Electrocatalytic performance of NiNH₂BDC MOF based composites with rGO for methanol oxidation reaction

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Present work comprehensively investigated the electrochemical response of Nickel-2 Aminoterephthalic acid Metal–Organic Framework (NiNH₂BDC) and its reduced graphitic carbon (rGO) based hybrids for methanol (CH₃OH) oxidation reaction (MOR) in an alkaline environment. In a thorough analysis of a solvothermally synthesized Metal–Organic Frameworks (MOFs) and its reduced graphitic carbon-based hybrids, functional groups detection was performed by FTIR, the morphological study by SEM, crystal structure analysis via XRD, and elemental analysis through XPS while electrochemical testing was accomplished by Chronoamperometry (CA), Cyclic Voltametric method (CV), Electrochemically Active Surface Area (EASA), Tafel slope (b), Electron Impedance Spectroscopy (EIS), Mass Activity, and roughness factor. Among all the fabricated composites, NiNH₂BDC MOF/5 wt% rGO hybrid by possessing an auspicious current density (j) of 267.7 mA/cm² at 0.699 V (vs Hg/HgO), a Tafel slope value of 60.8 mV dec⁻¹, EASA value of 15.7 cm², and by exhibiting resistance of 13.26 Ω in a 3 M CH₃OH/1 M NaOH solution displays grander electrocatalytic activity as compared to state-of-the-art platinum-based electrocatalysts.

At present, to fulfill the emergent worldwide energy demands and to replace the non-renewable energy sources, the invention and development of renewable, green, and economical energy sources is the field of attention and investigation for scientists and researchers¹⁻⁵. Amongst the Fuel Cells, Direct Methanol Fuel Cell (DMFC) is the prospective candidate for handy devices and light-duty vehicles owing to prerequisite low temperature requirement, liquid nature of the fuel, quick refueling, eminent power density, facile charging, minimum environmental influence, and high yield synthesis of H₂⁶⁻¹⁶.

The complete oxidation process with Ε⁰ values versus RHE is represented as follows:¹⁷

CH₃OH + 3/2O₂ → CO₂ + 2H₂O  Ε⁰ = 1.213 V  (Overall reaction).

The MOR proceeds identically in an acidic and basic media except that CO to CO₂ conversion occurs by OH⁻ group (provided by alkali) very smoothly in basic media while the same conversion takes place after water dissociation in an acidic environment with a low reaction rate¹⁸. To overcome the problems of (a) depressed redox process, (b) high manufacturing cost, (c) catalyst inactivation by reaction intermediates, and (d) sluggish kinetics, the development of a most appropriate and low-cost electrocatalyst with (i) flexible morphology, (ii) prompt electrons, ions, and reaction products transport (iii) The strong interaction between catalyst and reactants with adequate contact area, and (iv) upright inherent activity are the requirements of current research to replace highly active but expensive and less stable Pt metal-based catalysts¹⁹⁻²¹. Currently, contrary to noble metals, transition metal-based oxides, carbides, nitrides, borides, as well as double layered hydroxides (LDH) are embryonic materials with a tremendous performance for the MOR²²⁻²₅. Additionally, the transition metal-based coordination polymers (MOFs) based electrocatalysts are the area of interest for researchers due to their less density, gigantic surface area, porosity, tunable, and stable nature²⁶⁻²⁸.

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Moreover, in nickel-based MOFs (a) easy access to economical precursors (b) variable valency of Ni metal (+1 to +3), predominantly higher oxidation state (c) formation of nickel oxides and hydroxides on the surface, and (d) conversion of Ni(OH)$_2$ ($\beta$) $\rightarrow$ NiOOH ($\beta$) $\rightarrow$ NiOOH ($\gamma$) during electrochemical testing all are responsible for the excellent electrocatalytic response. Moreover, the inclusion of mesoporous, conductive supports (GO, rGO, Graphene, CNTs) is an important strategy to promote catalyst stability and charge transfer proficiency by the development of new pores and control over pore size which in turn enhances the surface area and leads to improved electrocatalytic activity$^{29-31}$.

In 2018, Li et al. reported highly active spongy nickel frameworks deposited metal Pt-Ni nanoparticles with improved MOR activity and stability due to high CO tolerance, great surface area, and effective utilization of active sites. The Pt-Ni/C electrocatalyst was prepared by Ortega and colleagues in the same year where the presence of double metals, reduction in particle size of Pt due to Ni inclusion, huge surface area, the formation of metal oxides and hydroxides, and reformed electronic structure due to synergistic effect leads to excellent MOR activity while Pt Nanostructured Carbon (Pt/NC) composite prepared by Ferrer and collaborators shows greater current density than Pt/rGO and Pt/C due to enhanced electron transport at the electrode–electrolyte interface along with hierarchical structure$^{32-34}$.

Stephanie and colleagues in 2016 fabricated Fe–Ni NPs as a MOR catalyst. During the reaction, the Fe (core)-Ni (shell) nanoparticles show the oxidation of Ni shell to α-Ni(OH)$_2$ and β-NiOOH, and the formation of metallic nanoparticles as well. The tested sample provides the forward current density of 0.048 A cm$^{-2}$ at an anodic potential of 1.58 V vs RHE and current density rises with an increase of methanol concentration$^{35}$.

Yaqoob et al. in 2019 fabricated Ni-BTC MOF/1–5 wt% rGO composites for MOR through a solvothermal technique. The hexagonal shape Ni-BTC/4 wt% rGO composite with high current density, minimum Tafel slope and capacitance, and long-term stability show a good response towards MOR. Furthermore, the product analysis by NMR confirms the oxidation of methanol to formic acid with 62% conversion efficiency$^{36}$. In the same year, a series of spindle-shaped bimetallic MOFs (Fe-Co $\text{NH}_2\text{BDC}$) with a variable Fe/Co ratio was successfully synthesized via a one-pot solvothermal approach by Bushra et al. In an alkaline medium, the best material (Fe/Co = 1) with high porosity and synergetic effect between MOF and two metals results in low overpotential, high Tafel slope, and long-term stability for 6 h during the OER process$^{41}$.

In this study, a solvothermally fabricated NiNH$_2$BDC MOF/1, 2, 5 wt% reduced graphene oxides hybrids (NiNH$_2$BDC/rGO) were thoroughly analyzed for the CH$_3$OH oxidation process in 1 M NaOH/3 M CH$_3$OH solution. In MOF/rGO composites diverse aspects such as; (a) availability of manifold Ni oxidation states; $n + 2$ to $n + 3$, smoothed redox process via facile electron movement (b) coordination compound formation propensity of nickel (c) development of defects and vacancies (d) rGO sheets tremendous stability and conductivity (e) escalated surface area of MOF (f) MOF NPs homogenous dispersal on the surface of the support, and (g) synergistic effect between rGO and MOF, all support the incredible enactment of as-synthesized materials for the methanol oxidation reaction. According to our literature survey, the catalytic tendency of NiNH$_2$BDC MOF/1, 2, 5 wt% reduced graphene oxide hybrids for the CH$_3$OH oxidation process has not been conveyed in the literature to date.

**Experimental section**

The 99% pure reagents and chemicals without further treatment were utilized for synthesis. Prerequisite chemicals for the fabrication purpose include Ni(NO$_3$)$_2$$\cdot$6H$_2$O, 2-Aminoterephthalic acid (NH$_2$BDC), potassium permanganate (KMnO$_4$), sodium nitrate (NaNO$_3$) which were procured from Sigma Aldrich while Dimethylformamide (DMF), hydrazine hydrate, hydrogen peroxide, and sulphuric acid were picked up from Merck.

**Fabrication of Ni NH$_2$BDC MOF.** Synthesis of NiNH$_2$BDC MOF was carried out by an already described solvothermal scheme after slight modification$^{35}$. 1 mol solution of both Ni(NO$_3$)$_2$$\cdot$6H$_2$O and 2-Aminoterephthalic acid in 15 ml DMF were prepared simply by stirring with subsequent slow mixing of nickel nitrate clear solution in linker solution. The homogenous mixture of MOF precursors acquired after one hour of stirring was distilled to a 23 ml capacity autoclave (Teflon lined) and retained for twenty-four hours at 393 K in an electric oven. After reaction accomplishment, the room temperature was attained by slow cooling of the autoclave. Light
green powdered material was achieved after repetitive washing of autoclave product with DMF and ethanol via centrifugation and vacuum drying at 348 K for 24 h.

**Fabrication of GO and rGO.** Reported Hummer’s method was utilized for GO Synthesis while rGO was synthesized through reduction of GO by hydrazine hydrate via 24 h reflux at 373 K43,44.

**Fabrication of Ni NH2BDC MOF/rGO composites.** A NiNH2BDC MOF/rGO hybrids (MOR catalyst) series was prepared by following the above-stated procedure. A clear solution of MOF obtained by the above-mentioned scheme and appropriate amount rGO was sonicated for two hours to acquire a uniform blend and then transmitted to stainless steel autoclave with Teflon inner cavity for 24 h reaction at 393 K. A dry solid product was obtained after 3–4 times washing with DMF/ethanol via centrifugation followed by 24 h vacuum drying at 348 K (Fig. 1).

**Materials characterization.** For comprehensive characterization of as-synthesized samples, a Scanning Electron Microscope (VEGA 3 TESCAN) was employed for exterior structure and morphology analysis. X-ray Powder Diffractometry (STOE Germany) was implemented for phase purity and crystalline nature scrutinization (Ka = Cu radiation, 0.1.54 Å, scanning range = 5°–80°, step size = 4°/s at 5 mA and 20 kV) while validation of functional groups and metal–ligand strong interaction was corroborated through FTIR Spectrophotometer (Perkin spectrum) by selecting wavenumber range of 500–4000 cm⁻¹. Binding energy and composition records
were collected by XPS (MI-600) respectively. The degree of defects and graphitization, as well as the extent of crystallinity, was ascertained via Raman Spectroscopy, and stability of material was observed through Thermo gravimetric analyses (TGA) by using a thermo-gravimetric analyzer (Perkin Elmer Pyris 1, Champaign, IL, USA). The temperature was increased from 20 to 500 °C at a heating rate (5 °C min⁻¹) under an airflow rate of 20 ml min⁻¹.

**Electrocatalytic measurements.** An inclusive electrochemical evaluation was done in 3 M CH₃OH/1 M NaOH mixture through the Gamry apparatus (Ref 3000/3000 AE). To get homogenous ink of electrocatalyst, 2.0 mg of sample (0.85 mg/cm²), 97 µl ethanol, and 3 µl Nafion were sonicated for 40 min, and then 0.003 ml of electrocatalyst ink was plunged on a glassy carbon electrode (GCE = working electrode) by micropipette. Pt wire and Hg/HgO were chosen as auxiliary and reference electrodes correspondingly. The selected voltage window for electrocatalytic response through Cyclic Voltammetry (CV) and stability testing for 3600 s via chronoamperometry at a fixed potential of 0.69 V was −0.1−0.7 V (vs Hg/HgO). Moreover, the frequency range of 1−1×10⁵ Hz was picked to find out system resistance at an amplitude of 0.005 V.

**Results and discussion**

NiNH₂BDC MOF/1,2,5 wt% rGO hybrids were systematically evaluated through XPS, FTIR, XRD, SEM, Cyclic Voltammetry, Tafel slope, Electrochemical Impedance Spectroscopy, EASA, Mass Activity, roughness factor, and Chronoamperometry.

In the FTIR spectrum of fabricated samples (Fig. 2a) the COO⁻ group symmetric and asymmetric stretching vibrations generate resilient adsorption bands at the position of 1568 and 1374 cm⁻¹ and the gap between these two bands designates the connection of the COO⁻ group of the linker with nickel-metal through the bidentate mode of linking. The band at 1655 cm⁻¹ besides 1250 cm⁻¹ indicates the N−C group stretching mode of vibration as well as divulges the coordinated DMF group manifestation while NH₂ group stretching and bending vibrations bands appear at 3309 and 1684 cm⁻¹, respectively⁴⁵–⁴⁸. The region between 3300 and 3000 cm⁻¹ was occupied by asymmetric & symmetric vibration bands of the H−N group⁴⁵. C−H peak appears at 754 cm⁻¹ while the evident peak at 587 cm⁻¹ approves the presence of nickel and its coordination with the COOH group oxygen. Figure 2b represents the comparison of FTIR spectra of NiNH₂BDC/5 wt% rGO composite before and after the stability test⁴⁹,₅₀.

In the reported samples XRD pattern (Fig. 3), less significant peaks within 20 range of 42°−52° correspond to the Ni NH₂BDC MOF distinctive peaks, while less intense peaks at 15°, 25°, 35°, 38°, 40°, and 61° ensure the development of Ni (OH)₂ during the reaction accompanied with DMF peak at 2θ, 7.5° and attributed to restricted oxygen. Figure 4b represents the comparison of FTIR spectra of NiNH₂BDC/5 wt% rGO composite before and after the stability test⁵₀,₅₁.

The particle size, crystalline shape, and morphology appraised at different magnifications via SEM study display the presence of hexagonal shape particles while Reduced Graphene Oxide sheets working as a MOF support not only control the size of MOF nanoparticles but also helps in a MOF NPs fine dispersal on its panes and prevents the agglomeration. During the optimization of the synthetic conditions, it was observed that the addition of a small amount of PVP further controls the growth, shape, and size of hexagonal particles. Furthermore in EDX analysis for elemental composition, the increase in carbon content from MOF towards 5 wt% rGO composite validates the successful synthesis of rGO and composites synthesis. The XRD pattern closely resembles the literature data⁵₂,⁵₃.

The information about elemental composition, binding energy, and metal oxidation state was obtained by XPS (Fig. 4). The C 1 s spectrum comprises 3 peaks at B.E (binding energy) value of 284, 286, and 288 eV stipulate the existence of C−C, C−O, and C = O groups, respectively while oxygen spectra deconvolution in 3 peaks with a binding energy value of 530, 531, and 532 eV specifies the existence of M−O, C = O, and C−O. Fragmentation of nitrogen XPS spectra into two peaks of 402 and 403 eV represents the presence of the amine and pyrrolic nitrogen, respectively⁵₆. In the nickel spectrum, the presence of Ni²⁺/Ni³⁺ was verified by the peaks in the range of 853−875 eV. The peaks at 871.8 eV for Ni 2p₁/₂ and 853.1 eV for Ni 2p₃/₂ indicate the spin-orbital coupling of Ni (+ 2) while peaks positioned at binding energy value of 874.73 eV (Ni 2p₁/₂) and 856.80 eV (Ni 2p₃/₂) are due to spin-orbital coupling of Ni (+ 3). The energy difference of 17.6 eV not only confirms the existence of Ni²⁺/Ni³⁺ but also supports the nickel hydroxide manifestation⁵₅,⁵₇–⁶₂.

Raman spectrum obtained after interaction and scattering of electromagnetic radiation with matter gives an idea about crystalline and the defects rich nature of material⁶³–⁶⁷. Raman spectra of NiNH₂BDC MOF rGO hybrids have been presented in Fig. 5. In the selected range of analysis (4000−500 cm⁻¹) the G and D band appears due to graphitic carbon vibrations and carbon defects, respectively. The calculated Iᵰ/Iₓ ratio is in following order; NiNH₂BDC (0.95) < 1 wt% rGO composite (0.98) < 2 wt% rGO composite (1.003) < 5 wt% rGO composite (1.008). The (a) amplified Iᵰ/Iₓ ratio in 5 wt% rGO composite due to rearrangements and structural defects promote the extensive π bonding and electron transfer from donor towards acceptor sites, and (b) ~ 5 and ~ 65-time shifting of G and D bands results in the smooth charge transfer process. Both of these factors are attributed to the enhanced catalytic activity of a 5 wt% reduced graphitic carbon (rGO) hybrid than parent MOF⁶⁸.

The TGA (Thermo gravimetric analysis) was performed for the investigation of the stability of the electrocatalysts. The thermal behavior of MOF and 5 wt% rGO composite is divided into four domains of mass loss (Fig. 6). The first step at 75 °C corresponded to the solvated DMF molecules, (5% loss). A second step between 100−240 °C was assigned to surface adsorbed water loss (18%). The third step at 290 °C corresponds to the loss of coordinated DMF(23% loss), and after that 61% weight loss at 388 °C represents structure collapse with the linker decomposition (Fig. 6)⁶⁹–⁷₂.
Electrochemical testing of NiNH₂BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids for MOR. The electrocatalyst (1–3 mg) was mounted on GCE to evaluate the optimized catalyst amount. The gradual increase in current density by increasing catalyst amount was due to easy access to abundant and exposed electroactive sites and after that decline in current density is due to; (i) restricted utilization of bottom layered material due to upper thick layer (ii) inferior charge transfer process, and (iii) active sites blockage by reaction intermediates (Fig. 7a)⁷³–⁷⁶. Likewise, during methanol concentration optimization (1–5 M), the 3 M concentration with the maximum delivered current was found to be the optimum amount. At low content of CH₃OH, the boosted current response is owing to excess of available OH⁻ ions owing to diffusion-controlled methanol transport process while at high CH₂OH concentration, excess of methanol limit the OH⁻ adsorption, and reaction intermediates block the active sites and consequently depress the catalytic activity, Fig. 7b⁷⁷–⁷⁹.

The electrocatalytic response of all samples in the presence and absence of CH₃OH is compared and analyzed at 50 mV/s in Fig. 8a,b. Without methanol, the 5.76 mA/cm² current density is produced while current density

![Figure 2.](attachment:image.png)

(a) Fourier transformed infrared spectrum of NiNH₂BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids (b) FTIR spectra of NiNH₂BDC/5 wt% rGO composite before and after stability test.
response of NiNH₂BDC MOF/1–5 wt% reduced graphitic carbon hybrids is 181.01 (NiNH₂BDC) < 186.86 (1 wt% rGO) < 218.94 (2 wt% rGO) <, and 267.77 (5 wt% rGO). Among all the analyzed composites the prime reason for the extraordinary current density of NiNH₂BDC/5 wt% rGO composite is; (a) synergistic effect between MOF and rGO (b) enhanced surface area, greater stability, and excellent conductivity due to sheet-like morphology of rGO. However, the excessive rGO amount in NiNH₂BDC/6 wt% rGO composite results in (i) rGO sheets restacking due to pi–pi interaction and choked active sites (ii) inhibited methanol diffusion, and (iii) firmly attached reaction intermediate (CO) limiting OH⁻ ions adsorption on electrode surface²⁴,⁵³,⁸⁰–⁸².

The Cyclic Voltametric investigations were executed at the scanning speed of 2, 5, 10, 25, and 50 mV/s by selecting the voltage window of −0.1 to 0.7 to recognize the influence of scanning speed on the current density of the tested samples. At the highest scanning speed, the easy and maximum approach of electroactive species towards the electrode surface leads to maximum current density Fig. 8b–f⁸³,⁸⁴.

To get information about the diffusion-controlled process, a straight line obtained by directly relating the peak current density with (scan rate)⁻¹/², provides a slope that is equivalent to diffusion coefficient (Fig. 9). Furthermore, the diffusion coefficient (D) is calculated by inserting the value of the α (charge transfer coefficient) in the Randles Sevcik equation⁸⁵.

For non-reversible oxidation process, the calculated D (diffusion coefficient) value are; 13.2 × 10⁻⁵ cm² s⁻¹ for NiNH₂BDC MOF, 16.1 × 10⁻⁵ cm² s⁻¹ for 1 wt% rGO composite, 21.8 × 10⁻⁵ cm² s⁻¹ for 2wt% rGO composite, and 31.8 × 10⁻⁵ cm² s⁻¹ for 5wt% rGO composite, respectively (Table 1). R² value ≈ 1 and absolute value of diffusion coefficient for NiNH₂BDC 5 wt% rGO composite prove it to be active MOR catalyst³⁶.

The EIS (Electrochemical Impedance Spectroscopy), an important parameter tends to explore the kinetics and reaction mechanism. The EIS evaluation was accomplished in 3 electrode systems within the selected frequency domain of 1–1 × 10⁵ Hz in an alkaline solution. Figure 10a,b illustrate the Nyquist plot of the bare electrode and NiNH₂BDC MOF/rGO composites. A depressed semicircle of NiNH₂BDC/5 wt% rGO hybrid illustrates the lowermost resistance (highest conductivity) than other counterparts due to homogenous scattering of MOF NPs on rGO surface having high surface area, exposed electroactive sites with maximum OH⁻ adsorption, facile CO oxidation, smooth charge, and mass transfer, and accelerated CH₃OH oxidation process⁸⁶. Besides, modification of interfacial structure as a result of rGO inclusion is also an important kinetic controlling factor⁸⁷–⁸⁹. The extracted EIS data obtained after fitting a suitable circuit represent the minimum contact resistance, electrolyte resistance, and substrate inherent resistance with consequent excellent conductivity and electrocatalytic activity of NiNH₂BDC/5 wt% rGO (Table 2)⁹⁰,⁹¹.

Tafel plot is another important parameter utilized for evaluation of methanol oxidation activity, reaction mechanism, and kinetics of catalytic process by correlating ln current density (ln j) with overpotential (η) (Fig. 11). Over potential is the required potential greater than the requisite potential for a reaction to occur. The kinetic behavior of as-synthesized samples is determined by the given below Tafel equation⁹².

\[
\eta = A + b \log j
\]
Figure 4. X-ray photoelectron spectra of NiNH$_2$BDC (a) Survey scan (b) Carbon (c) Oxygen (d) Nitrogen, and (e) Nickel.
At low overpotential (0.388 V), the NiNH$_2$BDC MOF/1, 2, 5 wt% rGO composites calculated Tafel slope values are in order of: 62.0 (pure MOF) > 61.6 (1 wt% rGO) > 59.6 (2 wt% rGO) > 57.3 mV/dec (5 wt% rGO), respectively. Moreover, at comparatively greater overpotential (0.410 V), the Tafel slope follow the sequence of: 65.4 (pure MOF) > 65.1 (1 wt% rGO) > 63.0 (2 wt% rGO) > 60.8 mV/dec (5 wt% rGO) (Table 3). Two different informations are obtained by calculating the Tafel slope at low and high overpotential region as (a) Hydrogen removal (dehydration) from CH$_3$OH is the rate controlling step in low potential region while (b) CO exclusion during oxidation process occur in the escalated potential domain. The NiNH$_2$BDC/5 wt% rGO composite lowermost Tafel slope value (57.3 mV/dec) reflects the fast removal of hydrogen from CH$_3$OH during oxidation process$^{93–97}$.

The utmost requirement for the practical application of electrocatalyst is its long-term stability under experimental conditions. A Chronoamperometry (i/t) experiment is conducted in N$_2$ saturated alkali solution at peak potential 0.69 V vs Hg/HgO in three electrodes set up for 60 min. The graphical response of the oxidation process can be elaborated as (i) initial maximum j (current density) is due to strong binding of catalyst at the electrode surface, minimum gas bubbles, and large available active sites. (ii) The rapid decline in current density after a short period is associated with (a) extreme gas release and reaction intermediates formation which block the electroactive sites, and (b) material detachment due to excessive bubbling (iii) finally, a steady-state is achieved.

![Raman spectra](image1)

**Figure 5.** Raman spectra of (a) rGO (b) NiNH$_2$BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids.

![Thermograms](image2)

**Figure 6.** The Thermograms of NiNH$_2$BDC MOF and NiNH$_2$BDC/5 wt% reduced graphitic carbon hybrids.
which persists for 3600 s due to the reaction intermediates passive adsorption\textsuperscript{96–101}. According to chronoamperometry graph, the stability retained by NiNH\textsubscript{2}BDC/5 wt% rGO composite is 60.6% while the stability retained by remaining samples is; NiNH\textsubscript{2}BDC/2 wt% rGO 59.3%, NiNH\textsubscript{2}BDC/1 wt% rGO 59.0%, and NiNH\textsubscript{2}BDC MOF 57.3%, respectively (Fig. 12a,b). The minimum loss in current density of NiNH\textsubscript{2}BDC/5 wt% rGO composite attributed to (a) large specific surface area provided by 2D rGO sheets (b) tolerance towards poisonous reaction intermediates (c) fine scattering of small size MOF nanoparticles on rGO surface, and trivial charge transfer resistance\textsuperscript{96}.

The greater stability of NiNH\textsubscript{2}BDC/5 wt% rGO composite was further evaluated through Cyclic Voltamogram. The current density reserved by electrocatalyst after 200 cycles are presented in Fig. 13. The sample stability tends to decline after successive cycling due to the blockage of active sites owing to excessive bubbling during MOR with electrode surface coverage, inhibited transport of electrolyte toward electrocatalytic material, and decrease in Electrochemical Active Surface Area. This problem can be settled by refreshing the electrolyte via a subsequent cathodic reduction in reverse scan and by performing the CV for few cycles\textsuperscript{98,102,103}.

The recommended mechanism for the CH\textsubscript{3}OH oxidation process is as under\textsuperscript{104,105}.

\[
\begin{align*}
\text{Ni}^0 & + 2\text{OH}^- & \rightarrow & \text{Ni}^{+2}(\text{OH})_2 \\
\text{Ni}^{+2}(\text{OH})_2 & \rightarrow & \text{Ni}^{+3}(\text{OH})_2 & + \text{e}^- \\
\text{Ni}^{+3}(\text{OH})_2 & + & \text{OH}^- & \rightarrow \text{Ni}^{+3}(\text{OH})_3 \\
\text{Ni}^{+3}(\text{OH})_3 & \rightarrow & \text{NiOOH} & + \text{H}_2\text{O} \\
\text{NiOOH} & + & \text{CH}_3\text{OH}_{(ads)} & \rightarrow \text{Ni}^{+2}(\text{OH})_2 & + & (\text{CH}_2\text{O})_{ads} \\
\text{NiOOH} & + & (\text{CH}_2\text{O})_{(ads)} & \rightarrow \text{Ni}^{+2}(\text{OH})_2 & + & (\text{CHO})_{ads} \\
\text{NiOOH} & + & (\text{CHO})_{(ads)} & \rightarrow \text{Ni}^{+2}(\text{OH})_2 & + & (\text{CO})_{ads} \\
\text{NiOOH} & + & (\text{CHO})_{(ads)} & \rightarrow \text{Ni}^{+2}(\text{OH})_2 & + & \text{CO}_2
\end{align*}
\]

In the case of a Nickel-based system, NiO smoothened the CO oxidation by providing required oxygen while the NiOOH group promotes the MOR by Ni\textsuperscript{1+}/Ni\textsuperscript{3+} oxidation/reduction process where +2 to +3 oxidation further promote CO oxidation\textsuperscript{92,106}.

The mass activity of all electrocatalysts is determined from the ratio of the current density vs deposited mass
Figure 8. Cyclic Voltamogram of (a) NiNH₂BDC MOF/1–5 wt% reduced graphitic carbon hybrids at 50 mV/s (b) NiNH₂BDC MOF/1–6 wt% reduced graphitic carbon hybrids at 50 mV/s (c) NiNH₂BDC MOF (d) NiNH₂BDC/1 wt% reduced graphitic carbon hybrids (e) NiNH₂BDC/2 wt% reduced graphitic carbon hybrids, and (f) NiNH₂BDC/5 wt% reduced graphitic carbon hybrids in 3 M CH₃OH/1 M NaOH solution at scanning speed 2–50 mV/s.
**Figure 9.** A graphical representation of the direct relationship of peak current density ($j$) versus under root of scan rate ($v$) in 3 M CH$_3$OH/1 M NaOH solution.

**Table 1.** The comparative statement of the magnitude of the diffusion coefficient and $R^2$ of NiNH$_2$BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids at 50 mV/s.

| Electrocatalyst           | $R^2$     | Diffusion coefficient (cm$^2$ s$^{-1}$) |
|---------------------------|-----------|----------------------------------------|
| NiNH$_2$BDC MOF           | 0.9991    | 13.2 x 10$^{-5}$                       |
| NiNH$_2$BDC/1 wt% rGO     | 0.9993    | 16.1 x 10$^{-5}$                       |
| NiNH$_2$BDC/2 wt% rGO     | 0.9996    | 21.8 x 10$^{-5}$                       |
| NiNH$_2$BDC/5 wt% rGO     | 0.9997    | 31.8 x 10$^{-5}$                       |

**Figure 10.** Nyquist plot (a) Bare and (b) NiNH$_2$BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids in 3 M CH$_3$OH/1 M NaOH solution at oxidation potential 0.699 V.
The Mass Activity (M.A) of tested samples at an overpotential of 0.331 V is as under; NiNH2BDC MOF 113.8 mA/mg < NiNH2BDC/1 wt% rGO composite 120.4 mA/mg < NiNH2BDC/2 wt% rGO composite 133.8 mA/mg < and NiNH2BDC/5 wt% rGO composite 168.7 mA/mg.

To calculate the electrocatalytic activity of as-synthesized samples, EASA is determined by dividing Cdl (double-layer capacitance) with Cs (specific capacitance). The specific capacitance is a constant factor for each specific system while double-layer capacitance is determined through multiple CV scans or EIS in the non-faradic region. The estimated EASA of NiNH2BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids at voltage 0.19 was observed to be; 7.6 (pure MOF) < 9.1 (1 wt% rGO) < 14.4 (2 wt% rGO) < 15.7(5 wt% rGO), correspondingly.

The comparatively heightened catalytically active surface area of NiNH2BDC/5 wt% rGO composite proves the superb electrocatalytic performance of material for MOR (Supplementary information Fig. 1). The given data also authenticate the CV, EIS, and Tafel results.

Moreover, the EASA is divided by the geometrical area of the electrode to calculate the R.F (roughness factor). It is a unitless factor, as it is a ratio.

\[
\text{R.F} = \frac{\text{EASA}}{\text{Electrode geometrical area}}
\]

### Table 2

| Electrocatalyst | Rs (Ω) | Rct (Ω) | Q (5° Ω⁻¹) | W (Ω) |
|-----------------|--------|---------|------------|-------|
| Bare            | 18.84  | 86.24   | 492.1 × 10⁻⁴ | 33.89 × 10⁻⁴ |
| NiNH2BDC MOF    | 14.24  | 67.13   | 538.5 × 10⁻⁴ | 39.97 × 10⁻⁴ |
| NiNH2BDC/1 wt% rGO | 14.10 | 63.10   | 540.8 × 10⁻⁴ | 40.09 × 10⁻⁴ |
| NiNH2BDC/2 wt% rGO | 13.33 | 58.35   | 548.8 × 10⁻⁴ | 43.16 × 10⁻⁴ |
| NiNH2BDC/5 wt% rGO | 13.26 | 35.50   | 1.072 × 10⁻² | 92.33 × 10⁻⁴ |

### Figure 11

Tafel plot (η vs ln j) of NiNH2BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids in 3 M CH₃OH/1 M NaOH solution.

### Table 3

| Electrocatalyst | Tafel slope (mV dec⁻¹) η = 0.388 V | Tafel slope (mV dec⁻¹) η = 0.410 V |
|-----------------|-----------------------------------|-----------------------------------|
| NiNH2BDC MOF    | 62.0                              | 65.4                              |
| NiNH2BDC/1 wt% rGO | 61.6                          | 65.1                              |
| NiNH2BDC/2 wt% rGO | 59.6                          | 63.1                              |
| NiNH2BDC/5 wt% rGO | 57.3                          | 60.8                              |

Mass Activity = J/m

The Mass Activity (M.A) of tested samples at an overpotential of 0.331 V is as under; NiNH2BDC MOF 113.8 mA/mg < NiNH2BDC/1 wt% rGO composite 120.4 mA/mg < NiNH2BDC/2 wt% rGO composite 133.8 mA/mg < and NiNH2BDC/5 wt% rGO composite 168.7 mA/mg.

To calculate the electrocatalytic activity of as-synthesized samples, EASA is determined by dividing Cdl (double-layer capacitance) with Cs (specific capacitance). The specific capacitance is a constant factor for each specific system while double-layer capacitance is determined through multiple CV scans or EIS in the non-faradic region. The estimated EASA of NiNH2BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids at voltage 0.19 was observed to be; 7.6 (pure MOF) < 9.1 (1 wt% rGO) < 14.4 (2 wt% rGO) < 15.7(5 wt% rGO), correspondingly.

The comparatively heightened catalytically active surface area of NiNH2BDC/5 wt% rGO composite proves the superb electrocatalytic performance of material for MOR (Supplementary information Fig. 1). The given data also authenticate the CV, EIS, and Tafel results.

Moreover, the EASA is divided by the geometrical area of the electrode to calculate the R.F (roughness factor). It is a unitless factor, as it is a ratio.

\[
\text{R.F} = \frac{\text{EASA}}{\text{Electrode geometrical area}}
\]
The heightened roughness factor reflects the excellent catalytic performance of material due to the direct relationship between EASA and R.F. Roughness factor of NiNH$_2$BDC MOF/1–5 wt% reduced graphitic carbon hybrids were found in the following order; 107, 128, 204, and 222 respectively (Table 4 and Fig. 14$^{107}$).

The comparative statement of the electrocatalytic response of tested materials with already reported materials is provided in Table 5 given below.
Conclusions
The NiNH₂BDC MOF/1–5 wt% reduced graphitic carbon hybrids (NiNH₂BDC/rGO) fabricated by sonication-assisted solvothermal approach were studied for the CH₃OH oxidation process under alkaline condition. The NiNH₂BDC MOF/5 wt% rGO composite by possessing auspicious current of 267.7 mA cm⁻² at voltage 0.69, Tafel slope of 60.8 mV dec⁻¹, the resistance of 13.26 Ω, EASA 15.7 cm², mass activity 168.7 mA/mg and roughness factor 222 in 3 M CH₃OH/1 M NaOH solution displays better activity as compared to the state-of-the-art platinum-based materials and prove to be a proficient substitute of costly materials exploited for MOR in the direct CH₃OH fuel cell.

Table 4. EASA, Mass activity, and Roughness factor comparison of NiNH₂BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids.

| Catalyst                  | EASA (cm²) | Mass activity (mA/mg) | Roughness factor |
|---------------------------|------------|------------------------|------------------|
| NiNH₂BDC MOF              | 7.6        | 113.8                  | 107              |
| NiNH₂BDC/1 wt% rGO        | 9.1        | 120.3                  | 128              |
| NiNH₂BDC/2 wt% rGO        | 14.1       | 133.8                  | 204              |
| NiNH₂BDC/5 wt% rGO        | 15.7       | 168.7                  | 222              |

Table 5. The electrocatalytic activity of synthesized samples in comparison with reported materials.

| Electrocatalytic materials | Molarity of Methanol solution (M) | Scan rate (mV s⁻¹) | Oxidation potential (V) versus RHE | Anodic current density (mA cm⁻²) | Resistance (Ω) | References |
|----------------------------|-----------------------------------|-------------------|-----------------------------------|---------------------------------|----------------|------------|
| Pt/rGO                     | 3                                 | 50                | 1.72                              | 32                             | –              | 108        |
| NiO-MOF/rGO                | 3                                 | 50                | 1.83                              | 276                            | 22.8           | 23         |
| Cu BTC/5 wt% rGO           | 3                                 | 50                | 1.84                              | 120                            | 20.53          | 22         |
| Ni Cr LDH                  | 3                                 | 50                | 1.63 V                            | 7.82                           | –              | 109        |
| NiNH₂BDC MOF               | 3                                 | 50                | 1.614 V                           | 180.0                          | 14.24          | This work  |
| NiNH₂BDC/1 wt% rGO         | 3                                 | 50                | 1.614 V                           | 186.8                          | 14.10          | This work  |
| NiNH₂BDC/2 wt% rGO         | 3                                 | 50                | 1.614 V                           | 218.94                         | 13.33          | This work  |
| NiNH₂BDC/5 wt% rGO         | 3                                 | 50                | 1.614 V                           | 267.77                         | 13.26          | This work  |

Figure 14. The comparison of EASA, Mass activity, and Roughness factor of NiNH₂BDC MOF/1, 2, 5 wt% reduced graphitic carbon hybrids.
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Supplementary Information

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