



Room-temperature synthesis of $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets with interfacial coupling for enhanced oxygen evolution reaction

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ABSTRACT

Constructing high-performance electrocatalysts for oxygen evolution reaction (OER) using a simple and economical strategy is considerably meaningful yet still challenging. Herein, $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ (where T_x represents the surface functional groups, -O, -OH and -F) hetero-nanosheets were facilely prepared by the *in situ* topochemical transformation at room temperature towards efficient OER. The integrity of $\text{Co}(\text{OH})_2$ nanosheets and $\text{Mo}_2\text{TiC}_2\text{T}_x$ nanosheets affords interfacial coupling to optimize the electronic structures of Co and Mo ions, which endows the high electron transfer efficiency and rapid reaction kinetics. As a result, the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets exhibit excellent OER performances with low overpotentials of 283 mV on glass-carbon electrode, and 227 mV on nickel foam at 10 mA/cm². Furthermore, the decent anti-alkali ability underpins superior operational stability exceeding 100 h, demonstrating grand potential in practical applications. This work provides a new insight for the synthesis of efficient and cost-effective two-dimensional (2D) material-based electrocatalysts.

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Hydrogen energy presents a promising solution to alleviate the energy crisis and environmental pollution owing to its zero-carbon emission and high calorific value [1,2]. Electrochemical water splitting, consisting of hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode, is an eco-friendly and efficient technology for hydrogen production [3]. OER is a four-electron transfer process that suffers from a higher energy barrier and sluggish kinetics, so it is regarded as the bottleneck step of the whole water splitting [4,5]. Therefore, finding an efficient and stable OER catalyst to reduce the anode reaction overpotential is vital to improve the efficiency of hydrogen production. So far, precious metal-based catalysts (such as RuO_2 , and IrO_2) show optimum OER activity, however, their large-scale practical applications are still hindered by high cost and low storage capacity [6,7]. Consequently, the development of highly efficient non-precious metal catalysts is crucial for the future applications of OER.

To date, a great deal of non-precious metal catalysts has been reported to boost OER performance. Thereinto, transition metal hydroxides (TMHs) have attracted increasing attention because of their large specific surface area, abundant metal active sites and low cost [8–11]. Nevertheless, inferior electrical conductivity and strong aggregation tendency of TMHs lead to low catalytic activity and unideal stability in OER process [12–14]. Metal-organic frameworks (MOFs) have become promising materials in various applications due to their unique structural advantages [15,16]. In recent years, some studies have shown that TMHs derived from MOFs precursors by means of hydrolysis, chemical etching, ion-exchange, *etc.* can effectively restrain their agglomeration [17–21]. For instance, Chen *et al.* used 2D Hofmann-MOFs as self-sacrificial templates to synthesize FeNi-LDH nanosheets *via* a hydrolysis transformation assisted by NaBH_4 , which effectually inhibited the self-stacking of LDHs, resulting in excellent OER activity [19]. The group reported the self-transforming $\text{Co}(\text{OH})_2$ nanosheet arrays from ZIF-67, which bring high exposure of active sites for OER [20]. Although the unique structure of TMHs obtained from the MOFs template endows improved OER performance, it is still necessary to take other measures to further boost their OER conductivity and reactivity.

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Recently reported that integrating TMHs with other functional materials (such as MXene, graphene, and NiP_x) to construct heterostructured composites is a promising way to solve the aforementioned problems [22–24]. This is mainly attributed to the fact that interfacial coupling can induce the redistribution of local electrons and regulate the electronic structure of atoms, thereby improving electrochemical reactivity, conductivity and stability [25,26]. Among the functional materials, MXenes are deemed as ideal substrate material to fabricate heterostructures for effectively modulating the electronic structures of target catalysts. Since the abundant surface negative terminations produced during the synthesis process, MXenes can easily anchor the functional units to form versatile hybrids *via* electrostatic absorption, hydrogen bonding, or covalent bonding [27–29], which is important for inhibiting MXene self-restacking and generating strong interface interactions at the molecular level. They are usually written as M_{n+1}X_nT_x, where M is an early transition metal, X is C and/or N, T_x represents surface functional groups such as -O, -OH and -F [30]. As the most studied material, Ti₃C₂T_x has been widely used as a substrate material to design extended heterostructures for energy storage and conversion applications [31,32]. In 2015, Anasori *et al.* discovered an ordered double-transition bimetallic Mo₂TiC₂T_x MXene with two layers of Mo atoms located on the outer side, while Ti atoms occupy the middle metal layer [33,34]. Unlike the conventional Ti₃C₂T_x, Mo atoms are present on the surface of Mo₂TiC₂T_x, thus the type of interface bonds can be tuned when it is combined with other components [35–38]. Moreover, related research has shown that Mo₂TiC₂T_x possesses a relatively stronger Ti-C chemical bond than that of Ti₃C₂T_x [39]; however, compared with Ti₃C₂T_x, there is relatively less research on coupling Mo₂TiC₂T_x with other functional materials to regulate the OER performance [40].

Herein, Co(OH)₂/Mo₂TiC₂T_x hetero-nanosheets were prepared using ZIF-67 as a raw material through simple topochemical transformations at room temperature. Detailed XPS and XANES analyses reveal that the interfacial coupling between Co(OH)₂ and Mo₂TiC₂T_x enables the electron transfer from Co(OH)₂ to Mo₂TiC₂T_x, thereby increasing the valence state of Co ions and the electron density around the Mo species, which contributes to the high OER reactivity. Moreover, in the process of topological structure conversion, ZIF-67 was *in situ* converted into Co(OH)₂ nanosheets, which strongly combined with the Mo₂TiC₂T_x nanosheets. Such hetero-nanosheets endow the composites with abundant active sites and well-developed electron transport channels as well as robust structural stability. As a result, the Co(OH)₂/Mo₂TiC₂T_x hetero-nanosheets exhibit excellent OER performances with low overpotentials of 283 mV on glass-carbon electrode, 227 mV on nickel foam at 10 mA/cm² and can be stable for 100 h in alkaline solution, holding great promise for practical applications.

As depicted in Fig. S1 (Supporting information), Co(OH)₂/Mo₂TiC₂T_x hetero-nanosheets were synthesized through a convenient room temperature topochemical transformation strategy, involving the successive preparation of Mo₂TiC₂T_x and ZIF-67/Mo₂TiC₂T_x composites. The details of the procedure are as follows: Mo₂TiC₂T_x nanosheets were first obtained by a combined method of NaF/HCl etching and liquid exfoliation. Notably, during the etching procedure, Al atoms were removed from between layers, while fluorine and oxygen-containing functional groups were adsorbed on the surface of Mo atoms. These terminated Mo₂TiC₂T_x nanosheets can easily adsorb the Co²⁺ ions in cobalt salts by the electrostatic interactions, which greatly facilitates the direct growth of ZIF-67 on Mo₂TiC₂T_x nanosheets. Subsequently, under the continued ultrasound process, the ZIF-67 in ZIF-67/Mo₂TiC₂T_x composites undergoes rapid hydrolysis and self-transforms into Co(OH)₂ nanosheets, thereby leading to the *in-situ* formation of tightly contacted Co(OH)₂/Mo₂TiC₂T_x hetero-

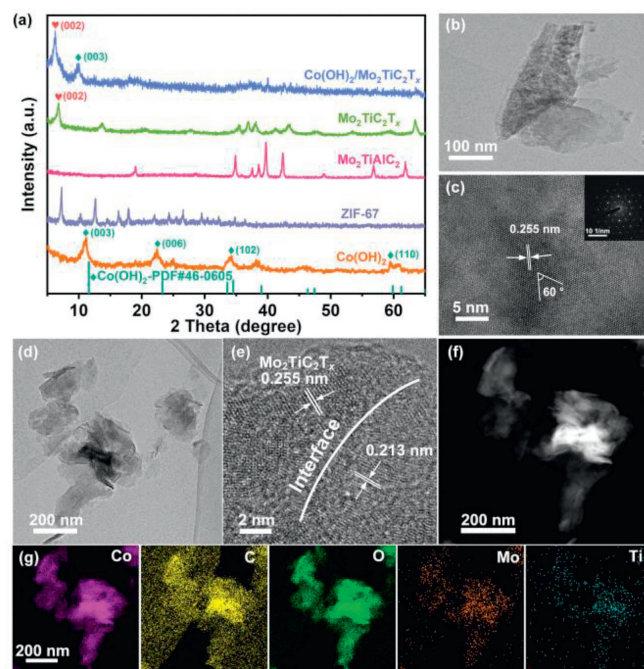


Fig. 1. (a) XRD patterns of the as-obtained samples. (b) TEM image of Mo₂TiC₂T_x nanosheets. (c) HRTEM image and the corresponding FFT (inset) of Mo₂TiC₂T_x nanosheet. (d) TEM image of Co(OH)₂/Mo₂TiC₂T_x nanosheets. (e) HRTEM image of Co(OH)₂/Mo₂TiC₂T_x nanosheet. (f, g) HAADF and corresponding EDS element mapping images of Co(OH)₂/Mo₂TiC₂T_x nanosheets.

nanosheets. The Co(OH)₂/Mo₂TiC₂T_x (*i.e.*, Co(OH)₂/Mo₂TiC₂T_x-3 in the performance section) with the 40 mg Mo₂TiC₂T_x loading is discussed in the following characterizations because it shows the highest electrocatalytic activity, see below. And the inductively coupled plasma emission spectrometer (ICP-OES) reveals the content of Co, Mo and Ti in this composite is 42.22 wt%, 8.5 wt% and 2.17 wt%, respectively, so the hybrid atomic ratio of Co:Mo:Ti is approximately 8:1:0.5.

X-ray diffraction (XRD) technique was performed to study the structural information of the as-prepared samples, as shown in Fig. 1a. Compared with Mo₂TiAlC₂ precursor, the characteristic peak at 39° disappears of Mo₂TiC₂T_x and the (002) peak appears at 6.9°, indicating the successful transformation from the Mo₂TiAlC₂ phase to the Mo₂TiC₂T_x structure *via* NaF/HCl etching. Meanwhile, the XRD pattern of the obtained ZIF-67 precursor is in good match with the previous report [20]. Under continuous ultrasound treatment at room temperature, ZIF-67 experiences a topochemical transformation and its diffraction peaks completely disappear. Moreover, a set of diffraction peaks corresponding to α -Co(OH)₂ appear (JCPDS card No. 46-0605), which confirms that ZIF-67 is completely converted to Co(OH)₂ at room temperature. When Mo₂TiC₂T_x is added into the above system, the XRD pattern of the product shows the characteristic diffraction peaks of Co(OH)₂ and Mo₂TiC₂T_x, demonstrating the successful preparation of Co(OH)₂/Mo₂TiC₂T_x composite. Additionally, compared with pure Mo₂TiC₂T_x, the (002) peak of Co(OH)₂/Mo₂TiC₂T_x shifts towards a lower angle direction (from 6.9° to 6.3°), indicating that coupling Co(OH)₂ can increase the layer spacing of Mo₂TiC₂T_x nanosheets, thereby preventing them from stacking. The microstructure information of these samples was detected by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As displayed in Fig. S2a (Supporting information), the etched Mo₂TiC₂T_x displays a typical accordion-like structure. After ultrasonic treatment in NMP, the layered Mo₂TiC₂T_x was exfoliated into ultrathin nanosheets with a lateral size of

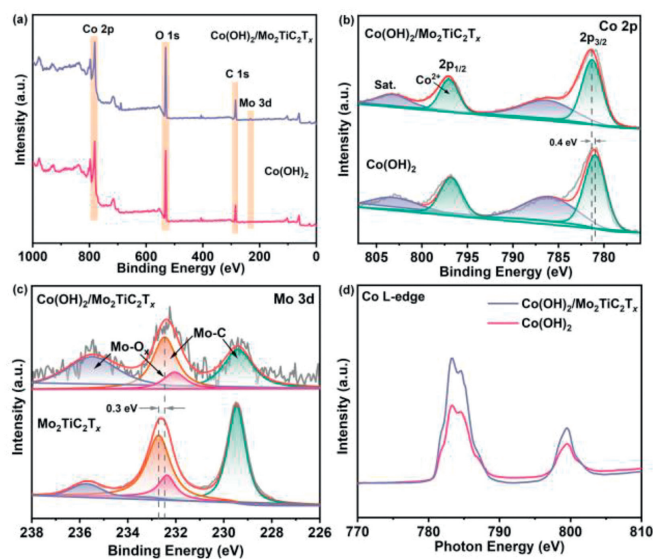


Fig. 2. XPS spectra of (a) survey, (b) Co 2p, (c) Mo 3d and (d) Co L-edge.

about several hundreds of nanometers, as is confirmed by the TEM image (Fig. 1b). In the HRTEM image (Fig. 1c), the lattice fringe of 0.255 nm corresponds to the diffraction peak at $2\theta = 35^\circ$ of $\text{Mo}_2\text{TiC}_2\text{T}_x$. Furthermore, from the inserted fast Fourier transform (FFT) image, the typical hexagonal symmetry of $\text{Mo}_2\text{TiC}_2\text{T}_x$ nanosheets can be seen. The SEM image in Fig. S2c (Supporting information) shows that Co(OH)_2 derived from rhombohedral dodecahedron ZIF-67 (Fig. S2b in Supporting information) also possesses nanosheets structure, which ensures intimate contact with $\text{Mo}_2\text{TiC}_2\text{T}_x$ nanosheets, providing abundant active sites and facilitating electron transport channels. The SEM (Fig. S2d in Supporting information) and TEM (Fig. 1d) images confirm that the hetero-nanosheets morphology of as-obtained $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ with a lateral size of several hundred nanometers, and the high transparency of TEM indicates their ultrathin feature. Moreover, the corresponding HRTEM image of the $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ (Fig. 1e) demonstrates the formation of a heterogeneous interface between Co(OH)_2 and $\text{Mo}_2\text{TiC}_2\text{T}_x$. Wherein, the lattice fringe of 0.213 nm belongs to the (200) crystal plane of CoO , since the ultrathin Co(OH)_2 nanosheets are extremely sensitive to electron beam irradiation and can be quickly converted to CoO under electron beam [41], which is further confirmed by TEM and HRTEM images of the single Co(OH)_2 nanosheets (Figs. S3a-c in Supporting information). Meanwhile, the lattice fringe of 0.255 nm matches well with the diffraction peak at 35° of $\text{Mo}_2\text{TiC}_2\text{T}_x$. These two crystal planes are consistent with that of individual Co(OH)_2 and $\text{Mo}_2\text{TiC}_2\text{T}_x$, respectively, further proving the existence of heterogeneous interfaces in $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets. The heterostructure is believed to play an important role in boosting electron transfer and stability as well as tuning electron structure [42]. In addition, the high-angle annular dark-field (HAADF) image of $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ and the corresponding element mapping images show a uniform distribution of Co, C, O, Mo and Ti (Figs. 1f and g) across the nanosheet. These results confirm the achievement of $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets.

X-ray photoelectron spectroscopy (XPS) was used to study the chemical valence state of $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ and the electronic interaction between Co(OH)_2 and $\text{Mo}_2\text{TiC}_2\text{T}_x$. As shown in Fig. 2a, the survey XPS spectra further confirm the elemental composition of the samples. The high-resolution Co 2p spectrum of the Co(OH)_2 demonstrates the Co $2p_{3/2}$ (781.0 eV) and Co $2p_{1/2}$ (796.8 eV) peaks as well as two shakeup satellite peaks, respectively, indicating the

valence state of Co species is +2 (Fig. 2b). Interestingly, compared with the Co(OH)_2 , the Co 2p peaks of $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ are shifted towards higher binding energies, implying that a decrease in local charge density of Co ions accompanied with higher valence state [32]. The Mo 3d spectrum of $\text{Mo}_2\text{TiC}_2\text{T}_x$ (Fig. 2c) can be divided into four peaks, of which the peak located at 229.5 and 232.7 eV correspond to the Mo $3d_{5/2}$ and $3d_{3/2}$ levels for the Mo-C bonds, which shows that 4+ is the dominant oxidation state. Two small peaks at 232.4 and 235.7 eV belong to Mo $3d_{5/2}$ and $3d_{3/2}$ levels of surface Mo-O bonds (Mo^{6+}), which can be attributed to the surface oxide-containing terminations [36,40]. Compared with $\text{Mo}_2\text{TiC}_2\text{T}_x$, an obvious shift of Mo-C bond to the lower binding energy is observed for the $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$, showing an increase in the charge density around the Mo atoms. Moreover, in the XPS O 1s spectra (Fig. S4 in Supporting information), except for the Co-OH peak (531.5 eV) and adsorbed water peak (532.9 eV), a new peak at 530.5 eV attributed to the Co-O-Mo bonds appears in the $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$, which are favourable for the electron transfer between Co(OH)_2 and $\text{Mo}_2\text{TiC}_2\text{T}_x$ [43,44]. To go further, the interface electronic interaction between Co(OH)_2 and $\text{Mo}_2\text{TiC}_2\text{T}_x$ in $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets was also examined by soft X-ray adsorption near-edge structure (XANES). As shown in Fig. 2d, the Co L-edge splits into lower energy L_{3-} edge and higher energy L_{2-} edge due to spin-orbit splitting. Although the peak positions of Co L-edge for $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets have almost no change by comparison with that of Co(OH)_2 , their peak area is higher than that of Co(OH)_2 . As is known, the normalized peak area of the sample can explain the occupied state of electrons. The larger peak area shows that there are more empty orbitals with higher valence state [45]. Compared with Co(OH)_2 , the Co ions in $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ have more empty orbitals, indicating that higher Co ions are generated, which is consistent with the results of Co 2p XPS. High valence Co ions have been proven to be beneficial for improving OER reactivity [46,47].

To shed light on the role of interfacial coupling play in the OER, the electrocatalytic performances of the obtained $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets, pure Co(OH)_2 and $\text{Mo}_2\text{TiC}_2\text{T}_x$ were examined using a three-electrode system in 1.0 mol/L KOH solution at room temperature. Moreover, to achieve optimal OER performance, $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ composites with different amounts of $\text{Mo}_2\text{TiC}_2\text{T}_x$ were synthesized and tested. As shown in Fig. 3, the OER performance of the sample with 0.285 mg/cm² loaded on the glass-carbon (GC) electrode was first evaluated. Fig. 3a shows the polarization curves of different samples, in which $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -3 has the best OER activity. The overpotentials that correspond to Co(OH)_2 and four $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ composites at 10 mA/cm² are 323, 309, 298, 283 and 358 mV, respectively (Fig. 3b). From the above values, it can be seen that the amount of $\text{Mo}_2\text{TiC}_2\text{T}_x$ has a significant impact on the OER activity of the composites, which may be attributed to the strength of interface coupling. The $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -3 achieves an optimized interface coupling effect. Moreover, to reveal the effect of the surface Mo atom on the OER activity of $\text{Mo}_2\text{TiC}_2\text{T}_x$, $\text{Co(OH)}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites were also prepared (Fig. S5 in Supporting information) and tested. Compared with the $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -3, the $\text{Co(OH)}_2/\text{Ti}_3\text{C}_2\text{T}_x$ has a larger η_{10} of 334 mV, which directly proves the beneficial role of surface Mo atoms on $\text{Mo}_2\text{TiC}_2\text{T}_x$ OER process. The corresponding Tafel slope in Fig. 3c further unravel the best OER kinetics of the $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -3 (80 mV/dec) by comparison with the $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -1 (116 mV/dec), $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -2 (95 mV/dec), $\text{Co(OH)}_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ -4 (108 mV/dec) and $\text{Co(OH)}_2/\text{Ti}_3\text{C}_2\text{T}_x$ (93 mV/dec), which could be attributed to the moderate interfacial coupling between $\text{Mo}_2\text{TiC}_2\text{T}_x$ and Co(OH)_2 .

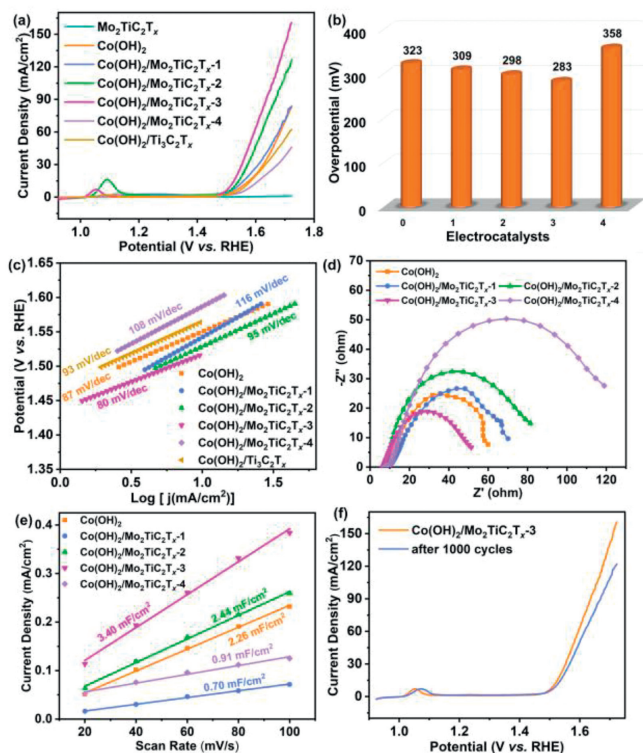


Fig. 3. OER performances of catalysts coated on GC electrode: (a) Polarization curves. (b) Comparison of the overpotential of different samples at 10 mA/cm^2 . (c) The corresponding Tafel plots. (d) Nyquist plots. (e) Linear fitting of C_{dl} of the catalysts versus scan rate for the estimation of the ECSA. (f) LSV curves of $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ initially and after 1000 CV cycles.

The charge transfer kinetics of as-prepared catalysts during the OER process were further estimated by electrochemical impedance spectroscopy (EIS). As shown in Fig. 3d, compared with other samples, the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ has the smallest semicircular diameter with charge-transfer resistance of $44 \ \Omega$, suggesting its fastest charge transfer kinetics, which is consistent with the result of the Tafel slope. The double-layer capacitance (C_{dl}) was measured in the non-Faraday range (Fig. S6 in Supporting information) to assess the electrochemical surface area (ECSA) of the samples. As displayed in Fig. 3e, among all the catalysts, $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ has the highest C_{dl} value of 3.40 mF/cm^2 , indicating that more active sites are exposed for OER, which contributes to the excellent OER activity. Besides, stability is an important indicator for the practical application of catalysts. Therefore, a long-term CV cycling test was carried out to assess the stability of the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$. As shown in Fig. 3f, slight differences between LSV curves can be observed before and after 1000 CV cycles, demonstrating the good durability of the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ hybrid nanosheets.

To explore whether the performance of the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ remains unchanged when the amount of catalyst is increased by dozens of times. The obtained samples were coated on the common nickel foam (NF) collector with a high loading amount of 10 mg/cm^2 to further investigate the OER activity, which is conducive to the industrial application. As shown in Figs. 4a and b, Figs. S7 and S8 (Supporting information), the comparative trend for OER performance of these samples coated on NF is similar to that of the samples with GC electrode as the substrate, where $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ still has the best OER activity of 227 mV at 10 mA/cm^2 , demonstrating the outstanding substrate-independent OER activity. This overpotential is also comparable to previously reported advanced OER electrocatalysts, as displayed in Table S1 (Supporting information). Moreover, the chronopotentiometry curve at 10 mA/cm^2 (Fig. 4c) shows no significant change in OER activity over 100 h, indicating that the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ has excellent long-term OER stability. Besides, the XRD and TEM were conducted to confirm the structure and morphology of $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ after a long-term chronopotentiometry test (Fig. S9 in Supporting information). By the analysis of post-OER characterization, $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ still presents the nanosheet morphology, while partially $\text{Co}(\text{OH})_2$ is oxidized to CoOOH during OER process. To reveal the OER intrinsic activity of the obtained catalysts, density functional theory (DFT) was performed to study the free energy of OER intermediates. In the calculation, the structural models of the reconstructed CoOOH , $\text{Mo}_2\text{TiC}_2\text{T}_x$ and $\text{CoOOH}/\text{Mo}_2\text{TiC}_2\text{T}_x$ heterostructure were established for DFT calculations. The OER process in alkaline media involves the * , OH^* , O^* and OOH^* intermediates, where * stands for the active sites. Moreover, the step with the largest change in Gibbs free energy (ΔG) is considered to be the rate-determining step (RDS). As displayed in Fig. 4d, the RDS of CoOOH is the formation of OOH^* intermediate from the O^* , with the largest free energy barrier of 1.63 eV . For $\text{Mo}_2\text{TiC}_2\text{T}_x$, the OOH^* intermediate reacts with OH^- and further converts into O_2 is the RDS, with the largest free energy barrier of 2.76 eV . As for the $\text{CoOOH}/\text{Mo}_2\text{TiC}_2\text{T}_x$, the generation of O^* from OH^* is the RDS, and the free energy barrier is 1.41 eV . The reduction of RDS energy barrier reveals that the coupling of $\text{Mo}_2\text{TiC}_2\text{T}_x$ onto the CoOOH can optimize the intermediate adsorption and provide favourable OER kinetics, thereby enhancing the OER catalytic activity.

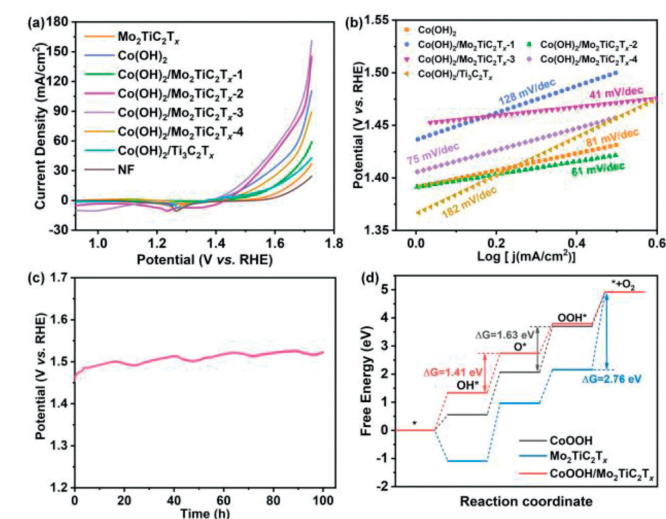


Fig. 4. OER performances of catalysts coated on NF: (a) Polarization curves. (b) The corresponding Tafel plots. (c) Chronopotentiometry of $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ at 10 mA/cm^2 . (d) Free energy diagram for OER process on catalysts.

tiometry curve at 10 mA/cm^2 (Fig. 4c) shows no significant change in OER activity over 100 h, indicating that the $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ has excellent long-term OER stability. Besides, the XRD and TEM were conducted to confirm the structure and morphology of $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x-3$ after a long-term chronopotentiometry test (Fig. S9 in Supporting information). By the analysis of post-OER characterization, $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ still presents the nanosheet morphology, while partially $\text{Co}(\text{OH})_2$ is oxidized to CoOOH during OER process. To reveal the OER intrinsic activity of the obtained catalysts, density functional theory (DFT) was performed to study the free energy of OER intermediates. In the calculation, the structural models of the reconstructed CoOOH , $\text{Mo}_2\text{TiC}_2\text{T}_x$ and $\text{CoOOH}/\text{Mo}_2\text{TiC}_2\text{T}_x$ heterostructure were established for DFT calculations. The OER process in alkaline media involves the * , OH^* , O^* and OOH^* intermediates, where * stands for the active sites. Moreover, the step with the largest change in Gibbs free energy (ΔG) is considered to be the rate-determining step (RDS). As displayed in Fig. 4d, the RDS of CoOOH is the formation of OOH^* intermediate from the O^* , with the largest free energy barrier of 1.63 eV . For $\text{Mo}_2\text{TiC}_2\text{T}_x$, the OOH^* intermediate reacts with OH^- and further converts into O_2 is the RDS, with the largest free energy barrier of 2.76 eV . As for the $\text{CoOOH}/\text{Mo}_2\text{TiC}_2\text{T}_x$, the generation of O^* from OH^* is the RDS, and the free energy barrier is 1.41 eV . The reduction of RDS energy barrier reveals that the coupling of $\text{Mo}_2\text{TiC}_2\text{T}_x$ onto the CoOOH can optimize the intermediate adsorption and provide favourable OER kinetics, thereby enhancing the OER catalytic activity.

In summary, we have successfully prepared $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets as efficient catalysts for OER via a simple MOF-derivative method at room temperature. The introduction of $\text{Mo}_2\text{TiC}_2\text{T}_x$ effectively optimizes the electronic structures of $\text{Co}(\text{OH})_2$, leading to improved reactivity and conductivity. Moreover, the hetero-nanosheets offer rich active sites and ensure structural stability. With these merits, the optimal $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ hetero-nanosheets deliver excellent OER performance and good stability. Besides, the OER activity of $\text{Co}(\text{OH})_2/\text{Mo}_2\text{TiC}_2\text{T}_x$ is superior to that of $\text{Co}(\text{OH})_2/\text{Ti}_3\text{C}_2\text{T}_x$, indicating the advantage of double transition metal carbide as a substrate material. Therefore, this work not only provides an economical and convenient strategy for designing advanced electrocatalysts for OER but also expands the breadth of study in double transition metal MXenes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2024.109774.

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