Enhancing the Overall Electrocatalytic Water-Splitting Efficiency of Mo$_2$C Nanoparticles by Forming Hybrids with UiO-66 MOF

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ABSTRACT: For efficient electrocatalytic water-splitting, developing a nonprecious-metal-based stable and highly active material is the most challenging task. In this paper, we have devised a synthesis strategy for a hybrid catalyst composed of molybdenum carbide (Mo$_2$C) and a Zr-based metal–organic framework (MOF) (UiO-66) via the solvothermal process. Synergistic effects between Mo$_2$C and UiO-66 lead to a decrease in the hydrogen adsorption energy on the catalysts, and Mo$_2$C/UiO-66 hybrids offer excellent catalytic activity in an alkaline environment for water-splitting. Particularly, the optimized Mo$_2$C/UiO-66 hybrid, termed MCU-2 with 50:50 wt % of both components, displayed the best catalytic performance for both hydrogen and oxygen evolution reactions (HER/OER). It offered a small overpotential of 174.1 mV to attain a current density of 10 mA/cm$^2$ and a Tafel plot value of 147 mV/dec for HER. It also offered a low overpotential of around 180 mV to attain a current density of 20 mA/cm$^2$ and a Tafel plot value of 134 mV/dec for OER. Additionally, the catalyst was stable for over 24 h and ~1000 cycles with a very minute shift in performance, and the electrolyzer indicates that a potential of ~1.3 V is required to reach 10 mA/cm$^2$ current density. It can be inferred from the results that the Mo$_2$C/UiO-66 hybrid is a promising candidate as a nonexpensive and active catalyst for overall electrocatalytic water-splitting as the devised catalyst exhibits enhanced kinetics for both OER and HER, a more exposed surface area, faster electron transport, and enhanced diffusion of the electrolyte.

1. INTRODUCTION

Currently, fossil fuels are the main sources for the generation of energy. However, these reserves are rapidly depleting, and their use is also responsible for environmental pollution. With the ever-increasing global energy requirements and the dwindling of fossil fuel reserves as well as the aggravation of environmental concerns, it is urgent and crucial to explore progressively more clean and sustainable alternate energy sources.1–3 Hydrogen as a fuel is a promising energy source with limitless potential as it provides an energy solution that is carbon-free. Hydrogen is a green, power-rich fuel (possessing 120 MJ/kg energy density compared to gasoline, which has 44 MJ/kg) that is nontoxic and sustainable in nature, and its consumption produces clean exhaust products (i.e., water).4–6

The market for hydrogen is continuously increasing across the globe. Hydrogen demand has increased more than three times since 1975, and it keeps growing. Countries that support policies for investment in technologies for clean hydrogen are constantly increasing as well. In addition to being a potential fuel of the future, hydrogen is also being utilized in many industrial practices, e.g., in production of ammonia, crude oil hydrocracking, and methanol manufacture.6

However, hydrogen does not exist independently on earth, and it has to be generated from alternative sources. Presently, the direct source for industrial-scale hydrogen manufacture is fossil fuels. Of the entire world’s supply of hydrogen, over 96% is produced via oil and natural gas steam reforming and coal gasification.9,10 It trounces the intention of not depending on fossil fuel reserves. To get rid of this reliance on fossil fuels, generation of hydrogen must be from abundant and green resources with environmentally benign processes. Record improvements are being made to increase the sustainable hydrogen production capacity.

Disassociation of water into its components is a highly promising process for the production of green hydrogen as water is the most prevalent compound on earth (covering 70% of the earth’s surface). Water-splitting can produce hydrogen with virtually zero environmental impact since water as a feedstock is employed, which can be reprocessed back into nature indefinitely. Oxygen is the byproduct of this process,
and it does not affect the environment negatively and can be exploited for additional applications to increase the economic value of the process. At present, around 4% of the world’s hydrogen is being manufactured by electrolysis due to the extreme energy needed to break down the hydrogen bonding of the water molecule as well as due to the substantial investment. Disassociation of water comprises the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Kinetics for these reactions is sluggish. It is necessary to employ a catalyst to help conquer the powerful chemical bonds in the water molecule so the process can function in a favorable manner. In general, the catalysts that are being employed in electrolysis are noble metal-based (Ir/Ru, Pt, etc.). Some disadvantages of these catalysts are their high cost, sparse reserves, and poor durability (stability and catalyst lifetimes), which constrain the water-splitting process from being employed on a commercial scale.

Thus, inexpensive, abundant, and active non-noble-metal-based catalysts are being explored as potential candidates for efficient water-splitting. Transition-metal dichalcogenides (TMDs), carbides, nitrides, and metal–organic frameworks (MOFs) are being studied extensively for this purpose with promising results as they are easily obtainable and display remarkable stability and activity. Among them, molybdenum carbide (Mo2C) is believed to be one of the best candidates due to its electronic structure, which resembles platinum, remarkable stability, economical price, and catalytic activity. However, its electrocatalytic activity is not comparable to that of Pt-based materials due to its poor conductivity, lack of hierarchical porosity, and slow interfacial reaction kinetics. To achieve enhanced catalytic performance, the most recent and effective practice is to couple two or more functional components of dissimilar catalysts with diverse characteristics to construct a hybrid structure that can overcome the shortcomings of the individual counterparts and create synergistic effects between the various components, making them tempting for practical and commercial-scale applications.

Metal–organic frameworks (MOFs) are fabricated by combining metal centers with organic linkers. Recently, their high surface area has been explored as an active catalyst for H2 production via water-splitting. MOFs possess exceptional physical, spatial, chemical, and electronic adaptability capable of supporting and sustaining water-splitting reactions. MOFs have high porosity (90% free volume), a dynamic structure, design flexibility, an ultrahigh surface area, and a crystalline nature. MOFs also boost an intrinsic property that makes them capable of maintaining their functionality and structural attributes post synthetic alteration. It allows them to be engineered for effective catalysis. However, the performance of MOFs toward OER and HER is poor because of harsh oxidizing conditions at which MOFs are generally unstable.

The first MOF that was employed for OER-based water oxidation was Zr-based MOF (UiO-66) in 2011. The main barrier toward the efficient exploitation of a catalyst is its exposure of active sites to reactants as well as reaction intermediates. This can be solved using MOFs as they have a high surface area. In this regard, Li et al. fabricated CoP/Mo2C/Mo2Co4C and Ni/Ni3P/Mo2C nanoparticles encapsulated in porous graphene shells along with some other compounds from bimetallic MOFs (CoMOMo) and NiMo4Co. It was noted that CoP/Mo2C/Mo2Co4C@C needs overpotentials of 182 and 362 mV at 10 mA/cm2 for HER and OER, respectively. Also, the prepared catalysts possessed decent stability in both basic and acidic electrolytes. Liang et al. designed inexpensive, stable, and highly active bifunctional electrocatalysts (Co@NC@Mo2C complex) via the facile MOF-based approach. This catalyst displayed excellent activity in alkaline media as it presented low overpotentials of 99 and 347 mV for HER and OER, respectively, at the current density of 10 mA/cm2. Chai et al. proposed the synthesis of ultrathin molybdenum carbide nanoparticles implanted uniformly in a hollow N-doped carbon polyhedron by employing the MOF-supported self-sacrificial template approach. The as-prepared catalysts displayed efficient and rapid HER response with nearly 0.0 V onset potential and only requiring an overpotential of 89 mV in 0.5 M H2SO4 and 87 mV in 1.0 M KOH to reach 10 mA/cm2. Ali et al. developed Co nanoparticles embedded in β-Mo2C. Co@β-Mo2C:NC had overpotentials of 188 and 330 mV to reach a current density of 10 mA/cm2 in an alkaline media for HER and OER, respectively. Zhang et al. worked on N-doped and carbon-wrapped Co-Mo2C heterostructures. These were constructed by carbonization of bimetallic Co-Zn MOF for electrolysis of water. The catalysts displayed rapid kinetics and small overpotentials of 92 mV (for HER) and 338 mV (for OER) to attain a current density of 10 mA/cm2 in 1 M KOH electrolyte. It was inferred from the literature that simply depositing MOF on a metal-based catalyst surface could not create an ideal interface. It will only result in poor charge separation and transmittance, so our strategy was to incorporate the two components in one structure so it retains beneficial properties of both Mo2C and MOF. Inspired by the idea of designing the hybrid structures to improve physical and chemical properties that are associated with the synergistic effects, we propose developing a Mo2C/MOF hybrid to significantly improve the catalytic activity of Mo2C nanoparticles toward both HER and OER.

2. RESULTS AND DISCUSSION

2.1. Material Characterization. The X-ray diffraction (XRD) graphs for hybrids MCU-1, MCU-2, MCU-3, pure Mo2C, and pure MOF UiO-66 are shown in Figure 1a–e, respectively. Observed characteristic peaks of the prepared UiO-66 are at 2θ values of 7.3, 8.5, 26, and 44° corresponding to planes (111), (002), (006), and (110) and are similar to those in the literature. Observed characteristic peaks of the prepared Mo2C are at 2θ values of 34.3, 37.9, 39.3, and 52.1° corresponding to planes (110), (002), (101), and (102) and are identical to JCPDS card No. 35-0787 and those in the literature. Positions of peaks observed for the synthesized hybrids MCU-1, MCU-2, and MCU-3 are in agreement with pure compounds employed. It is observed that the characteristic peak of Mo2C is suppressed in hybrids. With the decrease in the Mo2C content, its characteristic peak intensity is also reduced in the hybrid. Mo2C peaks in the range of 40° ≤ 2θ ≤ 44° are significantly shifted toward a higher angle with a slight broadening in the hybrids. This shift in angles can be explained in terms of structural deformation. For the synthesis of hybrids, the prepared pure Mo2C was added in the synthesis of UiO-66 and was incorporated in the interstices of the UiO-66 lattice. Shifting of peaks to a higher 2θ angle and overlapping of peaks can be attributed to the structural changes associated with crystal growth and nucleation. The decrease in intensity and the peak shifting to a higher 2θ angle are indicative of the change in the crystal
parameters such as lattice parameters, crystalline sizes, and d-spacing. The increase in interplanar spacing and particle size along with defect concentration is possibly responsible for the peak shifting. Broader diffraction peaks for hybrids are indicative of the relatively poor crystallinity compared to pure compounds. Average crystallite sizes for the hybrid MCU-2, MCU-1, and MCU-3 using the Scherer formula were calculated to be 207.6 Å, 219.2 Å, and 271.5 Å, respectively.

Scanning electron microscopy (SEM) images for pure Mo2C and UiO-66 are shown in Figure 2a and b, respectively, and their morphology is in accordance with the cited literature. Figure 2c and d shows SEM images for hybrids MCU-1 and MCU-3, respectively. Figure 3 shows SEM images for hybrid MCU-1 at various resolutions. On the synthesis of the hybrid, it is proposed that both components are interconnected together, and hence, no single unique morphology of either compound can be observed. This synthesis process leads to formation of disordered porous structures, and particle aggregation reduces the crystallinity of hybrids. Due to the unique synergistic effects and the high activity of materials, this nanolayered structure offers a rapid current response. Energy-dispersive X-ray (EDX) mapping of hybrid MCU-2 was performed to indicate the homogeneous presence of all of the key elements, i.e., molybdenum, zirconium, carbon, and oxygen, with ratios shown in the inset of Figure 4. It is to be noted that the composition was uniform throughout. The EDX elemental graph provides additional confirmation of the successful formation of UiO-66 and Mo2C hybrids.

The Brunauer–Emmett–Teller (BET) analysis providing the nitrogen adsorption–desorption isotherm of the optimized catalyst MCU-2 is shown in Figure 5a. It can be observed that the catalyst shows a hysteresis loop at high P/P0 with a type IV isotherm (mesoporous 2 nm < pore size < 50 nm). A large, single-point BET surface area of 793.756 m2/g was observed, which is many times greater than the reported Mo2C surface areas of 25.1413 and 23.458 m2/g. Pore size distribution curve for the catalyst MCU-2 obtained through the density functional theory (DFT) method is given in Figure 5b. It further solidifies the claim that the incorporation of MOF with Mo2C nanoparticles enhances the surface area and porosity with an average pore radius of 2.23 nm and an average pore volume of 0.798 cm3/g.

2.2. Electrochemical Measurements. As-synthesized hybrid catalysts were tested for their HER catalytic activity in 1.0 M KOH solution and on a three-electrode assembly of Ag/AgCl as the reference electrode, Pt-wire as the counter electrode, and the desired catalysts coated on nickel foam (NF) as the working electrode. Porous Ni-foam provides mechanical as well as conductive support to the catalysts. Figure 6a shows the linear sweep voltammetry (LSV) plot for
all of the prepared catalysts. LSV plots for the Pt-wire and the bare Ni-foam under the same testing conditions are also presented for comparison purposes as Pt/C is considered to be the strongest catalyst for HER. In 1 M KOH electrolyte solution, the overpotential of Pt/C calculated is 53 mV.\textsuperscript{47,48} It can be inferred from Figure 6a,b that pure Mo\textsubscript{2}C, MCU-1, and MCU-3 showed inferior HER performance with overpotentials of 301.1, 310.3, and 195.4 mV, respectively, at a current density of 10 mA/cm\textsuperscript{2}. In comparison, the Pt-wire (\(\eta_{10} = 74.8\) mV) exhibits the most prominent and the bare NF (\(\eta_{10} = 316.8\) mV) exhibits limited HER activity. The hybrid MCU-2 with a Mo\textsubscript{2}C/MOF ratio of 1:1 shows the maximum HER catalytic activity with an overpotential of 174.1 mV to reach a current density of 10 mA/cm\textsuperscript{2}, revealing the synergistic effects of Mo\textsubscript{2}C and UiO-66. With a small concentration of Mo\textsubscript{2}C in the hybrid, sufficient charge transfer is not achieved until the ratio of Mo\textsubscript{2}C is equal to MOF. Further increasing the Mo\textsubscript{2}C concentration in the hybrid lowers its electrocatalytic activity due to the problems of agglomeration and Mo\textsubscript{2}C blocking and reducing the porous sites of the structure. These results confirmed the successful fabrication of the hybrid composed of Mo\textsubscript{2}C and UiO-66, indicating that the presence of the porous MOF exposes more catalytic sites and allows uniform charge transfer.

Figure 3. SEM images of the catalyst MCU-2 at different magnifications.

Figure 4. EDS spectrum for the hybrid MCU-2.

Figure 5. (a) N\textsubscript{2} absorption and desorption of MCU-2; (b) pore size distribution curve for MCU-2.
distribution of Mo$_2$C for improved electrocatalytic water-splitting. To gain further knowledge about the HER mechanism, the Tafel slopes of all of the as-synthesized catalysts are shown in Figure 6c. The HER rate-limiting step is determined from its Tafel slope, and the smaller Tafel slope depicts a higher HER rate. Tafel slopes are obtained by plotting the overpotential vs log of current density linearly using eq 1:

$$\eta = b \log j + a$$

where $\eta$ is the overpotential,$a = \text{Tafel constant}$,$b = \text{Tafel slope}$,$j = \text{current density}$.

Figure 6c shows the Tafel plots of the catalysts acquired by plotting the overpotential vs log of current density linearly. The benchmark catalyst for HER, Pt/C, shows a Tafel slope of 39 mV/dec. The pure Mo$_2$C showed a Tafel slope of 423 mV/dec, which is the highest due to the high charge transport resistance, while the hybrid MCU-2 demonstrated the smallest Tafel slope of 147 mV/dec, suggesting the fast rate of hydrogen generation. Other hybrids MCU-1 and MCU-3 also displayed smaller Tafel plots compared to the bare Mo$_2$C (196 mV/dec for MCU-1 and 162 mV/dec for MCU-3). These findings prove that 1:1 Mo$_2$C/UiO-66 delivers the maximum yield for HER in the electrochemical process, and it is comparable to some very effective reported HER catalysts. A comparison of some very effective reported Mo$_2$C and MOF-based catalysts for HER activity in the literature has been shown in Table 1.

The catalytic activity for OER of as-synthesized electrocatalysts was also investigated through LSV polarization curves (Figure 7a). To compensate for the effect of oxidation peaks, the overpotential was measured at 20 mA/cm$^2$ for all catalysts. It is observed from Figure 7b that the overpotential needed for MCU-2 to attain the current density of 20 mA/cm$^2$ is around 180 mV and is lower than MCU-1 (200 mV), MCU-3 (370 mV), pure Mo$_2$C (380 mV), and NF (540 mV). The results depict successful incorporation of two entities UiO-66 and Mo$_2$C in the correct proportion for optimal synergistic effects without drawbacks of one overpowering the other. The OER catalytic performance of MCU-2 is comparably less than that of the benchmark OER electrocatalyst, i.e., RuO$_2$@NF, in 1.0 M KOH solution as it requires an overpotential of 283 mV to achieve 10 mA/cm$^2$. The enhanced OER performance of MCU-2 may be because of synergistic effects of Mo and Zr with the porous nature of the MOF structure. The Tafel plot is

Figure 6. (a) HER polarization curves of catalysts MCU-1, MCU-2, MCU-3, pure Mo$_2$C, Pt-mesh, and bare Ni-foam at a scan rate of 10 mV/s in 1.0 M KOH electrolyte. (b) Comparison of the overpotential needed at 10 mA/cm$^2$ by different catalysts for HER. (c) Tafel plots of catalysts MCU-1, MCU-2, MCU-3, and pure Mo$_2$C.

Table 1. Comparative $R_p$, $R_u$, and $C_\text{f}$ Values

| electrocatalyst | $R_p$ ($\Omega$) | $R_u$ ($\Omega$) | $C_\text{f}$ ($\text{F}^{-1}$) |
|----------------|-----------------|-----------------|-----------------|
| Mo$_2$C        | 15.20           | 1.332           | 420             |
| MCU-1          | 30.2            | 1.65            | 0.96            |
| MCU-2          | 13.20           | 1.969           | 0.165           |
| MCU-3          | 31.47           | 2.07            | 0.087           |

The results depict successful incorporation of two entities UiO-66 and Mo$_2$C in the correct proportion for optimal synergistic effects without drawbacks of one overpowering the other. The OER catalytic performance of MCU-2 is comparably less than that of the benchmark OER electrocatalyst, i.e., RuO$_2$@NF, in 1.0 M KOH solution as it requires an overpotential of 283 mV to achieve 10 mA/cm$^2$. The enhanced OER performance of MCU-2 may be because of synergistic effects of Mo and Zr with the porous nature of the MOF structure. The Tafel plot is
an important constraint to estimate the reaction kinetics for OER; as shown in Figure 7c, MCU-2 showed the smallest Tafel slope (134 mV/dec) in comparison with MCU-1 (248 mV/dec), MCU-3 (230 mV/dec), and pure Mo$_2$C (301.2 mV/dec). A comparison of some efficient reported Mo$_2$C- and MOF-based catalysts for OER activity in the literature is shown in Table 2.

To study the correlation between current density and scan rate, cyclic voltammetry (CVs) of hybrid MCU-2 in 1.0 M KOH electrolyte at scan rates ranging between 5 and 150 mV/s are given in Figure 8a. CV curves clearly show well-characterized two redox peaks in the potential region of 0−0.6 V. Higher current densities are attained with an increase in the scan rate because of the reduction in diffusion-layer resistance. The form of the CV curves is left unchanged with the rise in scan rate, implying the cyclic stability and smaller resistance of electrocatalysts. An important parameter to understand the kinetic model of the prepared samples is electrochemical impedance spectroscopy (EIS). The Nyquist plot is constructed between real and imaginary impedance in the region of 0.1 Hz to $20 \times 10^5$ Hz, and the equivalent circuit is shown in the inset of Figure 8b. EIS provides a straight line in the low-frequency domain and a semicircle-shaped curve in the elevated-frequency region. The Nyquist plot with the simple Randles equation gives information regarding the solution-induced resistance at the electrode/electrolyte interface ($R_u$), the polarization resistance ($R_p$), also known as the charge-transfer resistance, and the Faradic capacitance ($C_f$). Low charge-transfer resistance is associated with the small diameter of the semicircle, while the value of solution resistance is accountable for the improved performance of the material.\textsuperscript{56,57}

The small semicircle of MCU-2 depicts the small charge-transfer resistance, which decreases further with an increase in the potential and maximum conductance, which translates to improved catalytic ability (Table 3).

To determine the overall water-splitting potential of the prepared catalyst, a bifunctional device was fashioned with MCU-2 on Ni-foam acting as both the cathode and anode in a two-electrode assembly electrocatalytic cell. Bare Ni-foam was also examined under the same conditions, and a comparison is shown in Figure 9a. A cell voltage of around 1.3 V was required to attain a current density of 10 mA/cm$^2$ (0.01 A/cm$^2$). Catalyst stability is an important constraint when considering commercialization of the electrocatalyst for water-splitting

![Figure 7](https://doi.org/10.1021/acsomega.1c03115)

**Figure 7.** (a) OER polarization plot for catalysts MCU-1, MCU-2, MCU-3, and pure Mo$_2$C at a scan rate of 10 mV/s in 1.0 M KOH electrolyte. (b) Comparison of overpotential needed at 10 mA/cm$^2$ by different catalysts for OER. (c) Tafel plot of catalysts MCU-1, MCU-2, MCU-3, and pure Mo$_2$C.

### Table 2. Catalyst Nomenclature by Ratios

| sl. no | name of catalysts | ratios of Mo$_2$C/ZrCl$_4$ |
|--------|------------------|-----------------------------|
| 1      | MCU-1            | 1:3                         |
| 2      | MCU-2            | 1:1                         |
| 3      | MCU-3            | 3:3                         |

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applications. MCU-2 was also tested for long-term stability (60 h) at 10 mA to obtain the chronopotentiometric curve (Figure 9b). MCU-2 showed a stable behavior, which can be attributed to its structural characteristics. Once the hybrid catalyst was activated, the potential response became constant without any considerable loss in its activity. High stability and lower cell voltage indicate the potential of MCU-2 as an encouraging electrocatalyst with bifunctional characteristics for overall water-splitting in an alkaline environment.

3. CONCLUSIONS

In this research study, pure Mo2C, UiO-66, and Mo2C/UiO-66 hybrids were successfully synthesized by employing the solvothermal method. These catalysts were utilized for HER and OER by electrocatalytic water-splitting. The as-synthesized 50:50% Mo2C/UiO-66 hybrid (MCU-2) had a higher activity for both HER and OER. Moreover, MCU-2 demonstrated high stability for 24 h and around 1000 cycles. This enhanced activity is because of the complementary properties of Mo2C and UiO-66, consequentially increasing the synergistic effects and spatial uniform distribution, as the presence of Mo2C improves the stability and catalytic activity, while the UiO-66 structure provides an increased surface area with better electrical conductivity and charge transmittance during the reaction. This study provides an understanding of designing bifunctional MOF-based catalysts for the overall water-splitting process where each component in the hybrid possesses indispensable functions for the desired application with
improved activity. To explore the potential of MOF-based hybrids further, a deep investigation into the design strategies and reaction mechanism can be done to obtain more improved and active catalysts that can be employed at the commercial scale.

4. EXPERIMENTAL SECTION

4.1. Materials. Reagents and chemicals of analytical grade were used (with no processing or purification) for the synthesis of all of the samples. Chemicals used include ammonium molybdate tetrahydrate (\((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\)), zirconium(IV) chloride (\(\text{ZrCl}_4\)), and poly(vinylidene fluoride) (PVDF)-\((-\text{C}_2\text{H}_2\text{F}_2)_n-\)) from Sigma-Aldrich. Terephthalic acid (\(\text{C}_8\text{H}_6\text{O}_4\)), dimethylformamide (DMF) (\(\text{C}_3\text{H}_7\text{NO}\)), and i-Te were from Merck. Hexamethylenetetramine (\(\text{C}_6\text{H}_{12}\text{N}_4\)) was from Daejung Chemicals. Activated carbon powder was from Duksan Pure Chemicals. Ethanol (\(\text{C}_2\text{H}_5\text{OH}\)) was from BDH, and deionized water was from Vitro diagnostics laboratories.

4.2. Synthesis of \(\text{Mo}_2\text{C}\). Pure molybdenum carbide was synthesized following the procedure reported by Wang et al.\(^{13}\) In the first step, the \(\text{Mo}_2\text{C}\) precursor was prepared by dissolving 2.48 g of ammonium heptamolybdate (AHM) in 25 mL of deionized water followed by addition of 7.1 g of hexamethylenetetramine (HMT) in 25 mL of deionized water with continuous stirring for 2 h at room temperature. The solution was aged for 3 h, and the solvent was evaporated by heating at 80 °C for 24 h to obtain a white solid precursor. The precursor was then introduced to a tube furnace where it was treated at 700 °C under an Ar flow for 2 h. Annealing of the precursor with the above-mentioned conditions led to the formation of the final black powder of molybdenum carbide.

4.3. Synthesis of UiO-66. Zirconium-based MOF, termed UiO-66, was prepared by an acid-promoted solvothermal process reported by Qiu et al.\(^{38}\) with slight modifications for optimized results. Typically, 150 mg of \(\text{ZrCl}_4\) and 115 mg of 1,4-benzenedicarboxylic acid (BDC) were dissolved in 30 mL of DMF solvent; 2 mL of acetic acid was introduced into the solution with constant mixing for 2 h and ultrasonication for 20 min. This solution was then transferred to 100 mL of deionized water followed by addition of 7.1 g of \(\text{TeCl}_2\) in 25 mL of deionized water and aged for 3 h, and the solvent was evaporated by heating at 80 °C for 2 h. Annealing of the mixture of the reaction mixture was then transferred to a tube furnace, where it was treated at 120 °C overnight. Finally, the product was separated by centrifugation and rinsed thrice with DMF and distilled water for half an hour and then by absolute ethanol for 15 min. It was then dried at 60 °C in a drying oven for 2 h. The ink was prepared by mixing 85% of the active catalyst with 5% PVDF (binder), 10% carbon black (conductive additive), and 0.5–1 mL of 1-methyl-2-pyrrolidone (NMP) as the solvent in a sonicator to form a slurry. Ink was then deposited on the NF and dried at 80 °C in an oven overnight. The mass loading of the catalyst achieved was approximately 1.5–2 mg/cm².

4.4. Synthesis of \(\text{Mo}_2\text{C}/\text{UiO-66}\) Hybrids. \(\text{Mo}_2\text{C}\) and MOF hybrids were prepared with different concentrations by a one-pot solvothermal synthesis. \(\text{Mo}_2\text{C}\) and \(\text{ZrCl}_4\) were introduced in various ratios (1–3, 1–1, 3–1) (wt %) to the solution of BDC, DMF, and acetic acid. The solution was stirred for 30 min with sonication mixing for around 4 h for complete inclusion of the reactants. Mixture was placed in a Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. After the completion of the reaction time, the autoclave cooling to room temperature, and the solid product is separated by centrifuging. The product was rinsed thrice with DMF and ethanol to get rid of the residual reactants and dried overnight at 70 °C.

4.5. Electrode Preparation. Electrodes were prepared by depositing the catalyst on pretreated Ni-foam (NF), which acts as a conductive support for our catalyst. The NF substrate (dimension 1 × 1 cm²) was pretreated to clean it from the oxide layer by first sonicating with 2 mL of HCl in 10 mL of distilled water for half an hour and then by absolute ethanol for 15 min. It was then dried at 60 °C in a drying oven for 2 h. The ink was prepared by mixing 85% of the active catalyst with 5% PVDF (binder), 10% carbon black (conductive additive), and 0.5–1 mL of 1-methyl-2-pyrrolidone (NMP) as the solvent in a sonicator to form a slurry. Ink was then deposited on the NF and dried at 80 °C in an oven overnight. The mass loading of the catalyst achieved was approximately 1.5–2 mg/cm².

4.6. Catalyst Characterizations. An X-ray diffractometer (XRD, STOE Germany) was employed to study the compositional analysis and phase purity of the designed catalyst, using 2θ values from 10 to 80° using Cu Kα radiation. Scanning electron microscopy (JEOL instrument JSM-6490A) equipped with an EDX was used to observe and analyze the morphology and structure of the prepared samples. Surface area and pore structure of the optimized catalyst were analyzed by BET (Quantachrome, Virginia), at 200 °C for 6 h.

4.7. Electrochemical Study. Electrocatalytic response of the catalysts was studied on the GaN Potentiostat at room temperature with a three-electrode cell assembly and in 1.0 M KOH solution as an electrolyte. The working electrode was composed of a catalyst deposited on NF, the reference electrode was Ag/AgCl, and the counter electrode was a Pt-wire. For ease, the potential for the reversible hydrogen electrode was used for further calculations, which was obtained by the following equation

\[
E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.059 \text{pH} + E_0^{\circ}\text{Ag}/\text{AgCl}
\]

\[
\text{pH} = 14; E_0^{\circ}\text{Ag}/\text{AgCl} = 0.1976
\]

The linear sweep voltammetry (LSV) technique was applied in the potential range from 0 to 1.5 V at a scan rate of 10 mV/s. Cyclic voltammetry measurements were recorded at different scan rates (10, 20, 50, 100, 150) and reported at 100 mV/s in the specific potential range of 0–0.6 V. Electrochemical
impedance spectroscopy (EIS) was performed at a frequency range of 0.1–1 MHz, by providing an alternating voltage amplitude of 10 mV. Chronopotentiometry was employed to test the stability of the as-prepared electrocatalyst.

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### Notes

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