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Supplementary Information

Exploring Structural and Electronic Properties of Transition Metal carbides (T = Ti, V, Mo, & W) as efficient catalysts for overall water splitting with DFT study

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Note S1. Experimental section

Characterizations

The X-ray diffraction (XRD) pattern of all the samples were recorded in the 20 range of 5-100° using a Rigaku X-ray diffractometer (D/MAZX 2500V/PC, Japan) with Cu Ka radiation (0.154 nm). Raman spectroscopy (DXR Raman spectrometer, Thermo scientific) was used to analyze the Raman shift and symmetry variations. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250 Xi, Thermo Fished Scientific, USA) using Al Ka X-ray radiation (hv = 1486.6 eV) was used to determine the oxidation states of the constituent elements. The morphologies of the as-synthesized catalyst surfaces were observed through a field emission scanning electron microscope (JEOL JSM-6500F, Japan) and a high-resolution transmission electron microscope (JEOL JEM-2100F, Japan). The surface analyses of the samples were performed on a Thermo Fischer Scientific ESCALAB 250 Xi (USA) using a monochromatic Al-ka as a radiation source (1486.6 eV). The nitrogen adsorption-desorption isotherms were recorded at 77 K using a Quantachrome Quadrasorb SI automated surface area and pore size analyzer to determine the surface area of the as-synthesized catalysts.

Electrocatalytic measurements

All electrochemical measurements were carried out using a three-electrode system. Hg/HgO electrode with 1.0 M NaOH solution was used as reference electrode, a graphite rod was used as counter electrode and the 1×1 cm² nickel foam drop-casted with the individual carbides was used as the working electrode. The catalysts were dispersed in absolute EtOH (1 mg·mL⁻¹) and 4 µL of the dispersion was deposited on the nickel foam surface. The 5% nafion in isopropyl alcohol was used as binder. The HER and OER were examined through monitoring the linear sweep voltammetry (LSV) scan within a range of $0V \sim -0.6$ V and 0 V to 1.8 V with respect to RHE at a rate of 10 mV·s⁻¹. The electrochemical impedance spectroscopy (EIS) studies were carried out at a frequency range of 100 kHz and 1 Hz. The electrocatalytic process was carried out in 1.0 M KOH electrolyte. The references electrode potentials were converted in reversible hydrogen electrode (RHE) scale though the following expression,

$$E_{RHE} = E_{Hg/Hg0} + E_{Hg/Hg0}^{0} + 0.059 \times pH$$
(S1)

where, E_{RHE} is the converted potential. $E_{Hg/Hg0}$ and $E_{Hg/Hg0}^{0}$ are the measured potential at reference electrode and standard redox potentials of Hg/HgO electrode, respectively. Hg/HgO electrode was calibrated to obtain the potential of 0.927 V in 1.0 M KOH. The overpotentials (η) were calculated with respect to the RHE using the following expression.

$$\eta = E_{RHE} - E_{theo}^{0} (V)$$
 (S2)

For HER and OER, the E_{theo}^{0} values are and 1.23 V respectively. The plot of η vs. log J (J = current density) represents the Tafel plot. The Tafel equation can be

The plot of η vs. (0.9) (f = current density) represents the Tatel plot. The Tatel equation can be represented as,

$$\eta = b \log J + a \tag{S3}$$

where the slope $(^{b})$ is the Tafel slope that can be obtained by fitting the linear region of the experimental data on eq. (S3). Extrapolation of the as-obtained slope would intersect to the $\eta = 0$ axis to provide the value of exchange current, J_0 . The ECSA of a catalyst was then calculated by using the formula,

$$ECSA = \frac{C_{dl}}{C_s}.$$
 (S4)

where C_{dl} can be calculated from the slope of the relative current density $\left(\Delta J = \frac{J_a - J_c}{2}\right)$ vs. root of scan rate $(v^{\frac{1}{2}})$ equation over the non-faradaic region during scanning at scan rates within 20-100 mV·s⁻¹. The value of C_s specific capacitance of the catalyst per unit area under the same condition was considered to 0.035 mF·cm⁻² under experimental conditions.

The catalytic activity was further confirmed through calculation of turnover frequency (TOF) using the following equation ¹,

$$TOF = \frac{J \times A}{n \times F \times q} \tag{S5}$$

where J is the current density at a certain overpotential (for HER 200 mV and for OER 400 mV was used), A is the geometric surface area of the electrode (1.0 cm²), F is Faraday constant (96,500 C·mol⁻¹), and q is the number of catalytic active sites.

The CV and LSV curves were obtained at a scan rate of 5 mV·s⁻¹ with in the potential window of -0.6 to 2.0 V (CV), -0.6 to 0 V (HER) and 0 to 2.0 V (OER) and the efficiency were calculated following the equations that includes theoretical Gibbs free energy as a function of temperature, 2 ,

$$\eta_{Faradaic} = \frac{1 \cdot 23 V}{E_{cell}} \quad @ 25^{\circ}C \dots (S6)$$

ORR was measured at a potential window of 1.0 to 0.2 V with 5 mV·s⁻¹ scan rate at different rotating speeds. The numbers of electrons transferred (n) during ORR was calculated by the following Koutecky-Levich equation at various electrode potentials based on the different rotating speeds,

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{J_k} + \frac{1}{\frac{1}{B\omega}}$$

$$B = 0.62nFC_0 D_0^{\frac{2}{3}} v^{-\frac{1}{6}}$$
(S7)

where J is the measured current density, J_k and J_L are the kinetic and diffusion-limiting current densities, ω is the angular velocity, n is transferred electron number, F is the Faraday constant (96485 C· mol⁻¹), C₀ is the bulk concentration of O₂ (1.2×10⁻⁶ mol·cm⁻³ for 0.1 M KOH), D₀ is the diffusion coefficient of O₂ (1.9×10⁻⁵ cm²·s⁻¹ in 0.1 M KOH), and v is the kinematic viscosity of the electrolyte (0.01 cm²·s⁻¹ in 0.1 M KOH). For the RRDE test, a GC disk (0.2475 cm²) surrounded by a Pt ring (0.1861 cm²) was used. The current was collected in O₂-saturated 0.1 M KOH from GC disk and Pt ring, respectively.

Computational details

All the DFT calculations were completed using Vienna ab initio simulation package (VASP)^{3,4}. We utilized the generalized gradient approximation (GGA)-Perdew-Burke-Ernzerhof (PBE)⁵ and the projector augmented wave (PAW) method with an energy cutoff of 520 (400) eV for bulk (slab) structures.⁶ A Γ -centered fine k-spacing of 0.02 (0.03) $\times 2\pi/\text{\AA}$ was used for bulk (slab) calculations.⁷ All atoms in bulk (slab) geometry were relaxed until the net forces on each atom reached < 0.001 (0.02) eV Å⁻¹. The self-consistent-field electronic energies were converged to a precision of $1 \times 10^{-8} (1 \times 10^{-4})$ eV for bulk (slab). The optimized lattice constants, which are a/b/c (a/b/c) = 4.74/6.06/5.23 (4.74/5.22/6.09) Å for Mo₂C (W₂C), were found to be consistent with our experimentally observed lattice parameters with the error of less than 0.5% for each dimension for both the compounds. The experimentally observed (200) surface in this study was used to cleave the surface for the systems used in this study. The DFT-D3 type Van der Waals dispersion correction and dipole corrections were included for all the slab geometries optimization ⁸. A total of eleven alternative metal-carbon layers were used for the computation, with the bottom six fixed layers. A vacuum of 15 Å was used for the slab. The structural models for Mo₂C (200) and W₂C (200) with different adsorbates were already displayed in Fig. 1 (inset). The (200) surface for both the systems was stabilized by decorating the surface with oxygen monolayer.⁹ Crystal structure was visualized using VESTA software.10

Note S2. Raman peak fitting

Combination of Breit-Wigner-Fano (BWF) profile along with Lorentzian peak fitting is used for all TMC's where the BWF line shape, which arises from the coupling of a discrete mode to continuum is addressed through:

$$I(w) = \frac{I_0 [1 + 2(\omega - \omega_0)/Q\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2}$$

Here I_0 is peak intensity at the peak position ω_0 , Γ is full width half maximum (FWHM) and Q^{-1} is BWF coupling coefficient. Whereas the Lorentzian shape is analyzed when $Q^{-1} \rightarrow 0$. A positive or a negative sign of Q gives the relative position of the observed symmetry. The

maximum of a BWF peak is not at ω_0 as the primary peak profile is asymmetric which laterally shifts according to

$$\omega_{max} = \omega_0 + \frac{\Gamma}{2.Q}$$

As Q<0 all G peaks will be shifted towards lower ω although this effect is larger when FWHM is large especially at the disordered carbon atoms.

Note S3. XPS depth profiling

Where the metal salts initially get dissociated and then reduced into their zero oxidation states through solvent mediated reduction process in EG followed by the nucleation and aggregation of particles. The oleylamine present in the reaction medium is a good stabilizing agent, which would get attached easily to the metal surface and create a carbon layer within the atomic space of the metal aggregate¹¹ which would lead to the M-C bond formation where C would have higher sp³ character. In the next step while the as-obtained particles are being calcinated at higher temperature at inert condition, the carbon atoms are incorporated within the metal lattice providing the carbide functionalities as at such high temperature the other functional groups of the ligand are removed leaving only the carbon backbone over the metal aggregation ¹². The inert condition prevented the metallic oxide formation at the bulk of the aggregate and allowed close packing of atoms in the crystal, but the surface atoms tend to get oxidized might be due to the erg of coordination compensation. This is further evident in XPS spectra and XRD patterns. Fig. S7 showed that the oxidation states of metals at the surface differed from that of bulk with introduction of multivalency under the influence of surface oxidation along with evident M-O and C-O bonds. Such surface properties helped carbides to act efficiently as electrode materials for electrocatalytic oxidation and reduction of water since electrocatalysis is a surface phenomenon that involves direct electron transfer within the redox species.¹³⁻¹⁶ The surface involved redox reactions were further examined through postscanning XPS depth profiles of the optimized materials for HER and OER in the following sections.

Note S4. DFT calculations; DOS and band structure of MoC and WC

Solid material dynamic properties are affected directly or indirectly through phonon dispersion spectra (PDS) and density of states (Projected DOS). PDS helps to understand several peculiar properties like dynamic lattice stability/instability, phase transition, vibrational contribution, Helmholtz free energy, and capacity of heat. Optical properties of materials are basically controlled by optical phonons where the electron-phonon interaction at sub-level is also controlled by optical phonons. To calculate DOS of Mo₂C and WC density functional perturbation theory (DFPT) and finite displacement method (FDM) are used. In Fig. S22, the band structure and DOS of Mo₂C and WC are displayed with the dispersion curves along the high-symmetry towards the Brillouin zone (BZ). If the phonon frequencies over the whole BZ are positive, the compound is dynamically stable. Soft phonon modes and dynamic instability are ensured by the existence of imaginary (negative) phonon frequency. Both phases are devoid of imaginary vibrational frequencies throughout the BZ, indicating their dynamical stability. In each unit cell, there are three times as many phonon modes as there are atoms. N atoms make up a unit cell, which has (3N-3) optical modes and 3 acoustic modes. There are two transverse and one longitudinal acoustic branch within the acoustic modes. The coherent vibrations of atoms in a lattice that are out of equilibrium are what produce acoustic phonons. The optical phonon, on the other hand, is caused by out-of-phase oscillations of the atoms in the lattice when one atom travels to the left and its neighbor to the right.^{15–18} Acoustic phonons are connected to crystal rigidity and contribute to sound propagation in crystals. The orthorhombic structure's unit cell is made up of 12 atoms, resulting in 36 normal lattice vibration modes, including three acoustics and 33 optical modes. Optical phonons have non-zero frequencies at the -point. A hexagonal unit cell includes four atoms in total, resulting in 12 vibrational modes with three acoustics and nine optical branches. For orthorhombic structures, the dispersion of acoustic modes away from the center of the BZ flattens rapidly. The optical branches substantially influence a material's optical behavior. Optical modes are sometimes divided into two branches: lower and upper optical branches. Because of the atomic mass difference between Mo and C atoms, as well as W and C atoms, there is a frequency gap between two branches for both phases. In contrast to orthorhombic structure, this gap is wider, and the branches are more concentrated. There is no phononic bandgap between the acoustic and optical branches in any of the two situations when the lower optical branches overlap with the acoustic branches.¹⁹ Additionally, it forecasts how well the investigated chemicals' thermal transport will work. The highest phonon frequency for optical mode appears around Γ point where the values are 20.9 THz and 23.17 THz.

One crucial component that aids in the explanation of a material's microscopic electrical, optical, and magnetic capabilities is its electronic band structure. Calculating the effective masses of charge carriers is also helpful. To a significant extent, it also influences the bonding qualities. However, if one can determine the nature of dominating bands close to the Fermi level, one can gain a deeper understanding of a material's charge transport capabilities. The electronic energy band structures of the orthorhombic MoC and WC are calculated with energy smearing widths of 0.2 eV and 0.1 eV along with high symmetry direction towards the Brillouin zone. Here both electron-like and hole-like features were along different directions towards BZ. The calculated total density of states (TDOS) at fermi energy of O-MC, H-MC, O-WC, and H-WC at Ef are 6.21, 1.47, 5.98, and 1.52 states per eV of a unit cell. DOS calculations observed show that near Fermi level the main contribution for Mo₂C comes from Mo 4*d*, 2*s* and C 2*p*, 2*s* same as for WC it comes from W 4*d*, 2*s* and C 2*p*, 2*s* electronic states at Fermi energy indicates that a strong covalent bonding has formed. The electron-electron interaction (Coulomb pseudopotential) is estimated through below equation:

$$\mu^* = \frac{0.26N(E_F)}{1 + (E_F)}$$

The calculated Coulomb pseudopotential of Mo2C and WC are 0.24 and 0.17 respectively.

Note S5. Water splitting mechanism through DFT calculations

OER is commonly referred to as a 4e⁻ transfer process. In the OER, water molecules are oxidized, releasing oxygen gas and generating protons and electrons. The overall reaction can be represented as:^{20,21}

$$4H_2O(l) \rightarrow 4H^+ + 4e^- + 2O_2$$
 (S1)

The net energy change, ${}^{\Delta G_0}$, associated with above OER process is 4.92 eV. This reaction is assumed to pass through four consecutive steps with a change in energy of 1.23 eV for every step.²² These steps involve different intermediates (*O, *OH, and *OOH) and mathematically can be expressed using following equations:

$$H_2O(l) + * \rightarrow *-OH + H^+ + e^- ; {}^{\Delta G_1}$$
(S2)

*-OH
$$\rightarrow$$
 *-O + H⁺ + e⁻ ; ${}^{\Delta G_2}$ (S3)

$$H_2O(l) + *-O \rightarrow *-OOH + H^+ + e^-; {}^{\Delta G_3}$$
(S4)

*-OOH
$$\rightarrow$$
 *+O₂(g) + H⁺ + e⁻ ; ${}^{\Delta G_4}$ (S5)

where * is used to represent the adsorption site of the catalyst. The other symbols associated with * represent the reaction intermediates adsorbed on the catalyst site. ${}^{\Delta G_i}(i=1-4)$ is the Gibbs free energy for each reaction step. Here, an electron and a proton pair, H⁺(aq.) + e⁻, are transferred in each step. Calculating the energy of a proton and of an electron is not straightforward.²³ To simplify the comprehension of these reactions, a concept, known as the computational hydrogen electrode (CHE) which equates the energy associated with one H⁺ + e⁻ pair to that of a hydrogen molecule, ${}^{0.5 * E_{H_2}}$ vs. reversible hydrogen potential (U_{RHE}), was used.²³ ${}^{\Delta G_i}(i=1-4)$ for equations (S2-S5) was used to calculate the thermodynamic progression of Fig. S24. The expressions for the computation of ${}^{\Delta G_i}(i=1-4)$ can be found elsewhere¹⁸ The overall efficiency of the OER process is heavily influenced by the height of ${}^{\Delta G_i}(i=1-4)$. The step having highest ${}^{\Delta G}$ represents the most sluggish reaction. The thermodynamic over potential, ${}^{\eta_{TD}}$, can be calculated as following:

$$\eta_{TD} = max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \} / e - 1.23 V$$
(S6)

where 1.23 eV refers to the equilibrium potential of the reaction vs. U_{RHE} (reversible hydrogen electrode).²⁴



Fig. S1. Raman-depth profiling spectra for the prepared TMCs; (a) TiC, (b) VC, (c) MoC, and (d) WC.



Fig. S2. 2D mapping obtained from Raman-depth profiling for the prepared TMCs; (a) TiC, (b) VC, (c) MoC, and (d) WC.



Fig. S3. XPS survey spectra of the prepared TMCs; (a) TiC, (b) VC, (c) MoC, and (d) WC.



Fig. S4. XPS depth profiles of the prepared TMCs; (a) TiC, (b) VC, (c) MoC, and (d) WC.



Fig. S5. Atomic content from the XPS depth profiles for the prepared TMCs; (a) TiC, (b) VC, (c) MoC, and (d) WC.



Fig. S6. High resolution XPS spectra of TiC with depth profiles; (a, d) Ti 2p, (b, e) C 1s, and (c, f) O 1s.



Fig. S7. High resolution XPS spectra of VC with depth profiles; (a, d) V 2p, (b, e) C 1s, and (c, f) O 1s.



Fig. S8. Schematic illustration of the formation mechanism of TMCs as deduced from the XPS depth profile.



Fig. S9. (a-c) FE-SEM images of TiC and (d-f) its elemental mapping of Ti and C elements with EDX spectrum.



Fig. S10. (a-c) FE-SEM images of VC and (d-f) its elemental mapping of V and C elements with EDX spectrum.



Fig. S11. HR-TEM images, lattice fringes, and SAED patterns of (a-c) MoC and (d-f) WC.



Fig. S12. XPS spectra of MoC coated on the nickel foam; (a) the survey spectrum, (b-d) high resolution XPS spectra of Mo3d, C1s and O1s. (e-g) XPS depth profiling of MoC on the nickel foam and (h-j) the corresponding 2D images.



Fig. S13. XPS spectra of WC coated on the nickel foam; (a) the survey spectrum, (b-d) high resolution XPS spectra of W4f, C1s and O1s. (e-g) XPS depth profiling of WC on the nickel foam and (h-j) the corresponding 2D images.



Fig. S14. HER performance of TMCs; (a) Current densities at certain potentials, (b) overpotentials at certain current densities, (c) Current densities with respect to ECSA and electrode surface area, (d) Tafel slopes at higher overpotential region, (e) XRD patterns change for post-HER, and (f) TOF values in 1.0 M KOH during HER.



Fig. S15. (a) Chronoamperometric study for WC over 60 h HER operation. (b) XPS survey spectra and (c, d) high resolution XPS spectra of W4f and C1s of WC after chronoamperometric study. (e) Chronoamperometric study for other TMCs over 60 h HER operation.



Fig. S16. OER performance of TMCs; (a) Current densities at certain potentials, (b) overpotentials at certain current densities, (c) current densities with respect to ECSA and electrode surface area, (d) Tafel slopes at higher overpotential region, (e) XRD patterns change for post-HER, and (f) TOF values in 1.0 M KOH during OER.



Fig. S17. (a) Chronoamperometric study for MoC over 60 h OER operation. (b) XPS survey spectra and (c, d) high resolution XPS spectra of Mo3d and C1s of MoC after chronoamperometric study. (e) Chronoamperometric study for other TMCs over 60 h OER operation.



Fig. S18. Comparative study of the XRD patterns of TMCs after HER and OER; (a) TiC, (b) VC, (c) MoC, and (d) WC.



Fig. S19. XPS Depth profile spectra of MoC after HER. (a) Mo3d, (b) C1s, and (c) O1s. (d-f) The corresponding 2D depth scan images.



Fig. S20. XPS Depth profile spectra of WC after HER. (a) W4f, (b) C1s, and (c) O1s. (d-f) The corresponding 2D depth scan images.



Fig. S21. (a) Schematic mechanistic steps for OER/ORR. (b) LSV curves at 1600 rpm, (c) Tafel slope plots, and (d) Nyquist plot for WC and MoC in 0.1 M KOH



Fig. S22. LSV plots at different rotation speed for (a) MoC and (b) WC. Calculation of electron transfer number form K-L plot for (c) MoC and (d) WC. (e) Chronoamperometric study with methanol crossover for 1 hr for MoC and WC. (f) OER and ORR activity of MoC.



Fig. S23. PDOS and band structure of (a) MoC and (b) WC using DFT calculations



Fig. S24. Activation barriers for water dissociation over Mo_2C and W_2C surfaces



Fig. S25. Projected density of states (PDOS) of H adsorbed (a) Mo_2C and (b) W_2C surfaces



Fig. S26. Projected density of states (PDOS) of OH adsorbed a) Mo₂C and b) W₂C surfaces



Fig. S27. Comparison of energy profile diagrams of WC and MoC for (a) HER and (b) OER.



Mo₂C (200)

Fig. S28. Reaction schemes on the Mo_2C (200) surface (*) with the reaction intermediates adsorbed of *-OH, *-O, *-OOH, and *-H.



Fig. S29. Reaction schemes on the W_2C (200) surface (*) with the reaction intermediates adsorbed of *-OH, *-O, *-OOH, and *-H.

Parameter	TiC	VC	МоС	WC
Crystal structure	Cubic	Cubic	Orthorhombic	Orthorhombic
Space group	Fm-3m (225)	Fm-3m	Pbcn (60)	Pbcn (60)
a (Å)	4.32781 (1)	4.164 (3)	4.733 (1)	4.75 (2)
b (Å)	4.32781 (1)	4.164 (3)	6.035 (3)	5.23 (5)
c (Å)	4.32781 (1)	4.164 (3)	5.203 (1)	6.11 (1)
	Ti-4a (0, 0, 0)	V-4a (0, 0, 0)	Mo-8d (0.245, 0.079, 0.087)	W-8d (0.244, 0.081, 0.127)
Wyckoff position (x , y , z)	C-4b (0, 0, ½)	C-4b (½, 0, 0)	C-4c (½, ¾, 0.84)	C-4c (¹ / ₂ , ³ / ₄ , 0.121)
Diffractometer	Rigaku AFC6R	Rigaku AFC6R	Rigaku AFC6R	Rigaku AFC6R
Temperature	23°C	23°C	23°C	23°C
Scan method	ω - 2θ	ω - 2θ	ω - 2θ	ω - 2θ
Absorption correction	DIFABS	DIFBAS	DIFBAS	DIFBAS
Goodness of fit	1.1	1.01	0.71	2.26
Crystallite size (nm)	6774 (56)	547 (2)	8.74 (4)	268.25 (3)
Strain (%)	0.033 (1)	0.001 (1)	0.4 (1)	0.3391 (4)
Volume (Å ³)	81.26	72.09	149.1	152.21
Density (g·cm ⁻³)	4.89	5.81	9.07	16.58

Table S1. Crystal data intensity collection for TMCs.

Material	Element	Main peak (eV)	ΔE (eV)	FWHM	Area (%)
	${\rm Ti}2{\rm p}^{+4}{}_{3/2}{\rm C}$	454.54	4.5	1.27	11.19
	$Ti2p^{+4}_{3/2}O$	457.18	5.58	1.52	38.5
	C-M	281.11		1.59	9.93
	C-C	283.17		1.20	8.83
TiC	C=C	284.43	-	1.90	68.11
Ti2p/C1s/O1s	C-0	285.58		1.23	5.20
	C=O	288.35		1.42	6.34
	O-M	528.09	-	1.73	9.50
	O-C	529.89		2.29	61.94
	О-Н	531.90		2.21	22.71
	$V2p^{+4}_{3/2}$	515.84	7.08	1.29	8.33
	$V2p^{+6}_{3/2}$	524.60	7.47	1.29	23.82
	O-M	529.18	-	1.37	0.83
	O-C	529.95	-	1.41	38.56
VC	О-Н	531.34	-	1.37	6.84
V2p/C1s/O1s	C-M	282.63		1.68	6.92
	C-C	284.15		1.51	69.24
	C=C	285.29	-	1.18	9.38
	C-0	286.20		0.98	7.06
	C=O	288.45		1.40	5.76

Table S2. Details of the peak positions and individual bonds as obtained from the XPS spectra.

Material	Element	Main peak (eV)	ΔE (eV)	FWHM	Area (%)
	Mo3d ⁺² _{5/2}	228.59	2.96	0.42	0.18
	Mo3d ⁺⁴ _{5/2}	232.58	3.11	1.29	43.55
	Mo3d ⁺⁶ _{5/2}	235.69	2.0	1.40	29.52
	C-M	283.05	-	1.09	4.22
M-C	C-C	284.32		1.26	72.73
MoC	C=C	285.60		1.01	7.36
Mo3d/C1s/O1s	C-O	286.16		1.15	5.15
	C=O	288.47		1.18	5.65
	O-M	529.14	-	0.95	2.02
	0-C	530.35		1.32	72.01
	0-Н	531.70		2.04	25.98
	$W4f^{+4}_{7/2}$	30.74	2.6	1.48	30.33
	W4f ⁺⁴ _{7/2} -O	31.69	2.8	1.43	2.86
	W4f ⁺⁶ _{7/2} -O	36.94	2.0	1.40	22.82
	C-M	282.33	-	1.60	19.54
WC	C-C	283.85		1.95	62.40
wC	C=C	285.73		1.34	4.78
W4f/C1s/O1s	C-O	287.36		0.85	2.00
	C=O	288.11		1.01	5.18
	O-M	529.40	-	1.93	70.23
	O-C	530.99		1.71	21.30
	О-Н	532.40		1.37	7.25

(continued)

	Atomic %				
TMCs	C 1s	O1s	TM-2p/3d/4f (TMCs= Ti, V, Mo, and W)		
TiC	30.8954	49.2126	19.8919		
VC	57.4084	42.5916	0*		
МоС	36.3501	45.1593	18.4907		
WC	49.8743	48.6602	1.46553		

 Table S3. Account of atomic % of individual elements of TMCs from XPS.

*The weak signal of V2p might have suppressed by high intensity of O1s.

Catalysts	Electrolyte	η ₁₀ (mV)	b (mV·dec ⁻¹)	$egin{array}{c} R_{CT} \ (\Omega) \end{array}$	J₀ (mA·cm ⁻²)	Ref.
VC-NS*	$0.5 \mathrm{MH}_2\mathrm{SO}_4$	98	56	19		13
α -MoC _{1-x}	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	250	95	-	-	14
MoC aerogel	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	185	65	-	0.02	25
Mo ₂ C/C	$0.5 \mathrm{~M~H_2SO_4}$	264 (η_{50})	82	$1.5 (\eta_{400})$	-	26
WC	0.5 M H ₂ SO ₄ 1.0 M KOH	87 62	55.5 38.89	-	-	27
η-MoC	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	122	53	15	-	28
Ni/Fe ₃ C	0.5 M H ₂ SO ₄ 1.0 M KOH	112 93	97 63	-	-	29
Mo ₂ TiC ₂ T _x	1.0 M KOH	32	30	0.235	-	30
Co ₆ Mo ₆ C ₂ /Co ₂ Mo ₃ O ₈ /N PCRGO*	1.0 M KOH	220	104.7	-	-	31
NC*@Cu-Co-W-C	1.0 M KOH	98	50	-	-	32
Co ₄ Mo ₂ @NC/Ti	1.0 M KOH	218	78.5	-	-	33
Ni-MoC@NGC*	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	338 (η_{100})	69	-	-	34
WC	1.0 M KOH	295 (η_{100})	45	$1.66(\eta_{400})$	0.083	This work

Table S4. Comparison of HER performances with other reported works.

 * VC-NS: vanadium carbide encapsulated by graphitic carbon network.

NPCRGO: N,P-doped reduced graphene oxide.

NC: nitrogen-doped carbon.

NGC: N-doped graphitic carbon.

 Table S5. Comparison of OER performances with other reported works.

Catalysts	Electrolyte	η ₁₀ (mV)	b (mV·dec⁻¹)	R_{CT} (Ω)	Ref.
Mo ₂ TiC ₂ T _x	1.0 M KOH	320	86	-	30
Co ₆ Mo ₆ C ₂ /Co ₂ Mo ₃ O ₈ /NPC RGO*	1.0 M KOH	403	89.7	-	31
NC*@Cu-Co-W-C	1.0 M KOH	238	59	-	32
Co ₄ Mo ₂ @NC/Ti	1.0 M KOH	330	48.7	-	33
Ni-MoC@NGC*	0.5 M KOH	520 (η ₁₀₀)	-	-	34
TiTaF _x C ₂ NP*/rGO	$1.0 \mathrm{~M~HClO}_4$	490 (η_{100})	36	-	35
Co ₆ Mo ₆ C ₂ /NCRGO	1.0 M KOH	260	50	9.0	36
B,N:Mo ₂ C@BCN*	1.0 M KOH	$360 (\eta_{100})$	61	1.5	37
Co–Ni ₃ C/Ni@C	1.0 M KOH	325	67.76	-	38
CoP/Mo ₂ CT _x	1.0 M KOH	78	66	-	39
Co-doped Fe ₃ C@CNO*	1.0 M KOH	271	48.9	32.6	40
МоС	1.0 M KOH	$373~(\eta_{100})$	33	132.0	This work

* NPCRGO: N,P-doped reduced graphene oxide. NC: nitrogen-doped carbon. NGC: N-doped graphitic carbon. NP: nanoparticles

BCN: B,N-doped carbon network

CNO: carbon nano-onions

TMCs (n	C _{dl}	ECSA	RF	то	TOF	
	(mF)	(cm ²)		HER	OER	
TiC	1.33	33.25	33.25	0.046	0.0121	
VC	0.767	21.9	21.9	0.032	0.016	
МоС	1.584	45.25	45.25	0.044	0.043	
WC	1.822	53.77	53.77	0.075	0.017	

 Table S6. Details of electroactive surface area and TOF for the synthesized TMCs.

Electrodes	Electrolyte	Cell voltage@\eta ₁₀ (V)	Ref.
$Mo_2TiC_2T_x \mid Mo_2TiC_2T_x$	1.0 M KOH	1.57	30
Co ₆ Mo ₆ C ₂ /Co ₂ Mo ₃ O ₈ /NPCRGO Co ₆ Mo ₆ C 2/Co ₂ Mo ₃ O ₈ /NPCRGO	1.0 M KOH	1.81	31
NC@Cu-Co-W-C NC@Cu-Co-W-C	1.0 M KOH	1.566	32
Co ₄ Mo ₂ @NC/Ti Co ₄ Mo ₂ @NC/Ti	1.0 M KOH	1.74	33
Ni-MoC@NGC Ni-MoC@NGC	1.0 M KOH	1.75	34
₩С ∥ Мо С	1.0 M KOH	$1.89@\eta_{100}$	This work

Table S7. Comparison of OWS performances with other reported works

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