| 0.28 | 9.67 | 16.92 | 241.75 |
| 0.37 | 21.23 | 37.15 | 530.75 |
| 0.46 | 11.45 | 20.04 | 286.25 |

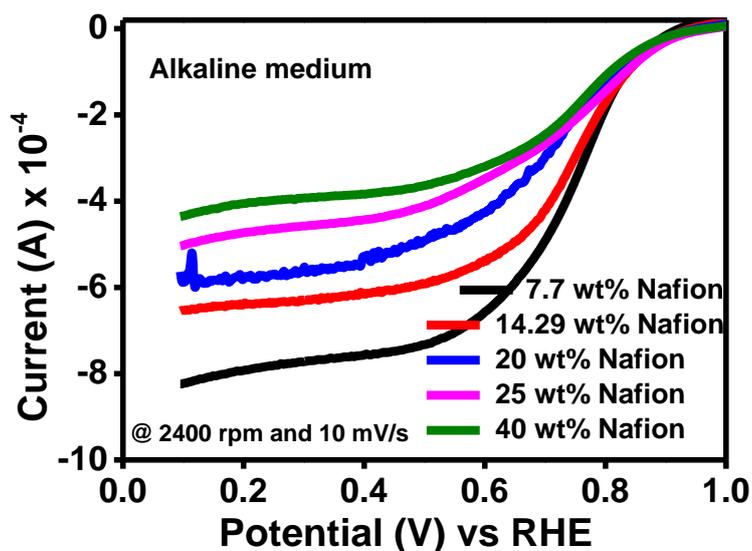


Fig S13: ORR LSV-RDE polarization curve of state-of-the-art Pt/C catalyst with different nafion binder percentage used during ink preparation (in O₂ saturated 0.1 M NaOH solution at scan rate 10 mV/s and 2400 rpm rotation).

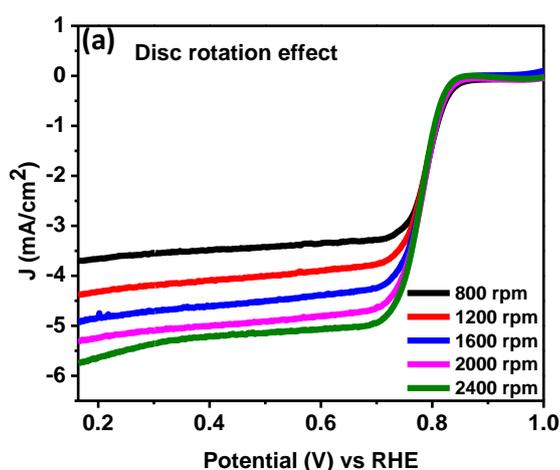


Fig S14:(a) ORR LSV-RDE polarization curve of as prepared Co-N-C@750 at different rotation speed from 800 to 2400 rpm (in O₂ saturated 0.1 M NaOH solution at scan rate 10 mV/s).

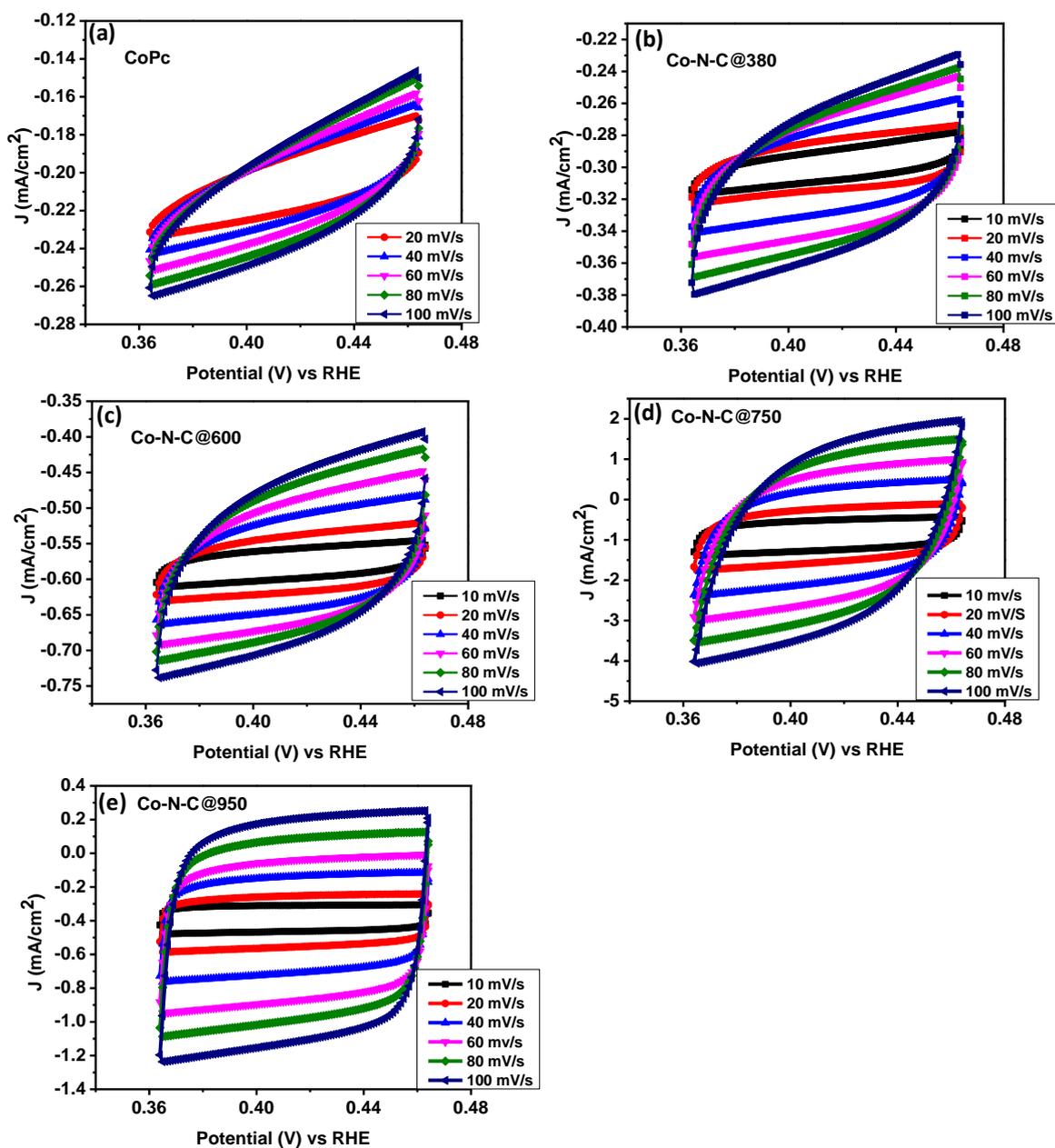


Fig S15 : Cyclic voltammograms in oxygen saturated alkaline 0.1 M NaOH electrolyte at the scan rate of 10-100 mV/s in non-faradaic region for (a) CoPc and (b-e) Co-N-C@T (T= 380,600, 750, 900°C), respectively.

Table S2: C_{dl} , ECSA, R_f of CoPc and Co-N-C@T (T= 380, 600, 750, 900°C).

| Electrocatalysts loading | C_{dl} (mF/cm ²) | ECSA (cm ²) | R_f |
|--------------------------|---------------------------------|--------------------------|-------|
| CoPc | 0.17 | 0.30 | 4.25 |
| Co-N-C@380 | 0.42 | 0.74 | 10.50 |
| Co-N-C@600 | 1.07 | 1.87 | 26.75 |

| | | | |
|------------|-------|-------|--------|
| Co-N-C@750 | 21.23 | 37.15 | 530.75 |
| Co-N-C@900 | 6.47 | 11.32 | 161.75 |

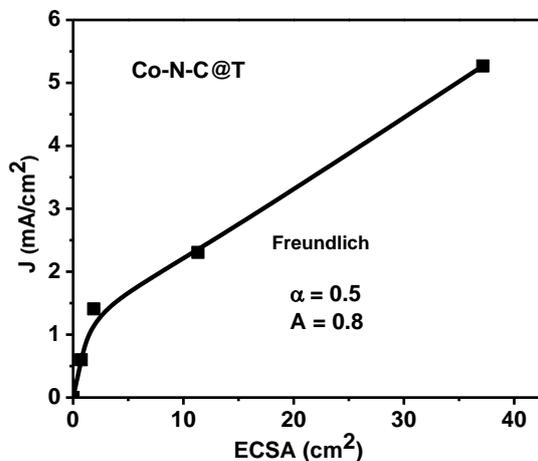


Fig. S16 : Freundlich adsorption isotherm for Co-N-C@T (T= 380, 600, 750 and 900).

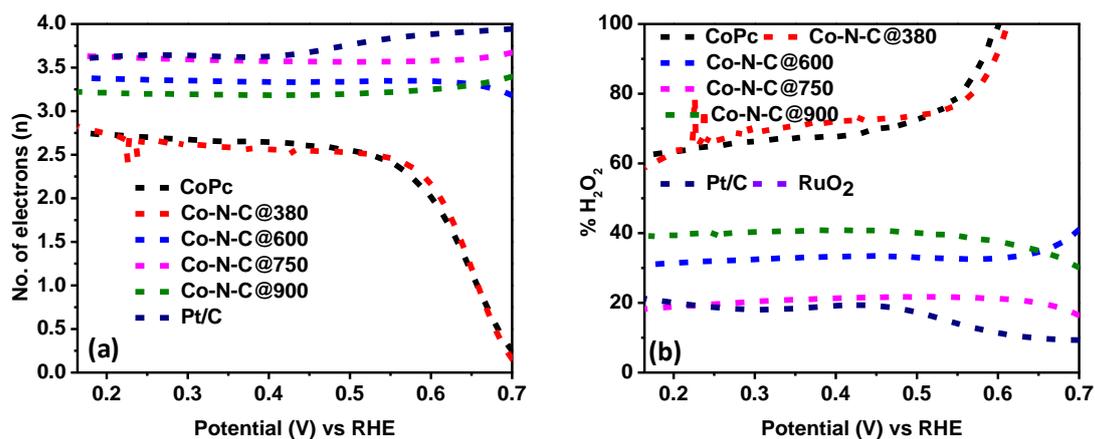


Fig S17: (a) No. of electron transfer and (b) % H_2O_2 generation of CoPc and Co-N-C@T (T=380, 600, 750, 900°C), state-of-the-art Pt/C and RuO_2 catalysts measured from their respective RRDE-LSV polarization curve.

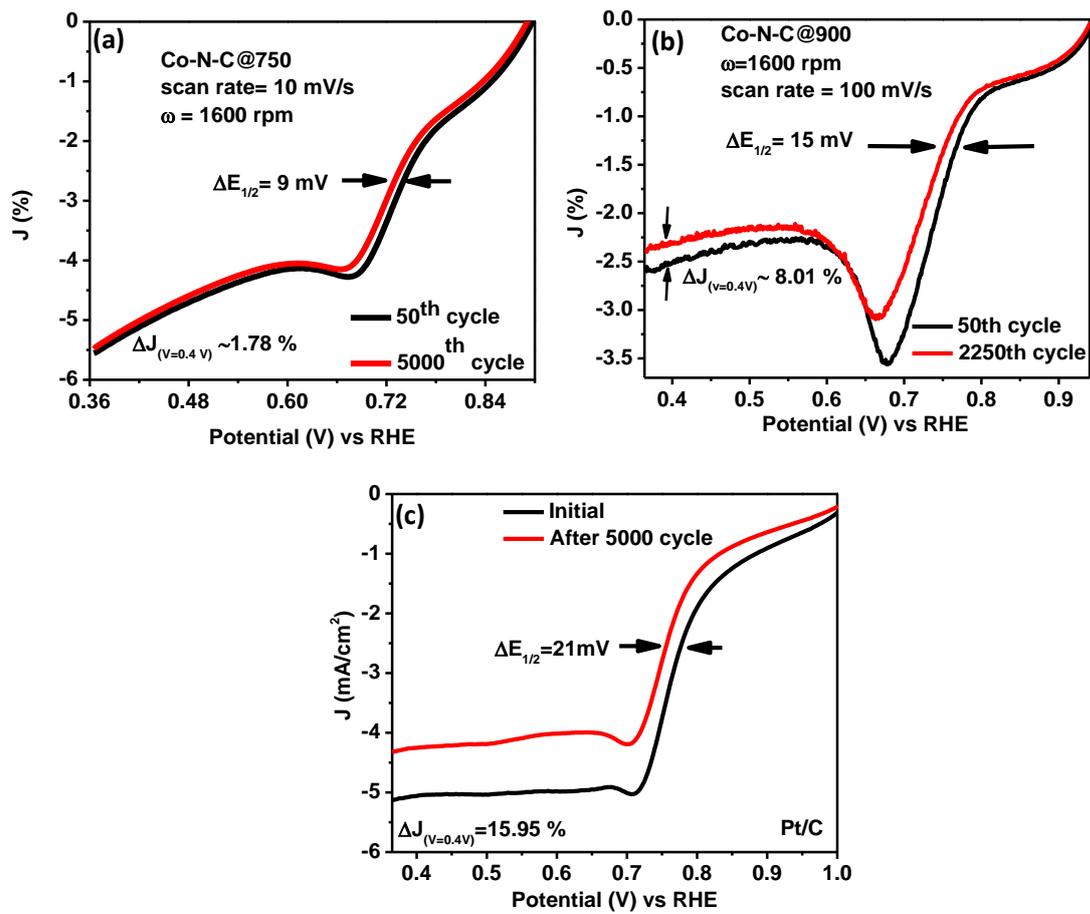


Fig S18: The accelerated stability test in O_2 saturated 0.1 M NaOH electrolyte at the scan rate of 100 mV/s and rotation speed of 1600 rpm for (a) Co-N-C@750 and (b) Co-N-C@900 and (c) Pt/C

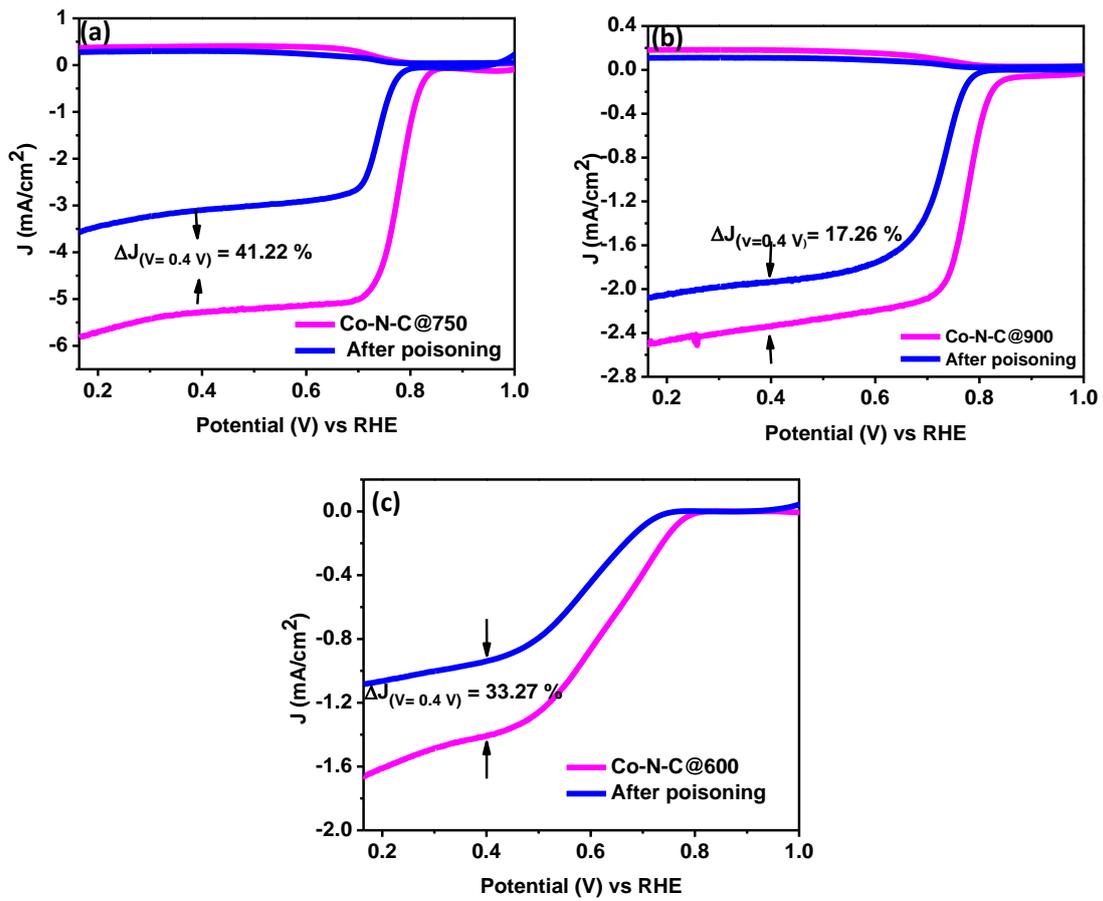


Fig S19: ORR-LSV RDE curve at 10 mV/s @2400 rpm in O₂ saturated 0.1 M NaOH and 0.1 M NaOH+ 10 mM NaCN electrolyte for (a) Co-N-C@750, (b) Co-N-C@900 and (c) Co-N-C@600.

Table S3: Summary of previously reported catalysts in terms of their ORR half wave potential in basic media.

| Catalyst | $E_{1/2}$ (mV vs RHE) | Loading (mg/cm²) | References |
|--|---|------------------------------------|-------------------|
| NCAC-Co | 743 | - | 6 |
| Co _{0.25} -N _{0.32} /C-800 | 700 | 0.4 | 7 |
| NGM-Co | 770 | 0.25 | 8 |
| CoNC | 780 | - | 9 |
| Co@NCNT | 779 | - | 10 |
| Co/N-C CNFs | 710 | 0.2 | 11 |
| FeN _x C/C-S | 720 | 0.8 | 12 |
| NPMC-800 | 750 | | 13 |
| B-FeCNTs | 739 | 0.75 | 14 |
| Co-NC-900 | 800 | 0.40 | 15 |
| CoNP@NC/NG-700 | 780 | - | 16 |
| Co-N-C@750 | 778 | 0.37 | Present study |

Table S4: Summary of previously reported catalysts in terms of their ORR mass activity in basic media.

| Catalysts | Mass activity (mA/mg) | Loading (mg/cm ²) | References |
|-----------------|-----------------------|-------------------------------|---------------|
| CNTs@Co-N-PC | 9.333 | 0.6 | 17 |
| Co/N-C CNFs | 12.5 | 0.2 | 11 |
| Co-NC | 13.0 | 0.4 | 18 |
| FeNxC/C-S | 6.625 | 0.8 | 12 |
| B-FeCNTs | 8.533 | 0.75 | 14 |
| cobalt-based CP | 8.04 | 0.5969 | 19 |
| Co-N- GA | 5.892 | 0.611 | 20 |
| Co SAs/N-C(900) | 13.5 | 0.408 | 21 |
| Co-NC-900 | 11.4 | 0.40 | 15 |
| Co-N-C@750 | 14.24 | 0.37 | Present study |

Table S5: Summary of few recently featured reports based on Co-N-C based systems, where acid leaching has been used to develop Co-N-C based systems.

| Catalysts/Materials | Commercial Chemicals Used | Special Chemicals | Synthesis Conditions | Journal |
|---|--|--|--|---|
| Cobalt single atoms anchored on nitrogen-doped porous carbon (Co-N-C) | Magnesium oxide (MgO), CoCl ₂ ·6H ₂ O, 1,10-phenanthroline | 5 M hydrochloric acid (HCl) with reflux for 30 minutes 2 M H ₂ SO ₄ at 80 °C for 6 h Solvent used: Ethanol | Four steps First: Preparation of a MgO template Second: Precursor can be obtained from the mixture of MgO, CoCl ₂ ·6H ₂ O and 1,10-phenanthroline in ethanol solvent and stirred and heated at 60°C for 2 h. | Green Chemistry, 2020, 10.1039/d0gc03498c |

| | | | | |
|---|--|---|---|--|
| | | | <p>Third: Pyrolysis at 700. 800. 900°C (Ar gas flow during synthesis)</p> <p>Fourth: 5 M HCl with reflux for 30 minutes and 2 M H₂SO₄ treatment at 80 °C for 6 h.</p> | |
| Single Co atom and N codoped carbon nanofibers (Co–N/CNFs) | <p>polyacrylonitrile (PAN), 4-dimethylaminopyridine (DMAP), cobalt acetate (Co(Ac)₂)</p> | <p>5M H₂SO₄ treatment for 24 h at 80°C</p> <p>Solvent used: dimethylformamide (DMF)</p> | <p>Four steps</p> <p>First: Electrospinning at 16-18 kV of the mixture of PAN, DMAP and Co(Ac)₂ in DMF solvent ,</p> <p>Second: annealing in Muffle furnace at 250°C in air atmosphere,</p> <p>Third: pyrolysis at 900 °C,</p> <p>Fourth: 5 M H₂SO₄ treatment for 24 h at 80°C</p> | <p><i>ACS Catal.</i> 2017, 7, 6864–6871</p> |
| Atomically dispersed Co–N–C@F127 catalyst derived from surfactant-assisted MOFs | <p>2-methylimidazole, zinc nitrate hexahydrate, cobalt(II) nitrate hexahydrate, F127 (surfactant)</p> | <p>2 M HCl solution treatment for 5 h at 50°C</p> <p>Solvent used: Methanol and ethanol</p> | <p>Three steps</p> <p>First: Precursor can be obtained from the mixture of 2-methylimidazole, zinc nitrate hexahydrate, cobalt(II) nitrate hexahydrate and F127 in Methanol solvent and centrifuged with ethanol and dried at 60°C for 12 hours,</p> | <p><i>Energy Environ. Sci.</i>, 2019, 12, 250–260</p> |

| | | | | |
|---------------------------------------|--|---|---|--|
| | | | <p>Second: Pyrolysis at 900°C (N₂ gas flow during synthesis)</p> <p>Third: 2 M HCl solution treatment for 5 h at 50°C</p> | |
| Single atom cobalt catalysts (Co-SAC) | Co(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, 2-methylimidazole | <p>3 M HCl treatment for 6 hour at 80°C</p> <p>Solvent used: Methanol</p> | <p>Three steps</p> <p>First:- ZnCo-biMOF can be obtained from mixture of 2-methylimidazole, zinc nitrate hexahydrate and cobalt(II) nitrate hexahydrate in Methanol solvent and centrifuged with ethanol and freeze dried overnight,</p> <p>Second: Pyrolysis at 900°C (N₂ gas flow during synthesis)</p> <p>Third:-3 M HCl solution treatment for 6 h at 80°C</p> | ChemSusChem 2018, 11, 3473 – 3479 |
| Single-atom dispersed Co–N–C catalyst | Co(phen)₂(OAc)₂, Mg(OH)₂ | <p>Nitric acid treatment</p> <p>Solvent used: tert-butyl alcohol</p> | <p>First: Precursor can be obtained from the mixture of Co(phen)₂(OAc)₂ and Mg(OH)₂</p> <p>Second: Pyrolysis at 700°C (N₂ gas</p> | Chem. Sci., 2016, 7, 5758 |

| | | | | |
|-----------------------------|---|---|--|--|
| | | | <p>flow during synthesis)</p> <p>Third: Nitric acid treatment to remove MgO template</p> | |
| Single atom Co-N-C catalyst | <p>SiO₂ nanospheres (50 nm),cobalt chloride hexahydrate (CoCl₂·6H₂O), dicyandiamide (C₂H₄N₄)</p> | <p>0.15 M HF acid treatment</p> <p>0.5 M HCl overnight to remove excess Co</p> <p>Solvent used: N-methyl-2-pyrrolidone (NMP)</p> | <p>Four steps</p> <p>First: Precursor can be obtained from the mixture of SiO₂ nanospheres, CoCl₂·6H₂O and C₂H₄N₄ in NMP solvent and stirred and heated at 80°C for several h.</p> <p>Second: Solid were heated at 500°C for 2 h and then 750°C for 2 h.</p> <p>Third: 0.15 M HF solution treatment for completely remove the SiO₂ Spheres.</p> <p>Fourth: 0.5 M HCl Overnight treatment to remove excess Co</p> | <p>Chemical Engineering Journal 389 (2020) 124377</p> |
| Co-N-C/750 | <p>Dicyandiamide, Cobalt phthalocyanine</p> | <p>Acid and Organic solvent Not used</p> | <p>No gas flow, Single step Pyrolysis temperature 750 °C</p> | <p>Present study</p> |

Table S6: Summary of previously reported M-N-C based systems in “Green Chemistry” where melamine/urea/ phthalocyanine as well as ZnO as a sacrificial agent has been used to develop M-N-C based systems

| Catalysts/Materials | Commercial Chemicals Used | Special Chemicals | Synthesis Conditions | Journal |
|---|--|---|--|--|
| Atomic Fe embedded in bamboo-CNTs grown on graphene (Fe-N-G/bC) | Melamine, 1-butyl-3-methylimidazolium tetrachloroferrate | Before annealing Hot 2 M HCl acid at 80 °C for 12 h (Twice repetition) 0.5 M H ₂ SO ₄ treatment for 24 h after annealing | Three steps First: Electrochemical charging at 4V, Second: Ball Milling Third: pyrolysis at 800 °C | <i>Green Chem.</i> , 2018, 20 , 3521-3529 |
| Ni catalysts supported on nitrogen doped carbon (Ni/NDC) | Urea, Glucose, ZnO nanoparticles, Semolina | 0.1 M HCl solution treatment for 10 h under continuous stirring | N ₂ gas flow during synthesis (8 h N ₂ gas flow) Pyrolysis at 950 °C | <i>Green Chem.</i> , 2020, 22 , 2755-2766 |
| Fe containing N-doped carbon | Activated carbon, FeCl ₃ , ammonium peroxydisulphate, iron(II) phthalocyanine | 6 M HCl treatment to activated carbon for 24 h 0.5 M HCl for aniline polymerization with (NH ₄) ₂ S ₂ O ₈ | First:- Pyrolysis of material between 700 and 900 under N ₂ gas flow Second:- 0.5 M H ₂ SO ₄ treatment for 8 h at 80 °C after first pyrolysis Third:- Repeating the pyrolysis after H ₂ SO ₄ treatment for 3 h at 700-900 °C | <i>Green Chem.</i> , 2016, 18, 1547–1559 |
| Co-N-C@750 (Present study) | Dicyandiamide, Cobalt phthalocyanine | Not used | No gas flow, Single step | |

| | | | | |
|--|--|--|------------------------------------|--|
| | | | Pyrolysis temperature 750 °C | |
|--|--|--|------------------------------------|--|

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