## **Electronic Supplementary Information**

# Mechanistic insight into the Co-Based metal-organic framework as an efficient oxygen electrocatalyst via in-situ FT-IR study

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## Section-1

#### **1. EXPERIMENTAL**

## **Materials and Methods**

#### Materials

This analysis utilized organic linkers benzene-1,2,4,5-tetracarboxylic acid (H<sub>4</sub>BTC) and imidazole (Him) supplied by Sigma-Aldrich, India respectively. Additionally,  $Co(NO_3)_2.6H_2O$ , and potassium hydroxide (KOH), were indeed purchased from Sigma-Aldrich, India. However, dimethylformamide (DMF) [(CH<sub>3</sub>)<sub>2</sub>NC(O)H] and methanol, organic solvents were utilized as obtained from Spectro-chem, India, with no further purification. The water used in all the experiments was purified through a Millipore system.

#### Synthesis of Co-MOF material:

A mixture of Him (0.068 g, 1 mmol),  $Co(NO_3)_2.6H_2O$  (0.291 g, 1 mmol) and benzene-1,2,4,5tetracarboxylic acid (0.254 g, 1 mmol) was dissolved in 12 mL of DMF and methanol (1:1) and stirred for 1 hour. The resulting solution of the mixure was sealed in 20 mL steal autoclave and heated at 100 °C for 96 h under autogenous pressure. After cooling to room temperature, the purple colored block shaped crystals were obtained and washed with DMF and methanol. The yield of the synthesized crystal material was based on Co(II) by approximately 70 wt%.



#### Synthesis of Co-MOF/G catalyst material:

Synthesis of Co-MOF/G was carried out by electrochemical exfoliation technique using graphene sheet of  $1*1 \text{ cm}^2$  as cathode and anode into a dispersed solution of Co-MOF in 0.1 M phosphate buffered saline (PBS) solution. The exfoliation has been done with 40 mg of Co-MOF in 20 mL PBS solution at 4.0 V for 45 min followed by the sonication at 30 min and continuous stirring for 6 hours. After that, the precipitate was washed several times with DI water and ethanol. Finally, the material Co-MOF/G as represented was obtained by washing with DI water and ethanol and collected through centrifuges under 8000 rpm and dry under vacuum at 70 °C. Similarly, the exfoliation has also been done with different amount of Co-MOF (20 mg, 40 mg, and 60 mg) in 20 mL 0.1 M PBS solution at constant applied potentials (4V) for different time (20 min, 45 min and 60 min) followed by the sonication at 30 min and materials represented as Co-MOF/G<sub>40/45/4</sub>, Co-MOF/G<sub>20/45/4</sub>, Co-MOF/G<sub>60/45/4</sub>, Co-MOF/G<sub>40/30/4</sub>, and Co-MOF/G<sub>40/60/4</sub> catalysts. Here the catalyst represents (Co-MOF/G<sub>mg/t/V</sub>), mg indicates the amount of the Co-MOF taken, t denotes that the time used for exfoliation and V represents the voltage used for the exfoliation. The solution was stirred for 3 hours. The solution was washed with water and ethanol and collected through centrifuged under 8000 rpm and dry under vacuum at 70 °C.

#### Instrumentation.

Powder X-ray diffraction (PXRD) (Bruker D8 Advances instrument with Cu-K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation in the 20 range from 10° to 70° with an acceleration voltage of 40 KV) was used to analysis the crystal structure of the all synthesized materials. The single-crystal diffraction data of the complex was collected on a Bruker diffractometer with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 150 K. Data reduction and the unit cell parameters were determined by using CrysAlisPro 1.171.38.43. With the help of Olex2 software with the SHELXL program, crystal data was solved by direct method and refined by the least square procedure. All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. The detailed surface morphology of samples was analyzed by a high-resolution transmission electron microscope (HRTEM, JEM2100 instrument). The Raman spectra obtained from WITEC

Focus Innovations Alpha-300 Raman confocal microscope under an excitation laser of 532 nm. The bonding configuration and surface elemental composition of the synthesized samples were determined using X-ray photoelectron spectroscopy (XPS) spectrometer (K-Alpha 1063) instruments in an ultrahigh vacuum chamber (7X10<sup>-9</sup> torr) using Al-K<sub> $\alpha$ </sub> radiation (1486.6 eV). The UV-Vis absorbance spectra obtained from CARY5000 UV-Vis G9825 CARY instrument. The Extended X-ray absorption fine structure spectrum (EXAFS) was performed at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India with the dispersive EXAFS beam line (BL-9) at Indus-2 synchrotron radiation source. The beam source was operated at 2.5 GeV (300 mA). A bent crystal Si (111) polychromator for selection of a band energy was used in this beamline (BL-9), all the data for this work was collected in transmission mode for Cobalt foil, Co-MOF and Co-MOF/G catalysts. All the spectra of the synthesized materials were measured under ambient condition. DEMETER programs were used for data analysis. Athena and Artemis codes were used to fit the profiles and extract the measured data. The k range used for Fourier transform is 2-11 Å<sup>-1</sup> for both the samples. The extraction, processing and fitting of the EXAFS data has been done using a set of EXAFS data analysis program available within the Demeter software package. The complete information about the atomic environments surrounding central absorbing Co atom, mean deviation of distances ( $\sigma$ ) as of the absorbing atoms, the nearest neighbor distances (R), and coordination numbers (N), were obtained from the Fourier transform  $|\chi(\mathbf{R})|$  of the EXAFS oscillation curves.

## **Electrode preparation:**

The ink of the catalysts was prepared by dispersing 2 mg of the Co-MOF/G in 1 mL of water and isopropanol (1:1) by ultra-sonication for hour to form homogenous ink. Prior to drop casting, the Glassy carbon electrode (GC), rotating disk electrode (RDE), rotating ring disk electrode (RRDE) working were cleaned thoroughly by using alumina powder with 1, 0.3, and 0.05  $\mu$ m and washed ultrasonically in millipore water. The optimized mass loading of the catalyst ink was dropcasted on the surface of electrode and was then vacuum-dried for overnight. Similarly, the ink of other synthesized control samples also prepared. For comparison, a separate Pt/C (20 wt%) catalyst was prepared by dispersing the Pt/C in a water and isopropyl alcohol mixture (1:1) containing Nafion (5 %) followed by ultrasonication for 60 min. The standard RuO<sub>2</sub> ink also

prepared by using similar method for OER analysis. Nickel foam used for electrode modification for the OER analysis in all the study. The materials were drop-casted on the porous nickel foam and used as a working electrode. All the electrochemical measurements of the materials have been done at room temperature.

## **Electrochemical Measurements**

Electrochemical characterizations were performed in a three-electrode cell using a Metrohm multichannel Autolab (M204) electrochemical workstation at room temperature. A catalyst coated rotating ring-disk electrode (RRDE; GC disk area 0.196 cm<sup>2</sup>; Pt ring area 0.041 cm<sup>2</sup>) was used as working electrode, Ag/AgCl (3 M KCl) as reference electrode and graphite rod as counter electrode.

The electrocchemical surface area analysis of Co-MOF and Co-MOF/G have been done by using cyclic voltammetry curve which were taken with three electrode system at different scan rates from 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup> in 0.1 M KOH electrolyte solution. The CV curves in a non-faradaic region were plotted as a function of various scan rates (10, 20, 40, 60, 80, 100, mV s<sup>-1</sup>). Double layer capacitance (C<sub>dl</sub>) for the both as synthesized materials calculated from the slope of the linear regression between the current density differences in the middle of the potential window of CV curves vs the scan rates. The electrochemical surface area (ECSA) was calculated by using following equation which is give below.

$$ECSA = \frac{C_{dl}}{C_s}$$
(1)

All the electrochemical measurements cyclic voltammetry (CV) and linear sweep voltammetry (LSV), chronoamperometry were carried out in 0.1 M KOH (pH >13) solution that was saturated with  $O_2$  for 30 min prior to the reaction and also during the reaction  $O_2$  saturation was maintained. As the system achieved equilibrium, the data was recorded at the scan rate of 10 mV

s<sup>-1</sup>. During linear sweep voltammetry test, the rotation speed of the working electrode was increased from 625 to 4900 rpm at the scan rate of 10 mV s<sup>-1</sup>. The diffusion-limiting (JL), kinetic current densities (J) and the number of electrons transferred (n) per O<sub>2</sub> molecule were calculated from the slopes (B) of the best linear fit lines of KL plot using KL equation which is given by:

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm K}} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_{\rm K}}$$
(2)

Where *j* is the measured current density, diffusion-limiting (JL), kinetic current densities (JK) and the number of electrons transferred (n) per O<sub>2</sub> molecule,  $\omega$  is the angular velocity of the disk ( $\omega = 2\pi N$ , N is the linear rotation speed), and B is the Levich slope.

B is given by:

$$B=0.62nFC_0 D_0^{2/3} \vartheta^{-1/6}$$
(3)

$$J_{\rm K} = n F k C_0 \tag{4}$$

Where *J* is the measured current density,  $J_L$  and  $J_K$  are the diffusion-limiting and kinetic current densities, F is the Faraday constant (F = 96485 C mol<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> in the solution, n is the overall number of electrons transferred in oxygen reduction reaction, D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.93 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), and  $\vartheta$  is the kinematic viscosity of the electrolyte (1.09× 10<sup>-2</sup> cm<sup>2</sup> s<sup>-1</sup>).

The number of electrons transferred (n) and  $H_2O_2$  production yield is calculated from the RRDE measurement using equations:

$$\boldsymbol{n} = \boldsymbol{4} \times \frac{I_{\rm D}}{I_{\rm D} + \frac{I_{\rm R}}{N}} \tag{5}$$

$$\% H_2 O_2 = 200 \times \frac{\frac{I_R}{N}}{\frac{I_R}{N} + I_D}$$
(6)

where n is the number of electrons transferred (n) during the ORR process,  $I_D$  and  $I_R$  is the absolute value of the disk and ring current respectively and N is the current collection efficiency of the Pt ring (0.249 in this work).

The calculation of Tafel slope for OER

$$\boldsymbol{\eta} = \boldsymbol{a} + \boldsymbol{b} * \log \boldsymbol{j} \tag{7}$$

where  $\eta$  is known as the overpotential, j is represented as the current density and b is the Tafel slope,. All the onset potentials were calculated based on the very beginning of the linear region in Tafel plots.

The calculation of overpotential for OER

$$\boldsymbol{\eta} = \boldsymbol{E}_{RHE} - 1.23 \tag{8}$$

## Section-2

#### Physical and electrochemical characterization



Figure S1. Selected bond lengths of Co-MOF



Figure S2. (a-b) HRTEM images of exfoliated graphene material.



Figure S3. (a) AFM image and (b) height profile of Co-MOF/G catalyst material.



Figure S4. Thermogravimetric analysis (TGA) of Co-MOF material.



Figure S5. FTIR spectrum of Co-MOF and Co-MOF/G catalyst material.

The determination of the binding modes of the tetracarboxylate was done by analyzing the Fourier-transform infrared (FTIR) spectrum of Co-MOF, where the difference in the asymmetric and symmetric stretching frequencies were used as the significant parameters. In the FTIR spectrum of Co-MOF, the asymmetric and symmetric stretching vibrations were observed at 1602 and 1375 cm<sup>-1</sup>, respectively (Figure S5). The difference between these two frequencies was found to be 227 cm<sup>-1</sup>, indicating a monodentate binding mode of the tetracarboxylate ligand to the central metal centre. We have also performed the FT-IR analysis of the Co-MOF/G hybrid material and found almost similar peaks to Co-MOF material. But few peaks diminished due to stacking of the Co-MOF material in between the graphene sheets in the Co-MOF/G material. (Figure S5)



Figure S6. Raman spectra of Co-MOF/G and EG materials



Figure S7. Electrical sheet resistance (I-V) curves of Co-MOF and Co-MOF/G materials



Figure S8. XPS full survey spectra of Co-MOF/G material



**Figure S9.** R space EXAFS fitting spectra of (a) Co-MOF (inset smallest unit structure of Co-MOF) and (b) Co-MOF/G material (inset unit structure of Co-MOF/G material)



**Figure S10.** (a) UV-Vis spectra of Co-MOF and Co-MOF/G material. (b) ss-PL spectra of Co-MOF, EG and Co-MOF/G materials.



**Figure S11.** Cyclic voltammetry (CV) analysis of Co-MOF/G catalyst in the presence of Argon and  $O_2$  gas saturated 0.1 M KOH electrolyte solution.



**Figure S12.** (a) LSV analysis of Co-MOF/G catalyst with different ratio for ORR in the O<sub>2</sub> gas saturated 0.1 M KOH electrolyte solution. (b) LSV analysis of Co-MOF/G catalyst and other control samples for ORR in the Ar-saturated 1 M KOH electrolyte solution. (Here Co-MOF/G<sub>mg/t/V</sub>, the mg denotes amount of the Co-MOF, t denotes time taken for exfoliation, and V denotes voltage used for the exfoliation)



**Figure S13.** Electrochemical active surface area analysis (a) CV curves of Co-MOF/G at different scan rate (b) Linear fitting of capacitive currents of the Co-MOF/G electrocatalyst vs scan rate (c) CV curves of Co-MOF at different scan rate (d) Linear fitting of capacitive currents of the Co-MOF electrocatalyst vs scan rate.



**Figure S14.** Electrochemical impedance spectroscopy (EIS) spectra of Co-MOF/G and Co-MOF. (b) EIS fitted circuit diagram of Co-MOF and Co-MOF/G catalyst.



Figure S15. Linear sweep voltammetry (LSV) polarization curve of Co-MOF/G catalyst at all rotation speeds 625 to 4900 rpm in  $O_2$  saturated 0.1 M KOH electrolyte solution.



**Figure S16.** Linear sweep voltammetry (LSV) polarization curve Co-MOF/G catalyst at 1600 rpm in  $O_2$  saturated 0.1 M KOH electrolyte solution with ring and disk current.



Figure S17. Durability test (i-t) curve of Co-MOF/G catalyst and comparison with Pt/C catalyst



**Figure S18**. Linear sweep voltammetry polarization curve before and after stability of Co-MOF/G catalyst.



**Figure S19.** Methanol cross over durability (i-t) curve of Co-MOF/G in presence of 1 M methanol in  $O_2$ -saturated 0.1 M KOH solution.



**Figure S20.** CV analysis of Pd-NC<sub>800</sub> catalyst with 1 M CH<sub>3</sub>OH and without CH<sub>3</sub>OH in O<sub>2</sub>-saturated 0.1 M KOH electrolyte.



Figure S21. CV analysis of Pt/C catalyst with 1 M CH<sub>3</sub>OH and without CH<sub>3</sub>OH in O<sub>2</sub>-saturated 0.1 M KOH electrolyte.



Figure S22. Tafel slope of all the catalysts in 1 M KOH electrolyte for OER activity.



**Figure S23.** Stability curve of Co-MOF/G catalyst in 1 M KOH electrolyte at constant potential for OER activity.



Figure S24. PXRD analysis of Co-MOF/G catalyst before and after stability measurement.



Figure S25. FTIR analysis of Co-MOF/G catalyst before and after stability measurement.



Figure S26. Full survey of XPS analysis of Co-MOF/G catalyst after stability measurement.



**Figure S27.** XPS analysis of Co-MOF/G catalyst after stability measurement (a) High-resolution deconvoluted C1s XPS spectra, (b) N1s, (c) O1s, and (d) Co 2p deconvoluted spectra after stability measurent.



Figure S28. In situ ATR-IR spectra of Co-MOF/G in Ar-saturated alkaline media.

**Table S1.** Crystallographic parameters for complex Co-MOF

Parameter	<b>Co-MOF</b> (at 150K)
Empirical formula	C <sub>11</sub> H <sub>9</sub> CoN <sub>4</sub> O <sub>4</sub>
Formula weight	320.15
Crystal system	Triclinic
Space group	P-1
a/Å	7.8979(2)
b/Å	9.6092(2)
c/Å	9.6699(2)
α/°	117.062(2)
β/°	96.564(2)
$\gamma/^{\circ}$	103.049(2)
Volume/Å <sup>3</sup>	616.40(3)
Ζ	2
$\rho_{calc}g/cm^3$	1.725
$\mu/mm^{-1}$	1.412
Temperature/K	150.00(10)
$2\Theta_{\text{max}}$	50
Radiation	MoK
λ[Å]	0.71073
Reflns	22619
Ind. reflns	2178
Goodness-of-fit on $F^2$	1.079
R <sub>1</sub>	0.0255
wR <sub>2</sub>	0.0610

Table S2: Selected bond lengths and bond angles for Co-MOF material

Atom	Atom	Length (Å)	]	Bond Angle	Value (°)
Col	N11	2.0319		∠N11-Co1-N21	103.23(7)
				∠N11-Co1-O11	114.94(7)
Col	N21	2.0038		∠N21-Co1-O11	96.85(7)
Col	011	1 9858		∠011-Co1-O13	102.80(6)
001	011	1.7050		∠N11-Co1-O13	120.76(7)
Co1	031	1.9849		∠N21-Cu11-O13	116.08(7)

**Table S3:** Atoms involved in intermolecular hydrogen bonding and its corresponding bond distances and bond angles in Co-MOF (with symmetry equivalents).

\$1 = x, y+1, z; \$2= x+1, y, z;

H-Bond Donor(D)- Acceptor(A)	DA (Å)	∠DHA (°)
N41-H41O21_\$1	2.767(2)	179.5
N21-H21O11_\$2	2.918(3)	150.9

S No.	Elements	Co-MOF/G (	Co-MOF/G Catalyst after stability	
		Binding Energy (eV)	Atomic (%)	Atomic (%)
1.	Carbon (C)	285.05	65.26	63.14
2.	Oxygen (O)	531.91	30.17	32.51
3.	Nitrogen (N)	400.32	1.56	1.40
4.	Cobalt (Co)	782.22	3.01	2.95

**Table S4**. Elemental analysis of Co-MOF/G catalyst obtained from XPS analysis.

**Table S5.** Different parameters obtained from the EXAFS fitting of Co-MOF and Co-MOF/Gcatalyst

Catalysts	Coordination Number	Bond length	Bond disorder	ΔE0 (eV)	R factor
	(N)	R (Å)	σ <sup>2</sup> (*10 <sup>-3</sup> Å <sup>2</sup> )		
Co-MOF at Co K-edge	3.94	1.98	6.10	0.496	0.03
Co-MOF/G at Co K-edge	4.03	1.96	3.24	1.8	0.04

**Table S6.** Performance comparison of Co-MOF/G catalysts synthesized with different ratio through exfoliation technique for ORR and OER application

S. No.	Catalysts	ORR		OER	$\Delta E = E_{ORR} - E_{OER}$ (V vs RHE)
		E <sub>1/2</sub>	$J_{L}$	Overpotential	
		(V vs RHE)	(mA cm <sup>-2</sup> )	(E <sub>j=10</sub> )	
				(mV vs RHE)	
1	Co-MOF/G <sub>40/45/4</sub>	0.78	5.6	302	0.75
2	Co-MOF/G <sub>20/45/4</sub>	0.71	2.96	360	0.88
3	Co-MOF/G <sub>60/45/4</sub>	0.75	4.01	320	0.80
4	Co-MOF/G <sub>40/30/4</sub>	0.72	3.17	352	0.86
5	Co-MOF/G <sub>40/60/4</sub>	0.74	5.11	339	0.82

**Table S7.** All the synthesized catalysts performances on the basis of electrocatalytic parameters for ORR

S. No.	Catalyst	Onset potential E <sub>onset</sub> (V)	Half-wave potential E <sub>1/2</sub> (V)	Limiting current density J <sub>L</sub> (mA cm <sup>-2</sup> )	Tafel slope (mV dec <sup>-1</sup> )
1	Co-MOF/G	0.901	0.78	5.6	74
2	Co-MOF	0.810	0.68	3.22	115
7	Pt/C	0.995	0.85	5.77	80

**Table S8.** All the synthesized catalysts performances on the basis of electrocatalytic parameters for OER analysis

S.	Catalyst	Onset	Over potential	Tafel slope
No.		potential	E <sub>i=10</sub> (mV vs RHE)	(mV dec <sup>-1</sup> )
		E <sub>onset</sub> (V vs RHE)		
1	Co-MOF/G	1.483	302	85
2	Co-MOF	1.542	369	132
5	RuO <sub>2</sub>	1.494	321	87

**Table S9.** Literature comparison of ORR/OER performances with recently reported catalysts in alkaline electrolytes.

S.	catalyst	Half wave	Overpotential	$\Delta E = E_{ORR} - E_{OER}$	Reference
No.		potential	E <sub>j=10</sub>	(V vs RHE)	
		E <sub>1/2</sub>	(V vs RHE)		
		(V vs RHE)	, ,		
1	Co-MOF/G	0.78	1.532	0.75	This work
2	CoFe/N-GCT	0.79	1.67	0.88	1
3	Fe-Co <sub>4</sub> N@N-C	0.83	1.55	0.72	2
4	Co/CoxSy@SNCF	0.76	1.54	0.78	3
5	FeCo-NCNFs800	0.81	1.686	0.86	4
6	CoNi/BCF	0.81	1.60	0.80	5
7	CoNi@CoO-NiO/NH <sub>2</sub> - CNTs-3	0.794	1.607	0.813	6
8	CoS2(400)/N,S-GO	0.79	1.61	0.82	7
9	ZnCo <sub>2</sub> O <sub>4</sub> /NCNT	0.87	1.65	0.78	8
10	Ni <sub>3</sub> Fe/N-C	0.78	1.60	0.82	9
11	NiCo/PFC	0.79	1.63	0.84	10
12	NiO/CoN	0.68	1.53	0.85	11
13	Co9S8/N-C	0.76	1.58	0.82	12
14	NiCo/CNF@NC/NiF	0.78	1.58	0.80	13
15	1D-NiCo <sub>2</sub> O <sub>4</sub>	0.78	1.62	0.84	14
16	FeNi <sub>3</sub> N/NG	0.79	1.64	0.85	15
17	FeCo-NCps	0.84	1.78	0.935	16
18	meso/micro-FeCo-Nx-CN	0.832	1.71	0.878	17
19	Co <sub>1</sub> -PNC/Ni <sub>1</sub> -PNC	0.88	1.62	0.74	18

20	CoNi-SAs/NC	0.76	1.57	0.81	19
21	Ni-N4/GHSs/Fe-N4	0.83	1.62	0.79	20
22	FeCo-N-C	0.896	1.60	0.71	21

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