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ORIGINAL REPORT



Study of unique and highly crystalline MoS₂/MoO₂ nanostructures for electrochemical applications

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ABSTRACT

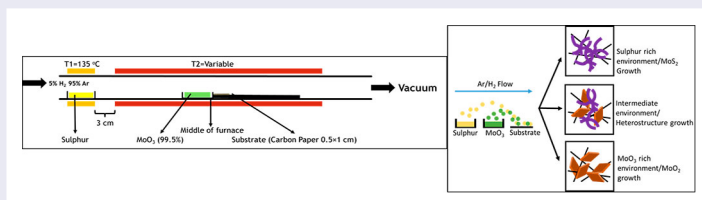
We report the synthesis of a spectrum of highly crystalline molybdenum sulphide/oxide-based materials such as MoS₂ (2-H), MoO₂ and unique hybrid MoS₂/MoO₂ nanostructures through chemical vapour deposition (CVD). The as-fabricated samples were scrutinized with materials characterization techniques. Our results reveal that, by tuning growth parameters, different samples demonstrate unique morphologies, which can be unequivocally tied to their chemical composition. We also explore their potential application as electrochemical catalysts, which we found that in addition to using large specific surface area and conductive substrate to improve interlayer conductivity, chemical heterogeneity and efficient charge transport are also essential for good catalytic activity.

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KEYWORDS

MoS₂/MoO₂; hybrid structures; nanoflowers; nanoflakes; electrocatalyst



IMPACT STATEMENT

We successfully fabricated an array of uniquely shaped MoS₂/MoO₂ nanostructures through a one-step chemical vapour deposition process. The practical application of said nanostructures as electrochemical catalysts has also been demonstrated.

1. Introduction

The scientific community is dedicated to find energy generation schemes other than fossil fuels, as they cause pollution and will eventually deplete [1]. Hydrogen evolution reaction (HER) is showing great promise as a source of clean, renewable hydrogen fuel [2–4]. However, energetically efficient effective hydrogen production requires an electrocatalyst. Noble metals, such as Platinum and Palladium, exhibit some of the best electro-catalytic properties [5,6], but their high price and limited availability make them unfeasible for large-scale implementation [7]. As such, cheaper and more abundant materials have been studied as potential alternatives. Examples include cobalt phosphide, nitrogen-infused carbon nanotubes,

nickel phosphide, molybdenum carbide and transition metal dichalcogenides etc. [8–12]

Among the transition metal dichalcogenide, molybdenum disulphide (MoS₂), has been intensively studied for its promise as an effective HER catalysis [12,13]. It is widely believed that bulk MoS₂ has poor HER activity for lacking exposed active edges and having poor interlayer conductivity, hence enormous efforts have been dedicated to acquire favourable morphologies such as nanosheets, nanoparticles [14–16] and nanocomposites [17,18] and to improve the conductivity by using conducting substrates [19–21]. Despite these efforts, however, relatively little attention has been spent on studying the effect of MoS₂ crystallinity and chemical composition

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on the HER performance. There are many contradictory reports stating that pure crystalline MoS₂ samples possess little, if any, catalytic activity [22–25]; the apparent HER performance was due to incorporation of MoO₂ impurities/composites. These arguably counter-intuitive results beckon a systematic approach. We present in this work, therefore, a comprehensive study on the MoS₂/MoO₂ composite material.

We are able to synthesize various crystalline nanostructures with tuneable compositional variation such as MoS₂ nanoflowers, MoO₂ nanoflakes and MoS₂/MoO₂ heterostructures/hybrid on porous carbon paper by direct chemical vapor deposition (CVD) growth. The substrate is thoughtfully chosen to ensure maximum electrode-electrolyte contact and good current transport. We systematically studied the correlation between morphology, composition and HER activity of the nanostructures through a set of material characterization and electrochemical techniques. Our results show that despite many exposed edges and highly conductive substrate, less HER activity is observed from MoS₂ nanoflowers. MoS₂/MoO₂ heterostructures/hybrid show better HER

performance, where MoO₂ nanoflakes show the best. As such, we can glean, from the HER performances of these samples, an unambiguous corollary that MoS₂ by itself does not exhibit much activity. In other words, our work confers a tenacious testament to the speculation on the inadequacy of MoS₂ catalytic activity. We show that the best MoS₂ based material for HER may actually be a heterostructure/hybrid of MoS₂ and MoO₂ with properly tuned stoichiometry.

2. Experimental details

The samples were fabricated through CVD process with controlled parameters such as temperature, carrier gas mass flow. The as-fabricated samples were characterized by X-ray Photoelectron Spectroscopy (XPS), X-Ray-Diffraction (XRD), Scanning Electron Microscopy (SEM), Raman spectroscopy and High-resolution transmission electron microscopy (HRTEM) and were investigated for their HER activity. Full detailed CVD growth study can be found in the supplementary document.

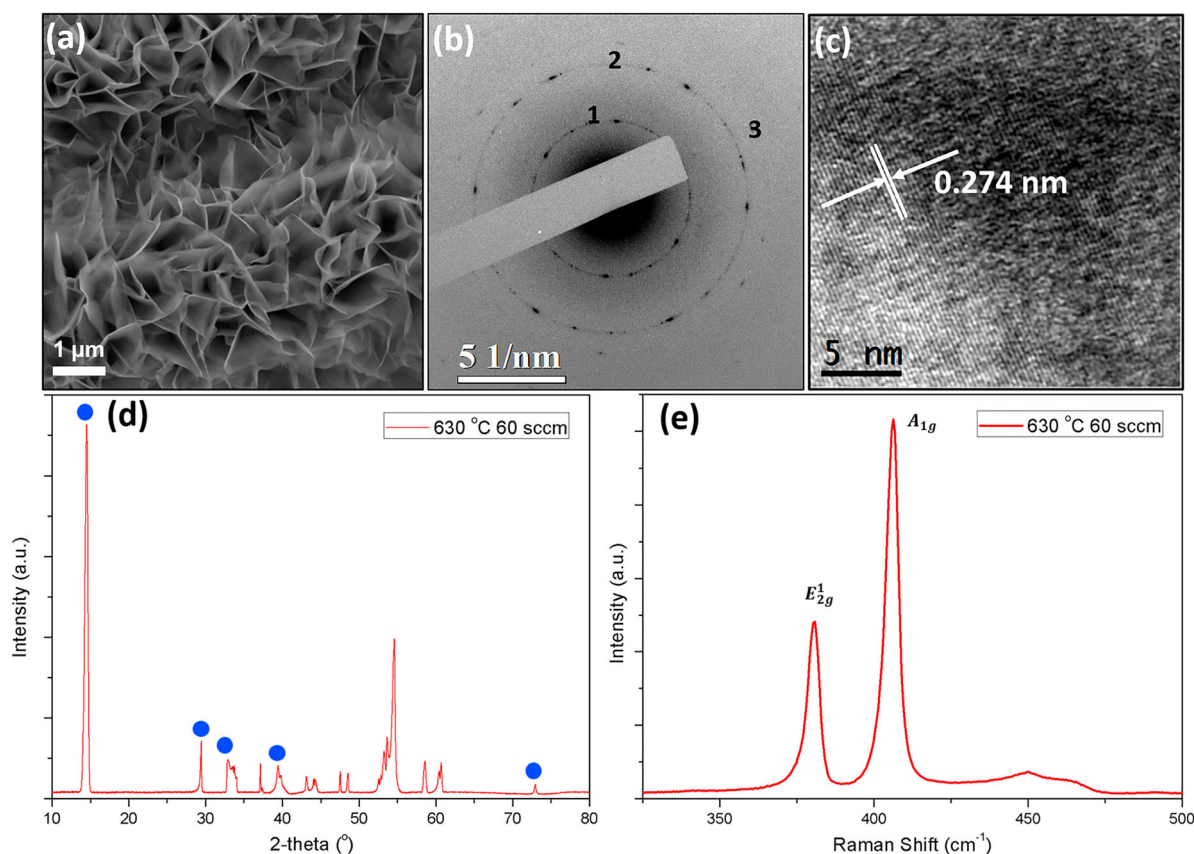


Figure 1. (a) SEM image of the distinct nanoflower structures. (b) SAED pattern on nanoflowers shows the polycrystalline rings 1, 2 and 3 which attribute to the (100), (110) and (200) of 2-H MoS₂ respectively. (c) HRTEM image of single nanoflowers shows the d- spacing of 2-H MoS₂ (100). (d) XRD exhibits the respective 2-H MoS₂ peaks (marked with the blue dot). (e) Raman spectroscopy reveals the high degree of crystallinity.

3. Results and discussion

Our samples display unique morphologies under SEM; the morphologies can be grouped under three motifs: nanoflowers, nanoflakes and a hybrid that exhibit both. Material characterizations, especially XRD and TEM, can evidently distinguish the motifs and each motif can be specifically correlated to a certain composition. Namely, nanoflowers have a MoS_2 composition; nanoflakes have a MoO_2 composition, and hybrid displays an intermediate composition between $\text{MoO}_2/\text{MoS}_2$.

Figure 1 (a) shows the SEM image of the distinct nanoflower motif grown at 630°C and 60 sccm. The TEM-energy dispersive X-ray (EDX) elemental mapping images shown in Figure S3 exhibit uniform distributions of Mo and S components throughout the nanoflower structure. The selected area electron diffraction (SAED) pattern (Figure 1(b)) on nanoflowers shows the polycrystalline rings 1, 2 and 3 which attribute to the (100), (110) and (200) of 2-H MoS_2 respectively [JCPDS-77-1716]. The HRTEM image (Figure 1 (c)) of single nanoflowers shows the d- spacing of 2-H MoS_2 (100). The XRD pattern in Figure 1 (d) clearly reveals the characteristic (002), (004), (100), (103), (110) peaks of 2-H MoS_2 at

respective 2θ angles (marked with the blue dot) [26]. The unmarked high peak at around $2\theta = 54.5^\circ$ corresponds to the carbon paper substrate and other unmarked peaks may be due to impurities. The TEM and XRD results confirm the high degree of crystallinity of the nanoflowers. Raman spectroscopy in Figure 1 (e) corroborates the above results as it displays peaks at Raman shift of 382 and 406 cm^{-1} , which corresponds to the E_{2g}^1 and A_{1g} shift of MoS_2 [27].

Figure 2(a) is the SEM image of the nanoflakes motif growth at 650°C and 50 sccm. The bright field low magnification TEM image of the nanoflakes is shown in Figure 2(b). The HRTEM image of single nanoflake along the $[\bar{1}2\bar{3}]$ zone axis and its Fast-Fourier Transform (FFT) (Figure 2(c) insert) show the d- spacing of monoclinic MoO_2 ($\bar{1}11$), which confirms the highly crystalline nature of the flakes. As shown in Figure 2(d), the XRD pattern of this sample, shows the characteristic MoO_2 (011), (200), (022), (130), (131), (311), and (040) peaks at respective 2θ angle (marked with blue square) [JCPDS 76-1807] which supports the TEM results. Raman spectroscopy (Figure 2(e)), however, is able to pick up signals from both MoO_2 and MoS_2 resonant modes [28]. This is perhaps due to surface sulphidation and the mechanism of

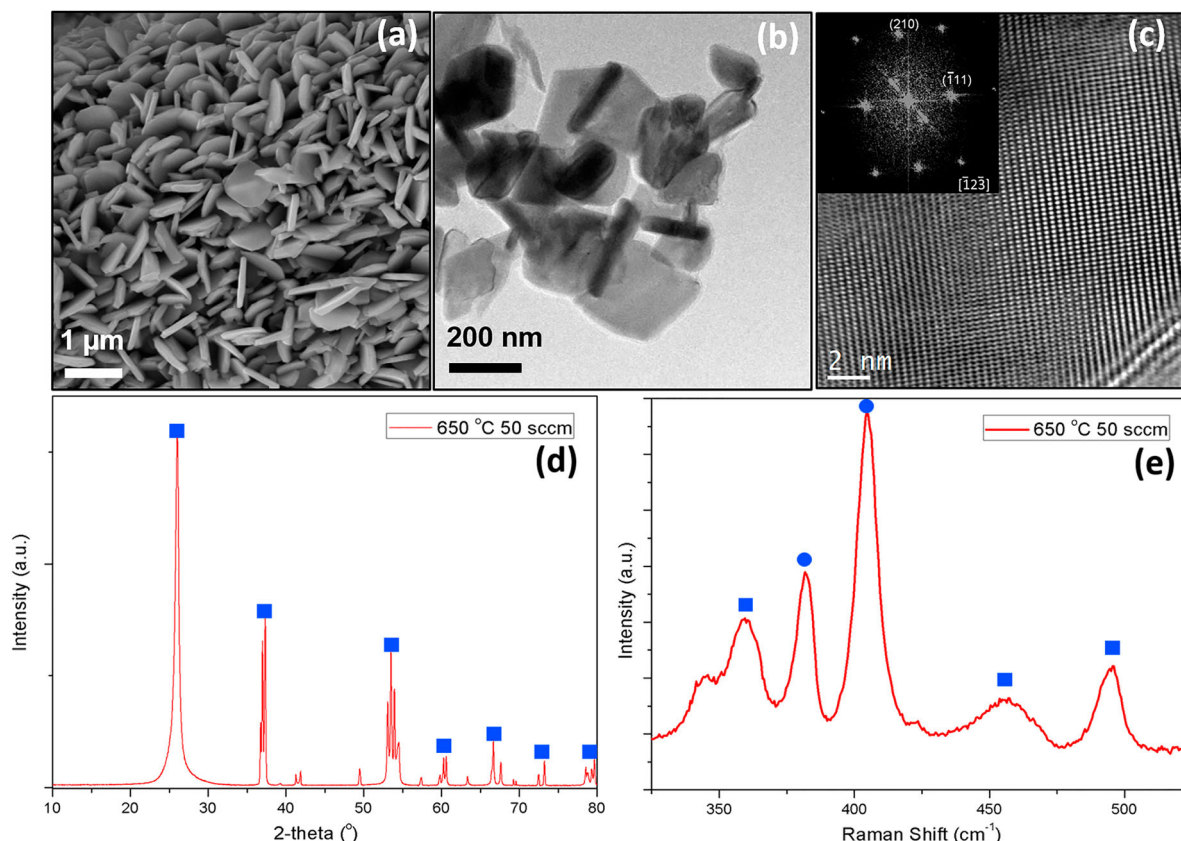


Figure 2. (a) SEM image and (b) Bright-field low magnification TEM image shows the nanoflakes (c) HRTEM image of single nanoflake taken along the $[\bar{1}2\bar{3}]$ zone axis and its FFT (inset Figure) show the d- spacing of Monoclinic MoO_2 ($\bar{1}11$). (d) XRD exhibits the crystalline MoO_2 phase (marked with the blue square). (e) Raman spectroscopy shows signals from both MoS_2 (blue dot) and MoO_2 (blue square).

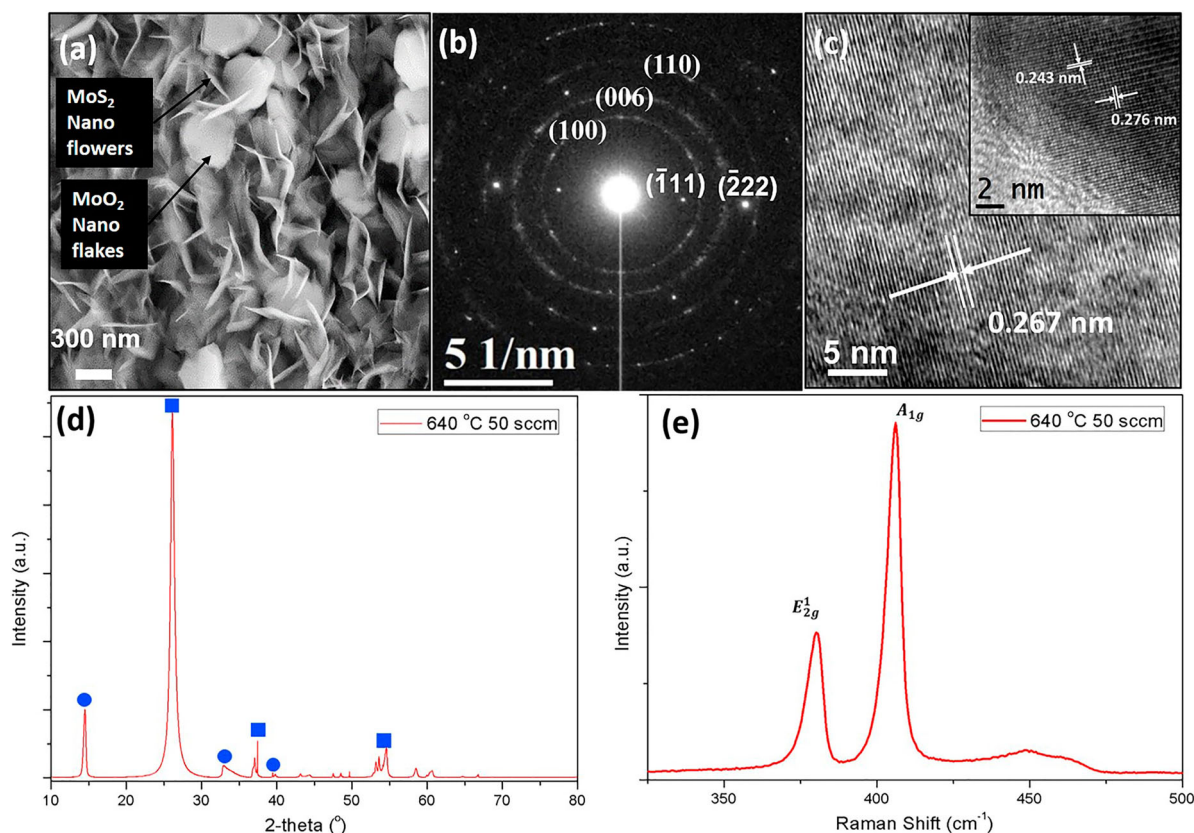


Figure 3. (a) SEM image featuring both nanoflowers and nanoflakes morphology (b) SAED pattern on the heterostructures shows the polycrystalline rings and crystalline spots which attributed to planes of 2-H MoS₂ and monoclinic MoO₂ respectively. (c) HRTEM images of a single nanoflower and single nanoflake (inset Figure) show the d-spacing correspond to (101) plane of 2-H MoS₂ and (002) plane of monoclinic MoO₂ respectively. (d) XRD exhibits both 2-H MoS₂ peaks (marked with the blue dot) and MoO₂ peaks (marked with the blue square). (e) Raman spectroscopy shows a dominant MoS₂ signal, corresponding to the largely nanoflowers (MoS₂).

competing growth, which corroborates to the XPS study (Figure 4)

For the sample with hybrid chemical composition grown at parameters of 640°C and 50 sccm, the characterizations are summarized in Figure 3. Figure 3(a) is the SEM image revealing the presence of both nanoflakes and nanoflower structures. The SAED pattern of the heterostructures shows the polycrystalline rings and crystalline spots (Figure 3(b)). The rings are attributed to (100), (006) and (110) planes of 2-H MoS₂ [JCPDS-77-1716]. The crystalline spots are attributed to the ($\bar{1}11$) planes of monoclinic MoO₂. The HRTEM images of a single nanoflower and single nanoflake (inset Figure) show the d-spacings correspond to the (101) plane of 2-H MoS₂ and the (002) plane of monoclinic MoO₂ respectively (Figure 3(c)). The XRD pattern (Figure 3(d)) reveals characteristic MoO₂ (011), (200), (022) peaks (marked with the blue square) at the respective 2θ angle [JCPDS 76-1807] in conjunction with 2-H MoS₂ peaks (marked with the blue dot) [26,29]. TEM and XRD results confirm the formation of highly crystalline MoS₂-MoO₂ heterostructures. Raman

spectroscopy (Figure 3(e)) shows a dominant MoS₂ signal correspond to nanoflowers, which again can be attributed to the surface sulphidation and competing growth mechanism.

In XPS data (Figure 4), we can observe that the MoS₂ (Mo⁴⁺), MoO₂ (Mo⁴⁺), and MoO₃ (Mo⁶⁺) peaks can be found in all of the three samples. This is perhaps due to the fact that, on the surface of the sample, the competing growth mechanism (see part 3, supplementary document) dictates that the sulphides and oxides, as well as just-evaporated precursor vies with each other to be deposited on the substrate. Since we supplied our source materials in abundance (to ensure no particular reagents runs out before reaction terminates), as the reaction stops and furnace temperature drops, the materials at the surface ‘freeze’ and cannot be driven to complete reaction, hence we see the residues of all three materials (MoS₂, MoO₂, and MoO₃). However, we still can observe a trend consistent with other characterizations. That is: the MoO₂ to MoS₂ peak ratio increases from the MoS₂, to the hybrid and finally to the MoO₂ sample. This further proves the fact that, by tuning our growth parameters, we

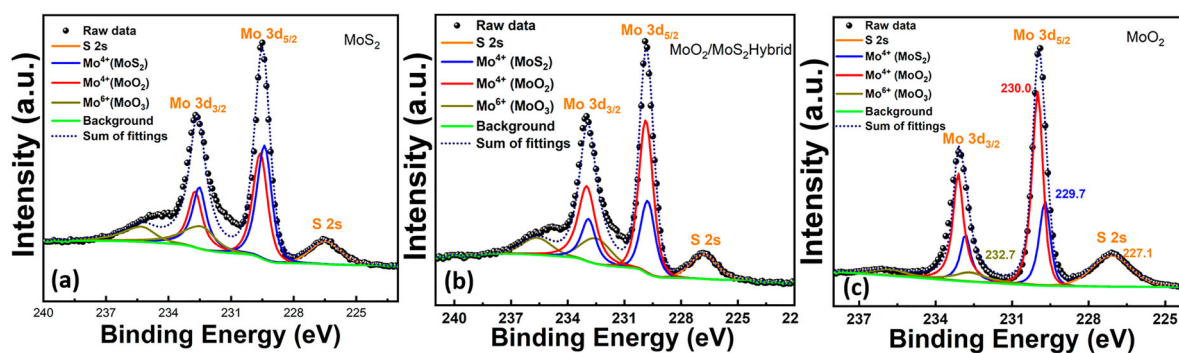


Figure 4. XPS studies of (a) MoS₂ (b) MoO₂/MoS₂ Hybrid and (c) MoO₂.

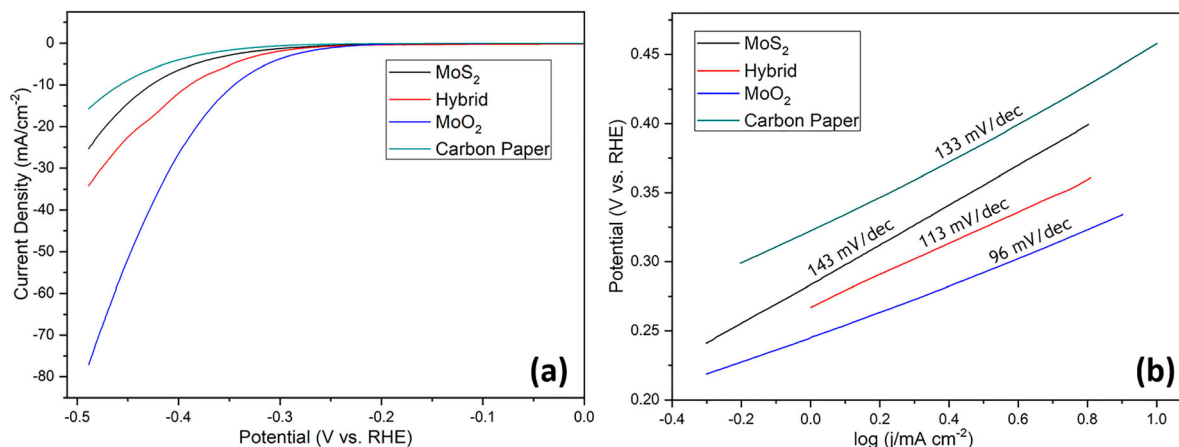


Figure 5. (a) Linear polarization curves of the three samples and (b) the corresponding Tafel plot. It can be clearly observed that the crystalline MoS₂ sample is, in fact, the worse performing sample, showing a Tafel gradient that is even larger than the carbon paper control sample.

are able to shift the balance of reactants on the sample surface, and hence ultimately determine and control the composition of the bulk material. The sulphur 2p_{3/2} and 2p_{1/2} peaks and the overall detailed binding energy information can be found in the supporting document (Figure S4 and Table S1).

Figure 5(a) is a summary of HER linear polarization curves for the three samples and Figure 5 (b) is the corresponding Tafel plot. One salient observation is that the crystalline MoS₂ (630°C 60 sccm) shows worse performance than either MoO₂ (650°C 50 SCCM) or the hybrid (640°C 50 sccm), having a current density of 25 mA/cm² at 0.5 V overpotential. The Tafel plot also shows lowest performing MoS₂ with gradient at 143 mV/dec, which is even higher than that of the carbon paper control sample (possibly due to the increased resistance as MoS₂ is not a conductor). Our HER results are similar to works done by Yao et al. and Ruiz et al. [30,31], with Tafel slopes around 90 mV/dec. However, in our study we found, contrary to these authors, that MoS₂ alone might not be sufficient for good HER performance, even with the copiously exposed edges; the role of MoO₂ can be quite important. This

notion corroborates well with the study of Jiang et al. and Yang et al. [32,33], where they also find the importance of MoO₂ as a catalyst support (in Jiang's case, the MoO₂ is used to support the active Ruthenium, a noble metal). As such, we are able to conclude quite decisively from our study, that the combination of MoO₂ support/interface with MoS₂ is the best strategy towards HER efficiency.

As mentioned before, our motivation is to verify the contended view that MoS₂ is not an innate electrocatalyst. While our result does testify this view, we believe this phenomenon can be explained further through a two-fold reasoning. First, several studies have postulated that MoS₂ is merely the basis to provide the truly active apical and terminal S²⁻ ions, and chemical heterogeneity is required to facilitate the formation of those ions [22,23,28,34]. A large degree of chemical heterogeneity is often observed in solution-processed amorphous samples which accounts for their often superior performance in HER activity [28]. Second, 2H MoS₂ is a semiconductor with a bandgap of 1.67 eV [35]; it is not known for having good electrical conductivity regardless of its morphology [36–38]. However, the efficiency

of the electrochemical process (i.e. HER) depends on the efficiency of its individual component steps and charge transport efficiency is one of them [39]. The poor conductivity of MoS₂ could mean that the transport step becomes rate-limiting, and hence compromises the overall efficiency. On the other hand, MoO₂ has been shown to possess metallic properties [40] with low electrical resistivity. The bulk and surface MoO₂ content (shown by XRD/TEM/XPS) may permit efficient charge transport and less potential drop. In addition, XPS shows that the MoO₂ sample does have surface sulphur content, which will provide the active apical S²⁻ ions. Our HER result exhibits a positive linear dependence of catalytic activity on the proportion of MoO₂ implying that the transport efficiency could indeed be rate-determining. Greater MoO₂ content while still maintaining surface sulphur presence might be the best strategy towards HER efficiency.

4. Summary and conclusions

We are able to synthesize samples through the vacuum CVD method with a well-studied growth mechanism; the manipulation of input parameters (temperature and flow rate) permits us to control the chemical composition of grown samples. Characterizations with TEM, SEM, Raman spectroscopy, XPS and XRD reveal the distinct and unique morphologies corresponding to the different chemical compositions. HER testing of the samples demonstrates that crystalline 2-H MoS₂ is chemically inert, and the HER activity comes from the chemical heterogeneity of MoO₂. The inclusion of MoO₂/MoS₂ heterogeneity works much more favourably for its promotion of the active apical S²⁻ ions and its better transport efficiency, resulting in an overall improvement of HER activity. Our work testifies the inadequacy of MoS₂ working as the sole catalyst and suggests prospective directions for better materials engineering to improve HER activity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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