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Mechanistic insight into a Co-based metal-organic framework as an efficient oxygen electrocatalyst *via* an *in situ* FT-IR study[†]

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The slow rate of reaction and significant energy consumption associated with the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are acknowledged as substantial obstacles within the realm of electrocatalysis. Hence, the quest for cost-effective and exceptionally efficient electrocatalysts for the ORR/OER holds huge demand to enhance energy conversion and storage capabilities. Herein, we have synthesized a cobalt-imidazole-tetracarboxylate metal–organic framework (Co-MOF) and further modified it with graphene (G) by an electrophoretic exfoliation technique to develop a conducting electrocatalyst (Co-MOF/G). The heterogeneous electrocatalyst is successfully utilized as a bi-functional catalyst towards the ORR and OER in alkaline media. The half-wave potential for the ORR and overpotential for the OER of the as-synthesized electrocatalysts were obtained at 0.78 V vs. RHE, and 302 mV vs. RHE, respectively. *In situ* Fourier transform infrared (FT-IR) spectroscopy coupled with an electrochemical technique reveals the intermediates formed during the reactions that help to draw the mechanism for the ORR and OER electrocatalytic processes. This approach opens up new possibilities for sustainable, low-cost and user-friendly catalysts for Zn-air batteries that might be a good alternative for future electronic applications.

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Introduction

In recent times, numerous studies have been accomplished to develop cost-effective and structured materials for renewable electrochemical energy conversion and storage systems, including fuel cells and metal-air batteries (MABs).1-4 The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the two critical reactions and integral parts of ZABs which occur on air cathodes that constitute an essential bifunctional electrocatalyst.5-7 Due to the lack of systematic investigation and underlying mechanism of ORR/OER, the kinetics of these reactions presents a huge barrier. This necessitates real-time monitoring and analysis of the ORR and OER using various spectroscopic techniques, conducted under operating conditions. As an alternative to various noble metal (Pt, Pd, Ru, Rh, and Ir)-based catalysts that served as a benchmark for the OER and ORR,8-12 non-noble metals, such as transition metal (Fe, Ni, Co, etc.)-based catalysts have been

explored widely, owing to their elemental abundance, affordability and durability.13,14 Among them, single-atom catalysts (SACs) are studied extensively because they consist of plenty of active sites and exhibit high mass activity. However, transition metal-based SACs have several drawbacks like strenuous synthesis procedures, difficulty in precisely controlling the active sites and moderate durability of a few transition metals, forcing researchers to search for alternative materials.^{15,16} In the past decade, porous organic polymers (POPs), covalent organic frameworks (COFs), covalent organic polymers (COPs), and metal-organic frameworks (MOFs) have drawn remarkable recognition and manifested excellent ORR/OER activity in alkaline media.¹⁷⁻¹⁹ Therefore, there is an urgent need to design a cost-effective, highly durable catalyst to enhance the electrochemical process by minimizing the reaction energy barriers and overpotential.20,21

MOFs are highly ordered crystalline polymers that consist of transition metal ions coordinated with organic ligands. MOFs have gained huge popularity due to their high surface area, permanent porous structure and tailorable and well-defined active sites. The high tunability of MOFs provides a unique platform for tailoring their characteristic properties and conducting comprehensive mechanism studies as a new electrocatalyst.²² However, the low electrical conductivity of the MOFs and the blocking of the active metal centers by organic ligands still restrict their use as promising electrocatalysts.^{23,24} Although

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several researchers have been using pyrolysis of MOFs as an alternative solution, it is inevitably an energy consuming procedure. Moreover, due to the unavoidable loss of organic linkers during high-temperature treatment, they often sacrifice their structural integrity and homogeneity in MOF-derived electrocatalysts via pyrolysis. Therefore, irrespective of their moderate catalytic performances, it is difficult to divulge real catalytic active sites and perform a reaction mechanism study of MOF-derived materials for further rational electrocatalyst design. Electrophoretic exfoliation of graphite in the presence of MOFs is an alternative approach to synthesize hybrid nanostructures of MOF and graphene (MOF/G). This method not only helps to improve the electrical conductivity of the electrocatalyst but also promotes the electronic transport from the catalyst to the electrode surface. Furthermore, the mechanisms of the ORR and OER follow the complicated intermediate steps and 4e⁻ pathway. The reaction mechanism selectivity of the ORR/OER is dictated by the different intermediates binding on the active sites of the catalyst. The OH-adsorbed intermediate will desorb or protonate to form water, or it might strongly adsorb onto the surface, influencing the long-term stability of the catalyst. The blocking of active sites by strongly adsorbed OH* is a common issue, especially in doped metal or cluster sites, leading to a reduction in their stability.^{25,26} One effective strategy to mitigate this poisoning effect involves electronically tuning the active sites using other coordinated heteroatoms, known as the ligand effect. This tuning lowers the adsorption energy of OH*, consequently decreasing the poisoning effect. However, despite these advancements, the detailed mechanistic understanding of the ORR/OER pathway and the specific roles of individual metal sites in the MOF materials still need to be made clearer. This is primarily because exploring the reaction mechanism through operando techniques has yet to be extensively accomplished.27

Cobalt metal containing coordination polymers (CPs) and metal organic frameworks (MOFs) have been proved to be promising candidates for bi-functional activity toward the ORR and OER in alkaline media.²⁸⁻³⁰ In addition to well-defined chemical structures resembling molecular electrocatalysts of Co-MOFs, they maintain their crystallinity and chemical stability in adverse conditions.31 Cobalt metal has favorable redox properties, making it suitable for bifunctional ORR and OER activities.^{32,33} Herein, we have adopted an effective and facile strategy to synthesize a two-dimensional (2D) cobalt imidazole-tetracarboxylate-based MOF (Co-MOF) through a single-step solvothermal synthesis procedure and a further electrophoretic exfoliation technique was employed to develop a conducting graphene MOF hybrid 2D electrocatalyst (Co-MOF/G) for the ORR and OER. Electrophoretic exfoliation is a straightforward, in situ, and environmentally friendly method for generating highly stable catalyst-grafted graphene layers. In contrast to conventional techniques like chemical vapor deposition (CVD) and mechanical exfoliation, which involve multistep processes and suffer from limitations such as hightemperature requirements, extended duration, scalability challenges, low yield, and potential use of hazardous reagents, electrophoretic exfoliation stands out. This technique allows in

situ synthesis and functionalization of graphene sheets in a single step by exfoliating graphite in the presence of a catalyst through π - π interactions in an aqueous medium. The uniform deposition achieved through electrophoretic exfoliation promotes efficient charge transfer, enhancing the electrocatalytic activity of the resulting hybrid material. In the Co-MOF, the Co metal together with imidazole and carboxylate ligands play a key role in the expansion of the MOF in the 2D framework via hydrogen bonds that facilitate the adsorption/ desorption of oxygen intermediate species, such as O2, OH* and OOH*, during the ORR/OER, which was proved by in situ electrochemical FT-IR study. So overall the underlying conductive graphene support improves the electrochemical performance of the catalyst and the ligand effect contributes to its long-term stability. Interestingly, the Co-MOF/G catalyst exhibits a small potential gap ($\Delta E_{ORR/OER}$) of 0.75 \pm 0.01 V vs. the reversible hydrogen electrode (RHE) in an alkaline medium which is highly useful for practical applications.

Experimental details

Materials and methods

All the detailed information about the materials used in this work is provided in the ESI file.[†] The details about the electrochemical methods are also provided in the ESI file.[†]

Catalyst synthesis

A mixture of HIm (0.068 g, 1 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1 mmol) and benzene-1,2,4,5-tetracarboxylic 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 mixture was sealed in a 20 mL steel 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 approximately 70 wt% based on Co(II).

All experimental procedures, associated materials and electrochemical experimental techniques are described in Section 1 of the ESI.† Thereafter, the as-synthesized Co-MOF was further modified with graphene through an electrophoretic exfoliation technique (detailed procedures are given in the ESI†) in phosphate buffer solution (PBS) to obtain the electrocatalyst, namely cobalt based MOF with graphene (Co-MOF/G). The remarkable advantage of utilizing graphene as the underlying support for the Co-MOF material has been substantiated through various experimental techniques. This advantage was ultimately confirmed through the electrocatalytic performance of the catalysts, as elaborated in the Results and discussion section.

Formula used for conversion to standard electrode potential

All the experiments in this study were performed using a three electrode setup, glassy carbon (GC)/rotating disk electrode (RDE)/rotating ring disk electrode (RRDE) as a working electrode, graphite rod as a counter electrode and a Ag/AgCl (3 M KCl) reference electrode and all the potentials were converted to the standard reversible hydrogen electrode (RHE) potential

using as reported in this manuscript. For 0.1 M KOH (pH > 13) the following equation was considered:

$$E_{\text{RHE}}$$
 (V) = $E_{\text{Ag/AgCl (3 M KCl)}}$ (in V) + (0.059 × pH) + 0.210 V(1)

Some other formulae involved in this work for calculation of the number of electrons, H_2O_2 (% yield) involved during the ORR, Tafel calibration, and electrochemical active surface area (ECSA) in alkaline medium are briefly discussed in the ESI file.[†]

Results and discussion

Physical characterization of materials

MOF³⁴ The cobalt imidazole-tetracarboxylate-based $[Co(HIm)_2(BTC)_{1/2}]_n$ was synthesized by a new approach using a one-step solvothermal method and further modified with graphene via an electrophoretic exfoliation technique, as shown in Scheme 1. The details of the synthetic procedure are given in the ESI.[†] Here, the BTC surfactant regulates the orientation of cobalt species and imidazole to form Co-MOF. It is noteworthy to mention that the imidazole moiety plays a vital role in ORR and OER applications by serving as a coordination site for metal centers and enhancing the adsorption of reaction species by stabilizing reaction intermediates, facilitating charge transfer and participating in proton-coupled electron transfer processes. Its versatile properties make it a valuable component in the design of catalysts for efficient electrochemical energy conversion reactions. Purple colored block shaped crystals were grown and can be clearly seen from the microscope images as shown in Scheme 1. The single-crystal X-ray diffraction (SCXRD) reveals that the Co-MOF $[Co(HIm)_2(BTC)_{1/2}]_n$ crystallizes in the triclinic crystal system with $P\bar{1}$ space group. All the crystal data is presented in Table S1[†] and bond length and bond angles in Table

S2.† The asymmetric unit (Fig. 1a) consists of central metal ion cobalt that is in a +2 oxidation state and has distorted tetrahedral geometry. Close observation reveals that two imidazole (HIm) moieties and a fragment of one 1,2,4,5-benzene tetracarboxylic acid (BTC) are present with the average bond length of 2.0 Å and 1.98 Å for Co–N_{im} and Co–O_{BTC}, respectively. Fig. 1a discloses one carboxylate group of BTC and two imidazole units bind to one Co centre in the asymmetric unit and the extension in the ac plane as shown in Fig. 1b. The extended structure is connected by the oxygens of the BTC ligand on both sides, forming 1D chains. The H present on the imidazole nitrogen is involved in hydrogen bonding with the oxygen present in the BTC unit (N–H...O_{BTC} \approx 2.76 Å), giving the extended stability of the 2D structure (Fig. 1a-e). The bond distances and bond angles of the atoms involved in intermolecular hydrogen bonding in Co-MOF are summarized in Table S3.† The bond lengths and bond angles match with similar types of structures reported earlier.³⁵⁻³⁷ The three-dimensional (3D) supramolecular architecture of the Co-MOF in the abc plane is shown in Fig. 1e. The phase purity and crystal structure were analysed via the powder X-ray diffraction patterns (PXRD), as shown in Fig. 2a. The sharp peaks in XRD data clearly indicate high crystallinity of the synthesized Co-MOF material. Moreover, the good agreement between the PXRD pattern and the simulated pattern from the SCXRD suggests the phase purity of the synthesized Co-MOF electrocatalyst. Moreover, Pawley refinements were performed in order to have full profile matching and achieved good agreement of the initial and refined unit cell parameters. The unit cell parameters of the refined Co-MOF structures were closely matched with the predictions with good agreement factors (R_{wp}) of 3.74%.

The morphological analysis of the Co-MOF and Co-MOF/G catalysts was performed by field emission scanning electron



Scheme 1 Schematic representation of the synthesis of Co-MOF and Co-MOF/G catalysts.



Fig. 1 Crystal structure of Co-MOF. (a) Asymmetric unit of Co-MOF. (b) The Co-MOF in the ac plane extended in 1D. (c) The Co-MOF extended in 2D via hydrogen bonding through N-H...O in the ab plane. (d and e) Extended framework in 2D in the bc plane and abc plane.



Fig. 2 (a) Pawley refinement of Co-MOF. Shown are the experimental (black), refined (red), and difference (blue) patterns. The Bragg positions are marked as green bars. (b) FESEM image of Co-MOF, (c) FESEM image of the Co-MOF/G catalyst, (d and e) HRTEM image of the Co-MOF/G material, (f) SAED pattern of the Co-MOF/G catalyst. (g) The elemental composition mapping of the Co-MOF/G catalyst.

microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM), as shown in Fig. 2b-e. Fig. 2b demonstrates the 2D sheet-type morphology of the Co-MOF material. The HRTEM images of exfoliated graphene (EG) as shown in the ESI and Fig. S2a and b[†] confirm the thin sheet-like morphology of the material. HRTEM images of the Co-MOF/G material (Fig. 2d-e) reveal a sheet-like morphology of the hybrid material, where Co-MOF sheets are stacked in between the graphene sheets. The presence of ordered carbon layers and crystallinity of the synthesized Co-MOF/G were also confirmed from the selected area electron diffraction (SAED) pattern (Fig. 2f), where the distinctly diffracted rings are displayed. The elemental mapping of the Co-MOF/G catalyst confirms the presence of cobalt, carbon, nitrogen and oxygen elements in the material and their uniform distribution (Fig. 2g). For further confirmation of the Co-MOF and graphene, the tapping-mode atomic force microscopy (AFM) technique was employed for the characterization of the Co-MOF/G catalyst, as depicted in Fig. S3a and b.† As anticipated, the results reveal that the Co-MOF material is effectively stacked onto the graphene sheets, as illustrated in Fig. S3a.† The measurement of the thickness of the 2D sheet-like Co-MOF/G indicates a thickness of approximately 2 nm for the graphene sheet and approximately 27 nm for the Co-MOF material, as demonstrated in Fig. S3b.† Moreover, thermogravimetric analysis (TGA) was conducted for the investigation of thermal stability of the Co-MOF catalyst. TGA was performed under a nitrogen atmosphere at the rate of 10 °C per minute with alumina pans (Fig. S4[†]). The weight loss was depicted at the temperature of ~330 °C, which indicates the thermal stability of Co-MOF up to 330 °C and the material was completely degraded at \sim 565 °C. The determination of the binding modes of the tetracarboxylate was done by analyzing the Fourier-transform infrared (FTIR) spectrum of Co-MOF and Co-MOF/G materials (Fig. S5[†]), and a detailed explanation is given in the ESI.^{†38} Further, Raman spectroscopic analysis of Co-MOF/G and exfoliated graphene (EG) was accomplished to confirm the stacking of the Co-MOF materials in between graphene sheets, as shown in Fig. S6.[†] In the Raman spectrum of Co-MOF/G, D and G bands appeared at 1327.67 and 1575.03 cm⁻¹ along with a broad peak in between 2400 and 3000 cm⁻¹ with a maximum at 2695 cm⁻¹, which revealed the 2D nature of the extended pi-conjugated polymer network of the hybrid catalyst. The D and G bands in the Raman spectrum of exfoliated graphene (EG) were also obtained at 1340.46 and 1577.13 cm⁻¹ positions respectively. There was red shifting in the D and G bands of the Co-MOF/G catalyst indicating proper stacking of the material in between the graphene support. The $I_{\rm D}/I_{\rm G}$ ratio was calculated for Co-MOF/G (0.84) and EG (0.96), which recommended a slight lowering of defects in the hybrid Co-MOF/G materials due to proper stacking of the Co-MOF material with the graphene sheets through π - π interaction.³⁹

The electronically well-interconnected two-dimensional (2D) structure of Co-MOF/G was anticipated to exhibits superior conductivity in comparison to the Co-MOF catalyst. To validate this, a comparative assessment of sheet resistance was conducted with the synthesized materials using a 2-probe technique, while varying the bias from -1 to +1 V within the device.

The *I–V* characteristics of Co-MOF/G demonstrated a linear plot with a steeper slope in contrast to the slope of the Co-MOF material (depicted in Fig. S7, ESI[†]). Remarkably, the electrical sheet resistance value for Co-MOF/G ($7.65 \times 10^3 \Omega$) was $\sim 10^5$ times lower than that of the Co-MOF catalyst ($1.77 \times 10^8 \Omega$). The electrical sheet resistance of the pristine exfoliated graphene is considered to be the same as that of our previous study.⁴⁰ However, comparing the MOF and graphene-stacked-MOF, the notably low resistance observed in the Co-MOF/G material could be attributed to an unhindered and facile electronic transport of the system due to stable π - π interaction in the hybrid material, which is suitable for electrocatalytic applications.

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the surface chemical composition of the elements C, N, O, and Co and their valence states in the Co-MOF/G material, as shown in Fig. 3a-d, and S8, ESI.† The elemental composition of the Co-MOF/G catalyst was summarized in ESI Table S4.† The deconvoluted peaks of C1s XPS spectra for the Co-MOF/G material appeared at 284.30 (C=C/C-C), 285.85 (C=N), 286.70 (C-O) and 288.23 eV (C=O), respectively (Fig. 3a).41 The N1s spectra could be deconvoluted into three sub-peaks due to the spin-orbit coupling, including pyridinic-N (399.78 eV), pyrrolic protonated-N (401.49 eV), and pyridine-N-oxide groups (404.95 eV), respectively⁴² (Fig. 3b). The O1s peaks (Fig. 3c) appeared at 531.01 and 531.78 eV for O-Co-O and 532.93 eV for O-C=O bonds. The Co 2p XPS spectrum of the Co-MOF/G material exhibited two split peaks with two satellite signals at 782.07 eV, 788.49 eV (satellite peak) for Co 2p3/2, and 797.20 eV, 804.79 eV (satellite) for Co $2p_{1/2}$ as shown in Fig. 3d. The doublet peaks might be attributed to Co(II) species.43,44 It was clear from the above results that the structure of the Co-MOF is retained after stacking with the graphene sheets in the Co-MOF/G hybrid material. To gain further insight into the chemical environment and oxidation state of the metal present in both Co-MOF and Co-MOF/G, extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near-edge structure (XANES) spectroscopy were conducted. The XANES spectra at the Co Kedge for Co-MOF, Co-MOF/G and Co foil (as a reference) were recorded to analyze their chemical states (Fig. 3e). The absorption edge line positions of both the catalysts were almost at a similar position and away from the Co foil, which indicates that the cobalt that is present in these two materials is in $Co(\pi)$ form and also matches with the results obtained from the XPS measurements. The Fourier transformed (FT) EXAFS spectra at the Co K-edge for Co-MOF and Co-MOF/G, as shown in Fig. 3f, display a peak at \approx 1.56 Å that corresponds to Co-N/Co-O and no peaks appeared at the position of Co-Co.45 The coordination environment of the Co-MOF was already confirmed from the SCXRD data, but for the comparison of the results of Co-MOF and Co-MOF/G hybrid materials, fitting of the EXAFS was carried out. On the basis of the fitting results for Co-MOF, it can be further confirmed that the coordination number of cobalt is four with a bond length of \sim 1.98 Å in the framework, which is shown in Fig. S9a[†] and the predicted structure is shown in the inset of Fig. S9a.[†] The fitting parameters at the Co K-edge of the Co-MOF catalyst are summarized in ESI Table S5.† Similarly, the



Fig. 3 XPS spectra of the Co-MOF/G catalyst: (a) XPS C1s spectra, (b) XPS N1s spectra, (c) O1s spectra, and (d) Co 2p spectra of the Co-MOF/G catalyst. Structural characterization of the Co-MOF and Co-MOF/G catalysts. The normalized XANES spectra and the Fourier transform of EXAFS spectra at the (e and f) Co K-edge of the Co-MOF and Co-MOF/G catalysts and Co foil.

EXAFS fitting of the Co-MOF/G catalyst was performed and it confirmed the retention of the Co-MOF structure after stacking in between the graphene. The fitting results indicated that the cobalt was present in four coordination with average bond length (~1.96 Å) as shown in Fig. S9b⁺ and the proposed structure is shown in the inset of Fig. S9b[†] and fitting parameters are listed in ESI Table S5.† These data further confirm the retention of structural integrity and the bonding environment in the framework after the exfoliation of the material. To study the electronic interactions between Co-MOF and exfoliated graphene in the Co-MOF/G hybrid material, ultraviolet-visible (UV-vis) absorbance and solid-state photoluminescence (ss-PL) spectroscopy analyses were performed, and the results are shown in Fig. S10a and b.† Interestingly, after incorporation of the Co-MOF with graphene, the characteristic peak of Co-MOF at 291 nm shifted to 310 nm as shown in Fig. S10a.[†] This shows the existence of electronic transition between Co-MOF and graphene in the Co-MOF/G material through π - π stacking. The p orbitals of the Co-MOF linker were stacked with the p orbitals of the graphene sheets via non-covalent interaction. Further confirmation of electronic interaction in the Co-MOF/G catalyst was obtained with photoemission spectroscopy measurement. The ss-PL spectroscopy of Co-MOF, exfoliated graphene and Co-MOF/G was performed as shown in Fig. S10b.[†] All the materials were excited at 290 nm and emission was recorded in the range of 352-385 nm with 600 nm min⁻¹ rates. The Co-MOF shows higher emission intensity but in case of the Co-MOF/G catalyst the emission intensity gets lower due to aggregation-caused quenching (ACQ). The emission intensity was quenched due to

the strong π - π interaction between the phenyl ring of the ligand of Co-MOF and graphene substrate in the Co-MOF/G catalyst.^{46,47} The interesting structure of the Co-MOF, crystallinity, high thermal stability and excellent electrical conductivity provoked us to explore its bifunctional activity toward the ORR/OER.

Electrochemical analysis for the ORR and OER

The electrochemical performance of the Co-MOF and Co-MOF/G materials for the oxygen reduction reaction was performed via cyclic voltammetry (CV) and linear sweep voltammetry (LSV) tests in alkaline electrolyte solution (0.1 M KOH). Initially, the CV data was recorded in argon and O2-saturated alkaline solution at 10 mV s⁻¹ scan rate. The Co-MOF/G catalyst depicts a sharp cathodic peak in O₂-saturated solution, which was absent in the Ar-saturated solution (Fig. S11, ESI[†]), confirming the material is active toward the ORR.48 The LSV data were recorded using a rotating disk electrode (RDE) in O2-saturated alkaline solution for all the synthesized materials and commercially available Pt/C (20 wt%) catalyst at 1600 rpm with 10 mV s⁻¹ scan rate (Fig. 4a). The Co-MOF/G catalyst displays excellent ORR activity with a positive half-wave potential $(E_{1/2})$ of 0.78 V vs. RHE and limiting current density $(J_{\rm L})$ of 5.6 mA cm⁻², which is better than that of Co-MOF ($E_{1/2} = 0.68$ V vs. RHE, $J_L = 3.22$ mA cm⁻²) and comparable to that of Pt/C catalyst ($E_{1/2}$, 0.85 V, J_L , 5.7 mA cm⁻²). This excellent catalytic activity of Co-MOF/G originated from the large number of metal active sites and bridging ligand that helps achieve better charge transportation from the framework to the electrode surface. All the parameters of the ORR are given in



Fig. 4 (a) LSV curves of the as-synthesized electrocatalysts and Pt/C catalyst for the ORR in O_2 -saturated alkaline (0.1 M KOH) electrolyte solution. (b) Tafel plots of all catalysts and comparison with Pt/C catalyst. (c) K–L plots of Co-MOF/G catalyst and (d) number of electrons involved and $%H_2O_2$ yield during the ORR with Co-MOF/G catalyst in alkaline solution. (e) LSV curves of Co-MOF and Co-MOF/G catalysts and the RuO₂ catalyst for the OER in 1.0 M KOH. (f) Overall polarization plots in the ORR and OER potential window for the Co-MOF/G and commercial (Pt/C + RuO₂) catalysts.

Table S6[†] for comparison purposes. The optimization of the amount of Co-MOF (20 mg, 40 mg, and 60 mg) and exfoliation time (20 min, 45 min and 60 min) in the synthesized Co-MOF/G catalyst was evaluated by recording LSV for the ORR in alkaline media, as shown in Fig. S12a.† The best response obtained with the catalyst that was synthesized with 40 mg of Co-MOF exfoliation was conducted for 45 minutes at 4 V in 0.1 M PBS solution. The ORR results of the controlled samples are summarized in the ESI, Table S7.[†] Further, the electrochemical active surface area (ECSA) was calibrated by using CV analysis at different scan rates starting from 10 mV s^{-1} to 100 mV s^{-1} in the non-faradaic region, as shown in Fig. S13a and c.[†] The double layer capacitance (C_{dl}) values of the Co-MOF/G and Co-MOF catalysts were calculated from the slope of the current vs. scan rate plot (Fig. S13b and d[†]). The ECSA values of Co-MOF/G and Co-MOF were calculated by using eqn (1), ESI,^{\dagger} and were found to be 15.07 cm² and 0.16 cm², respectively. The high ECSA value of the Co-MOF/G catalyst was also responsible for the better catalytic performance towards the ORR. The faster reaction kinetics of the Co-MOF/G catalyst toward the ORR was confirmed from the Tafel slope, which was obtained from the LSV curve, which was recorded at 2 mV s^{-1} scan rate at 1600 rpm. The Tafel slope of Co-MOF/G (115 mV dec^{-1}) was higher than those of Co-MOF (74 mV dec^{-1}) and commercial Pt/C catalyst (80 mV dec^{-1}) (Fig. 4b), reflecting faster kinetics of the catalyst toward the ORR.49-51 Electrochemical impedance spectroscopy (EIS) was conducted and lower solution resistance (R_s) was found for the Co-MOF/G catalyst as compared to the Co-MOF material, as shown in Fig. S14a.† The EIS

technique is instrumental in assessing the characteristics of the modified electrode interface, particularly in relation to electron transfer kinetics. A smaller charge transfer resistance (R_{ct}) indicates superior control over electron transfer kinetics at the catalyst material interface. In the Nyquist diagram as shown in Fig. S14b,^{\dagger} the semi-arc part corresponds to R_{ct} , reflecting the faster charge transfer processes during the catalysis on the Co-MOF/G catalyst as compared to the Co-MOF material. The EIS data further confirmed the faster kinetics of the Co-MOF/G catalyst during the ORR. In addition, the linear Koutecky-Levich (K-L) plots confirmed the first order reaction kinetics of Co-MOF/ G, which were obtained from LSV measurements that were taken with different rotation speeds of 625 to 4900 rpm at different potentials (0.67 to 0.47 V) using the RRDE electrode (Fig. 4c). The limiting current density in the LSV gradually increases with increasing the rotation speed (Fig. S15[†]) due to the shortening of the diffusion layer over the electrode surface and maximum transportation of the oxygen towards the electrode surface.52 It is very important to check the number of electrons involved and whether the undesirable intermediate product (%H2O2) was formed during ORR electrocatalysis. These are examined by using the rotating ring disk electrode (RRDE) technique that was performed at various potentials (0.67 to 0.47 V vs. RHE) at 1600 rpm in O₂-saturated alkaline media. The polarization curve for ring current and disk current of Co-MOF/G is shown in Fig. S16, ESI.[†] The average value of number of electrons (*n*) involved was determined by using ESI eqn (5) and (6)[†] and found to be ~ 3.55 and the undesirable intermediate product (H2O2 yield) of the Co-

MOF/G catalyst remains below 30% during the ORR electrocatalysis (Fig. 4d). From the above results, it was confirmed that Co-MOF/G was almost following the 4-electron pathway during the ORR electrocatalysis and O_2 was directly reduced to $OH^$ rather than to HO_2^- through the 4e⁻ reaction pathway in alkaline media.

Apart from the catalytic activity, the durability measurement of the Co-MOF/G catalyst was performed by the chronoamperometry technique at a constant potential. As shown in Fig. S17,† the relative current of the Co-MOF/G catalyst remained at 92% of its initial value after 16 hours, and was better than that of Pt/C catalyst. The stability results indicate that the synthesized Co-MOF/G catalyst was highly stable in alkaline media toward the ORR. Further, LSV was compared before and after stability measurement at 1600 rpm with 10 mV s^{-1} scan rate and a negligible negative shift was found in the half-wave potential of the Co-MOF/G catalyst (Fig. S18[†]). In addition, the methanol tolerance effect was also examined by using the i-t chronoamperometry technique and CV analysis in the presence of 1 M methanol under similar O₂-saturated alkaline conditions. The current density of the Co-MOF/G catalyst in the chronoamperometry curve recovered rapidly after transitory disturbance. However, the current density dropped sharply in case of the Pt/C catalyst (Fig. S19[†]). The methanol tolerance effect was also confirmed from the CV measurement of Co-MOF/G and Pt/C catalysts in the presence and absence of the methanol solution. The CV response of the Co-MOF/G catalyst remains similar (Fig. S20[†]) while the shape of the CV curve for the standard Pt/C catalyst was changed, (Fig. S21[†]) indicating the methanol oxidation occurred on the Pt/C electrode.53 These results confirm the excellent methanol resistance ability of the Co-MOF/G catalyst and further can be utilized for material fuel cell applications.

For understanding the bi-functional nature of the Co-MOF/G catalyst, OER performance was checked in 1.0 M KOH electrolyte solution at 5 mV s⁻¹ scan rate and compared with the controlled samples, such as Co-MOF and commercial RuO₂ under similar reaction conditions, as shown in Fig. 4e. To evaluate the OER activity of the catalyst, the potential required to achieve a 10 mA cm^{-2} current density ($E_{i=10}$) and Tafel slopes are the commonly used descriptors. The overpotential of the Co-MOF/G catalyst was calculated to be 302 mV at 10 mA cm⁻² current density, which was better than those of the Co-MOF (369 mV) and RuO₂ material (321 mV). The optimization of exfoliation time (20 min, 45 min and 60 min) and amount of Co-MOF (20 mg, 40 mg, and 60 mg) in the synthesized Co-MOF/G catalyst was evaluated by recording the polarization curve for the OER in basic media, as shown in Fig. S12b.† The best response obtained with the catalyst that was synthesized with 40 mg of Co-MOF exfoliation was conducted for 45 minutes at 4 V in 0.1 M PBS solution. The OER results of the controlled samples are summarized in the ESI, Table S7.† Moreover, the electron transfer rate at the electrode-electrolyte interfaces was investigated using Tafel slope measurement by recording the LSV at slow scan rate (1 mV s^{-1}). The lowest Tafel slope of 85 mV dec⁻¹ was observed for the Co-MOF/G catalyst, whereas Co-MOF and RuO2 show Tafel slopes of 132 and 87 mV dec^{-1} , respectively, (Fig. S22[†]), suggesting the highest electron transfer ability with superior kinetics of Co-MOF/G.54 The value of onset, overpotentials and Tafel slope of all the catalysts are summarized in Table S8, ESI.[†] Further, the long-term stability was evaluated at a constant potential of $1.532 \text{ V} \nu s$. RHE for $30\ 000$ s. The OER stability test of the Co-MOF/G showed almost no current attenuation (Fig. S23[†]) indicating outstanding durability of the catalyst.

In the alkaline media, the reaction mechanisms and kinetics of the OER process depend on the binding strength of OH* species on the catalyst surface. However, the conversion from O* to *OOH was reported to be the rate-determining step (RDS) to control the OER efficiency. The abundant active sites, facile electron/mass transportation through a bridging linker and the binding strength of OH* species on the Co-MOF/G material were responsible for the excellent activity and faster kinetics toward the OER. The potential gap (ΔE) between the half-wave potential of the ORR and $E_{i=10}$ for the OER is widely used to estimate the bifunctional activities (ORR/OER) that further govern the performance of ZAB. In case of Co-MOF/G, ΔE was found to be lower (0.75 V vs. RHE) as compared to Co-MOF (0.91 V vs. RHE), and comparable to standard Pt/C + RuO₂ (0.70 V vs. RHE) (Fig. 4f). The bifunctional catalytic activity of the Co-MOF/G catalyst was compared with the state-of-the-art catalysts recently reported in the literature and found to be comparable to or better than almost all the catalysts, as shown in Table S9, ESI,† demonstrating superior bifunctional (ORR/OER) electrocatalytic activity of the material. The durability of the catalyst is a major issue for any catalytic process. To verify the durability of the Co-MOF/G catalyst, PXRD, FTIR, and XPS analyses were carried out after stability measurement. From Fig. S24,† the PXRD spectra of Co-MOF/G before and after the test were similar. The peaks in the FTIR spectra of Co-MOF/G were found at the same position after the electrochemical measurement as shown in Fig. S25,† which confirms the structural stability of the Co-MOF/G catalyst material. We have performed the XPS analysis of the Co-MOF/G material to further confirm the chemical composition of the catalyst after stability. We found the elemental composition of the catalyst before and after stability similar, which is summarized in the Table S4.[†] The C1s, N1s, O1s and Co 2p peaks were also deconvoluted and found at a similar position as before the stability measurement (Fig. S26 and S27[†]). From the above results, it can be concluded that the Co-MOF/G catalyst is highly stable toward bifunctional oxygen electrocatalysis and can be utilized for practical applications.

ORR/OER reaction kinetics study by in situ FT-IR spectroscopy

A thorough understanding of the mechanistic aspects involved in reversible oxygen electrocatalysis (ORR/OER) is of utmost significance. This understanding aids in elucidating the catalyst's role in determining reaction selectivity *via* a 4-electron transfer pathway leading to water generation. Robust adsorption-desorption processes at the active site and charge polarization on the active material's surface, with the ability to influence electron cloud polarization of stable, neutral molecules, facilitate the breaking of O-O bonds. This becomes pivotal in the conversion of molecular oxygen into water. While the ORR follows a 2-electron route resulting in hydrogen peroxide formation as an intermediary when O–O cleavage is limited, evidence of the 4-electron ORR kinetics has been substantiated through RRDE experiments utilizing the Co-MOF/ G catalyst. This discovery has spurred us to offer automated insights to illuminate catalytic mechanisms. Both the ORR and OER follow the $4e^-$ path, and considering the intermediates formed during the ORR to be O*, OOH*, and OH*, the four reaction paths in a basic medium are described in eqn (2)–(5), whereas the OER proceeds in the reverse direction.⁵⁵

$$O_2 + 2H_2O + 4e^- \Leftrightarrow OOH^* + H_2O + OH^- + 3e^-$$
 (2)

$$OOH^* + H_2O + OH^- + 3e^- \Leftrightarrow O^* + H_2O + 2OH^- + 2e^-$$
 (3)

$$O^* + 2OH^- + H_2O + 2e^- \Leftrightarrow OH^* + 3OH^- + e^-$$
 (4)

$$OH^* + 3OH^- + e^- \Leftrightarrow * + 4OH^-$$
(5)

To delve into the interactions of intermediates formed during the reaction, we conducted in situ electrochemical Fourier transform infrared (FT-IR) spectroscopy on the Co-MOF/G catalyst within alkaline electrolyte solutions saturated with Ar and O₂. Fig. 5a illustrates the schematic setup of the *in situ* FT-IR study. Fig. S28[†] depicts that no peaks emerge in the Ar-saturated electrolyte solution. Intermediates generated during the ORR/OER process are depicted in Fig. 5b and c. Conversely, peaks corresponding to ORR intermediates during electrocatalysis become evident when performing a chronoamperometry study at various potentials in an O₂-saturated solution. The chronoamperometry study at different potentials (1.1, 1.0, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, and 0.20 V vs. RHE) in O2-saturated alkaline electrolytes was recorded. Fig. 5b portrays peaks at 1048 cm⁻¹ and 1397 cm⁻¹ corresponding to *O²⁻ intermediates' O-O stretching mode and a peak at 1538 cm⁻¹ for H–O–H bending observed during the ORR. The increase in the 3300–3500 cm^{-1} peak intensity as ORR



Fig. 5 (a) Schematic representation of the *in situ* ATR-FTIR cell setup. (b) *In situ* FTIR spectra of the Co-MOF/G catalyst at various potentials for the ORR in O_2 -saturated alkaline solution. (c) *In situ* FTIR spectra at various potentials for OER analysis. (d) Mechanistic reaction kinetics for the ORR and (e) OER in alkaline media. (f) M.O. diagram of the Co-MOF/G for the ORR and (g) for the OER in alkaline media.

limiting current rises confirms water production during the ORR (Fig. 5b).^{56,57} A similar approach was undertaken for the OER in Ar-saturated alkaline solution at various potentials (1.10 V, 1.20 V, 1.30 V, 1.40 V, 1.50 V, 1.60 V, and 1.70 V vs. RHE). The evolving process was tracked *via* a peak ranging from 980 to 1100 cm⁻¹ (Fig. 5c). Notably, an infrared absorption peak at approximately 1058 cm⁻¹ signifies the emergence of a pivotal dynamic intermediate *OOH during the OER process (Fig. 5c).56,58,59 The mass transportation during the ORR/OER occurs through diffusion transmission in which there is diffusion in the electrolyte directly to the active sites in the Co-MOF/G catalyst. The intermediate formation during the catalytic process is schematically illustrated in Fig. 5d for the ORR and in Fig. 5e for the OER, respectively. For further understanding the mechanism from the molecular orbital (MO) approach, the energy gap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) plays a key role in the interaction of the precursors on the active sites. The reaction will occur if the HOMO in a donor molecule can overlap with the LUMO in the acceptor molecule. Thus, the strength of the interaction between the donor and acceptor depends on the energy gap between HOMO and LUMO involving orbitals.60 The mechanism of ORR and OER over the cobalt metal sites in the Co-MOF/G catalyst and the p_z - d_{z^2} orbital interaction involved in the whole catalytic process (ORR/OER) are shown in Fig. 5f for the ORR and Fig. 5g for the OER.61,62 The MO diagram reflected electron transfer between the energy-symmetric electronic levels of the bonding and antibonding orbitals of oxygen 2p and cobalt 3d. This generated a fresh set of energy levels that exhibited degeneracy, corresponding to the reaction intermediates involved in the ORR and OER processes. These new energy levels were pivotal in driving the reaction steps further kinetically.

Conclusions

In summary, a Co-based 2D MOF catalyst was synthesized using a single-step solvothermal process. In order to overcome the inherent low conductivity of MOFs in electrocatalysis, we adopted the electrophoretic exfoliation technique without the need for thermal treatment. This approach enabled the creation of a conducting carbon support, enhancing the electronic transport capabilities of the catalyst. The Co-MOF/G shows excellent bifunctional electrocatalytic activity toward oxygen electrocatalysis. The bridging linkers in MOF advocate for better charge transportation during the electrocatalysis. The ligand effect contributes to the long term stability of the catalyst and overall the underlying conductive support improves the electrochemical performance of the catalyst. The kinetics of the catalytic reaction was examined by applying in situ Fourier transform infrared spectroscopy in an alkaline environment. This analysis corroborated the occurrence of reversible oxygen catalysis through the complete process, adhering to the 4-electron pathway. This environmentally friendly, uncomplicated, and economically viable technique is poised to introduce a fresh opportunity for enhancing the performance of less conductive MOF materials in tasks related to the ORR/OER and other electrochemical applications in the foreseeable future.

Author contributions

RSD and GK conceived the idea of this work. GK did the synthesis and detailed physical characterization. GK did the electrochemical measurements and wrote the manuscript with the aid of all authors. RH and MS helped with SCXRD data analysis. RSD supervised the work, review and corrected the manuscript. All the authors have checked the final draft of the manuscript and approved the submission.

Conflicts of interest

There are no conflicts to declare.

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