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Vertically Aligned MoS₂ on Ti₃C₂ (MXene) as an Improved HER Catalyst

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Abstract

We have demonstrated the microwave-assisted growth of vertically aligned interlayer expanded MoS₂ on conductive two-dimensional Ti₃C₂ MXene nanosheets (MoS₂⊥Ti₃C₂) and investigated the produced material as an electrocatalyst for the hydrogen evolution reaction (HER). MoS₂⊥Ti₃C₂ offers a unique inorganic hybrid structure that allows an increased exposure of catalytically active edge sites of MoS₂, compared to pure MoS₂ with a platelet-like morphology. The vertically aligned few-layer MoS₂ sheets have an expanded interlayer spacing of 9.4 Å. The MoS₂⊥Ti₃C₂ catalyst exhibited a low onset potential (-95 mV vs RHE) for the HER and a low Tafel slope (~40 mV dec⁻¹). The catalyst maintained a steady catalytic activity for the HER for over 20 hours.

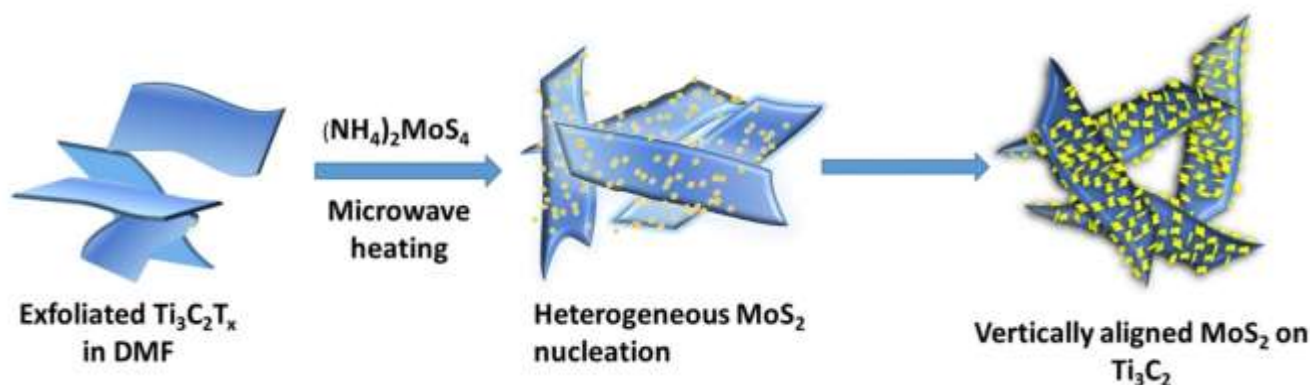
Text

The storage of electrical energy generated from solar to a large enough extent is still limited by the relatively low energy storage capacities of current devices, such as batteries. A feasible way to larger-scale storage is to use chemical bonds to store potential energy. Hydrogen is one of the most important molecules in the context of energy storage.¹⁻⁴ Using photovoltaics to convert solar energy to electric energy and using electrolyzers to reduce protons to hydrogen gas through water splitting is an attractive solution.⁵ Stable and efficient electrolyzers are an important part of the process and the search for Earth abundant materials that can catalyze the reduction of protons with the lowest possible energy is an active area of research.⁶

Theoretical investigations of the hydrogen evolution reaction (HER) have suggested that materials which display low binding free energies for atomic hydrogen ($\Delta G_{\text{H}} \sim 0$) are the most suitable candidates.⁷⁻⁸ In particular, it has been shown that the edge sites of 2-dimensional (2D) MoS₂ sheets are associated with ΔG_{H} values close to zero.^{6, 9-10} Relatively weak van der Waals forces bind the 2D MoS₂ sheets into a layered structure with an interlayer spacing of ~ 6.2 Å.¹⁰⁻¹² Two polymorphic forms of MoS₂ have been studied extensively for HER: the semiconducting 2H (trigonal prismatic co-ordination) and the metallic 1T (octahedral co-ordination) phase. 2H-MoS₂ is the more stable phase and prior research has shown that the basal plane of this phase is largely inactive towards the electrochemical HER.^{6, 9, 11, 13-14} The 1T-MoS₂ phase has been shown to have a higher electrical conductivity along both the basal plane and at its edges making it a better HER electrocatalyst than 2H-MoS₂.^{13, 15} The long term instability of 1T-MoS₂ for the HER has prevented 1T-MoS₂ from being an optimal catalyst. Thus, considerable effort has been expended to create 2H-MoS₂ nanostructures that optimize the exposure of edges and which exhibit an improved conductivity.¹⁶⁻²⁰

Recent research¹⁷ has shown that expansion of the interlayer spacing of MoS₂ improves HER catalysis.²¹ The growth of vertically aligned interlayer expanded MoS₂ (IE-MoS₂) on conductive substrates and scaffolds have been shown to lead to materials with efficient charge transfer from electrode to catalyst and more exposed edge sites.²² Many carbon based materials have been extensively studied as the conductive support for MoS₂ and other HER catalysts.²³⁻²⁵ Carbon nanotubes (CNTs),²⁶⁻²⁷ carbon cloth,²⁸⁻²⁹ graphene oxide/reduced graphene oxide (GO/rGO),^{18, 30-32} amorphous carbon supports,³³ and glassy carbon^{20, 34} have all been studied as support materials. In this study, we present

a novel method to grow vertically aligned MoS₂ directly on a 2D layered inorganic material, titanium carbide (Ti₃C₂) to further improve HER catalysis for IE-MoS₂. Ti₃C₂ belongs to the family of 2D transition metal carbides and nitrides, called MXenes.³⁵⁻⁴⁰ MXenes have the general formula M_{n+1}X_nT_x, where, M is an early transition metal (Ti, V, Nb, Mo, etc.), X is carbon or nitrogen, and *n* = 1-3. T_x is the surface termination group (typically -O, -OH or -F) left after the selective extraction of certain atomic layers in a top-down etching process of their precursors. More than twenty different MXenes have been synthesized and studied to date, such as Ti₂CT_x, Mo₂CT_x, Ti₃C₂T_x, V₂CT_x, Mo₂TiC₂T_x.³⁸ We drop the T_x notation referring to the surface termination when referring to the samples in the current study. MXenes are mostly metallic (conductivity is up to 9880 S/cm for Ti₃C₂),⁴⁰ because of their metal carbide core layers, and hydrophilic due to their surface terminations.³⁵⁻³⁷ Conductivity of Ti₃C₂ MXene, is higher than that of CNTs,



Scheme 1: Schematic of the synthesis process for the growth of vertically aligned IE-MoS₂/Ti₃C₂. In the first step, Ti₃C₂ flakes were homogeneously distributed in DMF by sonication and then (NH₄)₂MoS₄ was added to the Ti₃C₂ loaded DMF solution. Exposure of the (NH₄)₂MoS₄ and Ti₃C₂ containing solution to microwave radiation led to the nucleation and then vertically oriented growth of MoS₂ on the conductive Ti₃C₂ support.

graphene or GO materials, which makes it an excellent candidate to support MoS₂ catalyst for the HER.⁴⁰

Our hypothesis that motivates the present study is that vertically aligned IE-MoS₂ grown on Ti₃C₂ will serve as an excellent HER catalyst. The hypothesis rests largely on the realization that Ti₃C₂ exhibits a metal-like conductivity, likely making it a better substrate than GO for the growth of vertically aligned MoS₂.⁴¹⁻⁴² The conductivity between the substrate and catalyst is a crucial factor in determining the charge transfer kinetics of the catalyst. Exfoliated Ti₃C₂ MXenes provide a large surface area and moreover show better conductivity than reduced graphene/GO and most other 2D materials hence, Ti₃C₂ would make a superior substrate for the growth of MoS₂.^{24, 38, 40, 43-44} Furthermore, we hold out the possibility that a higher density of vertically aligned MoS₂ layers can be grown on Ti₃C₂ than can be grown on the more studied graphene support.^{18, 30-32, 45} The hydrophilicity of the MXene support can aid the binding of ionic precursors (MoS₄²⁻) on their surfaces and dispersion in polar solvents unlike hydrophobic graphene supports.

To grow vertically aligned MoS₂ on Ti₃C₂, we used a microwave assisted colloidal synthetic method. Ammonium tetrathio molybdate ((NH₄)₂MoS₄) in N,N-dimethyl formamide (DMF) was used as the precursor solution for IE-MoS₂.¹⁷ Microwaves interacting with charges on the MXene sheets generates the heat that help nucleate MoS₂ sheets on a support as depicted in Scheme 1.^{32, 46-48} Ti₃C₂ was expected to be an ideal surface for this process, since it provides metallic conductivity, a large surface area, and a charged surface for nucleation and growth of MoS₂. We support this contention by noting that prior studies have shown that Ti₃C₂ exhibits a very high absorption of electromagnetic waves (e.g., in the microwave region), even at very small thicknesses.⁴⁹⁻

⁵⁰ The synthesis of IE-MoS₂ vertically aligned on Ti₃C₂ (IE-MoS₂⊥Ti₃C₂) was achieved at four different temperatures (200, 220, 240, and 260 °C). For each growth temperature, the electrochemical performance of the IE-MoS₂⊥Ti₃C₂ for HER was determined. The heterostructures obtained at the different growth conditions were characterized with scanning electron microscopy (SEM), scanning tunneling electron microscopy energy dispersive spectroscopy (STEM-EDS), Raman spectroscopy, transmission electron microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and X-ray diffraction

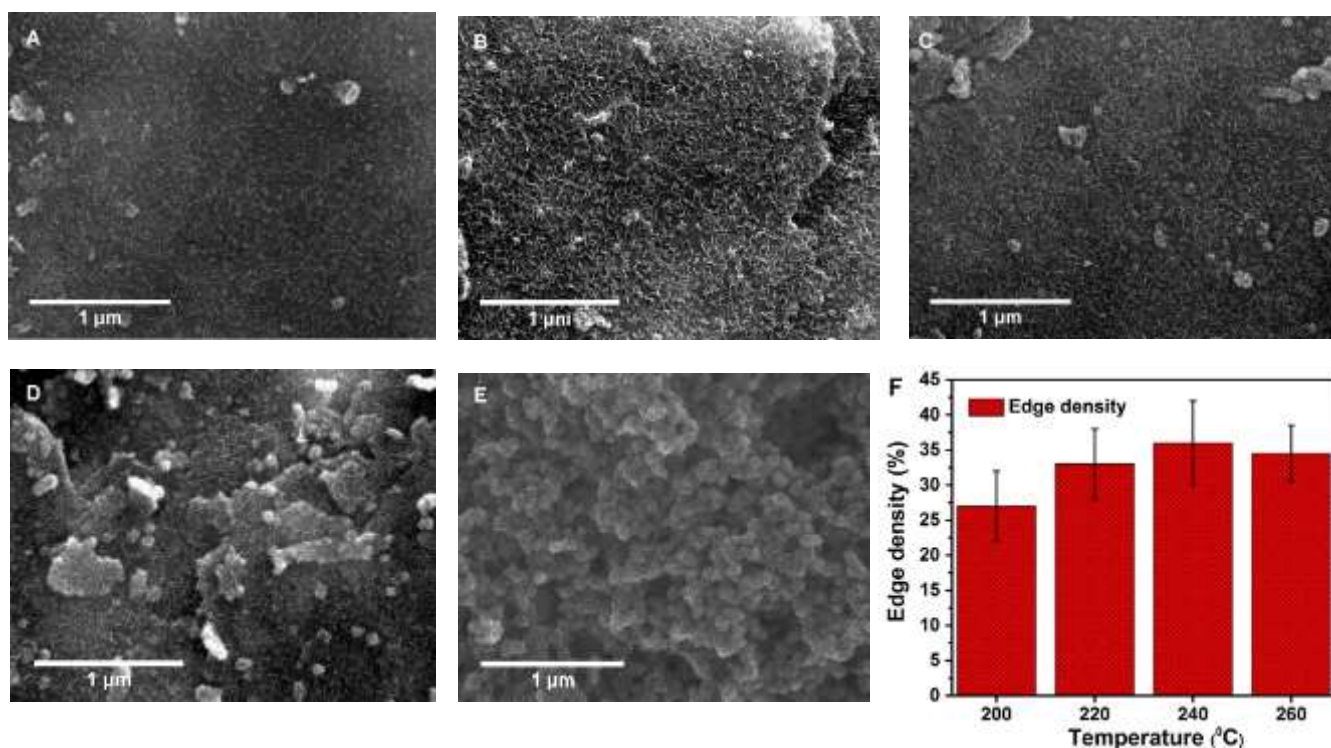


Figure 1: SEM micrographs of IE-MoS₂⊥Ti₃C₂ at growth temperatures of A) 200 °C, B) 220 °C, C) 240 °C, and D) 260 °C. E) IE-MoS₂ grown without the MXene substrate. F) Calculated % edge densities of MoS₂ sheets (see supporting information, Figure S1 and Table S1) based on the area of the images as a function of growth temperature. IE-MoS₂⊥Ti₃C₂@240 exhibits the highest edge density without flower-like aggregates (i.e., MoS₂⊥Ti₃C₂@260). Lower growth temperatures (e.g., 200 and 220 °C) result in lower MoS₂ edge densities.

(XRD).

SEM micrographs presented in Figure 1 provide direct evidence for the vertically aligned structural motif for IE-MoS₂⊥Ti₃C₂. Analysis of the images (Figure S1 and Table S1) also suggests that the vertically aligned MoS₂ sheets became denser (i.e., area of the edges of MoS₂ relative to the area of the Ti₃C₂ sheets) on the MXene support as the growth temperature was increased from 200 (i.e., IE-MoS₂⊥Ti₃C₂@200) to 240 °C (i.e., IE-MoS₂⊥Ti₃C₂@240). IE-MoS₂⊥Ti₃C₂@260 exhibited flower-like aggregates of MoS₂ coexisting with a vertically aligned MoS₂ component (Figure 1D), leading to a reduction in the density of vertically aligned edges of MoS₂ sheets, relative to IE-MoS₂⊥Ti₃C₂@240. We mention that a prior study by Wu *et al.* used a hydrothermal method to obtain vertically aligned MoS₂ on Ti₃C₂ MXene stabilized by carbon nanoplating.⁵¹ In contrast to the microwave synthesis approach, this prior study showed that the Ti₃C₂ MXene support, in the absence of carbon nanoplating, was unstable under hydrothermal synthesis conditions.

Our experimental observations from SEM suggest that at a microwave-assisted synthesis temperature of 260 °C there is some formation and nucleation of MoS₂ sheets in solution prior to binding to the MXene support. This homogeneous reaction would appear not to occur at a synthesis temperature of 240 °C where formation of MoS₂ sheets during microwave heating occurs exclusively at the MXene surface. At the lower synthesis temperatures (200 and 220 °C) we believe that incomplete reduction of the MoS₄²⁻ precursor within the reaction time of 2 h leads to the lower density of vertically aligned MoS₂ sheets. The atomic ratio, Mo:S, of IE-MoS₂⊥Ti₃C₂@240 obtained with EDS was ~1:2 (Figure S2 and S3) consistent with the growth of MoS₂ sheets. A STEM-EDS elemental map of IE-MoS₂⊥Ti₃C₂@240 (Figure S3) shows the distribution of Ti, Mo and

S on the MXene sheets. The SEM images suggest that a growth temperature of 240 °C is optimal for the synthesis of IE-MoS₂⊥Ti₃C₂, since it led to the highest density of vertically aligned sheets without the presence of flower-like aggregates (Figure 1F).

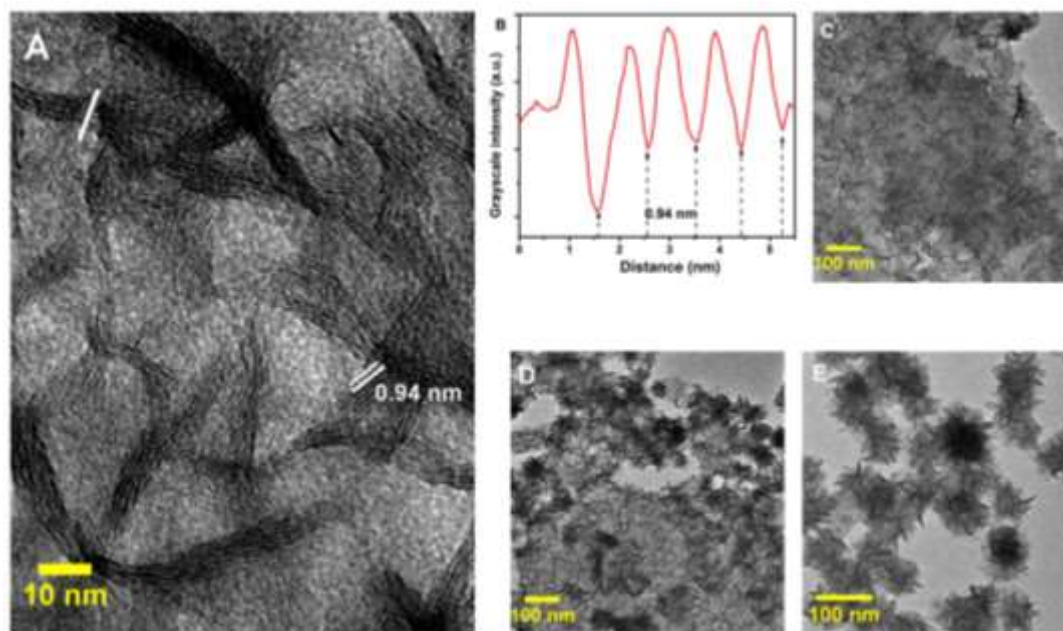


Figure 2: A) HRTEM of IE-MoS₂⊥Ti₃C₂@240 and B) Height profile of MoS₂ along the white line on image 2A, C) and D) TEM images of IE-MoS₂⊥Ti₃C₂@240 and MoS₂⊥Ti₃C₂@260 and E) IE-MoS₂ without the MXene support.

High-resolution TEM (HRTEM) (Figure 2A and Figure S4) was used to characterize the interlayer spacing of IE-MoS₂⊥Ti₃C₂. XRD was not useful for such a determination, since the relatively weak Bragg reflections of the MoS₂ component of IE-MoS₂⊥Ti₃C₂ were obscured by the strong reflections associated with the Ti₃C₂ support (Figure S5). TEM (Figure 2A) shows MoS₂ nano clusters with their edge-on morphology confirming the presence of vertically aligned clusters of sheets in IE-MoS₂⊥Ti₃C₂@240. The number of sheets making up the clusters ranged from two (i.e., a bilayer) to 10 layers. Contrast profiles of these stacked sheets in the HRTEM were used to determine the interlayer

spacing that was associated with IE-MoS₂∥Ti₃C₂@240 (Figure 2B). Analysis of these data show a uniform interlayer spacing of ~9.4 Å. This spacing does not vary with the synthesis temperature of IE-MoS₂∥Ti₃C₂ (see Figure S4 for samples synthesized at 200, 220 and 260 °C). Previous research showed that the microwave assisted synthesis of unsupported colloidal MoS₂ (using the same precursors as in this study) also gave rise to stacked MoS₂ with an interlayer spacing ~9.4 Å (an expansion of ~3.2 Å relative to 2H-MoS₂).¹⁷⁻¹⁸ To further validate this statement, we synthesized MoS₂ with no MXene (IE-MoS₂@260) and performed XRD on the resulting powder. Analysis of this material showed a similar interlayer spacing of ~9.4 Å (Figure S5). The expansion of the interlayer spacing could be due to the intercalation of oxidized DMF and/or to interlayer NH₄⁺ (retained from the (NH₄)₂MoS₄ precursor).¹⁷ TEM micrographs in Figure 2 also show that IE-MoS₂∥Ti₃C₂@240 (Figure 2C) is composed of uniform sheets of MoS₂ vertically aligned on the MXene substrate. With regard to IE-MoS₂∥Ti₃C₂@260, TEM shows the presence of flower-like aggregates of MoS₂ (Figure 2D) in addition to vertically aligned MoS₂ sheets, consistent with the SEM result shown above. These flower-like structures resemble the aggregates of IE-MoS₂ that grow in the absence of the MXene substrate (Figure 1E and 2E). As mentioned above, this morphology associated with IE-MoS₂∥Ti₃C₂@260 is likely due to the homogeneous nucleation of (NH₄)₂MoS₄ in solution at 260 °C in the presence of the microwave electromagnetic field interacting with the ion dipoles of MoS₄²⁻.^{17-18, 48}

Samples were further characterized with Raman spectroscopy. Figure S6 exhibits Raman data for IE-MoS₂∥Ti₃C₂@240, IE-MoS₂∥Ti₃C₂@260, and commercially purchased 2H-MoS₂. For the IE-MoS₂ samples, peaks at 402 and 376 cm⁻¹ are assigned to

the E_{12g}^1 and A_{1g} vibrational modes of MoS_2 , respectively. The peaks show a red shift relative to those analogous Raman features associated with 2H- MoS_2 (407 and 381 cm^{-1}) that does not have an expanded interlayer. A possible reason for this shift in vibrational frequencies is that the larger interlayer spacing for IE- $\text{MoS}_2 \perp \text{Ti}_3\text{C}_2$ reduces the coupling between the sheets (relative to reference 2H- MoS_2).^{17, 52-53} The intensity of the out-of-plane A_{1g} mode is greater than the in-plane E_{12g}^1 mode suggesting that IE- MoS_2 and IE- $\text{MoS}_2 \perp \text{Ti}_3\text{C}_2$ have abundant edge sites with less S-Mo-S interactions in between layers due to the relatively large interlayer spacing.¹⁷ XPS was used to identify the phase and the oxidation states of Mo, S and Ti. Characteristic Mo^{4+} peaks at binding energies of 228.8 and 231.8 eV, corresponding to $3d_{5/2}$ and $3d_{3/2}$ spectroscopic features, respectively, were observed in the fitted spectrum (SI Figure S8A). Moreover, a higher oxidation state Mo species ($\text{Mo}^{5+}/\text{Mo}^{6+}$) was apparent. The presence of $\text{Mo}^{5+}/\text{Mo}^{6+}$ oxidation states have been observed in previous studies and their presence is believed to be due to some oxidation of the $(\text{NH}_4)_2\text{MoS}_4$ precursor.³² S 2p XPS shows no oxidation of the S^{2-} groups (Figure S8B). We note that overall, the binding energies of Mo and S are lower in energy ($\sim 0.6\text{ eV}$) than those respective features associated with the semiconducting 2H- MoS_2 phase. This difference could conceivably be due to the differences in electronic structure (i.e., the metallic like 1T- MoS_2 phase versus the semiconductor 2H- MoS_2 phase). Ti-2p XPS shows a range of peaks assigned to various functional groups on the surface (Figure S7 and S8). Ti is primarily bonded to C and O, but spectroscopic features associated with Ti-F are present which presumably results from the etching process, that leads to at least a fraction of the Ti_3C_2 sheets being fluorine terminated.

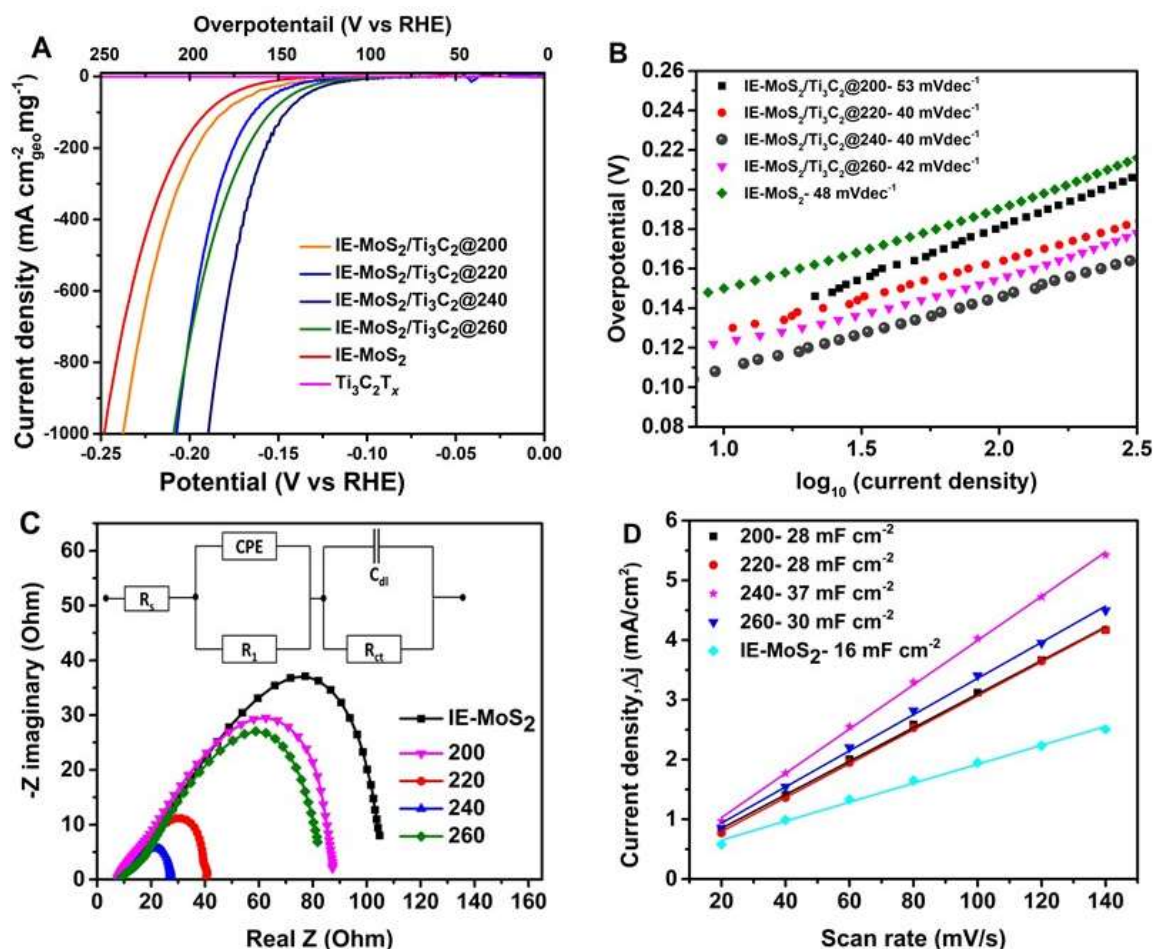


Figure 3: HER kinetics for samples prepared at different temperatures, A) polarization curves of heterostructures synthesized at 200, 220, 240, 260 °C, and IE-MoS₂ obtained at a scan rate 10 mVs⁻¹ in 0.5 M H₂SO₄, B) Tafel plots for the samples derived from the polarization plots of A, C) Impedance spectra (Nyquist plots) inset: equivalent circuit used to simulate the Nyquist plot where, R_s-solution resistance, CPE-constant phase elements, R₁-resistance in the catalyst, R_{ct}-charge transfer resistance and C_{dl}-double layer capacitance, D) scan rate vs current density (j_0) with C_{dl} values in the legend.

To prepare samples for the determination of catalytic activity for the electrocatalytic HER, MoS₂ with and without MXene support were individually drop-cast on a 3 mm diameter glassy carbon electrode with no added binder. The total mass loading of each sample was 0.071 mg cm⁻². As the heterostructure is composed of both MXene and MoS₂,

the samples were decomposed in nitric acid and the concentration of Mo and Ti were determined with Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES). We used this mass data to normalize the linear sweep voltammetry current densities for MoS₂ and MoS₂⊥Ti₃C₂ samples prepared at different growth temperatures. We believe that normalization based on mass is more revealing, since only the MoS₂ in the heterostructure is active towards HER.⁵⁴ Figure 3A (see Figure S9B for polarization plots with a graphite counter electrode) shows the cathodic polarization plots corrected for *i*R losses in solution. A polarization plot normalized to geometric surface area is included in the SI for comparison (Figure S10). Analysis of the polarization curves shows that the onset (η_0) for the HER for IE-MoS₂⊥Ti₃C₂@240 is ~95 mV (Figure 3A). It is noted that the polarization curves shown were obtained after cycling the catalyst 30 times between 0 and -0.70 V vs RHE (Figure S10B). After cycling, polarization plots with no background capacitive current in the non-faradaic region (i.e., before the onset potential) were obtained. The overpotential (η) to reach a current density of 10 mA/cm²mg for IE-MoS₂⊥Ti₃C₂@240 was 110 mV. At the same current density, IE-MoS₂ deposited on glassy carbon required an overpotential of ~160 mV to achieve a 10 mA/cm²mg current density. We attribute the increased catalytic activity (i.e., lower onset and overpotential) of IE-MoS₂⊥Ti₃C₂@240 for the HER relative to the unsupported MoS₂ to the ease of electron transfer from the substrate to the MoS₂ catalyst. Overall our results show that the current density at 50 mV beyond the onset potential of each sample increases with an increasing density of edge sites (Figure S11). The higher current densities observed for samples synthesized at higher temperatures at a given potential is a result of the availability of more active edge sites. With regard to the Tafel slope, another merit of

electrocatalytic performance, samples synthesized at 220, 240, 260 °C all had similar values ($\sim 40 \text{ mV dec}^{-1}$) to IE-MoS₂ (Figure 3B). The exception was IE-MoS₂⊥Ti₃C₂@200, which had a Tafel slope of 53 mV dec^{-1} . Based on our data, however, we cannot determine why this particular sample had a higher slope. Differences in Tafel slope are typically taken to indicate changes in reaction mechanism. Considering that all our samples contained vertically aligned IE-MoS₂, as the catalytic component, a change in mechanism would not be expected.

Figure 3C exhibits impedance spectra for all the samples investigated in this study. The impedance spectra are not perfect semi circles, implying that there is a charge transfer resistance (R_{ct}) between the electrolyte and the catalyst, as well as a resistance in the catalyst and the substrate (R_1). The charge transfer resistance R_{ct} is lower (6.8Ω) for MoS₂⊥Ti₃C₂ compared to MoS₂ alone ($\sim 48 \Omega$) for the stimulated circuit shown in the inset of Figure 3C. The higher impedance for IE-MoS₂⊥Ti₃C₂@260 is not surprising given the heterogeneity and agglomeration of MoS₂ sheets into nano flower-like aggregate structures for this sample. The lower charge transfer resistance between the MXene and MoS₂ sheets helps improve the catalytic activity of the MoS₂⊥Ti₃C₂ hybrid system. It has been suggested in prior research that the IE motif of MoS₂ allows the MoS₂ sheets to act as monolayer sheets which can allow isotropic electron transfer from substrate to the MoS₂ sheets.¹⁷ This effect is more pronounced in IE-MoS₂⊥Ti₃C₂ which provides a better conductivity for the MoS₂ sheets with the current supplying cathode, reducing R_{ct} for the heterostructures relative to IE-MoS₂ directly deposited on the glassy carbon electrode. The electrochemical double layer capacitance (C_{dl}) value is widely used to determine the electrochemically active surface area (ECSA) of electrocatalysts (Figure

S12), since the value of the C_{dl} is proportional to the ECSA.⁵⁵⁻⁵⁷ Our data show that all the samples (Figure 3D) have at least twice the active surface area compared to IE-MoS₂. The improved activity for IE-MoS₂⊥Ti₃C₂@240 is also reflected by it having the highest ECSA value among all the samples in this study. Chronopotentiometry was used to evaluate the stability of the electrocatalysts during the HER. Figure S13 shows the chronopotentiometric curve for IE-MoS₂⊥Ti₃C₂@240 and IE-MoS₂ for a reaction time of 20 h, carried out at a current density of 10 mA cm⁻²_{geo}. Both samples show excellent catalyst stability, with each sample showing less than a 7% change in the potential required to maintain 10 mA cm⁻² during the 20 h period. Polarization plots obtained after the stability test (Figure S14) showed little difference from the respective polarization plots obtained before the test.

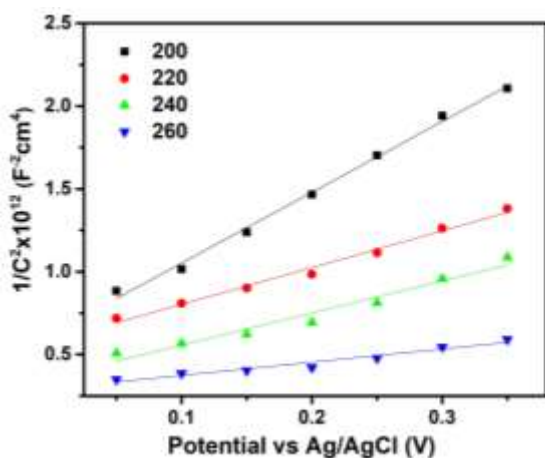


Figure 4: Mott Schottky plots for MoS₂⊥Ti₃C₂ heterostructures prepared at different temperatures of 200, 220, 240 and 260 °C obtained in 0.5 M Na₂SO₄.

The presence of a Schottky-like barrier (metal-semiconductor junction) between the metallic Ti_3C_2 and semiconducting MoS_2 can have an effect on the onset potential for the $\text{MoS}_2 \perp \text{Ti}_3\text{C}_2$ samples. We believe the difference in the onset potential for samples at different temperatures to be a result of the energy barrier for charge transfer between the MXene and MoS_2 interface. The carrier concentration of the different $\text{MoS}_2 \perp \text{Ti}_3\text{C}_2$ samples were investigated using the linear region of the Mott Schottky plots. The inverse value of the slope of these plots is proportional to the carrier density of the catalyst.⁵⁸⁻⁶⁰ Analysis of the data shows that there is a direct correlation between the charge carrier concentration and the activity of the samples. The positive slopes of the Mott Schottky plots in Figure 4 are characteristic of n-type semiconductors.^{58, 60-61} The formation of a Schottky barrier can result in an energetic penalty for electron transfer. The lower the barrier, the faster the electron transfer between the interface and catalyst. With a higher carrier concentration in MoS_2 this barrier would be more like a metal-metal junction with no barrier, thus causing enhanced electron transfer.⁶⁰ For samples synthesized at higher temperatures (240 and 260 °C) the carrier density is significantly higher than the samples synthesized at lower temperatures (200 and 220 °C). The carrier concentrations are summarized in Table S2.

Table 1: Comparison of onset potentials and Tafel slopes of studies on vertically aligned MoS₂ synthesized on different substrates.

Catalysts	Synthesis technique	Onset potential (mV vs RHE) ^d	Tafel slope (mV/dec)	Ref.
^a VA-MoS ₂ on Glassy carbon	Thermal evaporation	-250	105-120	Kong <i>et al.</i> ²⁰
^b VO-MoS ₂ on carbon cloth	Solvothermal	-100	50	Yan <i>et al.</i> ²⁹
MoS ₂ nanoparticles on graphene	Solvothermal	-100	41	Li <i>et al.</i> ³¹
IE-MoS ₂ on ^c GO/rGO	Microwave	-75	63	Chatti <i>et al.</i> ³²
Self-templated 1T-2H MoS ₂	Solvothermal	-119	60	Xiang <i>et al.</i> ³³
1T-MoS ₂ on glassy carbon	Thermal evaporation	-110	44	Wang <i>et al.</i> ³⁴
VA-MoS ₂ on carbon cloth	Hydrothermal	-100	39	Zhang <i>et al.</i> ²⁸
IE-MoS ₂ on rGO	Microwave	-117	42	Sun <i>et al.</i> ¹⁸
MoS ₂ on Ti ₃ C ₂ with carbon nanoplating	Hydrothermal	-20	45	Wu <i>et al.</i> ⁵¹
IE-MoS ₂ on Ti ₃ C ₂ MXene	Microwave	-95	40	This work

(^a VA-vertically aligned, ^b VO- vertically oriented, ^c GO-graphene oxide). ^d Onset potentials were derived from their respective Tafel plots.

Conclusions

Table 1 summarizes the results from relevant literature for vertically aligned MoS₂ on a range of substrates. A comparison of the HER onset for IE-MoS₂⊥Ti₃C₂@240 to those obtained in prior studies for other vertically aligned samples shows that IE-MoS₂⊥Ti₃C₂@240 is one of the most active materials to date. It is noted that while IE-MoS₂⊥Ti₃C₂@240 exhibits a relatively low overpotential for the HER, the value is comparable to vertically aligned MoS₂ on reduced graphene oxide.³² We mention that

MoS₂ grown on carbon nanoplated Ti₃C₂⁵¹ exhibits a low onset potential of -20 mV, but it is noted that in the same study the hydrothermal synthesis of MoS₂ on MXene without nanoplating led to oxidation of Ti₃C₂ and a relatively high onset potential of -260 mV. Based in part on this comparison, we contend that the microwave synthetic method for IE-MoS₂∥Ti₃C₂ detailed in this contribution is a scalable and relatively fast synthetic method using Earth abundant materials to produce a highly active MoS₂ catalyst for the HER. The improved activity is attributed to the enhanced conductivity between the highly conductive MXene and IE-MoS₂ and also the higher carrier densities in the MoS₂ and higher number of exposed edges of the catalyst. This high activity taken together with the excellent stability of the IE-MoS₂∥Ti₃C₂ catalyst makes the material a potentially attractive electrocatalyst for HER in the context of clean energy generation.

Conflicts of interest

“There are no conflicts to declare”.

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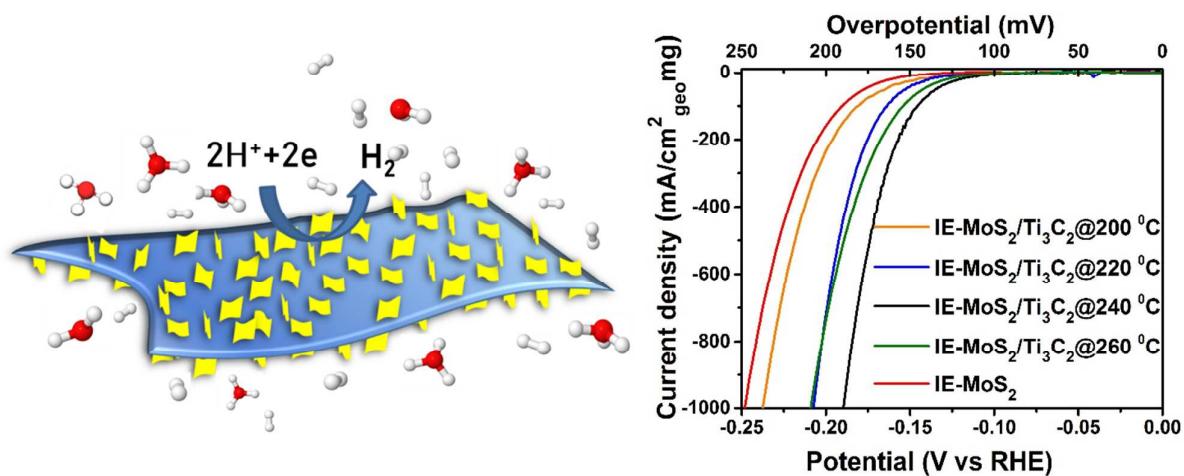
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BRIEFS. Vertically aligned interlayer expanded (IE) MoS₂ on Ti₃C₂T_x (MXene) support as an efficient electrocatalytic HER catalyst.



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