Towards molecular doping effect on the electronic properties of two-dimensional layered materials

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Abstract. In recent advancements of an atomically-thick, flat, and flexible two-dimensional (2D) material has attracted tremendous interest. Graphene and 2D layered semiconductors such as transition-metal dichalcogenides (TMDs) pave the way on the exploration of their unique layer-number dependent electronic and optical properties. The latter have a promising future on the microelectronics due to their sizeable bandgaps, i.e., the crossover from indirect-direct bandgap transition occurs as the thickness of TMDs is decreased to a monolayer. In this work, we systematically investigated the optimum growth parameter of chemical vapor deposition of MoS² and WSe², respectively. It turns out that the temperature and the duration growth plays role to produce a large area of TMDs monolayers. Our studies suggest that a well-controlled high quality of TMDs could serves as template and interlayer in the TMD-organic heterointerfaces. Thus it is potentially an attractive approach towards a wide-ranging application in optoelectronics, nanoelectronics and energy-harvesting applications.

1. An attempt of molecular doping of two-dimensional layered dichalcogenides

Recent significant interest of two-dimensional (2D) layered materials is fueled by the birthmark of graphene monolayer and its rich physical phenomenon [1-3]. Inorganic graphene analogues such as two-dimensional layered atomic structure transition metal dichalcogenides (TMDs) have attracted tremendous amount of effort by the condensed matter community [4-7]. In terms of electronic structure, graphene pose a semimetal behavior which is eventually led to a lack of bandgap and thereby hindering its promising practical applications. In the other hands, 2D layered materials possessed remarkable semiconducting properties such as a tunable bandgap via controlling number of layers, strain-mediated or chemical stoichiometric compositions.

The most intense recent subjects of TMDs so called MoS² have been dictated so far aiming for an optimum growth parameter of large single crystals and simultaneously preserving the quality of an atomically-thick film. Another class of TMDs, tungsten diselenides (WSe₂) is also potentially intriguing as their electronic properties could lead to the avenues of valley and spin polarization studies [8,9]. Monolayer WSe₂ has shown a smaller band gap than a monolayer MoS₂ (1.65 eV versus 1.8 eV) [3-9], whereas their bulk bandgaps showed a similar value of about 1.2 eV. Interestingly, single-layer TMDs is widely known to present a rather unique signature in its optical spectrum. It
manifested a strong photoluminescence (PL) signal due to indirect-direct bandgap transition as the layered structure is down to a monolayer-thick [2]. Taking these advantages, respective approaches could be dedicated to implement these materials in optoelectronic devices such as photodetectors, light-emitting diodes and photovoltaics. However, a niche growth method of particularly WSe$_2$ is seems lacking. In this regard, a well-controlled synthesis of both TMDs is prerequisite for its tremendous promising application in many areas of energy storage, electronics, photonics, catalysis and biomedical applications.

It is of interest that a controlled-molecular doping could potentially harness the feasibility of the electronic properties of 2D-TMDs beyond the regular electrically-control means. The emergence of the molecular-dopant studies of TMDs perpetually attracted numerous efforts [10-14]. The addressed question is how one could realize the existence of noncovalent interactions between the organic molecules and the underlying basal plane of TMDs. It is worth noting to mention that the molecule-substrate interaction in this system is subtle. That is, the bandgap of TMDs can be efficiently affected as the orientation of the evaporated organic molecules could exhibit a fully-stacked or slightly tilted with respect to the surface. For example, Yu Jing *et al.* demonstrated that the optical properties of MoS$_2$ significantly enhances when TCNQ molecules were deposited onto TMDs substrate [14]. In order to evaluate such observation, a large and homogenously TMDs surface is required to facilitate a systematically intriguing charge-transfer study. Therefore, our focus consist of two parts: An optimization of robust method to growth MoS$_2$ and WSe$_2$ using chemical vapour deposition (CVD) technique, respectively. Second, a highlight of our preliminary results in terms of TMDs-molecule heterointerface is a CVD-grown WSe$_2$ is suspended on a highly ordered pyrolytic graphite (HOPG) surface using wet transfer technique. Thus, we investigate the topographic and electronic properties by means of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) at low temperature.

2. Experimental methods used in this study

The high yield quality of two-dimensional layered materials is needed in this investigation. Therefore, we focused on systematically investigated the optimum parameters to grow two TMDs: MoS$_2$ and WSe$_2$ based on CVD technique.

2.1. CVD growth of monolayer and few layer MoS$_2$ and WSe$_2$

Both materials were synthesized using the same furnace with their respective heating profile and stoichiometric ratio. A heating zone furnace (OTF-1200X, MTI Corp.) was used to grown TMDs samples. A highly purity of MoO$_3$ (99%, Aldrich) and Sulphur powder (99.5%, Alfa) were placed in two separate Al$_2$O$_3$ quartz boat crucibles. Si/SiO$_2$ substrate was oriented face-down and situated on the upper side of MoO$_3$ powder. Surface substrate was treated with standard chemical cleaning prior to use. Quartz reaction tube was flushed with N$_2$ gas for 5 min prior to pre-heating. The MoS$_2$ flakes were fabricated using a furnace temperature with a heating rate of 15 °C/min to reach 105 °C. The heating zone was kept at this temperature for 30 min with constant gas rate of 300 sccm. Then it was followed by ramping to 660 °C at 15 °C/min with 20 sccm. Then the gas was changed to the N$_2$ (16 sccm) and H$_2$ (4sccm) mixed gas. The furnace was ramped to 700 °C at 15 °C/min and kept at this temperature for 5 min and slowly cooled down to reach 570 °C without feedback gas for 20 min. During the growth procedure, furnace pressure was kept in atmospheric condition. The temperature furnace is naturally cooling down after the reaction was completed. For WSe$_2$ samples, selenium powders (440 mg, 99.5% Sigma-Aldrich) and WO$_3$ powders (260 mg, 99.5% Sigma-Aldrich) were used. The temperature heating profile is slightly different than MoS$_2$ in which the furnace was ramped in 33 min from room temperature to reach 850 °C. The whole process is maintained with a constant gas flow of N$_2$ (72 sccm) and H$_2$ (8 sccm). We kept the temperature for 5-15 min and the remaining procedure is similar to the previous MoS$_2$ sample preparation.
2.2. Optical characterization of the CVD-grown samples
Optical micrographs were measured using Olympus BX51. The Raman and photoluminescence (PL) spectra of the CVD grown-TMDs flakes were performed in alpha300 R Witec equipped with a confocal spectrometer using 532 nm excitation laser. Typical laser spot is 1-2 µm. The morphological studies of the flakes were characterized using a commercial atomic force microscopy (AFM, BRUKER Dimension FastScan). A standard cantilevers with spring constant of 40 N/m and tip curvature <10 nm was used as a probe.

2.3. Wet-transfer technique
For the substrate transfer, the WSe\textsubscript{2} film on Si wafer was first coated with a layer of PMMA (950K, A3) by spin-coating (step 1: 500 rpm for 10 s; step 2: 2000 rpm for 70 s), followed by baking at 130 °C for 2 min. The PMMA at the edge of SiO\textsubscript{2}/Si substrate was gently peeled out at the corner using a knife in order to facilitate the following exfoliation of PMMA-capped MoS\textsubscript{2} from substrate. Subsequently, NaOH (3 mol/L) solution at 100 °C was used to exfoliate PMMA-capped MoS\textsubscript{2} from SiO\textsubscript{2}/Si. PMMA-supported MoS\textsubscript{2} film was immediately transferred to deionized (DI) water to remove the etchant and residues. HOPG substrate was then used to ‘fish out’ the PMMA-capped MoS\textsubscript{2} film. It was followed by drying on a hot-plate (75 °C for 5 min and then 100 °C for 10 min). The PMMA was removed by acetone and cleaned by isopropyl alcohol (IPA).

2.4. STM measurements
The experiments were performed in a custom-built multichamber ultra-high vacuum (UHV) system housing Omicron LT-STM equipped by a Nanonis controller. The base pressure was kept above 10\textsuperscript{-10} mbar. An electrochemically-etched tungsten tip was used to probe the samples. The working temperature is maintained at 77K during the entire measurements. The STM images were recorded in constant current mode with tunneling current in the range 60-70 pA. For dI/dV spectra, the tunneling current was obtained by a lock-in amplifier, with a modulation of 625 Hz and 40 mV.

3. Experimental result
CVD technical process in this study is partially performed by referring to van der Zande et al. [15] in combination with Lee et al. [16] procedure. Further details of CVD process can also be found in references herein [17-21]. Our contribution is employing an emphasis that the growth temperature can be very crucial for a successful synthesis of large area of TMDs monolayer. Here, we have varied a different growth temperature profile from 750 °C up to 950 °C to investigate their influence to the output monolayer MoS\textsubscript{2} flakes size. It turns out that when both precursors (MoO\textsubscript{3} and sulphur) were heated in the range of 850 °C, the optimum formation of a high yield distribution of single and few-layers of MoS\textsubscript{2} is achieved as illustrated in Fig. 1(a). A common triangular island of MoS\textsubscript{2} is clearly shown under optical microscopy. Further, some area were displayed the triangular-shaped islands that span its dimension from a few to 20 micron meter shown in Fig. 1(b). Although our triangular-shaped size is relatively smaller than the existing records [15-16], this could be governed by the current furnace geometry. Our furnace zone poses a rather limited separation between the involved precursors (~11 cm). Thus it basically hampered our ultimate goal to produce much large and homogenous single layer of MoS\textsubscript{2} onto a designated substrate. Nevertheless, it is worthwhile to mention that the triangular island of CVD-grown MoS\textsubscript{2} is reasonably promising as it is potentially merged into a large stacked-grain depicted in the half-part of Fig. 1(a).

The origin of triangular shape is unambiguously reflecting the symmetry of the intrinsic feature of inorganic 2D-TMDs crystal [2-5,10]. According to its crystal structure, three atomic layers of X-M-X of TMDs composed the height profile with the range of 0.6-0.9 nm has been widely reported in both mechanically exfoliated and CVD-grown monolayer TMDs [5,10] Interestingly, Fig. 1(c) shows typical AFM topographic inspection extracting a lateral height of 3 nm. This is correspond to the cross sectional depicted in Fig. 1(d)). In other words, this means that our sample could be comprised of trilayers. Thus, in the following complimentary techniques such as optical-based characterizations were thoroughly carried out to evaluate further in a rather large inspection area.
We next performed photoluminescence emission and Raman response as indicated in Fig 1(e) and Fig 1(f), respectively. As a result, two emission signals, namely, a small shoulder at 610 nm and a broad peak centered close to 660 nm were observed in PL spectrum in which these signatures of MoS$_2$ monolayer are in agreement with the findings of Mak et al. [2] and Splendiani et al. [21]. The addressed peaks are associated to the direct band gap originating from the intrinsic nature of the K point of the relevant Brillouin zone. Interestingly, another MoS$_2$ sample showed an outstanding strong emission signal manifested in the PL spectrum that eventually surpassed the detection limit of our instrument as illustrated in the inset Fig. 1(e). In addition, we have also performed several measurements in different area suggesting that indeed the formation of CVD-grown area covered by a monolayer of MoS$_2$ flakes. Fig 1(f) displays Raman spectrum implies that a monolayer of MoS$_2$ was successfully formed. The peculiar characteristic of in plane (E$_{2g}^1$) phonon mode and out-of-plane (A$_{1g}$) phonon mode were recognized at 398.77 cm$^{-1}$ and 418.30 cm$^{-1}$, respectively. Thus the different between the two (~ 19 cm$^{-1}$) has been used to identify the monolayer of MoS$_2$. Our results is fairly agrees with the previous findings in literatures [23-25]. It is emphasizing the fact that a typical thickness in our sample is predominantly covered the SiO$_2$/Si substrate in single-layer fashion.

Figure 1. CVD growth and microscopic characterization of monolayer MoS$_2$. (a) Optical microscopy image at large area. (b) High yield triangular shaped islands of MoS$_2$. (c) 30 x 30 µm$^2$ AFM image of
single monolayer of MoS$_2$ (d) Cross sectional extracted from grey line as indicated in Fig. (c). (e) Photoluminescence spectrum collected from laser spot size of 1µm. The inset depicted another PL spectrum collected from another area with a high and a strong emission signal. (f) Raman spectrum taken with 532 nm excitation laser.

Figure 2. CVD growth and microscopic characterization of monolayer WSe$_2$. (a) Optical microscopy depicted triangular shaped island of WSe$_2$. (b) 30 x 30 µm$^2$ AFM phase image of pyramid-like structure of MoS$_2$. Inset shows the topographic image of similar scanning range. (c) Cross sectional extracted from black line as indicated in Fig. (b). (d) A corresponding lateral profile close to the center of pyramid-like structure of WSe$_2$ as indicated in the blue line Fig (b). (f) Raman spectrum taken with 532nm excitation laser shown the main phonon modes of WSe$_2$. (g) The evolution of three subsequent Raman peaks that are largely concentrated at the vicinity of 350-385 cm$^{-1}$.

A rather distinguished feature was observed in the attempt to grow WSe$_2$ on SiO$_2$/Si surface. In contrast to the previous case, the crystalline size ranges from 5-11 µm with the most common dimension is approximately ~7 µm. The formation of a relatively small size of WSe$_2$ is hindered due
to less reacted of selenium powder in comparison to the sulphur case. Energetically, the typical separation between the precursors should be larger than 55 cm such that the chemical reaction is thermodynamically favorable toward the formation of large WSe$_2$ flakes. The regular trigonal shape of island was observed in the topographic image as shown in the inset Fig. 2(b). Interestingly, a simultaneous phase image exhibited a pyramid-like feature in which the smallest step height close to 30 nm (~equal to 33 layers from Fig. 2(c)) can be extracted from the black dashed line at the edge of structure.

This multi-thick layer of WSe$_2$ formation could be mediated due to two-fold. First, substrate effect, as the SiO$_2$/Si is reasonably rough compare to the other flat and well-ordered epitaxy such as sapphire. Secondly, low concentration of the reactants. Despite such formation, we also observed that the two cross sectional profiles blue and red lines in Fig. 2 (d) and (e) reflects unequivocally single layer of WSe$_2$ was formed at the center of pyramid-like structure. This finding is usually addressed to a screw-dislocation-driven (SDD) growth fashion that previously reported by Chen et al. [26]. Unlike MoS$_2$, Raman characterization of WSe$_2$ monolayer revealing two Raman active modes at 250 cm$^{-1}$ and a small shoulder of $A_{1g}$ phonon mode close to 261 cm$^{-1}$ as presented in Fig. 2 (f). For multilayered WSe$_2$, the van der Walls interaction between adjacent layers manifested in the Raman spectrum as a distinguished peak at 308 cm$^{-1}$ [27, 28]. In our experiment we did not observe such appearance in Raman spectrum shown in Fig. 2 (g). This finding is in agreement with the earlier reports in which the softened phonon mode was decreased from few-layer down to monolayer. In addition, there are three additional Raman peaks concentrated in the region of 360 cm$^{-1}$ – 400 cm$^{-1}$ that we can be assigned from the evolution of the inactive $B_{2g}$ phonon mode. It conclusively indicated that a true single layer formation was largely established.

We have investigated, in a systematic way, the role of growth temperature to the output size of triangular crystal-shaped of WSe$_2$. Fig. 3 exhibited a temperature dependence study of WSe$_2$ grown on SiO$_2$/Si surface with a series of sample CVD-grown at the different temperature ranges from 750-900 $^\circ$C. In this case, we observed several trends that the growth temperature is unambiguously play important role to obtain a large domain flakes size. Initially, most of the product was composed of particles as depicted in Fig. 3(a) and (b). As the temperature raise to 810-850 $^\circ$C, the triangular shaped island was formed as depicted in Fig. 3 (c) and (d). However, the shape of triangular island of WSe$_2$ is started to form hexagonal and much irregular shape at the growth temperature 900 $^\circ$C shown in Fig 3 (e). The resulted crystal size as a function of growth temperature is depicted in Fig.3 (f). Based on the statistical analysis of several flakes, we determine that growth temperature at 850 $^\circ$C is the most reliable parameter to form a continuous triangle domain-shape of WSe$_2$. 
Figure 3. Temperature dependence of the average triangular size of WSe$_2$. (a) Optical micrograph at 750 °C. (b) Optical micrograph at 780°C. (c) Optical micrograph at 810°C. (d) Optical micrograph at 850 °C. (e) Optical micrograph at 900 °C. (f) Summary of the average triangular size vs temperature.

We performed scanning tunneling microscopy (spectroscopy) of the CVD-grown WSe$_2$ as a profound result for integrating organic molecules in the later stage. First, we relocate the TMDs surface onto a conducting substrate such as highly ordered pyrolytic graphite (HOPG) using wet transfer technique (further detail can be found in the method). Fig. 4 (a) displays the large scan area which gives an idea that the as-transferred WSe$_2$ flakes were successfully embedded on HOPG. The upper part of the image was covered by a single layer of WSe$_2$ as the extracted cross-sectional profile of the grey line indicated a value of 5 Å. In Fig. 4 (b), whereas the below region is HOPG surface as their exclusively identified with its regular honeycomb lattice structure depicted in Fig 4. (c). A submolecular resolution implies the well-known formation of hexagonal symmetry with the periodicity of ~ 3.4 Å (shown in Fig. 4 (d)). This finding is in agreement with the early study of the atomic resolution of WSe$_2$ using STM technique [29,30]. Further, we examined the electronic properties of WSe$_2$ by means of STS method. Indeed, we are able to gain information that electronic bandgap of WSe$_2$ is close to 1.91 eV as shown in Fig. 4 (f). It is of great interest that this value is quite comparable to a direct band gap that can infer a WSe$_2$ thickness is down to a single layer.
4. Conclusions
In summary, we performed a systematical study to grow monolayers of MoS$_2$ and WSe$_2$ directly on SiO$_2$/Si substrates using CVD technique. Within our furnace geometry, a simultaneous feedstock of the transition metal oxides and the dichalcogenides powders as source materials heated with an optimized growth temperature of 700 °C and 850 °C exhibiting a monolayer of MoS$_2$ and WSe$_2$, respectively. Thus, the typical grown-crystal flake ranges from 5-12 µm in length. We confirmed the
existence of monolayer flakes based on the photoluminescence and Raman investigation that unambiguously dictated a characteristic feature of their respective TMDs case. Using wet transfer technique, we successfully embedded WSe$_2$ monolayer that intentionally serves as an interlayer and templating agent on HOPG surface. Subsequently the topographic and the electronic properties were studied using STM/STS technique. Thus we are one step closer to our ultimate goal in the corresponding research field, that is, a direct access of tuning the electronic properties of organic molecules on atomically-thin layered dichalcogenide materials.

Acknowledgements
Arramel acknowledges MOE Tier 3 WBS number R-143-000-625-112 for financial support. The NUS Centre for Advanced 2D Materials and Graphene Research Centre is greatly thankful for facilitating the wet-transfer, optical and topographic measurements.

5. References
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