

Effect of Precursor on Growth of MoS₂ Monolayer and Multilayer

Shraddha Ganorkar, Jungyoon Kim, Young Hwan Kim and Seong-II Kim*

Abstract—The rise of two-dimensional (2D) material is one of the results of the successful efforts of researchers which laid the path to the new era of electronics. The size and dimensionality will reveals the new limits of electronic devices and applications. One of the most exciting materials is MoS₂. In the last few years the MoS₂ has been studied extensively to understand its chemical kinematics and possible practical applications. Synthesis has been always a major issue as electronic devices need reproducibility along with similar properties for mass productions. Chemical vapor deposition (CVD) is one of the successful methods for 2D materials including graphene. Much of this research is still in its infancy, but this and other techniques will be developed and improved in the near future. Furthermore, there are various starting materials available for Mo and S source. The different source has different effects on the layers and morphology of MoS₂ films. In this work, we have extensively studied the CVD technique to grow few layers of MoS₂ with different starting materials and compare their results. We investigated the results of two precursors MoO₃ and MoCl₅, show remarkable changes. The MoO₃ source gives a triangular shaped MoS₂ monolayer with Raman-shift $\Delta k=21.5\text{ cm}^{-1}$ while that of MoCl₅ can achieve uniform MoS₂ without triangle. The photoluminescence spectra of monolayer MoS₂ grown from MoO₃ shows absorption peaks at 1.83 eV (675.73 nm) and 1.99 eV (621.78 nm). While bilayer MoS₂ film from MoCl₅ precursor shows absorption at 1.88 eV (657.44 nm) and 2.04 eV (605.10 nm). The film synthesized by MoCl₅ is more continuous and it would be a good choice for device applications. Eventually, we tried to explain the formation of continuous monolayer of MoS₂ without any triangle on the basis of chemical reaction formalism mostly like due to one step reaction process and formation of MoS₂ from gas phase to the solid phase.

Keywords—2D Materials, MoS₂ monolayer, CVD, Raman Spectra

I. INTRODUCTION

SILICON is the backbone of semiconductor industries from the last few decades. Owing to its remarkable properties like tunable bandgap (via doping) and switchable conductivity via magnetic or electric fields, temperature and even mechanical deformation; silicon behaves as ideal material for transistor or sensing device. This traditional semiconductor

now faces a daunting task. The new era of the high power and nano size are forcing electronic devices to reach new limits in fabrication. With the miniaturization of transistors (expected 14 nm in this year) the issues like short channel effects and defects densities will become harder to hold back. When the electronic industries seeking for a new material, the rise of 2D materials gave a light of hope.

Just over 10 years ago, isolation of graphene [1], the very first 2D carbon, a strong contender rose as a 2D device material. It has the extraordinary property of high electron mobility, excellent optical transmittance, thermal conductivity, large Young's modulus and chemical inertness [2]-[4]. These properties are highly sought after in a semiconducting industry. However, lack of a band gap and metallic behavior rules it out as a semiconductor. A strong bandgap engineering required for graphene for which it suffers its other properties. Nevertheless, graphene triggered a great deal of attention towards the 2D material. The search of 2D materials has thus grown to encompass other materials which exhibit similar properties to graphene and traditional semiconductors.

Among the new systems transition metal chalcogenides (TMCs) has shown the very similar properties demanded by electronic devices. One of the TMCs, molybdenum disulfide, MoS₂, has a similar layer structure like graphene, the hexagons consist of covalently bonded Mo and S atoms. The Mo layer is covalently sandwiched between two S layers to give S-Mo-S layers which are stacked over each other by Van der Waals forces. It is an excellent candidate for device fabrication. It is well known that structures with nanometric dimensions have different electronic, chemical, optical and magnetic properties. Similar way, monolayer of MoS₂ has vastly different properties as compared to its bulk counterpart. Bulk MoS₂ has an indirect band gap of 1.29 eV while that of its monolayer has a large direct band gap of 1.8 eV [5]. The layered structure enables MoS₂ to have a tunable band gap based on the number of layers grown. Theoretical studies have also predicted the tunable band gap also possible with external electric field [6]. There are several sparkling properties of MoS₂ which makes it to be used in the potentials devices. MoS₂ has stiffness, resistant for braking, excellent mechanical properties [7], very high current density [8], high on/off ratio and electron mobility similar to silicon [9]. Furthermore, MoS₂ has strong fluorescence by virtue of its direct band gap. These properties coupled with its aforementioned tunable band gap, allow MoS₂ used in fabrication of ion of flexible electronics and optical sensing or

This work was supported by Korea Institute of Science and Technology (2E25373). Shraddha Ganorkar, Jungyoon Kim, Young Hwan Kim and Seong-II Kim* are with the Center for Nano Photonics, Korea Institute of science and Technology, 5, Hwarangro 14-gil, Seongbuk-gu, Seoul, 136-791, South Korea (phone: 82-2-958-5737 ; fax: 82-2-958-5739 *email:s-ikim@kist.re.kr).

emitting devices at different optical frequencies and wavelength. Every new material needs a unique characterization tool. Since the 2D material has remarkably different properties from bulk, researchers have designed way to characterize and identify different types of monolayers. Raman spectroscopy and resonant Raman spectroscopy are one of the tools which allows one to distinguish and identify the material and the number of layers [10].

Synthesis of MoS₂ is still an open challenge for researchers. There are several methods to grow or fabricate monolayer MoS₂. Some of which have been very successful. Top-down approaches like mechanical exfoliation and lithium intercalation assisted exfoliation which has less control on the thickness of layers. Chemical vapor deposition (CVD) has proven one of the successful technique for growing monolayer to few layers of 2D materials including graphene [11]-[17]. The number of layers critically depends on several factors in CVD like temperature, pressure, position of precursor and substrate, etc. Nevertheless, sources of Mo and S also play an important for deciding the morphology of the films. In this paper, we have investigated the CVD method. We used two different Mo precursors (MoO₃ and MoCl₅) to grow MoS₂ films and compare their results. It has been observed that for practical application purposed the films grown with MoCl₅ can be a better choice for device fabrication.

II. EXPERIMENT

The growth of MoS₂ monolayer and few layers were carried out in a home-built CVD furnace with 1 inch quartz tube. The precursor MoO₃ (Sigma-Aldrich 99.999%), MoCl₅ (Sigma-Aldrich 99.999%) and S (Sigma-Aldrich 99.999%) were used for MoS₂ synthesis. 300 nm SiO₂ on Si was used as substrate. The substrate was sonicated with trichloroethylene, acetone, methanol and DI water for 15min each. Since the two precursor need the different treatment the method is described below briefly.

A. Synthesis with MoO₃ precursor

The MoO₃ was placed in a quartz boat at the center of the furnace with the substrate held upside down. The S was placed at upstream at 14 cm from the center of the furnace. Furnace was heated to 700 °C in 40 min with N₂ flow of 10 sccm. The temperature was held about 5 min and allow it to cool naturally to 500 °C followed by rapid cooling by opening furnace and flowing 500 sccm N₂. With this method we able to grow MoS₂ monolayer and bilayer films.

B. Synthesis with MoCl₅ Precursor

The MoCl₅ powder placed at the center of the furnace and the S powder is placed in the quartz crucible at the upstream of the furnace. The substrate was placed at downstream (next to Mo precursor) from 1-4cm away from the center of the furnace. The growth was carried out in 2 torr Ar atmosphere at 50 sccm flow. The furnace was heated to 800 °C in 30 min and held for 5 min followed by natural cooling to room temperature. With this method we could able to get MoS₂ mono, bi, tri and tetra layer films.

The films synthesized as above were characterized by optical microscope, Raman spectroscopy and photoluminescence spectroscopy (Uni-RAM 5500, UniNanoTech, Korea) with frequency-doubled Nd:YAG (532 nm) laser.

III. RESULT AND DISCUSSION

Figure. 1 shows the optical images of MoS₂ layers grown using MoO₃. The monolayer of MoS₂ can be clearly seen in Fig. 1 (a). Various size triangle-shaped MoS₂ grains can be clearly seen in the image. Some grains are merged to form star shapes and many arbitrary shapes which indicate the formation of

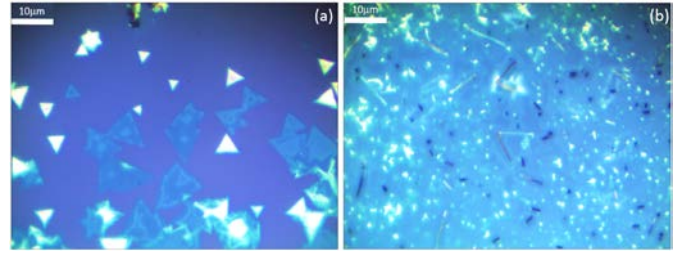


Fig. 1 Optical images of MoS₂ synthesized from MoO₃ precursor (a) Monolayer (1L) (b) Bilayer (2L)

continuous layer. Such an overlapping of grains turn into bilayer film, which can be seen from Fig. 1 (b). It is difficult to get very clean film using MoO₃ as source. We characterized the synthesized films using Raman spectroscopy. It is a powerful nondestructive characterization tool for MoS₂. Raman spectra of the films grown using MoO₃ is shown in Fig. 2. Two characteristic Raman modes can be found in the Raman spectra. The off resonance first-order Raman active modes E_{2g}^1 (387

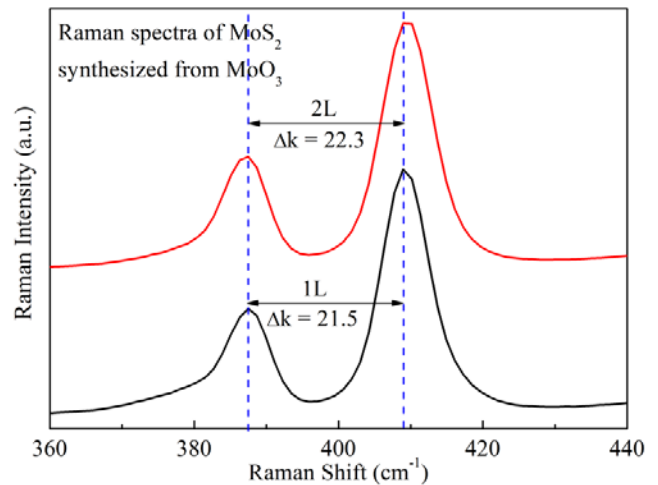


Fig. 2 Raman spectra of MoS₂ monolayer (1L) and bilayer (2L) synthesized from MoO₃

cm⁻¹) and A_{1g} (408 cm⁻¹) are generally observed for bulk MoS₂. The A_{1g} mode results from opposite vibration of two S atom with respect to Mo atom while A_{1g} mode arises from out of plane vibration of S atoms in the opposite direction [10]. These modes are closely related to number of layers. The Raman spectra of monolayer and bilayer MoS₂ grown from MoO₃ is

depicted in Fig. 2. The frequency difference (Δk) between the Raman modes for monolayer is found to be $\Delta k = 21.5 \text{ cm}^{-1}$ while that of for bilayer it is found to be $\Delta k = 22.3 \text{ cm}^{-1}$. The grown films show excellent optical quality. Photoluminescence (PL) for monolayer MoS₂ is shown in Fig. 3. Two PL peaks can be observed around 675 nm (1.83 eV) and 621 nm (1.99 eV) corresponding to the A₁ and B₁, respectively for direct excitonic transitions with the energy split from the valence band spin-orbital coupling [18]. It is difficult to grow controlled multilayer with MoO₃ source

The second precursor was MoCl₅. Though the method of synthesis was CVD but MoCl₅ need the different growth conditions to grow MoS₂ multilayers. The optical images of

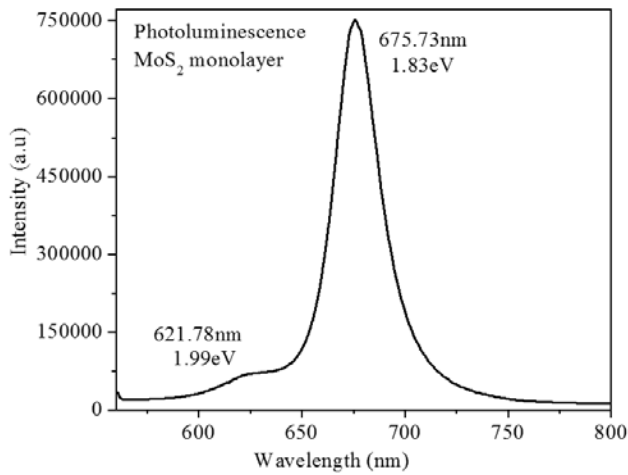


Fig. 3 Photoluminescence of MoS₂ monolayer grown by MoO₃

MoS₂ grown by MoCl₅ source are depicted in Fig 4 (a) monolayer 1L and Fig. 4 (b) bilayer (2L). One can notice there are no triangle observed like MoO₃ growth. In contrast to earlier Mo source, these films are found to be very uniform. We have successfully grown the various layers by tailoring the

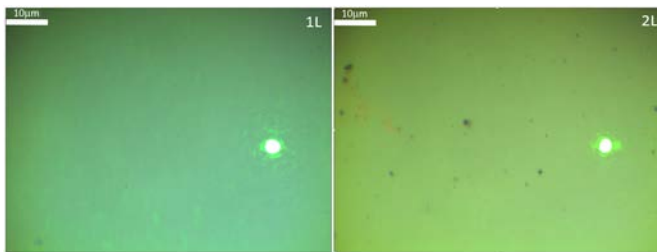


Fig. 4 Optical images of MoS₂ synthesized from MoCl₅ precursor (a) Monolayer (1L) (b) Bilayer (2L)

substrate position (1 to 4 cm from the source). We obtained the thicker film for the larger distance between the source and substrate. The Raman spectra of MoS₂ multilayers are shown in Fig. 5. One can observe the significant increase in the Raman frequency difference Δk with increases of MoS₂ thickness from monolayer to tetralayer. A systematic correlation is found between the Raman modes and number of layers. PL spectra of bilayer MoS₂ grown from MoCl₅ source is presented in Fig. 6. PL peaks A₁ (657.44 nm, 1.88 eV) and B₁ (605.10 nm, 2.04 eV)

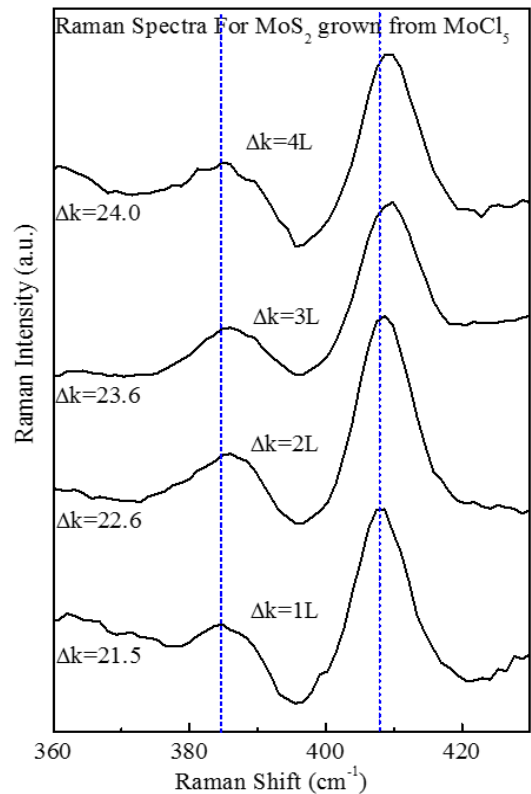


Fig. 5 Raman spectra of MoS₂ monolayer (1L), bilayer (2L), trilayer (3L) and tetralayer (4L) synthesized from MoCl₅

observed at lower wavelength than monolayer, as expected due to increases in the band gap of bilayer film. One can notice drastic decrease in PL peak intensity as compared to monolayer. This justifies the evolution of bandgap with an

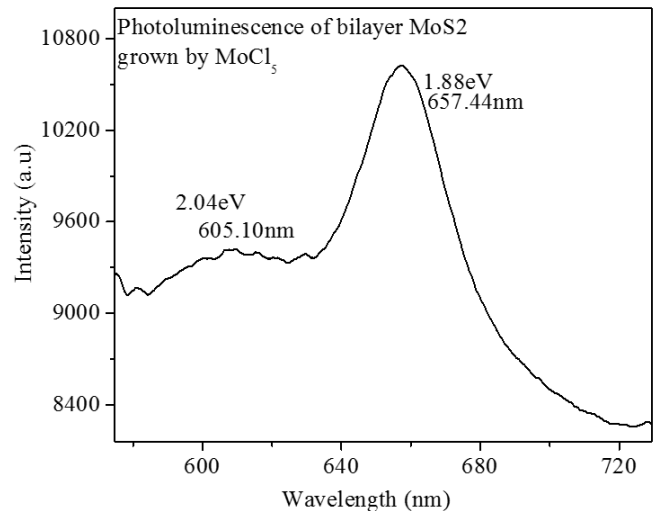
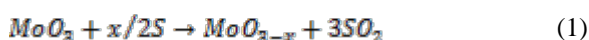


Fig. 6 Photoluminescence spectra of MoS₂ bilayer film grown by MoCl₅ source

increase in the number of layers. It is well known fact that there is no observable PL spectra in bulk MoS₂ is due to local field effect while strong PL spectra of monolayer shows that luminescence quantum efficiency is much higher in monolayer than in multilayer and bulk [18].

From the above studies once can see that in CVD process the

source materials play an important role for deciding the morphology of the film. MoS₂ monolayer grows in different geometrical shapes triangular to hexagonal when MoO₃ is used as source material. There are several factors in the CVD process which decide the shapes of monolayer MoS₂. A possible explanation for shape evolution can be given by a principle of crystal growth in which the shape change of domains is attributed to local changes in the source ratio (Mo:S) as well as its influence on the kinetic growth dynamics of edges [19]. The mechanism of reduction of MoO₃ to MoS₂ in the absence of H is still not known. It is believed that the reaction between MoO₃ and S involves stepwise reduction of Mo^{VI} in MoO₃ to Mo^{IV} in MoS₂. This transition is supposed to involve reduction and sulfuration. A postulated stepwise process is given by the following equations [20], [21]



In these steps there is possibility of formation of oxysulfide (MoOS₂), which is a composite of MoS₂ and MoO_(3-x). MoO₂ is one of the most stable intermediate in this process. Substituting $x=1$ in equation (1) realized the formation of MoO₂. Where as in case of MoCl₅ in presence of excess S is possibly one step process. The chemical reaction between MoCl₅ and S is not clearly reported as per best of our knowledge. The possible process can be given as follows.



Furthermore the growth of MoS₂ multilayers with MoCl₅ source is believed to be “self-limiting” process. It is most postulated that formation MoS₂ in gas phase followed by its diffusion onto receiving substrate and further precipitation to MoS₂ solid phase [15]. This indeed supports for our assumption of one step chemical reaction of MoCl₅ and S. From this scenario, we can conclude that the one step chemical reaction is the key point to get uniform monolayer of MoS₂ without formation of triangles. Since in this particular process there is no need of nucleation, which is the main reason for formation of geometric shapes (mostly triangular) of MoS₂ monolayer. In device application of MoS₂ monolayer the geometric shapes can create the issues related to grain bounties. Hence MoCl₅ or similar sources can be a good choice as a precursor for MoS₂ deposition.

REFERENCES

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, “Electric field effect in atomically thin carbon films,” *Science*, vol. 306, pp. 666-669, Oct, 2004 DOI: 10.1126/science.1102896
- [2] K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, “A roadmap for graphene,” *NATURE*, vol. 490, pp. 192-200, Oct, 2012 DOI:10.1038/nature11458
- [3] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, “Graphene and graphene oxide: synthesis, properties, and applications,” *Adv. Mater.*, vol. 22, pp. 3906-3924, Jun, 2010 DOI:10.1002/adma.201001068
- [4] X. Song, J. Hu, H. Zeng, “Two-dimensional semiconductors: recent progress and future perspectives,” *J. Mater. Chem. C*, vol. 1, pp. 2952-2969, Jan, 2013 DOI: 10.1039/C3TC00710C
- [5] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, “Atomically thin MoS₂: a new direct-gap semiconductor,” *Physical Rev. Lett.*, vol. 105, pp. 136805(1-4), Sep, 2010 DOI: 10.1103/PhysRevLett.105.136805
- [6] A. Ramasubramanian, D. Naveh, E. Towe, “Tunable band gaps in bilayer transition-metal dichalcogenides,” *Physical Review B*, vol. 84, pp. 205325(1-10), Nov, 2011 DOI: 10.1103/PhysRevB.84.205325
- [7] S. Bertolazzi, J. Brivio, A. Kis, “Stretching and breaking of ultrathin MoS₂,” *ACS Nano*, vol. 5, pp. 9703-9709, Nov, 2011 DOI: 10.1021/nn203879f
- [8] D. Lembke, A. Kis, “Breakdown of high-performance monolayer MoS₂ transistors,” *ACS Nano*, vol. 6, pp. 10070-10075, Oct, 2012 DOI: 10.1021/nn303772b
- [9] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, “Single-layer MoS₂ transistors,” *Nat. Nanotechnol.*, vol. 6, pp. 147-150, Jan, 2011 DOI:10.1038/nnano.2010.279
- [10] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, D. Baillargeat, “From bulk to monolayer MoS₂: evolution of Raman scattering,” *Adv. Funct. Mater.*, vol. 22, pp. 1385-1390, Jan, 2012 DOI: 10.1002/adfm.201102111
- [11] J. Mann, D. Sun, Q. Ma, J. R. Chen, E. Preciado, T. Ohta, B. Diaconescu, K. Yamaguchi, T. Tran, M. Wurch, et al. “Facile growth of monolayer MoS₂ film areas on SiO₂,” *Eur. Phys. J. B*, vol. 86, pp. 226(1-4), May, 2013 DOI: 10.1140/epjb/e2013-31011-y
- [12] Y. H. Lee, X. Q. Zhang, W. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, J. T. W. Wang, C. S. Chang, L. J. Li, et al. “Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition,” *Adv. Mater.*, vol. 24, pp. 2320-2325, May, 2012 DOI: 10.1002/adma.201104798
- [13] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J. C. Idrobo, P. M. Ajayan, J. Lou, “Vapor phase growth and grain boundary structure of molybdenum disulphide atomic layers,” *Nat. Mater.*, vol. 12, pp. 754-759, Jun, 2013 DOI:10.1038/nmat3673
- [14] Y. C. Lin, W. Zhang, J. K. Huang, K. K. Liu, Y. H. Lee, C. T. Liang, C. W. Chu, L. J. Li, “Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization,” *Nanoscale*, vol. 4, pp. 6637-6641, Aug, 2012 DOI: 10.1039/c2nr31833d
- [15] Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, L. Cao, “Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS₂ films,” *Sci. Rep.*, vol. 3, pp. 1866, May, 2013 DOI:10.1038/srep01866
- [16] S. Balendhran, J. Z. Ou, M. Bhaskaran, S. Sriram, S. Ippolito, Z. Vasic, E. Kats, S. Bhargava, S. Zhuiykov, K. Kalantar-Zadeh, “Atomically thin layers of MoS₂ via a two-step thermal evaporation-exfoliation method,” *Nanoscale*, vol. 4, pp. 461-466, Nov, 2012 DOI:10.1039/C1NR10803D
- [17] Q. Ji, Y. Zhang, T. Gao, Y. Zhang, D. Ma, M. Liu, Y. Chen, X. Qiao, P. H. Tan, M. Kan, “Epitaxial monolayer MoS₂ on mica with novel photoluminescence,” *Nano Lett.*, vol. 13, pp. 3870-3877, Jul, 2013 DOI: 10.1021/nl401938t
- [18] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli and F. Wang “Emerging photoluminescence in monolayer MoS₂” *Nano Lett.*, vol 10 (4), pp. 1271-1275 Mar 2010 DOI: 10.1021/nl903868w
- [19] S. Wang, Y. Rong, Y. Fan, M. Pacios, H. Bhaskaran, K. He and J. H. Warner, “Shape evolution of monolayer MoS₂ crystals growth by chemical vapor deposition,” *Chem. Mater.* vol 26, pp. 6371-6379 Nov 2014 DOI: 10.1021/cm5025662
- [20] Y. D. Li and X. L. Li, “Formation of MoS₂ inorganic fullerenes (Ifs) by reaction of MoO₃ nanobelts and S,” *Chem. Eur. J.*, vol 9, pp. 2726- 2731 Jun 2003 DOI: 10.1002/chem.200204635
- [21] B. Li, S. Yang, N. huo, Y. Li, J. Yang, R. Li, C. Fan and F. Lu, “Growth of large area few-layer or monolayer MoS₂ from controllable MoO₃ nanowire nuclei,” *RSC Adv.*, vol 4, pp. 26407, Apr 2014 DOI: 10.1039/c4ra01632g