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Operando Analyses of Highly Enhanced Water Splitting by Electronically Modulated Non-noble Metal Carbides

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Abstract

Designing non-noble metal based electrocatalysts for efficient overall water splitting (OWS) solves a critical bottleneck of sustainable water electrolyzer technology. Here, we elucidate real-time mechanistic insights into the promotional effect of Ni substitution on the bifunctional OWS activity of N-doped graphite carbon (NGC) supported molybdenum and tungsten carbides (Ni-MoC/WC@NGC). Ni substitution yields multi-fold improvement in water splitting activity over the pristine systems that are comparable to commercial Pt/C for HER and better than IrO₂ in case of OER. Ni-MoC@NGC champions in HER activity exhibiting an onset overpotential of 65 mV and current density of 140 mA/cm² at -370 mV (v RHE) in acidic media. Their excellent OWS activity in alkaline media prompted us to construct a H₂O electrolyzer where the bifunctional Ni-MoC@NGC system shows a comparable cell voltage to the PtIrO₂ pair and could split water aided by a 1.5V AAA commercial battery. First principle calculations and in-situ probing of the local Ni and W sites through quick-XAS during electrochemical processes provide valuable insights into how the adsorption energies of intermediates and reaction kinetics are modulated at different catalytic sites with the promotional electronic effect of Ni substitution.

Keywords: Water splitting; alkaline electrolyzer; transition metal carbides; operando XAS analyses

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1. Introduction

The juxtaposing global scenario of increasing energy demands (1.1×10^{21} J/hour by 2050)¹ and incumbent regulations on carbonaceous fossil fuels, triggered by an alarming increase in atmospheric CO₂ level (~410 ppm), calls for urgent scientific breakthroughs in establishing alternative fuel economies.² Hydrogen, owing to its high gravimetric energy density (143 kJ kg⁻¹) and environmentally benign nature, poses as a potential alternative green fuels.³ Electrocatalytic water splitting, empowered by renewable energy sources, is one of the most efficient, and sustainable technologies for pure H₂ generation that can be easily coupled with fuel cell applications.⁴⁻⁶ Thermodynamically uphill processes of hydrogen evolution (HER) at cathode and oxygen evolution (OER) at anode involves overpotentials, which determines the overall cell voltage (E_{cell}) governing an electrolyzer's practical viability.^{7,8} In spite of extensive research explorations over the last decade,⁹⁻¹⁴ both acidic and alkaline water electrolysis, alike, are still most efficiently catalyzed by noble metal based catalysts (Pt for HER and Ir/Ru oxides for OER)^{4,7,15} which are prohibitively expensive and scarce.^{16,17} Thus, new catalyst engineering concepts influencing and progressing the limits of the state-of-the-art is of utmost importance in this regard.

Earth-abundant transition metal (TM) based electrocatalysts (phosphides,¹⁸⁻²¹ carbides,^{10,22-24} nitrides,²⁵⁻²⁷ borides,^{12,28} chalcogenides²⁹⁻³⁵) have strongly emerged as a new class of low-cost and efficient electrocatalysts for HER, OER and water splitting.^{14,31,32,36,37} Among them Mo and W carbides (interstitial compounds)³⁸ stands out owing to their noble metal like electronic structure around Fermi level,³⁹ high electrochemical stability and adaptability to different structural engineering techniques.^{3,6,40} A plethora of interesting approaches⁴¹⁻⁴³ has been undertaken over the last few years to improve the activities of pristine Mo and W carbide which include phase, shape & size modulation,^{3,4,44-47} active site enhancement, interface/strain engineering,^{5,48-50} introducing interacting supports,^{6,51,52} incorporating heteroatoms like N,^{40,53} alloying or doping secondary metals^{43,54} etc. In spite of these efforts, till date, very few reports exist for structurally engineered Mo and W carbides exhibiting highly efficient overall water splitting, with equivalent cathodic and anodic activity.^{3,5,12,40}

To achieve the desired activities it is important to understand the underlying catalytic features governing the descriptors that modulate the electrochemical processes. Optimizing adsorbate-metal interactions, d-band centre tuning, increasing ECSA and chemical state modulation of active centres are among the most important factors that can modulate a catalyst's electrochemical activity.^{32,48,55-62} ECSA and partial oxidation states of active metals, on the other hand, determines the site-density and electron transfer kinetics of an electrocatalyst. To tap into the potential of all these factors, tuning chemical composition and electronic

structures of W and Mo centres by substitution of a secondary TM appears as one of the most efficient and facile approaches.^{14,17,54,60} In this work, we have chosen Ni as the suitable substituent owing to its superior activity for HER/OER in both acidic and alkaline media, valence electron rich surface and adaptability to charge transfer interactions.^{5,60,63-66} The proton adsorption capability and high electrical conductivity of defect enriched N-doped graphitic carbon (NGC)^{6,67,68} prompted us to exploit its potential as a useful support for dispersing and stabilizing the Ni-doped Mo and W carbide nanoparticles (NPs).

Through a one-step in-situ carbonization technique we synthesized Ni substituted WC and MoC nano-systems dispersed on NGC. Both the catalysts (Ni-WC@NGC & Ni-MoC@NGC) exhibit multi-fold improvement in activity in terms of current densities, onset values, Tafel slopes and electron transfer resistances as compared to the undoped carbide catalysts. Synthetic optimization yields Ni-MoC(1:5)@NGC as the best HER electrocatalysts in acidic media with an onset overpotential of 65 mV and current density of 140 mA/cm² at -370 mV (v RHE). Both Mo and W samples show enhanced and durable OER activity in alkaline medium with onsets of 1.5 V (vs. RHE) and current densities as high as 150 mA/cm² at 1.86 V, which is close to state-of-the-art activity as bifunctional OWS catalysts triggered us to construct a low E_{cell} H₂O electrolyzer device. Ni-MoC@NGC exhibits a comparable cell voltage to the PtIrO₂ pair and can split water aided by a 1.5V AAA commercial battery. The electronic and structural roles of Ni in enhancing the catalytic activity have been extensively studied through operando quick X-ray absorption spectroscopic (QXAS) studies and density functional theory (DFT) calculations. In-situ probing of the local Ni and Mo/W sites during different electrochemical processes provides valuable insights into relative mechanisms of HER and OER in different media. These studies elucidate, in real time picture, how the adsorption energies of intermediates and reaction kinetics are modulated at different catalytic sites with the promotional effect of Ni substitution.

2. Results and Discussions

2.1. Synthesis, Structural Analyses and Characterization

The Ni-substituted W/Mo carbide-based hybrid nanocatalysts are synthesized through a facile one-step synthetic procedure following the scheme shown in **Figure 1a**. The precursors, polyoxometalate (H₃PMo₁₂O₄₀/H₃PW₁₂O₄₀), nickel chloride (NiCl₂), and melamine (C₃H₆N₆) are thoroughly mixed at various molar ratios of Mo/W:Ni (5:1, 5:2, 5:3) followed by subsequent ball milling. The ball-milled mixture is vacuum-sealed in quartz tube and pyrolyzed at 900 °C (based on the TGA, **Figure S1**, and suitable temperature profile, **Figure S2**) resulting in the formation of well-dispersed Ni-substituted Mo and W carbide NPs on nitrogen-doped graphitic carbon (Ni-W/MoC@NGC, see synthetic details in ESI for details, **Figure 1b-d**, **S3-S4**, **Figure 2**).

Figure 1. Synthesis and characterization of Ni-WC@NGC & Ni-MoC@NGC: (a) Synthetic scheme for Ni-W/MoC@NGC showing different steps of precursor mixing, carbonization and Ni substitution into W/MoC lattice and N doping in carbon matrix, (b) Comparative PXRD patterns of Ni-WC@NGC & Ni-MoC@NGC, (c) PXRD shift in 100 plane of Ni-MoC having different precursor mole ratios and (d) PXRD shift in 101 plane of Ni-MWC having different precursor mole ratios.

In addition to enabling efficient diffusion of Ni into the metal carbide lattice, ball milling also enhances the microstructural disordering and defects in the graphitic carbon,⁵ as evident from the comparative I_D/I_G ratios (Figure S4-S5). Melamine precursor acts as the reductant, which carbonised the metal-oxy clusters, onto a graphitic carbon matrix, enriched in nitrogen from the melamine molecular unit. Gases like CH_4 , NH_3 generated in-situ from melamine at high temperatures induce a chemical pressure facilitating Ni diffusion and dopes the carbon sheets with nitrogen during graphitisation. The nitrogen defects enhances the electronic properties and conductivity of the graphitic carbon promoting efficient proton adsorption during electrocatalysis.^{53,68,69} The same precursor mixture calcined under H_2/Ar in an open boat, results in additional metallic oxide impurities owing to incomplete carbonization & Ni diffusion. Thus, the use of vacuum-sealed quartz ampules is essential to ensure an oxygen free atmosphere and induction of chemical vapour pressure for Ni diffusion and N-doping. The substituted carbides crystallize in the hexagonal $P6m2$ space group of MoC/WC phase (Figure 1b) with right shift in the diffraction peak positions (Figure 1c-(100) of MoC at 35.7° , 1d-(101) of WC at 48.4°) due to lattice shrinkages on substitution of the smaller Ni ions (Ni^{2+} :69 pm, Mo^{6+} :79 pm and W^{6+} :80 pm) in the carbide lattices.⁷⁰ The absence of additional peaks of metallic Ni or nickel carbide phases implies the substitution of Ni in the carbide lattice. Molar ratio of 5:1 with respect to W:Ni is found to be the optimum, as higher Ni percentages (Ni-WC(2:5) or Ni-WC(3:5)) lead to similar or lesser Ni substitution with excess of metallic Ni phases (Figure S3a, peaks at 44.3° & 51.6°), owing to solid solubility limit. The controlled reactions, devoid of Ni (Ni-WC(0:5) or Ni-MoC(0:5)), yield mixed phases of MoC ($Fm\bar{3}m$) and Mo_2C ($Pbcn$), (Figure S3b) for Mo, while primary phase of WC ($P6m2$) was obtained in the case of W variant. Ni incorporation triggered the formation of the hexagonal phase in both Mo and W systems, through substantial lowering of the

formation energy (values, Table S1). Interestingly, profile fitting (Figure S3c, d), revealed that Ni substitution affected the relative intensities of the (100) (MoC-Structure Factor (SF):31, WC-SF:54) and (101) (MoC-SF:29, WC-SF:50) plane differently in case of Mo and W carbide systems (see ESI for details). In case of MoC, the intensity of (100) plane (consisting of only Mo) at 35.7° was enhanced, while in WC the (101) (having structure factors from both W and C atoms) at 48.4° plane reached a higher intensity than the (100) plane (Figure S3e, f).

Elemental analyses of Ni-Mo/WC@NGC ($\text{X}_5\text{Ni}_1\text{C}@NGC$) was carried out through FESEM-EDS, TEM-EDS and ICP studies (Table S2, S3). From a cumulative elemental analyses, it can be seen that ball milling (BM) enhances the Ni diffusion into the carbide lattice. The average ratio of Ni:Mo/W (1:4.16 for Mo, 1:4.27 for W) for the ball-milled sample was double of that (Ni:Mo/W = 1:9.19 Mo, 1:8.77 W) in the non-ball milled samples (Table S3). TEM images show that the Ni-substituted W/MoC (particle size ~ 10-30 nm) nanoparticles are encapsulated and well-dispersed over the graphitic carbon matrix (Figure 2). The incorporation of Ni in the Mo/W carbide lattice is further confirmed from the elemental mapping on selected particles which showed a uniform mixed distribution of Ni and Mo/W (Figure 2a, b and 2j, k). High resolution TEM (HRTEM) images, show a d-spacing of 0.249 nm corresponding to the 100 plane (Figure 2h) in the Ni-MoC system and 0.28 & 0.25 nm for the Ni-WC corresponding to 001 and 100 facets (Figure 2m), respectively. Selected area electron diffraction (SAED) patterns display the concentric rings of diffractions, characteristic of the low index exposed planes (001, 100, 101) in either systems (Figure 2d, 2n). Elemental line scanning on the particles of Ni-MoC@NGC (Figure 2g) confirms the Ni substitution in the carbide structure. SEM images show the microstructural arrangement where the semi-spherical carbide NPs are found to be grafted on the thicker carbon matrix (Figure S4a, S4b).

Figure 2. TEM analysis of Ni-WC@NGC & Ni-MoC@NGC: (a) & (b) Colour mapping on particles of Ni-MoC@NGC, (c) & (e) Particle distribution in Ni-MoC@NGC, (d) SAED pattern of Ni-MoC@NGC showing presence of corresponding lattice planes, (f) & (g) Line scanning EDS spectra of Ni-MoC@NGC, (h) HR-TEM image Ni-MoC@NGC particle showing the d-spacing corresponding to 100 plane, (i) & (l) Particle distribution in Ni-WC@NGC, (j) & (k) Colour mapping on particles of Ni-WC@NGC, (m) HR-TEM image Ni-WC@NGC particle showing the d-spacing corresponding to 001 plane and (n) SAED pattern of Ni-WC@NGC showing presence of corresponding lattice planes.

XPS studies (Figure S4c, S4d) depicts the electronic effect of Ni substitution on Mo/W, where in addition to the expected Mo/W⁺⁴ peaks, a notable presence of Mo and W⁺⁶ species can be seen. This is attributed to the substitution of Ni, which being a divalent cation induces an increase in the usual oxidation state of Mo/W (+4 in carbides) to +6 in the substituted system. Near surface composition analyses through XPS also prove the elemental presence and electronic nature of C, and N in the nano hybrids (Figure S5a). The peaks centred at 284.6, 285.8, 287, 289.7 eV of the C1s spectra (Figure S5b) correspond to C-C/C=C, C-N, C-O and C=O of the graphitic carbon sheets. The typical presence of pyrrolic (397.5 eV), pyridinic (394.8) and graphitic (401.5 eV) N species in the N 1s spectra (Figure S5c) confirm the doping of N in the carbon matrix.^{71,72} Furthermore, Raman studies manifest the degree of graphitisation in the carbonized nanocomposites with enhanced D and G bands around 1350 and 1598 cm⁻¹ respectively. The I_D/I_G values obtained (Figure S6a, b, see the SI for details) indicate the presence of defects, attributable to N doping in the carbon matrix. This is expected to favours active site accessibility, electrical conductivity and enhanced electrochemical performance in the composites.^{3,6,40}

2.2. Hydrogen Evolution Reaction (HER)

The series of Ni-W/MoC@NGC compounds were investigated for electrochemical HER activity in a conventional three-electrode setup under acidic and basic conditions. Figure 3a shows a comparison of the polarization curves of W/MoC@NGC, Ni-W/MoC@NGC, 20 wt% Pd/C and 20 wt% Pt/C obtained from the iR-corrected linear sweep voltammograms at a scan rate of 5 mV/sec. Multi-fold enhancement in terms of onset potential and current densities can clearly be observed, in the Ni-substituted samples as compared to the undoped carbides. Though Ni samples exhibit similar onset potentials (at 66 mV for Ni-WC@NGC and 69 mV of Ni-MoC@NGC), Ni-MoC@NGC excels in the overall activity, in terms of current density and the reaction kinetics (Figure 3a, Table S4).

The marked decrease in the Tafel slope values (Figure S7a, Table S4) from the undoped carbides to the Ni-substituted ones indicates a clear enhancement in reaction kinetics and mechanism, stemming from a more facile electron and mass transfer process in the modulated catalysts. The Tafel slope values which is an

indicative of the mechanism and the rate determining step (r.d.s.) of HER, show that the Ni-substituted carbides exhibit intermediate Tafel values (between Volmer and Heyrovsky) signifying occurrence of spill over mechanism.¹⁷ Both the Ni-substituted catalysts show highly enhanced (~10 times higher) intrinsic exchange current densities (*j*₀) of 0.32 × 10⁻⁴ A/cm² (Ni-WC@NGC) and 0.56 × 10⁻⁴ A/cm² as compared to the unsubstituted systems (WC@NGC: 0.34 × 10⁻⁵ A/cm² & MoC@NGC: 0.79 × 10⁻⁵ A/cm²).^{15,17} The Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) reveal that the Ni-substituted nano-carbides suffer extremely low charge-transfer resistance (*R*_{CT}, one order less: 117 Ω for Ni-WC@NGC & 78 Ω for Ni-MoC@NGC) (Figure 3b), as compared to the undoped catalysts (1169 for WC@NGC & 530 for MoC@NGC). The decrease in charge-transfer resistance signifies enhancement in electron transfer kinetics during electrocatalysis, arising from Ni-substitution. Ni-MoC@NGC which exhibits quite low Tafel slope value (76 mV/dec) and *R*_{CT} (78 Ω) for HER in acidic media is seen to approach the activity of the state-of-the-art catalysts Pd/C and Pt/C at higher potentials (Figure 3a). Between the unsubstituted and Ni-substituted MoC@NGC catalysts we observe a decrease of ~150 mV in onset, ~5 fold increase in current density (@ -370 mV), ~30 mV/dec decrease in Tafel slope and almost an order decrease in the charge transfer resistance (@ -0.13 V). Thus, all in all it can be concluded that the Ni-substituted carbide catalysts exhibit supreme catalytic activity surpassing most of the earlier reported carbides and non-noble metal catalysts tested under similar conditions (Table S5).

The catalysts are ultrastable under both electrochemical cycling (accelerated durability test, ADT, Figure S7b) and chronoamperometric modes of stability tests (@10 mA/cm² (Figure S7c, d). A marginal increase in activity during the initial 250 cycles (ADT between 0 to -0.33 V vs RHE) (Figure S7b), can be attributed to the leaching induced vacant sites creation, and chemical state optimization of the active centers.⁷³ However, after the marginal dissolution of Ni and W/Mo atom during the initial cycles, the catalysts (Ni-WC@NGC, Ni-MoC@NGC) show high electrochemical durability till 2000 cycles with no further change in the polarization current.

Figure 3. (a) Comparative polarization curves of **Ni-WC@NGC** & **Ni-MoC@NGC** for HER in 0.5M H_2SO_4 under a scan rate of 5 mV/s using SCE as the reference and Pt coil as the counter electrode. (b) Electrochemical Impedance Spectra (EIS) of **Ni-WC@NGC**, **Ni-MoC@NGC** and undoped catalysts showing R_{CT} during HER in 0.5M H_2SO_4 . (c) Comparative polarization curves of **Ni-WC@NGC** & **Ni-MoC@NGC** with Pd/C & Pt/C for HER in 0.5M KOH. (d) EIS spectra of **Ni-WC@NGC**, **Ni-MoC@NGC** and undoped catalysts showing R_{CT} during HER in 0.5 M KOH. (e) Comparative polarization curves of **Ni-WC@NGC**, **Ni-MoC@NGC** and **IrO₂** for electrochemical OER in 0.5M KOH under a scan rate of 5 mV/s using Hg/HgO as the reference and Pt coil as the counter electrode. (f) EIS spectra of **Ni-WC@NGC**, **Ni-MoC@NGC** and **IrO₂** showing R_{CT} during OER in 0.5 M KOH.

The catalysts after electrochemical HER were analysed through XANES, XAFS, TEM-imaging and TEM-EDS studies. The slight decrease in the XANES edge jump at Ni before and after HER (250 cycles) (Figure S7e), indicates a slight decrease in Ni amount as a result of initial electrochemical leaching and activity enhancement. The post-electrochemical comparative elemental and microscopic analyses through TEM (Figure S8) show that the catalysts are structurally and compositionally stable. Electrochemically active surface area (ECSA) is a critical kinetic factor influencing the activity and current densities of a catalyst.¹⁵ To deconvolute the role of ECSA in activity enhancement, double layer capacitances (C_{dl}) of the catalysts are determined (Figure S7f), where the current response is majorly associated with the double-layer charging (Figure S9).¹³ As shown in Figure S7f, the Ni-substituted catalysts (Ni-WC@NGC: 14.9 mF/cm², Ni-MoC@NGC: 21.4 mF/cm²) exhibit larger C_{dl} values than the pristine carbides (WC@NGC: 3 mF/cm², MoC@NGC: 10 mF/cm²) which indicates an increase in ECSA upon Ni-substitution. The activity difference between the Ni-WC@NGC and Ni-MoC@NGC catalysts can be partially attributed to the larger ECSA in case of the latter.

As mentioned earlier, the difference in relative intensities and shifts of the (100) and (101) peaks in PXRD (Figure 1b-d, Sc-d) indicates that Ni is majorly substituting at two different planes in case of the WC and MoC systems. This is further corroborated from the formation energy calculations showing the 100 plane (more exposed than 101) in case of MoC systems to achieve a higher stabilization energy (-3999 Ha, Table S1) upon Ni substitution. Mo ionic radii being slightly lesser than that of W (Lanthanide contraction), may prefer higher d-spacing plane (100) for Ni²⁺ incorporation.

The effect of synthetic conditions on the electrocatalytic activity is analyzed by testing a number of controlled catalysts like Ni-W/MoC(2:5)@NGC, Ni-W/MoC(3:5)@NGC, Ni-W/MoC(1:5)-NBM@NGC (NBM: non-ball milled). The polarization curves shown in Figure S10a, b demonstrate that 5:1 W/Mo:Ni ratio yields the best electrochemical activity among the variants of Ni substitution. From diffraction pattern analyses, it can be concluded that the highest Ni substitution occurs in the case of 5:1 (W/Mo:Ni) sample as higher percentages (5:2 or 5:3) result in elemental Ni impurities (Figure S3a). Presence of excess elemental Ni in hetero-structured form or isolated sites does not really enhance the activity. Milling of the precursors is crucial for

more Ni diffusion into the carbide systems, as reflected in the enhancement of HER activity in Ni-W/MoC(1:5)@NGC as compared to the NBM variant (Figure S10c, d). The electrocatalytic studies on the controlled catalysts revealed three important points: (a) Electronic interaction between Ni & W/Mo centres is the key governing factor for the HER activity, (b) Isolated/electronically non-interacting Ni cannot enhance the activity to a similar extent and (c) HER activity is proportional to the amount of substituted Ni in the carbide lattice.

Subsequently, we investigate the HER activity of the Ni-substituted catalysts in alkaline media of 0.5 M KOH. HER activity across extreme pH ranges from 0.5 M H_2SO_4 to 0.5M KOH is crucial for practical applications, which is rarely exhibited by non-noble metal electrocatalysts. Both Ni-WC@NGC and Ni-MoC@NGC catalysts exhibit excellent and equivalent alkaline HER activities with respective low overpotentials (Figure 3c, Table S5). The catalysts exhibit very low Tafel slope values of 135 mV/dec (Ni-WC@NGC) and 124 mV/dec (Ni-MoC@NGC) (Figure S11a, Table S4) as compared to the reported carbide and non-noble metal based systems (Table S5), indicative of facile reaction kinetics. The current densities (200 mA/cm²) at higher potentials match the activity of state-of-the-art catalyst, 20 wt% Pt/C, and surpass 20 wt% of Pd/C at ~ 60 mA/cm². The catalysts exhibit lower Tafel slope values than that of Pd/C (193 mV/dec) in the alkaline media. Multi-fold enhancement in activity in terms of onset potential (Ni-WC@NGC: 120 mV, Ni-MoC@NGC: 90 mV), Tafel slopes and current densities is observed upon Ni substitution (Table S4). The Ni-substituted catalysts exhibit very low R_{CT} values (Figure 3d, Ni-WC@NGC: 133 Ω & Ni-MoC@NGC: 95 Ω) indicative of facile electron transfer processes during the electrocatalysis. HER activity of most non-Pt catalysts in alkaline media suffers from the sluggish water activation step (usually the r.d.s.) resulting in a more complicated proton adsorption process (Volmer reaction, $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$),^{13,70,74} In case of the pristine W/MoC@NGC for HER in KOH we observe a Tafel slope of 206 mV/dec and 159 mV/dec which confirms that the Volmer step (proton adsorption step) is the r.d.s in these carbide catalysts.^{66,75,76} However, a stark decrease in the Volmer limited Tafel slopes in the substituted catalysts indicates that the water activation step becomes more facile upon Ni substitution. H_2O activation (H-OH bond breaking) in alkaline condition involves adsorption of the H_2O molecule on the active site through the interaction of the O atom with the $\delta(+ve)$ metal ion (in this case

W/Mo) and that of H with the $\delta(-ve)$ C.¹⁷ The breaking of the H-OH bond is facilitated by the induction of a higher partial charge on the W/Mo centres by Ni²⁺ resulting in an improved activity in the substituted nano-catalysts.

The catalysts exhibit highly durable alkaline HER activity under both dynamic potential (5000 cycles ADT, **Figure S11b**) with $\leq 1\%$ degradation in catalytic current densities (after 5000 cycles) and static amperometric conditions (24 hrs, CA) with no significant drop at the operating current density of 20 mA/cm² for 24 hrs (**Figure S11c, d**). The activity and stability of Ni-doped W/MoC@NGC (**Figure S12a, b**) is far better than undoped catalysts (**Figure S12c, d**) after comparing the LSVs of various catalysts at different number of ADT cycles. The Ni-doped catalysts, unlike in the acidic media, do not show any significant improvement in the polarization curves during initial cycling (**S12e**), as negligible dissolution of Ni is observed in the alkaline electrolyte, from the edge jump in Ni XANES spectra before and after electrochemistry (**Figure S12f**). The similarity in Ni-WC@NGC and Ni-MoC@NGC catalysts' activity in alkaline media can be attributed to the more active role of 101 plane, for HER in KOH owing to its uniform distribution of metal and carbon atoms.

2.3. Oxygen Evolution Reaction (OER)

Figure 3e depicts the OER polarization curves of the substituted catalysts in 0.5 M KOH in comparison to the benchmark catalyst IrO₂. Both Ni-WC@NGC and Ni-MoC@NGC exhibit excellent activities for electrochemical OER with onset potentials of 1.45 V (vs. RHE) and overpotentials of 310 mV, 340 mV, 410 mV and 520 mV at 10, 20, 50 and 100 mA/cm² respectively. The overpotentials obtained for IrO₂ under similar conditions are 380 mV (η_{10}), 460 mV (η_{20}) and 690 mV (η_{50}). The Tafel slopes of Ni-WC@NGC & Ni-MoC@NGC are 57 mV/dec & 60 mV/dec respectively, which are substantially less than that of IrO₂ (75 mV/dec) (**Figure S13a**). The R_{CT} values (Ni-WC: 71 Ω ,

Ni-MoC: 60 Ω) measured at 1.6 V (vs. RHE, ~ 20 mA/cm²) decreases by $\sim$ one-third from IrO₂ (188 Ω) suggesting a faster electron transfer process for hydroxyl anion oxidation in (**Figure 3f**). Ni-MoC@NGC exhibited superior electrocatalytic OER activity as compared to many of the recently reported OER catalysts, operating under similar electrochemical conditions (**Table S6**). Both the compounds showed robust OER stability under dynamic potential cycling (1.3 V to 1.7 V vs RHE), with no degradation in activity after 1000 cycles of ADT as shown in **Figure S13b, c**. Ni is known to be very active during OER,⁷⁷ and thus unlike in HER, is expected to participate as the active centre along with the W/Mo sites. The oxidized Ni atoms forms Ni-(oxy)hydroxide species which is believed to be the actual catalytic centre for OER.^{17,77,78} This can be proved from the comparison of XANES spectra during and after electrochemistry (see the mechanism section), which shows a pronounced increase in white line intensity associated with the operando oxidation of Ni sites to the Ni-(oxy)hydroxide species. The identification of the Ni-OOH phase from PXRD is tricky due to substantially low Ni content and its low crystallinity owing to fast in-situ formation.¹⁷

2.4. Overall water splitting

To investigate their potential as bifunctional OWS catalysts, commercial and customized GCE was used in a two electrode setup (**Figure 4a, inset**). The OWS studies were done in 0.5 M KOH at current densities of 7, 10, 25, 50, 75, 100 mA/cm². The overall cell potentials (E_{cell}) obtained experimentally at various current densities under the two-electrode setup, are almost equal to the calculated E_{cell} as the sum of the cathodic and anodic potentials obtained from the HER/OER polarization curves (**Figure 4b-c, Table S7**). The E_{cell} at onset of water splitting, depicted as a hump in the upward I-V curve in **Figure 4a**, was found to be 1.34 V for Ni-MoC@NGC and 1.4 V for Ni-WC@NGC, which are very close to the thermodynamic potential (1.23 V) required for water splitting.

Figure 4. Overall water splitting activity of Ni-WC@NGC & Ni-MoC@NGC in 0.5 M KOH: (a) Comparative overall water splitting activity and stability of Ni-WC@NGC & Ni-MoC@NGC electrolyzers @10mA/cm² powered by a Keithly Source Meter. The comparison of overall cell potentials obtained experimentally at various current densities under the two electrode setup with the calculated E_{cell} as the sum of the cathodic and anodic potentials at those current densities during individual HER/OER activity in 0.5 M KOH for (b) Ni-MoC@NGC and (c) Ni-WC@NGC. (d) The evolution of H₂ and O₂ gas bubbles at the cathode and anode (single chamber cell, two electrode setup) respectively aided by a 1.5 V AAA commercial battery, after 30 sec of voltage application.

The cell voltages @10 mA/cm² are obtained to be 1.75 V & 1.8 V for the Ni-MoC@NGC and Ni-WC@NGC electrolyzers respectively, which are very close to the experimental E_{cell} value (1.68 V) observed for the combined state-of-the-art catalysts (Pt/C||IrO₂) system, with 20% Pt/C as the cathode and IrO₂ as the anode. Interestingly, the lowest cell potential of 1.60 V is exhibited by 20% Pt/C as the both cathodic and anodic catalyst. Furthermore, controlled experiments using different combinations of cathode and anode (**Table S4**) reveal that the HER in alkaline media is the limiting faradaic process for both the catalysts, as using [Pt/C||Ni-MoC or Ni-WC] we can easily achieve an E_{cell} of 1.6 V (**Table S7**). This highlights the excellent OER activity of the substituted catalysts under total water splitting conditions. Interestingly, for Ni-MoC||Pt/C electrolyzer, the obtained E_{cell} is 2.06 V whereas, that for Ni-WC||Pt/C system is 2.15 V which indicate that both HER and OER are getting limited by Ni-MoC@NGC/Ni-WC@NGC at the cathode and Pt/C at the anode respectively. Pt-wire||Pt-wire coupled electrolyzer requires a cell potential of 2.1 V to reach the same H₂O splitting current density of 10 mA/cm². The durability of the Ni substituted WC@NGC and MoC@NGC catalysts were tested under the overall water splitting conditions for 2 hours, where both the catalysts exhibited a constant potential with negligible increase in E_{cell} . The Faradaic efficiencies (FE) for HER and OER of the Ni-MoC@NGC catalyst in the overall water splitting mode were obtained as 100% using a customized cell (**Figure S14a and Video S1**).

Finally to explore the practical applicability of the bifunctional Ni-MoC@NGC catalyst, a commercial 1.5 V AAA battery was used to split H₂O in 0.5 M KOH. **Figure 4d, S14b and and Video S2** show the simultaneous and continuous hydrogen and oxygen evolution at the cathode and anode respectively in the Ni-MoC@NGC||Ni-MoC@NGC electrolyzer powered by a 1.5 V commercial battery. Thus, the combined OWS studies on the Ni-substituted carbides demonstrate their tremendous potential for practical OWS applications. They can be further used as a case study for related non-noble metal systems depicting high electrocatalytic enhancement upon promotional secondary TM substitution.

2.5. Mechanistic Analyses

The electronic effect of Ni substitution and mechanistic understanding of activity enhancement is elucidated through density functional theory (DFT) analyses, which is corroborated by a series of systematic ex-situ (XPS, PXRD, discussed in earlier section) and in-situ XANES studies. HBE (hydrogen binding

energy) was computationally evaluated through d-band centre and H-adsorption energy calculations (or Free Energy of Hydrogen adsorption, ΔG_{Hads}) using first-principles theoretical analysis. Ni substitution at M sites in the (100) and (101) surfaces of MC (M = Mo/W) stabilizes the system. Gibbs free-energies of H-adsorption (ΔG_{H}) on Ni-substituted WC (100) and MoC (101) surfaces are close to optimum, $\Delta G_{\text{H}} \sim -0.3$ eV and -0.4 eV, respectively. Reduction in work function and enhanced activity of MC upon Ni substitution leads to facile evolution of H₂. The hydrogen evolution potential is close to Fermi energy of Ni substituted (100) and (101) surfaces of MC, corroborating their viability as electrocatalysts for HER. These results are in good agreement with experiments revealing multi-fold enhancement in onset potential and current densities upon Ni substitution. To assess feasibility of Ni substitution, we modelled a 3x3 supercell of (100) surfaces and a 3x2 supercell of (101) surfaces of WC and MoC, substituting Ni atoms at the surface and in bulk like layers (**Figure S15, S16**), at the 1a site in M₅₄C₅₄ and M₃₂C₃₂ (M = W/Mo) respectively, and estimated formation energies (See ESI for details). As is evident from **Table S9**, Ni substitution at M sites (1a Wyckoff site) of both (100) and (101) surfaces of MC is energetically favourable, and its stability improves with concentration. To test the catalytic activity of surfaces of pristine and Ni substituted MC (M = W/Mo), we have simulated adsorption of H-atom at various surface sites (**Figure S15, S16**) and determined the strength of its interaction with M_{1-x}Ni_xC is determined (See ESI for details). We have estimated the Gibbs free energy of H adsorption (ΔG_{H}), a descriptor of catalytic activity of surface towards HER (See ESI for details).⁷⁹

Interaction of H with surface having vanishingly small ΔG_{H} points to optimal catalytic activity of the surface. Our simulations show that interaction of adsorbate (H-atom) with (100) and (101) surfaces of pristine MC (**Figure S17**) is relatively strong. For Ni-W/Mo(1:10) substituted MC, we find a slight reduction in activity of the catalyst towards HER. However the Ni-W/Mo(1:5) substituted MC surfaces exhibit a nearly optimum interaction with hydrogen. Out of the surfaces considered here, Ni-W/Mo(1:5) substituted WC (100) and MoC (101) surfaces exhibit most optimal interaction of H-atom with, $\Delta G_{\text{H}} \sim -0.3$ eV and -0.4 eV respectively. Chemical nature of H interaction with surfaces has been uncovered using projected density of states (PDOS) (**Figures 5 and S18**).

Figure 5. Projected density of states (PDOS) of structures with H-adsorbed on pristine (top) and Ni-Mo/WC(1:5) substituted surfaces (bottom) of (a) MoC (100), (b) MoC (101), (c) WC (100) and (d) WC (101) surfaces. Dashed black lines represent the Fermi level (E_{F}). PDOS (zoomed out) including all the orbitals is shown in **Figure S18**.

For pristine MoC (100) surface, the adsorbate orbital is degenerate (**Figure 5a**), partially occupied and has energy just below the Fermi level (E_F). The broad and split peak associated with HOAO shows a covalent interaction between H and the surface. PDOS of H-atom adsorbed on pristine MoC (101) surface exhibits a sharp HOAO peak at energy below E_F (**Figure 5b**) denoting more ionic nature of its interaction with the surface involving charge transfer. The HOAO of H-atom adsorbed on Ni-MoC(1:5) (100) and (101) surfaces is deeper in energy than that on pristine surfaces (**Figure 5a, 5b**) showing that H-atom interacts more weakly with the Ni-substituted surfaces. HOAO of H adsorbed on pristine WC (100)/(101) surfaces occurs at energy just below E_F and is partially occupied being degenerate with the W-6s and C-2s orbitals of the catalyst (**Figure 5c, 5d**). As a result, it resonates and facilitates charge transfer from the catalysts' surfaces. H-atom adsorbed on Ni-WC(1:5) (100) exhibits a much broader HOAO peak (**Figure 5c**), while the HOAO peak of H adsorbed on Ni-WC(1:5) (101) lies much lower in energy (**Figure 5c, 5d**), as expected. We estimated work functions (ϕ), a descriptor relevant to catalytic activity of metals towards water reduction reaction,⁸⁰ of the pristine, Ni-Mo/WC(1:5) substituted (100) and (101) surfaces using the following relation:

$$\phi = V_{\text{vac}} - E_F$$

where, V_{vac} is the potential energy in vacuum estimated from coarse-grained planar average of electrostatic potential. Water reduction potential is -4.44 V with respect to vacuum. As evident in **Table S10**, the work functions of WC and MoC surfaces correspond to E_F much below the hydrogen evolution potential. Ni substitution results in bringing shift in E_F closer to the HER potential, showing their viability as electrocatalysts. In summary, Ni-substitution in MCs permits engineering of Fermi surface/energy to weaken their interaction with H.

When Ni in +2 oxidation state substitutes W or Mo (in +4 oxidation state) in the carbide lattice,⁸¹ an incumbent need to maintain the charge balance can trigger the Mo and W to attain a higher partial oxidation state, as observed from the XPS (**Figure S4a, b, S4b**) and XANES spectra (**Figure S19a-b**). XANES measurements at the Ni (K-edge, 8.33 keV), Mo (K-edge, 19.99 keV) and W (L_{III} edge, 10.207 keV) edges (**Figure S19a, S19b, and Figure 6**) show a prominent increase in the white line intensity of the Mo/W centres upon Ni substitution (**Figure S19a, S19b**) which is indicative of the increase in unoccupied states of the d-orbitals.^{43,82} Interestingly, the Mo edge shows the appearance of an edge peak (**Figure S19b**), corresponding to an $1s \rightarrow 4p$ transition, presumably arising from a breaking in symmetry around the local coordination of Mo centres upon Ni substitution. The possibility of charge transfer between the

electronically linked Ni & W/Mo ions is expected to optimize the electrochemical adsorption desorption processes resulting in enhanced electrocatalytic activity.

To understand the mechanistic effect of Ni induced electronic modulation of W and Mo centres on the real-time electrocatalytic activity, operando quick-EXAFS measurements are done in a customized in-situ setup as shown in **Figure S20**. In the unsubstituted WC, a gradual increase in white line intensity in the normalized W-edge XANES spectra is observed during electrochemistry and cycling (**Figure 6a**). This suggests that during HER, the active site, W, has to attain a higher oxidation state for the electron transfer process of proton reduction which facilitates the electron transfer process from the electrode surface to the adsorbed H atom. Since in case of Ni-substituted WC, the W sites already exists at a partially higher oxidation state, the increase in white line intensity during electrochemistry is much lower (0.15 compared to 0.23 in WC@NGC) (**Figure 6b**), thereby allowing a much faster and enhanced electron transfer kinetics. Furthermore, during electrochemistry, the existence of a clear charge transfer process from W to Ni is evident from the corresponding decrease in white line intensity in the Ni edge (**Figure 6c**). This further facilitates the partial oxidation of W centre resulting in a more facile electron transfer process (**Figure S21**). As expected, W centres in WC@NGC and Ni-WC@NGC exhibit a contrasting variation in their chemical states after the 1hr-CA at the negative potentials. **Figure 6a and 6b** shows that after 1hr-CA, W in case of the pristine WC suffers a substantial decrease in the white line intensity, while that in case of Ni-substituted system remains stabilised at the higher oxidation state. This proves, beyond doubt, that the in-situ charge transfer interaction between Ni and W, helps the active W centre to achieve and maintain the desirable unfilled d-states, leading to a facile and stable electron transfer process during HER. The normalized in-situ XANES spectra of the Ni-WC@NGC catalyst during HER in basic media is shown in **Figure 6d**. The W-edge experiences an increase in the white line intensity on exposure to the 0.5 M KOH solution, which results from a partial surface oxidation of the WC by the action of hydroxyl anions. The increase in white line intensity during further HER process is less pronounced than that in acidic media which can be attributed to two reasons. Firstly, in basic media the extent of activity is somewhat hindered (at the same potential ~ -0.45 V vs RHE) by the sluggish water activation kinetics leading to a lower current density. Secondly, the adsorbed species in alkaline media happens to be H-OH*, in contrast to the H* in acid, where $\delta(-ve)$ O atom is expected to bind to the metallic W site. The proton reduction after water activation thus, can be presumed to occur on the C site, or from a spilled over metallic site.

Figure 6. In-situ XANES studies at (a) W edges of WC@NGC during HER in 0.5M H₂SO₄, (b) W edges of Ni-WC@NGC during HER in 0.5M H₂SO₄, (c) Ni edges of Ni-WC@NGC during HER in 0.5M H₂SO₄, (d) W edges of Ni-WC@NGC during HER in 0.5M KOH, (e) W edges of Ni-WC@NGC during OER in 0.5M KOH and (f) Ni edges of Ni-WC@NGC during OER in 0.5M KOH.

This suffices a moderate increase in W oxidation state during alkaline HER. The slight increase in W oxidation state is facilitated by a charge transfer process from W to Ni, like in the previous case, which was reflected in the decrease in white line intensity of Ni edge (Figure S19c, d).

Oxygen evolution in alkaline media occurs at a much higher potential, where the oxidation of the W and Ni centres becomes inevitable under constant operations. Thus the normalized XANES spectra for both W and Ni centres after ADT and CA exhibits a high increase in the white line intensities, as shown in Figure 6e, f. This can also be explained from the Pourbaix diagram of the W and Ni species which predicts the existence of higher oxidation state of the elements at the corresponding pH (13-14) and potential ranges (~ 0.6 to 1 V vs RHE).⁸³ Ni is speculated to play a role, alongside W, as an active centre in OER through the formation of the well-known Ni-OOH species in alkaline media as evident from the change in post edge XAS spectra of the Ni-edge during OER (Figure S21).

3. Concluding Remarks

In summary, we have designed and presented two nanocomposites of hexagonal Ni-W/MoC carbide nanoparticles grafted on NGC support, synthesized through a facile one-step in-situ carburization technique. Both the nano-hybrids performed excellently as cheap, highly efficient and stable electrocatalysts for hydrogen & oxygen evolution and overall water splitting. The superior activity of Ni-MoC@NGC for HER, OER and overall water splitting surpasses most of the reported carbide or non-noble metal systems, which is further showcased in the 1.5 V battery aided OWS activity. The Ni induced modulation of carbide electronic structure was proved through various techniques like XPS, XAS and DFT calculations. The colossal enhancement in activity is shown to stem from the multifunctional role of the Ni substituent, which on one hand enhances the kinetic factors like ECSA, and on the other, controls the thermodynamic aspects like intermediate adsorption energies, oxidation state modulation of the active centres and electronic DOS. Real time mechanistic analyses through operando XAS studies reveals that the synergistic electronic interactions through in-situ charge transfer between Ni and active centres promotes the HER kinetics. During OER Ni was found to play an active role in catalytic enhancement through the formation of Ni-oxyhydroxide species. The new mechanistic insights elucidated in this work will help in re-understanding the concepts of substituent induced synergistic enhancement of water splitting activity in a wide variety of electrocatalysts.

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Figures

Figure 1

Synthesis and characterization of Ni-WC@NGC & Ni-MoC@NGC: (a) Synthetic scheme for Ni-W/MoC@NGC showing different steps of precursor mixing, carbonization and Ni substitution into W/MoC lattice and N doping in carbon matrix, (b) Comparative PXRD patterns of Ni-WC@NGC & Ni-MoC@NGC, (c) PXRD shift in 100 plane of Ni-MoC having different precursor mole ratios and (d) PXRD shift in 101 plane of Ni-MWC having different precursor mole ratios.

Figure 2

TEM analysis of Ni-WC@NGC & Ni-MoC@NGC: (a) & (b) Colour mapping on particles of Ni-MoC@NGC, (c) & (e) Particle distribution in Ni-MoC@NGC, (d) SAED pattern of Ni-MoC@NGC showing presence of corresponding lattice planes, (f) & (g) Line scanning EDS spectra of Ni-MoC@NGC, (h) HR-TEM image Ni-MoC@NGC particle showing the d-spacing corresponding to 100 plane, (i) & (l) Particle distribution in Ni-WC@NGC, (j) & (k) Colour mapping on particles of Ni-WC@NGC, (m) HR-TEM image Ni-WC@NGC particle showing the d-spacing corresponding to 001 plane and (n) SAED pattern of Ni-WC@NGC showing presence of corresponding lattice planes.

Figure 3

(a) Comparative polarization curves of Ni-WC@NGC & Ni-MoC@NGC for HER in 0.5M H₂SO₄ under a scan rate of 5 mV/s using SCE as the reference and Pt coil as the counter electrode. (b) Electrochemical Impedance Spectra (EIS) of Ni-WC@NGC, Ni-MoC@NGC and undoped catalysts showing RCT during HER in 0.5M H₂SO₄. (c) Comparative polarization curves of Ni-WC@NGC & Ni-MoC@NGC with Pd/C & Pt/C for HER in 0.5M KOH. (d) EIS spectra of Ni-WC@NGC, Ni-MoC@NGC and undoped catalysts showing RCT during HER in 0.5 M KOH. (e) Comparative polarization curves of Ni-WC@NGC, Ni-MoC@NGC and IrO₂ for electrochemical OER in 0.5M KOH under a scan rate of 5 mV/s using Hg/HgO as the reference and Pt coil as the counter electrode. (f) EIS spectra of Ni-WC@NGC, Ni-MoC@NGC and IrO₂ showing RCT during OER in 0.5 M KOH.

Figure 4

Overall water splitting activity of Ni-WC@NGC & Ni-MoC@NGC in 0.5 M KOH: (a) Comparative overall water splitting activity and stability of Ni-WC@NGC & Ni-MoC@NGC electrolyzers @10mA/cm² powered by a Keithly Source Meter. The comparison of overall cell potentials obtained experimentally at various current densities under the two electrode setup with the calculated E_{cell} as the sum of the cathodic and anodic potentials at those current densities during individual HER/OER activity in 0.5 M KOH for (b) Ni-MoC@NGC and (c) Ni-WC@NGC. (d) The evolution of H₂ and O₂ gas bubbles at the cathode and anode (single chamber cell, two electrode setup) respectively aided by a 1.5 V AAA commercial battery, after 30 sec of voltage application.

Figure 5

Projected density of states (PDOS) of structures with H-adsorbed on pristine (top) and Ni-Mo/WC(1:5) substituted surfaces (bottom) of (a) MoC (100), (b) MoC (101), (c) WC (100) and (d) WC (101) surfaces. Dashed black lines represent the Fermi level (E_F). PDOS (zoomed out) including all the orbitals is shown in Figure S18.

Figure 6

In-situ XANES studies at (a) W edges of WC@NGC during HER in 0.5M H₂SO₄, (b) W edges of Ni-WC@NGC during HER in 0.5M H₂SO₄, (c) Ni edges of Ni-WC@NGC during HER in 0.5M H₂SO₄, (d) W edges of Ni-WC@NGC during HER in 0.5M KOH, (e) W edges of Ni-WC@NGC during OER in 0.5M KOH and (f) Ni edges of Ni-WC@NGC during OER in 0.5M KOH.

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