Fabrication of Ni–MOF-derived composite material for efficient electrocatalytic OER

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ABSTRACT
The poverty-stricken population cannot withstand the shocks of global warming and can hardly pay the soaring expenditure of fossil fuels whose reservoirs are already approaching the threshold limit. These adventures guided the researchers towards water oxidation as a source of energy. In this study, a metal-organic framework (MOF)-based material was fabricated and catalyzed the lethargic oxygen evolution reaction (OER). The synthesized material is characterized with different analytical techniques to confirm structural, morphological and textural properties. Its huge surface area (87 m²/g) rendered it a promising material to carry the OER. It exhibited shallow onset potential that is, 1.40 V vs. RHE and displayed an exceptionally low overpotential of 1.42 V vs. RHE to reach the benchmark current density (10 mA/cm²) with remarkably small Tafel slope that is, 34 mV/dec. It surpassed the state of the art electrocatalyst for OER, that is, IrO₂ and RuO₂ in efficiency as well as in stability.

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1. Introduction
To support economic development and keep pace with the modern world, every nation seeks an alternate energy source. The everlasting and vigorous energy for life on earth is the ultimate goal of today’s research. The type of energy that is everlasting and vigorous for the life on earth is the ultimate goal of today’s research. The scarce sources and byproducts released during their consumption in power generation houses and automobiles diminished the importance of fossil fuels [1,2]. These circumstances prompted the intellectual community to divert their focus from the conventional hazardous fossil fuels to other possible unconventional sources of energy [3]. Solar [4], wind [5], tidal [6], hydrodynamical [7] and geothermal [8] sources have endeavored for the generation of renewable energy, but the outcome was not up to the mark. Endless investigation on contemporary fuels revealed that hydrogen (H₂) as an alternative sustainable fuel has far better results in terms of efficiency and availability. Various origins for the generation of H₂ were tested, but photocatalysis and electrocatalysis of water were the most promising and the most dynamic H₂ [3,9].

Electrocatalytic water splitting is the blue-eyed phenomenon of the scientific community working on the energy problem to address the miserable energy issues, gloomy environmental adulteration, and consequently depressed economy. The dynamic water splitting has two complementary steps, namely hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode [10]. Among these, the lateral reaction, OER, is much explored. As its kinetics is lethargic and controls the overall efficiency of the reaction. Generally, reactants have to cross an uphill of energy (energy of activation) to be converted into the products. The four-electron transfer mechanism of OER has to travel a vast mountain of energy (activated complex) to accomplish the reaction. Electrochemical water splitting must occur under extreme conditions where HER is likely to be more efficient under acidic solid conditions [11–13]. To make the reaction efficient and to make it commercially feasible, it is crucial to devise a catalyst to alter the way of the reaction in a way with minimum activation energy. During a chemical reaction, intermediates have to adsorb on the surface of the electrocatalyst. A good electrocatalyst must have
an inexpensive origin and should offer a more
electrochemically active surface area for the adsorption of
reaction intermediates, and at the same time, it should
facilitate desorption of the molecules for the formation of
the end products. It should also offer this facility again
and again over a longer period of time, so that, the
reaction might be cost-effective [14]. In the case of OER
and hydrogen oxidation reaction (HOR), a wide variety of
electrocatalysts including metals [15], metal alloys
[16], metal oxides [17,18], metal chalcogenides [19–21],
metal phosphides [22,23], porous materials like zeolites
[24,25], MOFs [26,27], composites and a huge range of
nano-materials were employed to mitigate its energy
expenditure for activation energy. Many of these
displayed their propensity to drive the reaction through
a different route but still at the expense of a big deal of
energy. Noble metals like Ru and Ir, however, proved
their hegemony and carried the reaction in the way
with the least expense of energy [28]. However, they
too could not maintain their efficiency under such drasti-
c conditions over a longer period of time. High cost,
dearth sources and limited efficiency of these noble
metals triggered researchers to extend their vision to
replace these costly metals with the ones which have
earth abundance inexpensive sources with ultrahigh
durability [29].

Since their discovery by Omar M. Yaghi, metal
organic frameworks (MOFs) have been playing a tremen-
dous role in many vital procedures. Their intriguing
crystalline structure, versatile and tunable porosity (up
to 9.8 nm depending upon the length of the ligand),
huge surface area (from 1000 to 10,000 m²g⁻¹) and
tailored chemistry have made these materials the cor-
nor stone of the today’s research domains [30]. MOFs
are lovely combination of inorganic (metal nodes) and
organic (linkers) compounds for the service of human-
ity [31]. They are being tested from gas separation
to gas storage [32,33], from photocatalysis to electrol-
ysis [34,35], from dyes’ degradation to energy stor-
age devices [36–39] and from sensing to biomedicine
[40,41]. Although they are employed in their original
form in variety of applications, yet they can host the vari-
ety of nanoparticles to exert the synergistic effect. Now-
a-days, lots of innovative materials, whose preparation
is otherwise impossible, are being fabricated with the
help of MOF. Their unique composition, versatile crys-
talline structure and distinctive morphologies aroused
the interest of researchers to fabricate thousands of
innovative MOFs every year. More than 20,000 MOFs
have already been reported [42–47].

Carbon materials, making the backbone of organic
compounds, playing a crucial role in other fields of
chemistry and biological sciences, are here to serve humanity. A huge variety of carbon nano-materials,
including nano-tubes, nano-fibers, graphene, graphene
oxide, fullerene, carbon dots (CDs), etc., have played
crucial roles in many solid reactions and served human
beings for hundreds of years. With the passage of time,
innovative handling of these materials and unique syn-
thetic strategies make them a potential aspirant for
every novel endeavor. Sometimes, they act as the exclu-
sive reagent to accomplish the reaction with the superb
outcome, and sometimes, they are in combination with
other materials to exert a phenomenal synergistic effect
to fulfill the requirement [48–54].

Here in this work, a novel composite of Ni-based
mixed linkers MOF with CDs was fabricated via solvother-
mal reaction followed by calcining and performed
their electrochemical properties in 1 M KOH solution.
It was perceived that the presence of CDs in Ni-MOF
offered tremendous OER activity due to the contribu-
tion of Ni-atoms embedded in the enormous car-
bon structure of the calcinated material. The calcinated
composite attained the benchmark current density of
10 mA cm⁻² at only 194 mV and displayed an ideal
Tafel slope of 34 mV dec⁻¹, proposing easy and quick
electron–proton transfer during the reaction. All these
parameters advocated that the calcinated composite is
an auspicious material and a prospective contestant for
highly valued OER.

2. Experimental section

2.1. Chemicals

All the analytical grade chemicals, that is, ethanol
(Analar, 99.8%), acetone (Normapur, 99.8%), HNO₃
(Merk 65%), H₂SO₄ (Analar, > 98%), 1,5-benzenedi-
arylcarboxylic acid (BDC) (Sigma Aldrich, 89%), 4,4’-bipyridine
[bpy] (Sigma Aldrich, 98%), NN-dimethyldiformamide
[DMF] (Riedel-deHaen, 99%) and nickel nitrate hexahy-
drate (Ni(NO₃)₂·6H₂O), (Sigma Aldrich, 99.9%) were
utilized as such without additional refining and purifi-
cation.

2.2. CDs fabrication

Using green chemistry, Li Wang et al. devised a
grandiose scheme to synthesize CDs [55]. This proce-
dure is devoid of any chemical reagent and uses only
milk as a source of CDs and thus is benign for the envi-
ronment. In the said process, de-ionized water (20 mL)
was taken. To this water, 25 mL of milk was added
with vigorous and continuous stirring. A 50 mL stainless
steel autoclave with Teflon cup was taken washed thor-
oughly following the standard protocol to minimize the
risk of any impurity. The resultant mixture was trans-
ferred into the autoclave, placed in the oven for 2 h
at 180°C. The reaction mixture was obtained and cen-
trifuged when the period was over, and the autoclave
gradually cooled at room temperature. The obtained
precipitates were washed via ultrapure water and then
with ethanol before drying. For drying, these precip-
itates were kept in the oven for 18 h at 50°C. When
the drying period was over, brown precipitates of CDs were obtained, grounded finely with the help of pestle and mortar. These fine precipitates were stored for characterization and further applications.

2.3. Fabrication of metal-organic framework
To fabricate a mixed linkers MOF, slight modifications were made in the already devised scheme reported by Phan et al. [56]. Twenty millilitre of NN′-dimethylformamide (DMF) was taken in a reaction flask. The calculated amount of 1,5-benzenedicarboxylic acid (BDC, 0.332 g, 2 mmol) to this solvent was added and continuously stirred until a clear solution. After that, 4,4′-bipyridine (bpy, 0.112 g, 1 mmol) was added with constant stirring. After continuous stirring for 10 min, nickel nitrate hexahydrate [Ni (NO₃)₂·6H₂O, 0.58 g, 2 mmol] was added to the reaction mixture. The stirring lasted for a further 10 min. Then, the reaction mixture was transferred into the cleaned and dried autoclave, which was then placed in the oven for 48 h at 100°C. After the reaction duration was over, the system was allowed to cool at room temperature naturally. The resultant product was taken out of the autoclave. Further, DMF was added and stirred for 15 min. After that, it was filtered and washed with DMF, followed by drying at room temperature. The end product was stored for further evaluation.

2.4. Fabrication of composite
By following the same procedure as discussed above for the synthesis of MOF, we added 1,5-benzenedicarboxylic acid (BDC, 0.332 g, 2 mmol) and 4,4′-bipyridine (bpy, 0.112 g, 1 mmol) into 20 mL of NN′-dimethylformamide (DMF) with vigorous stirring and got a clear solution. At this point, we added CDs (0.8 g) along with nickel nitrate hexahydrate [Ni (NO₃)₂·6H₂O, 0.58 g, 2 mmol] into the reaction mixture with constant stirring. The rest of the method was identical as we followed for the synthesis of MOF. The obtained, washed and dried composite was stored for characterization and further application.

2.5. Calcination of MOF and its composite
The synthesized MOF and its composite were then calcinated at 400°C for 3 h in a muffle furnace. After 3 h, the calcined materials were allowed to acquire room temperature gradually. They were collected and stored for characterization and further application (Scheme 1).

2.6. Preparation of catalytic ink
For making a homogenous catalytic ink of all materials, 15 mg of the facilely synthesized composite was dissolved in 100 μL of de-ionized water without any binding agent. The mixture was sonicated for 45 min, and a homogenous catalyst ink was obtained.

2.7. Fabrication of the working electrode
To examine the electrochemical activity of the as-synthesized materials, these have to be deposited on a substrate. In the current study, nickel foam (NF) was used as a substrate. Small pieces of NF (1 cm × 1 cm) were cut down and were treated with acetone, hydrochloric acid (2M), ultrapure water and finally ethanol for 15 min each, respectively. After sonication, NF pieces were placed in an oven for 20 min at 60°C for drying. Then, the prepared catalytic ink was physically employed on the already clean NF pieces by the drop-casting method. For this purpose, 10 μL of ink was taken in a micropipette and was deposited on the NF. These loaded NF pieces were then dried at room temperature and then were engaged for electrochemical measurements.

2.8. Characterization of materials
Powder X-ray diffraction (XRD) illustrates whether a material exists in amorphous or crystalline form and to investigate the crystallite size. A Bruker Diffractometer (D8-advance, Japan), with Ni-filter and Cu-Kα radiations, was employed to study the crystallinity of synthesized materials with continuous mode. The linkage of the elements to form functional groups which impart the overall characteristics to the compound was unveiled by using the Fourier-transform infrared (FTIR). For this purpose, a Nicolet-170SX FTIR spectrometer ranging from 400 to 4000 cm⁻¹ was employed. EDX reveals the elemental analysis of the materials done via and energy dispersive spectrometer (S3700N, Hitachi, Japan). The Brunauer–Emmett–Teller (BET) surface area, pore sizes and pore volumes of the as-synthesized composite material were evaluated by using NOVA2200e. The morphology of the materials was expounded via Scanning Electron Microscope (S3700N, Hitachi, Japan) with an accelerating voltage of 20 kV. Surface topology and particle size were further confirmed by Atomic Force Microscopy (AFM) by using Agilent 5500 (USA) Atomic Force Microscope.

2.9. Electrochemical studies
With the help of Potentiostat [PGSTAT-204] computer-controlled AUTOLAB, electrochemical activities of the prepared materials were evaluated containing a typical three electrodes system cell in which Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. NF deposited was used as the working electrode. To assess the inherent catalytic activities of the materials toward OER, Cyclic Voltammery (CV), Linear Sweep Voltammetry (LSV), Electrochemical...
IEEE 5050-2009 (IEEE Standard for Safety Requirements for Industrial Control Systems) was used for the fabrication of the calcinated composite.

Impedance Spectroscopy (EIS) and Chronoamperometry (CA) were employed. Before using, the cell was cleaned by boiling it in a solution of H2SO4 and HNO3 (1:3), followed by boiling in de-ionized water and rinsed with de-ionized water and acetone. At 80°C, it was dried in the oven for some time. 20 per cent solution of HNO3 was used to wash the counter electrode (Pt wire). After treatment with acid, Pt wire was treated with plenty of de-ionized water. All the electrochemical measurements were taken at room temperature (298K). Prior to use, the solution was also purged with argon gas for 20 min. Positive as well as negative potential was intentionally applied at a scan rate of 5 mVs\(^{-1}\) during cyclic voltammetric measurements and only the positive potential was utilized during LSV.

The potential obtained vs. Ag/AgCl was also converted to the potential of RHE by using the following equation:

\[
E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{0}_{Ag/AgCl}
\]  

2.9.1. Tafel slope value
To take an insight into the charge transfer mechanistic studies of OER, Tafel slope values were acquired for all the materials from their respective CV cycles. From these values, it was revealed that catalytic performance has a strong bond with the Tafel slope values. As the relation between the Tafel slope and \(\alpha\) (charge transfer coefficient) is inversely proportional, its lower value corresponds to a higher value of charge transfer coefficient, which leads to easy and quick transfer of electrons and thus confers greater catalytic efficiency to the electrocatalyst and vice versa. Here too, the value of Tafel slope was exploited to have deep insight into the kinetics of the reaction and also sketching the rate-limiting step of OER. Only linear region of steady-state polarization curve was taken into account, and the linear equation was applied to extract the value of Tafel slope [56,57].

\[
\eta = a + b \log j
\]

here \(a\) represents the Tafel constant, \(b\) denotes the Tafel slope which is equal to \(2.303RT/\alpha nF\), \(\eta\) stands for overpotential, \(\alpha\) corresponds to charge transfer coefficient, \(n\) signifies the number of electrons and \(F\) symbolizes the Faraday constant while \(j\) characterizes the current density.

2.9.2. Turnover frequency
To assess the catalytic behavior of the fabricated materials, another crucial parameter called Turnover frequency (TOF) is also exercised. TOF determines the intrinsic potential of a catalyst to alter the reactants into end products in unit time under prevailing conditions. TOF is always determined at a specific overpotential (\(\eta\)) [58,59]. The equation used for TOF calculation is as under:

\[
\text{TOF}(\eta) = j \times A/4 \times F \times n
\]

here \(j\) denotes the current density (certain overpotential in mA cm\(^{-2}\)), \(A\) is the surface area of the deposited NF submerged in the electrolyte, \(F\) symbolizes Faraday constant and \(n\) corresponds to number of moles of the catalyst while 4 characterizes the number of shifting electron to produce one mole of O\(_2\). TOF, here, is determined at overpotential (\(\eta\)) = 1.42 V vs RHE.

2.9.3. Mass activity
When the loaded mass of the electrocatalyst is considered to normalize its current density instead of a geometrical area of the electrode, it is expressed as “Mass Activity”. To gain more insight into catalytic activity of an electrocatalyst predominantly the one with nano-nature, mass-loaded normalized current density of the electrocatalyst is also taken into account along with the geometrical area normalized \(j\). The lateral, expressed in mA cm\(^{-2}\), reflects the area of only planer electrodes with smooth surfaces while the former deals with the rough surface of the electrocatalyst. Mass activity is given by the following formula:

\[
\text{MA} = \frac{j(\eta)}{\text{active mass loading}}
\]

The overpotential (\(\eta\)) used in the above case is 1.42 V vs. RHE.

2.9.4. Specific activity
When the heterogeneous surface of the catalyst is used to normalize current density, then the activity is called...
specific activity, and it is denoted by \( J_s \) and calculated by the following formula:

\[
J_s = \frac{J_{\text{exc}}}{RF}
\]  \( (5) \)

Overpotential \( (\eta) \) used in the above case is 194 mV.

### 2.9.5. Exchange current density (mA cm\(^{-2}\))

For the calculation of exchange current density, charge transfer resistance \( (R_{ct}) \) at the electrode–electrolyte interface is taken into account and then using the following equation.

\[
J_{\text{exc}} = \frac{RT}{nAF\theta}
\]  \( (6) \)

where \( R \) represents the gas constant, \( T \) is the temperature, \( n \) symbolizes a number of electrons, \( F \) is the Faraday constant, \( \theta \) characterizes charge transfer resistance and \( A \) is the geometrical area electrode, that is, 0.5 cm\(^2\) in a current case.

### 2.9.6. Electrochemical active surface area

Electrochemical active surface area (ECSA) is one of the crucial parameters employed to assess the potential of a catalyst to carry the OER. More the value of ECSA, the larger will be the exposure of active sites, the higher will be the intensity of the reaction and greater will be the efficiency of the catalyst. For measuring ECSA, the non-faradic region is taken from the cyclic voltammetric graph. The potential window is chosen from this non-faradic region carefully. At various scan rates, CV cycles are recorded at this window range. The value of \( \Delta j \) is calculated from the difference of anodic and cathodic current densities obtained from these graphs and a straight line is obtained when a new plot is drawn between values of \( \Delta j \) and scan rates. Double-layer capacitance \( [C_{dl}] \) is acquired by dividing the slope of the new plot by 2. The value of ECSA is attained when \( C_{dl} \) is divided by the specific capacitance (0.01 to \( \sim \) 0.040 mF cm\(^{-2}\)). In present work, the potential window selected for the synthesized material was between 0 and 0.06. At this window, various plots were recorded at scan rates of 5–25 mV s\(^{-1}\). From the literature, the value of specific capacitance for flat electrode is mentioned between 0.01 and \( \sim \) 0.040 mF cm\(^{-2}\).

### 2.9.7. Electrochemical impedance spectroscopy

Metrohm Autolab electrochemical workstation was employed to do the EIS study. For this purpose, the applied potential was 0.5 V, and the frequency range was \( 1 \times 10^5 \)–0.1 Hz, while 0.01 V\(_{\text{rms}}\) was the amplitude. With the help of Randles circuit, values of \( R_s \) and \( R_{ct} \) were acquired. Faster kinetics necessitates minimum values of \( R_{ct} \) and \( R_s \) imparting high conductivity to the materials under study.

### 2.9.8. Stability and durability

The stability and the durability of an electrocatalyst are judged by its ability to withstand the harsh conditions of OER over a longer span of time performed on the AUTOLAB PGSTAT-204 in the same conditions, that is, in 1 M KOH solution with three-electrode system at room temperature. The catalyst should not only offer sustained superb activity but also maintain it for an enormous time span without altering its texture during unfavorable conditions. Generation of enormous catalytic activity and unaltered morphology over using again and again for longer time periods pave the way for its commercialization. These characteristics make it a potential candidate for swapping the costly noble metals for OER. Chronoamperometry is one of the tools to assess the intrinsic stability of materials. In the current case, chronoamperometric measurement of the sample was recorded at a potential of 0.8 V for about 12 h.

Furthermore, the constancy of the material can also be evaluated by recording multiple scans and analysing its ability to produce constant current density after hundreds of cycles. The as-synthesized material was also subjected to 1000 CV cycles in 1 M KOH solution. The potential window was \( \sim \) 0.2–1, and the scan rate was 50 mV s\(^{-1}\).

### 3. Results and discussions

#### 3.1. Structural, morphological, compositional and textural analysis

Different analytical techniques characterized synthesized materials. Crystallinity, phase and particle size were estimated by powder XRD analysis. Powder XRD patterns of the CDs, MOF, calcinated MOF and calcinated composite are shown in Figure 1(a). A single carbon peak justifies the amorphous nature of CDs at 20°, which corresponds to the turbostratic carbon phase. Due to the high dispersion of CDs in DMF during MOF formation, the broad peak was converted to the sharp peak, indicating the composite’s crystallinity. As MOF and composite possess crystalline nature, so distinct characteristic peaks of nickel and carbon were observed. After calcination, a slight change in MOF structure was observed due to heating at high temperature and the formation of Ni-MOF-derived carbon composite. Characteristics peaks of Ni in different forms are present in both the calcinated products.

FTIR analysis was also carried out to access the functional groups at different stages of the synthesis of the composite material (Figure 1(b)). Synthesized CDs show a distinct peak at 3400 cm\(^{-1}\) attributed to the hydroxyl groups present on CDs. The as-synthesized MOF shows characteristic peaks at 3350 cm\(^{-1}\) due to hydroxyl groups. This broad peak indicates the abundance of hydroxyl groups, which contributes to the MOF formation. Peaks at 1637 and 1370 cm\(^{-1}\) represent the
anti-symmetric and symmetric stretching of $-\text{COO}^-$ ion in MOF. These two peaks also indicate the bond formation between the metal ion and the ligand. IR bands appearing at 2900 cm$^{-1}$ were due to C–H stretching vibrations. Few peaks in the fingerprint region indicate the composite formation between a metal oxide and carbon after calcination. The absorption peak at 490 cm$^{-1}$ is characteristic peaks of Ni–O in calcinated materials. Peaks of hydroxyl groups also disappeared after calcination due to heating at high temperature.

EDS was carried out to determine the elemental composition of the materials. The mass percent and atomic percent of the elements also justify the formation of different products before and after calcination. EDS analysis of CDs shows only two prominent peaks of carbon and oxygen, with carbon dominating the mass percent (Figure S1). In pure MOF, nitrogen and nickel also appear, and the ratio of carbon is slightly decreased (Figure S2). Carbon content increased in the composite case due to the addition of CDs to MOF (Figure S3). In calcinated MOF (Figure S4) and calcinated composite, the ratio of carbon increased as the whole MOF structure was disturbed at high temperature, resulting in the formation of carbon-NiO composite (Figure 1(c)).

Surface area and porosity play a critical role in electrochemical catalysis and especially in water splitting applications. The surface area and porosity of calcinated composite were determined by BET adsorption isotherm presented in Figure 1(d). Results demonstrate that the high surface area (56 m$^2$/g) of the composite may be due to the attachment of CDs particles, resulting in the blockage of porous channels of the MOF.

Surface morphology and particle size of the CDs, MOF, composite, calcinated MOF and calcinated composite were evaluated by SEM. SEM image of CDs is given in Figure 2(a) that shows the spherical morphology with particle size less than 20 nm. Synthesized MOF shows a rod-like structure with varying particle size (Figure 2(b)). A slight change in the morphology and structure of the MOF is observed after composite formation, and Figure 2(c) (inset figure) shows the attachment of CDs to MOF crystals. The MOF and composite are slightly disturbed after calcination at 400°C and significant change in the morphology is observed in both the calcinated products due to the formation of Ni-MOF-derived carbon composite (Figure 2(d,e)). Morphology and particle size is further characterized by AFM, and a similar trend is observed in all the five synthesized materials (Figure 2(a–e)). These results indicate the successful synthesis of CDs, MOF, composite and their derived porous MOF and composite (after calcination at 400°C).

3.2. Electrochemical studies

To evaluate the intrinsic potential of the as-synthesized materials, that is, CDs, MOF, composite (CDs@MOF), calcinated MOF and calcinated composite (CDs@MOF), electrochemical examinations were carried out in 1 M...
KOH at room temperature through AUTOLAB Poten-
siosstat (PGSTAT-204 computer-controlled). CV and LSV
were used to evaluate the onset potentials and overpo-
tentials in addition to the Tafel slope of the synthesized
catalysts. Both the CV and LSV voltammograms demon-
strated a pre-oxidation peak before the beginning of
the OER shown in Figure 3, which is due to the con-
version of Ni$^{2+}$ to Ni$^{3+}$ species. The creation of Ni$^{3+}$
was the major step for OER initiation. The high inten-
sity of the peak demonstrated that active species Ni$^{3+}$
was in massive amount predicting larger values of ECSA
for the catalyst. It was the Ni$^{3+}$ species that is accred-
ited for the foundation of OER and provided a platform
for the adsorption of reaction intermediates, that is, oxy-
hydroxides to the surface of the electrocatalyst. This
trend of redox reaction via pre-oxidation peak prevails
in transition metal-based electrocatalysts exploited for
OER [60]. Just after the pre-oxidation peak, appearance
of an almost vertical massive line representing the pro-
cess of OER accompanied by the evolution of enormous
bubbling from the electrodes was witnessed. The initia-
tion of this peak was the onset potential of the materials
which were 1.73, 1.58, 1.49, 1.48, 1.41 and 1.40 V vs
RHE for bare nickel foam (BNF), CDs, MOF, composite,
calcinated MOF and calcinated composite respectively.
All these values revealed that the as-prepared calcin-
ated MOF and calcinated composite, possessed excel-
 lent propensity to initiate the OER at significantly low
onset potential surpassing numerous already utilized
MOF-based materials and pasting state of the art elec-
trocatalysts, that is, RuO$_2$ and IrO$_2$ for OER. A current
density of 10 mA cm$^{-2}$ is regarded as the benchmark
to assess the inherent potential of the electrocatalyst
to catalyze the electrolytic OER. The overpoten-
tials used by BNF, CDs, MOF, composite, calcinated
MOF and calcinated composite were 1.77 V (537 mV),
1.61 V (387 mV), 1.51 (280 mV), 1.50 V (272 mV), 1.44 V
(211 mV) and 1.42 V (194 mV), respectively vs. RHE to
achieve benchmark current density (Figure S5). Excep-
tionally low overpotential displayed by the calcinated
composite demonstrated its excellent potential for OER.
As redox potential of Ni$^{2+}$ to Ni$^{3+}$ species also lay
within the purview of benchmark current density, so,
the 10 mV cm$^{-2}$ for the materials regarding OER was

Figure 2. SEM and AFM images of (a, a’) CDs, (b, b’) MOF, (c, c’) Composite, (d, d’) Calcinated MOF and (e, e’) calcinated composite.

Figure 3. (a) CV and (b) LSV polarization curves of BNF, CDs, MOF, composite, calcinated MOF and calcinated composite obtained in
1 M KOH solution at a scan rate of 5 mV/s at room temperature.
calculated from the backward scan of the cyclic voltammogram. Calcinated composite was also able to attain higher current densities at relatively minimum overpotential values. It attained 50, 100, 200, 300, 400, 500, 600 and finally a maximum of 665 mV cm\(^{-2}\) at overpotential values of 1.50 V (270 mV), 1.56 V (336 mV), 1.66 V (431 mV), 1.74 V (512 mV), 1.81 V (587 mV), 1.88 V (658 mV), 1.95 V (729 mV) and 2 V (773 mV) vs. RHE, respectively (graphical comparison of overpotentials is given in Figure S6). This trend demonstrated the superb potential of calcinated composite and declared it as one of the most promising materials for OER surpassing many Ni-based electrocatalysts in efficiency [61–69] (Table 1).

Tafel slope is another vital criterion to have a deep look into the kinetics of OER. The linear region of the steady-state polarization curve was taken into account, and a linear equation was applied to extract the value of the Tafel slope. Lower values of Tafel slope are ascribed to easy adsorption/desorption via quick charge transfer across the surface of the catalyst and thus conferring superior activity to it while higher values render highly resistive behavior of the catalyst in charge transfer resulting in low adsorption/desorption conferring bad catalytic properties to the catalyst. The Tafel slope values for BNF, CDs, MOF, composite, calcinated MOF and calcinated composite were 212, 95, 53, 51, 57 and 34 mV dec\(^{-1}\), respectively, as shown in Figure 4(a) (Figure S7). Outstandingly small Tafel slope of the calcinated composite further confirmed its extraordinarily small values of onset and overpotential, leading to a superb electrocatalytic potential for OER. As CDs were incorporated into the MOF to formulate the composite, it demonstrated its effect in both the simple and the calcinated composites. Due to its synergistic effect with the MOF, it helped to increase the surface area of the composites with enormous porosity, which resulted in the exposure of more and more electrocatalytic active sites facilitating quick adsorption and desorption of lots of reaction intermediates. All these factors enabled calcinated composite to catalyze OER extraordinarily with the minimum values of onset and overpotentials along with extremely low value of Tafel slope. Acquisition of extremely high current densities further supported its outstanding potential for OER. Exceptionally low Tafel slope value envisaged four-electron transfer kinetics for this OER in accordance with the already established mechanism [70]. The proposed electrochemical oxide mechanism is given as under:

\[
\begin{align*}
\text{NiO(OH) + OH}^- &\leftrightarrow \text{NiO(OH)}_2 + e^- \\
\text{NiO(OH)}_2 + 2OH^- &\leftrightarrow \text{NiOOO} + 2H_2O + 2e^- \\
\text{NiOO} + OH^- &\rightarrow \text{NiO} - OH + O_2 + e^- \\
\text{Overall:} 4OH^- &\rightarrow O_2 + 2H_2O + 4e^- 
\end{align*}
\]

In this mechanism, the active sites of the fabricated product were represented by Ni–O. In the first step, the hydroxyl radicals were adsorbed on the surface of bare active sites because of the oxidation of OH\(^{-}\) resulting Ni–OH. The removal of coupled e\(^{-}\) and protons from the Ni–OH results the production of Ni–O. Conversely, nucleophilic attack on the Ni–O results the formation of metal hydroperoxide (Ni–OOH) when combined with one electron. The coupling of proton with one more electron causes the formation of free active centers and the discharge of oxygen molecule takes place.

EIS is another measure to gauge the conductivity of materials and the electrolyte. Charge transfer resistance value \((R_{ct})\) received from low-frequency region describes the resistance of the materials while solution resistance is given by the value of \(R_s\). The values obtained reflect the kinetics occurring at electrode–electrolyte interfaces during OER. The \(R_{ct}\) values for BNF, CDs, MOF, composite, calcinated MOF and calcinated composite were 21.55, 19.69, 4.35, 2.13, 0.948 and 0.248Ω, correspondingly (Figure S8). While solution resistance \((R_s)\) for BNF, CDs, MOF, composite, calcinated MOF and calcinated composite were 1.5, 1.6, 1.5, 1.4, 1.5 and 1.4Ω, respectively. The lowest values of \(R_{ct}\), \(R_s\) and smaller diameter of the semicircle for calcinated composite demonstrated that incorporation of CDs into MOF following their calcination greatly reduced the resistance and ultimately favored the fast and tranquil transport of electron–proton at the electrode–electrolyte interface during OER. It further supported that calcinated composite is highly conductive and possesses outstanding potential for catalyzing OER shown in Figure 4(b).

ECSA simply depicts the actual volume of the catalyst available to carry out the sluggish OER. The larger the value of ECSA, the greater will be the number of exposed active sites, and enormous will be the activity of the catalyst. Through the polarization curves of the CV, a non-faradic region was selected and CV plots were recorded at various scan rates, that is, 5–25 mV s\(^{-1}\) (Figure 5(a)). From these plots, values of \(\Delta j\) were obtained through the difference of the anodic and cathodic current densities, which were further plotted against the scan rates to get a straight line (Figure 5(b)). Half of the slope of this straight line illustrated double-layer capacitance \((C_{dl})\) which was 5, 7, 9.5, 10.05 and 25 mF cm\(^{-2}\) for CDs, MOF, composite, calcinated MOF and calcinated composite, respectively. When the values of \(C_{dl}\) were divided by specific capacitance, that is, \(\sim 0.040\) mF cm\(^{-2}\), ECSAs were obtained. The values were 125, 175, 237.5, 262.5 and 625 cm\(^{2}\) for CDs, MOF, composite, calcinated MOF and calcinated composite, respectively. The higher values of ECSA for calcinated composite demonstrated that it not only had enormous active sites but these sites
Table 1. A relative study of catalytic performances of various already reported MOF-based electrocatalysts.

| S. No. | Catalysts | Overpotential (η) At 10 mA/cm² | Tafel slope value | References |
|--------|-----------|-------------------------------|------------------|------------|
| 1      | Fe−Co−O—OH/ Ni | 250 mV | 40.28 mV dec⁻¹ | [61] |
| 2      | yolk-shell Ni₂P/ZnP₂ hollow microspheres (NZP HMSs) | 210 mV | 57.8 mV dec⁻¹ | [62] |
| 3      | C-MOF-C2-900 | 350 mV | 79 mV dec⁻¹ | [63] |
| 4      | 3D-CNTA | 360 mV | 89 mV dec⁻¹ | [64] |
| 5      | NiCoOS | 470 mV | – | [65] |
| 6      | V-CoP@NC NPs | 354 mV at 50 mA/cm² | 79 mV dec⁻¹ | [66] |
| 7      | Co₃P@FeCoP/NC YSMPS | 238 mV | 47.98 mV dec⁻¹ | [67] |
| 8      | Co₃O₄@C-MWCNTs | 320 mV | 62 mV dec⁻¹ | [68] |
| 9      | Co₃O₄@C-MWCNTs | 340 mV | 72 mV dec⁻¹ | [69] |
| 10     | MOF-based calcinated composite | 194 mV | 34 mV dec⁻¹ | This work |

Figure 4. (a) Tafel slope of BNF, CDs, MOF, composite, calcinated MOF and calcinated composite. (b) OER activity of BNF, CDs, MOF, composite, calcinated MOF and calcinated composite via EIS studies.

Figure 5. (a) CV cycles in non-faradic region at scan rates 5, 10, 15, 20 and 25 mV/s and (b) the respective slope value for the measurement of $C_{dl}$ and ECSA of calcinated composite.

The catalytic activities of the prepared materials to convert $H_2O$ into $H_2$ and $O_2$ in a unit time period under given conditions were further assessed via Turn over frequency (TOF). The greater the value of TOF, the higher will be the electrochemical activity and the superior will be the efficiency of the catalyst. CDs, MOF, composite, calcinated MOF and calcinated composite...
demonstrated 0.014, 0.7, 1.42, 0.25 and 0.44 s\(^{-1}\) TOF values, respectively. Comparatively, the superior value of TOF for calcinated composite with respect to its calcinated MOF simply supported its exceptional potential for electrochemical conversion and thus conferred brilliant activity.

Considering the loaded mass of the materials on to the BNF, mass loading, mass and specific activities, roughness factor (R\(_f\)) and exchange current density of the prepared materials were also calculated. Mass activities were 0.92, 1.22, 3.09, 0.72 and 1.92 Ag\(^{-1}\) while specific activities were 0.0092, 0.102, 0.019, 0.0106 and 0.008 mA cm\(^{-2}\) for the CDs, MOF, composite, calcinated MOF and calcinated composite respectively. Roughness factors were 250, 350, 475, 525 and 1250 while exchange current densities were 0.65, 2.95, 6.03, 13.54 and 51.77 mA cm\(^{-2}\) for the CDs, MOF, composite, calcinated MOF and calcinated composite, respectively. All these parameters supported the superb catalytic activity of the calcinated composite and offered it as one of the best contestants for OER.

Efficiency and stability go side by side to make an electrocatalyst viable for commercialization. The high stability and tremendous durability of an electrocatalyst are crucial considerations that pave the way for its large-scale applications. In the current case, a highly efficient calcinated composite was evaluated via running 1000 CV cycles and through chronoamperometric analysis for up to 12 h. Both these assessments demonstrated super stability of the calcinated composite over a longer period of time. Chronoamperometric analysis disclosed that the as-synthesized calcinated composite displayed superb activity for about 8 h (Figure 6(a)), and then, a little decay in efficiency was observed. However, it was successful to maintain a current density as high as 200–250 mA cm\(^{-2}\). Same trend was observed with 1000 CV cycles (Figure 6(b)). Early on, good stability was observed, which was slightly reduced with the passage of time. Overall the efficiency and stability of the as-synthesized material were outstanding. Its outperformed stability has proved it as one of the best-known electrocatalysts for OER.

4. Conclusion

In order to provide a promising substitute for fossil fuels, MOF-based material synthesized via solvothermal reaction followed by calcination was developed in a quest to harness H\(_2\) from water. In this study, MOF-based material, owing to its versatile porous morphology and massive surface area (625 cm\(^2\)), was exploited to address the hot issues of energy crisis and global warming. The incorporated CDs further boosted the activity by means of enhancing the surface area, thus exerting a synergistic effect. These factors facilitated the calcinated composite to perform outstandingly in initiating the OER at low onset potential as 1.40 V vs RHE. It was superb in attaining the benchmark current density, that is, 10 mA cm\(^{-2}\) at a remarkably low overpotential of 1.42 V vs RHE with attaining a current density as high as 665 mV/cm\(^2\). Its astoundingly small Tafel slope, that is, 34 mV/dec, further confirmed its amazing ability to quickly conduct the charge transfer at the electrode–electrolyte interface. Resultantly, it exhibited astonishingly a charge transfer resistance (R\(_ct\)) as low as 0.248Ω. Its double-layer capacitance was good, and it demonstrated a huge surface area as enormous as 625 cm\(^2\)/g. All these attributes favor calcinated composite to be a promising contender in a race for seeking a potential substitute of fossil fuel.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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