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**PREPARASI DAN KARAKTERISASI 'FEW-LAYER
MoS₂ NANOSHEETS'**

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Preparation and Characterization of Few-layer MoS₂ Nanosheets

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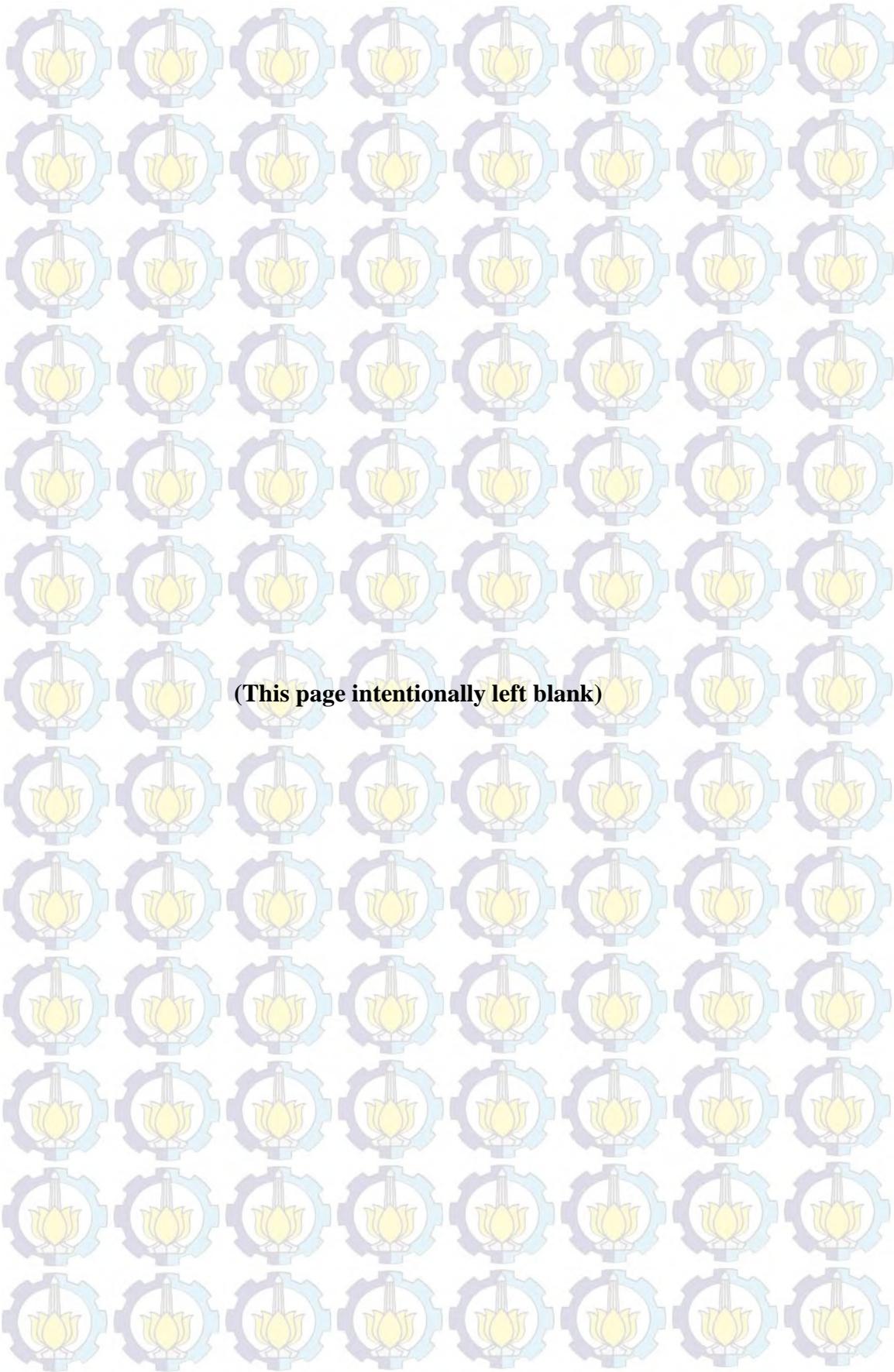
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ABSTRACT

Exfoliation of bulk MoS₂ via Li intercalation is an attractive route to large-scale preparation of MoS₂ few-layers and it can be used to realize their unique properties in practical applications. In general, solution-based exfoliation of layered materials results in flakes with lateral sizes of one micron or less on average. In this report, we performed the various preparations using a Li-intercalation method at room temperature to prepare MoS₂ few-layers with various flake sizes according to dynamic light scattering (DLS) analysis. MoS₂ few-layers with particle sizes ranging 85 to 145 nm are reported. We also characterize the few-layer MoS₂ nanosheets by various microscopic and spectroscopic techniques.

Keyword : MoS₂, nanosheets, , intercalation, exfoliation.



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Preparasi dan karakterisasi 'Few layer MoS₂ Nanosheets'

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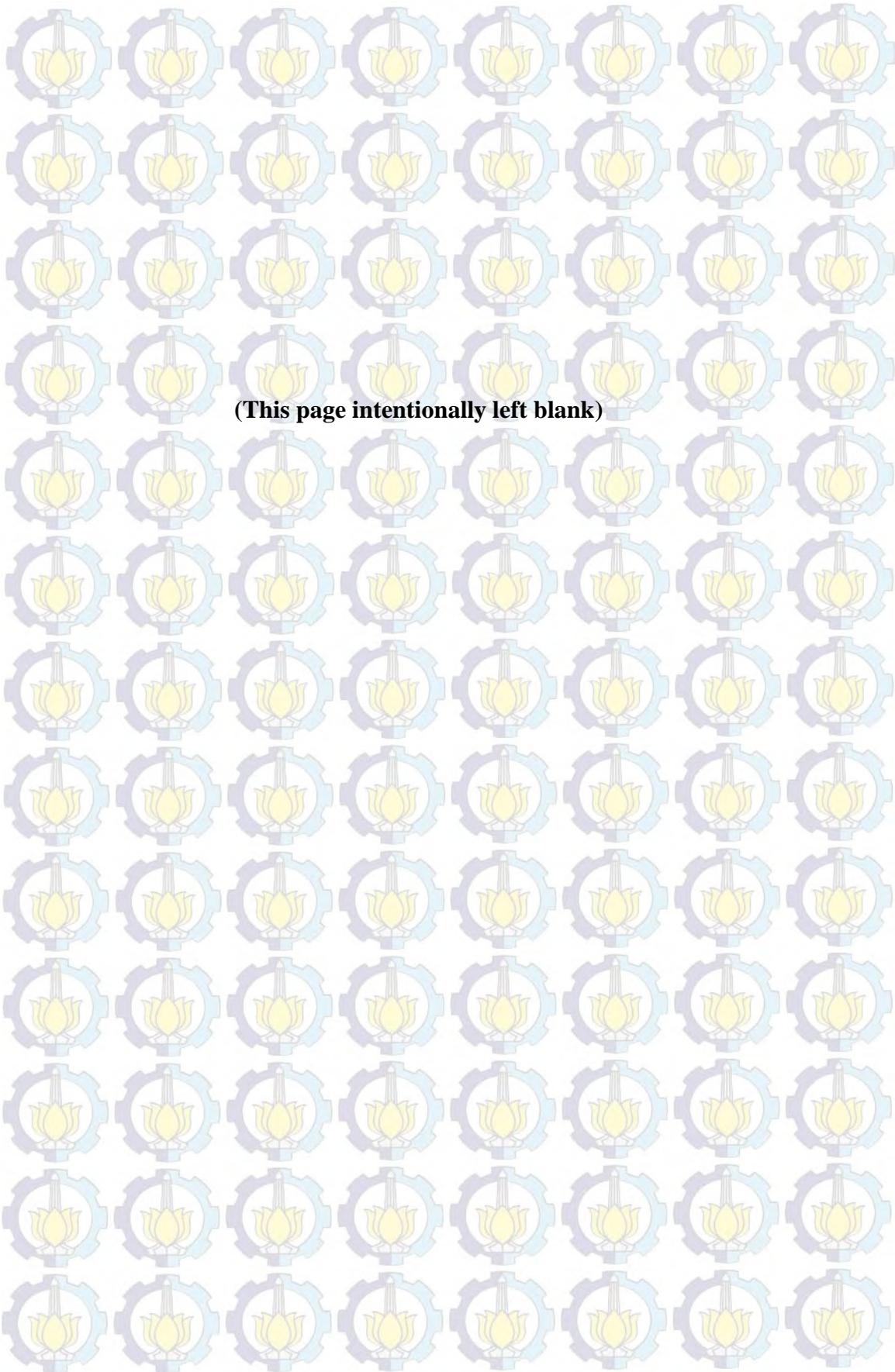
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ABSTRAK

Pengelupasan *bulk MoS₂* dengan menggunakan metode interkalasi lithium adalah metode yang menarik untuk preparasi *MoS₂ few-layers* dalam skala besar dan dapat digunakan untuk merealisasikan porperti-properti unik dari *MoS₂ few-layers* dalam aplikasi nyata. Pada umumnya, pengelupasan material berlapis yang didasarkan pada pengelupasan dengan menggunakan larutan menghasilkan serpihan dengan ukuran satu mikrometer atau masih jauh dari rata-rata. Di laporan ini, kita menunjukkan macam-macam preparasi nanosheet dengan menggunakan metode interkalasi lithium pada temperatur ruang untuk menyiapkan *MoS₂ few-layers* dengan variasi ukuran serpihan berdasarkan analisa *dynamic light scattering* (DLS). *MoS₂ few-layers* yang kita peroleh mempunyai ukuran dengan range 85-145 nm. Kita juga melakukan karakterisasi terhadap *MoS₂ few-layers* dengan menggunakan berbagai teknik mikroskopik dan spektroskopik.

Kata kunci: MoS₂, Nanosheets, Interkalasi, Pengelupasan.



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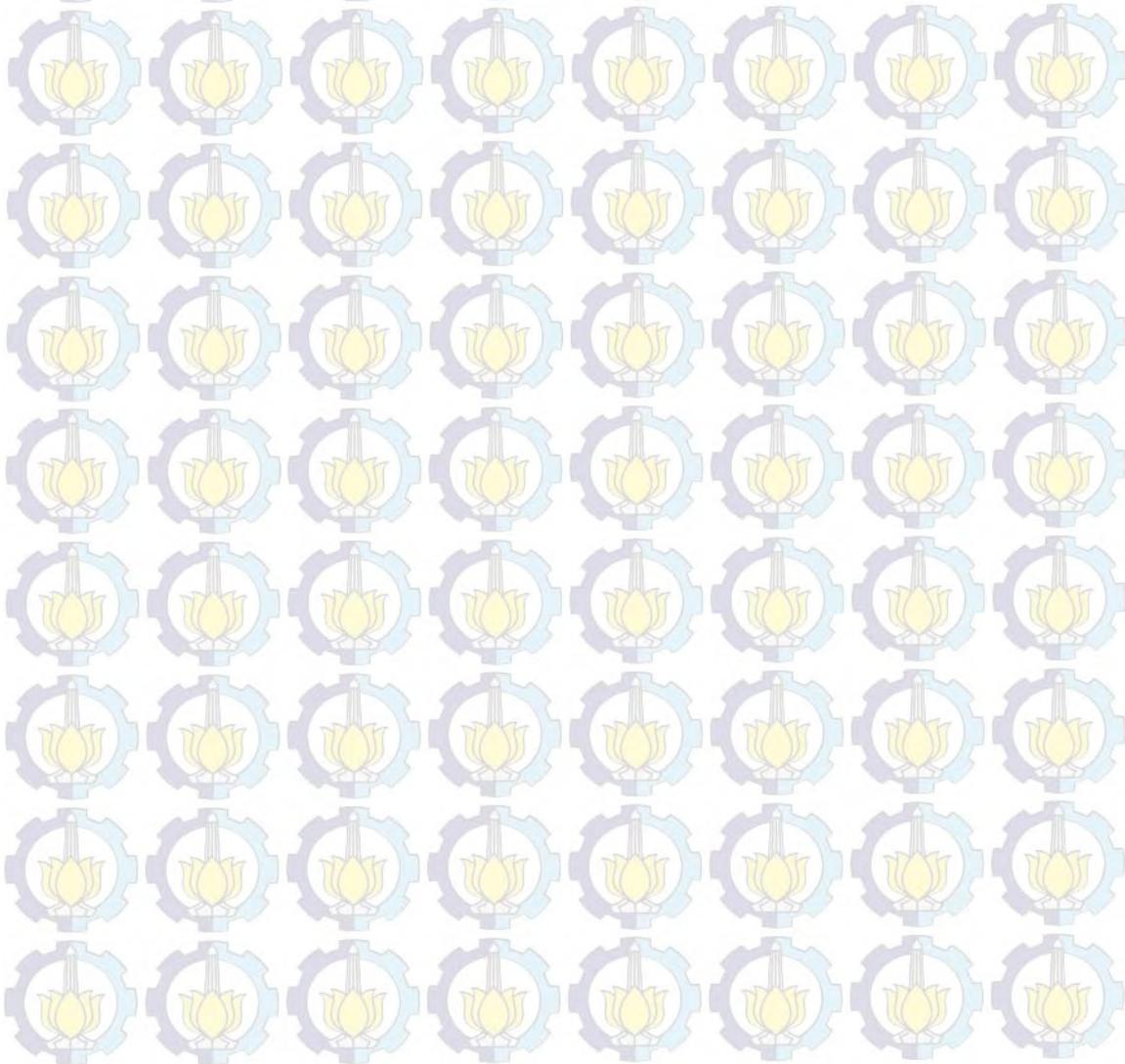
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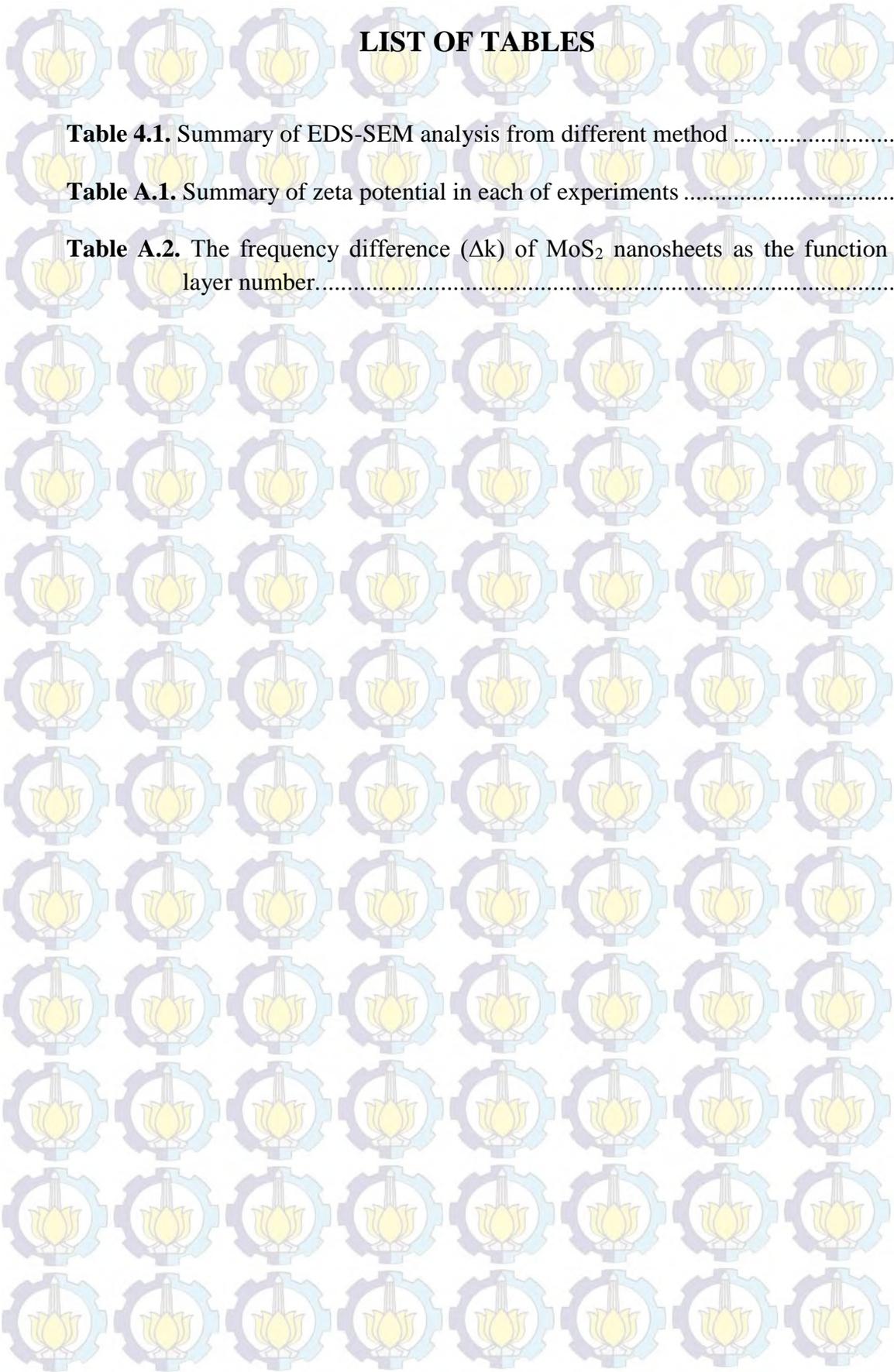
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CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent decades, nanomaterials have attracted major attentions due to their fascinating properties and wide ranges of applications. There are two categories of nanomaterials: organic (mostly carbon allotropes) and inorganic nanomaterials, such as iron, silver, gold, boron nitride nanosheets (BNNs), molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), etc. Inorganic nanomaterials, especially two-dimensional (2D) nanomaterials, have received tremendous attention in recent years because of unique both chemical and physical properties. The two-dimensional nanomaterials have completely different properties compared to the bulk materials (the quintuple layers). These properties includes high surface areas, mobility, conductivity, mechanical strength, transparency, electronics and optoelectronics. As one of the 2D nanomaterials, molybdenum disulfide possesses a sandwich structure which consist of covalent bonds in S-Mo-S structures that form by weak Van Der Waals forces between sheets. Therefore, it is probably easy to peel MoS_2 nanosheets from bulk material (Novoselov et al., 2005). Bulk MoS_2 is a semiconducting material with an indirect band gap of about 1.2 eV. When layered MoS_2 pristine is peeled to single-layer, it become a semiconductor with 1.8 eV direct band gap (Wang et al., 2012a, Yoon et al., 2011). The wide band gap, which is thickness-dependent (bulk to single-layer), makes MoS_2 a promising candidate for many applications, such as electronic devices (Choi et al., 2013), optoelectronic devices (Yin et al., 2012, Lopez-Sanchez et al., 2013, Fontana et al., 2013, Yu et al., 2013a), sensors (Zhang et al., 2014), and energy storage devices, like lithium ion batteries (LIB) (Park et al., 2013, Zhou et al., 2014, Li et al., 2015, Su et al., 2015), sodium ion batteries (SIB) (Bang et al., 2014), and capacitors (Cao et al., 2013). The other applications, which have become hot topics until now are utilization and optimization of exfoliated MoS_2 in either hydrogen evolution reaction (HER) (Ji et al., 2013, Lukowski et al., 2013, Voiry et al., 2013) or water splitting (Yin et al., 2014,

Singh et al., 2015). If MoS₂-based catalysts are to actualize their potential, there is an important need to increase the numbers of active sites and the catalytic activity by changing their electronic properties and conductivity via exfoliation of MoS₂ from bulk materials to nanosheets (Lukowski et al., 2013). And also the size of nanosheets is an important factor in the hydrogen evolution reaction (HER) (Varrla et al., 2015).

Recently, several methods have been reported for synthesizing single- and multi-layer MoS₂. In the synthesis of 2D nanomaterials, the synthetic routes can be divided into two fundamental categories. First, top-down methods use the external energy (mechanical or ultra-sound energy) as main sources to achieve the exfoliated nanomaterials. Second, bottom-up methods are via deposition of atoms in either thermal or chemical reactions on a substrate to synthesize exfoliated 2D nanomaterials (Das et al., 2014). Until now, single-, few- and multi-layer MoS₂ have all been prepared by both methods. For the top-down methods, there are the mechanical exfoliation method (Lee et al., 2014, Li et al., 2014), chemical lithium intercalation and exfoliation using *n*-butyllithium (Chou et al., 2013, Xiao et al., 2010), electrochemical lithium intercalation and exfoliation (You et al., 2014), liquid phase exfoliation using solvent and surfactants (Coleman et al., 2011b), (Gupta et al., 2015) and synthesis of MoS₂ nanosheets via shear exfoliation (Varrla et al., 2015). For the bottom-up methods, they include the thermal chemical vapor deposition (CVD) (Zhang et al., 2011, Liu et al., 2013a) and synthesis of MoS₂ nanosheets via hydrothermal reaction (Ma et al., 2012, Liu et al., 2013b, Liu et al., 2014, Ye et al., 2014). Recently, many researchers made good quality MoS₂ monolayers using a chemical vapor deposition (CVD) or a Scotch tape-based micromechanical exfoliation method. However, a low yield is generally achieved in the Scotch tape method and a high temperature and cost of instruments are required for experiments in the CVD method. Coleman et al. reported direct exfoliation of MoS₂ sheets with thickness of 3–12 nm and the lateral nanosheets size of 0.1–2 μm in organic solvents through sonication (Coleman et al., 2011b). However this method leads to a low yield and the major issue is that specific nanosheet sizes cannot be obtained. It is essential for various applications. For

example, composite reinforcement requires large nanosheets (May et al., 2012) at least around 2 μm in length, whereas a catalyst of hydrogen production requires small nanosheets with lateral size or length below 100 nm (Jaramillo and Horch, 2007). Significance of this work focuses on synthesis of few-layer MoS_2 nanosheets with specific lateral size via the lithium intercalation method and characterization of the material, even though some research on the intercalation of alkali metals into bulk MoS_2 has been reported (Somoano et al., 1973, Somoano and Woollam, 1979, Lacaze et al., 1997, Hara et al., 1990).

Nanotechnology and its applications are expanding in academic research and also moving into industry in recent years. The development in this area is supported by technological advancement, such as microscopy and spectroscopy. The microscopic images help us understand the morphology of nanomaterial, like lateral size, thickness, lattice, and the diffraction pattern with high resolution. The spectroscopic instruments include Raman spectroscopy, X-ray photoelectron spectroscopy, UV-vis spectroscopy, and Photoluminescence spectroscopy, which help us characterize nanomaterials, like lattice vibration of nanomaterial and excitation of electron.

1.2 Previous Studies

Joensen and co-workers (Joensen, 1986) have conducted experiments to prepare monolayer MoS_2 via the lithium intercalation using *n*-butyl lithium dissolved in hexane. In this method, the intercalation process would be an important step because of the formation of Li_xMoS_2 compound. This process can be tuned to control the yield of monolayers MoS_2 . The X-ray diffraction was used to distinguish single-, bi-, tri-, and quadratic-layer of MoS_2 .

Benevante and co-workers (Benevante et al., 2002) reported the successful preparation of MoS_2 nanosheets using *n*-butyl lithium as the intercalating agent and also demonstrated the influences of quasi-equilibrium voltage-composition to the number of lithium inserting into 2H- MoS_2 (semiconducting phase of MoS_2 with trigonal prismatic coordination) (Figure 2.1). Electrochemical behavior, spectroscopy and structural features, crystal structures of single-layers and

restacked MoS₂ were also studied. The main advantage of the lithium intercalation method is its ability to access the metallic phase (1T-MoS₂) with octahedral coordination phase that is induced through charge-transfer from *n*-butyl lithium to MoS₂ sheets and thus the semiconducting to the metallic phase occurs.

Ambrosi and co-workers (Ambrosi et al., 2015) studied the influences of various kinds of the lithium intercalation compound on electrochemical properties of exfoliated MoS₂. In this work, they used methyl lithium (Me-Li), *n*-butyl lithium (Bu-Li), and *t*-butyl lithium. The *n*-Bu-Li, and *t*-Bu-Li are more efficient than Me-Li. Based on both Raman and XPS spectra results, smaller lateral sizes and numbers of layers can be produced. Larger current signals (per unit mass) in KCl electrolyte are observed in electrochemical measurements, suggesting they are promising for the applications in rechargeable batteries and good energy storage.

Liu and co-workers (Liu et al., 2014) demonstrated the preparation of MoS₂ nanosheets with lithium hydroxide (LiOH) dissolved in ethylene glycol via hydrothermal exfoliation. (The materials are used as anode materials in lithium ion batteries (LIB)). This process uses lithium ion (Li⁺) for intercalating into MoS₂ layers to form Li_xMoS₂. It exhibited a good initial capacity of 1190 mAh/g and cyclic stability at constant current density of 50 mA/g and also still delivered reversibly sustained high capacity of 750 mAh/g after 50 cycles.

Wang and co-workers (Wang et al., 2013) demonstrated the continuous tuning of layer vertically aligned MoS₂ nanosheets through electrochemical intercalation of lithium ion (Li⁺) to different voltages vs. Li⁺/Li in nanofilms with perpendicular to the substrates and its application for electrochemical hydrogen evolution reaction (HER). So, the formation of Li_xMoS₂ and the reaction process can be tuned to control the characteristic and yield of nanosheets. The layer spacing changes, oxidation state, and the ratio of semiconducting to metallic phase due to their electron transfer from Li⁺ to MoS₂ layer were also studied. This paper mentioned that increasing the molar ratio of lithium in Li_xMoS₂ caused rearrangement of the atomic structure of MoS₂ from 2H semiconducting to 1T metallic phase. Related to hydrogen evolution reaction, HER activities are already

enhanced along with the lowered oxidation states of Mo before transformation of semiconducting to metallic phase occurs.

1.3 Problem Statement

As described previously, exfoliation of layered material via lithium intercalation method is considered as a useful method for preparation of discrete dimension of layered materials. The unique properties of MoS₂ nanosheets have attracted many researcher's interests in recent years to seek its applications on the lithium ion batteries (LIBs) and evolution of hydrogen. The nanosheet sizes are very important with respect to the catalytic performance. The development of nano-sized sheets as electrocatalysts for hydrogen production is a challenge for researchers. In this work we simultaneously solve that problem. We demonstrated the preparation of MoS₂ nanosheets with specific flake dimensions via the lithium intercalation method at room temperature with low cost, we will extend their use in applications of either LIBs or HER.

1.4 Research Objective

The objective of this study is to synthesize few-layer MoS₂ nanosheets via lithium intercalation method with simple experiments. Their morphology, flake dimensions, and thickness are characterized. The results are compared with the previous ones.

1.5 Research Organization

This thesis is divided into five parts which is organized as follows:

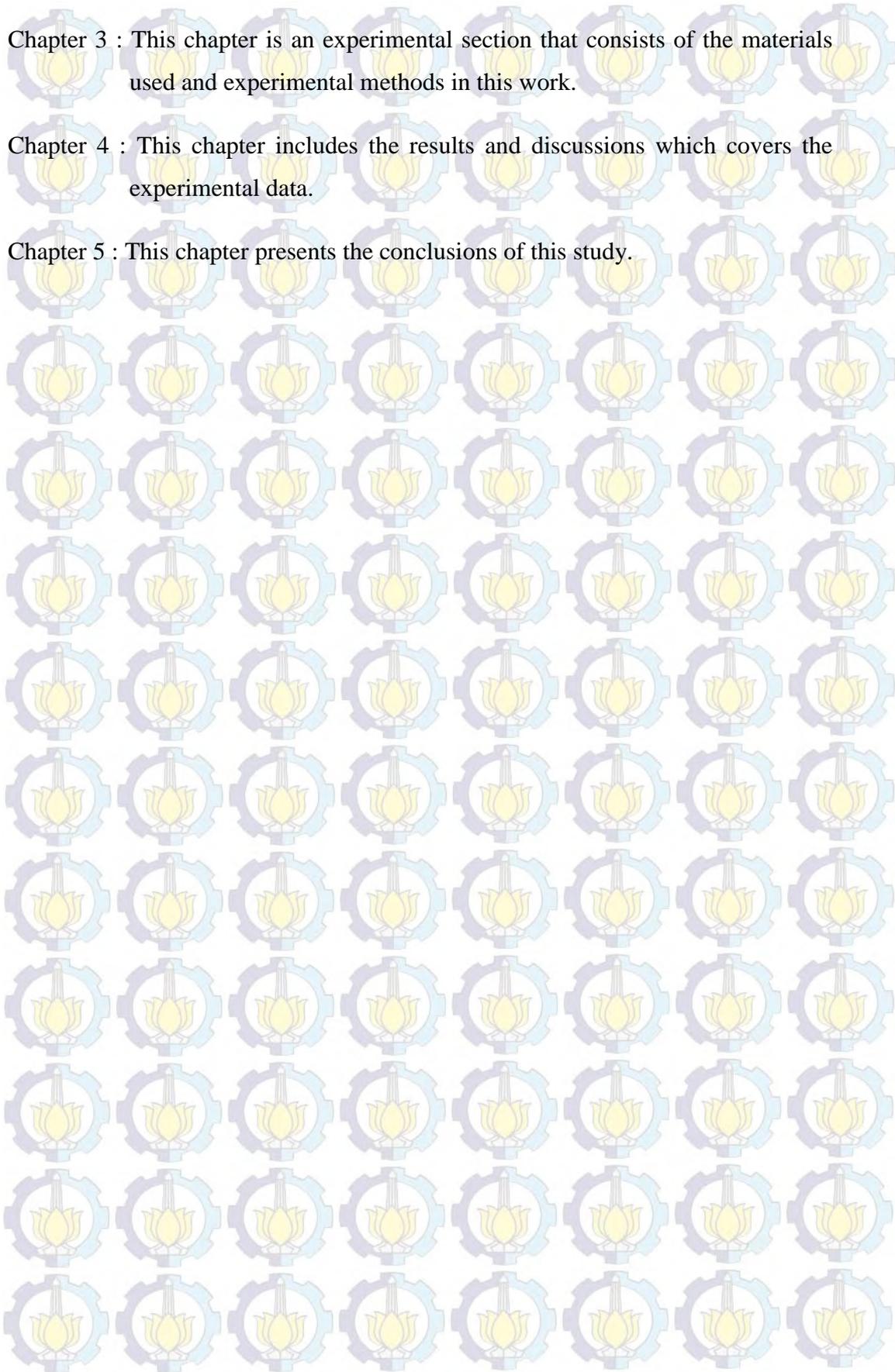
Chapter 1 : This chapter gives an introduction that provides the background of the research, previous studies, problem statement, and the objective of this study.

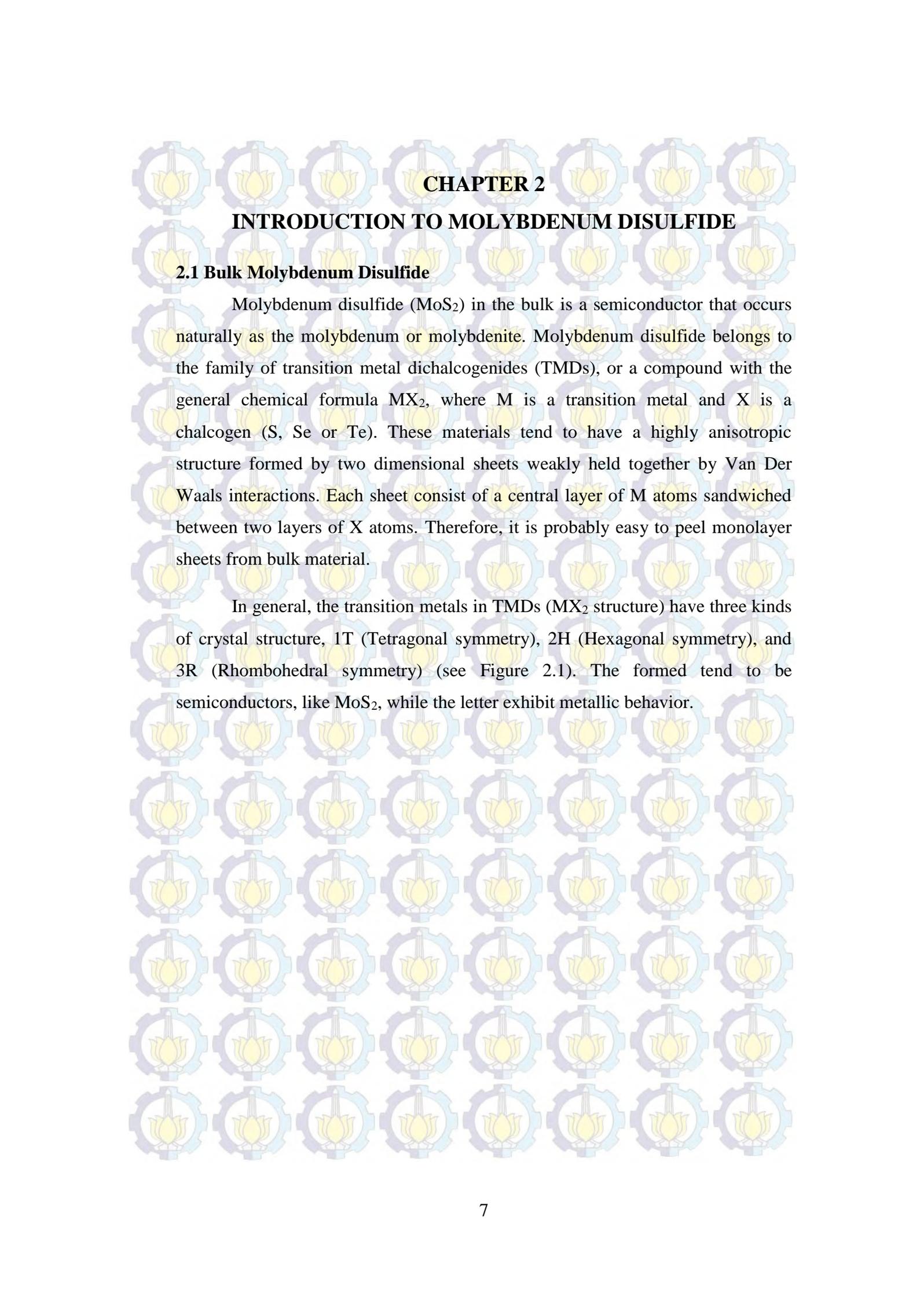
Chapter 2 : This chapter provides an introduction to molybdenum disulfide that presents a brief explanation about characteristics of molybdenum disulfide and potential applications of intercalation-exfoliated nanosheets.

Chapter 3 : This chapter is an experimental section that consists of the materials used and experimental methods in this work.

Chapter 4 : This chapter includes the results and discussions which covers the experimental data.

Chapter 5 : This chapter presents the conclusions of this study.





CHAPTER 2

INTRODUCTION TO MOLYBDENUM DISULFIDE

2.1 Bulk Molybdenum Disulfide

Molybdenum disulfide (MoS_2) in the bulk is a semiconductor that occurs naturally as the molybdenum or molybdenite. Molybdenum disulfide belongs to the family of transition metal dichalcogenides (TMDs), or a compound with the general chemical formula MX_2 , where M is a transition metal and X is a chalcogen (S, Se or Te). These materials tend to have a highly anisotropic structure formed by two dimensional sheets weakly held together by Van Der Waals interactions. Each sheet consist of a central layer of M atoms sandwiched between two layers of X atoms. Therefore, it is probably easy to peel monolayer sheets from bulk material.

In general, the transition metals in TMDs (MX_2 structure) have three kinds of crystal structure, 1T (Tetragonal symmetry), 2H (Hexagonal symmetry), and 3R (Rhombohedral symmetry) (see Figure 2.1). The formed tend to be semiconductors, like MoS_2 , while the letter exhibit metallic behavior.

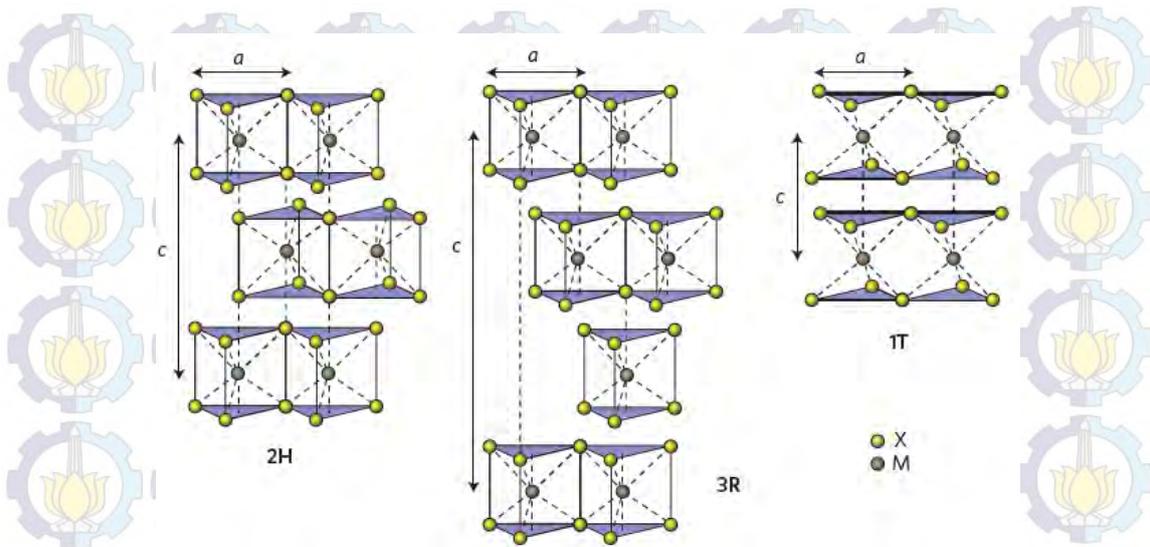


Figure 2.1. Schematics illustration of the structural polytypes in TMDs, with the chalcogen atoms (X) in yellow and the metal atoms (M) in grey: 2H (hexagonal symmetry, two layers per unit cell, trigonal prismatic coordination), 3R (rhombohedral symmetry, three layers per unit cell, trigonal prismatic coordination) and 1T (tetragonal symmetry, one layer per unit cell, octahedral coordination). The lattice constants a are in the range 3.1 to 3.7 Å for different materials, The stacking index c indicates the number of layers in each stacking order, and the interlayer spacing is ~ 6.5 Å. (Adapted from Wang et al. Nature Nanotechnology, 2012).

In the MoS_2 bulk also has three main polytypes of crystal structure: 1T, 2H and 3R, with 2H being the most stable form. This structure consists of the stacked trilayer structure with every 2 stacks offset such that two MoS_2 trilayers are included in the unit cell. The Van Der Waals gap, the (002) plane, has a spacing of around 0.6 nm (Figure 2.2A). In addition, the Mo atoms have trigonal prismatic coordination relative to the S atoms, this gives rise to a hexagonal structure when viewed along the c axis (normal to layers) (Figure 2.2B). The characteristic spacing of the (100) plane in the hexagonal lattice is 0.26 nm and 0.16 nm for the (110) plane. The covalent bonding results in an oxidation state of +4 for the Mo unit and -2 for each sulfur atom.

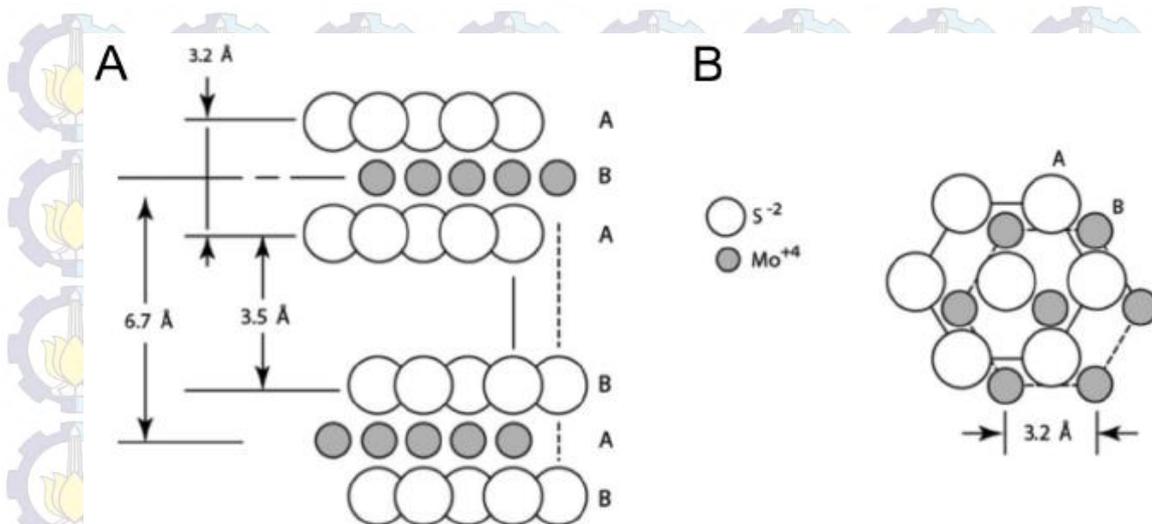


Figure 2.2. (A) Bulk MoS₂ observed parallel to basal plane shows stacked trilayer structure. (B) Perpendicular to the basal plane the trigonal crystal structure can be observed. (Adapted from W. G. S. B. C. Windom, and D. W. Hahn, Tribology Letters, 2011).

An interesting feature of many MX₂ compounds is that the layers can be separated through a procedure known as *exfoliation*. For example, when lithium (Li) is intercalated into MoS₂ layers, the Li atoms move into the crystal from the edges and diffuse in between the layers to form a compound Li_xMoS₂, where x is typically close to 1 (Joensen, 1986). In the intercalated materials, the coordination of the Mo atom changes from trigonal prismatic to octahedral, (Py and Haering, 1983) and thus the MoS₂ changes from semiconducting to metallic (Lin et al., 2014).

2.2 Exfoliation of Molybdenum Disulfide

The Scotch-tape based on mechanical exfoliation made famous because graphene, has also been applied to MoS₂. A bulk crystal is cleaved with adhesive tape repeatedly over a substrate, with single and few layers settling on the surface. The fragments or layers will be of different layer heights and lateral sizes, so this technique is not suited for producing uniform nanostructures on a large scale. This method involves locating a single nanostructure of interest on the substrate and micro-fabricating measurement electronics around it. Exfoliation of nanomaterial can be achieved by intercalation of lithium (Joensen, 1986). The MoS₂ is soaked

in a lithium containing solution for several hours to saturate the interlayer gaps, then exposed to water. The hydrolysis reaction produces hydrogen gas which causes the exfoliation. The suspension of few layer nanosheets can be produced in the presence of a support such as alumina to generate industrial catalyst material.

2.3 Exfoliated Molybdenum Disulfide

Preparation of single-layers has become increasingly in recent years. A simple mechanical exfoliation technique has been explored to prepare single-layer of MoS₂ (Splendiani et al., 2010). The robust enhancement of photoluminescence from few-layer to single layer of MoS₂ allows single-layer regions to be identified by optical microscopy. The robust enhancement is caused by a transition from an indirect bandgap of 1.3 eV from bulk material to a direct bandgap of about 1.83 eV in single-layer of MoS₂ (King et al., 2013, Geim and Grigorieva, 2013, Wang et al., 2012b). From single-layer to bilayer, the bandgap goes from the direct transition of 1.83 eV to indirect one of 1.6 eV (Mak et al., 2010). However from bilayer to hexa-layer, the bandgap changes slowly from 1.6 to 1.4 eV (Mak et al., 2010). Increasing to original multiple layers changes bandgap ultimately to 1.3 eV (Mak et al., 2010). Therefore, the value of the indirect bandgap depends on the number of layers within nanosheets. The simplicity of fabrication and analysis, as well as the high impact from such a novel material has made their study attractive. As graphene, single and few-layer of MoS₂ nanosheets were also produced by lithium intercalation.

2.4 Properties of Molybdenum Disulfide

Crystal structure. Layered molybdenum disulfide is made of stacked plane of covalently bonded Mo and sulfur atoms, and the neighboring layers are connected by weak Van Der Waals interactions. There are three main polytypes of bulk crystal structure: 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination), 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination) and 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination), where 2H is the most stable form in nature. Powder X-ray diffraction and TEM are direct method to study the crystal structure, and TEM can be used to study additionally the morphology of MoS₂.

However, we only can use TEM to identify the difference of diffraction pattern of single- and few-layer MoS₂. As we know that the 2H can transformed to 1T phase through lithium intercalation method. The lattice symmetry changes from 2H to 1T phase is followed by the change of density of state (DOS). Thus MoS₂ changes from the semiconducting (2H) to metallic (1T) phase (F. Wypych and R. Schollhorn, 1992).

Mechanical properties. Pristine graphene is one of strongest material that has been measured before, with having a breaking strength of 42 N/m and the Young's modulus of 1000 GPa (Huang et al., 2011). Therefore, it is to be a great interest and importance to examine the mechanical properties of the other 2D layered nanomaterials. Castellanos-Gomez *et al.* have measured the elastic properties of freely suspended exfoliated MoS₂, which have thickness ranging from 5 to 25 layers (Castellanos-Gomez et al., 2012). They reported that the average Young's modulus of suspended MoS₂ nanosheets is relatively high, $Y = 330 \pm 70$ GPa, which is comparable to that of graphene oxide. The Young's modulus of MoS₂ nanosheets is also higher than bulk MoS₂, $Y = 240$ GPa. The individual single-layers of MoS₂ have comparatively high values of both stiffness ($Y \approx 300$ GPa) and tensile strength ($\sigma_B \approx 23$ GPa) (Bertolazzi et al., 2011, Castellanos-Gomez et al., 2012), which are lower than graphene ($Y \approx 1000$ GPa, $\sigma_B \approx 130$ GPa) (Huang et al., 2011) but extremely higher than macroscopic materials such as steel ($Y \approx 200$ GPa, $\sigma_B \approx 1$ GPa). The superior elastic properties of single- and few-layer MoS₂ make them attractive semiconductors for both of electronic and optoelectronic devices, as well as for nanocomposite films (O'Neill et al., 2012).

Optoelectronic properties. MoS₂ nanosheets possess different optical and electrical properties than bulk form. For an example, MoS₂ nanosheets are semiconducting, with a direct electronic bandgap of ~ 1.9 eV, while the bulk material exhibits an indirect bandgap of 1.2 eV (Figure 2.3). The bulk material shows an indirect bandgap since the bottom of the conduction band and the top of the valence band is situated at different reciprocal lattice points (K, M, and Γ). Nevertheless, for single-layer MoS₂, the position of bottom of conduction band

and the top of the valence band are at the same K point of the x (wave factor) axis. Since this material exhibits direct bandgap behavior, it exhibits strong photoluminescence (Splendiani et al., 2010) and spin polarization (degree of alignment of electron's spin) (Mak et al., 2012). The unique optoelectronic properties of this material make it suitable for photovoltaics in which it can be used as absorber materials in thin film solar cell (Aruchamy, 1992). In addition, it has a potential applications in optoelectronic devices.

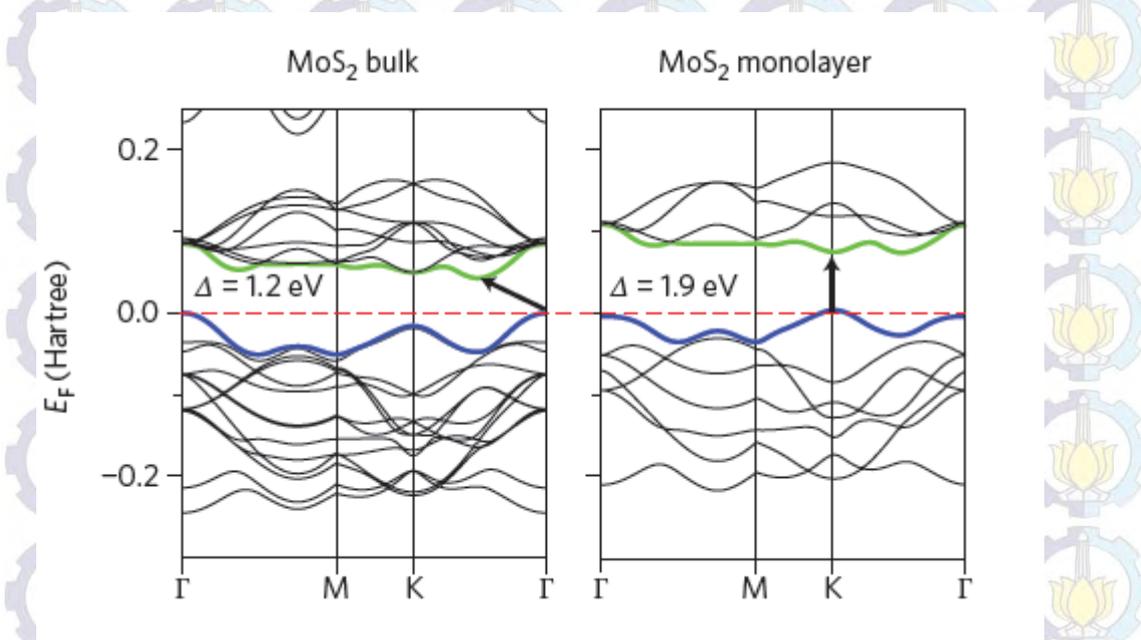


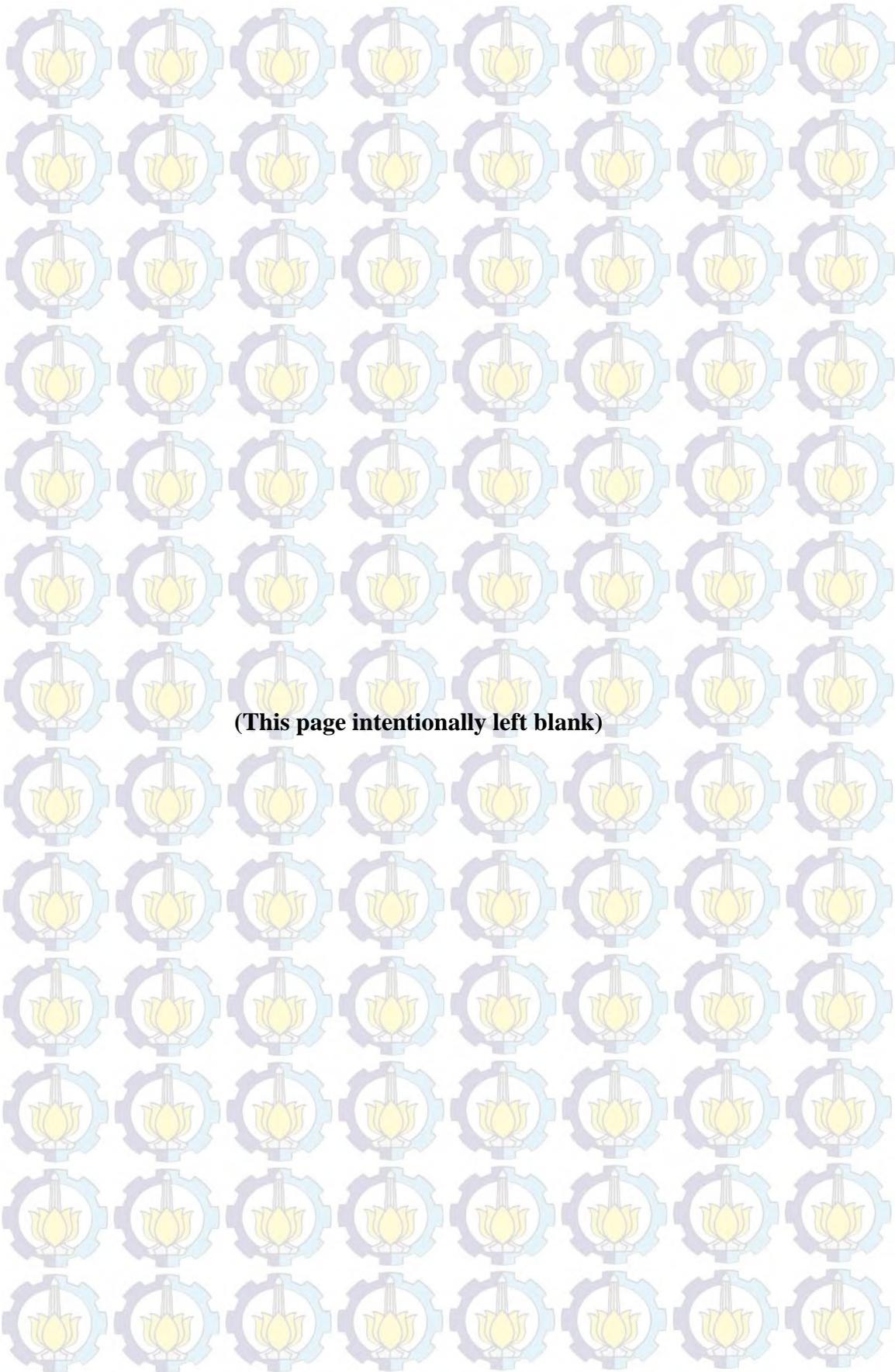
Figure 2.3. Electronic bandgap of bulk and monolayer MoS₂ (Adapted from Wang et al, Nature Nanotechnology, 2012).

Catalytic properties. When MoS₂ is exfoliated into sheets, the prismatic edge and basal plane are exposed. Many forms of MoS₂ are important in several catalytic reactions. The catalytic activity of the molybdenum disulfide is closely related to the structural properties of the material. As we know that the photoluminescence increases very significantly from an indirect bandgap to a direct bandgap which is followed by changes in orbital hybridization. The edge molybdenum and sulfur sites are highly active for hydrogen evolution reactions and thus are being considered as electrodes for water splitting by using sunlight.

Lubricant properties. The main industrial use of MoS₂ in addition to being catalysts as a dry lubricant where graphite is impractical. The lubrication is achieved by the easy shearing plane of the Van Der Waals interlayer gap. Graphite functions best when the graphene layers are lubricated by water vapor, whereas it is opposite for MoS₂. MoS₂ finds its use in space, vacuum and high temperature applications. In the form of suspended MoS₂ particles in micro sizes are often used in a grease for low-end applications. The high quality lubricating surfaces can be produced by coating a thin film of MoS₂, usually by magnetron sputtering. For the lubricating purpose, the MoS₂ surface should ideally present the basal plane for shearing as opposed to the edges, which are best for catalysis.

2.5 Potential Applications of Intercalation-Exfoliated Nanosheets

Lithium intercalation represents a versatile and sustainable route for production of molybdenum disulfide nanosheets. The successful intercalation is closely related to both charge transfer and diffusion rates. The high reduction potentials and mobility of lithium species are notably appropriate for such purposes. Lithium intercalates in which lithium is found occupying the octahedral sites in the MoS₂ interlaminar spaces are thus used as precursors of the other more complex intercalation compounds to increase the conductivity, such as molybdenum disulfide dialkylamine, Li_{0.1}MoS₂(HNR₂)_y (Sánchez et al., 1999). Also, the lithium intercalation method can be used to develop the lithium ion batteries. When molybdenum disulfide nanosheets are changed from 2H to 1T phase, effectivity of hydrogen evolution reaction is enhanced. This phase change can be achieved by electrochemical lithium intercalation method.



CHAPTER 3

EXPERIMENTAL SECTION

3.1 Synthesis

3.1.1 Materials

The Molybdenum disulfide (MoS_2) bulk powder used in these experiments was purchased from Alfa Aesar (99%) and 2.5 M n-butyl lithium in hexane was purchased from Chemetall.

3.1.2 Preparation of MoS_2 nanosheets

To make the single-layer MoS_2 suspension, molybdenum disulfide bulk powder (300mg) was placed in a 100 mL schlenk flask, to which a 2 mL of 2.5 M n-butyl lithium in hexane and 18 mL of hexane anhydrous were added under N_2 atmosphere. Then, the solution was stirred for 5 days at room temperature.

Lithium intercalation occurs according to the chemical reaction:



The resulting suspension was gravity-filtered under N_2 , and the solid washed with ~100 mL of anhydrous hexanes to remove any excess butyl lithium.

The Li_xMoS_2 was gravity-filtered under N_2 and the solution was removed using vacuum. The MoS_2 paste was transferred to a 100 mL round-bottom flask and sealed with a septum. Then, ~60 mL of distilled-water was added into round-bottom flask quickly to quench the sample. The MoS_2 paste was then taken from the round-bottom flask after the solution was removed by rotavapor.

When exfoliation occurred, excess distilled water was added to the MoS_2 paste, the lithium reacts strongly with the water, forming lithium hydroxide (LiOH), and visible bubbling occurs with the release of H_2 gas and original quintuple layers are homogeneously exfoliated due to the rapid expansion in the layers and forming suspensions of MoS_2 nanosheets. The following chemical reaction describes this process:



Next, 17.5 mg of the MoS₂ paste was suspended in 35 mL water in a 50 mL tube. Then, the mixture was sonicated continuously for 38 hours using a ½" (12.7 mm) diameter worn tip on replaceable tip (QSonica, 700W and 30% amplitude). The probe tip was adjusted to 2.5 cm from the liquid surface and bubble was formed. Bubbling by aeration at the middle of liquid and the morphology of worn tip can be helpful in the dispersion of nanosheets because the bubbling can produce a greater shearing which effect on the nanosheets in suspension. The system was kept at 5⁰C. The probe was pulsed on for 10 s and off for 5 s reduce solvent heating. After sonication, the solution was taken and then analyzed using UV-vis, dynamic light scattering (DLS), scanning electron microscopy (SEM), powder X-ray diffraction (P-XRD), transmission electron microscopy (TEM), and Raman Spectroscopy.

3.2.3 Preparation of few-layers MoS₂ with specific flakes dimension.

In our experiment, to achieve a certain size of few-layer MoS₂. We used four procedures to reduce sheet sizes to desired dimension. The first method is via centrifugation of the sample at 2000 rpm for 60 minutes (Method A). The second method involves filtration, through polyvinylidene difluoride (PVDF) membrane with pore size 450 nm, 47 mm diameter (Method B). The third one is via centrifugation at 2000 rpm for 60 minutes, followed by filtration (Method C). The fourth method involves filtration (PVDF membrane, pore size 450 nm, 47 mm diameter) followed by centrifugation at 2000 rpm for 30 minutes (Method D). In our experiments, after sonicated, 13 mL of solutions was placed in a vial. In Method A, 4.6 mL of 12 mL solutions in vials was taken and centrifuged at 2000 rpm for 60 minutes. The top 1/2nd part of the dispersion was collected by pipette. In Method B, 2.4 mL of remaining solution was dispersed in 12 mL Di-water. After that, the solution was filtered using PVDF membrane and the filtrate was collected. In Method C, 6 mL of remaining solution in vials was centrifuged at 2000 rpm for 60 minutes, then the top 1/2nd part of the dispersion was collected by pipette and was then filtered quickly. In method D, 6 ml of the filtrate from method B was taken and centrifuged at 2000 rpm for 30 minutes. Then, the top 1/2nd part of the solution was collected by pipette. Then, all of the solution (from

Method A, B, C, and D) were analyzed using UV-vis, dynamic light scattering (DLS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman Spectroscopy.

3.2 Characterization Method

The absorbance spectra of the few-layer MoS₂ were recorded using a varian Cary 5000 and samples were tested in quartz glass cuvettes having 10 mm path length. The morphology of the samples was examined using scanning electron microscopy (SEM) model ZEISS-GEMINI Ultra Plus, with an Oxford Instruments EDS apparatus operated at 5 kV. For the EDS measurements, the EDS-SEM was operated at 10 kV. The sample was dropped on Silicon wafer (Si substrate) and washed three times using Di-water and evaporated at room temperature. The measurements were performed in standard carbon tip. The TEM images were examined using transmission electron microscopy instrument (Model JEOL-2010) operated at an accelerating voltage of 200 kV. The lattice and corresponding SAED pattern were characterized in a JEOL JEM-2100F TEM operated at an accelerating voltage of 200 kV. In preparation of TEM measurement, 1.5 mL of the sample was taken and centrifuged to collect the sample. Then, 1.5 ml ethanol solution was added into each of samples to disperse the exfoliated MoS₂. 100 μ L of the solution was taken and diluted in 400 μ L ethanol, then dropped on copper grids, then washed three times using Di-water to remove the impurities which are probably attach on the Cu grids and let samples evaporated at room temperature. The X-ray diffraction (XRD) patterns were measured with a diffractometer (BRUKER, GADDS) using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation over the range of $10^\circ \leq 2\theta \leq 80^\circ$ under a voltage of 40 kV and a current of 40 mA. In the preparation of XRD measurements, for the MoS₂ nanosheets, 3 ml of main solution (after sonication) was taken and centrifuged to collect the sample paste, and then dropped on Glass-deck and dried at room temperature. The number of lithium before and after exfoliation were calculated using VARIAN ICP-OES. In the ICP-OES preparations, each of 8.6 mg of Li_xMoS₂ and 8.6 mg of MoS₂ nanosheets powder were dissolved in 20 ml aqua regia and allowed in the hood for overnight. Raman spectra were measured with in Via Confocal Raman

Spectroscopy (NTEGRA Spectra, NT-MDT) at excitation laser line 488 nm in air ambient environment. The power of the excitation laser line was kept well below 1 mW to avoid heating effect and the spot size of 50 μm with exposure time at 10 s and grating line at 1800/500 with range of $\lambda = 500$ nm. In preparation of Raman measurements, 1.5 mL of the sample was taken and centrifuged to collect the solid. Then, 1.5 ml ethanol was added into each of samples to disperse the exfoliated MoS_2 , and finally the dispersions were collected using pipette and dropped on Silicon wafer (Si substrate), then washed three times using Di-water and let samples evaporated at room temperature. Atomic force microscopy images was recorded on Veeco MultiMode VIII microscope in tapping mode. In AFM measurements, 1.5 mL of sample A, B, C and D were taken and centrifuged to collect the sample. Then, 1.5 ml ethanol was added into each of samples to disperse the exfoliated MoS_2 , and finally the dispersions were collected using pipette and dropped on freshly silicon wafer (Si substrate), dried, and then soaked in distilled water to remove any impurities which are attach on Si substrate and dried under vacuum at 50 $^{\circ}\text{C}$ for minimum 3 hours. The zeta potential and size distribution of the as-prepared MoS_2 nanosheets were measured by using dynamic light scattering (DLS). DLS measurements were performed using a Malvern Zetasizer Nano ZS with a 633 nm He-Ne laser. Samples were tested in low volume disposable sizing cuvettes. Malvern Zetasizer Nano ZS was operated in backscatter mode at an angle of 173 $^{\circ}$ and analyzed three times for each samples. Samples were equilibrated to 25 $^{\circ}\text{C}$ for 120 s prior to measurement. Viscosity and Refractive index of solvent (water) at 25 $^{\circ}\text{C}$ are 0.8872 cP and 1.330, respectively. An automatic measurement positioning and automatic attenuation. The samples were analyzed as prepared without further dilution. In this measurements, the dispersions (for sample A, B, C, and D) were taken 600 μL and sonicated for two minutes to avoid aggregation before measurements.

CHAPTER 4

RESULTS AND DISCUSSIONS

In recent years, MoS₂ based catalysts have been considered as promising material to replace platinum because of their high abundance and low cost. Promising catalytic activity of MoS₂ in the hydrogen evolution reaction (HER) is attributed to the active sites located along the edges of its two-dimensional layered crystals. If the MoS₂ based catalysts are to realize their potential, there is an urgent need to design MoS₂ nanosheets with more edge sites. The ability to control the nanosheets size during exfoliation process, achieved here by control of centrifugation and filtration, will be important for the number of applications. One of the most important applications is as catalyst for the evolution of hydrogen from proton-rich electrolytes (Jaramillo and Horch, 2007). Because the catalytically active sites reside on edge of nanosheets, Hydrogen evolution catalyst is strongly dependent on nanosheets length with small flakes performing much better than larger ones (Varrla et al., 2015). And the change of phase MoS₂ from semiconducting to metallic which happened during intercalation process is to be an important factor in evolution of hydrogen because in the previous research shown that the metallic phase has catalytic activity is better than semiconducting phase (Voiry et al., 2013). For another application, lithium ion batteries are still exist and high efficient energy in industrial battery. So, in here we reported the preparation MoS₂ nanosheets with specific flake dimensions using lithium intercalation method to provide material which can be applied in those applications.

4.1 Intercalation of Lithium

The intercalation of lithium into transition metal dichalcogenides is especially relevant both to technical applications and to fundamental knowledge of layered materials. This is notably valid for MoS₂, as a great part of its intercalation chemistry based on processes. Even though some research about synthesis of MoS₂ nanosheets using another alkali metal as intercalating agents and another method, such as mechanical exfoliation, chemical vapor deposition,

and liquid-phase exfoliation have been reported, much attention has been focused on intercalation of lithium, among others because of the potential of such materials as a high power component in batteries and a good component for hydrogen production.

Chemical exfoliation of layered materials is generally achieved by reacting the 2D nanomaterials with *n*-butyl lithium. The electrons from *n*-butyl lithium (as a guest) are transferred to the lowest-lying-unoccupied energy levels of MoS₂ (as a host), which are fundamentally transition metal d bands (as shown in Figure 4.1) (Knirsch et al., 2015). And also the charge transfer from *n*-BuLi to MoS₂ actually may induce structural changes in the host. Structural and electronic changes in the host of MoS₂ produced by lithium intercalation method often induce dramatic changes in the transport properties of MoS₂ from semiconducting to metallic (Benavente et al., 2002). The important thing is that when the bulk materials become nanosheets, the properties change, such as mechanical, electronic and thermodynamic properties (O'Neill et al., 2012).

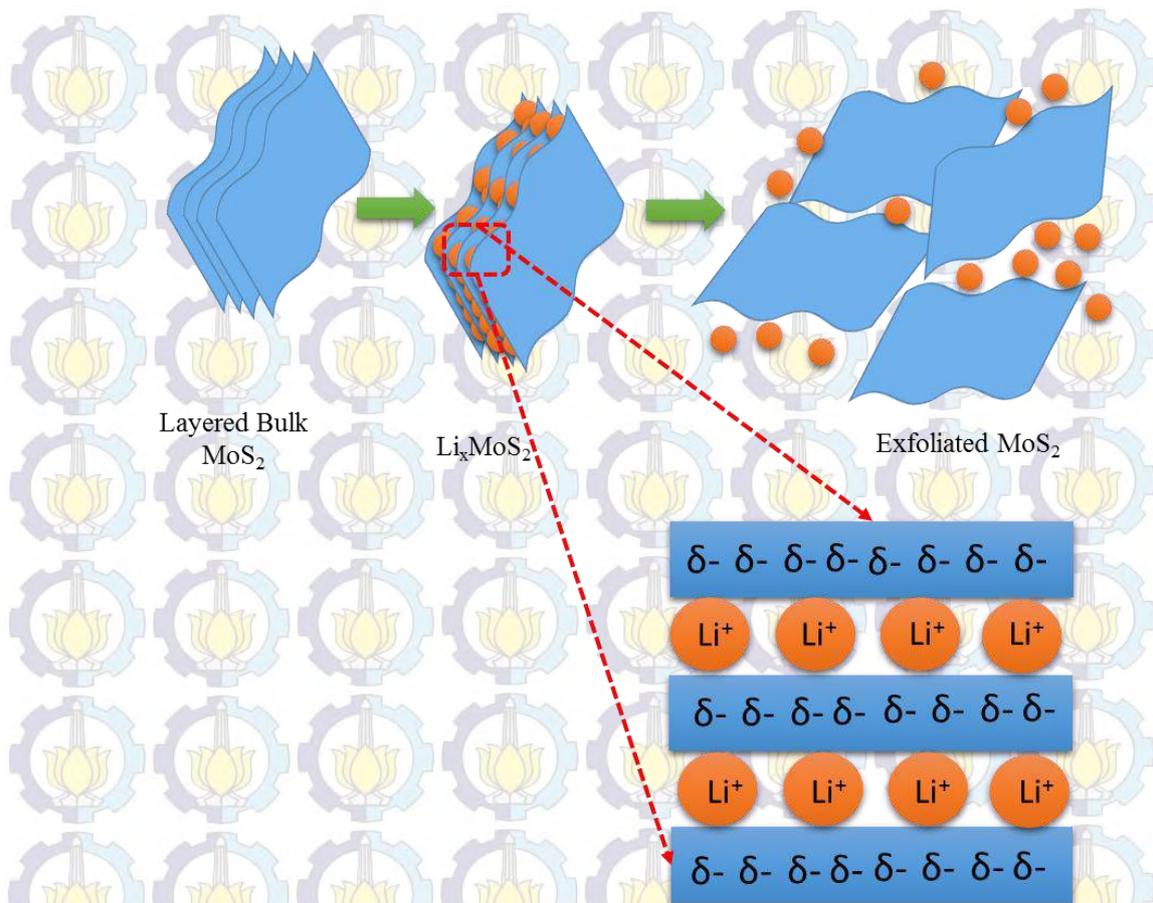


Figure 4.1. Schematic illustration of intercalation of lithium into MoS₂ layers.

Figure 4.1 illustrates the formation of MoS₂ nanosheets via lithium intercalation method from bulk material. The structure of molybdenum disulfide can be considered as layers coupling together by weak Van Der Waals forces, which make lithium ion being intercalated between layers under appropriate condition. During the stirring process, anhydrous hexane can serve as solvent, resulting in the lithium cations dispersed in the solvent being readily insert into MoS₂ layers with the formation of lithium intercalated MoS₂ (Li_xMoS₂) units according to the following chemical reaction,



Then when the Li_xMoS₂ units are exposed to water, the lithium in the unit become rapidly solvated and produces exfoliated MoS₂ layers, lithium hydroxide (LiOH), and hydrogen gas (H₂) based on another following chemical reaction,



During the reaction process, original quintuple layers are homogeneously exfoliated due to the rapid expansion in the layers and forming suspensions of MoS₂ nanosheets.

4.2 Exfoliation of Molybdenum disulfide

To promote exfoliation of MoS₂, here we used sonication. The MoS₂ exfoliated sheets were exposed to ultrasonication at room temperature for 38 h, followed by centrifugation to reduce sheet size to desired dimension. The reaction of the resulting lithiated phase of MoS₂ with water through the redox reaction (reaction 2) and can form few- or single-layer MoS₂ dispersion with partial negative charge (see Figure 4.1) (Joensen, 1986). In this work, after we got MoS₂ nanosheets, Zeta (ζ) potential measurements is used to prove it.

The zeta potential is an important factor for characterizing the stability of colloidal dispersions and provides a measure of the magnitude and sign of the effective surface charge. In this measurements the average value of zeta potential is about -29.18 mV (Figure 4. 2), which indicates that the MoS₂ nanosheets become negative charge after exfoliation due to the electron transfers from *n*-BuLi (guest) to MoS₂ surface (host).

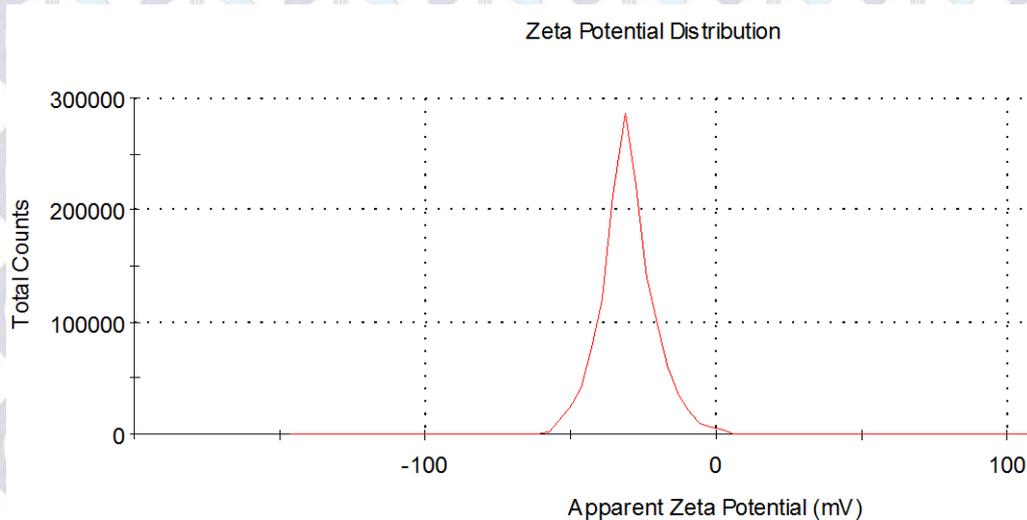


Figure 4. 2. The zeta potential distribution of the exfoliated MoS₂ dispersions

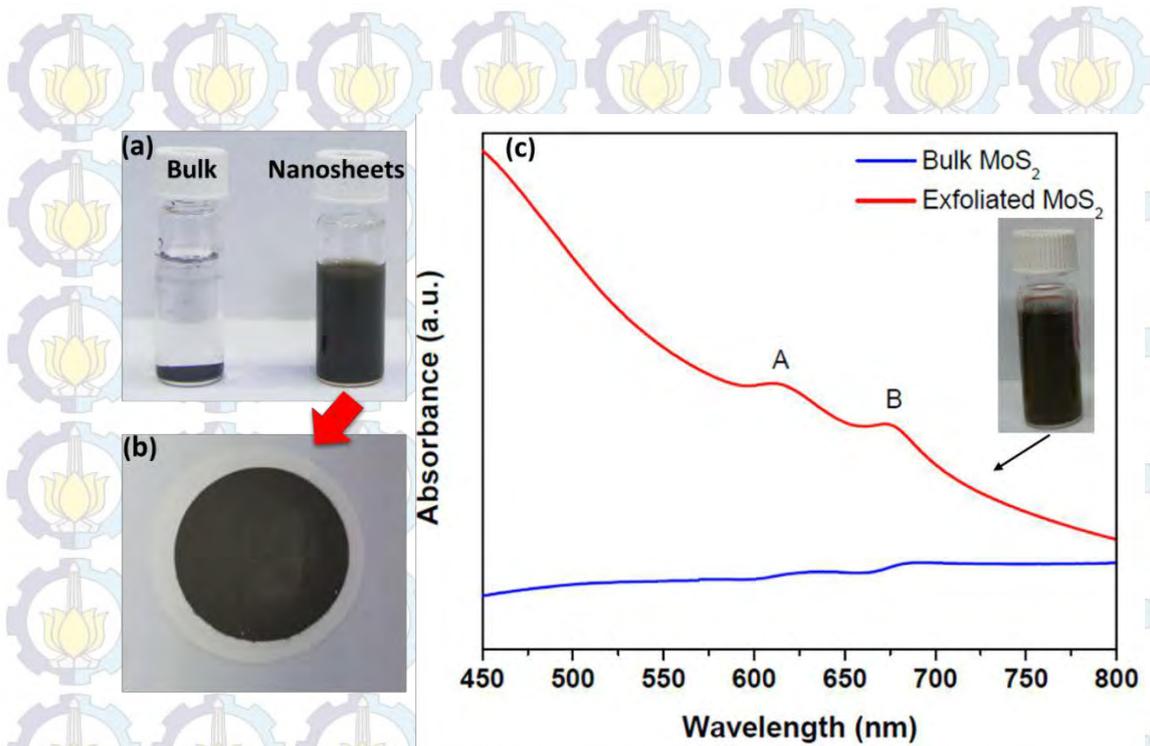
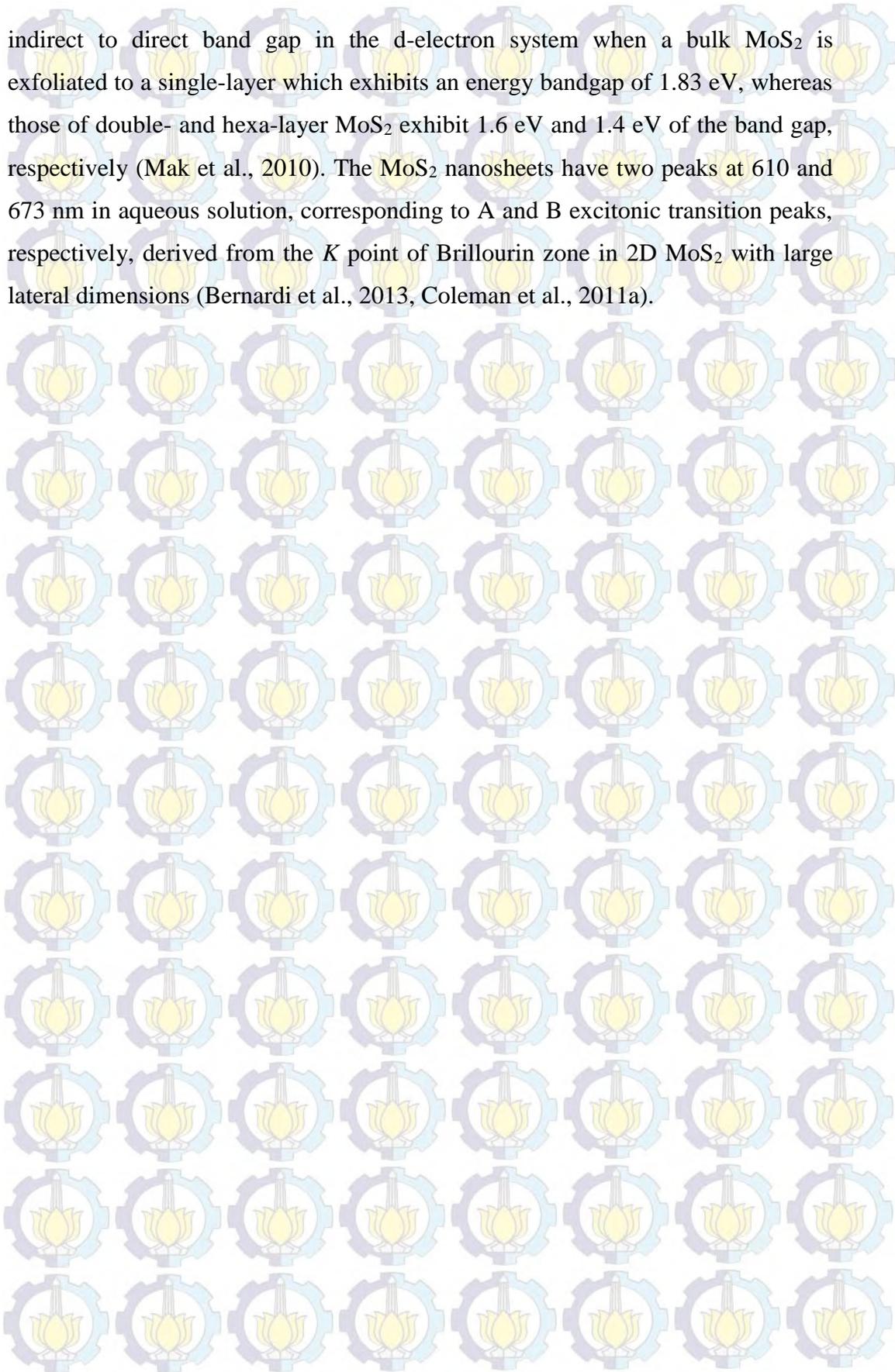


Figure 4.3. (a) Digital images of the change in the solution containing bulk MoS₂ before (left) and after (right) reaction; (b) Digital image of the MoS₂ nanosheets by filtration using PVDF membrane with 450 nm pore size; (c) UV-vis absorption spectra of bulk MoS₂ and exfoliated MoS₂ nanosheets (after sonication for 38 h) dispersed in water. The inset photo is the dilute solution of MoS₂ nanosheets.

Figure 4.3a illustrates the observable changes between the dispersion of MoS₂ bulk and nanosheets in water. In contrast to the former limpid solution containing a large number of MoS₂ bulk in the bottom, the aqueous dispersion of MoS₂ nanosheets presents a muddy and uniform dispersion state, implying the thin sheets of MoS₂ contained therein. The MoS₂ nanosheets can be obtained by filtration using porous polyvinylidene fluoride (PVDF) membrane (as shown in Figure 4.3b). Figure 4.3c shows typical UV-vis spectra of MoS₂ nanosheets and bulk suspended in water. The absorption spectrum of MoS₂ nanosheets suspension displays much higher peak absorption in visible region compared to that of the bulk suspension. Optical absorption is a characteristic related to band structure of a semiconductor. Bulk MoS₂ is a semiconducting material with an indirect band gap of about 1.3 eV. However, from the previous researches have shown an

indirect to direct band gap in the d-electron system when a bulk MoS₂ is exfoliated to a single-layer which exhibits an energy bandgap of 1.83 eV, whereas those of double- and hexa-layer MoS₂ exhibit 1.6 eV and 1.4 eV of the band gap, respectively (Mak et al., 2010). The MoS₂ nanosheets have two peaks at 610 and 673 nm in aqueous solution, corresponding to A and B excitonic transition peaks, respectively, derived from the *K* point of Brillouin zone in 2D MoS₂ with large lateral dimensions (Bernardi et al., 2013, Coleman et al., 2011a).



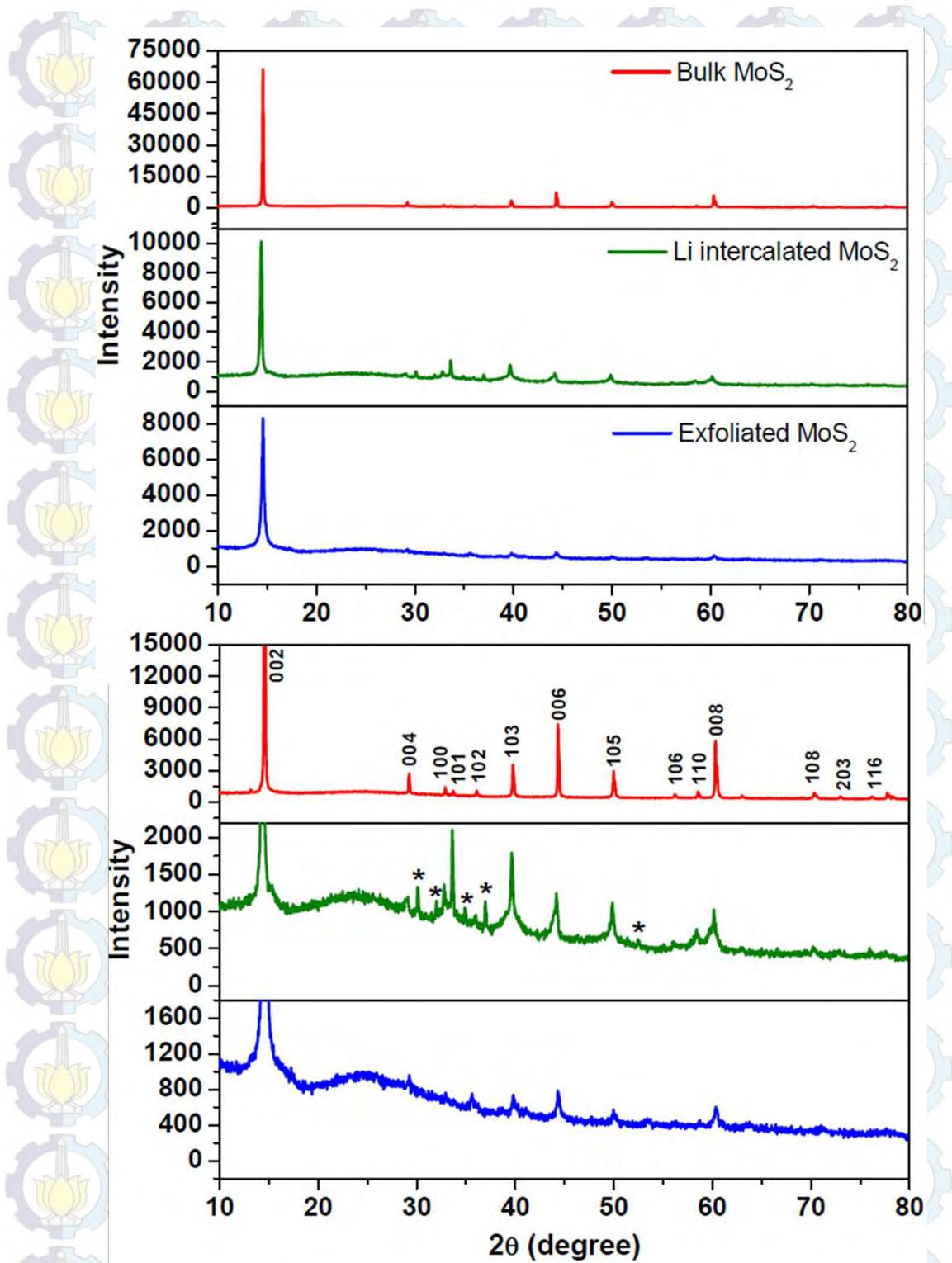


Figure 4.4. The XRD pattern of bulk MoS₂, Li intercalated MoS₂, and exfoliated MoS₂ nanosheets (top) with magnification of intensity of 5x (bottom).

Figure 4.4 shows the XRD results of raw bulk material, lithium intercalated MoS₂ and exfoliated MoS₂ nanosheets. All diffraction peaks of the sample were in good agreement with a hexagonal structure of MoS₂ (JCPDS No. 37-1492). As shown in Figure 4.4, the peak positions of MoS₂ bulk and nanosheets are in the same places, with different intensity, which indicates that the exfoliated MoS₂ has a hexagonal lattice structure and preserve well the crystalline phase of bulk MoS₂. Compared with those of bulk MoS₂ and exfoliated MoS₂ nanosheets, lithium intercalated MoS₂ has additional diffraction peaks at 30°, 32°, 35°, 37° and 52°. These XRD peaks are originated from MoS₂ being intercalated by Li to form Li_xMoS₂, which is consistent with previous results reported by Liu et al (Liu et al., 2013b). From XRD results, these additional peaks disappear after exfoliation, indicating that intercalated Li is removed when MoS₂ nanosheets are formed. To confirm that the lithium become disappear after exfoliation, we performed the Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (see appendix A). The result shows that before and after exfoliation of Li intercalated MoS₂, 95% of lithium can be removed. Therefore, in the XRD pattern of MoS₂ nanosheets we cannot see the lithium intercalated peaks. In XRD results of bulk material, the very sharp peaks with high intensity and a strong [002] peak indicate good crystallization and well-stacked layered structure. Furthermore, the XRD result of MoS₂ nanosheets shows broadened peaks and shortened [002] peak, which is consistent with previous results (Eda et al., 2011). And the results indicate a much smaller crystallite size of MoS₂ nanosheets compared to bulk material.

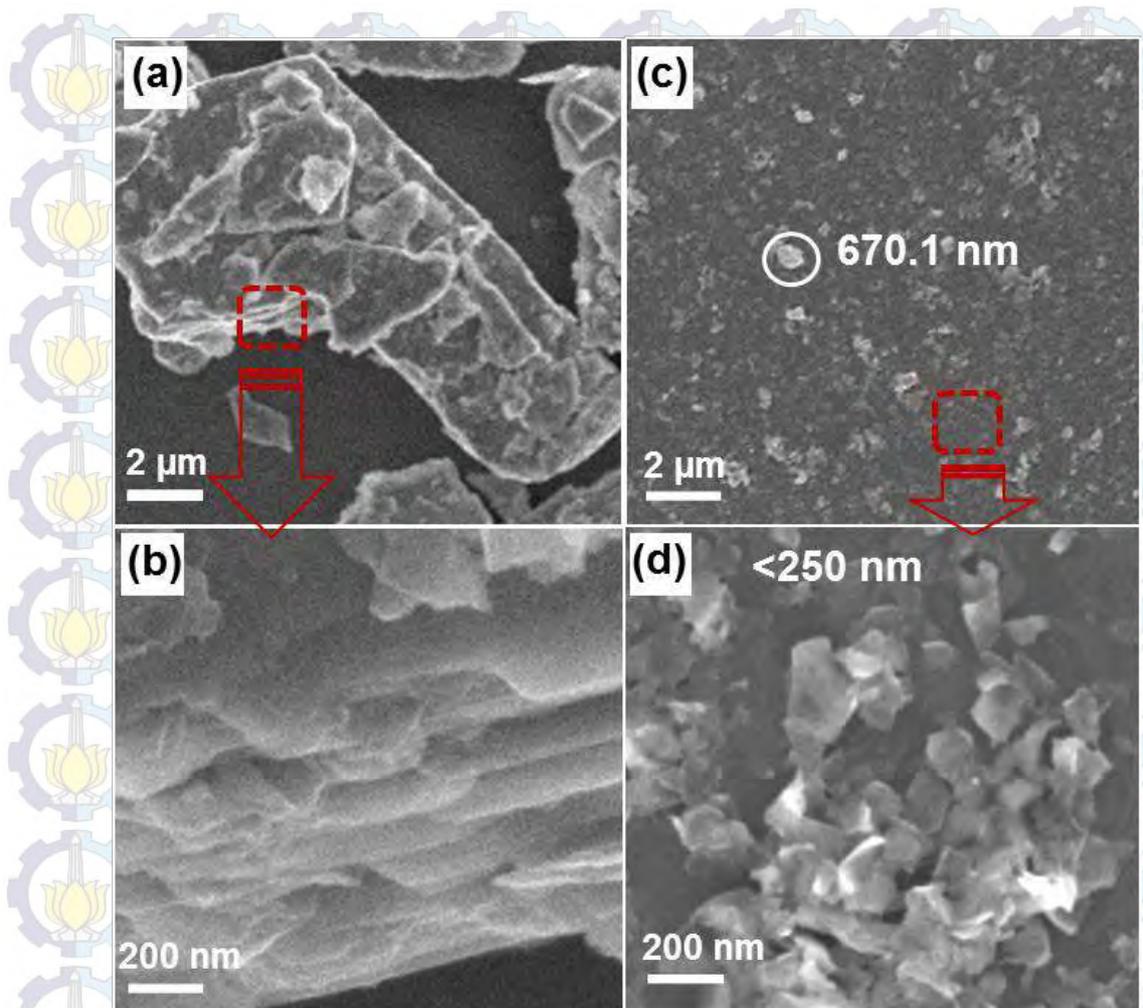


Figure 4.5. The typical SEM images: (a) and (b) Bulk MoS₂ powder with different resolution; (c) MoS₂ nanosheets with different lateral sizes; (d) MoS₂ nanosheets with lateral size <250 nm.

The morphology of the as-prepared MoS₂ samples was identified by SEM and high-resolution TEM (HRTEM). The SEM images of the MoS₂ both bulk material and exfoliated MoS₂ are shown in Figure 4.5. The original quintuple layers with several irregular lateral size of sheets can be observed clearly in Figure 4.5a. Figure 4.5b displays the stacked-layered structures and sharp edges of the MoS₂ flakes. The SEM image of the MoS₂ nanosheets is shown in Figure 4.5c. Many irregular MoS₂ nanosheets with different lateral sizes can be clearly observed. A bigger exfoliated MoS₂ with a size of 670.1 nm is observed in the

SEM image, and much smaller sheets are contained therein (as shown in Figure 4.5d with higher resolution).

This variation of size is mainly associated with the ultrasonic cavitation effect because in this preparation we used probe sonication to promote exfoliation.

When the resonance frequency of bubbles corresponds with that sound waves, the maximum energy coupling of acoustic field and bubbles will be generated, accompanying an obvious cavitation effect and finally, the flake MoS₂ nanosheets with different lateral sizes are produced.

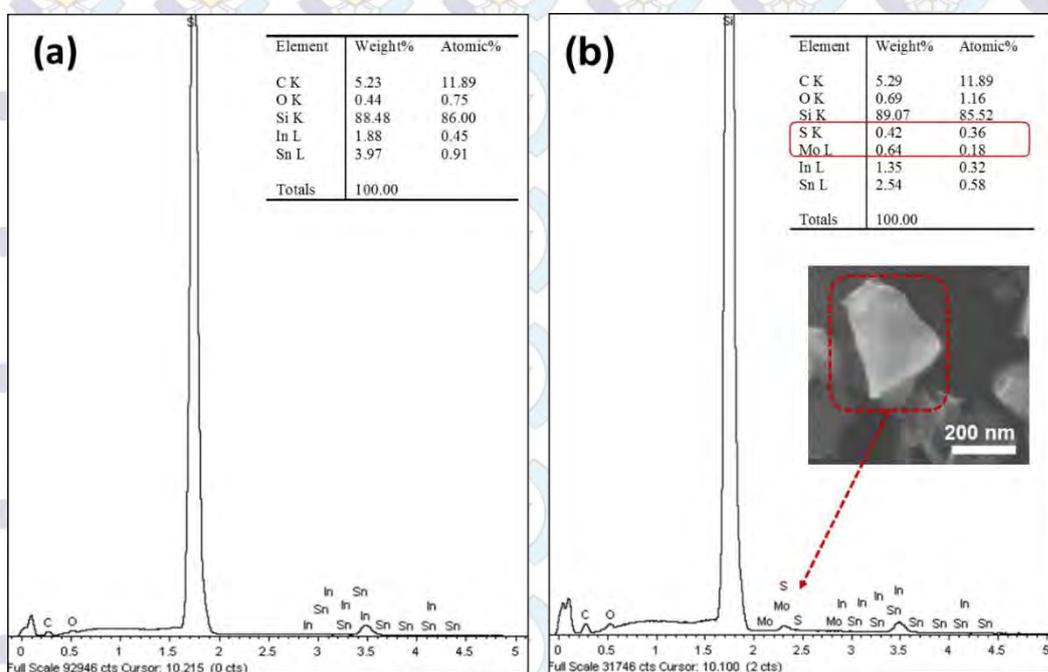


Figure 4.6. (a) EDS-SEM of silicon wafer; (b) A representative EDS-SEM spectrum collected from an individual MoS₂ nanosheets in silicon wafer. The inset image is the SEM image of MoS₂ nanosheets in EDS-SEM analysis.

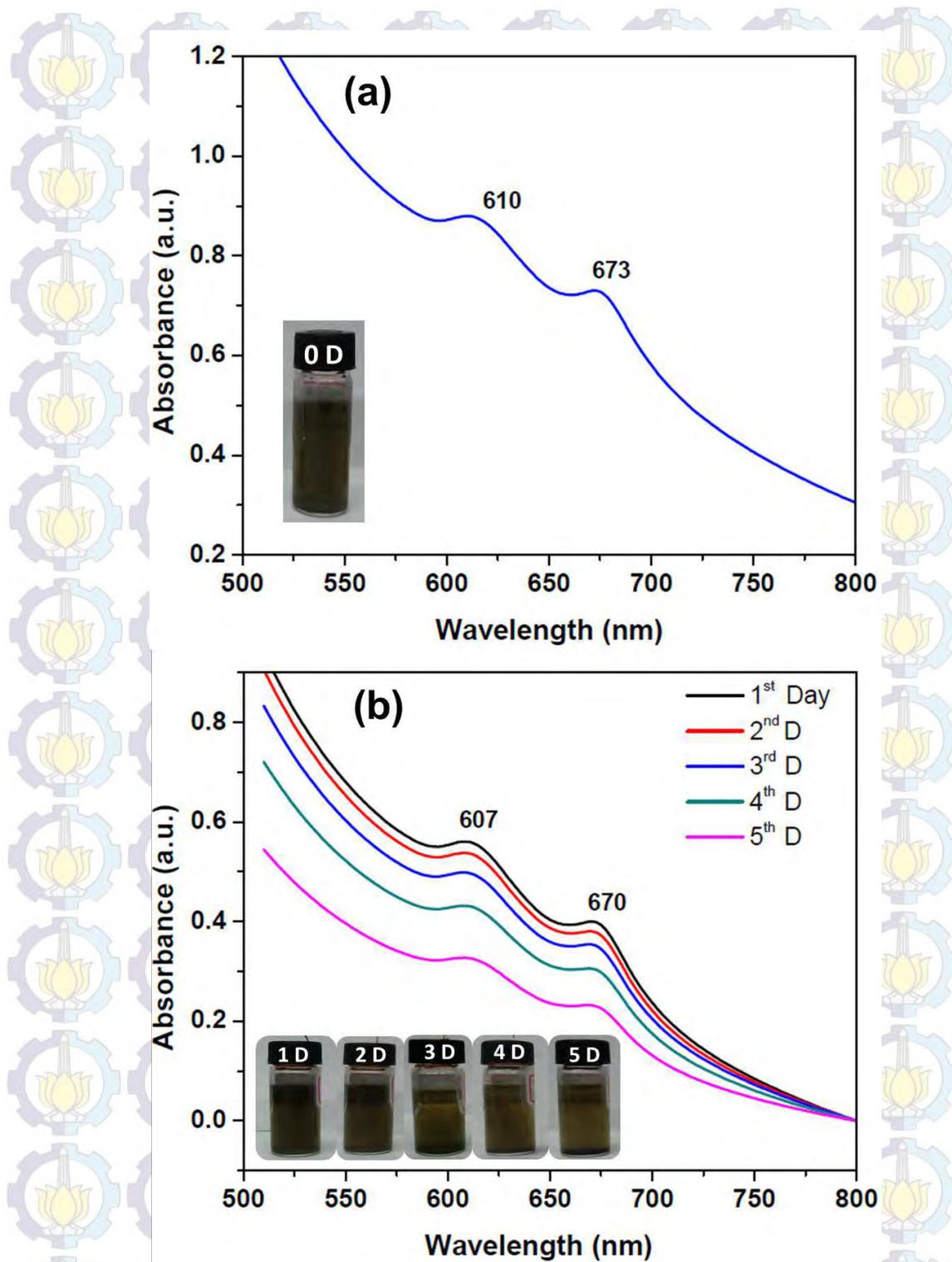


Figure 4.7. (a) Absorption spectrum of MoS₂ nanosheets after sonication (not further dilution). (b) Absorption spectra of MoS₂ nanosheets from (a) after 1 – 5 days. All of UV-Vis results in the same concentration: 0.6 ml of sample after sonication / 3 ml of Di-water.

The important thing in this process is the sonication with stronger cavitation and longer time produces the smaller flake sizes of MoS₂ nanosheets with narrow lateral size distribution. This effect is analogous to the previous results, which states that the flakes could be cut by the scission of low energy ball milling and sonication (Yao et al., 2012). Figure 4.6 illustrates the composition of elements of silicon wafer (left) and MoS₂ nanosheets (right) and the presence of C and O element actually comes from SEM machine. As shown in Figure 4.6b, in EDS spectrum, the atomic ratio of an individual MoS₂ nanosheet is 1:2, which indicates that MoS₂ nanosheets preserve well-qualified atomic structure of bulk MoS₂. We also provided UV-vis spectra to show the different lateral sizes of MoS₂ nanosheets in my sample as shown in Figure 4.7. The UV-vis spectrum of MoS₂ nanosheets after sonication (no further treatment) exhibits two peaks at 610 nm and 673 nm which are ascribed to the *K* point of the Brillouin zone in 2D MoS₂ with larger lateral dimensions (Bernardi et al., 2013). In contrast to Figure 4.7a, the excitonic peaks in Figure 4.7b at 607 nm and 670 nm are in accordance with the characteristic peaks of exfoliated MoS₂ with smaller lateral dimensions (Wang et al., 2014). In Figure 4.7b shows that after the sample is left up to 5 days, the bigger MoS₂ nanosheets precipitate in the bottom and the color of solution changed to be brighter. To confirm that the bulk MoS₂ has been successfully exfoliated into nanosheets with various sizes, we performed dynamic light scattering (DLS) on exfoliated MoS₂, as shown in Figure 4.8. The simplest way to do this is to measure the particle diffusion coefficient which can be used to infer its size via Stokes-Einstein relation. In this measurement a commercially available Malvern Zetasizer Nano ZS was used. By operating in backscatter mode (173° scattering angle) it was possible to use the machine's automatic beam positioning system. The focal position and attenuation of the incident beam were optimized by that system before data acquisition. These setting was used to probe the sample close to the cuvette wall, thus minimizing multiple scattering of the light by highly concentrated samples. So, in this measurements, the samples did not need to be diluted in order to record size data, even zeta potential data.

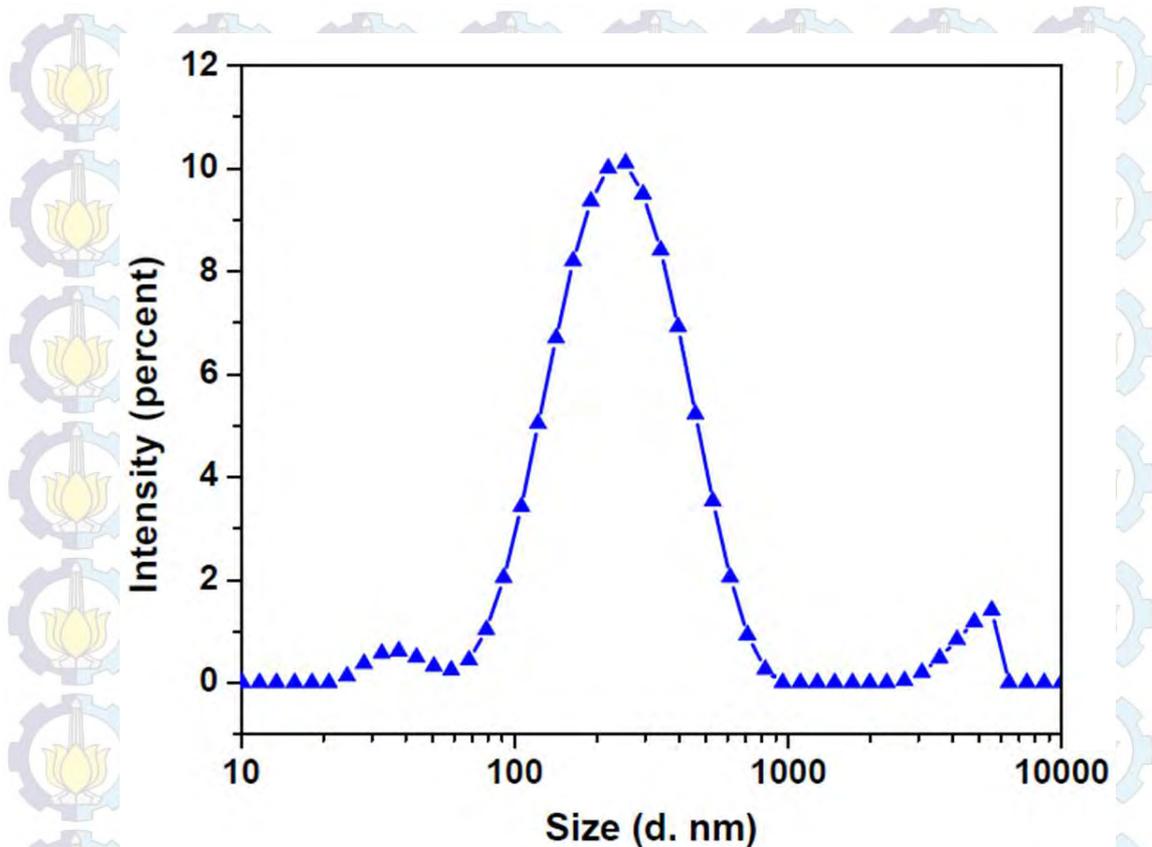


Figure 4.8. Size distribution of MoS₂ nanosheets by intensity

However, this measurements considerably work well for spherical objects, it is less reliable for non-spherical geometries, such as rods or platelets. At least here we can present the size distribution of MoS₂ nanosheets according to DLS measurements. The DLS software also computes an averaged particle size value known as the “Z-average diameter”. This value is derived from the entire intensity particle size distribution (PSD) and so is also strongly influenced by the presence of any spurious peaks.

In DLS results, a small peak around 38 nm is observed; this could be attributed to the presence of very small MoS₂ nanosheets. However, the primary peak of the distribution is centered at 220 nm which agrees well with the size distribution from SEM analysis shown in Figure 4.5d. A third small peak is observed at around 5.8 μm, this feature appeared in few samples. The origin of this peak is unclear as large objects around 5.8 μm in size were not observed in

SEM analysis. This feature may be due to small dust particles or air bubbles in this dispersions.

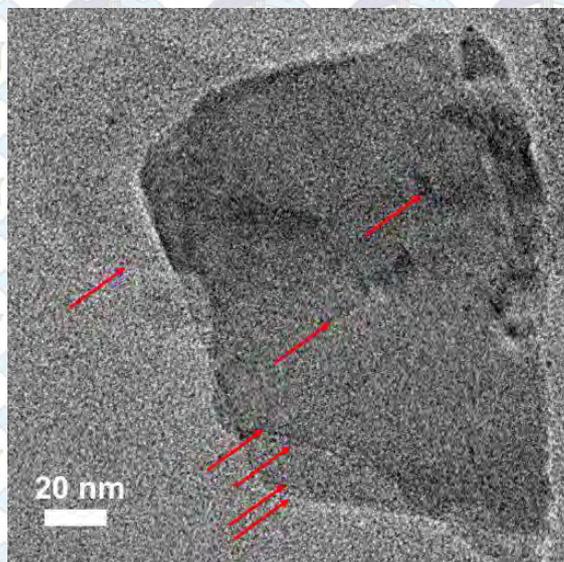


Figure 4.9. TEM image of MoS₂ nanosheets

The as-prepared MoS₂ nanosheets was also analyzed by TEM. The Figure 4.9 displays the typical TEM image of an individual MoS₂ nanosheets. It is clearly shown that the exfoliated MoS₂ was a thin layer with smooth surface. The TEM image also shows the presence of 7 layers of sheets. To confirm that the MoS₂ bulk has been successfully exfoliated into few-layers structure, we performed Raman spectroscopy on exfoliated MoS₂ and bulk MoS₂, as shown in Figure 4.10. The characteristic peaks of the bulk MoS₂ at 377 and 402.9 cm⁻¹ are assigned to the E_{2g}^1 and A_{1g} modes, respectively, while that of the exfoliated MoS₂ features these peaks at 383.9 and 407.8 cm⁻¹, respectively.

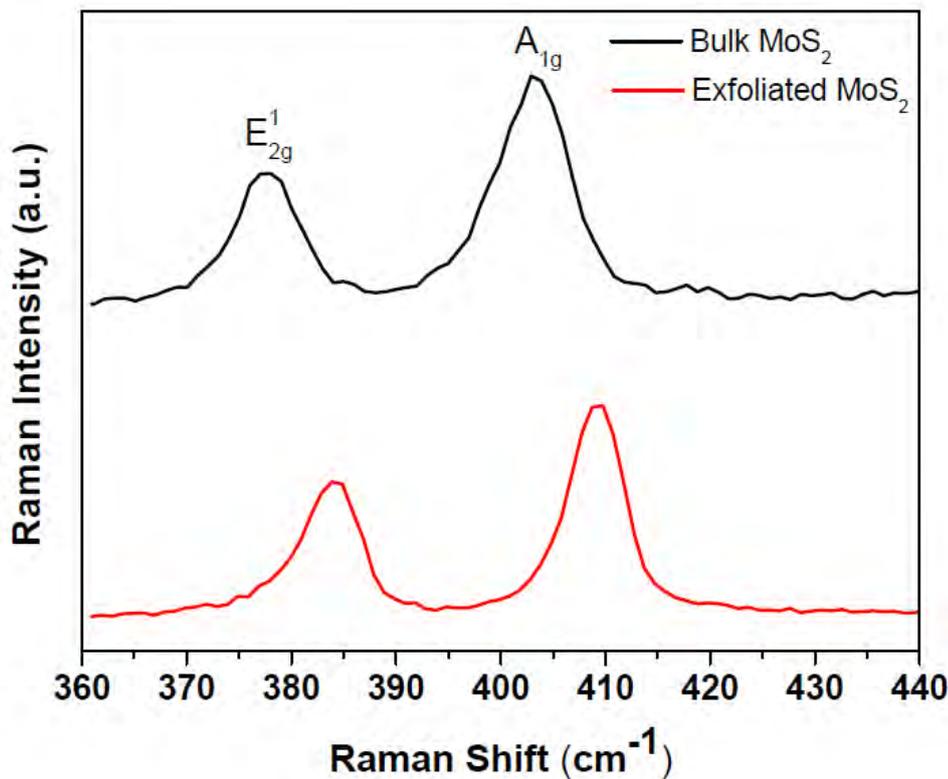


Figure 4.10. Raman spectra of bulk MoS₂ and exfoliated MoS₂ from lithium intercalation process.

The E_{2g}^1 mode is correlated with an in plane opposite vibration of Mo and S atoms, while the A_{1g} mode is caused by an out-of-plane vibration of sulfur atoms in opposite directions (Yu et al., 2013b). Particularly, the E_{2g}^1 mode is the shear mode, which is attributed to the relative vibration between the adjacent single-layers. The frequency difference (Δk) between the E_{2g}^1 and A_{1g} modes in the exfoliated MoS₂, $\Delta k = 23.9 - 24.9 \text{ cm}^{-1}$ is smaller than that in the bulk MoS₂, $\Delta k = 25.9 \text{ cm}^{-1}$, consistent with the Raman signatures of MoS₂ nanosheets comprising over than three layers (see **Error! Reference source not found.** in appendix A) (Lee et al., 2010).

4.3 Few-layer Molybdenum disulfide with Specific Flake Dimensions.

Recent research has indicated that graphene flakes can be selected by sizes by controlled centrifugation coupled with sediment recycling (Khan et al., 2012, May et al., 2012). Here we used centrifugation based on time and filtering to

control the size of few-layer MoS₂ nanosheets. While liquid exfoliation generally results in flakes which are small on average, the flake size distribution can be quite broad. In this work we developed methods to control sizes of MoS₂ nanosheets to predominately select flakes in the upper solution. To achieve this we used four methods as shown in experimental section, we combined centrifugation and filtration to reduce the bigger size of few-layer MoS₂ nanosheets. In method A, we used centrifugation at 2000 rpm for 60 minutes and then the top 1/2nd part of the supernatant was collected by pipette. When taking the supernatant we must be careful because sometimes the bigger size will be mixed into it. In method B, after the solution was filtered through PVDF membrane, the solution was taken while the solid sample was removed. In method C, the solution was centrifuged at 2000 rpm for 60 minutes and the followed by filtration. In the first step, the top 1/2nd part of the supernatant was collected by pipette and entered to vials and the next step the solution was filtered using PVDF membrane. Then the solution was taken while the solid sample was removed. In method D, we used the solution from method B after filtering, then the solution was centrifuged at 2000 rpm for 30 minutes, after that the top 1/2nd part of the supernatant was collected by pipette and entered to vials. After each centrifugation and filtration step, we performed spectroscopic measurements. The color of the resultant dispersions varied in different procedures (method A, B, C, and D) indicating that the nature of the nanosheets is indeed changed. As shown in Figure 4.11a, the color in the method B is the darkest than others, and after centrifuged, the color changes slowly to be brighter. According to the previous research (Wang et al., 2014), the peaks position at 673 and 610 nm are assigned to the *K* point of the Brillouin zone in 2D MoS₂ with relatively larger lateral dimensions (Method B). We also found large shift for the method A, C, and D in the optical absorption in comparison to those of MoS₂ nanosheets with relatively smaller lateral dimensions, arising from the quantum size effect of MoS₂ nanosheets (Figure 4.11b).

We also performed SEM, TEM and HRTEM to determine the quality and dimension of the flakes during controlled centrifugation and filtering regime. The

SEM images (Figure 4.12) illustrated that the MoS₂ was well exfoliated for all of methods. In addition, we noticed that size-selected few layer flakes tended to have smaller flakes adsorbed in many cases. As shown in Figure 4.12, the sample B had the largest lateral dimension, which agrees well with the UV-vis spectra (Figure 4.11).

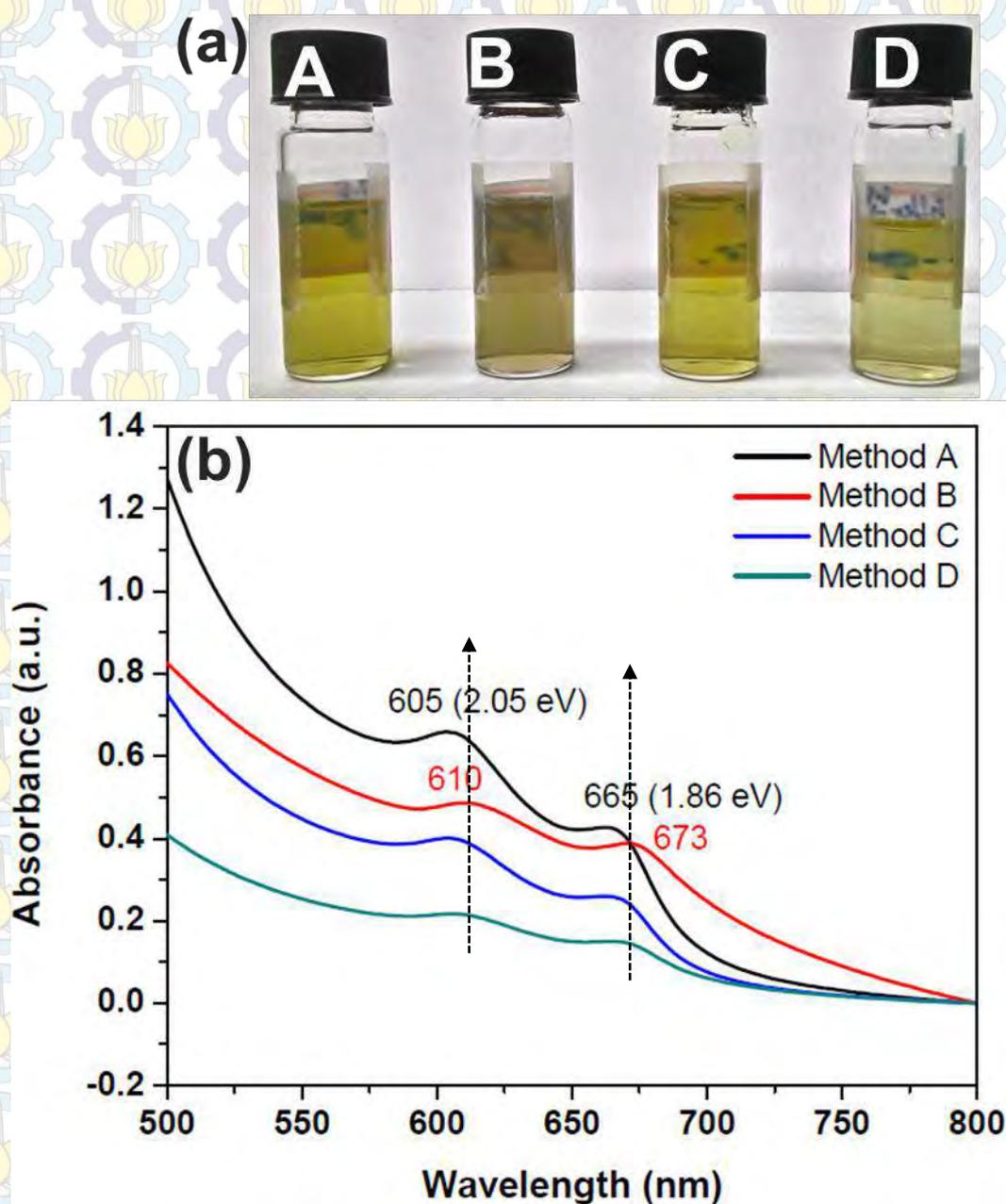


Figure 4.11. (a) Digital images of the dispersions after size selection; (b) Absorption spectra of few-layer MoS₂ nanosheets from different methods.

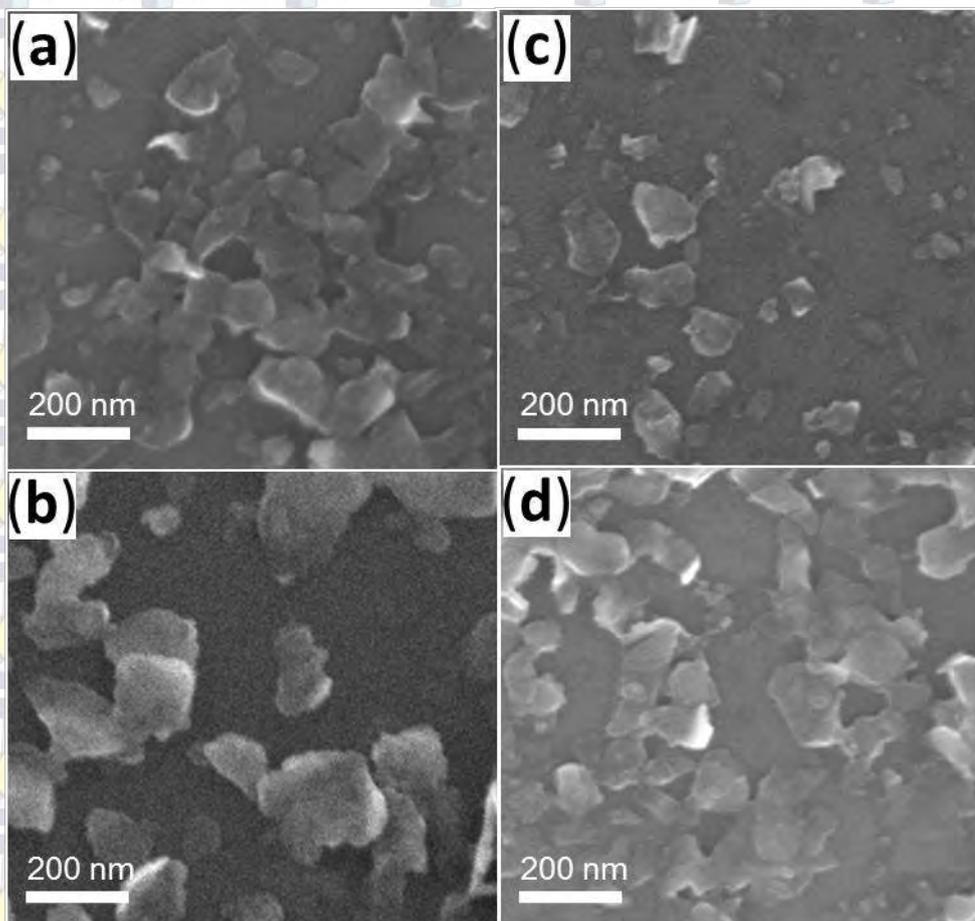


Figure 4.12. SEM images of size selected dispersions produced by (a) Method A, (b) Method B, (c) Method C, (d) Method D.

Table 4.1 shows that the molar ratio of every few-layer MoS₂ sample from different methods is close to 1:2, which is consistent with the formula. The completely EDS-SEM results can be found in appendix B (**Error! Reference source not found.**).

The lateral sizes of the few-layer flakes are also observed by SEM micrographs. The SEM micrographs illustrated that the MoS₂ bulk has been successfully exfoliated into few-layer MoS₂ nanosheets with different lateral size. Sample D displays a smaller lateral size than sample B, but it is bigger than sample A and B (see Figure 4.12).

Table 4.1. Summary of EDS-SEM analysis from different method

Method	Molar ratio (S/Mo)
A	2.27
B	1.97
C	1.93
D	2.13

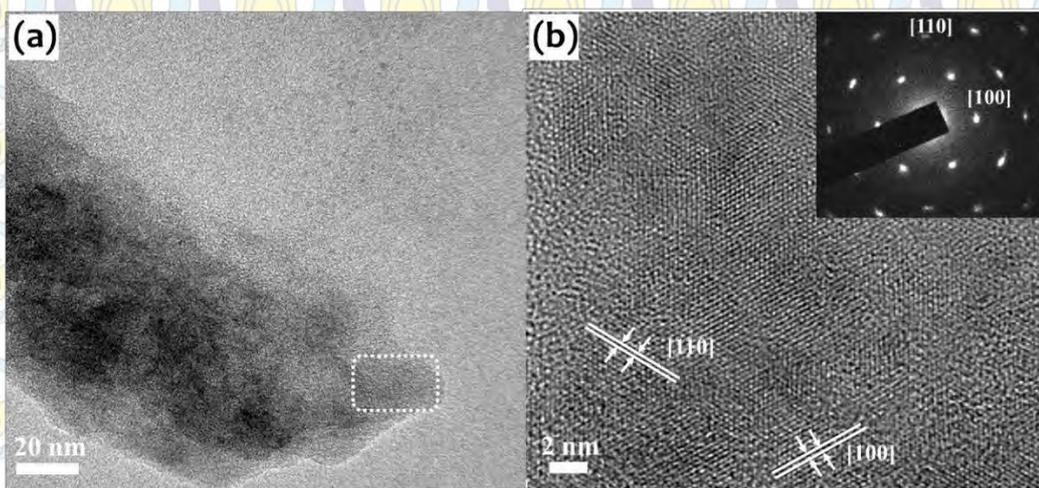


Figure 4.13. (a) TEM image of an individual few-layer MoS₂ nanosheet; (b) High resolution TEM image of an individual few-layer MoS₂ nanosheet, with an inset showing the SAED pattern. All images from sample A.

Figure 4.13 shows the transmission electron microscopy image for the few-layer MoS₂ from sample A. From Figure 4.13a shows that the layer-structure few-layer MoS₂ overlap each other. The high resolution TEM image (Figure 4.13b) and the corresponding selected area electron diffraction (SAED) pattern (inset of Figure 4.13b) reveal the hexagonal lattice structure, which had good agreement with XRD pattern. And in the SAED pattern, the lattice spacing of 0.27 nm and 0.16 nm assigned to the [100] and [110] planes have been observed. Moreover, as expected, the HRTEM illustrates that the MoS₂ nanosheets have 2D

hexagonal symmetry crystalline structure with lattice spacing of 0.30 nm (see **Error! Reference source not found.** in appendix B), consistent with bulk MoS₂ materials. We also performed DLS results to confirm that the MoS₂ has been exfoliated into few-layer MoS₂ nanosheets with different lateral dimensions.

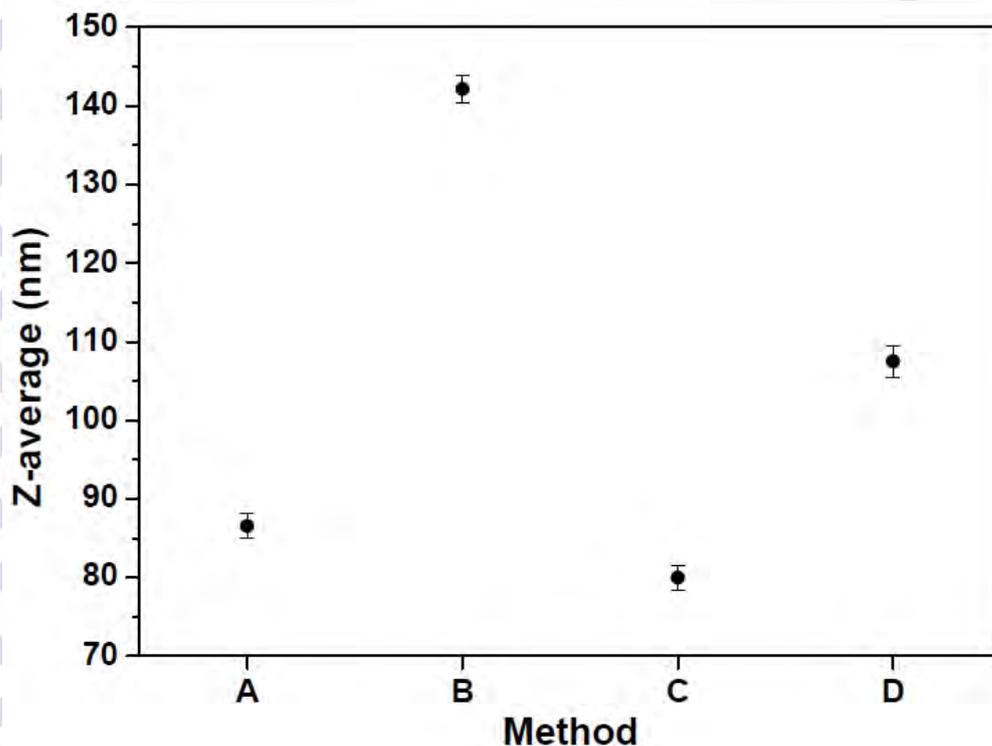


Figure 4.14. Various flake sizes according to DLS analysis.

Figure 4.14 shows that the few-layer MoS₂ nanosheets with different lateral sizes can be prepared using centrifugation and filtration. Dispersed few-layer MoS₂ nanosheets have Z-average particle size ranging 85-145 nm.

Sample A has a Z-average particle size of 87.5 ± 2.5 nm; sample B 142.5 ± 2.5 nm; sample C 80.5 ± 2.5 nm; and sample D 107.5 ± 2.5 nm. These results are consistent with the SEM results, which suggests that the sample B has the biggest size.

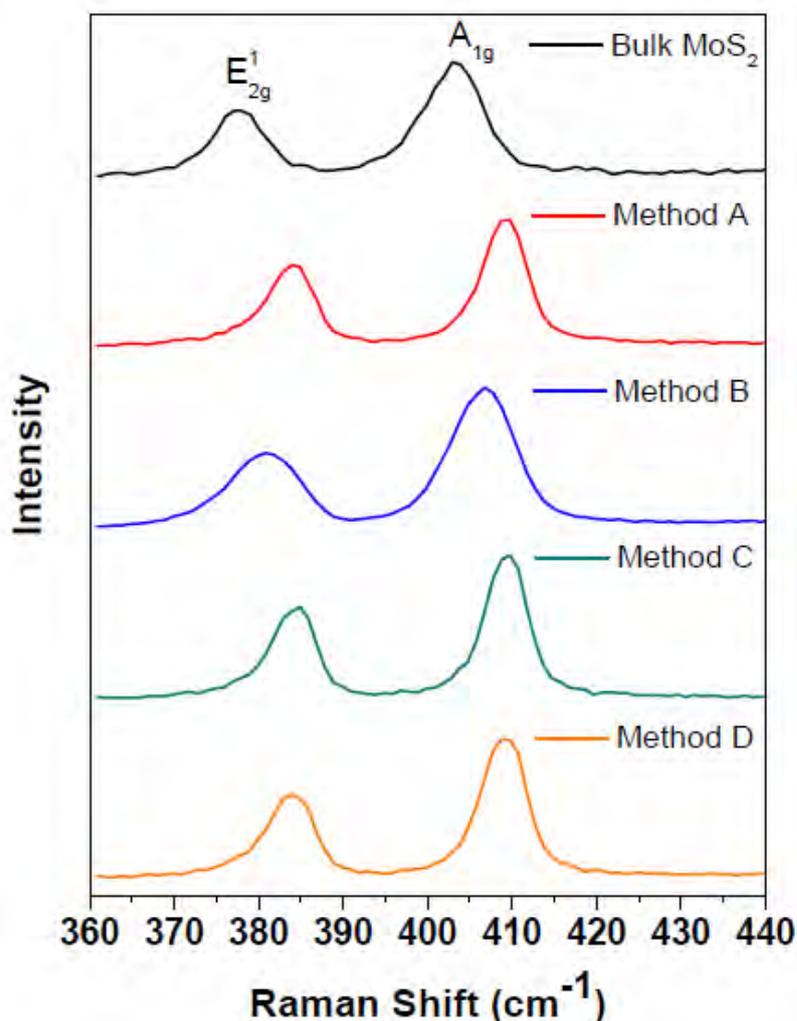


Figure 4.15. Typical Raman spectra of sample A, B, C, D and bulk MoS₂

Raman spectroscopy was usually used to study the crystalline structures and quantitatively identify the layer numbers of graphene and MoS₂. Figure 4.15 shows the two characteristic Raman modes (E_{2g}^1 and A_{1g}) of sample A, B, C, and D, which possess the similar Raman spectra like that of the sample after sonication. Sample A exhibits a smallest Δk (23.89 cm⁻¹), which is consistent with the reported value for 3-5 layers (Yu et al., 2013b). Actually, the frequency differences between E_{2g}^1 and A_{1g} peaks, instead of the intensities and widths of the peaks, were used as the reliable features to identify the layer of MoS₂. For instance, the frequency difference (Δk) 20-21.2 cm⁻¹ corresponds to a single layer MoS₂ (Yu et al., 2013b). A MoS₂ flake with Δk of ~23.6 cm⁻¹ has

been expected to possess three layers (Li et al., 2012) and a MoS₂ flake with Δk of $\sim 24.3 \text{ cm}^{-1}$ has been proposed contain four layers (Ye et al., 2014) and Δk of $\sim 24.9 \text{ cm}^{-1}$ to possess 6 layers (Lee et al., 2010). Thus, sample A are composed of three layers. Based on the reported data, sample B, C, and D with Δk of $\sim 24.89 \text{ cm}^{-1}$ are identified as MoS₂ nanosheets with six layers. Atomic Force Microscopy (AFM) are also used to confirm numbers of layers in nanosheets. Tapping mode of AFM is used to assess the thickness of 2D MoS₂ nanosheets. From AFM images, some aggregation or overlapping between individual sheets are found. The resulting dispersion on the Si substrate was nonhomogeneous due to partial aggregation. Some individual MoS₂ nanosheets can be identified to have average thickness of ca. 3 nm from sample A and ca. 4 nm from sample C, indicating that one sheet consists of ca. 4 and 6 layers, respectively (as shown in Figure 4.16) (Knirsch et al., 2015).

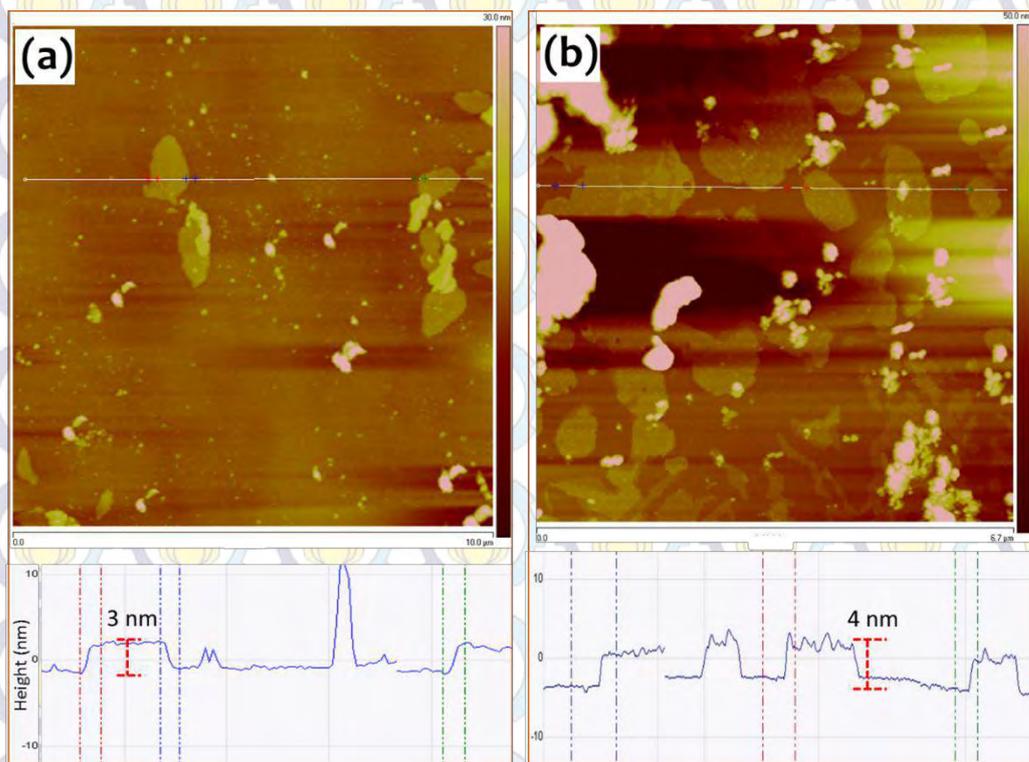
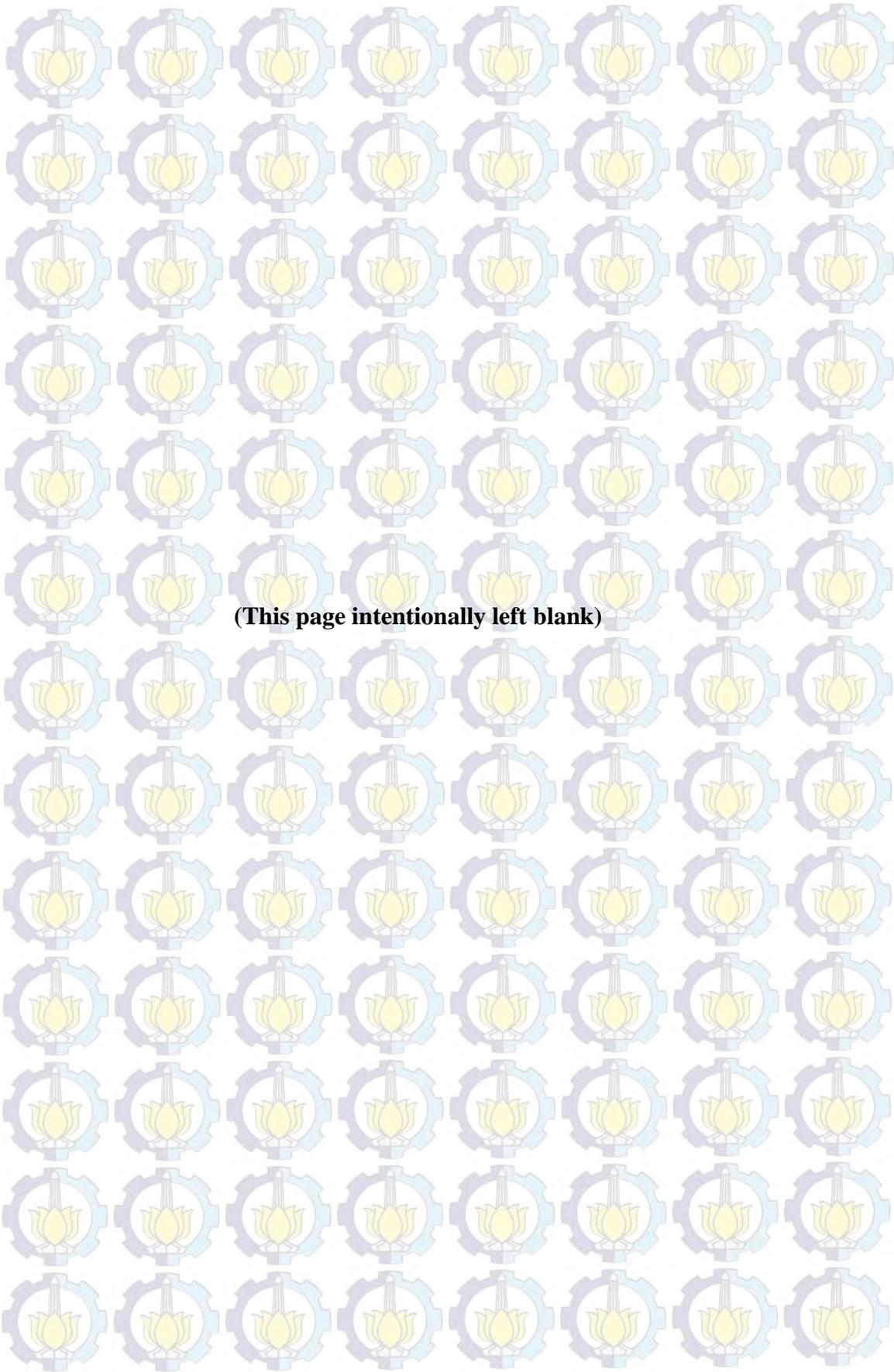
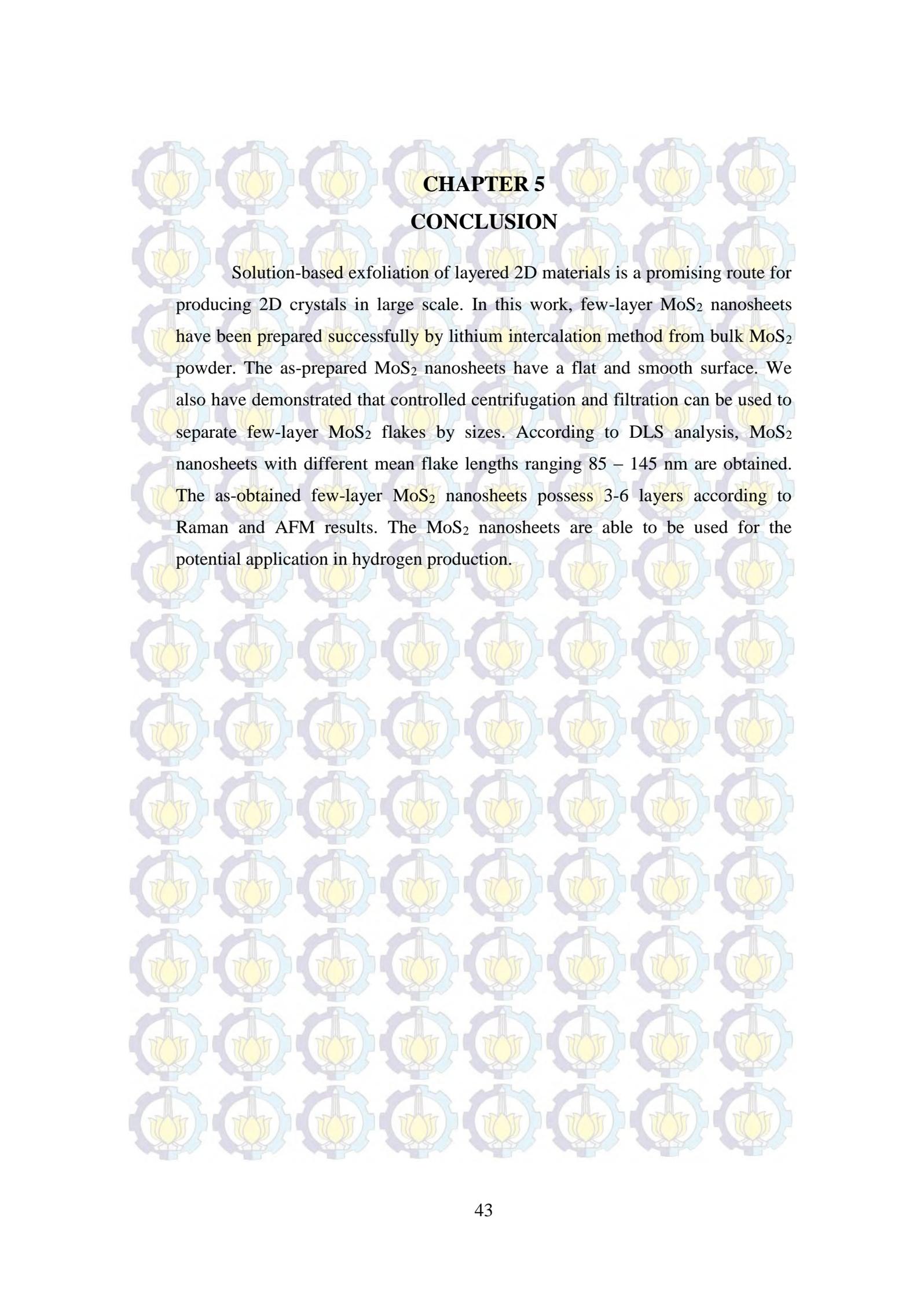


Figure 4.16. Atomic force microscopy (AFM) image of individual exfoliated MoS₂ sheets: (a) sample A; (b) sample C.

Here the DLS, Raman, and AFM results, imply that the large flake or sheet, dispersed without centrifugation, should be relatively thick. This suggests that thinner sheets could be obtained by centrifugation. The effect of aggregation on the electronic properties of MoS₂ is considerably different from that of graphene. For graphene, the electronic properties are largely correlated to the number of layers per sheet when it consists of less than 5 layers (Geim, 2009). On the other hand, for MoS₂, the effect is widely less significant for MoS₂. It is true that a large change occurs going from monolayer to bilayer where the bandgap increases from a direct bandgap of 1.83 eV to an indirect one of 1.6 eV (Mak et al., 2010). When the number of layers increases from two to six, the bandgap decreases from 1.6 eV to 1.4 eV. It eventually reaches 1.3 eV when the quintuple layers are achieved. In all cases multilayers have indirect bandgaps. This means the electronic properties of MoS₂ multilayers (larger than six layers) are relatively insensitive to flake thickness.

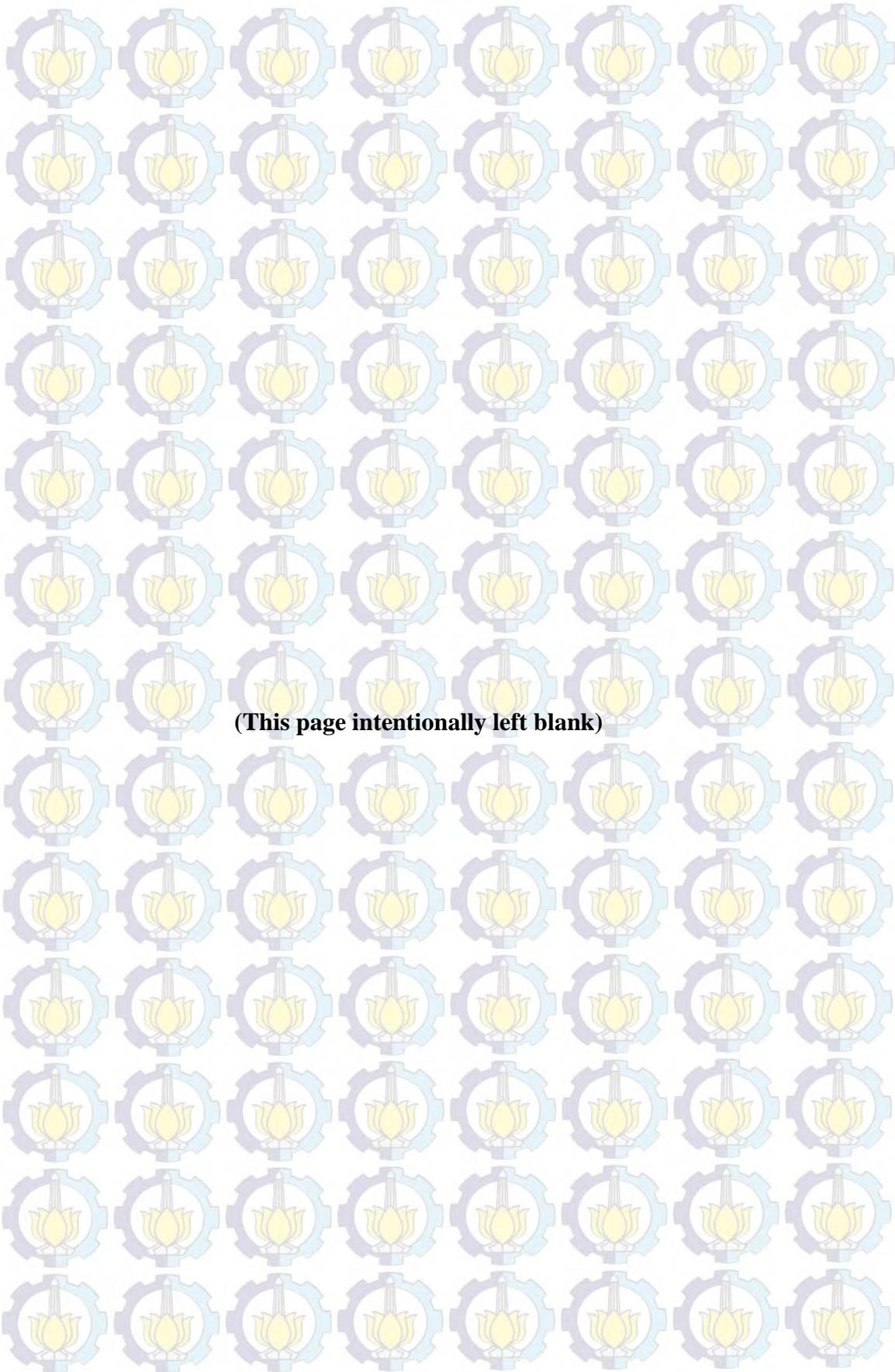




CHAPTER 5

CONCLUSION

Solution-based exfoliation of layered 2D materials is a promising route for producing 2D crystals in large scale. In this work, few-layer MoS₂ nanosheets have been prepared successfully by lithium intercalation method from bulk MoS₂ powder. The as-prepared MoS₂ nanosheets have a flat and smooth surface. We also have demonstrated that controlled centrifugation and filtration can be used to separate few-layer MoS₂ flakes by sizes. According to DLS analysis, MoS₂ nanosheets with different mean flake lengths ranging 85 – 145 nm are obtained. The as-obtained few-layer MoS₂ nanosheets possess 3-6 layers according to Raman and AFM results. The MoS₂ nanosheets are able to be used for the potential application in hydrogen production.



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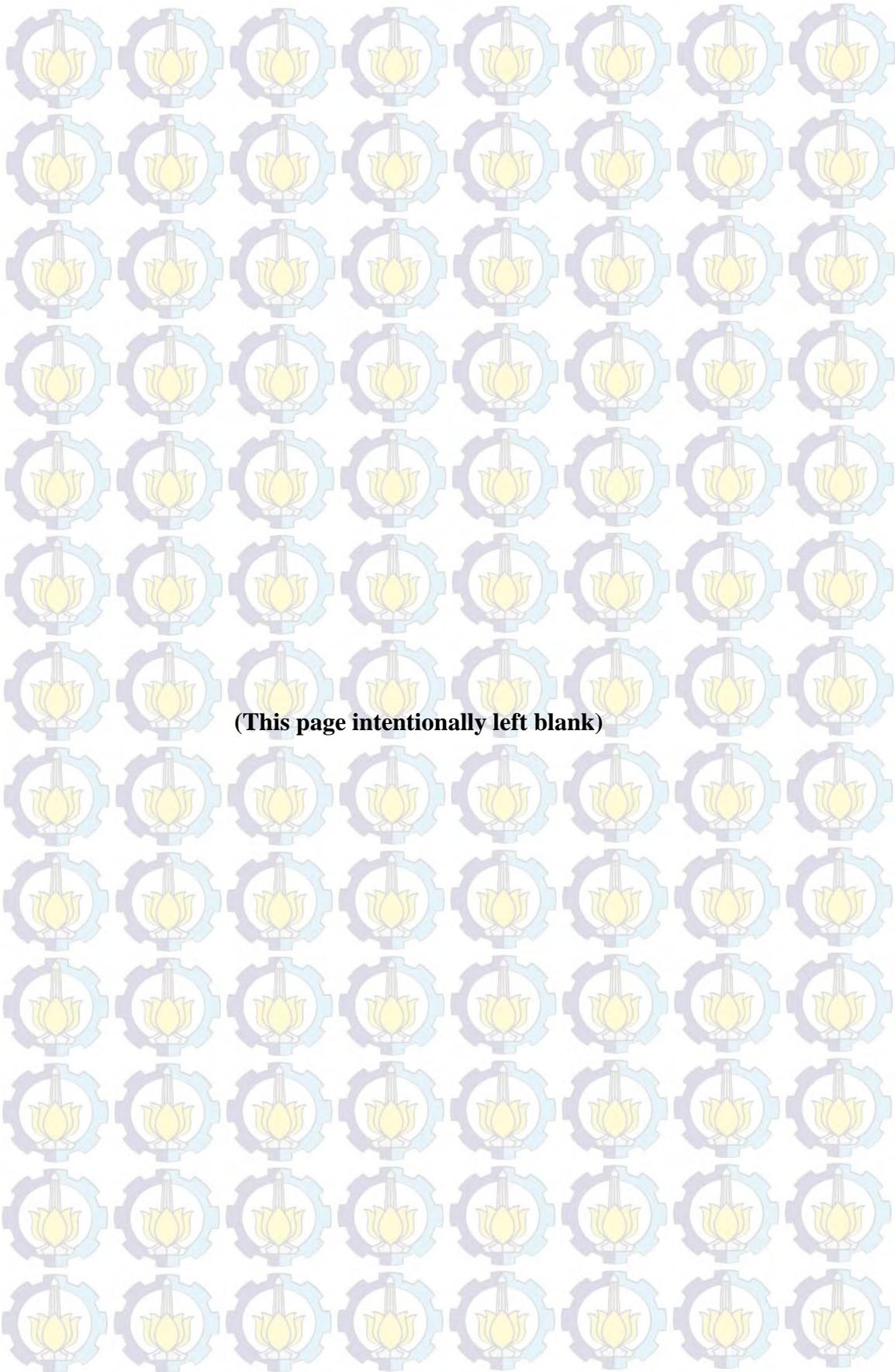
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APPENDIX A

Few-layer MoS₂ without Selection of Size

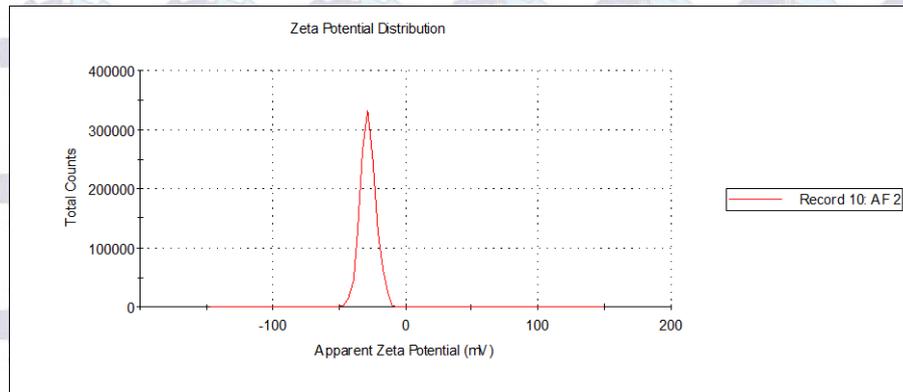


Figure A.1. Zeta potential distribution of 5th experiment

Table A.1. Summary of zeta potential in each of experiments

Experiment	1 st	2 nd	3 rd	4 th	5 th
Zeta Potential (mV)	-30	-30	-27.9	-29.9	-28.1

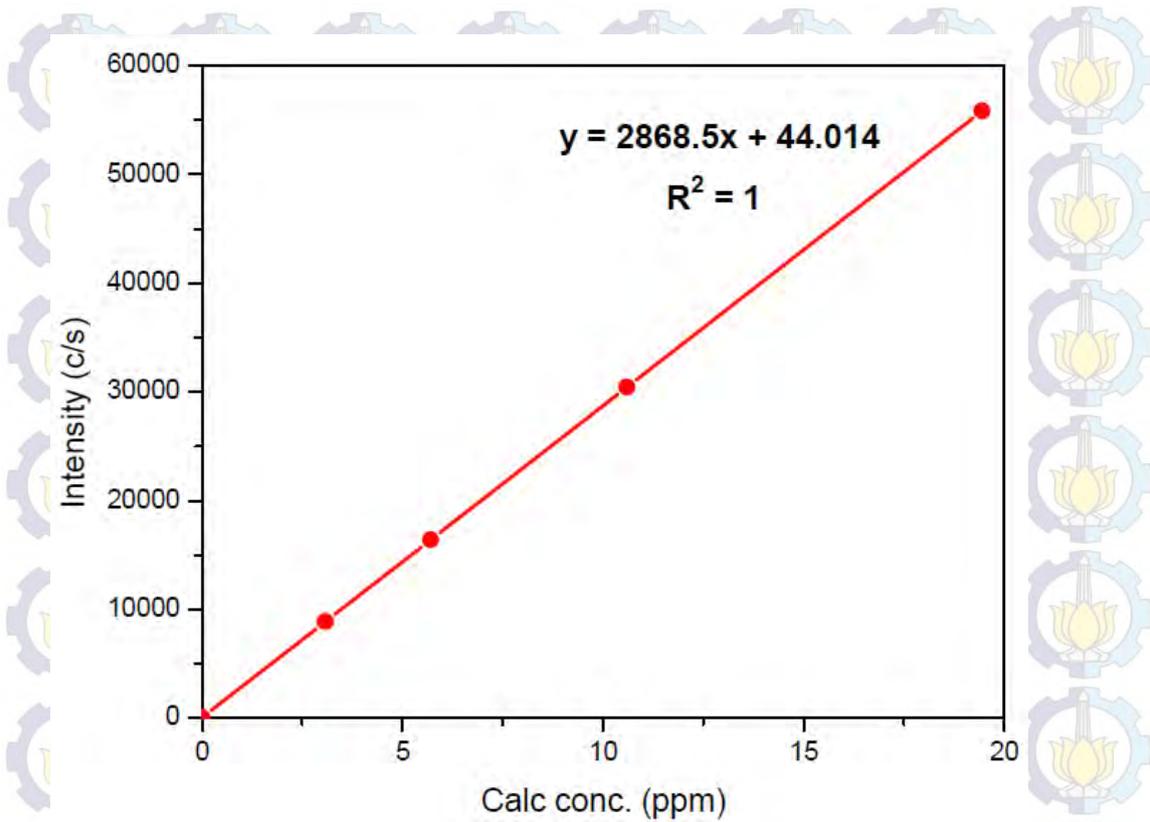


Figure A.2. The Calibration curve of lithium concentration in ICP-OES measurement

Li intercalated		MoS ₂ nanosheets	
Intensity (c/s)	Calc conc. (ppm)	Intensity (c/s)	Calc conc. (ppm)
3363.70	1.16	201.33	0.06

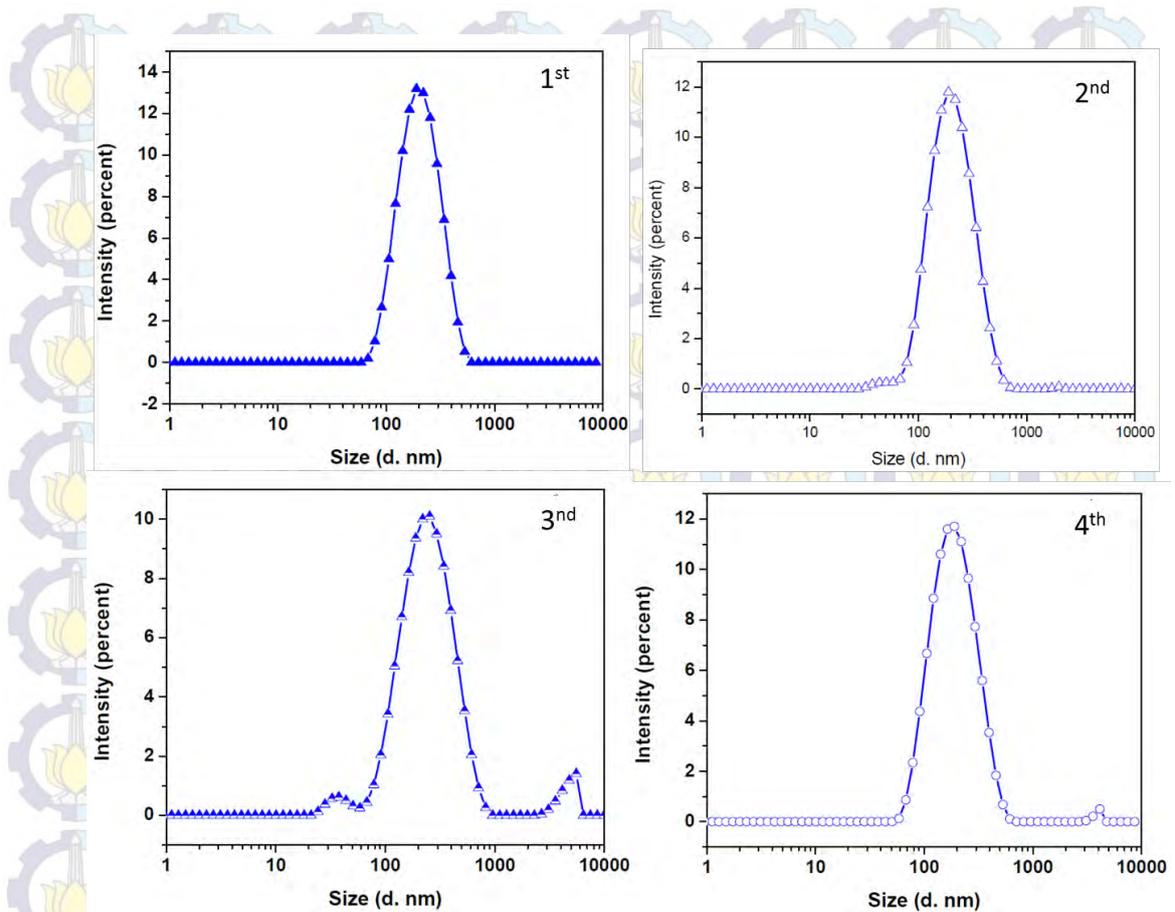


Figure A.3. Size distribution by intensity in repeating experiment.

Figure A.3 shows that in repeating experiment result the mean flake length of ~ 220 nm, and some of nanosheets with smaller mean flake length of ~ 38 and ~ 40 nm. And the maximum of the mean flake length of the MoS_2 nanosheets is about $3 \mu\text{m}$ (see 4th experiment). And also in 3rd experiment, the small peak is observed at around $5.8 \mu\text{m}$. But during the SEM and TEM analysis, we did not see large objects around $5.8 \mu\text{m}$. However, this feature may be due to small dust particles or air bubbles in this dispersion.

Table A.2. The frequency difference (Δk) of MoS₂ nanosheets as the function of layer number.

Reported by	Δk (A _{1g} -E _{12g}) cm ⁻¹	Layer number of MoS ₂
Korn, T. et al ⁷³	18	1 layer
Yu, Y. et al ⁶⁸	20-21.2	1 layer
Van Thanh, V. et al ⁷⁴	21.7	2 layers
Yu, Y. et al ⁶⁸	22.4-23.2	2 layers
Yu, Y. et al ⁶⁸	23.6-23.9	3 layers
Yu, Y. et al ⁶⁸	24.0-24.2	4 layers
Lee, C. et al ⁶⁹	24.9	6 layers
Lee, C. et al ⁶⁹	25.6	bulk
Van Thanh, D. et al ⁷⁴	27.2	bulk

Note: k = wavenumber.

APPENDIX B

Few-layer MoS₂ with Selection of Size

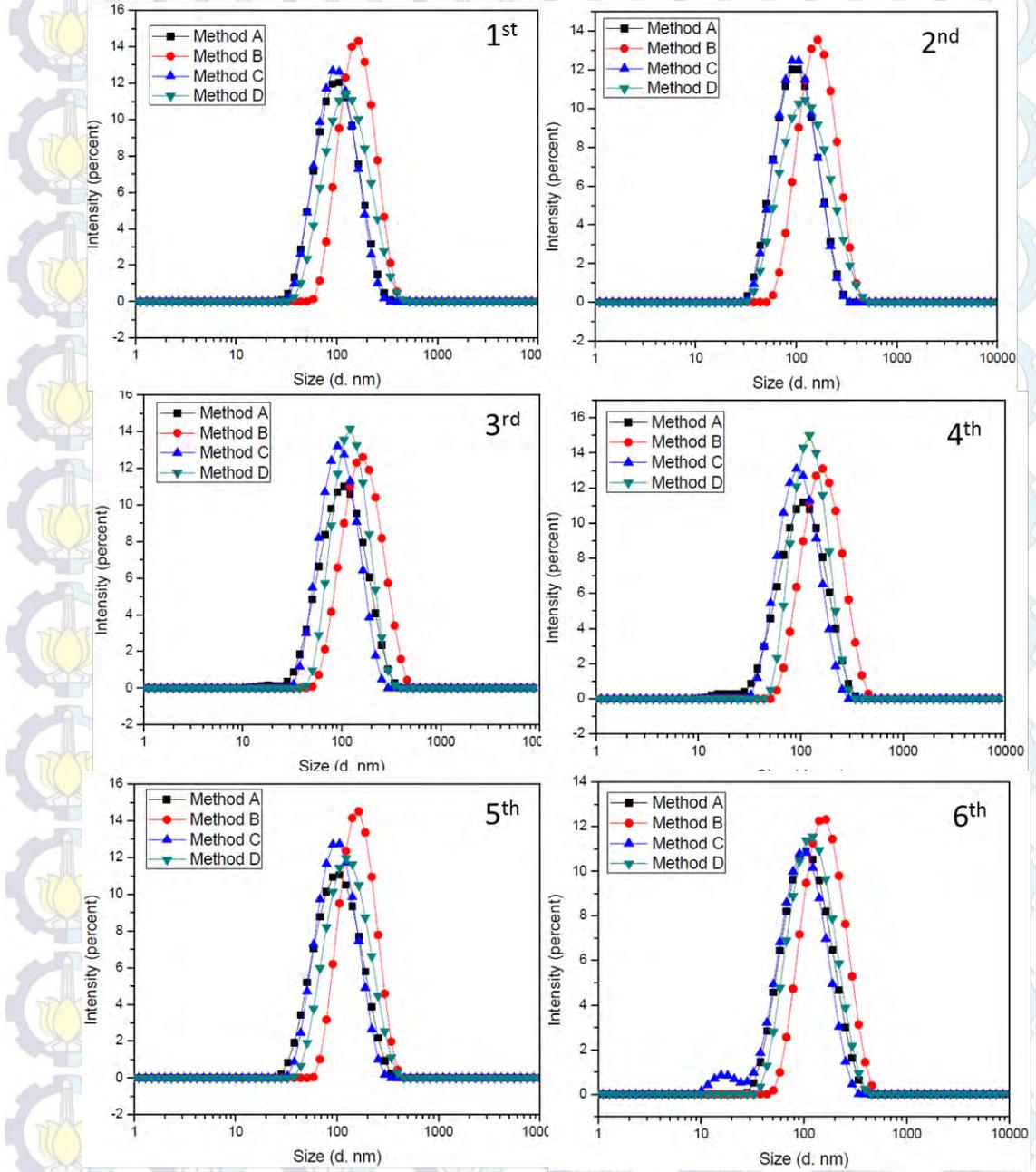


Figure B.1. Size distribution of Method A, B, C, and D by intensity in repeating experiment.

Figure B.1 shows that according to DLS measurements we have gotten MoS₂ nanosheets with different mean flake length. In the sixth experiment, the peak around 18 nm is observed, indicating the very small nanosheets contained therein. However, in others measurements we did not see this peak, may be the nanosheets were clustered by air bubbles in this dispersion.

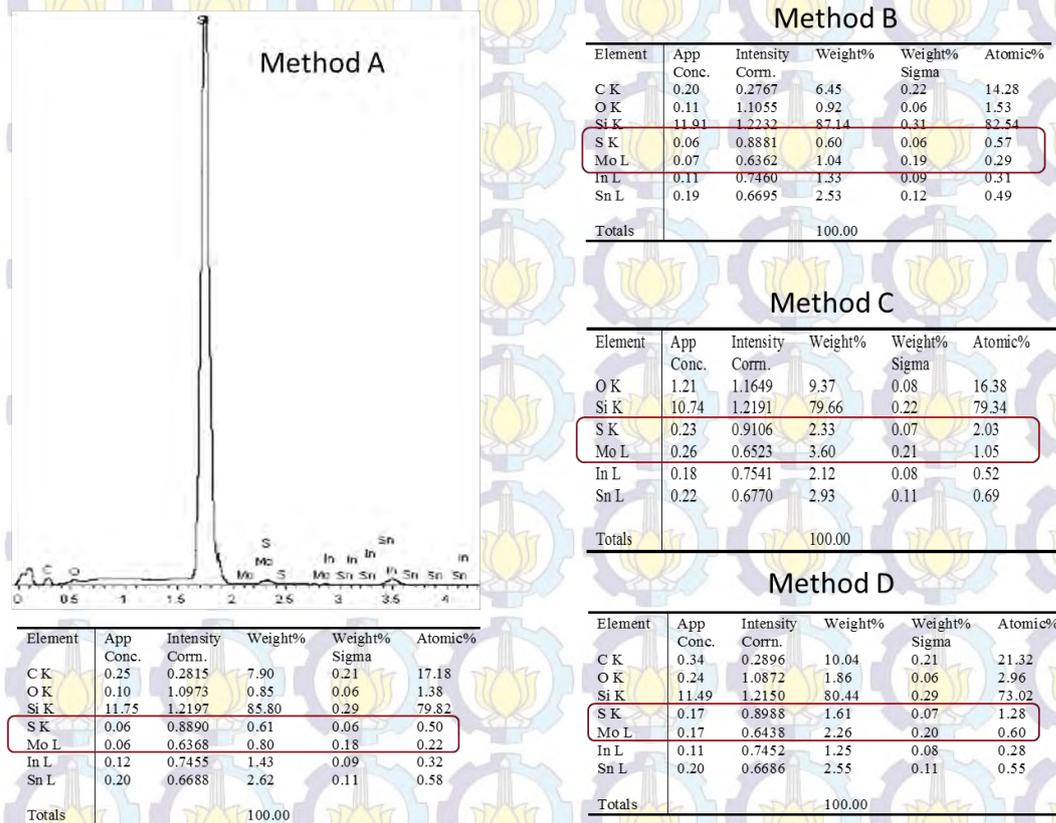


Figure B.2. EDS-SEM spectra of an individual few-layer MoS₂ processed by Method A, B, C, and D.

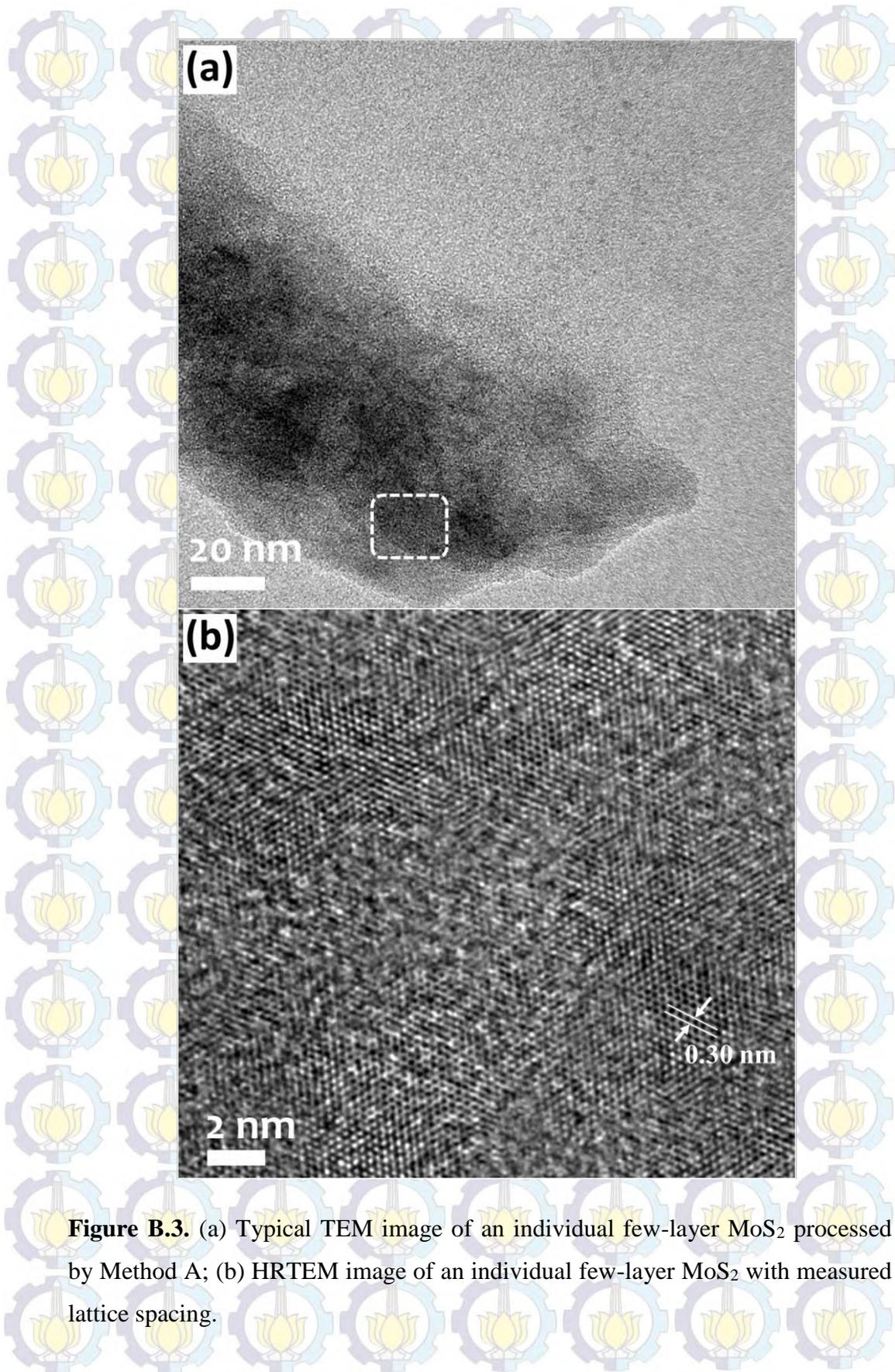
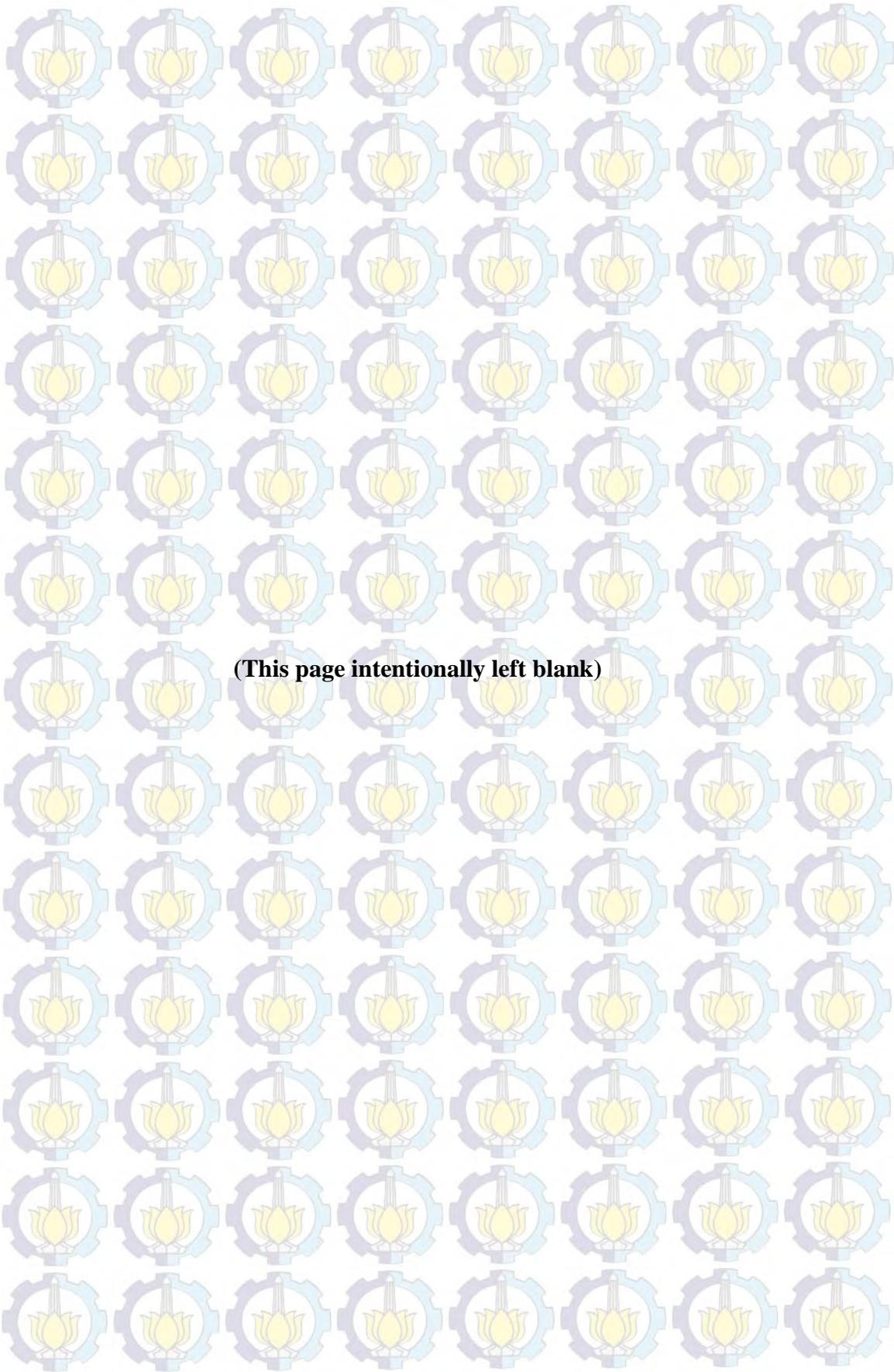


Figure B.3. (a) Typical TEM image of an individual few-layer MoS₂ processed by Method A; (b) HRTEM image of an individual few-layer MoS₂ with measured lattice spacing.



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BIOGRAPHY



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Thank you, 謝謝, Terima kasih ... Bye..bye...

“一切都很好”

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Preparation of MoS₂ Nanosheets for Energy Applications

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Abstract - Exfoliation of bulk MoS₂ via Li intercalation is an attractive route to large-scale preparation of MoS₂ few-layers and it can be used to realize their unique properties in practical applications. In general, solution-based exfoliation of layered materials results in flakes with lateral sizes of one micron or less on average. In this report, we performed the various preparations using a Li-intercalation method at room temperature to prepare MoS₂ few-layers with various flake sizes according to dynamic light scattering (DLS) analysis. MoS₂ few-layers with particle sizes ranging 85 to 145 nm are reported. We also characterize the few-layer MoS₂ nanosheets by various microscopic and spectroscopic techniques.

Keywords - MoS₂, Nanosheets, Intercalation, Exfoliation.

INTRODUCTION

In recent decades, nanomaterials have attracted major attentions due to their fascinating properties and wide ranges of applications. There are two categories of nanomaterials: organic (mostly carbon allotropes) and inorganic nanomaterials, such as iron, silver, gold, boron nitride nanosheets (BNNs), molybdenum disulfide (MoS₂), tungsten disulfide (WS₂), etc. Inorganic nanomaterials, especially two-dimensional (2D) nanomaterials, have received tremendous attention in recent years because of unique both chemical and physical properties. The two-dimensional nanomaterials have completely different properties compared to the bulk materials (the quintuple layers). These properties includes high surface areas, mobility, conductivity, mechanical strength, transparency, electronics and optoelectronics. As one of the 2D nanomaterials, molybdenum disulfide possesses a sandwich structure which consist of covalent bonds in S-Mo-S structures that form by weak Van Der Waals forces between sheets. Therefore, it is probably easy to peel MoS₂ nanosheets from bulk material.¹ Bulk MoS₂ is a

semiconducting material with an indirect band gap of about 1.2 eV. When layered MoS₂ pristine is peeled to single-layer, it become a semiconductor with 1.8 eV direct band gap.^{2,3} The wide band gap, which is thickness-dependent (bulk to single-layer), makes MoS₂ a promising candidate for many applications, such as electronic devices,⁴ optoelectronic devices,⁵⁻⁸ sensors,⁹ and energy storage devices, like lithium ion batteries (LIB),¹⁰⁻¹³ sodium ion batteries (SIB),¹⁴ and capacitors.¹⁵

The other applications, which have become hot topics until now are utilization and optimization of exfoliated MoS₂ in either hydrogen evolution reaction (HER)¹⁶⁻¹⁸ or water splitting.^{19,20} If MoS₂-based catalysts are to actualize their potential, there is an important need to increase the numbers of active sites and the catalytic activity by changing their electronic properties and conductivity via exfoliation of MoS₂ from bulk materials to nanosheets.¹⁷ And also the size of nanosheets is an important factor in the hydrogen evolution reaction (HER).²¹

Recently, several methods have been reported for synthesizing single- and multi-layer MoS₂. There are the mechanical exfoliation method,^{22,23} chemical lithium intercalation and exfoliation using *n*-butyllithium,^{24,25} electrochemical lithium intercalation and exfoliation,²⁶ liquid phase exfoliation using solvent and surfactants,^{27,28} and synthesis of MoS₂ nanosheets via sear exfoliation.²¹ Recently, many researchers made good quality MoS₂ monolayers using a chemical vapor deposition (CVD) or a Scotch tape-based micromechanical exfoliation method. However, a low yield is generally achieved in the Scotch tape method and a high temperature and cost of instruments are required for experiments in the CVD method.

Coleman et al. reported direct exfoliation of MoS₂ sheets with thickness of 3–12 nm and the lateral nanosheets size of 0.1-2 μm in organic solvents through sonication.²⁷ However this method leads to a low yield and the major issue is that specific nanosheet sizes cannot be obtained. It

is essential for various applications. For example, composite reinforcement requires large nanosheets²⁹ at least around 2 μm in length, whereas a catalyst of hydrogen production requires small nanosheets with lateral size or length below 100 nm.³⁰ Significance of this work focuses on synthesis of few-layer MoS₂ nanosheets with specific lateral size via the lithium intercalation method and characterization of the materials.

EXPERIMENTAL SECTION

Materials. The Molybdenum disulfide (MoS₂) bulk powder used in these experiments was purchased from Alfa Aesar (99%) and 2.5 M n-butyl lithium in hexane was purchased from Chemetall.

Preparation of MoS₂ nanosheets. To make the MoS₂ nanosheets suspension, molybdenum disulfide bulk powder (300mg) was placed in a 100 mL flask, to which a 2 mL of 2.5 M n-butyl lithium in hexane and 18 mL of hexane anhydrous were added under N₂ atmosphere. Then, the solution was stirred for 5 days at room temperature. The resulting suspension was gravity-filtered under N₂, and the solid washed with a few ml of anhydrous hexanes to remove any excess butyl lithium. Then, a few ml of distilled-water was added quickly to quench the sample. The MoS₂ paste was then taken after the solution was removed by rotavapor. To achieve the exfoliation of MoS₂, 17.5 mg of the MoS₂ paste was suspended in 35 mL water in a 50 mL tube. Then, the mixture was sonicated continuously for 38 hours using a 1/2" (12.7 mm) diameter worn tip on replaceable tip (QSonica, 700W and 30% amplitude).

Preparation of few-layers MoS₂ with specific flakes dimension. In our experiment, to achieve a certain size of few-layer MoS₂. We used four procedures to reduce sheet sizes to desired dimension. The first method is via centrifugation of the sample at 2000 rpm for 60 minutes (Method A). The second method involves filtration, through polyvinylidene difluoride (PVDF) membrane with pore size 450 nm, 47 mm diameter (Method B). The third one is via centrifugation at 2000 rpm for 60 minutes, followed by filtration (Method C). The fourth method involves filtration (PVDF membrane, pore size 450 nm, 47 mm diameter) followed by centrifugation at 2000 rpm for 30 minutes (Method D). In our experiments, after sonicated, 13 mL of solutions was placed in a vial. In Method A, 4.6 mL of 12 mL solutions in vials was taken and centrifuged at 2000 rpm for 60 minutes. The top 1/2nd part of the dispersion was collected by pipette. In Method B, 2.4 mL of remaining solution was dispersed in 12 mL Di-water. After that, the solution was filtered using PVDF membrane and the filtrate was collected. In Method C, 6 mL of remaining solution in vials was centrifuged at 2000 rpm for 60 minutes, then the top 1/2nd part of the dispersion was collected by pipette and was then filtered quickly. In

method D, 6 ml of the filtrate from method B was taken and centrifuged at 2000 rpm for 30 minutes. Then, the top 1/2nd part of the solution was collected by pipette. Then, all of the solution (from Method A, B, C, and D) were analyzed using UV-vis, dynamic light scattering (DLS), scanning electron microscopy (SEM), and Raman Spectroscopy.

Characterization Method. The absorbance spectra of the few-layer MoS₂ were recorded using a varian Cary 5000 and samples were tested in quartz glass cuvettes having 10 mm path length. The morphology of the samples was examined using scanning electron microscopy (SEM) model ZEISS-GEMINI Ultra Plus, with an Oxford Instruments EDS apparatus operated at 5 kV. For the EDS measurements, the EDS-SEM was operated at 10 kV. The TEM images were examined using transmission electron microscopy instrument (JEOL JEM-2100F) operated at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns were measured with a diffractometer (BRUKER, GADDS) using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation over the range of $10^\circ \leq 2\theta \leq 80^\circ$ under a voltage of 40 kV and a current of 40 mA. Raman spectra were measured with in Via Confocal Raman Spectroscopy (NTEGRA Spectra, NT-MDT) at excitation laser line 488 nm in air ambient environment. The power of the excitation laser line was kept well below 1 mW to avoid heating effect and the spot size of 50 μm with exposor time at 10 s and grating line at 1800/500 with range of $\lambda = 500 \text{ nm}$. Atomic force microscopy images was recorded on Veeco MultiMode VIII microscope in tapping mode. DLS measurements were performed using a Malvern Zetasizer Nano ZS with a 633 nm He-Ne laser. Samples were tested in low volume disposable sizing cuvettes. Malvern Zetasizer Nano ZS was operated in backscatter mode at an angle of 173° and analyzed three times for each samples. Samples were equilibrated to 25°C for 120 s prior to measurement. Viscosity and Refractive index of solvent (water) at 25°C are 0.8872 cP and 1.330, respectively. An automatic measurement positioning and automatic attenuation.

RESULTS AND DISCUSSION

In recent years, MoS₂ based catalysts have been considered as promising material to replace platinum because of their high abundance and low cost. Promising catalytic activity of MoS₂ in the hydrogen evolution reaction (HER) is attributed to the active sites located along the edges of its two-dimensional layered crystals. If the MoS₂ based catalysts are to realize their potential, there is an urgent need to design MoS₂ nanosheets with more edge sites. The ability to control the nanosheets size during exfoliation process, achieved here by control of centrifugation and filtration, will be important for the number of applications. One of the most important applications is as catalyst for the evolution of hydrogen

from proton-rich electrolytes.³⁰ Because the catalytically active sites reside on edge of nanosheets, Hydrogen evolution catalyst is strongly dependent on nanosheets length with small flakes performing much better than larger ones.²¹ And the change of phase MoS₂ from semiconducting to metallic which happened during intercalation process is to be an important factor in evolution of hydrogen because in the previous research shown that the metallic phase has catalytic activity is better than semiconducting phase.¹⁸ For another application, lithium ion batteries are still exist and high efficient energy in industrial battery. So, in here we reported the preparation MoS₂ nanosheets with specific flake dimensions using lithium intercalation method to provide material which can be applied in those applications.

Intercalation of Lithium - Chemical exfoliation of layered materials is generally achieved by reacting the 2D nanomaterials with *n*-butyl lithium. The electrons from *n*-butyl lithium (as a guest) are transferred to the lowest-lying-unoccupied energy levels of MoS₂ (as a host), which are fundamentally transition metal d bands (as shown in Figure 1).³¹ And also the charge transfer from *n*-BuLi to MoS₂ actually may induce structural changes in the host. Structural and electronic changes in the host of MoS₂ produced by lithium intercalation method often induce dramatic changes in the transport properties of MoS₂ from semiconducting to metallic.³² The important thing is that when the bulk materials become nanosheets, the properties change, such as mechanical, electronic and thermodynamic properties.³³

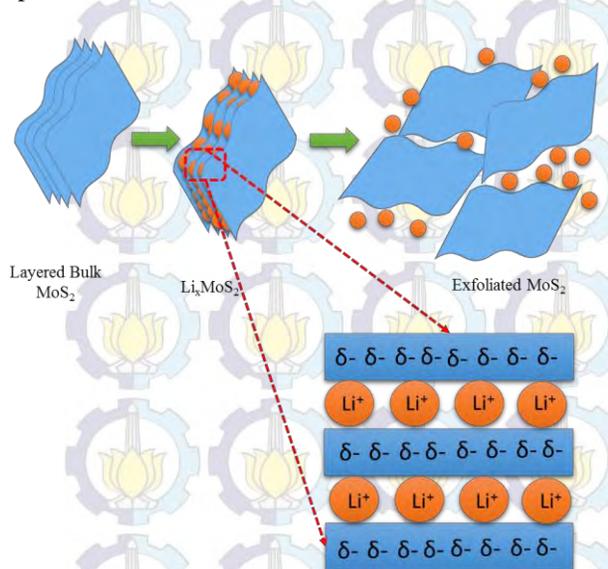
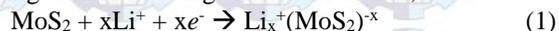


FIGURE 1. SCHEMATIC ILLUSTRATION OF INTERCALATION OF LITHIUM INTO MoS₂ LAYERS.

During the stirring process, anhydrous hexane can serve as solvent, resulting in the lithium cations dispersed

in the solvent being readily insert into MoS₂ layers with the formation of lithium intercalated MoS₂ (Li_xMoS₂) units according to the following chemical reaction,



Then when the Li_xMoS₂ units are exposed to water, the lithium in the unit become rapidly solvated and produces exfoliated MoS₂ layers, lithium hydroxide (LiOH), and hydrogen gas (H₂) based on another following chemical reaction,



During the reaction process, original quintuple layers are homogeneously exfoliated due to the rapid expansion in the layers and forming suspensions of MoS₂ nanosheets.

Exfoliation of Molybdenum disulfide - To promote exfoliation of MoS₂, here we used sonication. The MoS₂ exfoliated sheets were exposed to ultrasonication at room temperature for 38 h, followed by centrifugation to reduce sheet size to desired dimension. The reaction of the resulting lithiated phase of MoS₂ with water through the redox reaction (reaction 2) and can form few- or single-layer MoS₂ dispersion with partial negative charge (see Figure 1).³⁴ In this work, after we got MoS₂ nanosheets, Zeta (ζ) potential measurements is used to prove it.

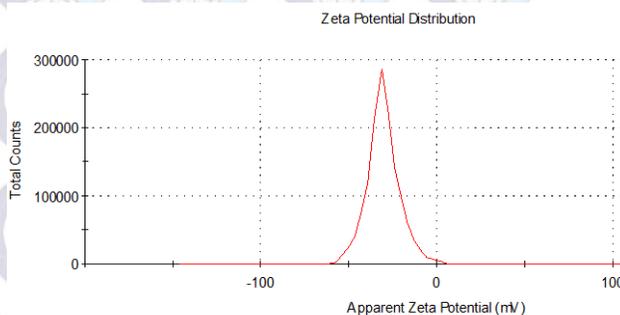


FIGURE 2. THE ZETA POTENTIAL DISTRIBUTION OF THE EXFOLIATED MoS₂ DISPERSIONS.

The zeta potential is an important factor for characterizing the stability of colloidal dispersions and provides a measure of the magnitude and sign of the effective surface charge. In this measurements the average value of zeta potential is about -29.18 mV (Figure 2), which indicates that the MoS₂ nanosheets become negative charge after exfoliation due to the electron transfers from *n*-BuLi (guest) to MoS₂ surface (host).

Figure 3 shows the XRD results of raw bulk material, lithium intercalated MoS₂ and exfoliated MoS₂ nanosheets. All diffraction peaks of the sample were in good agreement with a hexagonal structure of MoS₂ (JCPDS No. 37-1492). As shown in Figure 3, the peak positions of MoS₂ bulk and nanosheets are in the same places, with different intensity, which indicates that the exfoliated MoS₂ has a hexagonal lattice structure and

preserve well the crystalline phase of bulk MoS₂. Compared with those of bulk MoS₂ and exfoliated MoS₂ nanosheets, lithium intercalated MoS₂ has additional diffraction peaks at 30°, 32°, 35°, 37° and 52°.

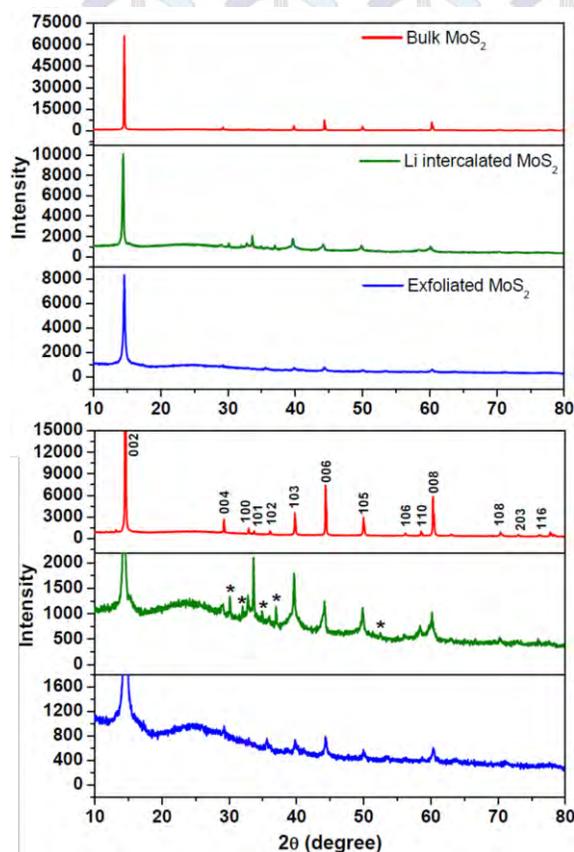


FIGURE 3. THE XRD PATTERN OF BULK MoS₂, LI INTERCALATED MoS₂, AND EXFOLIATED MoS₂ NANOSHEETS (TOP) WITH MAGNIFICATION OF INTENSITY OF 5X (BOTTOM).

These XRD peaks are originated from MoS₂ being intercalated by Li to form Li_xMoS₂, which is consistent with previous results reported by Liu et al.³⁵ From XRD results, these additional peaks disappear after exfoliation, indicating that intercalated Li is removed when MoS₂ nanosheets are formed.

Few-layer Molybdenum disulfide with Specific Flake Dimensions - Recent research has indicated that graphene flakes can be selected by sizes by controlled centrifugation coupled with sediment recycling.^{29,36} Here we used centrifugation based on time and filtering to control the size of few-layer MoS₂ nanosheets. While liquid exfoliation generally results in flakes which are small on average, the flake size distribution can be quite broad. In this work we developed methods to control sizes of MoS₂ nanosheets to predominately select flakes in the upper solution. To achieve this we used four methods as shown

in experimental section, we combined centrifugation and filtration to reduce the bigger size of few-layer MoS₂ nanosheets.

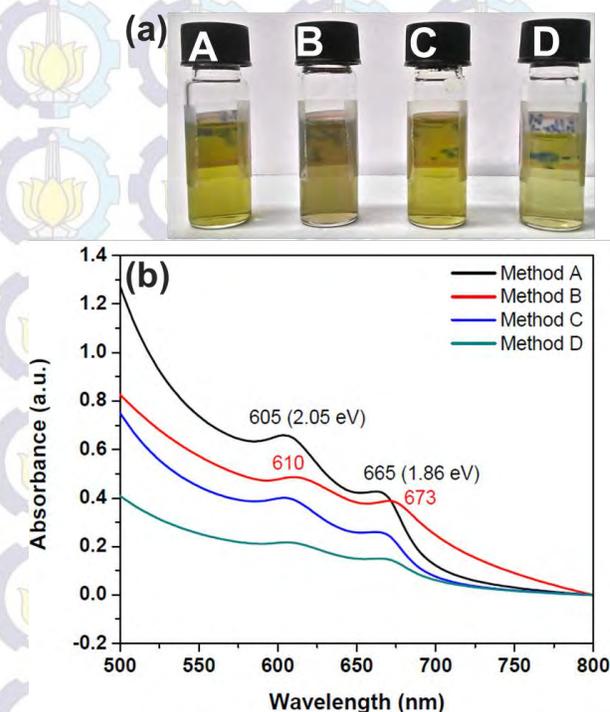


FIGURE 4. (A) DIGITAL IMAGES OF THE DISPERSIONS AFTER SIZE SELECTION; (B) ABSORPTION SPECTRA OF FEW-LAYER MoS₂ NANOSHEETS FROM DIFFERENT METHODS.

The color of the resultant dispersions varied in different procedures (method A, B, C, and D) indicating that the nature of the nanosheets is indeed changed. As shown in Figure 4a, the color in the method B is the darkest than others, and after centrifuged, the color changes slowly to be brighter. According to the previous research,³⁷ the peaks position at 673 and 610 nm are assigned to the *K* point of the Brillouin zone in 2D MoS₂ with relatively larger lateral dimensions (Method B). We also found large shift for the method A, C, and D in the optical absorption in comparison to those of MoS₂ nanosheets with relatively smaller lateral dimensions, arising from the quantum size effect of MoS₂ nanosheets (Figure 4b). We performed SEM, TEM and HRTEM to determine the quality and dimension of the flakes during controlled centrifugation and filtering regime. SEM images (Figure 5) illustrated that the MoS₂ was well exfoliated for all of methods. In addition, we noticed that size-selected few layer flakes tended to have smaller flakes adsorbed in many cases. As shown in Figure 5, the sample B had the largest lateral dimension, which agrees well with the UV-vis spectra (Figure 4b). The SEM micrographs illustrated that the MoS₂ bulk has been successfully exfoliated into few-layer MoS₂ nanosheets with different lateral size. Sample D

displays a smaller lateral size than sample B, but it is bigger than sample A and B (see Figure 5).

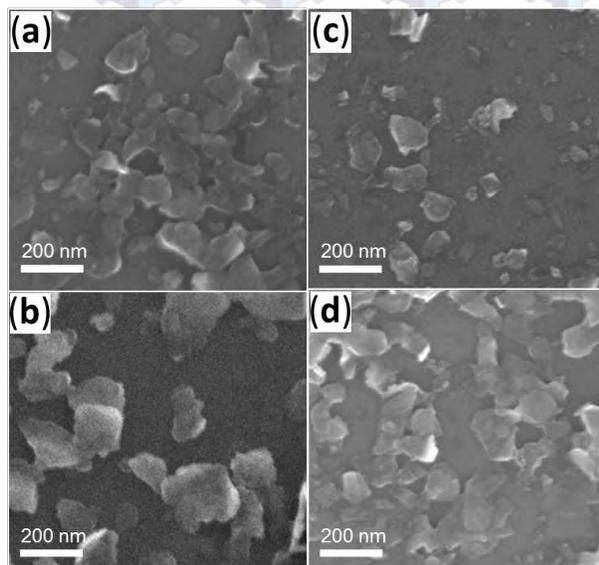


FIGURE 5. SEM IMAGES OF SIZE SELECTED DISPERSIONS PRODUCED BY (A) METHOD A, (B) METHOD B, (C) METHOD C, (D) METHOD D.

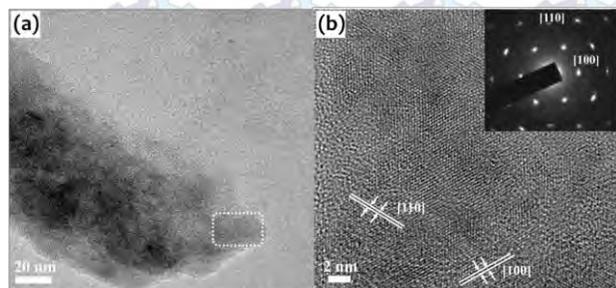


FIGURE 6. (A) TEM IMAGE OF AN INDIVIDUAL FEW-LAYER MoS_2 NANOSHEET; (B) HIGH RESOLUTION TEM IMAGE OF AN INDIVIDUAL FEW-LAYER MoS_2 NANOSHEET, WITH AN INSET SHOWING THE SAED PATTERN. ALL IMAGES FROM SAMPLE A.

The as-prepared MoS_2 nanosheets was also analyzed by TEM. Figure 6 shows the transmission electron microscopy image for the few-layer MoS_2 from sample A. From Figure 6a shows that the layer-structure few-layer MoS_2 overlap each other. The high resolution TEM image (Figure 6b) and the corresponding selected area electron diffraction (SAED) pattern (inset of Figure 5b) reveal the hexagonal lattice structure, which had good agreement with XRD pattern. And in the SAED pattern, the lattice spacing of 0.27 nm and 0.16 nm assigned to the [100] and [110] planes have been observed.

We also performed dynamic light scattering (DLS) results to confirm that the MoS_2 has been exfoliated into few-layer MoS_2 nanosheets with different lateral size.

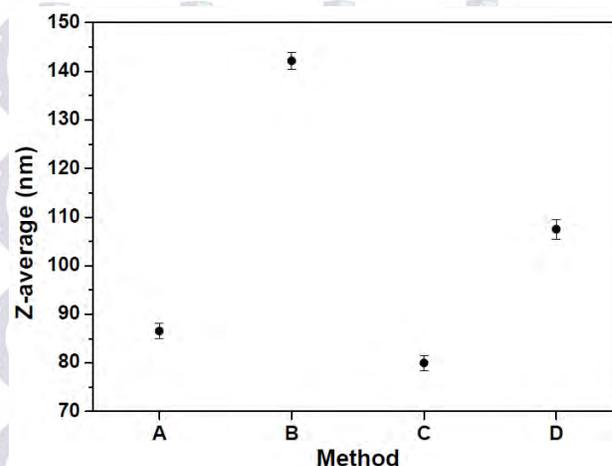


FIGURE 7. VARIOUS FLAKE SIZES ACCORDING TO DLS ANALYSIS.

Figure 7 shows that the few-layer MoS_2 nanosheets with different lateral sizes can be prepared using centrifugation and filtration. Dispersed few-layer MoS_2 nanosheets have Z-average particle size ranging 85-145 nm. Sample A has a Z-average particle size of 87.5 ± 2.5 nm; sample B 142.5 ± 2.5 nm; sample C 80.5 ± 2.5 nm; and sample D 107.5 ± 2.5 nm. These results are consistent with the SEM results, which suggests that the sample B has the biggest size. To confirm that the MoS_2 bulk has been successfully exfoliated into few-layers structure, we performed Raman spectroscopy on exfoliated MoS_2 and bulk MoS_2 , as shown in Figure 8. Raman spectroscopy was usually used to study the crystalline structures and quantitatively identify the layer numbers of graphene and MoS_2 . The E_{2g}^1 mode is correlated with an in plane opposite vibration of Mo and S atoms, while the A_{1g} mode is caused by an out-of-plane vibration of sulfur atoms in opposite directions.³⁸ Particularly, the E_{2g}^1 mode is the shear mode, which is attributed to the relative vibration between the adjacent single-layers. The characteristic peaks of the bulk MoS_2 at 377 and 402.9 cm^{-1} are assigned to the E_{2g}^1 and A_{1g} modes, respectively. The frequency difference (Δk) between the E_{2g}^1 and A_{1g} modes in the exfoliated MoS_2 , $\Delta k = 23.9 - 24.9 \text{ cm}^{-1}$ is smaller than that in the bulk MoS_2 , $\Delta k = 25.9 \text{ cm}^{-1}$. Sample A exhibits a smallest Δk (23.89 cm^{-1}), which is consistent with the reported value for 3-5 layers.³⁸ Actually, the frequency differences between E_{2g}^1 and A_{1g} peaks, instead of the intensities and widths of the peaks, were used as the reliable features to identify the layer of MoS_2 . For instance, the frequency difference (Δk) 20-21.2 cm^{-1} corresponds to a single layer MoS_2 .³⁸ A MoS_2 flake with Δk of $\sim 23.6 \text{ cm}^{-1}$ has been expected to possess three

layers.³⁹ and A MoS₂ flake with Δk of $\sim 24.3 \text{ cm}^{-1}$ has been proposed contain four layers⁴⁰ and Δk of $\sim 24.9 \text{ cm}^{-1}$ to possess 6 layers.⁴¹

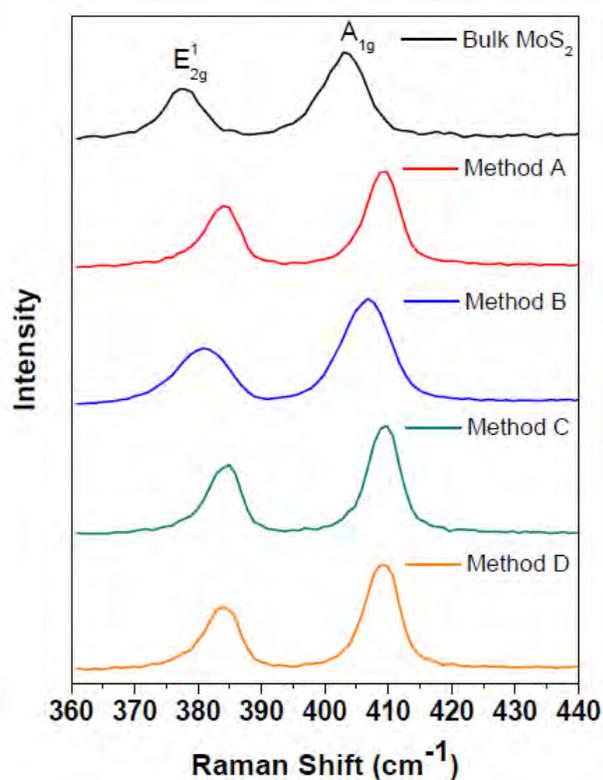


FIGURE 8. SEM IMAGES OF SIZE SELECTED DISPERSIONS PRODUCED BY (A) METHOD A, (B) METHOD B, (C) METHOD C, (D) METHOD D.

Thus, sample A are composed of three layers. Based on the reported data, sample B, C, and D with Δk of $\sim 24.89 \text{ cm}^{-1}$ are identified as MoS₂ nanosheets with six layers.

Atomic Force Microscopy (AFM) are also used to confirm numbers of layers in nanosheets. Tapping mode of AFM is used to assess the thickness of 2D MoS₂ nanosheets. From AFM images, some aggregation or overlapping between individual sheets are found. The resulting dispersion on the Si substrate was nonhomogeneous due to partial aggregation. Some individual MoS₂ nanosheets can be identified to have average thickness of ca. 3 nm from sample A and ca. 4 nm from sample C, indicating that one sheet consists of ca. 4 and 6 layers, respectively (as shown in Figure 9).³¹

Here the DLS, Raman, and AFM results, imply that the large flake or sheet, dispersed without centrifugation, should be relatively thick. This suggests that thinner sheets could be obtained by centrifugation. The effect of aggregation on the electronic properties of MoS₂ is considerably different from that of graphene. For graphene, the electronic properties are largely correlated to the

number of layers per sheet when it consist of less than 5 layers.⁴²

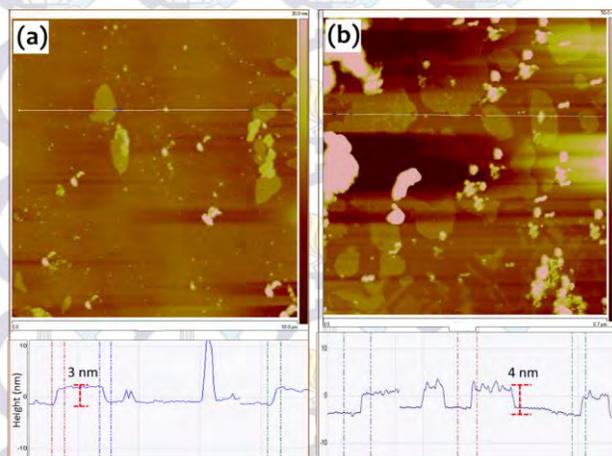


FIGURE 9. ATOMIC FORCE MICROSCOPY (AFM) IMAGE OF INDIVIDUAL EXFOLIATED MoS₂ SHEETS: (A) SAMPLE A; (B) SAMPLE C.

On the other hand, for MoS₂, the effect is widely less significant for MoS₂. It is true that a large change occurs going from monolayer to bilayer where the bandgap increases from a direct bandgap of 1.83 eV to an indirect one of 1.6 eV.⁴³ When the number of layers increases from two to six, the bandgap decreases from 1.6 eV to 1.4 eV. It eventually reaches 1.3 eV when the quintuple layers are achieved. In all cases multilayers have indirect bandgaps. This means the electronic properties of MoS₂ multilayers (larger than six layers) are relatively insensitive to flake thickness.

CONCLUSION

Solution-based exfoliation of layered 2D materials is a promising route for producing 2D crystals in large scale. In this work, few-layer MoS₂ nanosheets have been prepared successfully by lithium intercalation method from bulk MoS₂ powder. The as-prepared MoS₂ nanosheets have a flat and smooth surface. We also have demonstrated that controlled centrifugation and filtration can be used to separate few-layer MoS₂ flakes by sizes. According to DLS analysis, MoS₂ nanosheets with different mean flake lengths ranging 85 – 145 nm are obtained. The as-obtained few-layer MoS₂ nanosheets possess 3-6 layers according to Raman and AFM results. The MoS₂ nanosheets are able to be used for the potential application in hydrogen production.

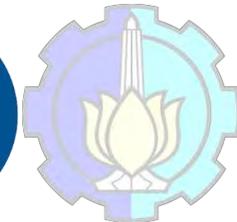
ACKNOWLEDGEMENTS

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Preparation and Characterization of Few-layer MoS₂ Nanosheets



薄層二硫化鉬奈米層片的合成與鑑定

Speaker :

Mohammad Sholeh

M10306821

Advisor :

Prof. Ming-Hsi Chiang

Prof. Shawn D. Lin



Outline



Introduction



Experimental



Results and Discussion



Conclusion

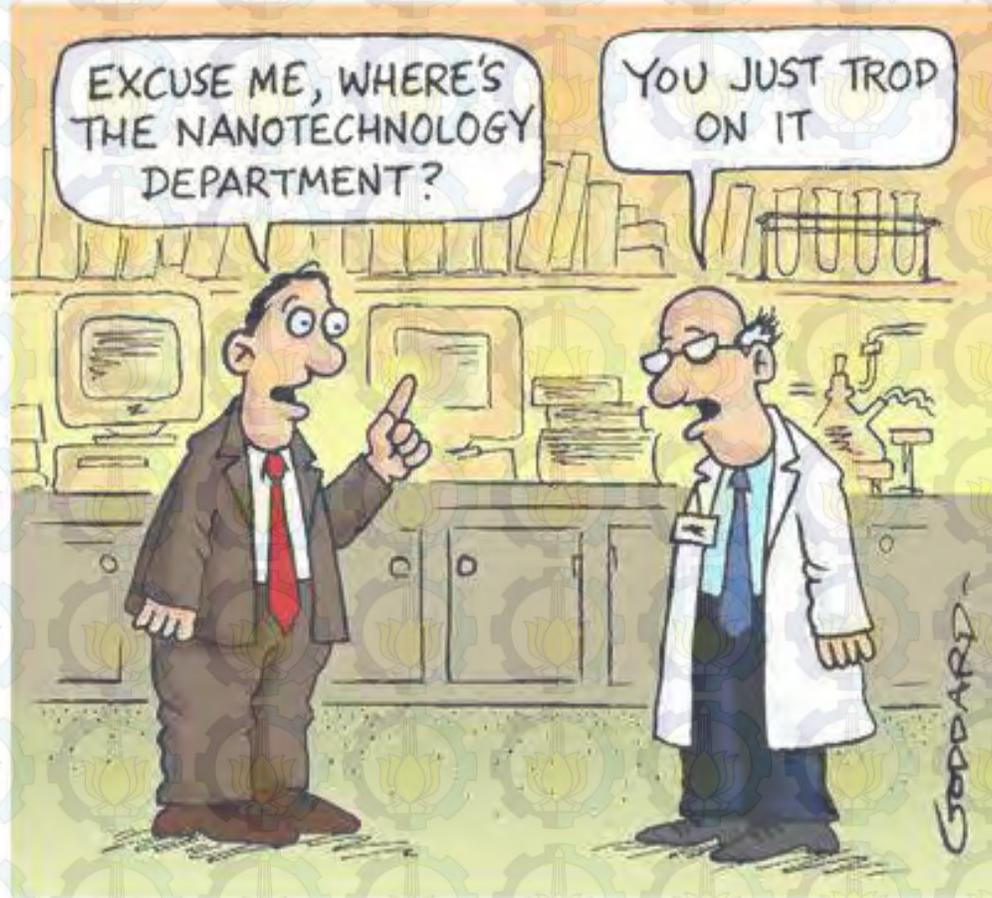


Acknowledgement

Introduction



Nanoscience: Small things can be surprisingly cool



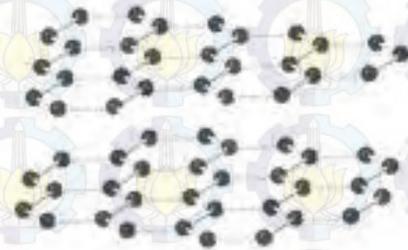
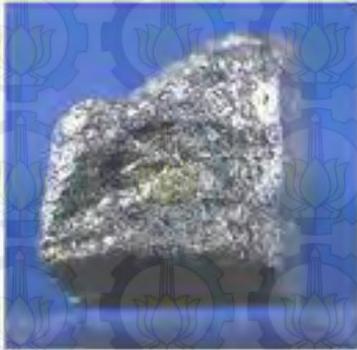
Below 100 nm, properties change, often improving



Introduction

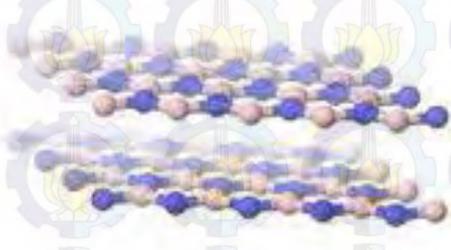
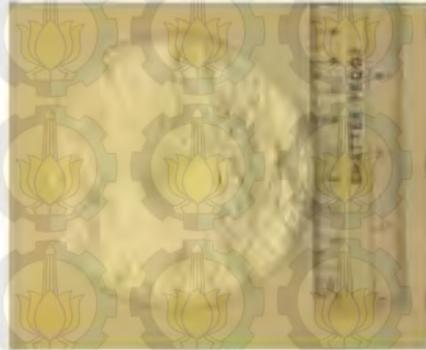


Graphite (C)



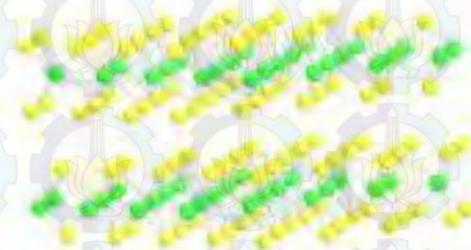
Electrical conductor

Boron Nitride (BN)



Electrical insulator

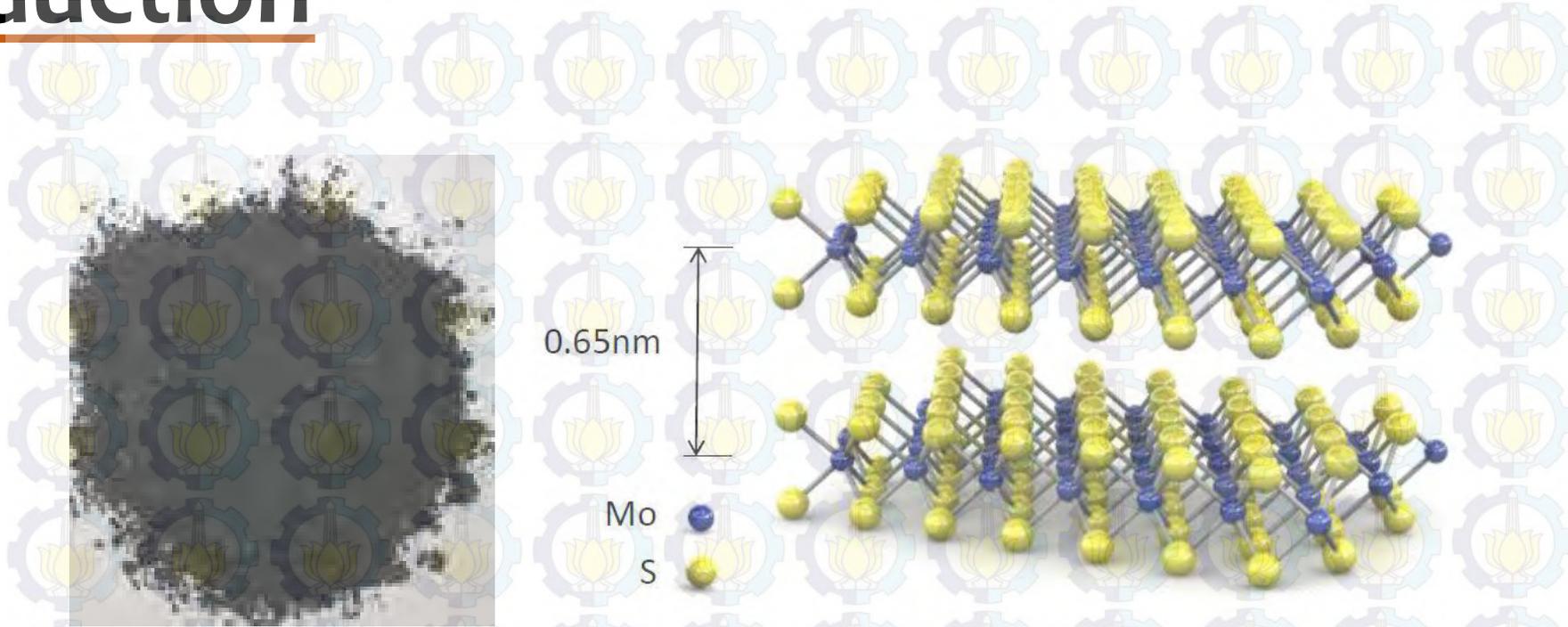
Moly disulphide (MoS_2)



Semiconductor



Introduction



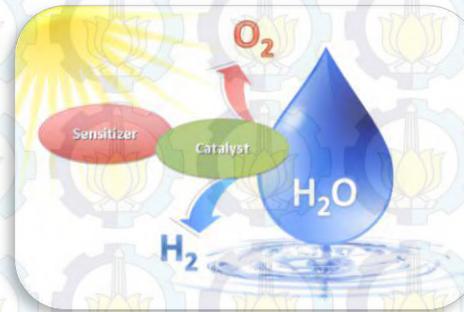
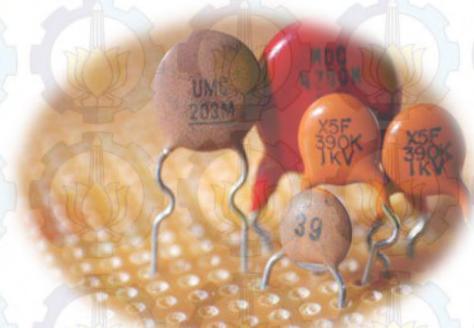
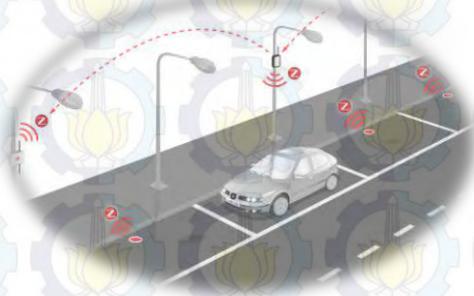
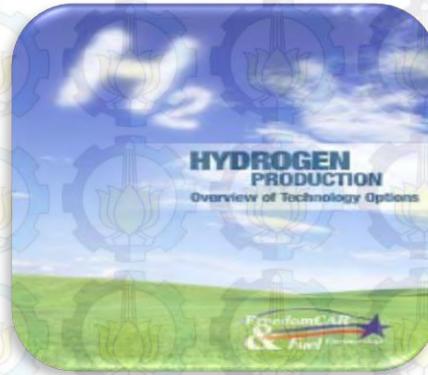
Band gap: 1.29 eV band gap (bulk); 1.83 eV direct gap (single layer)

Mobility: 200 (monolayer, RT) - 500 cm^2/Vs (bulk, 70 K)

Stability: > 1000 °C in inert atmosphere no dangling bonds

Availability: naturally occurring mineral, abundance similar to Ge

Introduction



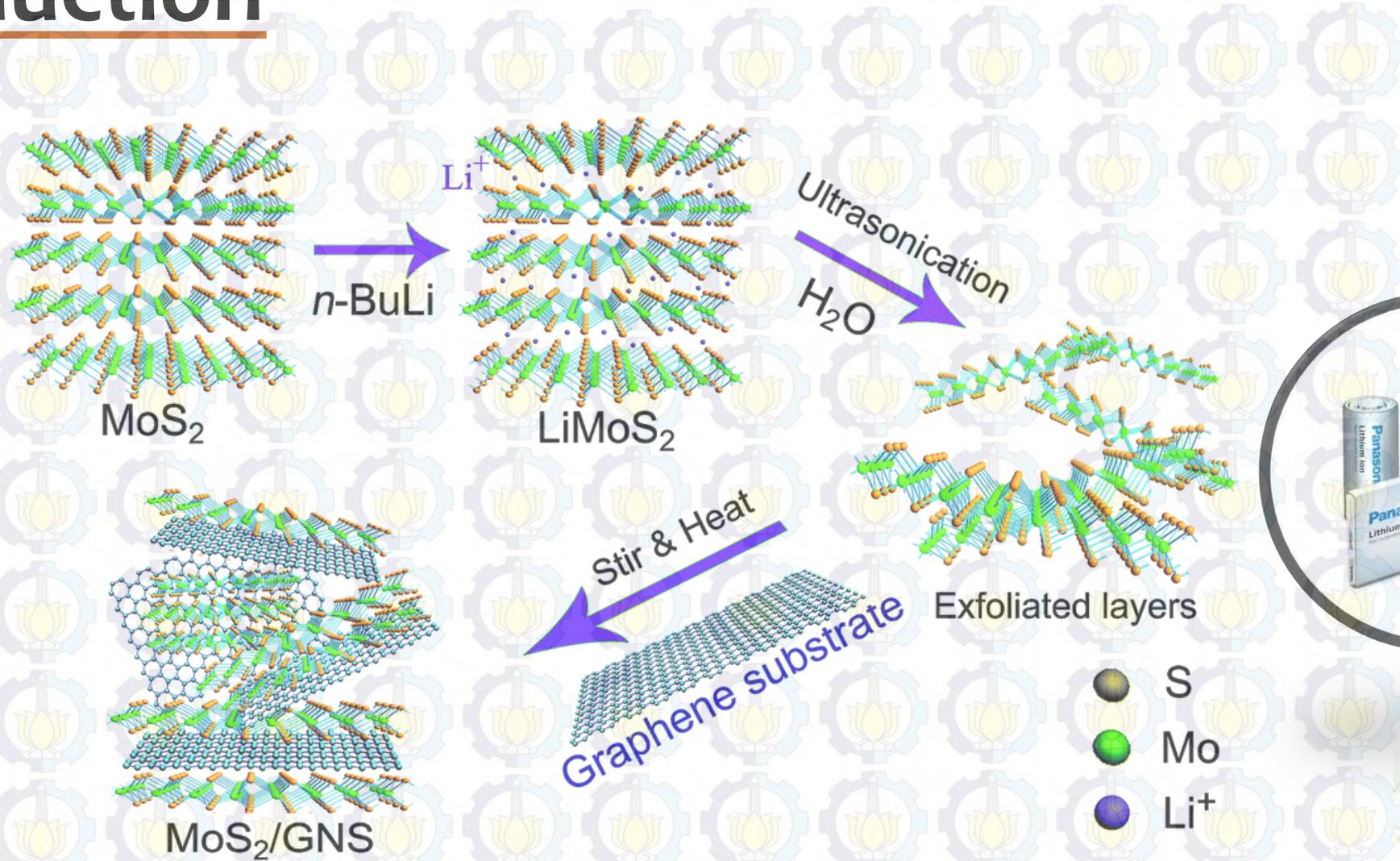
Yin, Z. Y. et al., *ACS Nano* **2012**, *6*, 74-80

Voiry, D. et al., *Nano lett.* **2013**, *13*, 6222-6227

Ma, G. et al., *Journal of power sources* **2013**, *229*, 72-78

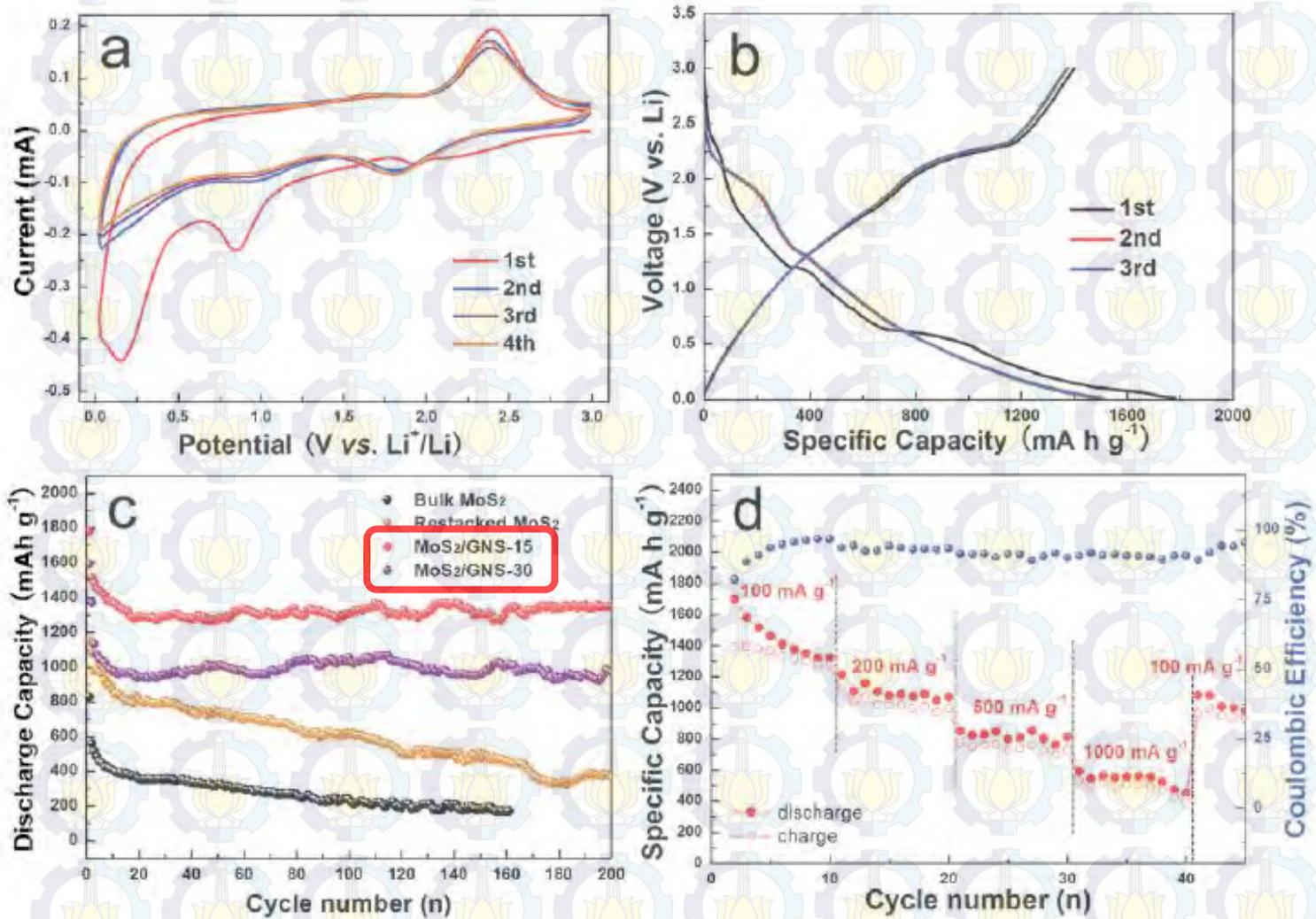
Zhang, S.-L. et al., *Current Applied Physics* **2014**, *14*, 264-268

Introduction



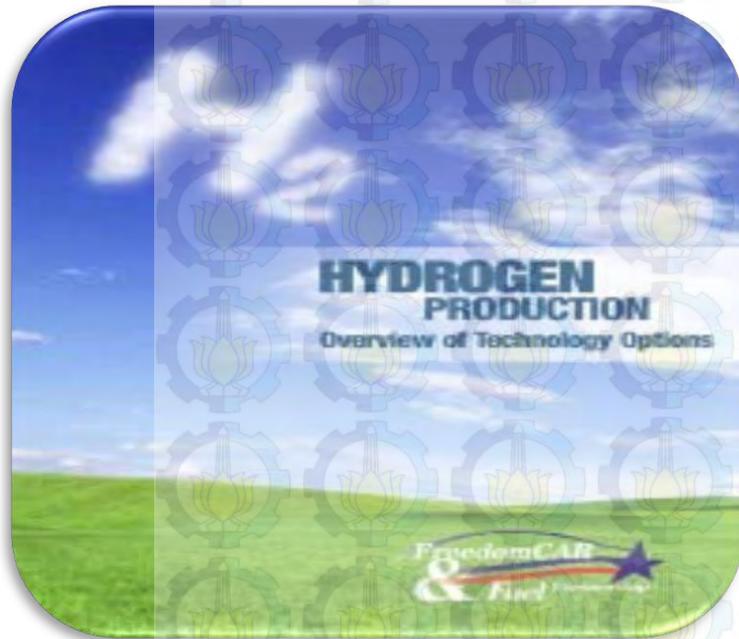
Liu, Y. D. et al., *Journal of Materials Chemistry A* **2014**, 2, 13109.

Introduction

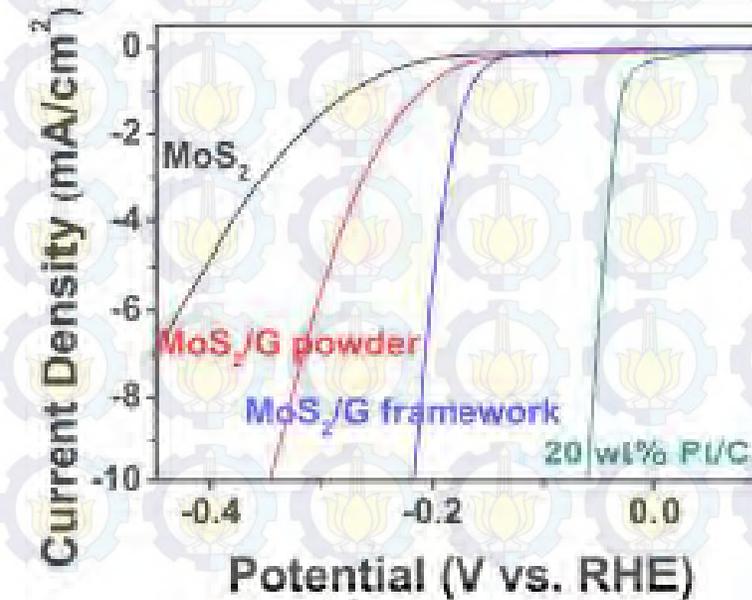
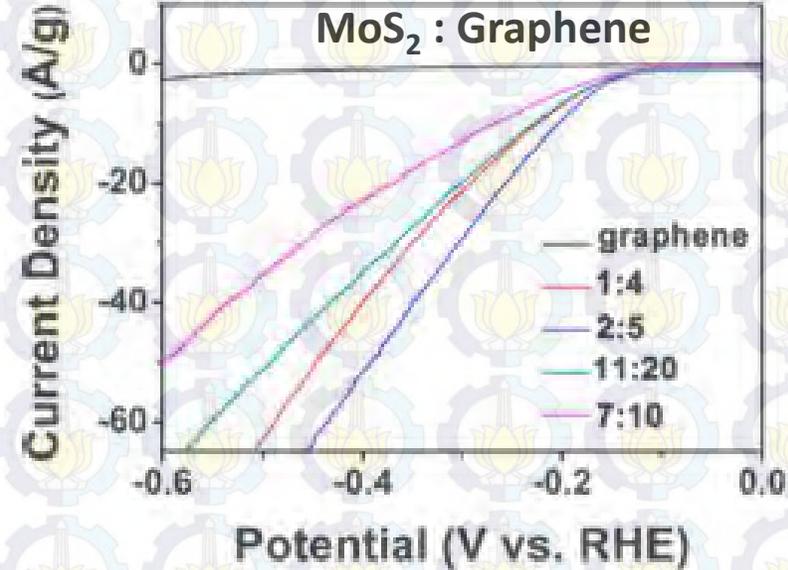


Liu, Y. D. et al., *Journal of Materials Chemistry A* **2014**, 2, 13109.

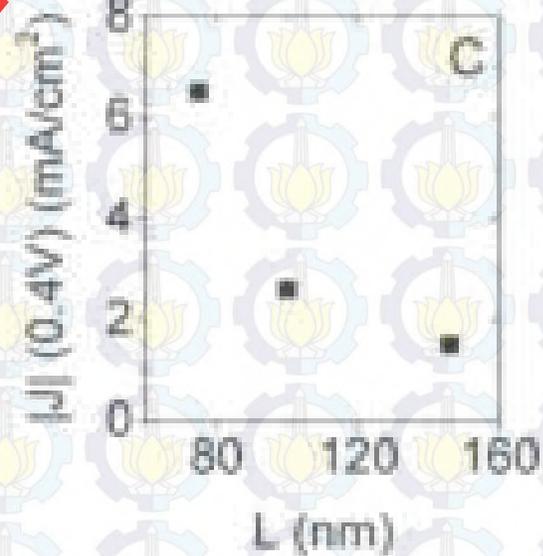
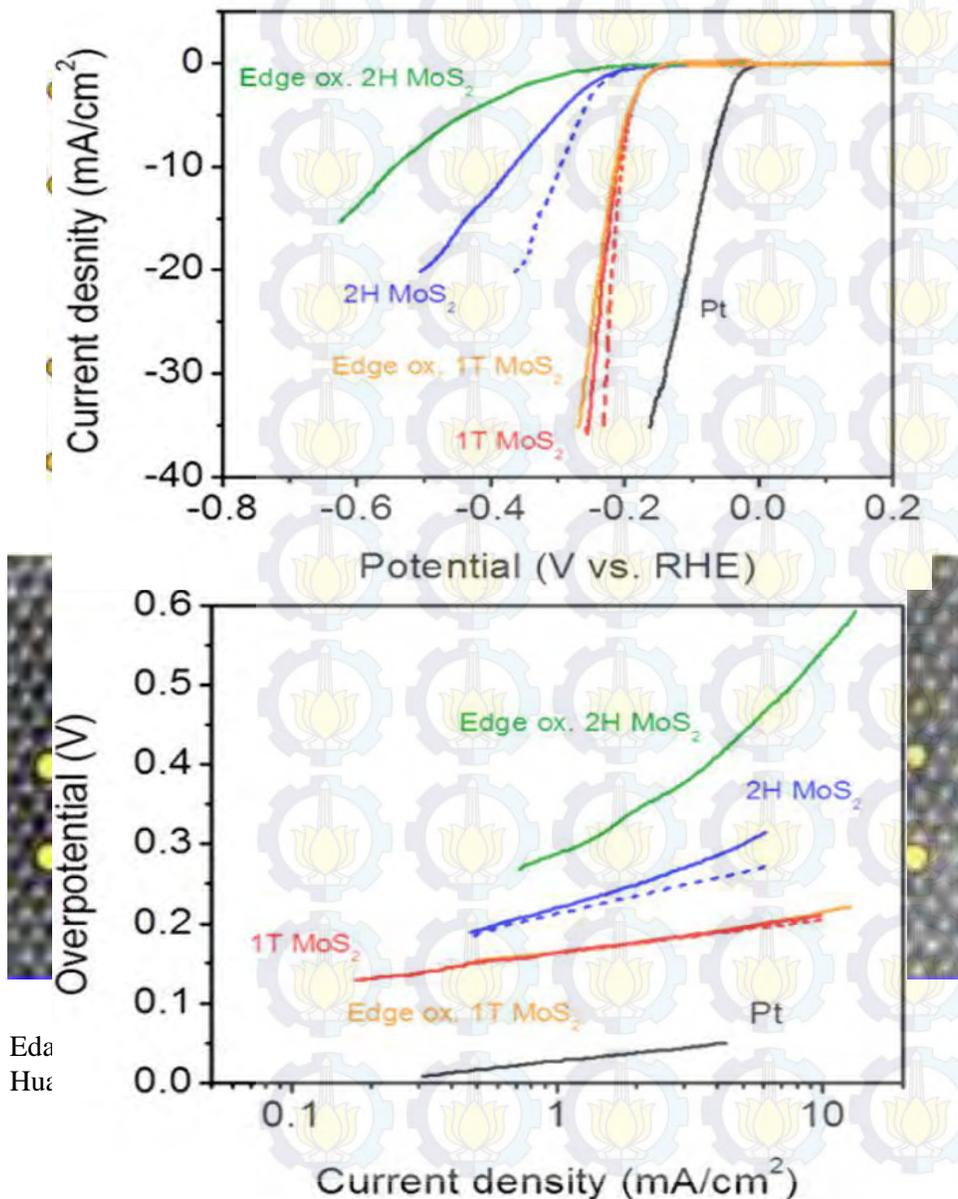
Introduction



Zhou, W. et al., *ACS Appl. Mater. Interfaces* 2014, 6, 21534.



Introduction



Current density produced at 0.4 V plotted versus nanosheet size.

Varrla, E. et al., *Chemistry of Materials* 2015, 27, 1129.



Eda
Huz

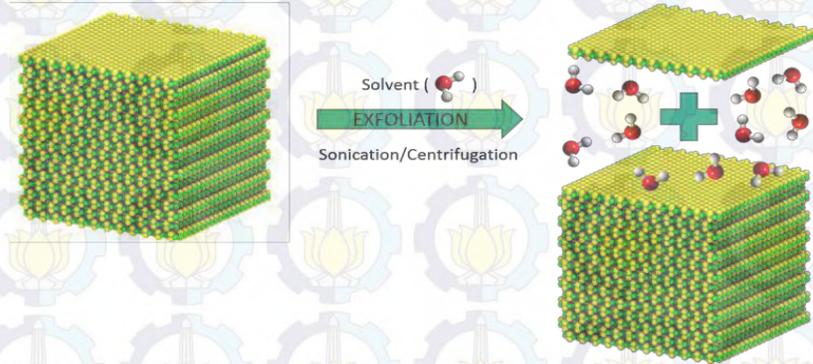
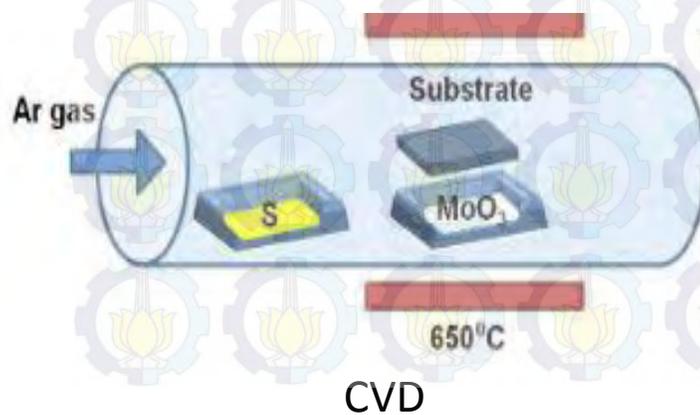
Introduction



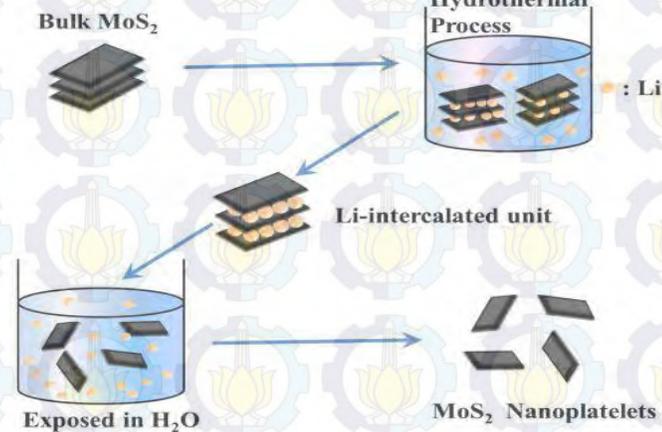
Preparation of MoS₂ nanosheets



Scotch-taped



Liquid-Exfoliation

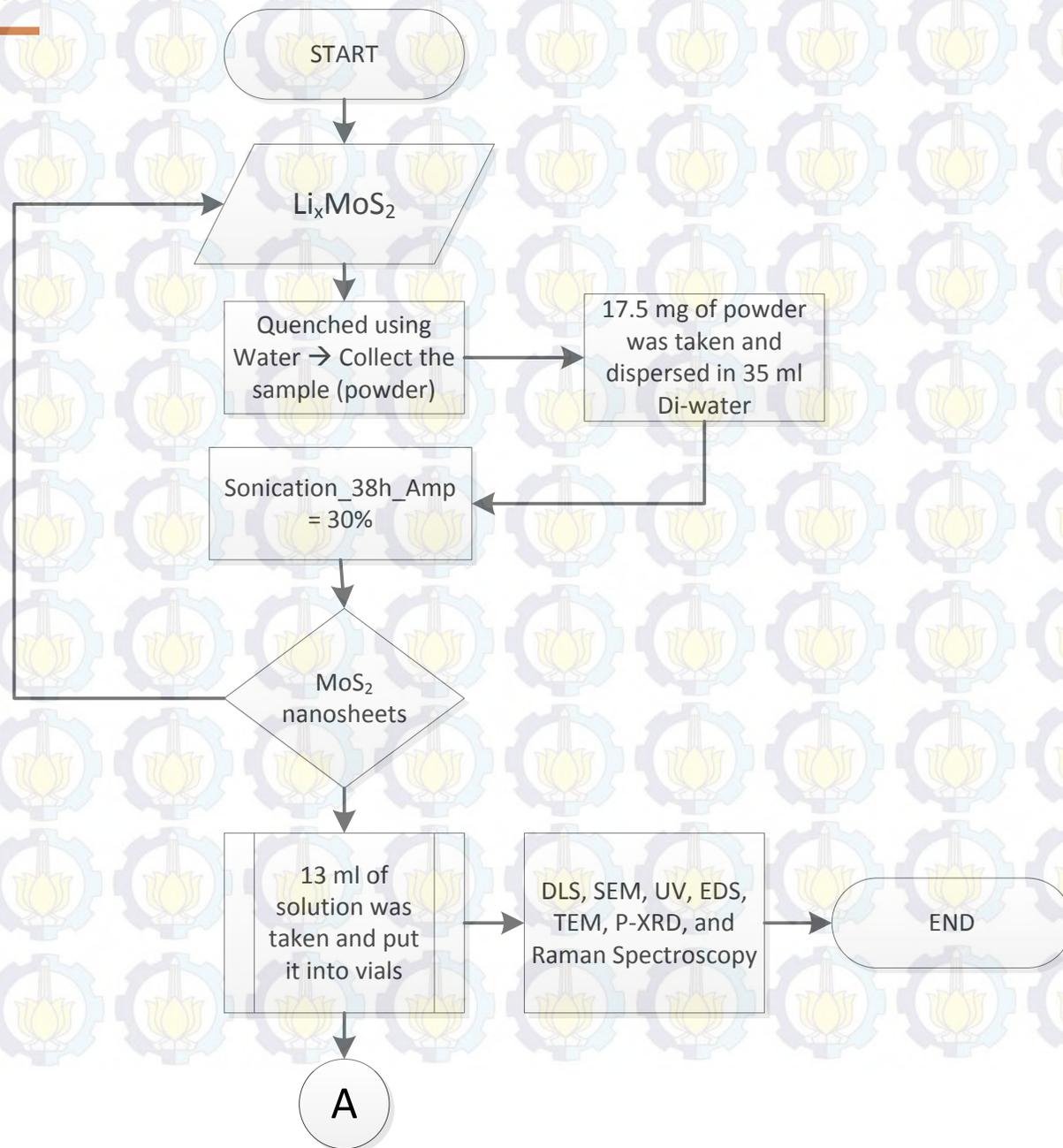


Hydrothermal

Experimental



1st Part

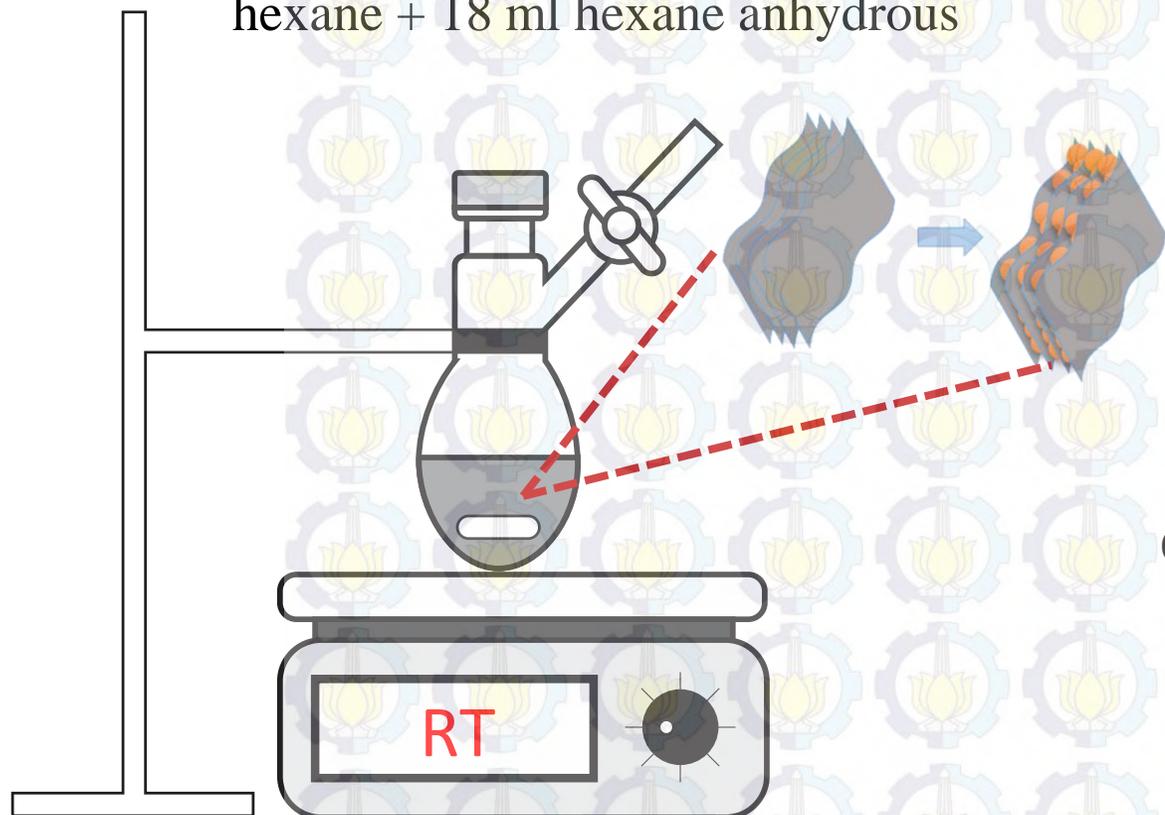


Experimental (1st Part)



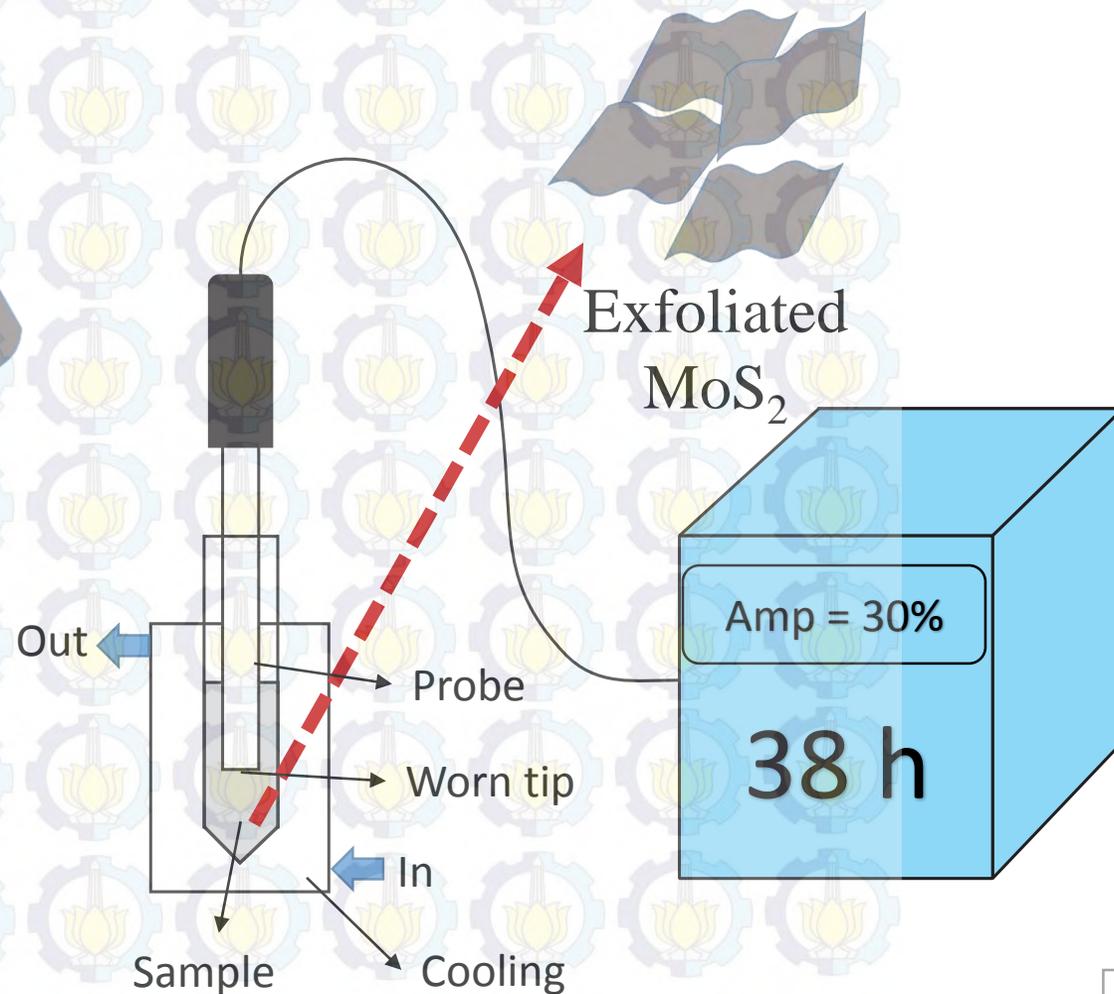
Intercalation Process

0.3 g Bulk MoS₂ + 2 ml of 2.5 M *n*-BuLi in hexane + 18 ml hexane anhydrous



Stirred for 5 days

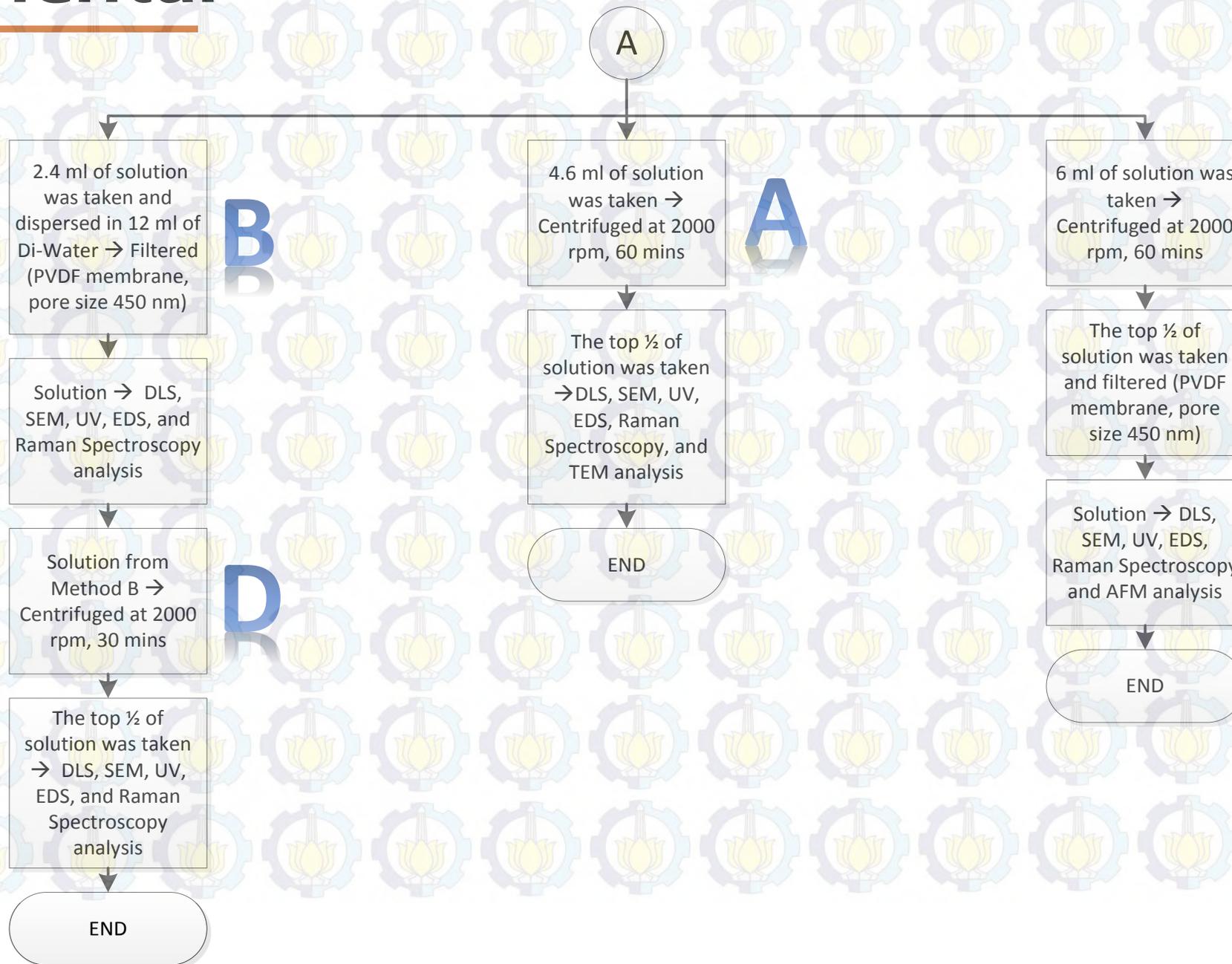
Exfoliation Process



Experimental



2nd Part

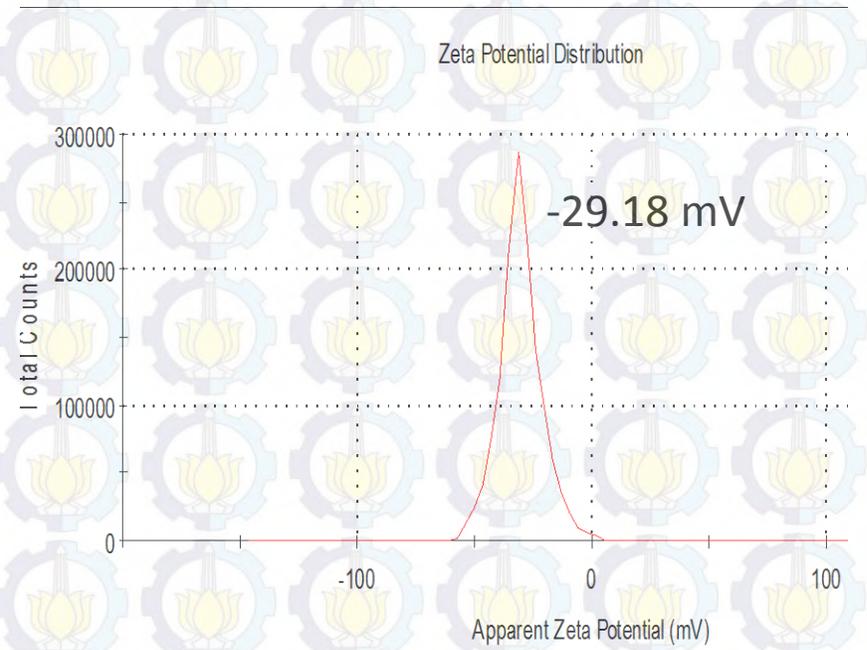
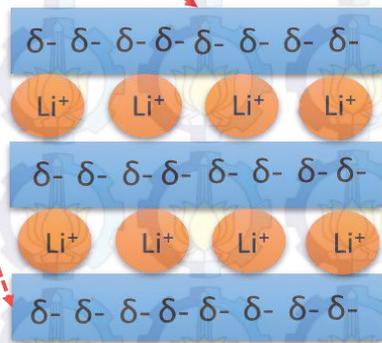
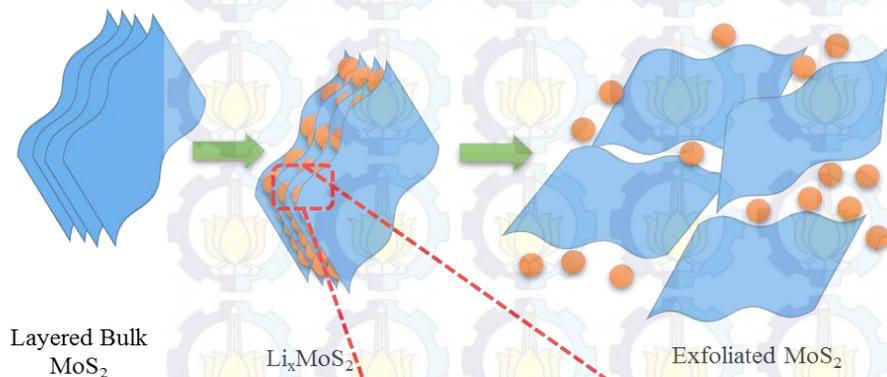




Results and Discussion



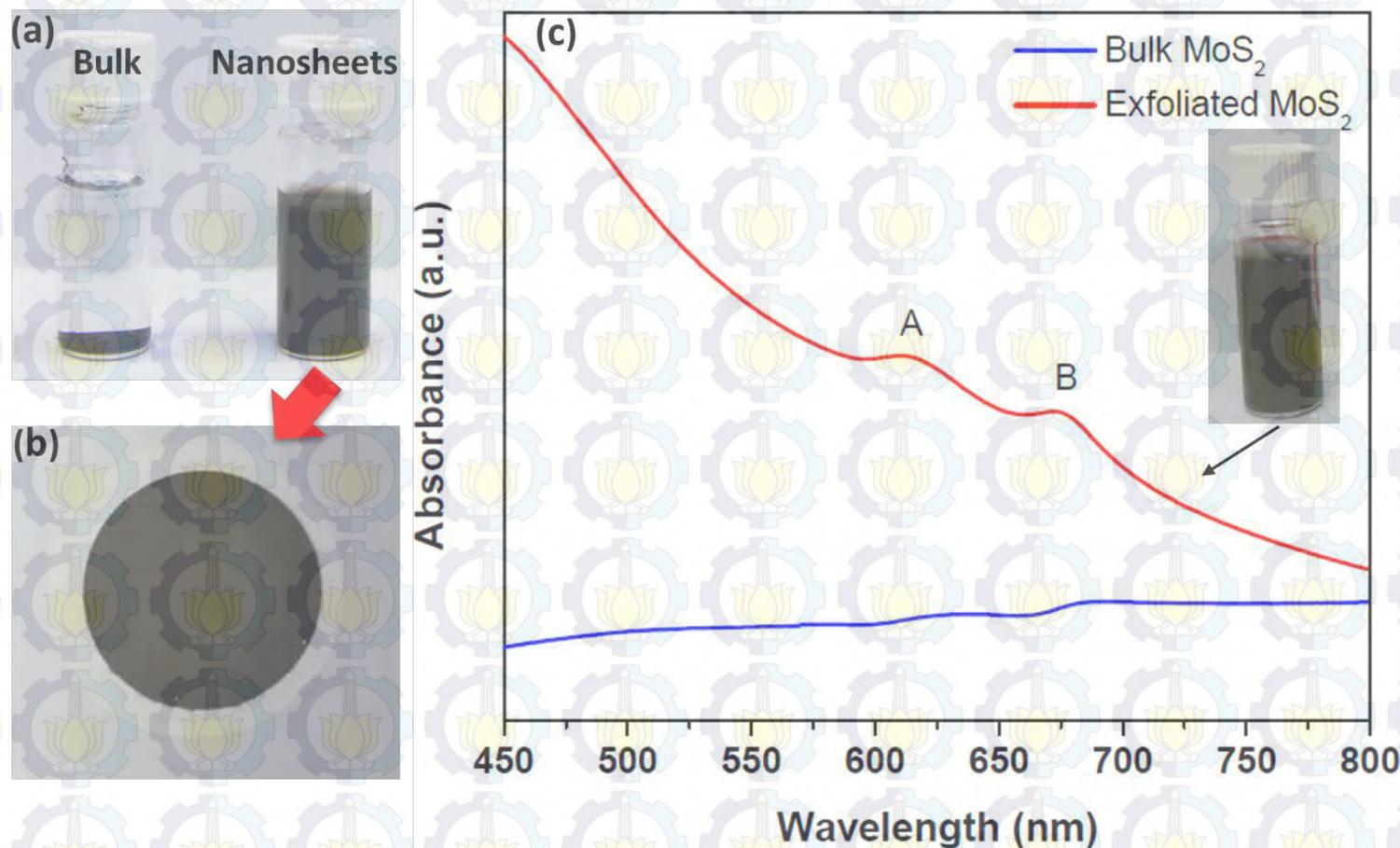
Results (1st Part)



Experiment	1 st	2 nd	3 rd	4 th	5 th
Zeta Potential (mV)	-30	-30	-27.9	-29.9	-28.1



UV – Vis Spectra

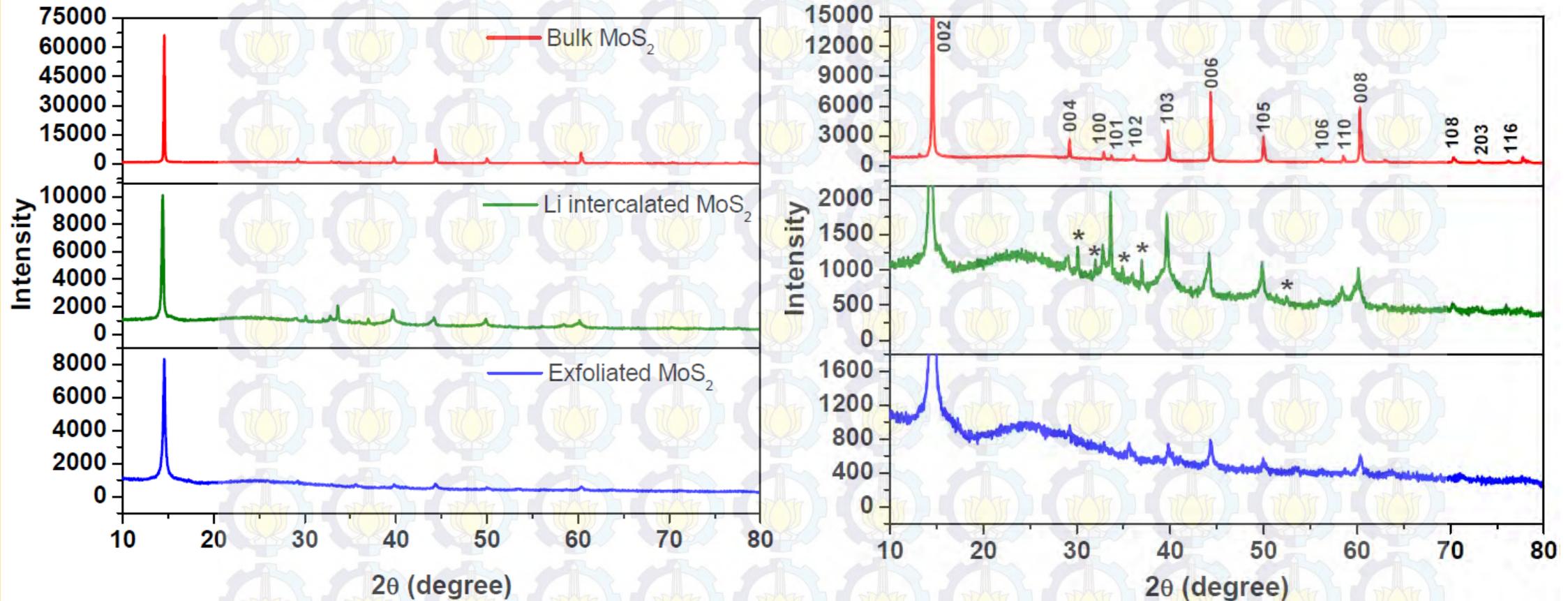


The two peaks centered at 610 nm (2.03 eV) and 673 nm (1.84 eV) can be attributed to the characteristic A and B direct-gap absorptions and excitonic transitions of MoS₂ with energy separation of 0.19 eV^{1,2}

1 Benavente, E., et al. *Coord. Chem. Rev.* **2002**, 224, 87–109

2 Bang, G. S., et al. *ACS Appl. Mater. Interfaces.* **2014**, 6, 7084–7089

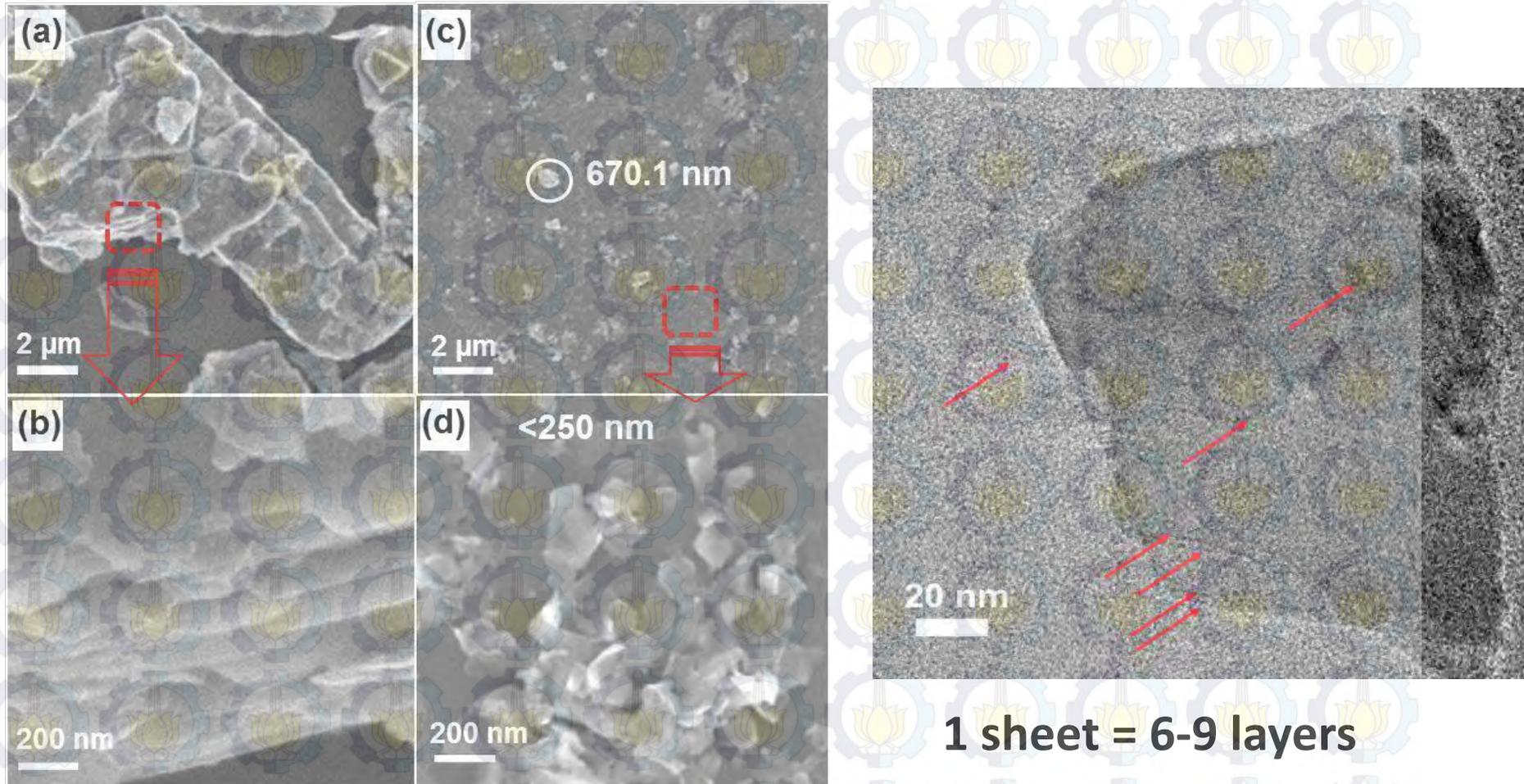
P-XRD Analysis



All diffraction peaks of the sample were in good agreement with a hexagonal lattice structure of MoS₂ (JCPDS No. 37-1492).

The additional diffraction peaks (stars) at 30°, 32°, 35°, 37° and 52° indicate the lithium intercalated MoS₂

SEM & TEM

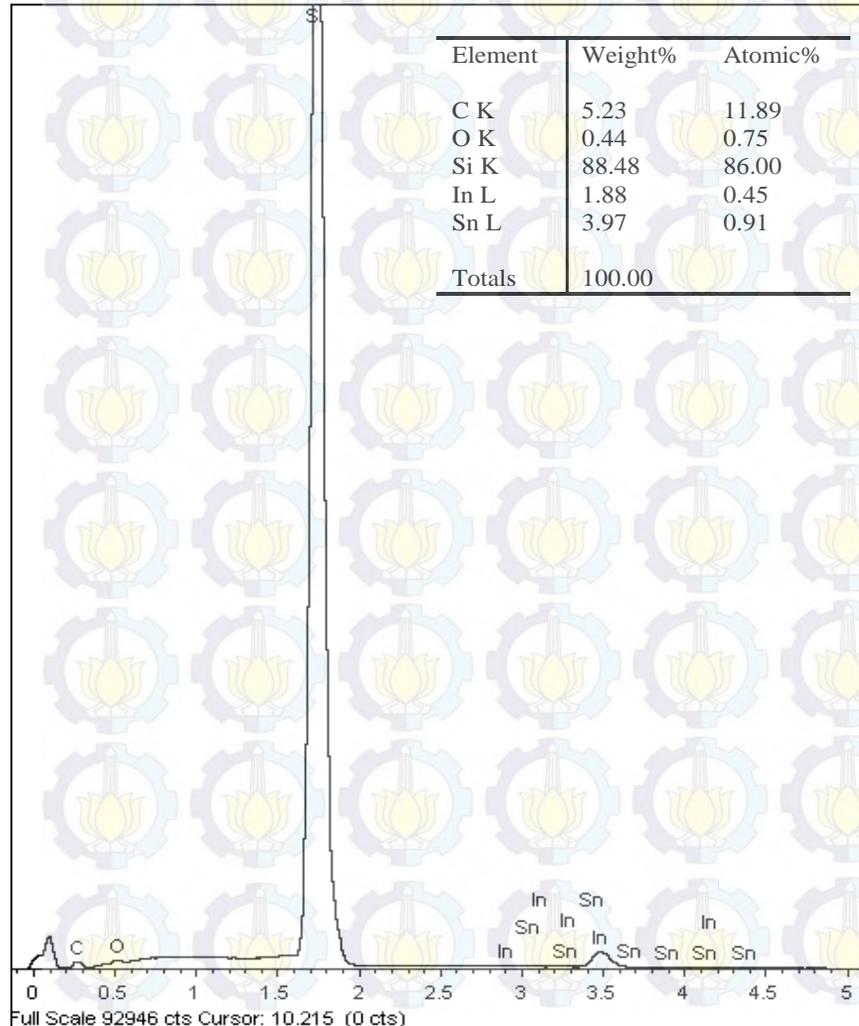


1 sheet = 6-9 layers

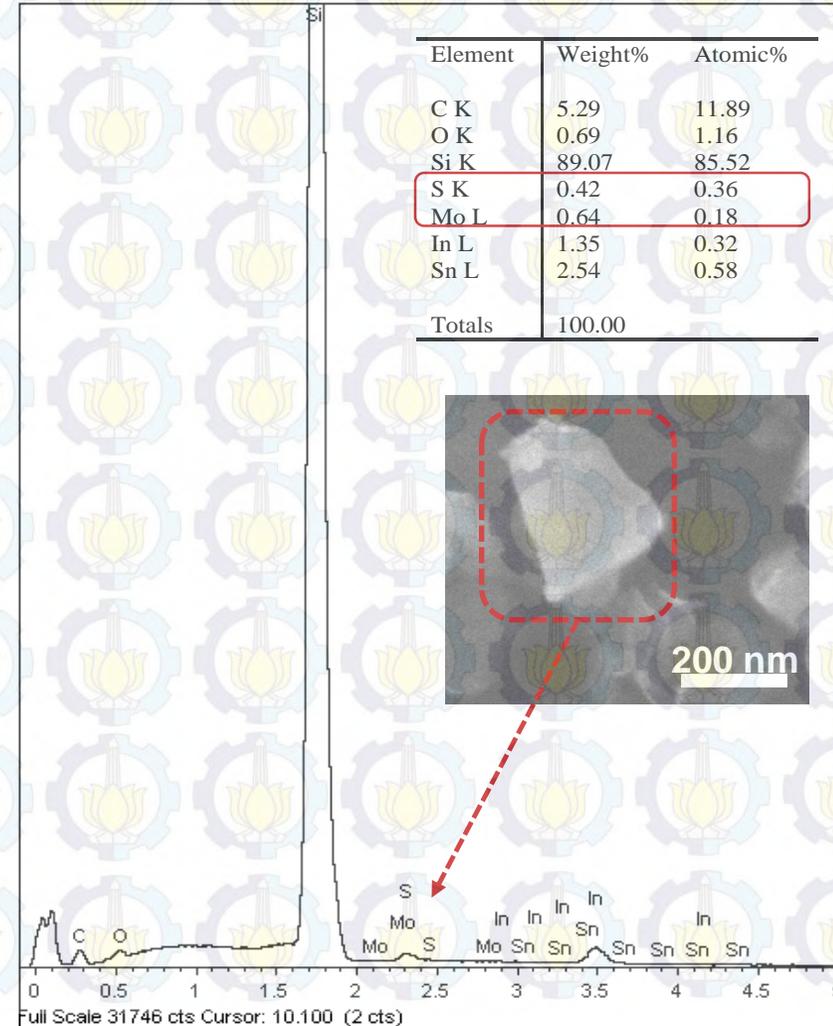
The typical SEM images: (a) and (b) Bulk MoS₂ powder with different resolution; (c) MoS₂ nanosheets with different lateral sizes; (d) MoS₂ nanosheets with lateral size <250 nm.



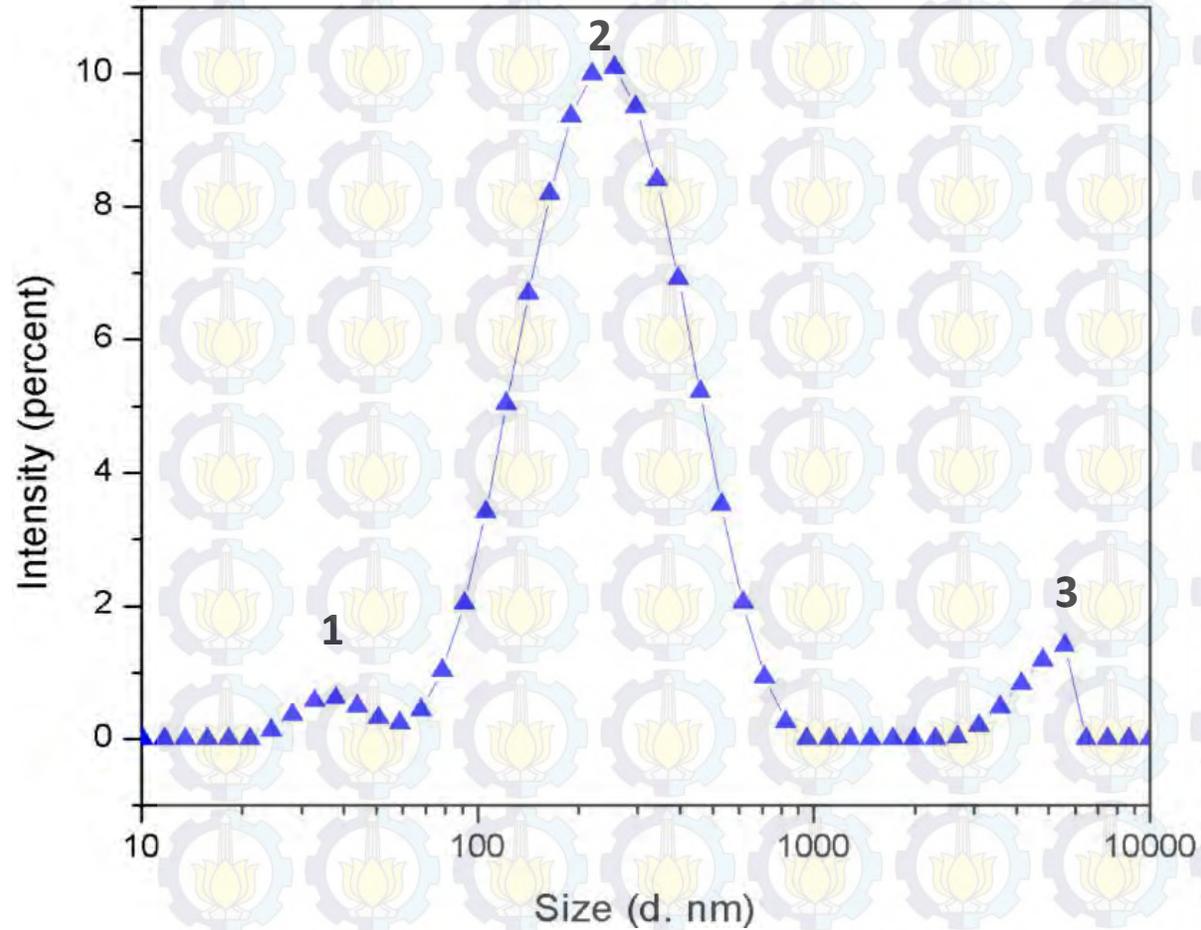
Background



After Sonication

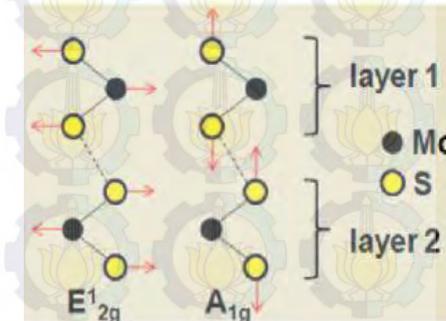
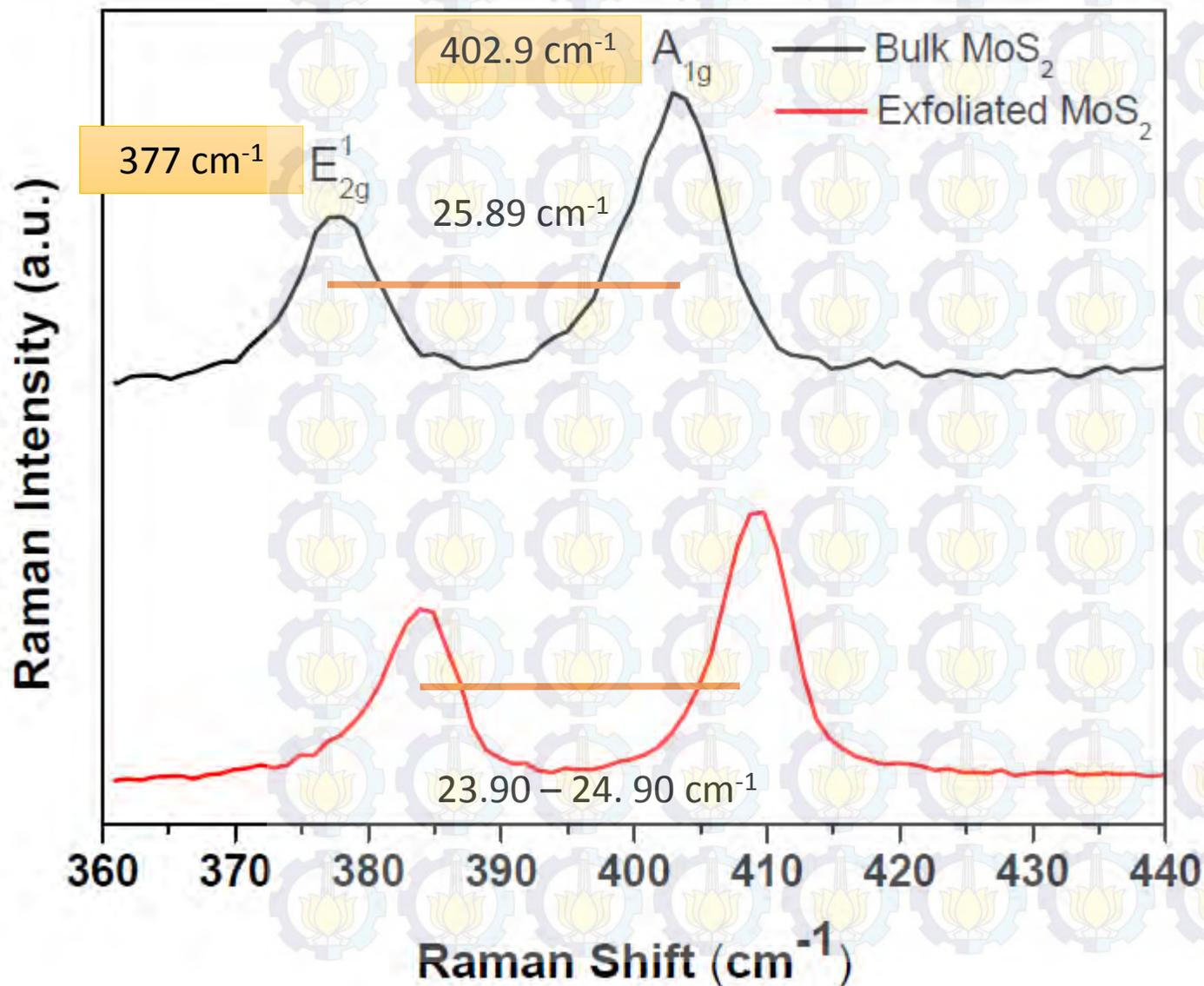


DLS Analysis



Peak	d. nm
1 st	38
2 nd	220
3 rd	5800

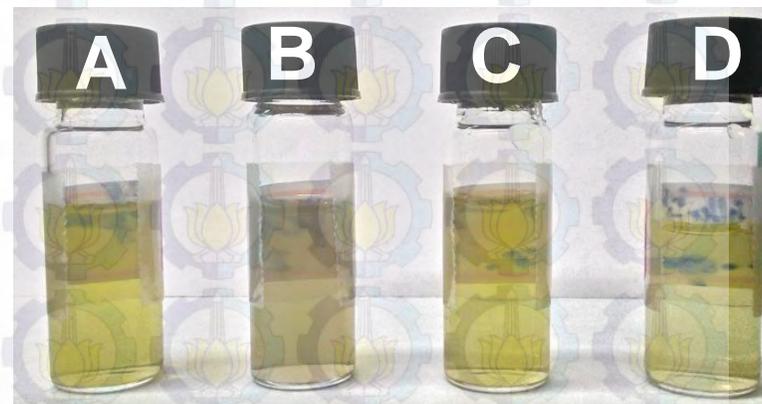
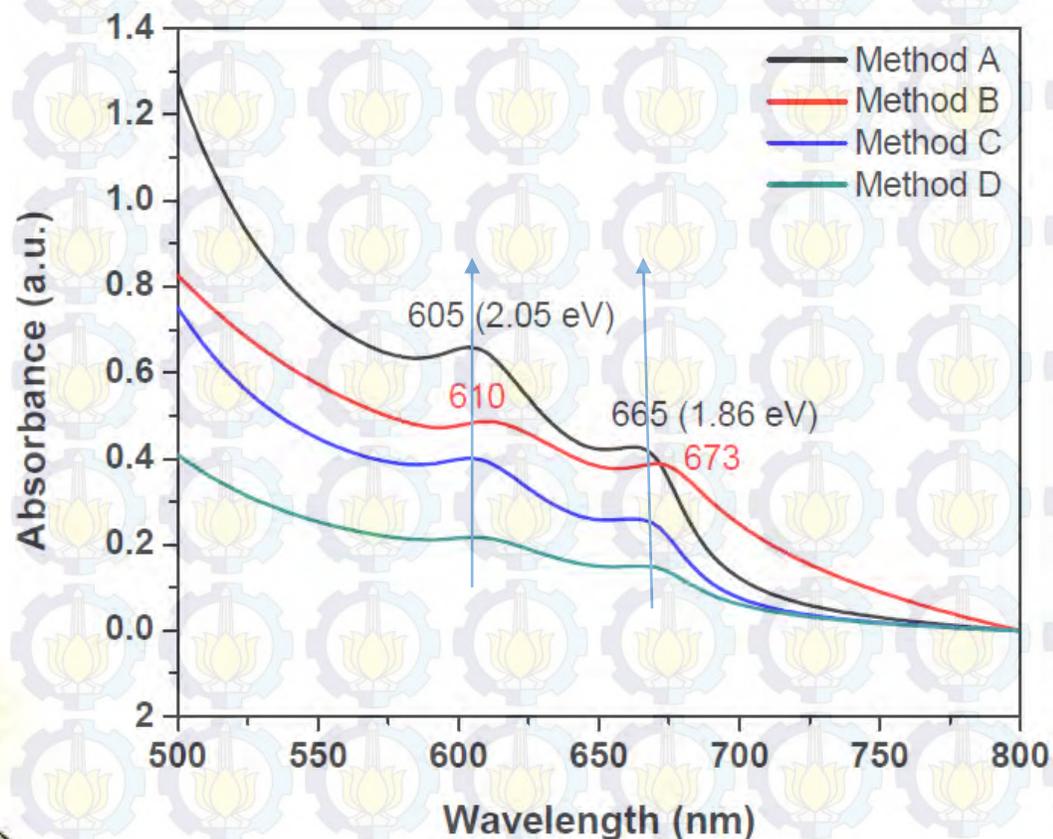
Raman Spectroscopy



Reported by	Δk ($A_{1g}-E_{2g}^1$) cm ⁻¹	Layer number of MoS ₂
Korn, T. et al ¹	18	1 layer
Yu, Y. et al ²	20-21.2	1 layer
Van Thanh, V. et al ³	21.7	2 layers
Yu, Y. et al ²	22.4-23.2	2 layers
Yu, Y. et al ²	23.6-23.9	3 layers
Yu, Y. et al ²	24.0-24.2	4 layers
Lee, C. et al ⁴	24.9	6 layers
Lee, C. et al ⁴	25.6	bulk
Van Thanh, D. et al ³	27.2	bulk

(1) Korn, T. et al., *Applied Physics Letters* **2011**, *99*, 102109.
 (2) Yu, Y. et al., *Sci. Rep.* **2013**, *3*, 1866.
 (3) Van Thanh, D. et al., *RSC Advances* **2014**, *4*, 15586.
 (4) Lee, C. et al., *ACS Nano* **2010**, *4*, 2695.

Results (2nd Part)



- A = Sonic_38h, 2000 rpm, 60 mins
- B = Sonic_38h, Filter, Solution
- C = Sonic_38h, 2000 rpm, 60 mins + Filter, Solution
- D = Sonic_38h, Filter, Solution + 2000 rpm, 30 mins



The peak positions for electronic transitions are at 605 nm (2.05 eV) and 665 nm (1.86 eV) with energy separation of 0.19 eV^{1,2} with smaller lateral dimensions^{3,4}

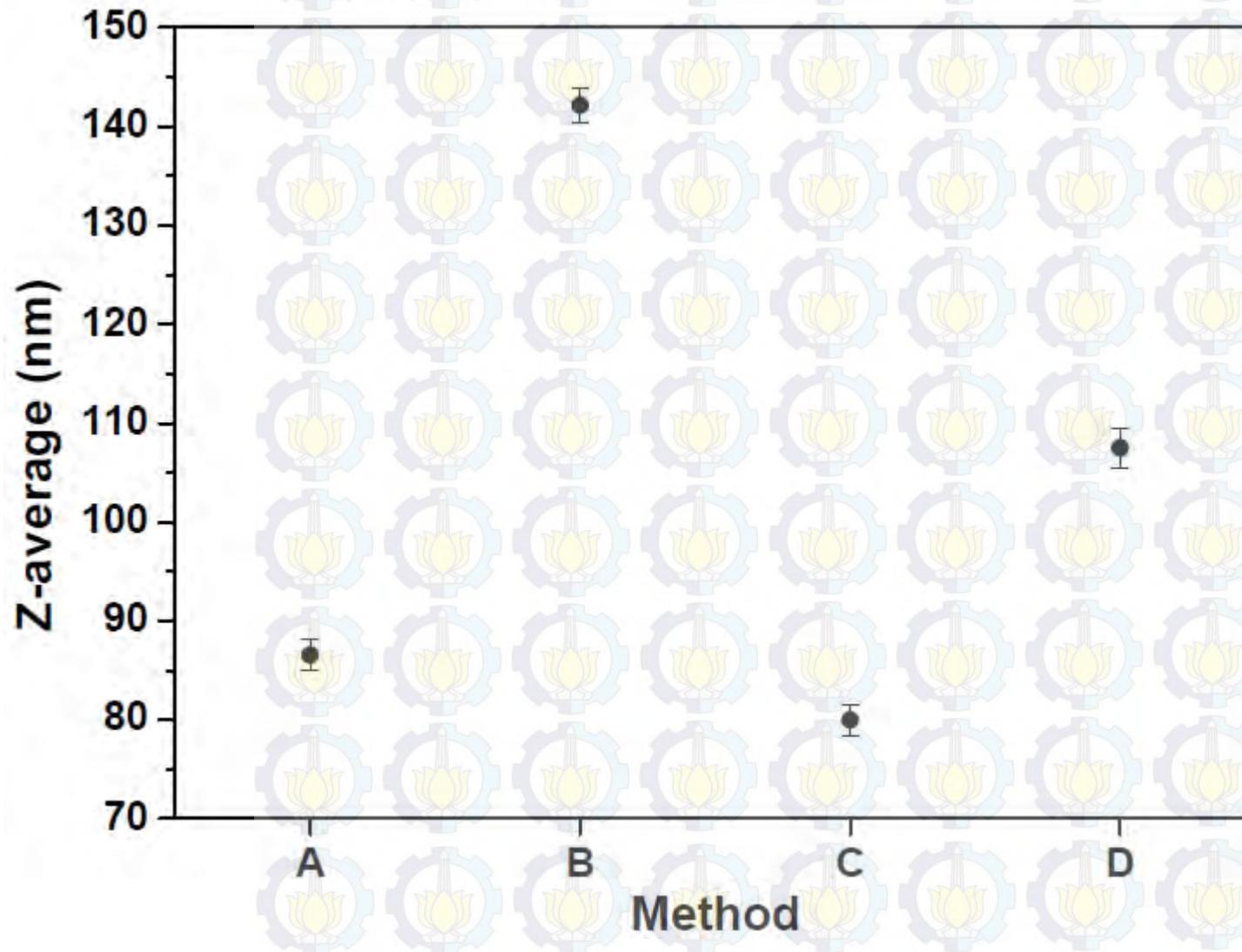
1 Benavente, E., et al. *Coord. Chem. Rev.* **2002**, 224, 87–109

2 Bang, G. S., et al. *ACS Appl. Mater. Interfaces.* **2014**, 6, 7084–7089

3 Bernardi, M., et al. *Nano Letters* **2013**, 13, 3664.

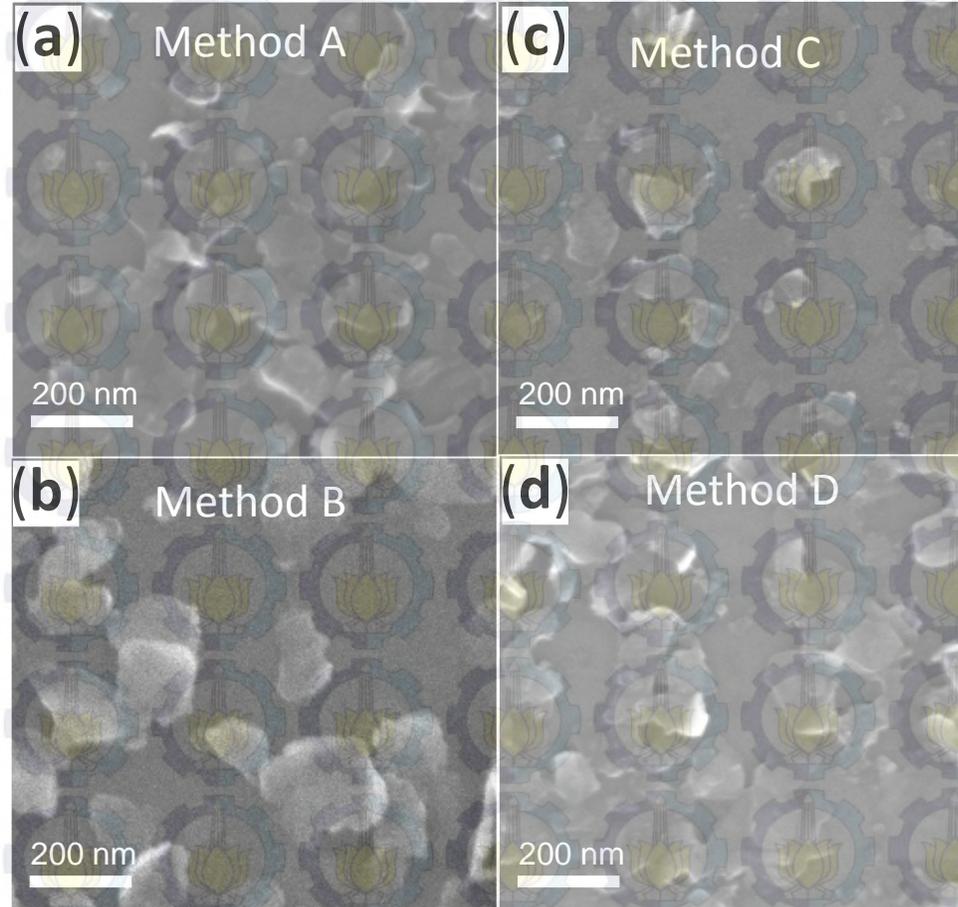
4 Coleman, J. N., et al. *Science* **2011**, 331, 568.

DLS Analysis



Method	Z-average (d. nm)
A	87.5 ± 2.5
B	142.5 ± 2.5
C	80.5 ± 1.5
D	107.5 ± 2.5

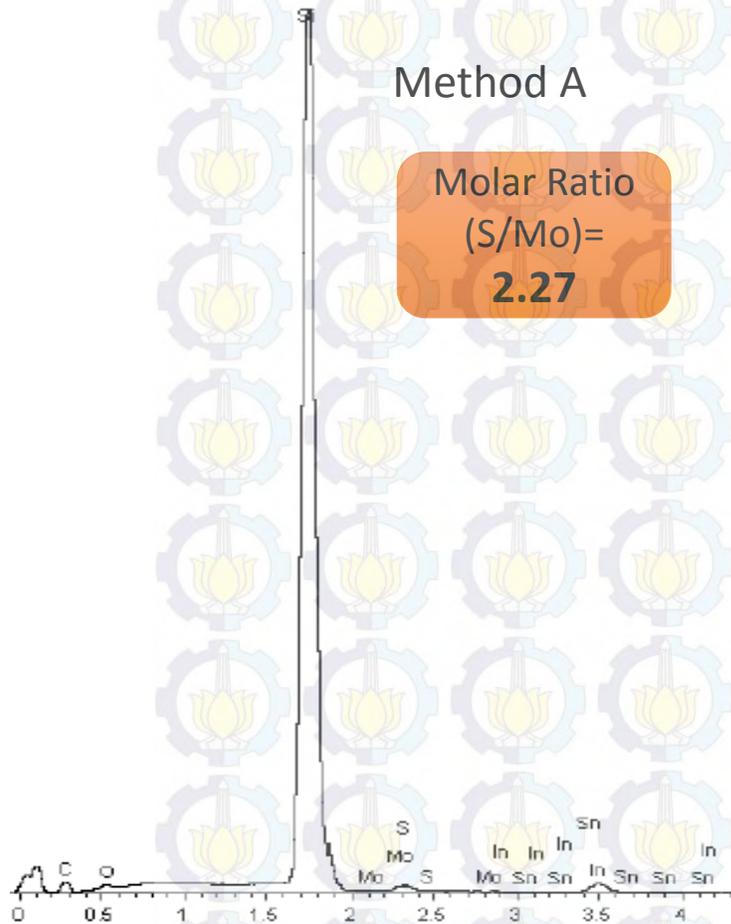
SEM Images



Sample B
is Biggest
one



EDS-SEM



Method A

Molar Ratio
(S/Mo)=
2.27

Element	App Conc.	Intensity Corr.	Weight%	Weight% Sigma	Atomic%
C K	0.25	0.2815	7.90	0.21	17.18
O K	0.10	1.0973	0.85	0.06	1.38
Si K	11.75	1.2197	85.80	0.29	79.82
S K	0.06	0.8890	0.61	0.06	0.50
Mo L	0.06	0.6368	0.80	0.18	0.22
In L	0.12	0.7455	1.43	0.09	0.32
Sn L	0.20	0.6688	2.62	0.11	0.58
Totals			100.00		

Method B

Element	App Conc.	Intensity Corr.	Weight%	Weight% Sigma	Atomic%
C K	0.20	0.2767	6.45	0.22	14.28
O K	0.11	1.1055	0.92	0.06	1.53
Si K	11.91	1.2232	87.14	0.31	82.54
S K	0.06	0.8881	0.60	0.06	0.57
Mo L	0.07	0.6362	1.04	0.19	0.29
In L	0.11	0.7460	1.33	0.09	0.31
Sn L	0.19	0.6695	2.53	0.12	0.49
Totals			100.00		

Molar Ratio
(S/Mo)=
1.97

Method C

Element	App Conc.	Intensity Corr.	Weight%	Weight% Sigma	Atomic%
O K	1.21	1.1649	9.37	0.08	16.38
Si K	10.74	1.2191	79.66	0.22	79.34
S K	0.23	0.9106	2.33	0.07	2.03
Mo L	0.26	0.6523	3.60	0.21	1.05
In L	0.18	0.7541	2.12	0.08	0.52
Sn L	0.22	0.6770	2.93	0.11	0.69
Totals			100.00		

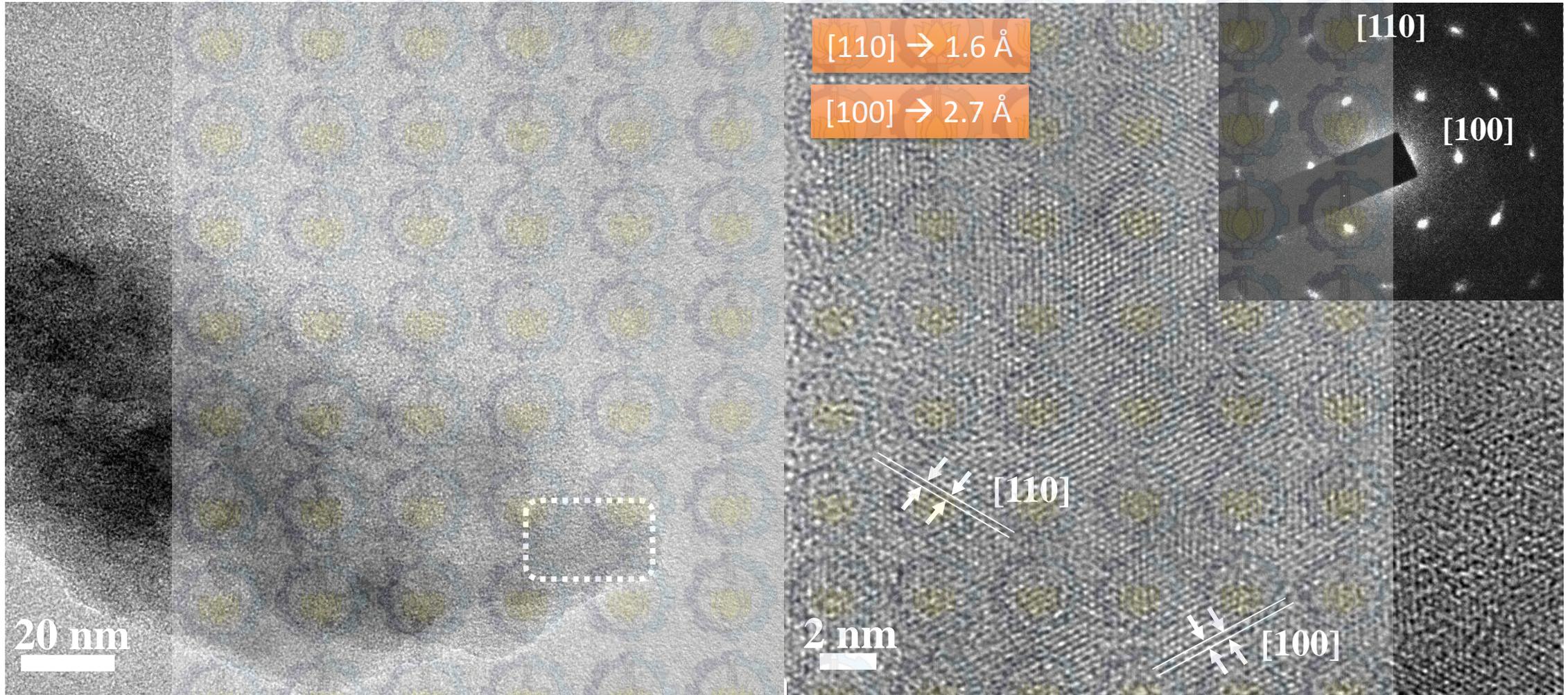
Molar Ratio
(S/Mo)=
1.93

Method D

Element	App Conc.	Intensity Corr.	Weight%	Weight% Sigma	Atomic%
C K	0.34	0.2896	10.04	0.21	21.32
O K	0.24	1.0872	1.86	0.06	2.96
Si K	11.49	1.2150	80.44	0.29	73.02
S K	0.17	0.8988	1.61	0.07	1.28
Mo L	0.17	0.6438	2.26	0.20	0.60
In L	0.11	0.7452	1.25	0.08	0.28
Sn L	0.20	0.6686	2.55	0.11	0.55
Totals			100.00		

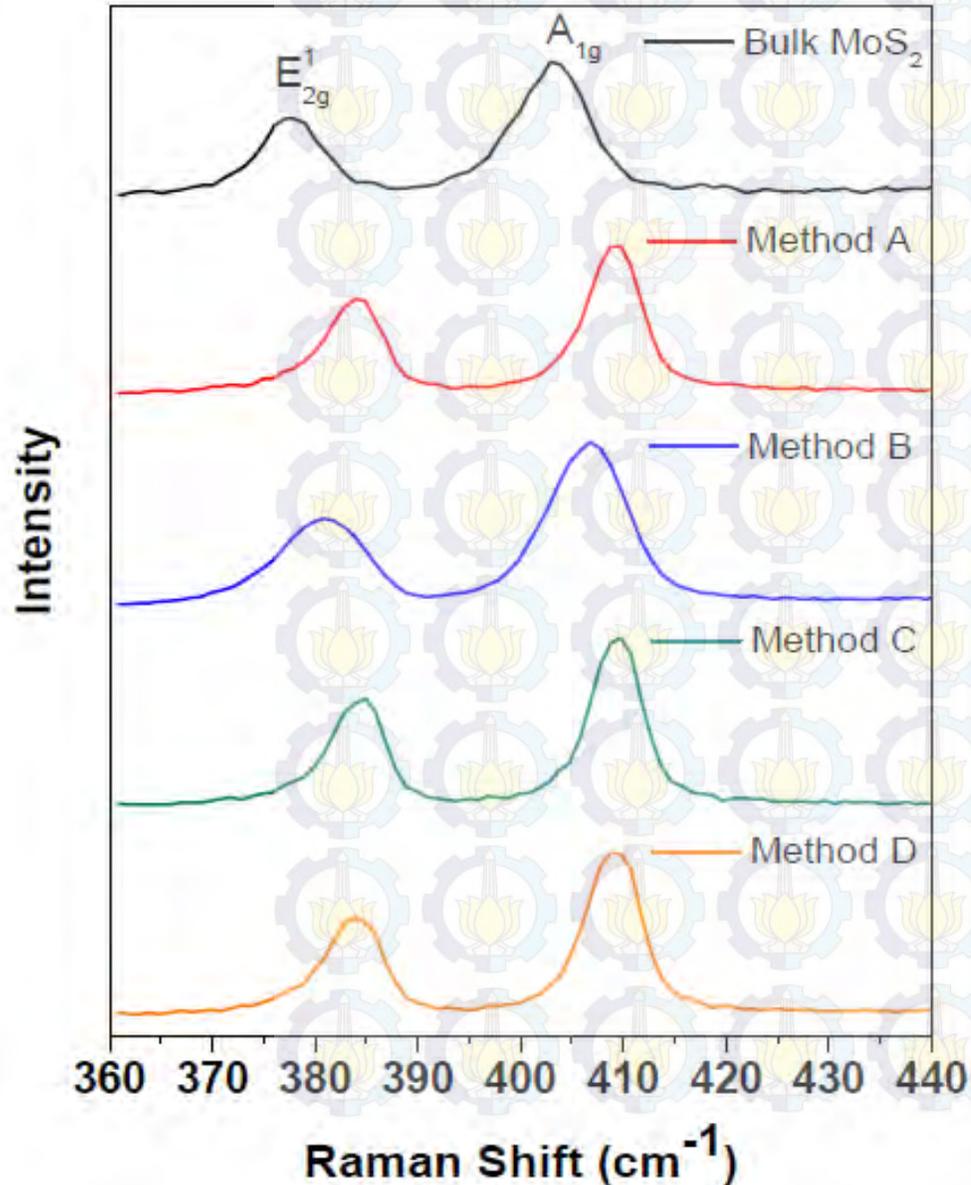
Molar Ratio
(S/Mo)=
2.13

TEM Analysis



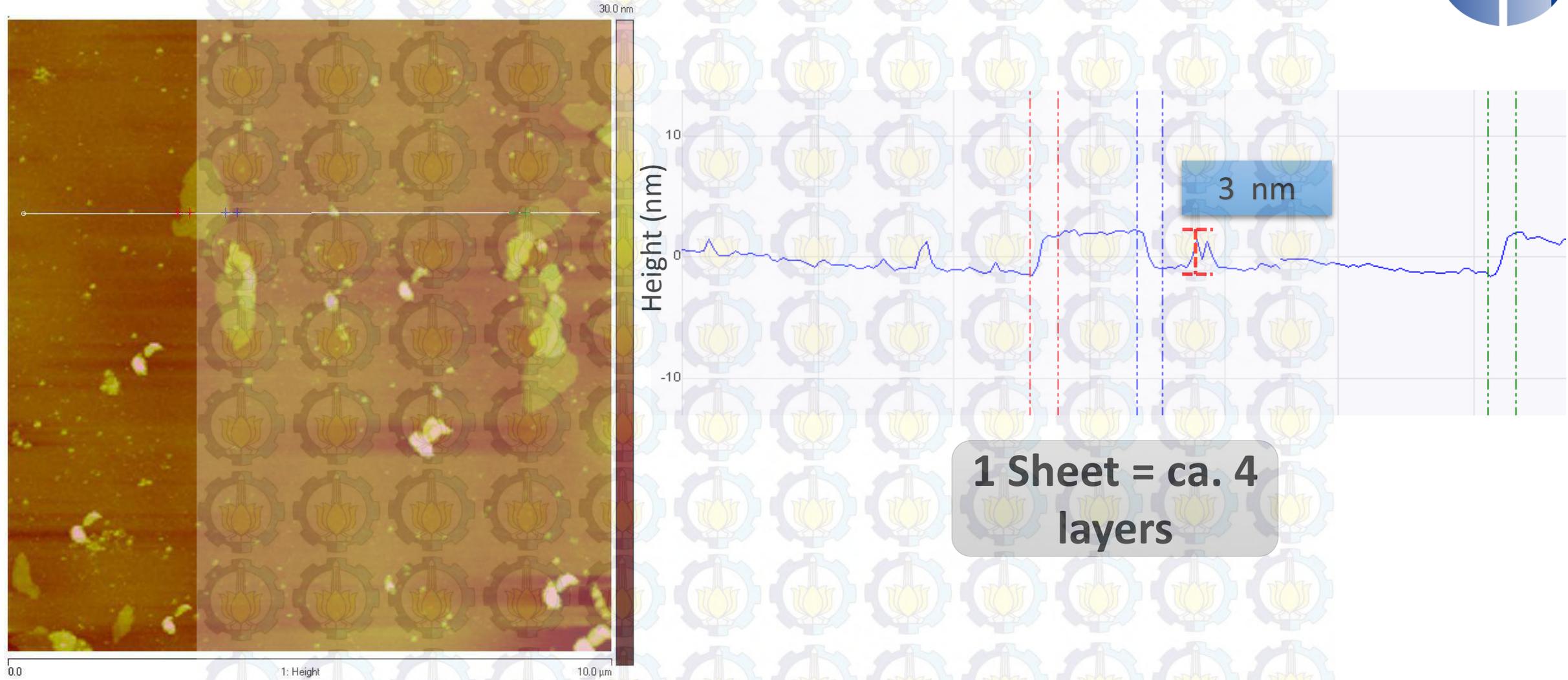
All of images were taken from sample A

Raman Spectroscopy



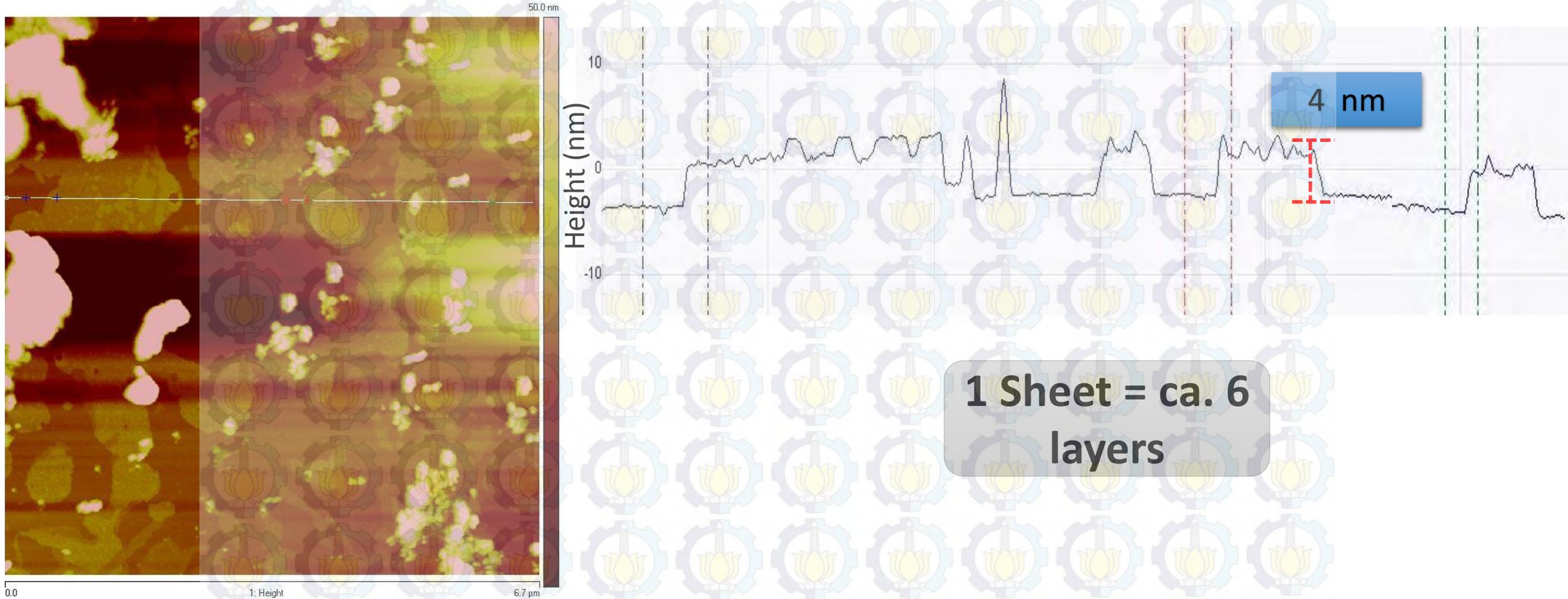
Method	Δk ($A_{1g}-E_{2g}^1$) cm^{-1}	Layer number of MoS_2
A	23.89	3-5 layers
B	24.88	6 layers
C	24.89	6 layers
D	24.88	6 layers

AFM Analysis



The image was taken from sample A

AFM Analysis



The image was taken from sample C



Conclusion

Conclusion



Few-layer MoS_2 nanosheets have been prepared successfully by the lithium intercalation method.



According to DLS and spectroscopic analysis, the MoS_2 nanosheets have different mean flake lengths ranging 85-145 nm with layer number of MoS_2 is *ca.* 3-6 layers

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