Study of unique and highly crystalline MoS$_2$/MoO$_2$ 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 MoS$_2$ (2-H), MoO$_2$ and unique hybrid MoS$_2$/MoO$_2$ 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.

IMPACT STATEMENT
We successfully fabricated an array of uniquely shaped MoS$_2$/MoO$_2$ 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 (MoS$_2$), has been intensively studied for its promise as an effective HER catalyst [12,13]. It is widely believed that bulk MoS$_2$ 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 conductive substrates [19–21]. Despite these efforts, however, relatively little attention has been spent on studying the effect of MoS$_2$ crystallinity and chemical composition...
on the HER performance. There are many contradictory reports stating that pure crystalline MoS$_2$ samples possess little, if any, catalytic activity [22–25]; the apparent HER performance was due to incorporation of MoO$_2$ impurities/composites. These arguably counter-intuitive results beckon a systematic approach. We present in this work, therefore, a comprehensive study on the MoS$_2$/MoO$_2$ composite material.

We are able to synthesize various crystalline nanostructures with tuneable compositional variation such as MoS$_2$ nanoflowers, MoO$_2$ nanoflakes and MoS$_2$/MoO$_2$ 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 MoS$_2$ nanoflowers. MoS$_2$/MoO$_2$ heterostructures/hybrid show better HER performance, where MoO$_2$ nanoflakes show the best. As such, we can glean, from the HER performances of these samples, an unambiguous corollary that MoS$_2$ by itself does not exhibit much activity. In other words, our work confers a tenacious testament to the speculation on the inadequacy of MoS$_2$ catalytic activity. We show that the best MoS$_2$ based material for HER may actually be a heterostructure/hybrid of MoS$_2$ and MoO$_2$ 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](image-url)

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 MoS$_2$ respectively. (c) HRTEM image of single nanoflowers shows the d-spacing of 2-H MoS$_2$ (100). (d) XRD exhibits the respective 2-H MoS$_2$ 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 MoO$_2$/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 2$\theta$ 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 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 [123] zone axis and its Fast-Fourier Transform (FFT) (Figure 2(c) insert) show the d-spacing of monoclinic MoO$_2$ (111), 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 2$\theta$ 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.](image-url)
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 MoS$_2$ [JCPDS-77-1716]. The crystalline spots are attributed to the $(11\bar{1})$ planes of monoclinic MoO$_2$. The HRTEM images of a single nanoflower and single nanoflake (inset Figure) show the d-spacings correspond to the (101) plane of 2-H MoS$_2$ and the (002) plane of monoclinic MoO$_2$ respectively (Figure 3(c)). The XRD pattern (Figure 3(d)) reveals characteristic MoO$_2$ (011), (200), (022) peaks (marked with the blue square) at the respective 2$\theta$ angle [JCPDS 76-1807] in conjunction with 2-H MoS$_2$ peaks (marked with the blue dot) [26,29]. TEM and XRD results confirm the formation of highly crystalline MoS$_2$-MoO$_2$ heterostructures. Raman spectroscopy (Figure 3(e)) shows a dominant MoS$_2$ signal corresponding to nanoflowers, which again can be attributed to the surface sulphonation and competing growth mechanism.

In XPS data (Figure 4), we can observe that the MoS$_2$ (Mo$^{4+}$), MoO$_2$ (Mo$^{4+}$), and MoO$_3$ (Mo$^{6+}$) 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 (MoS$_2$, MoO$_2$, and MoO$_3$). However, we still can observe a trend consistent with other characterizations. That is: the MoO$_2$ to MoS$_2$ peak ratio increases from the MoS$_2$, to the hybrid and finally to the MoO$_2$ sample. This further proves the fact that, by tuning our growth parameters, we
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\textsubscript{3/2} and 2p\textsubscript{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 Mo\textsubscript{S\textsubscript{2}} sample is, in fact, the worse performing sample, showing a Tafel gradient that is even larger than the carbon paper control sample.

**Figure 4.** XPS studies of (a) Mo\textsubscript{S\textsubscript{2}} (b) Mo\textsubscript{O\textsubscript{2}}/Mo\textsubscript{S\textsubscript{2}} Hybrid and (c) Mo\textsubscript{O\textsubscript{2}}.

**Figure 5.** (a) Linear polarization curves of the three samples and (b) the corresponding Tafel plot. It can be clearly observed that the crystalline Mo\textsubscript{S\textsubscript{2}} sample is, in fact, the worse performing sample, showing a Tafel gradient that is even larger than the carbon paper control sample.

As mentioned before, our motivation is to verify the contended view that Mo\textsubscript{S\textsubscript{2}} 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 Mo\textsubscript{S\textsubscript{2}} is merely the basis to provide the truly active apical and terminal S\textsuperscript{2−} 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 Mo\textsubscript{S\textsubscript{2}} 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.

Acknowledgement

Y.J., H.Y.W, A.R., S.J.P. and D.H.C.C., acknowledge the partial support from Ministry of Education (Grant numbers: R284-000-142-112, R284-000-150-112) and National Research Foundation, Prime Minister’s Office, Singapore under its Competitive Research Programme (CRP Award No. NRF-CRP 10-2012-6). Y.J. would like to acknowledge NUS Research Scholarship funding.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

Y.J., H.Y.W, A.R., S.J.P. and D.H.C.C., acknowledge the partial support from Ministry of Education - Singapore [grant number R284-000-142-112], [grant number R284-000-150-112] and National Research Foundation Singapore, Prime Minister’s Office, Singapore under its Competitive Research Programme (CRP Award No. NRF-CRP 10-2012-6). Y.J. would like to acknowledge NUS Research Scholarship funding.

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