

# EXPANSION OF TRANSITION METAL DICALCOGENIDES

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**Doctoral Dissertation**  
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EXPANSION OF TRANSITION METAL DICHALCOGENIDES

**Doctoral Dissertation**

RAZTEZANJE DIHALKOGENIDOV PREHODNIH KOVIN

**Doktorska disertacija**

**Supervisor:** Prof. Dr. Christoph Gadermaier

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*To Grandpa Vladimir*



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Lastly, I gratefully acknowledge the funding of this research by ARRS.



# Abstract

Layered two-dimensional materials have unique physical and chemical properties due to their highly anisotropic nature. These properties are modified and complemented by novel phenomena as their thickness is reduced to one or a few layers. Two-dimensional crystals have strong covalent or ionic bonds in the plane and a weak van der Waals interaction between planes. This allows them to be expanded into low density structures or delaminate them into a few or single-layer nanosheets. Many two-dimensional materials can also intercalate molecules or ions between their layers, thus opening up new functionalities.

Transition metal dichalcogenides form layered crystals of stoichiometry  $\text{MX}_2$  ( $\text{M}$ =transition metal,  $\text{X}$ =S, Se, or Te). The best known compound  $\text{MoS}_2$  is an earth-abundant mineral and has been used for decades as a solid lubricant and as a catalyst for petroleum desulphurization. All transition metal dichalcogenides have been studied in detail for their electronic properties. The methods of exfoliation have made huge progress recently, but are still limited to either ultrasound-mediated exfoliation in liquid phase, which requires lengthy sonication and produces nanoflakes of inferior quality, or chemical exfoliation using the strongest reducing agents – alkali metals – to intercalate the layers. A subsequent reaction with water flooding the interlayer spaces produces hydrogen that pushes them even further apart. However, most transition metal dichalcogenides also react with weaker reducing agents, and this interaction is still largely unexplored.

The purpose of this dissertation is to expand the possible uses of transition metal dichalcogenides by preparing new intercalation compounds and studying the expansion by (using) relatively mild reducing agents. The workhorse compounds of their respective classes are chosen:  $\text{MoS}_2$  as a semiconductor,  $\text{TiS}_2$  as a conductor, and  $\text{TaS}_2$  as a phase change memory material. All three are treated with hydrazine in a reaction which rapidly expands  $\text{TiS}_2$  and  $\text{TaS}_2$ , but is relatively inefficient in expanding  $\text{MoS}_2$ . We circumvent this obstacle by intercalating  $\text{MoS}_2$  with quaternary ammonium salts. This ambient reaction yields expandable layered crystals in many ways similar to expandable graphite.

The expansion process is investigated in detail by characterising the materials at different stages – the raw material, the intercalation compound, the expanded material – using scanning electron microscopy, thermogravimetric analysis, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. Intercalation does not result in any structural changes or chemical modification such as oxide formation. The intercalation compounds can be stored and remain expandable for at least a year. The expansion is studied in detail under a scanning electron microscope, which both provides the electron beam and allows real time observation of the process. The range of expansion depends on the energy and incident angle of the electrons: higher energy results in deeper penetration and in a higher exfoliation range. Crystals irradiated from the side expand significantly faster and more efficiently. This process is self-accelerating since an expanding crystal is being reduced in density and the electrons can propagate deeper. The expanded material is exfoliated to nanosheets in solution and pressed into foil as a proof of principle.



# Povzetek

Unikatne fizikalne in kemijske lastnosti dvodimenzionalnih plastovitih materialov izvirajo iz njihove anizotropne narave, saj ti materiali tvorijo močne-kovalentne vezi zgolj v dveh dimenzijah, medtem ko jih v tretji dimenziji povezujejo šibke Van der Waalove vezi. Posledično lahko medplastne prostore zapolnijo raznolike molekule. Pri tem se plasti razmaknejo, s čimer materiali pridobijo nove lastnosti, v skrajnem primeru pa se kristali razplastijo v nekaj ali celo eno plastne dvodimenzionalne nano delce.

Dihalkogeni prehodnih kovin tvorijo plastovite kristale v stehiometriji  $MX_2$  ( $M$ =prehodna kovina,  $X$ =S, Se, Ta). Njihov najbolj raziskan predstavnik,  $MoS_2$  se že desetletja uporablja kot trd lubrikant in kot katalizator pri desulfurizaciji nafte. Mnogi predstavniki te skupine so bili preiskovani zaradi njihovih zanimivih elektronskih lastnosti.

Metode razplastitve so v zadnjem času precej napredovale, a so večinoma še vedno osnovane na dolgotrajnem ultrazvočnem dispergiranju v tekočem mediju. Alternativno se uporablja kemično razslojevanje osnovano na interkalaciji alkalijskih kovin v dihalkogenide prehodnih kovin. Produkt te reakcije so reaktivne spojine, ki v stiku z vodo med plastmi tvorijo vodik in na ta način razpadejo na tanke sloje. Mnogo dihalkogenidov reagira tudi s šibkejšimi reducenti in ta reakcija je mnogo manj raziskana.

Namen te dizertacije je raziskati nove metode interkalacije in raztezanja nekaterih najpomembnejših dihalkogenidov prehodnih kovin z uporabo šibkejših reducentov, s katerimi je mogoče rokovati v zračni atmosferi. V ta namen smo se posvetili  $MoS_2$ , kot primeru polprevodnika, prevodniku  $TiS_2$  in superprevodniku  $TaS_2$ . Vse tri snovi smo tretirali s hidrazinom in ugotovili, da se  $TiS_2$  in  $TaS_2$  v vodni raztopini hidrazina hitro razširita.  $MoS_2$  je mnogo manj reaktiven, zato smo ga poskusili interkalirati z organskimi molekulami. Produkt te reakcije je interkaliran  $MoS_2$ , ki ga lahko smatramo kot analog interkaliranemu grafitu, saj imata več podobnih lastnosti. Obe snovi sta dolgotrajno stabilni v zraku a ju lahko razširimo s hitrim dvigom temperature. Zabeležili smo tudi razširjanje interkaliranega plastovitega kristala pod elektronskim snopom vrstičnega elektronskega mikroskopa. Ta proces smo posebej preučili, saj gre za popolnoma novo metodo razširjanja plastovitih kristalov. Ugotovili smo, da je razširjanje močno odvisno od pospeševalne napetosti in gostote elektronskega toka, pri čemer napetost igra pomembnejšo vlogo, saj je od nje odvisna udorna globina. Zgolj pri dovolj visokih napetostih elektroni prodrejo dovolj globoko, da se razpre celoten kristal. V nasprotnem primeru se razširi zgolj površinska plast, ki pred obsevanjem ščiti ostanek kristala in reakcija se ustavi. Opazili smo tudi, da je proces razširjanja pod elektronskim snopom samo-pospešujoč, saj se z razširjanjem kristala elektronskemu snopu izpostavlja vedno večji presek, kar pospešuje reakcijo. Razširjene kristale smo oblikovali v folijo in jih v tekoči fazi dispergirali do nanodelcev. Z modifikacijo metode nanosa nanodelcev iz stika dveh tekočin smo jih nanесли na substrate v obliki neprekinjenih atomsko tankih filmov.



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# Abbreviations

|                   |     |                                  |
|-------------------|-----|----------------------------------|
| eMoS <sub>2</sub> | ... | expanded MoS <sub>2</sub>        |
| iMoS <sub>2</sub> | ... | intercalated MoS <sub>2</sub>    |
| VdW               | ... | Van der Waals                    |
| ELM               | ... | expanded layered materials       |
| GO                | ... | graphite oxide                   |
| EG                | ... | expanded graphite                |
| BET               | ... | Brunauer, Emmett, Teller         |
| L-B               | ... | Langmuir-Blodgett                |
| SEM               | ... | scanning electron microscope/y   |
| XRD               | ... | X-ray diffraction                |
| XPS               | ... | X-ray photoelectron spectroscopy |
| CDW               | ... | charge density wave              |
| MS                | ... | mass spectroscopy                |
| QA                | ... | quaternary ammonium              |
| TBAI              | ... | tetrabutylammonium Iodide        |
| CTAB              | ... | cetrimonium bromide              |
| TBAOH             | ... | tetrabutylammonium hydroxide     |
| TG                | ... | Thermogravimetric                |
| TGA               | ... | thermogravimetric analysis       |
| CVD               | ... | chemical vapour deposition       |
| CB                | ... | conduction band                  |
| VB                | ... | Valence band                     |



# Symbols

$\tau$  ... mean crystalline domain size

$K$  ... dimensionless shape factor

$\lambda$  ... wavelength

$\beta$  ... FWHM linewidth

$\varphi$  ... Bragg angle



# Chapter 1

## Introduction

### 1.1 Background

#### 1.1.1 Layered materials

Layered materials have been used since ancient times. The group comprises members as common as clay or graphite extending to materials synthesised only recently in the lab.

The unique physical and chemical properties of these materials stem from their highly anisotropic nature. The atoms in these compounds form a crystalline lattice strongly bound in one plane only and by weak Van der Waals (VdW) interactions between the planes. This fact makes it possible to expand the crystals to form low density structures or to delaminate them completely to single-layer nanosheets by a process called exfoliation, and is responsible for excellent lubricating properties of some of the materials [1]. Some layered materials can be reduced, oxidised or linked to molecules either covalently or by VdW attractions, and the space between the layers can often be occupied by molecules or ions – in a process called intercalation. The layers also interact with the surrounding depending on the pH or ionic strength of the medium. For example, these processes make it possible for clay soils to hold nutrients and water, critically influencing agriculture [2, 3].

#### 1.1.2 Expansion of layered materials

A few layered materials, most notably graphite and vermiculite, can be expanded by a rapid rise of interplanar pressure. In order for expansion to proceed, molecules must be present in the interplanar spaces and must be transformed to gas upon the change of some external condition. This is most often achieved by rapid heating either in a furnace or by micro wave irradiation [4]. However, the reaction can also start due to introduction of a suitable reactant [5]. There are a few common principles that hold independently of the material used. Gas formation should be as rapid as possible. This is due to the fact that formed gas molecules will find a way out of the interplanar spaces given enough time. Expansion is only possible when gas forms faster than it diffuses out of the crystal. The greater the difference between the time scales of these two effects (Figure 1.1), the more the crystal will expand [6]. It follows that the intercalated crystals should be as big laterally as possible [7], since the lateral size of the crystal determines the path that the gas molecules must travel to reach the edge of the crystals. The longer the path, the more pressure can be built up before it is released at the plane edge, hence larger crystals tend to expand more than smaller ones [8, 9]. Since the expansion can only take place when the pressure between the planes is greater than the outside pressure, it follows that expansion in vacuum should be more efficient than in atmosphere. This effect presented in Figure 1.2: Expansion of oxygen intercalated graphite in atmosphere and vacuum. Derived from [10]. has also been confirmed by experiments [10]. After the expansion the surface area is increased due to pore formation and exfoliation but the extent of this effect varies considerably with material and method and never reaches the limit value for fully exfoliated material. In order to achieve complete delamination every interlayer space should deform to a bubble during gas formation. However, this is unachievable, since all crystals carry defects, imperfections and are torn to some degree during expansion due to strains. As a result a few layers aggregate to form a barrier impenetrable to gas, resulting in pockets that form the characteristic accordion structure common to all expanded layered materials (ELMs).

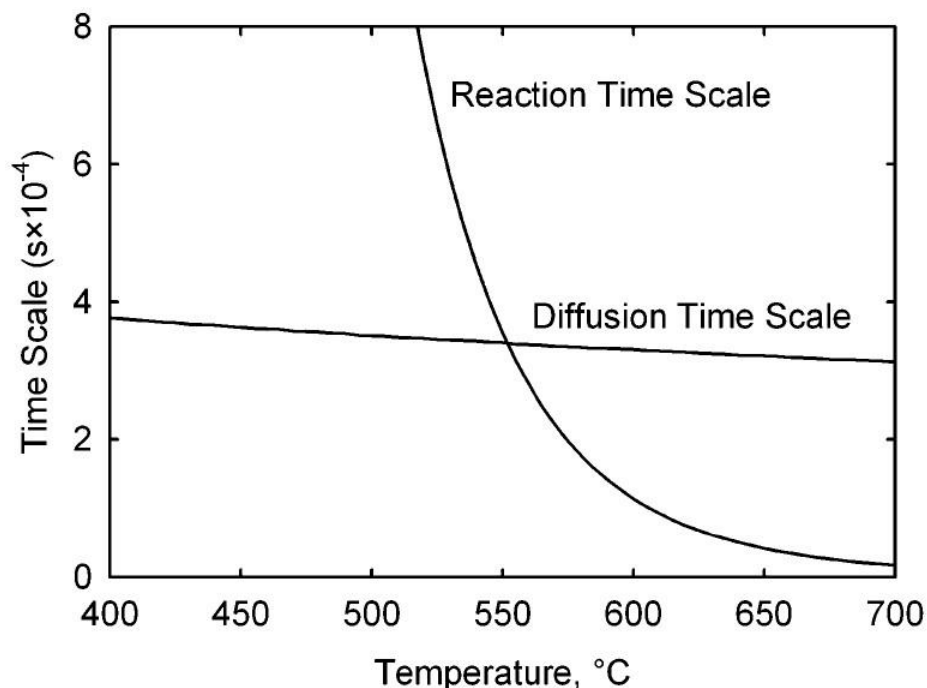


Figure 1.1: EG kinetics. Comparison of the diffusion and reaction time scale in expandable graphite. Adopted from [6]

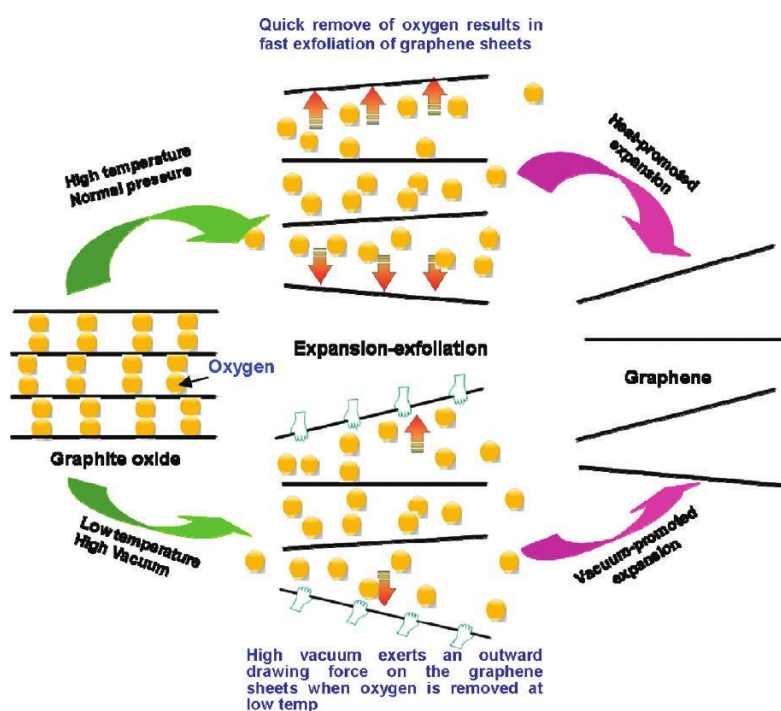


Figure 1.2: Expansion of oxygen intercalated graphite in atmosphere and vacuum. Derived from [10].

Clays are a type of 2D materials composed of parallel crystalline sheets bound by non-covalent interactions in out of plane direction. A few members of this family can be expanded by chemical treatment. Depending on composition the layers can contain negative charge balanced by interlayer cations and possibly water. Vermiculite is a clay mineral

having layers composed of two tetrahedral sheets encapsulating one octahedral sheet. The layers are heavily charged and can be significantly hydrated (Figure 1.3). Vermiculite (Figure 1.4) can be expanded by rapid heating due to this large amount of intercalated water, by simply inserting the sample in a furnace. A more efficient method [5] involves exchange of some of the water with hydrogen peroxide molecules at a low temperature followed by heating to a relatively low temperature of 100 °C. During this reaction the hydrogen peroxide molecules decompose rapidly and inflate the crystal by a factor of hundreds perpendicularly to the crystal planes (Figure 1.5).

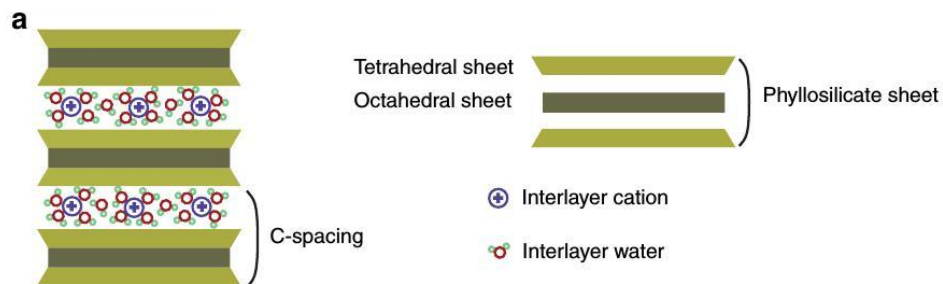


Figure 1.3: Molecular model of vermiculite. The interplanar space is occupied by solvated cations. Adopted from [131].



Figure 1.4: Expanded vermiculite crystals. Adopted from [131].

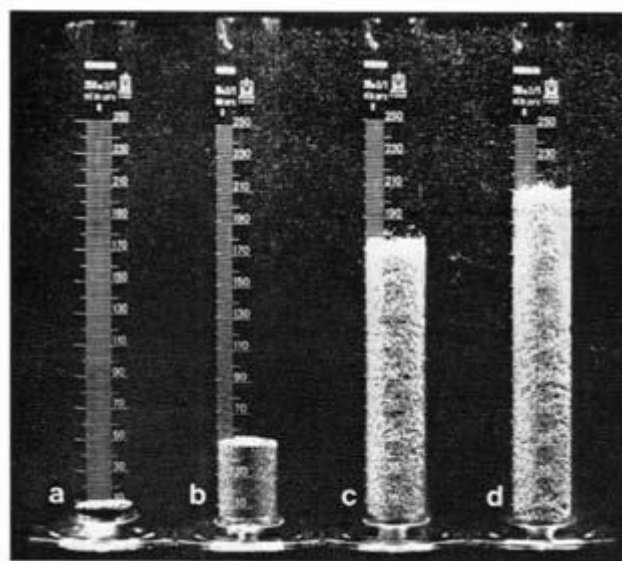


Figure 1.5: A comparison of volumes of expanded vermiculites. Vermiculite before treatment (a), expanded at 800 °C (b), expanded by  $\text{H}_2\text{O}_2$  at room temperature (c) and at low temperature (4 °C) (d) [5].

Graphite is a crystalline form of carbon composed of weakly linked sheets of two dimensional hexagonal lattice. Graphite can be oxidised by treatment with oxidants and strong acids to form a material known as graphite oxide (GO). The carbon lattice is partially preserved in the process but the oxygen-containing groups push the layers further apart from 0.34 nm to 0.71 nm (Figure 1.6) Although graphite can be intercalated by reduction with alkali metals as well [11], GO is used in the vast majority of applications due to the relative ease of synthesis. Upon rapid heating [6] or exposure to microwave radiation [4] these covalently linked groups transform to gas molecules (Figure 1.7) [6].

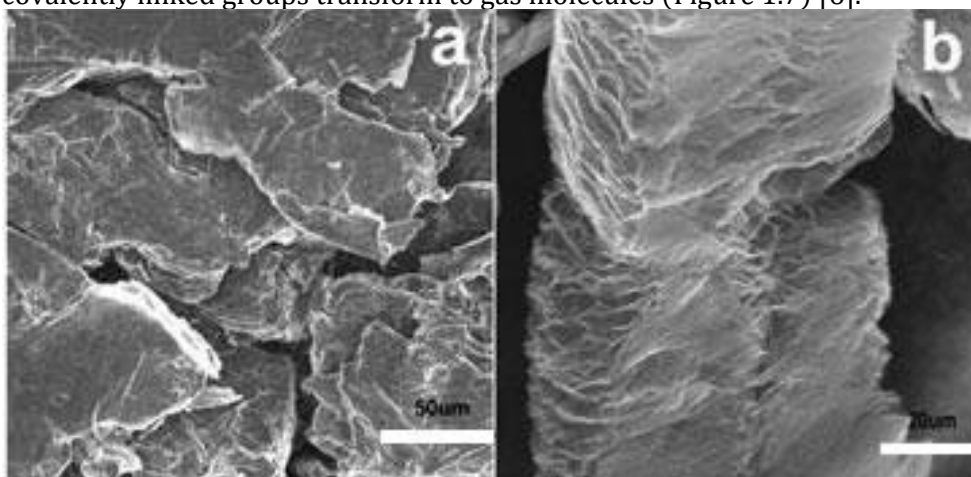


Figure 1.6: SEM micrograph of intercalated (a) and expanded graphite (b). Scale bars: 50  $\mu\text{m}$  (left) and 20  $\mu\text{m}$  (right). Adopted from [19].

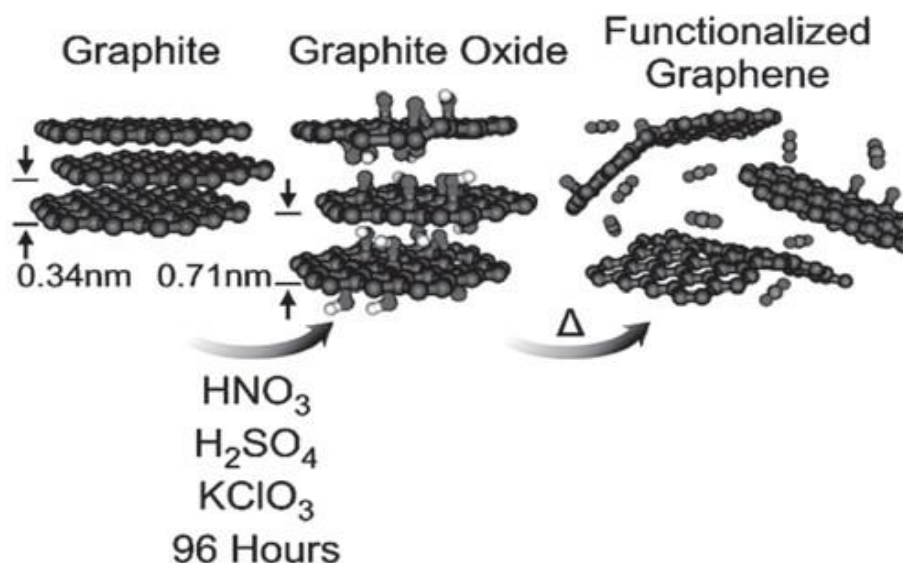


Figure 1.7: Graphite intercalation and expansion model. In the first step some of the carbon sites are oxidised. After rapid heating a part of those oxygen-containing groups exit the crystal as  $\text{CO}_2$ . [6]

The structure of expanded graphite has been investigated in some detail. The studies show that EG forms a network of bubbles with walls about 8 monolayers thick, however the extent of layer separation varies greatly between the methods as indicated by BET (Brunauer–Emmett–Teller) surface area measurements [6].

The chemical composition and crystal structure of GO change during oxidation and expansion. The C/O molar ratio of 2.2 before the expansion changes to 8.9 [12] afterwards, indicating expulsion of oxygen-containing molecules. The crystal ordering is restored to some degree, a fact that is reflected in the recovery of electric conductivity.

In general, expanded layered materials (ELMs) inherit some of the properties of their respective parent compounds whilst drastically increasing their volume and surface area. This makes them interesting for a range of applications. Clay-based ELMs like vermiculite are non-combustible and do not expel toxic gases on heating, which makes them suitable for fire barriers. Another use of ELMs due to their porosity and inertness is in agriculture. Vermiculite for example is widely used as a soil additive or a soilless medium. This is due to the fact that its pores can hold a large amount of water and nutrients but also allow the air to penetrate into the root zone. ELMs are often further modified or used as components in different polymers or resins. Mixing vermiculite into polymers can drastically decrease their flammability [13] and EG polymer composites can be made conductive and have been known to exhibit mechanical properties superior to pure polymers [14, 15]. Inclusion of ELMs into composite materials can also improve gas barrier properties [16]. However, gas expansion can also be a pretreatment step to complete exfoliation to mono layers. EG has been successfully exfoliated to graphene [4,12,17–19] and expanded  $\text{MoS}_2$  [20] has been shown to be a suitable precursor for exfoliation to single layers with a higher aspect ratio compared to untreated  $\text{MoS}_2$ . Gas expansion is also an important step in complete exfoliation of vermiculite [21].

### 1.1.3 Physics and chemistry of transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) are a group of layered materials defined by the formula  $\text{MX}_2$  (M=transition metal, X=chalcogen). The most studied member of the group  $\text{MoS}_2$  is also a mineral (Figure 1.8) widely used as a solid lubricant. Since other members of the group are not found in nature in significant quantities, they are not used in bulk due to their much higher costs. Nevertheless, many have found interesting uses in both the basic science and applications. Depending on a transition metal and a chalcogen in question, compounds can be metals, semimetals, or semiconductors. Additionally, many TMDs also

show temperature-dependent ordering phenomena, such as charge density waves (CDW) or superconductivity. Their properties can be notably changed by inclusion of atoms or molecules in the VdW gaps, a process called intercalation or by exfoliation to few or even single layers. Finally, hybrid compounds can be synthesised with mixed chalcogen or transition metals, expanding the array of possible properties even further.

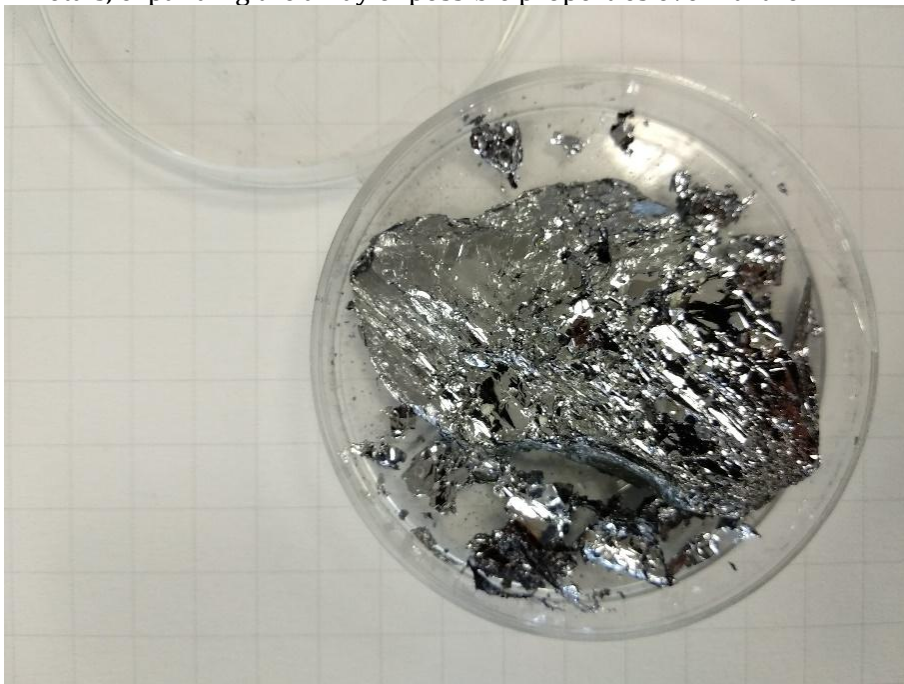


Figure 1.8: Mineral  $\text{MoS}_2$  –Molybdenite.

Synthesis of bulk powder is done from the elements in vacuumed ampules at high temperatures [22, 23]. The ampules can then be returned to a temperature gradient (zone) furnace and left to grow macroscopic single crystals by vapour phase transfer reaction. Often a transport-inducing agent, such as iodine or bromine, is included to facilitate the reaction. However, this can lead to inclusion of these atoms in the final product. After weeks the ampules are either quenched or left to be cooled and symmetric single crystals are harvested.

It is also possible to grow few layers of the compounds by a variety of methods. Chemical vapour deposition (CVD) is most commonly used method [24, 25], and with current methods precise control of layer thickness and crystal orientation on a wafer scale [26] is achievable [27, 28]. Molecular beam epitaxy has been used more recently [29–32].

All of the TMDs form crystal structures such that the metal atom forms bonds with 6 neighboring chalcogen atoms. However, there are two possible configurations: trigonal prismatic and octahedral (Figure 1.9). The  $c$  lattice parameter (perpendicular to the VdW gaps) is usually close to  $6\text{\AA}$ , whereas  $a$  and  $b$  (both in plane) fall in the range of  $3\text{--}4\text{\AA}$ .

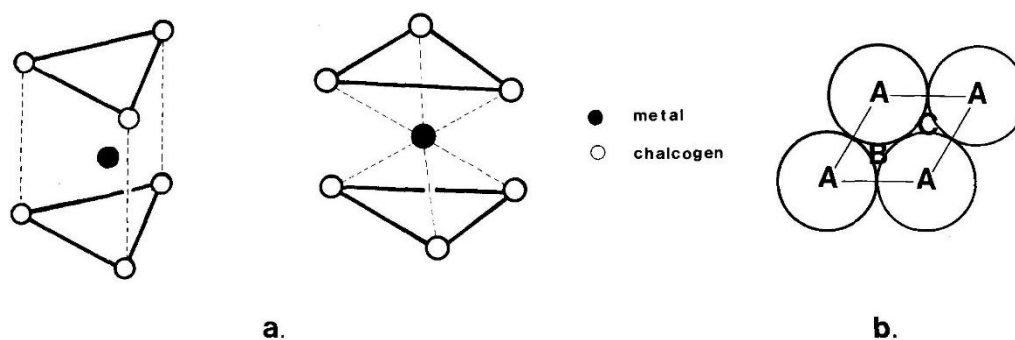


Figure 1.9: Possible configuration of atoms in TMDs. Trigonal prismatic (left) and octahedral (right) configuration of atoms in TMDs (a). Possible stacking of the planes (b). Edited from [35].

For the layer stacking there are several possibilities as presented in Figure 1.10. The exact configuration depends not only on the TMD in question, but also on the growth and annealing conditions, as well as on the chemical environment. Group 6 compounds, such as  $\text{MoS}_2$ , prefer the trigonal prismatic coordination. Stacking sequences are 2H for a material of geological origin, and 2H or 3R for a synthetic material [33]. Exfoliation via Li intercalation results in a metastable octahedral 1T polytype. On the other hand, for group 4 compounds like  $\text{TiS}_2$ , the octahedral 1T phase is the most stable one. Group 5 compounds exhibit several polytypes in both octahedral and trigonal prismatic coordination, and develop charge density waves (CDW) accompanied by a periodic lattice distortion [34].

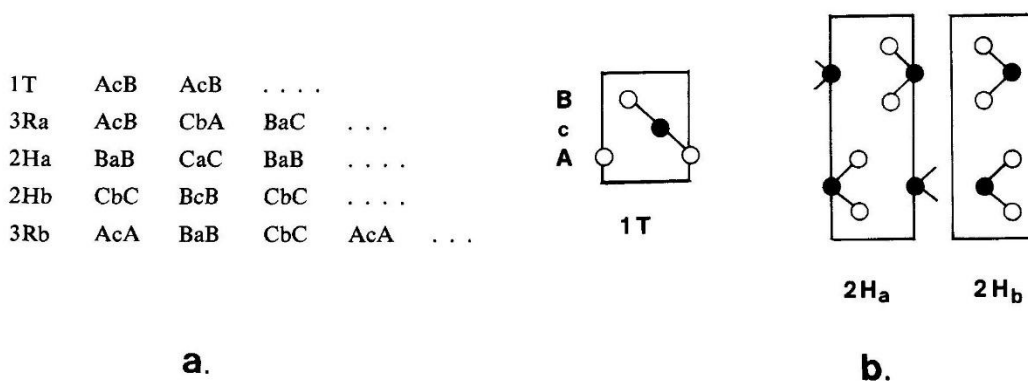


Figure 1.10: Different phases of TMDs depending on layer stacking (a) and representation of chalcogen and metal atom positions for 1T and 2H phases (b). Edited from [35].

The electronic structure of TMDs depends strongly on the choice of transition metal, as illustrated by the electronic density of states depicted in Figure 1.11 for several compounds [35]. With increasing metal group number the  $d$  orbitals are getting progressively filled. However, electronic structures vary considerably within the group, as well as with doping/intercalation.

Lattice vibrations probed by Raman spectroscopy are an important signal in the characterisation of TMDs. Due to the anisotropic nature of layered materials the intralayer modes can be significantly stronger than the interlayer modes. In  $\text{MoS}_2$  the relative spacing between the  $A_{1g}$  and  $E_{12g}$  peaks is a clear indicator of the layer number [36], since it changes from  $25 \text{ cm}^{-1}$  to  $18 \text{ cm}^{-1}$  when crystals are thinned from bulk to monolayer. For the group 4 TMDC  $\text{TiS}_2$ , on the other hand, a larger distance between the dominant Raman peaks has been predicted for the monolayer compared to the bulk [37], while for the group 5 TMDC  $\text{TaS}_2$  no appreciable shift has been observed [38].

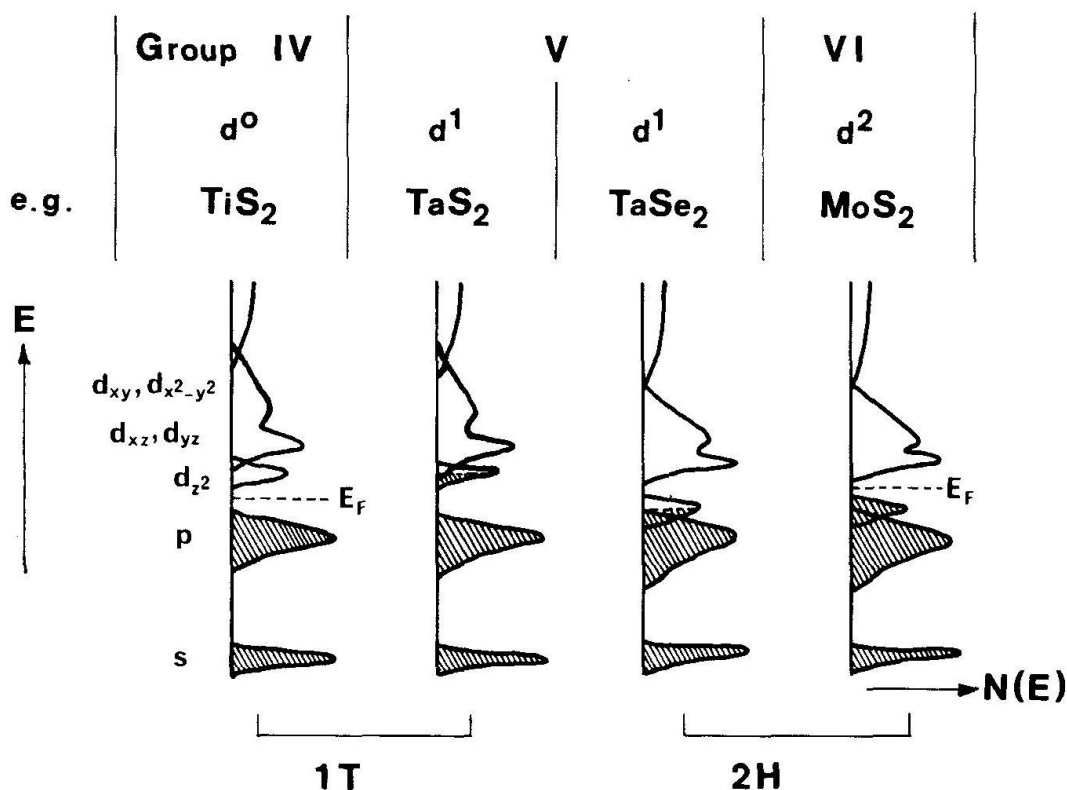


Figure 1.11: Electronic density of states of some common TMDs. Edited from [35].

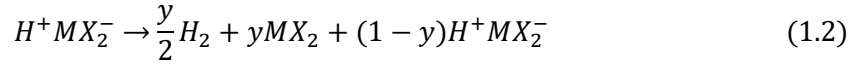
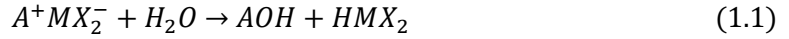
The ability of TMDs to act as host for a variety of molecules has already been observed in the early stages of TMD research [39]. Intercalation can be achieved by an electrochemical reaction at a cathode [40, 41]. In this reaction the TMDs are reduced and the VdW gap is occupied by charge balancing cations [40]. The process is reversible and neutral TMDs are obtained upon oxidation of the intercalants.

Alternatively, the TMDs can be intercalated by various Lewis bases – molecules containing filled nonbonding orbitals whose electron pairs can be donated to other molecules, called Lewis acids. Upon intercalation, electrons are transferred from the Lewis base to an unoccupied metal  $d$  band of the TMDC. The Coulombic attraction between the intercalant cation and the negatively charged layer is the main driving force for this reaction. For group 5 compounds, the conduction band is half filled and conductivity is given predominantly by holes. Electron transfer decreases the number of holes, and hence the conductivity. In group 4 and group 6 compounds, on the other hand, the electrons are transferred to an empty band and increase the conductivity, in particular for the semiconducting 2H compounds. In group 6 compounds, the donor electrons need to go into  $d$  orbitals of relatively high energies allowing intercalation of only strong donors, such as alkali metals [35, 42].

Both  $\text{TaS}_2$  and  $\text{TiS}_2$  can be intercalated by hydrazine [43] and various other amines [44], and this process can be utilized to ease exfoliation to single layers [45].

Many of intercalated compounds co-intercalate water molecules that solvate the intercalated cations [46], and intercalated ions can be exchanged for others even in aqueous medium [47, 48].

TMDs can be intercalated with the strongest of the Lewis bases, ie. with the alkali metals. In these reactions electrons are transferred to the TMD lattice, and the cations balance the charge by occupying the interplanar space. Such compounds are quite reactive and will exfoliate to single or few layered nanosheets when immersed in water [49], as the reactions denoted in equations (1.1) and (1.2) proceed. The first is a proton exchange reaction. The second is neutralisation of part of the charge by evolution of hydrogen gas that helps to separate the layers which results in substoichiometrically charged nanolayers.



The process can be made more efficiently by sonication [39] and by pretreatment with hydrazine [20]. Alkali metal intercalation can also induce structural rearrangement of the lattice. In MoS<sub>2</sub> alkali intercalation is accompanied by a 2H to 1T phase transition [50] as well as with retention of some charge [51]. However, both of these effects can be reversed by annealing. Lastly dispersed TMD nanolayers can even be precipitated by addition of cations or molecules to form inclusion compounds [52].

TMDs can be exfoliated without a chemical treatment as well. The simplest way is mechanical exfoliation [53], a variation of the scotch tape method famously used to exfoliate graphene [54]. However, although the method was used to prepare samples for most of the basic research of two-dimensional TMDs, it is clearly not scalable. In order to mass-produce 2D TMDs, liquid exfoliation methods were developed [55]. Choosing a proper solvent can be decided by matching the Hansen parameters [56]. This can easily be achieved by mixing different solvents [57, 58]. Due to a significant interest in liquid exfoliation research recently some methods have been developed to probe nanoflakes properties in solution [59].

#### 1.1.4 Electronic properties of TMDs

The band structure of semiconducting group 6 TMDs such as MoS<sub>2</sub> shows two important valence band (VB) maxima and two conduction band (CB) minima [62, 63]. Strong excitonic resonances across the direct gap at the K point dominate the optical absorption spectra with the two main peaks A and B in the range between 1.6 and 2.2 eV. The VB is split by spin-orbit coupling, resulting in the characteristic double peak with an energy difference ranging from 0.15 to 0.4 eV.

Monolayers show fluorescence of quantum yields (QY) in the 1% range, which decreases rapidly when shifting to a larger number of layers  $N$ . The band gap decreases for increasing  $N$ , and calculations suggest that such decrease is stronger for the indirect gap than for the direct one. As a consequence, monolayers are direct gap semiconductors while all  $N > 1$  are indirect gap semiconductors, which explains the  $N$ -dependent fluorescence QY.

The spectral position of the A resonance shifts slightly as a function of  $N$ . This has been used to develop a metric of the flake thickness [64], which allows determining the (average) thickness of a film or an ensemble of flakes in a dispersion by a simple measurement of the extinction spectrum rather than a much more time-consuming statistical analysis of an AFM image. Additionally, the extinction spectrum also depends on the lateral size  $L$  of flakes or crystal domains, which can be estimated by comparing the relative intensities using two different wavelengths for excitation. The larger the samples, the stronger is the extinction in the red part of the spectrum due to the stronger scattering contributions. Flakes from liquid phase exfoliation generally show larger  $L$  for larger  $N$  and can be separated via fractionated centrifugation.

MoS<sub>2</sub> and WS<sub>2</sub> have been explored for typical semiconductor applications such as transistors and solar cells, given that their bandgap is fairly close to the theoretical optimum for photovoltaic efficiency. Their use in transistors has been mostly precluded by poor mobility and low on/off ratios. Both shortcomings have been overcome by applying gate electrodes on both sides of the flake (monolayer MoS<sub>2</sub> in the case of the seminal publication) [65]. Subsequently, integration has been demonstrated by fabricating several interconnected transistors on a single flake [66]. Transistors have also been shown to work as efficient photodetectors [67], chemical sensors [68] and strain sensors [69]. Their efficiency in photovoltaic mode has been greatly enhanced by strategies to facilitate charge separation, such as vertical [62] or lateral heterostructures [70] or engineered p-n junctions via double gating [71]. High on/off ratios have also been achieved for thicker flakes or networks from liquid phase exfoliation via gating with an ionic liquid [72].

TaS<sub>2</sub> is in the centre of research attention because it has the richest phase diagram of all TMDs [73]. It exhibits a series of charge density wave (CDW) phases, starting from an incommensurate CDW (meaning that the periodicity of the electronic ordering and its

accompanying periodic lattice distortion is not an integer multiple of the crystal lattice constant) between 543 and 352 K, nearly commensurate from 352 to 183 K (for progressive cooling from 221 to 355 K upon heating), and finally a commensurate CDW below 183 K. The nearly commensurate CDW is formed by a periodic superstructure of commensurate and non-commensurate domains. The commensurate phase is characterised by groups of 13 Ta atoms in a David-star arrangement where the twelve outer atoms are strongly displaced towards the central atom of the star. While a classic phase diagram is obtained through slow, adiabatic changes of the relevant parameters (most prominently temperature), TaS<sub>2</sub> also exhibits an additional “hidden” phase that is accessible only via non-adiabatic pathways, induced via illumination with a short laser pulse [74] or via the application of a short current pulse [75]. The change in resistivity resulting from the transition to this hidden phase bears the potential for the use in a fast memristor device.

TiS<sub>2</sub> is the lightest of all TMDs and is therefore researched as battery electrode material due to its ability to intercalate Li and Na [76, 77] ions. Another interesting property is thermoelectricity of TiS<sub>2</sub> intercalated with organic molecules [78]. TiS<sub>2</sub> has also been used as a hole-transport material for perovskite solar cells [79].

### 1.1.5 Exfoliation of layered materials

Layered materials like graphene and transition metal dichalcogenides acquire new exciting properties when thinned to single atomic layers.

Exfoliation of layered materials is the process of splitting bulk into single or few-layer nanoparticles. Although layered crystals have been known for a long time, they have come in the spotlight with mechanical cleaving of graphene by the “scotch-tape method” and characterization of its electric properties [54]. This approach, however, is extremely inefficient and this has led to development of other methods. Layered materials are held together by weak interlayer Van der Waals forces that can be broken in various ways. These can be either chemical or mechanic. Intercalation by lithium compounds [20] is mainly used to produce single-layer flakes of TMDs whereas graphite is often oxidised to graphene oxide (GO) by introducing hydrophilic groups to increase the interlayer distance and to make the final product soluble in aqueous dispersions. Alternatively layered materials can be exfoliated mechanically by milling [80] or sonication in appropriate solvents [56]. Exfoliation efficiency very strongly depends on a suitable choice of a solvent. To this end the Hansen solubility parameters theory has been applied early on. Careful tuning of solubility parameters can be achieved by mixing two solvents [57, 58, 81]. Alternatively, layered materials can be exfoliated and dispersed by mechanical agitation in surfactant or polymer solutions [82–84]. High concentration dispersions have been achieved by a scalable approach applying mechanical agitation by shear mixers (blenders) [85]. Amongst less frequently used methods is intercalation by supercritical CO<sub>2</sub> and subsequent rapid expansion [86, 87], and there are reports of exfoliation in bio-polymers [88] and even in pure water [89].

### 1.1.6 Deposition from dispersions of exfoliated layered materials

Bottom-up solution-based technology is fast, cheap and can be scaled up easily. Bulk layered materials are first treated to produce 2D nanoflakes [55]. These can then be reassembled to thin films or nanostructures [90–105] leading to new applications. Efficient exfoliation leads to single or few-layer nanoflakes. To utilize their properties, however, they must be successfully deposited on a substrate. The deposition process is especially difficult for 2D nanoparticles since they are prone to restacking and aggregation.

If we want to harness the potential of solution dispersed nanolayers, we need suitable deposition methods. The methods should be fast and efficient (with little discarded material) and restacking of nanolayers should be limited or absent. Liquid-air methods like Langmuir-Blodgett deposition come close to meeting these criteria but deposition from liquid-liquid interface goes a step further by offering better stability and deposition speed. To this date various methods have been developed, each with its advantages and disadvantages. Here we note some of them and try to justify the method we used in this project.

*Spray coating*

With this method nanoparticle dispersion is sprayed using a paint gun. This method has been used to fabricate transparent graphene films [106,107]. Although this method is easy to implement, scalable and has successfully been used to deposit nanomaterials [106,107], we have found it impractical in our laboratory setting, since the substrates used are usually small and a homogeneous deposition requires a fair distance from the nozzle to the substrate. This necessarily leads to a huge loss of material. We also note that complete evaporation of the dispersion medium (which might be toxic) is a prerequisite for successful deposition, and this leads to further waste.

#### *Drop casting*

In this technique a drop of solution is cast upon a substrate. When the solution evaporates, a thin film of nanoparticles is left behind, but there are problems with uniformity and thickness. These particles are prone to aggregation during the drying, and the coffee ring effect [108] is commonly observed. The method is therefore unsuitable for a uniform thin film production.

#### *Spin coating*

It is a widely used method since it circumvents some of the problems appeared in drop casting. During or immediately after the deposition, the substrate is spinning. The centrifugal force pulls the liquid off the substrate, thus producing uniform coating. Uniform coatings can be produced this way, but a large amount of the material is discarded, therefore the method is poorly scalable.

#### *Langmuir-Blodgett*

Langmuir-Blodgett (L-B) is especially useful for deposition of nanoparticle monolayers. The physical basis is the fact that amphiphilic molecules (or nanoparticles) do not dissolve in the subphase (commonly water) but they cluster at the surface. In the low concentration regime they behave like a 2D gas. When their concentration increases, they start to interact behaving like a 2D liquid and finally like a solid. In a practical experiment this surface pressure is regulated with a moving barrier. When the desired concentration is reached, the substrate is slowly lifted through the liquid-air interface. The interfacial pressure forces the particles to move upwards and finally adhere to the substrate. The method is useful for depositing thin layers of nanoparticles. It has been applied in systems like GO [93, 95, 102, 105] and MoS<sub>2</sub> [105]. On the downside the film formation is time consuming since material is usually deposited on the water surface by introducing a volatile immiscible suspension that must evaporate before deposition can begin. One of the downsides is that the process cannot be made continuous. Another drawback is the instability of films in the liquid-air interface, which can be irreversibly destroyed by agitation. Some of the problems can be overcome by deposition from a liquid-liquid interface

#### *Liquid-liquid interface method*

Nanoparticles can act as surfactants when introduced to an interface between two immiscible liquids. This process is in fact similar to localisation of the particles at the liquid-air interface used in L-B but with certain advantages. Since the particles are in contact with the liquid on both sides of the interface, they are resistant to folding and stacking even when the interface is agitated. The material can be brought to the interface more rapidly by agitating the two liquids (this drastically increases the surface area of the interface). Since the nanoparticle films resist folding, they climb the receptacle surface after agitation [103]. A similar effect has been observed for conductive polymer nanoparticles [110] and in MoS<sub>2</sub> nanolayers [111]. Another advantage of this approach is the ease of deposition, since the film climbs up the substrate in the same way as it climbs the receptacle walls. A film can therefore be deposited without the need of L-B equipment. Interfacial pressure is raised by addition of material to the interface. Since the film is stable, excess material does not lead to restacking but to reversible structures like bubbles and folds that reform a homogeneous film when enough material is removed by deposition. For these reasons, we chose this method to deposit the nanomaterials synthesised in this work, including some extensions discussed in the results section.

### **1.1.7 Scanning electron microscopy**

Scanning electron microscopy is a type of microscopy where an electron beam focused by a system of electromagnetic lenses is driven across the surface of the sample in a raster pattern. The electron beam originates at the cathode, In order to prevent plasma generation,

filament burnout or contamination, the whole system must be pumped to high vacuum (below  $10^{-5}$  mbar) by a series of pumps.

At specific points in the raster, the detectors collect the signal (of electrons coming from the sample) and the signal strength is recorded as image brightness. The detected electrons result from interaction of the scanning beam and the samples, and can be separated into different categories. *Secondary electrons* – resulting from ionisation of the very first nanometers of the sample – carry the information of the sample surface. *Backscattered electrons* on the other hand result from elastic scattering of the scanning beam microns deep inside the samples. The interaction volume (Figure 1.12Error! Reference source not found.) is a representation of these and other processes governing the trajectories of the electrons in the sample. More detailed information on electron trajectories can be obtained by Monte Carlo simulations (Figure 1.13). As a rule of thumb, however, interaction volumes increase with increasing accelerating voltage and decreasing Z-number and sample density (Figure 1.12Error! Reference source not found.).

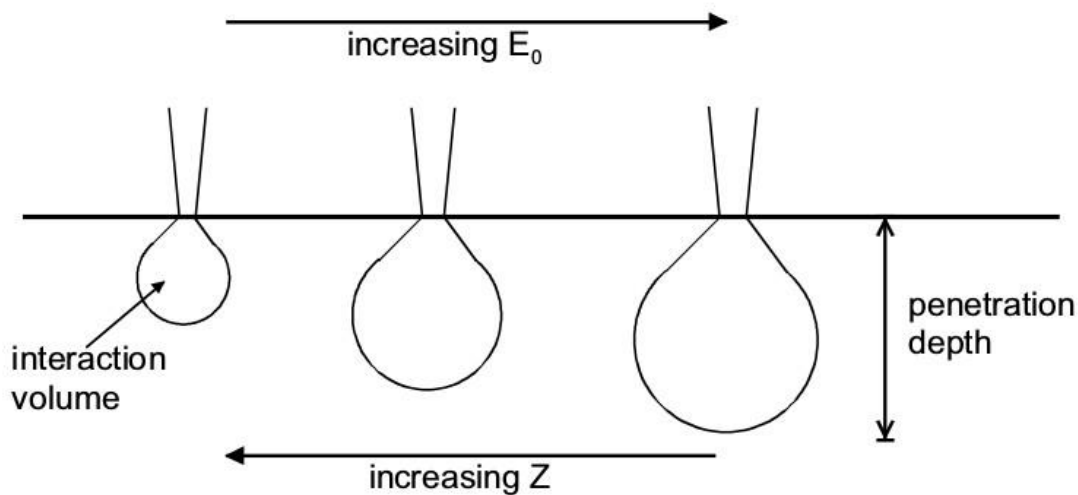


Figure 1.12: Change of the interaction volume in relation to acceleration voltage ( $E_0$ ) and atomic number ( $Z$ ). Adopted from [130].

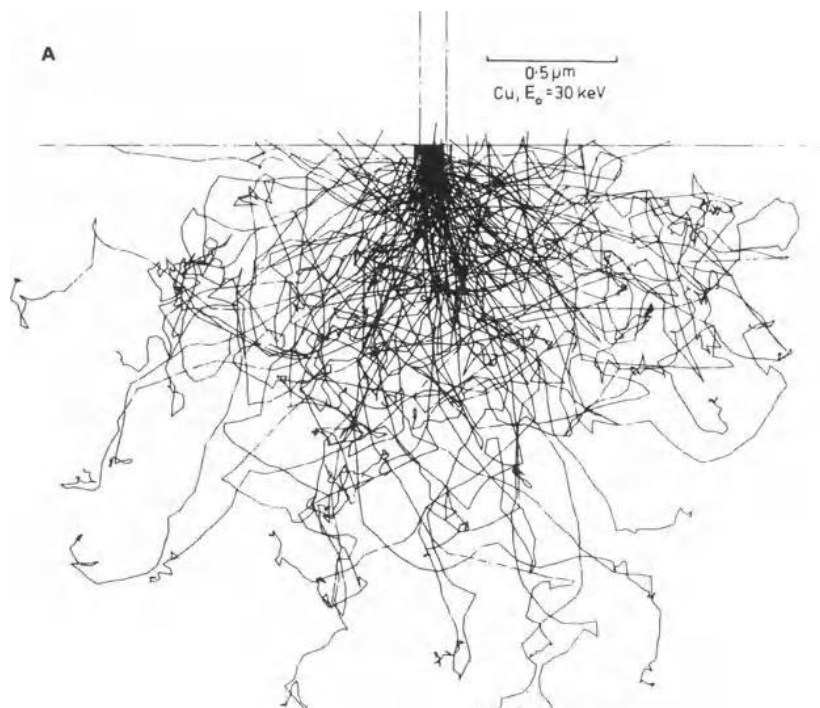


Figure 1.13: Electron trajectories calculated by a Monte Carlo simulation in copper. Adopted from [129].

The accelerating voltages of common SEMs range from a few kV to a few tens of kV and the electron current from a few pA to a few hundred nA. A large percentage of the beam power is deposited in the sample as heat, and this power can be quite significant, but is quickly dissipated into the surrounding in most cases, either by radiation or conduction through the sample holder [112]. The notable exceptions are poorly conducting organic materials which can be heated considerably – even to the point of decomposition – by electron irradiation. Organic materials are also susceptible to ionising damage by electrons accelerated to energies far beyond that of the valence electrons. It is difficult to evaluate SEM heating in expandable layered materials due to their complex morphology. On the one hand the materials can be good heat conductors, but on the other hand the expanded pore network of these materials prevents efficient heat flow and this is the reason why these materials can be used as thermal insulation.

## 1.2 Scope

This thesis focuses on one TMD from each of the groups 4, 5 and 6 of the periodic system. We focused the most on MoS<sub>2</sub>, since it is the most prominent member of the TMD family. It is also by far the cheapest one and therefore the only one feasibly used in bulk quantities, since it is the only one existing as a mineral and is also relatively chemically inert and resistant to heating.

Representing group 4 and 5 are TiS<sub>2</sub> and TaS<sub>2</sub> respectively. The former can be processed to form conductive layers and electrodes. The latter is a known charge density wave (CDW) compound that has recently been shown to switch to a hidden state (electronically ordered phase not accessible by adiabatic processes) and may hold the key to ultrafast nanoscale memory devices, an area that currently constitutes a bottleneck for computing power.

We focused on the sulphides, since these are the most studied of the dichalcogenides. We also note that all of the TMDs, especially less stable ones like TiX<sub>2</sub> and TaX<sub>2</sub> (X=S, Se), decompose to some extent, releasing H<sub>2</sub>X. Moreover, due to extreme toxicity of H<sub>2</sub>Se it was in our interest to avoid those reactions.

There were some other transition metal dichalcogenides tested, that we were unable to expand or intercalate. These are discussed in the appendix.

## 1.3 Outline

In chapter 1 we lay out theoretical foundation relevant to the thesis. The following chapter 2 encompasses the list of experimental techniques used in our work. Chapter 3 is the main chapter where we present the bulk of our results on  $\text{MoS}_2$  intercalation and expansion, and is followed by a shorter chapter of  $\text{TiS}_2$  and  $\text{TaS}_2$  expansion under action of hydrazine. Following the concluding chapter there is the appendix summing up some observations on our attempts to expand some other metal dichalcogenides.

## Chapter 2

# Experimental Methods

In this chapter we present both synthesis and characterisation methods used in our work.

### 2.1 Synthesis of TMDs

All of the metal dichalcogenides ( $\text{MoS}_2$ ,  $\text{MoSe}_2$ ,  $\text{WS}_2$ ,  $\text{TiS}_2$ ,  $\text{TaS}_2$  and  $\text{SnS}_2$ ) studied were synthesised from the elements as described in [22]. Stoichiometric amounts of the respective metals and chalcogen were put into quartz ampules. These were then put under high vacuum ( $10^{-6}\text{mbar}$ ) for three hours. After that the ampules were sealed and were put in a three-zone furnace for different lengths of time. The ampules were inspected regularly and were removed from the furnace when the material inside turned to reflective powder indicating growth of small  $\sim 10\text{ }\mu\text{m}$  crystals. The procedure differed only for the ampule containing  $\text{TaS}_2$  which was rapidly quenched in water to prevent the formation of the 2H phase, since the 1T phase was desired. An example of reacted powder is depicted in Figure 2.1.



Figure 2.1: Dichalcogenide powder in ampule after the reaction.

## 2.2 Materials

TMDs were grown from the following materials: sulphur (Aldrich, 99.98%), selenium (Aldrich 99.98%), molybdenum powder (Aldrich 99.99%), tantalum powder (Alfa Aesar 99.99%), tungsten powder (Sigma Aldrich 99.99%), titanium foil (Sigma Aldrich 99.7%) and tin powder (Sigma Aldrich 99.5%)

For intercalation reactions we used the following materials: hydrazine monohydrate (Acros Organics 97%), NaOH (Applichem 99%), TBAOH (Acros Organics 99%), CTAB (Acros Organics 99%), TBAI (Acros Organics 98%), choline chloride (Acros Organics 99%)

In exfoliation and deposition experiments we used ethanol (Carlo Erba absolute anhydrous), isopropyl alcohol (Carlo Erba absolute anhydrous), n-butanol (Sigma Aldrich anhydrous 99.8%) and n-hexane (Carlo Erba anhydrous).

## 2.3 Intercalation, Expansion, Exfoliation

The following reaction protocols were followed unless stated differently in the text.

1/6 (molar ratio) hydrazine/NaOH mixture was prepared by mixing 30 ml of hydrazine hydrate with 4 g of NaOH assisted by 2 hours of stirring by a magnetic stirrer. This mixture was freshly prepared before each use in all of the intercalation reactions with MoS<sub>2</sub>.

160 mg (1 mmol) of MoS<sub>2</sub> was mixed with 5 ml of hydrazine/NaOH mixture and 1 ml of TBAOH 30H<sub>2</sub>O or equivalent molar amount of other quaternary ammonium salts. The mixtures were left to react for different lengths of time as stated in the text. Afterwards, the crystals were washed with deionized water and filtered 3 times and were dried for 12 hours in an oven at 60 °C.

In the section 3.4, 0.1 mmol (16 mg) of MoS<sub>2</sub> was used in all of the reactions. Apart from this, the reaction conditions did not differ from those just described.

Expansions of intercalated MoS<sub>2</sub> were always started by putting the crystals on a hot plate set to 300 °C. After 5 seconds, the expanded crystals were removed from the hot plate and left to cool.

Exfoliation was achieved by dispersing TMDs in different solvents in an ultrasonic bath.

TaS<sub>2</sub> and TiS<sub>2</sub> crystals were expanded in pure hydrazine hydrate in all of the experiments and were washed and filtered with deionized water 3 times before letting them dry in an oven at 60 °C overnight.

Expanded TiS<sub>2</sub> and TaS<sub>2</sub> were exfoliated by sonicating the crystals in hydrazine hydrate for 1 minute. Afterwards, the dispersions were centrifuged as described in the text to remove unexfoliated material.

In order to deposit exfoliated nanoflakes to a substrate a few drops of the centrifuged dispersion (MoS<sub>2</sub>, TiS<sub>2</sub> or TaS<sub>2</sub>) were introduced to water/hexane interface in a centrifuge tube, and were brought to the interface by a brief stirring. The material was deposited to substrates by lifting the substrates through the liquid/liquid interface. Afterwards the substrates were dried in an oven at 60 °C for 12h prior to investigations.

## 2.4 Characterisation

This chapter contains descriptions of all the characterisation instruments used, as well as general settings. Some theoretical background relevant to our investigation is also detailed.

-SEM:

This is the characterisation method most used for this thesis. Its background is described in chapter 1.1.7. All SEM micrographs were taken in a Helios Nanolab 650 manufactured by FEI. All treated samples were put on a piece of a carbon tape and dried at 60 °C overnight before characterisation.

-XRD:

A dry sample was ground with pestle and mortar for 10 minutes and spread onto a Teflon holder. The samples were then scanned by an X-ray diffractometer (BRUKER AXS D4 ENDEAVOR) at Cu K $\alpha_1$  wavelength.

-AFM:

All of the AFM micrographs were recorded in tapping mode on a Veeco dimension 3100 AFM microscope.

-TGA:

TG-MS analyses were carried out in a Mettler Toledo TGA/DSC 1 Thermal Analyzer coupled to a Pfeiffer Vacuum ThermoStar Balzers Mass Spectrometer. The samples were measured in the temperature range of 25 - 600 °C in a platinum crucible (150  $\mu$  L), at the heating rate of 10 °Cmin<sup>-1</sup> in an air atmosphere with the flow-rate of 100 mLmin<sup>-1</sup>. The sample mass was approximately 4 mg. A baseline was subtracted from all measurements. Evolved gases were introduced into the mass spectrometer via a 75 cm long heated capillary.

-XPS:

X-ray photoelectron spectroscopy (XPS) analysis was performed on the PHI-TFA XPS spectrometer produced by Physical Electronics Inc. equipped with a monochromatic Al X-ray source. The analysed depth by XPS is 3 - 5 nm. The energy analyser operated at a resolution of about 0.6 eV, pass energy 29 eV, and accuracy about  $\pm 0.1$  eV. A neutralisation low-energy electron gun was used to eliminate possible charging of the sample surface.

-Optical microscopy:

Micrographs were taken by Leitz SM-LUX-HL optical microscope.

-Nitrogen (N<sub>2</sub>) physisorption:

Nitrogen physisorption measurements were carried out at liquid-N<sub>2</sub> temperature, -196 °C, using a Gemini VII 2390t instrument (Micromeritics). Before analysis, each sample was degassed at 250 °C in a dynamic vacuum (9 Pa) for 2 hours. The specific surface area was determined by a 5-point Brunauer-Emmett-Teller (BET) method and pore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) method.



## Chapter 3

# MoS<sub>2</sub> Intercalation and Expansion

### 3.1 Intercalation

MoS<sub>2</sub> reacts slowly with hydrazine hydrate even at room temperature. A macroscopic MoS<sub>2</sub> crystal will inflate over a period of months (Figure 3.1). A recent study has tried to overcome this by increasing the temperature to 130 °C by a reaction in an autoclave [20]. Even such conditions fail to expand microscopic crystals (Figure 3.2 right), hence the resulting material is only of limited use as an analogue to EG or as a precursor in liquid exfoliation. We intended to improve the reaction in a way that would lead to an intercalation compound that can be rapidly and consequentially efficiently expanded and is stable in air atmosphere.



Figure 3.1: Expanded MoS<sub>2</sub> after a year in hydrazine hydrate at room temperature.

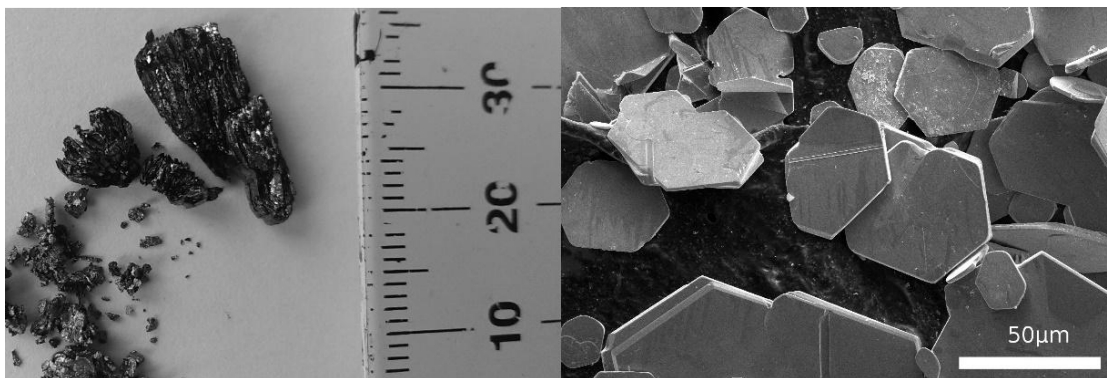


Figure 3.2: Macroscopic (left) and microscopic (right) MoS<sub>2</sub> crystals. These crystals were treated with hydrazine in an autoclave (as in [20]). Only macroscopic crystals expanded during the reaction.



Figure 3.3: MoS<sub>2</sub> expanded in N<sub>2</sub>H<sub>4</sub>:H<sub>2</sub>O/NaOH solution at 60 °C. The reaction lasted for 24h.

Firstly we synthesized (see experimental section) MoS<sub>2</sub> crystals tens of microns in diameter. These synthesized MoS<sub>2</sub> crystals of hexagonal shape were more appropriate for the expansion experiments than MoS<sub>2</sub> mineral because it was easier to follow the changes of their shape. The ability to expand smaller crystals, which cannot be expanded by current methods (Figure 3.2 right), it clearly shows the superiority of our method. Finally, by synthesizing the materials in our lab, we were able to have a complete control over their chemical composition.

In order to synthesise expandable MoS<sub>2</sub> the following criteria should be met: The interplanar spaces should be occupied by molecules, ions and/or chemical groups that are stable until an external stimulus (probably rapid rise of temperature) starts a reaction that

produces gas molecules. The reaction should take place below the decomposition temperature of  $\text{MoS}_2$ . To achieve these goals we postulated according to the literature presented in the introduction, that the  $\text{MoS}_2$ -hydrazine reaction could be utilised to produce intercalated crystals if:

- the reaction temperature could be brought down sufficiently to allow some relatively unstable organic molecules to co-intercalate;
- after washing and drying the molecules remained in the interplanar space.

We have found out that hydrazine becomes increasingly reactive by addition of strong alkalis ( $\text{NaOH}$ ,  $\text{KOH}$ ). In fact, bubbles appear as soon as a macroscopic  $\text{MoS}_2$  crystal is dropped in a saturated hydrazine hydrate/ $\text{NaOH}$  solution, and after 24h at 60 °C the crystals (Figure 3.3) resemble those treated by hydrazine-hydrate in an autoclave.

Several salts and hydroxides of quaternary ammonium (QA) were investigated as co-intercalants. We based our choice on the fact that these molecules are rather unstable and will decompose to various gaseous fragments upon heating. They are also heavily hydrated, and we believed co-intercalated water molecules would provide extra pressure when heated above the boiling point.

Since reduced TMDs can intercalate larger molecules by cation exchange [47], we postulated that a concentrated hydrazine solution might reduce  $\text{MoS}_2$  sufficiently to allow the reaction to take place.

$\text{MoS}_2$  crystals were intercalated by a reaction with a hydrazine hydrate /  $\text{NaOH}$  (1/6) solution including one of a few quaternary ammonium salts or hydroxides in a molar ratio with  $\text{MoS}_2$  in excess of 1:1. After the end of the reaction the samples were washed with distilled water and dried in the air at 50 °C. The samples were investigated by SEM, XRD, TGA, XPS and Raman spectroscopy in order to elucidate whether any material was intercalated or  $\text{MoS}_2$  underwent any chemical change in the process.

Compounds treated with various QAs were tested for expandability by heating small amounts of the samples on a hot plate at 300 °C – a temperature above the decomposition temperature of the organic intercalants [113], and just below the decomposition temperature of  $\text{MoS}_2$  in the air. The resulting compounds were characterised by optical microscopy and the results for different molecules are presented in Figure 3.4 and Figure 3.5. Depending on the compounds used, the crystals expanded to different degrees. Untreated  $\text{MoS}_2$ ,  $\text{MoS}_2$  treated only with hydrazine hydrate/ $\text{NaOH}$  and  $\text{MoS}_2$  intercalated with choline chloride do not expand significantly. Crystals intercalated with Tetrabutylammonium iodide (TBAI), Cetrimonium bromide (CTAB) and Tetrabutylammonium hydroxide (TBAOH) expand to different degrees in the following order:  $\text{TBAI} < \text{CTAB} < \text{TBAOH}$ . Accordingly, further investigations were based on TBAOH intercalation. It is also noteworthy that in contrast to some other QAs (CTAB) the alkyl chains are shorter in TBAOH, and hence more likely to leave the interplanar space after expansion, leaving the resulting material purer.

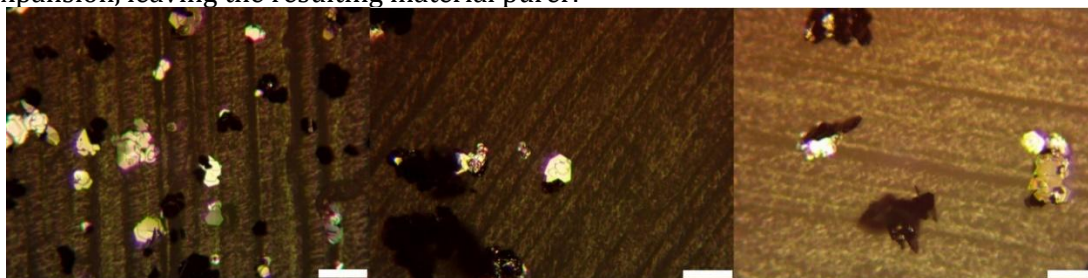


Figure 3.4: Expanded  $\text{MoS}_2$  depending on the intercalant used. Untreated (left), hydrazine hydrate treated (center) and choline intercalated (right)  $\text{MoS}_2$ . The crystals are photographed after 10s (negligible) expansion on a hot plate at 300 °C. Scale bars are 50 $\mu\text{m}$ .

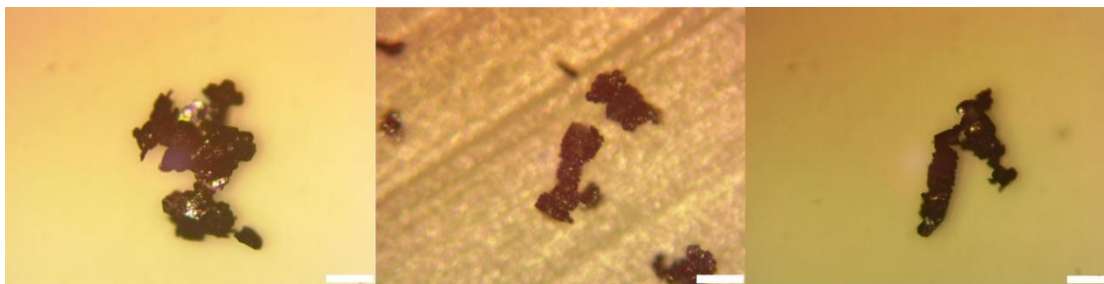


Figure 3.5: TBAI (left), CTAB (center) and TBAOH (right) intercalated MoS<sub>2</sub>. The crystals are photographed after expansion on a hot plate at 300 °C for 5 s. Scale bars are 50  $\mu$ m.

To determine the mass loss and thermal stability of intercalated compounds, we recorded the thermo gravimetric (TG) curves of the sample intercalated for 48h (Figure 3.6) by dynamical heating from ambient temperature up to 600 °C. Pure MoS<sub>2</sub> (black) remained stable up to 410 °C. The initial mass loss on the TG curve for pure TBAOH hydrate (blue) corresponds to the content of water in the sample ( $m/z$  18, 17; Figure 3.9). Above 110 °C the sample exhibits a sharp mass loss up to 200 °C, where thermal decomposition is complete (Figure 3.7) which is consistent with the reported decomposition temperature [113]. In this temperature range, besides water, the typical fragmentation for thermal decomposition of TBAOH occurred in the mass spectra ( $m/z$  100, 41, 56, 29, 30, 44). The decomposition onset (around 110 °C) is reflected in the sample intercalated with TBAOH. The TG curves show three overlapping steps up to 600 °C, where thermal decomposition is not completed yet. To follow the effect of shorter intercalation time, we recorded additional decompositions of the samples intercalated for shorter periods: 3 hours and 1 day (Figure 3.10 and Figure 3.11 respectively). A comparison of TG curves shows also that the course of thermal decomposition is similar, but the mass loss in the first step, which is completed at 300 °C, is 5.9 % for TBAOH (3h), and more than double (12.4 %) in the case of TBAOH (1d). Between 300 °C and 430 °C, where the second step occurs, the mass loss for TBAOH (3h) and for TBAOH (1d) is 1.4 % and 1.8 %, respectively. Further thermal decomposition up to 600 °C is associated with decomposition of MoS<sub>2</sub> evolving SO<sub>2</sub> ( $m/z$  64; Figure 3.8, Figure 3.9 and Figure 3.11) and SO ( $m/z$  48; Figure 3.8, Figure 3.10 and Figure 3.11) gasses. The mass loss in this step is 7.8% for TBAOH (3h) and 9.7% for the TBAOH 1d sample.

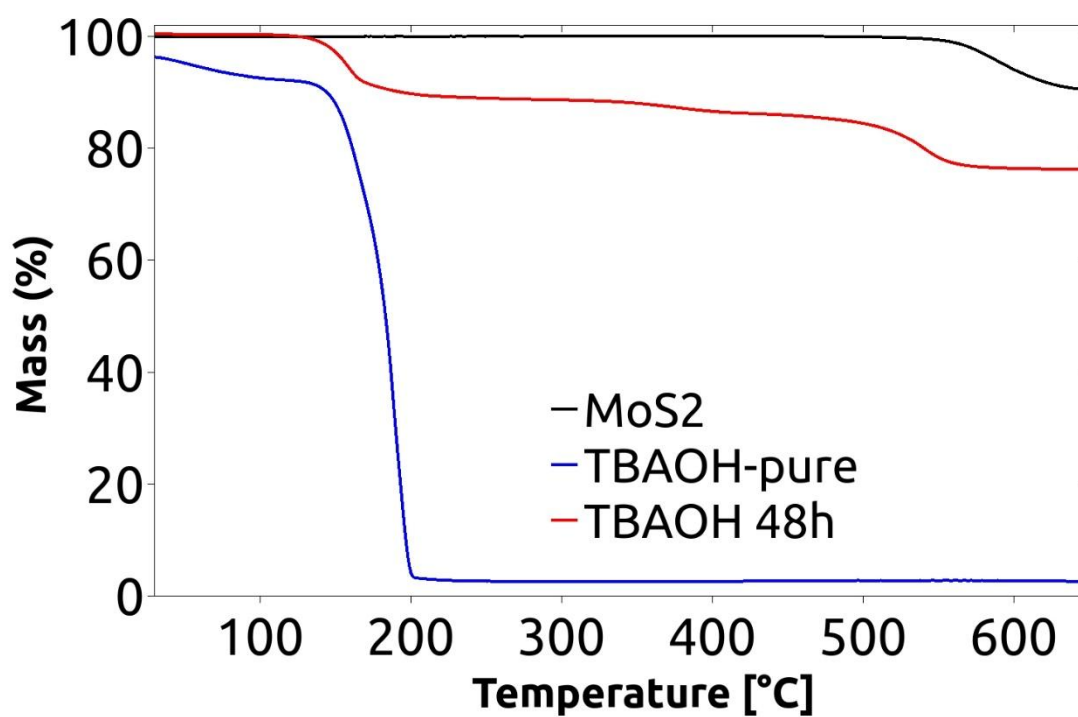


Figure 3.6: TGA plots of MoS<sub>2</sub> (black), pure TBAOH (blue) and MoS<sub>2</sub> intercalated for 48h (red).

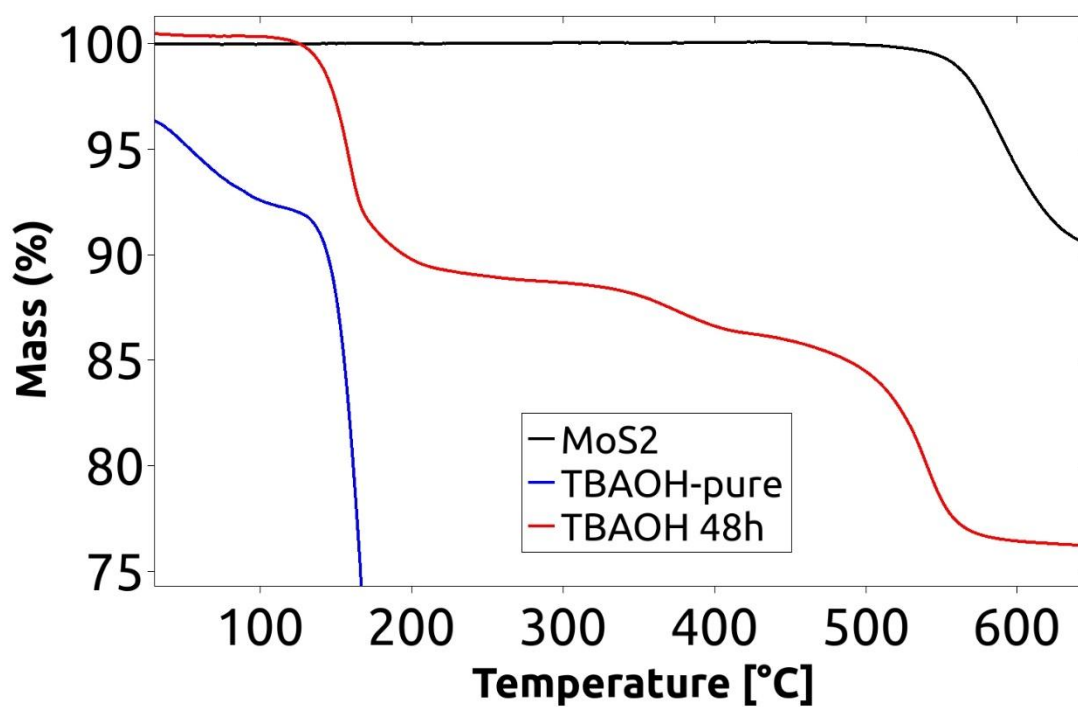


Figure 3.7: TGA plots in the significant range of iMoS<sub>2</sub> expansion/decomposition.

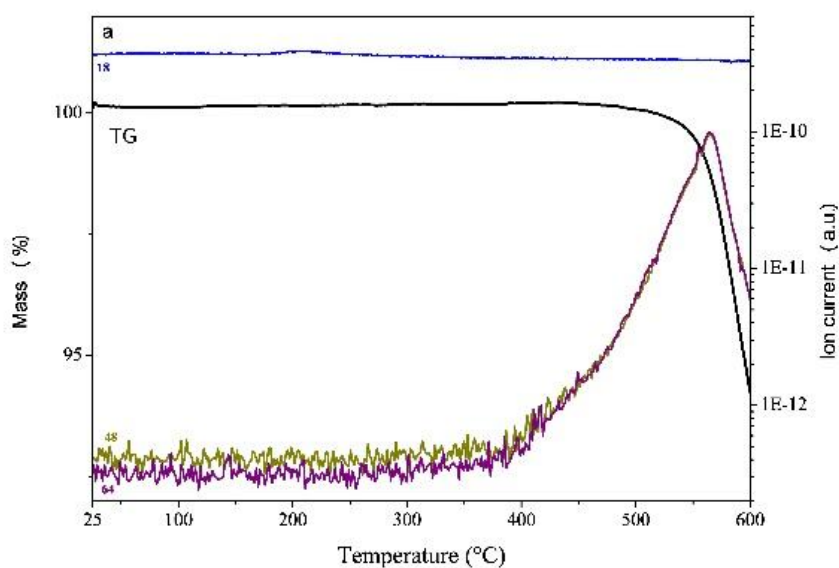


Figure 3.8: TG-mass spectroscopy curves of MoS<sub>2</sub>. Mass-to-charge ratios ( $m/z$ ) for MS curves are written beside each curve.

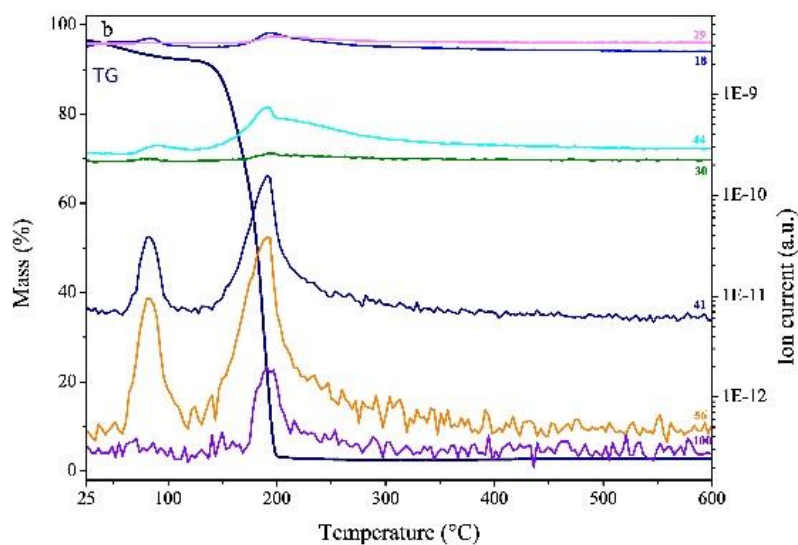


Figure 3.9: TG-mass spectroscopy curves of pure TBAOH. Mass-to-charge ratios ( $m/z$ ) for MS curves are written beside each curve.

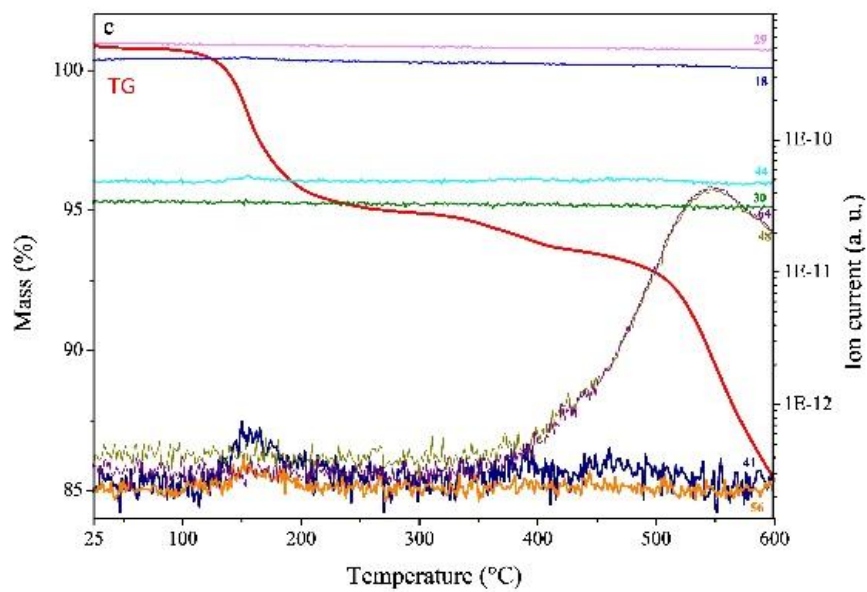


Figure 3.10: TG-mass spectroscopy curves of  $i\text{MoS}_2$  (3h). This sample was intercalated for 3h.

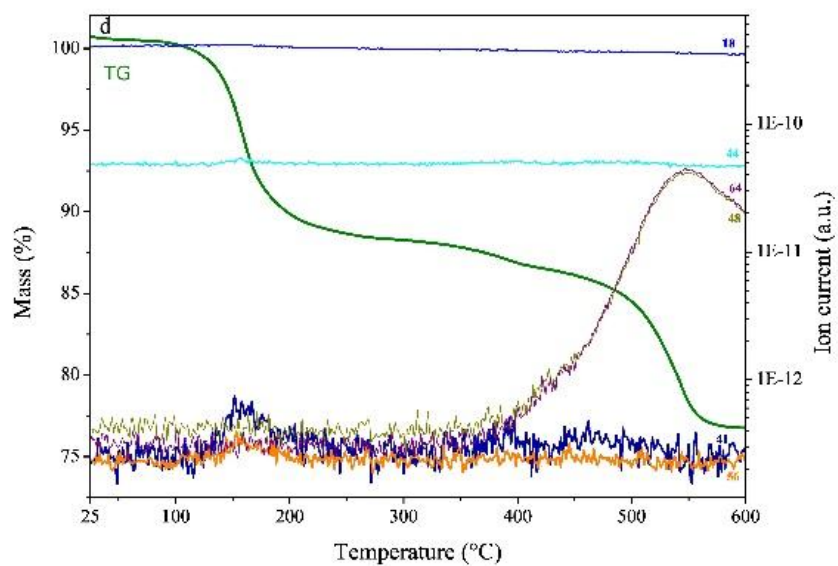


Figure 3.11: TG-mass spectroscopy curves of  $i\text{MoS}_2$  (1d). This sample was intercalated for 1d.

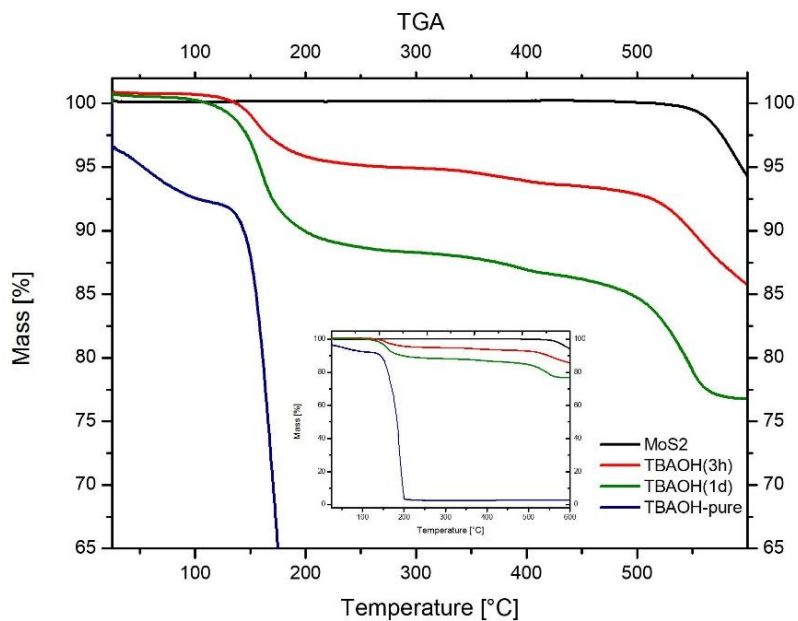


Figure 3.12: TGA plots for shorter intercalation times.

We also utilized TGA to investigate iMoS<sub>2</sub> intercalated by different compounds. The results summarised in Figure 3.13: TGA of iMoS<sub>2</sub> intercalated with different compounds are in line with observations from Figure 3.4 and Figure 3.5 with TBAOH resulting in the greatest intercalated mass and also the greatest observed expandability.

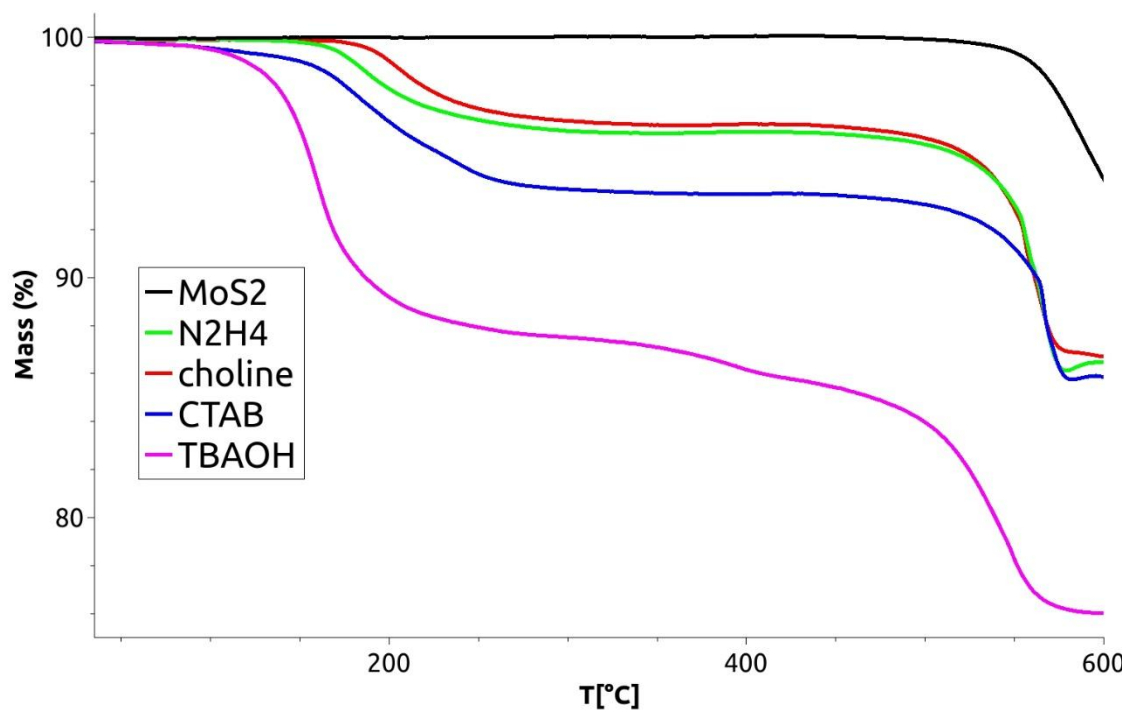


Figure 3.13: TGA of iMoS<sub>2</sub> intercalated with different compounds.

## 3.2 Expansion by Heating

In analogy with EG the materials were expanded by rapid heating. From TG measurements we knew that the onset of the decomposition of the intercalant molecules was at about 150 °C. So all of the experiments were done at higher temperatures. There is also an upper temperature limit of expansion set by the decomposition of MoS<sub>2</sub>. In the air MoS<sub>2</sub> is said to be stable up to 300 °C, but in vacuum it withstands far higher temperatures. While inspecting intercalated samples in an SEM, we noticed that the irradiated crystals were deforming. After increasing the magnification (and in consequence the electron current density) the crystals began expanding rapidly. To our knowledge this is the first description of expansion of layered materials under electron beam, so we are going to describe this phenomenon in chapter 3.3, while the characteristics of heat expanded crystals are discussed in this chapter.

In order to quantify the increase in surface and pore distribution, we measured the nitrogen physisorption isotherms. The 5 point BET surface area of untreated MoS<sub>2</sub> is below the detection limit and increases to 2.6 m<sup>2</sup>/g for eMoS<sub>2</sub>. For comparison, monolayer MoS<sub>2</sub> has a specific surface area of 615 m<sup>2</sup>/g. The specific surface area of eMoS<sub>2</sub> would correspond roughly to the surface of a 200 nm thick MoS<sub>2</sub> slab. This result agrees with the SEM images (Figure 3.14) showing 100 nm slabs still intact after expansion and XRD data indicating a crystallite size of the same order in the out of plane direction. The calculated pore distribution in Figure 3.15 **Error! Reference source not found.** indicates the absence of pores with diameter under 100nm. Although iMoS<sub>2</sub> expanded by heating shows a significant increase in volume, most of the layers remain intact, and the exposed surface remains far below the monolayer limit. This is in fact a common observation also in its analogue, i.e. in expandable graphite [114].



Figure 3.14: Unexpanded edges of MoS<sub>2</sub> crystals.

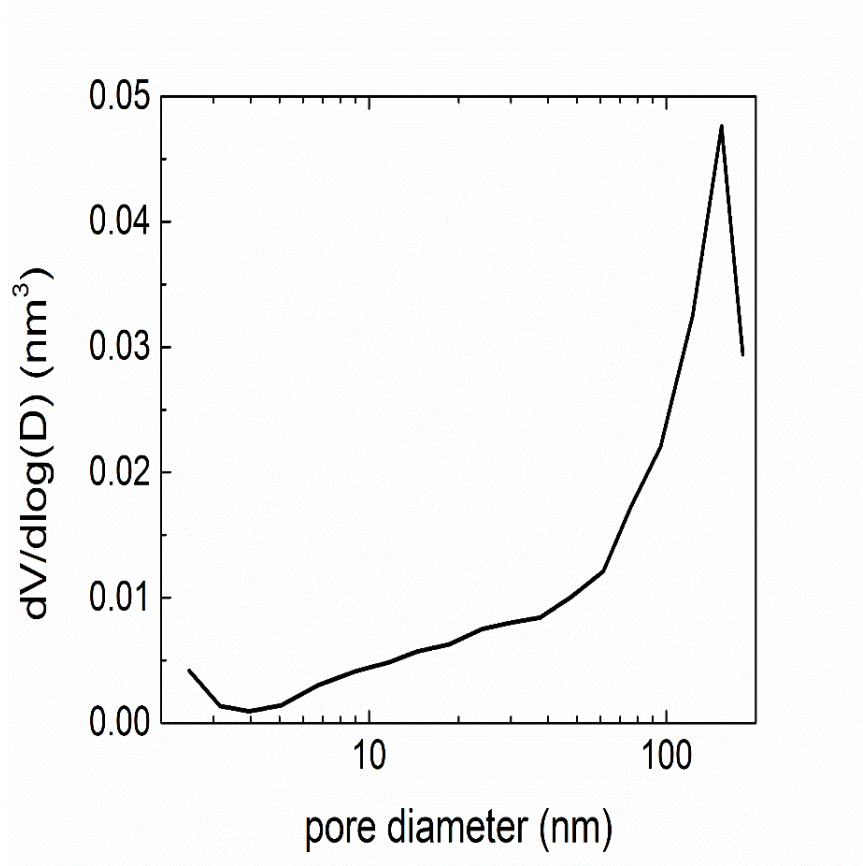


Figure 3.15: Pore distribution of eMoS<sub>2</sub> measured by nitrogen absorption.

The XRD diffraction pattern of iMoS<sub>2</sub> (Figure 3.16) contains extra lines due to intercalated molecules which disappear after heating (e MoS<sub>2</sub>). All spectra show persistent ordering in the out of plane direction, with the 002 peak getting progressively weaker and broader after intercalation and expansion. To evaluate the extent of delamination we used the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \phi} \quad (3.1)$$

where  $\tau$  is the mean size of ordered crystallite domains,  $K$  is a dimensionless shape factor,  $\beta$  is the line width at half the maximum intensity (FWHM) and  $\phi$  is the Bragg angle. The FWHM value of the 002 MoS<sub>2</sub> peak approximately doubles from 0.03 to 0.06° after expansion (Figure 3.17) indicating halving of the crystal domain size.

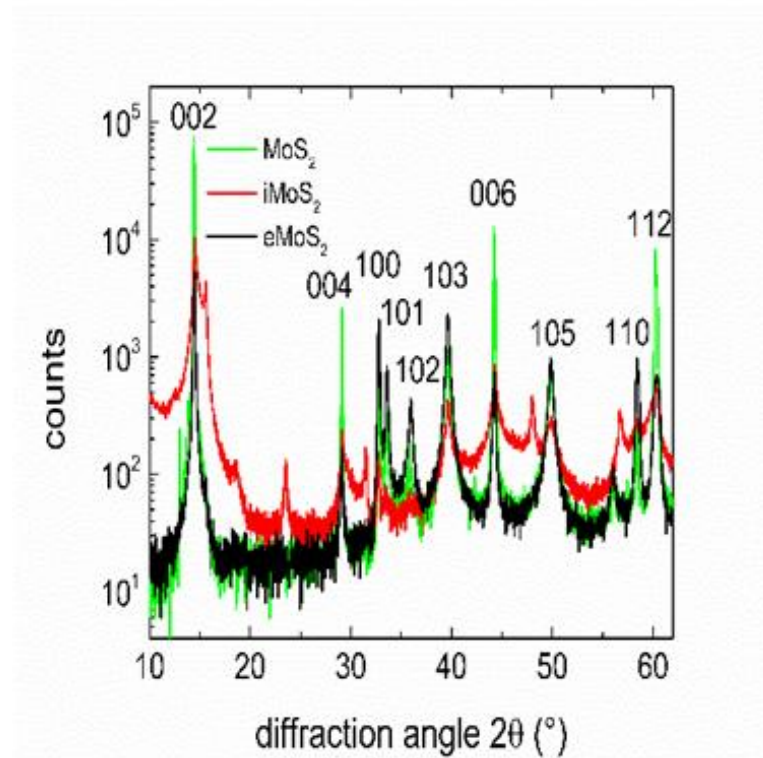


Figure 3.16: Powder XRD of native, intercalated and expanded (by heating)  $\text{MoS}_2$ . (JCPDS card No. 37-149)

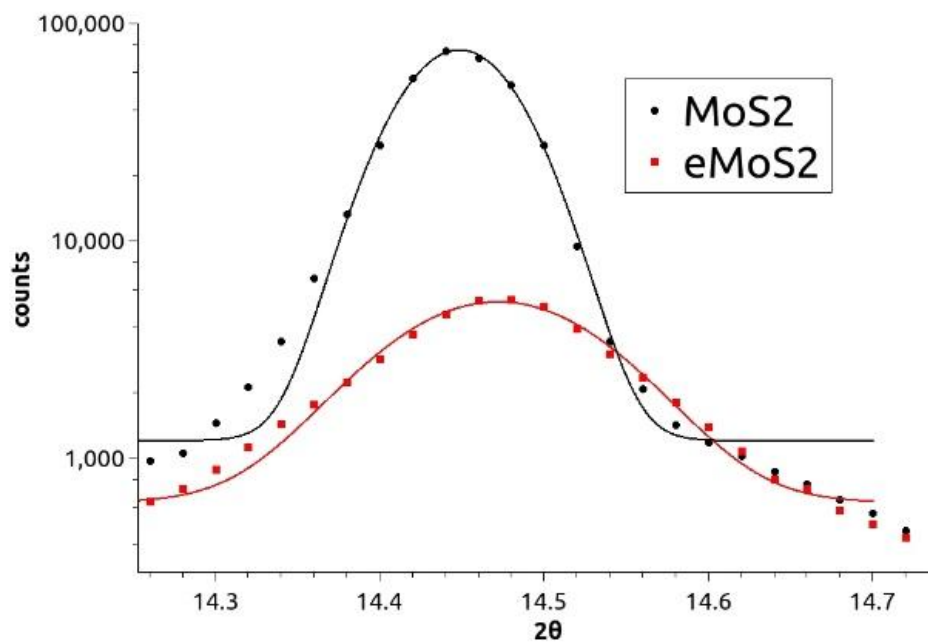


Figure 3.17: Gaussian fit of the 002 peaks for  $\text{MoS}_2$  and  $\text{eMoS}_2$ .

### 3.2.1 Particle size and reaction duration

In this section we investigate whether iMoS<sub>2</sub> behaves similarly to its graphite analogue with regards to the particle size and intercalation duration. To this end we prepared a ground mineral MoS<sub>2</sub> and separated it according to the particle size by sieving (Figure 3.18).

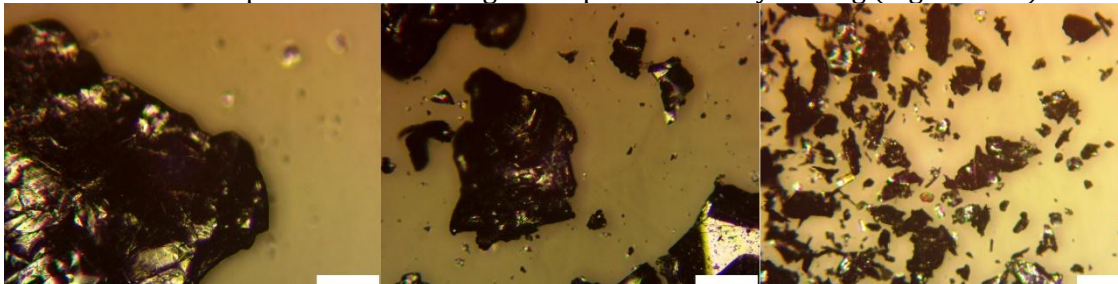


Figure 3.18: Different sizes of ground MoS<sub>2</sub> separated by 300 $\mu$ m and 60 $\mu$ m sieves. The scale bar is 100 $\mu$ .

The reaction time was set to 3 days to allow for intercalation of bigger particles. Otherwise we followed the protocol described in 3.1. The volumes of expanded MoS<sub>2</sub> were compared and the results are presented in Figure 3.19. The expansion of larger crystals is clearly more intense relative to the smaller ones in line with observations for EG [115].



Figure 3.19: Comparison of expansion volumes of equal amounts of MoS<sub>2</sub> of different sizes (as in Figure 3.18): >300 $\mu$ m (left), 300 $\mu$ m>60 $\mu$ m (center) and <60 $\mu$ m (right).

### 3.2.2 Raman characterization

Raman spectroscopy is an invaluable tool for studying structural as well as chemical changes in MoS<sub>2</sub>. Before investigating the effects of intercalation and expansion, we recorded spectra of both mineral and synthetic MoS<sub>2</sub> and MoS<sub>2</sub> treated in similar ways as iMoS<sub>2</sub> on a hot plate. Results presented in Figure 3.20 show that the crystals consist of a large number of layers (indicated by a A<sub>1g</sub>-E<sub>2g</sub> peak spacing greater than 25 cm<sup>-1</sup> in all samples [116]). The lack of pronounced MoO<sub>3</sub> peaks [117] in all spectra also indicates the absence of oxides in all samples. We conclude that the starting materials in our research are

not significantly oxidised, and do not oxidise even after relatively long heating on a hot plate at conditions similar to expansion.

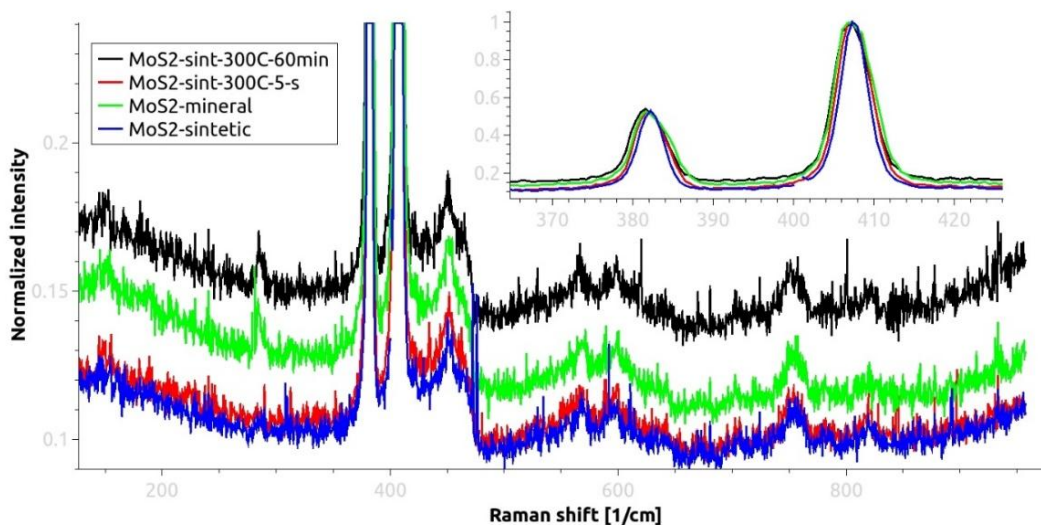


Figure 3.20: Raman spectra of mineral (green) and synthetic MoS<sub>2</sub> (blue), as well as of synthetic MoS<sub>2</sub> heated on a hot plate at 300 °C for 5s (red) and 1 hour (black). The inset shows the dominant peaks ( $A^1_g$  and  $E^2_g$ ) that are cut out in the main figure in order to visualize the weaker peaks.

Next we recorded spectra of intercalated and expanded MoS<sub>2</sub>. The results presented in Figure 3.21 indicate that there is no significant oxidation after intercalation and expansion since the spectra do not differ in any significant way from the spectra of hot plate treated MoS<sub>2</sub>.

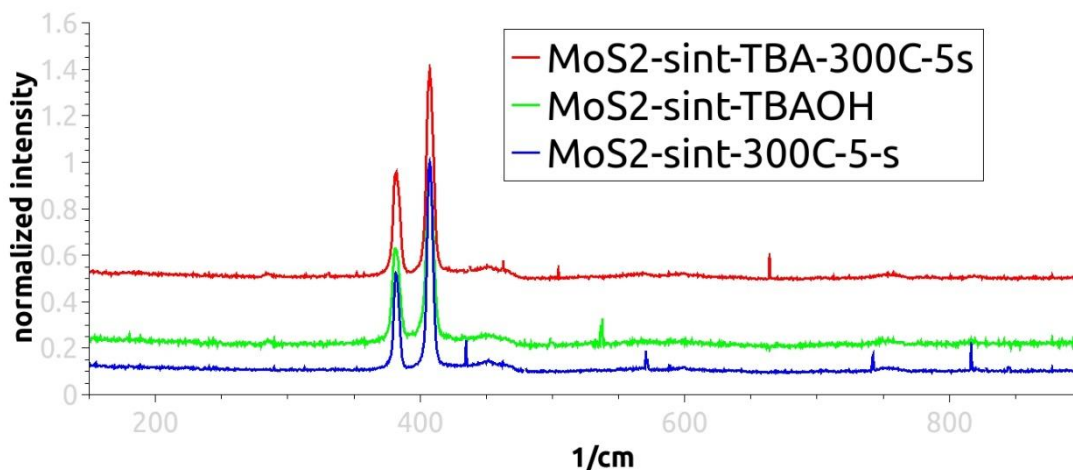


Figure 3.21: Raman spectra of intercalated MoS<sub>2</sub> (green), expanded MoS<sub>2</sub> (red) and native MoS<sub>2</sub> (blue) heated on a hot plate for 5 seconds. Smaller spikes are due to background radiation.

We conclude that intercalation and a fast hot plate treatment at 300 °C do not alter the structural or chemical characteristics of MoS<sub>2</sub>.

### 3.2.3 Stability of iMoS<sub>2</sub>

We have tested whether iMoS<sub>2</sub> remains expandable after long periods of time. A sample was tested after months of storage in the air at room temperature and the crystals expanded after both heating and electron beam expansion.

Figure 3.22 shows that iMoS<sub>2</sub> remains expandable by electron beam even after being stored in air atmosphere for over a year. The same applies to expansion by heating on a hot plate at 300 °C presented in Figure 3.23.

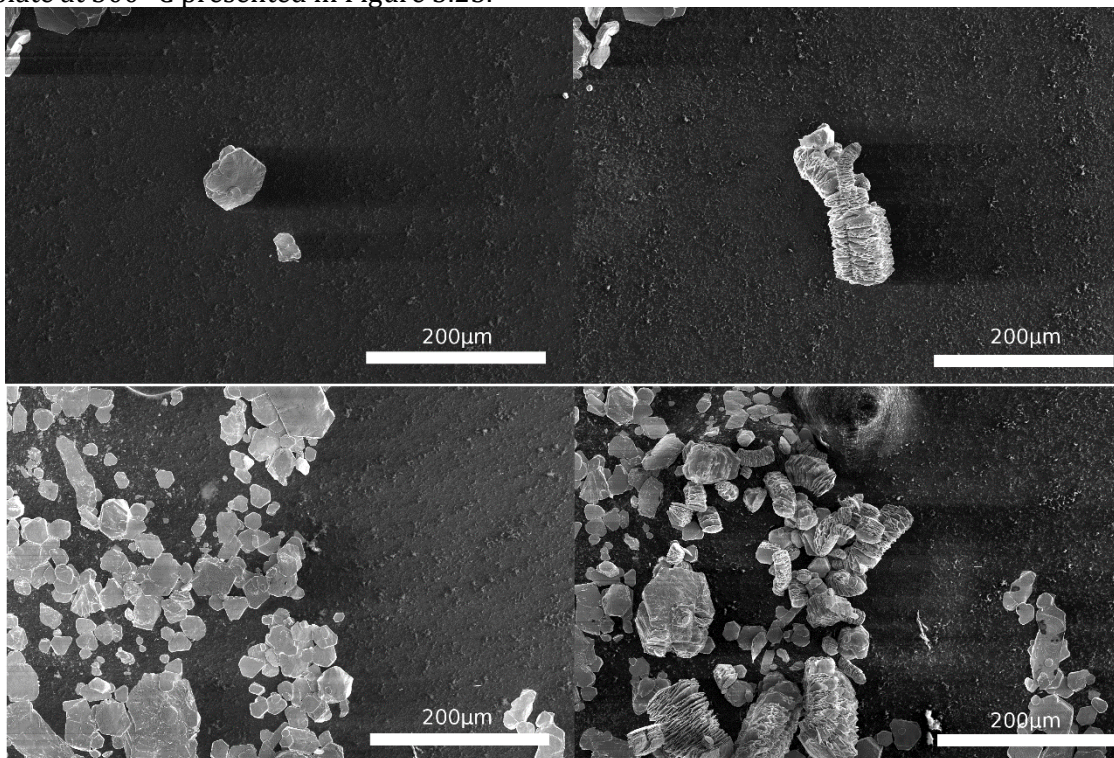


Figure 3.22: Comparison of freshly prepared (top) and aged (bottom) iMoS<sub>2</sub> expansion before (left) and after (right) expansion by electron beam.

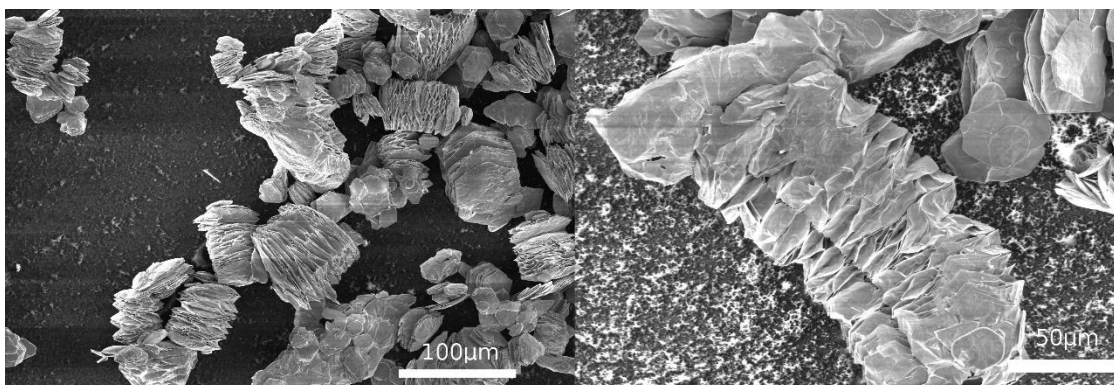


Figure 3.23: Aged (left) and freshly prepared (right) intercalated MoS<sub>2</sub> expanded on a hot plate.

We also investigated possible structural changes in aged iMoS<sub>2</sub> samples with Raman (Figure 3.24) spectroscopy and XRD (Figure 3.25). Results clearly show that MoS<sub>2</sub> expanded from aged iMoS<sub>2</sub> does not differ significantly from a freshly prepared sample.

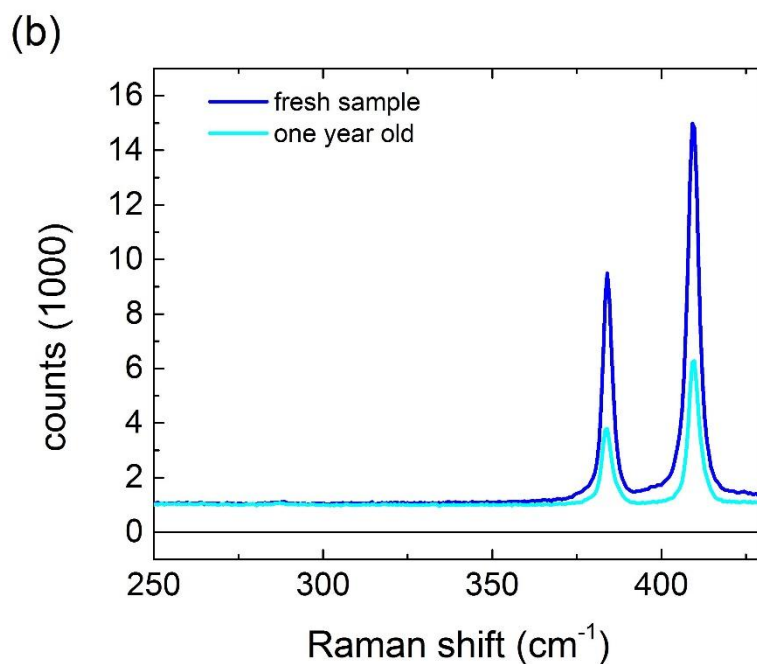


Figure 3.24: Raman spectra of freshly prepared and aged expanded iMoS<sub>2</sub>.

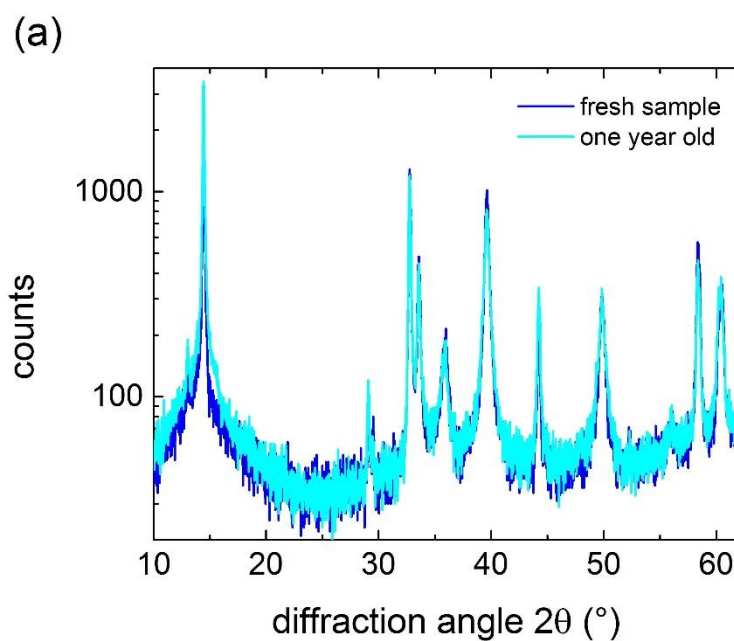


Figure 3.25: XRD of freshly prepared and aged MoS<sub>2</sub>.

### 3.3 Expansion by Electron Beam

While observing iMoS<sub>2</sub> in an SEM, we observed rapid expansion (Video 3.1, Figure 3.26). Since this is to our knowledge the first such observation in layered materials, we characterised the process further.

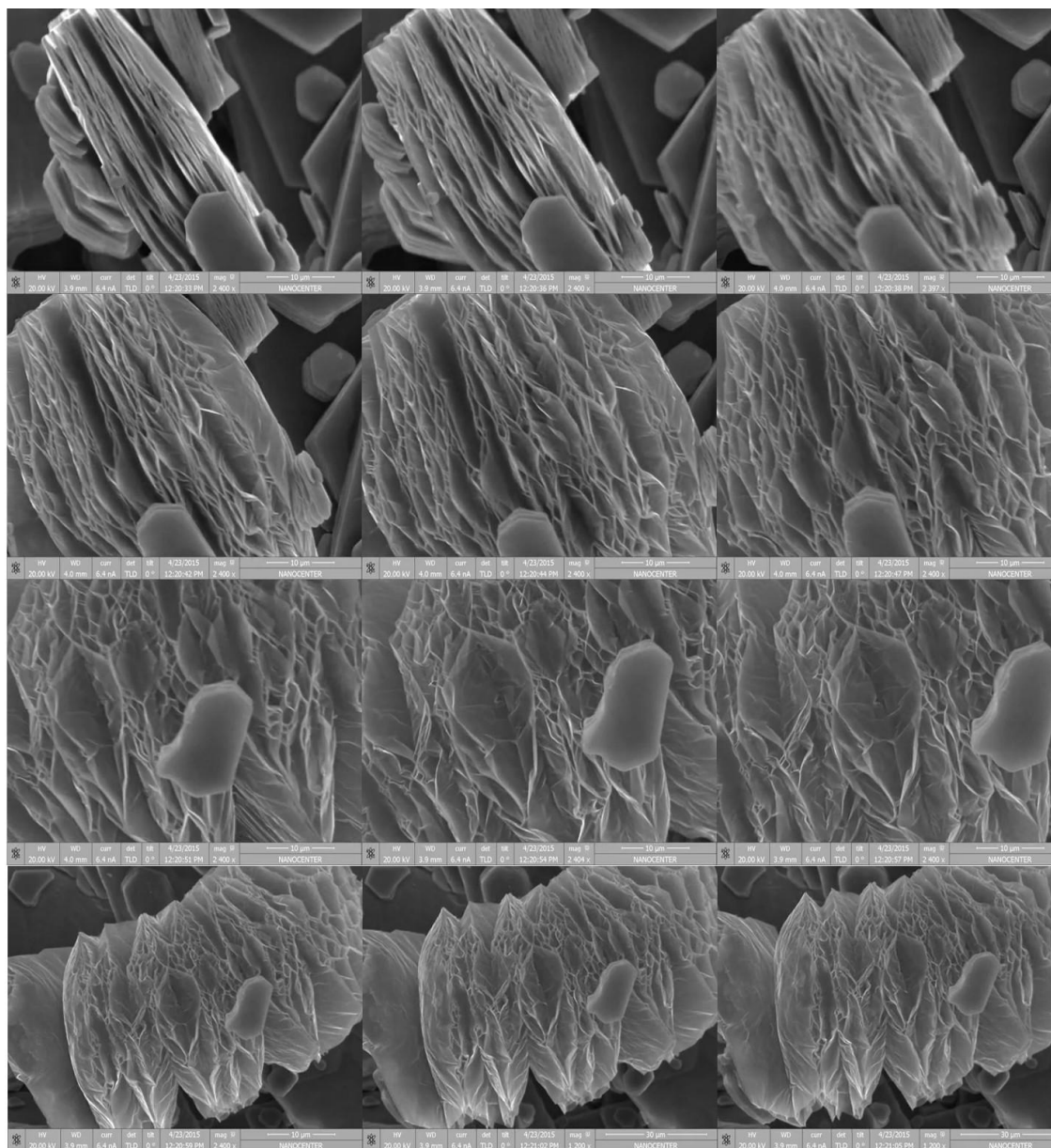


Figure 3.26: Expansion of iMoS<sub>2</sub> under electron beam. The time lapse was taken every 3 seconds. The accelerating voltage is set to 20 kV and electron current to 6.4 nA in all micrographs. The scale bar is 10  $\mu\text{m}$  in all but the last three micrographs, where it is 30  $\mu\text{m}$ .

We have also investigated in situ expansion of iMoS<sub>2</sub> by exposure to an SEM electron beam in detail. The Video 3.2 shows that the expansion rate depends heavily on an e-beam energy flux density, i.e. it increases by both increasing voltage and beam current density (achieved by zooming). We also note that the crystals are expanded to a greater extent when irradiated from the sides, rather than perpendicular to the basal (001) planes.

The different expansion rates depending on crystal orientation can be explained as follows: for irradiation perpendicular to the (001) planes the uppermost layers of the crystal form a protective layer for attenuating the electron flux. Conversely, crystals whose (001) planes lie perpendicularly to the substrate surface and are hence irradiated from the side are expanded significantly faster and more efficiently. An example of this behavior can be observed in Video 3.3. This process is self-accelerating: as the crystal expands its density is lowered and electrons can propagate deeper, facilitating expansion. At the same time the cross-section of the expanding crystal in the electron beam is larger. Therefore the expanded crystal is exposed to higher power of the electron beam.

We propose that a mechanism analogous to the expansion of graphite yields eMoS<sub>2</sub> both upon heating and e-beam irradiation. Throughout the crystal, gas is formed from the decomposition of intercalant molecules and diffuses between the crystal planes. The expansion is a result of gases generating faster than they are diffusing out of the crystal. The nature of these molecules depends on the material, but the similar kinetics of the process yields expanded materials of similar shapes.

Figure 3.27 shows eMoS<sub>2</sub> at the end of e-beam expansion, i.e. when no further expansion is perceivable during SEM monitoring. All images are taken at the same magnification. All rows are taken at the same current density, all columns at the same voltage, with all columns and rows related to their neighbours by roughly a factor 2 in voltage and current density, respectively. Clearly, a voltage of 5 kV is not enough to cause appreciable expansion at any current density. Comparing the columns with 10 and 20 kV, clearly the expansion at 20 kV is more efficient. Also when comparing images with the same energy flux density, e.g. 10 kV x 100 nA with 20 kV x 51 nA or 10 kV x 51 nA with 20 kV x 27 nA, the higher voltage (meaning higher electron penetration depth) still yields better expansion.

The expansion mechanism under electron beam depends on the electron current, the accelerating voltage, and the orientation of the crystals relative to the electron beam. A Monte Carlo simulation (Figure 3.28 **Error! Reference source not found.**) shows that the electron penetration depth is approximately 100 nm at 5 kV and almost 1  $\mu$ m at 20 kV. Hence, for the majority of crystallites, which lie flat on the substrate at 5 kV at most, a thin surface layer can be expanded. With higher voltages, a thicker layer is expanded, typically with uneven rate along the circumference. This tilts the surface and bends the “accordion”, thus allowing the electron beam to penetrate from the side, which greatly increases the expansion rate.

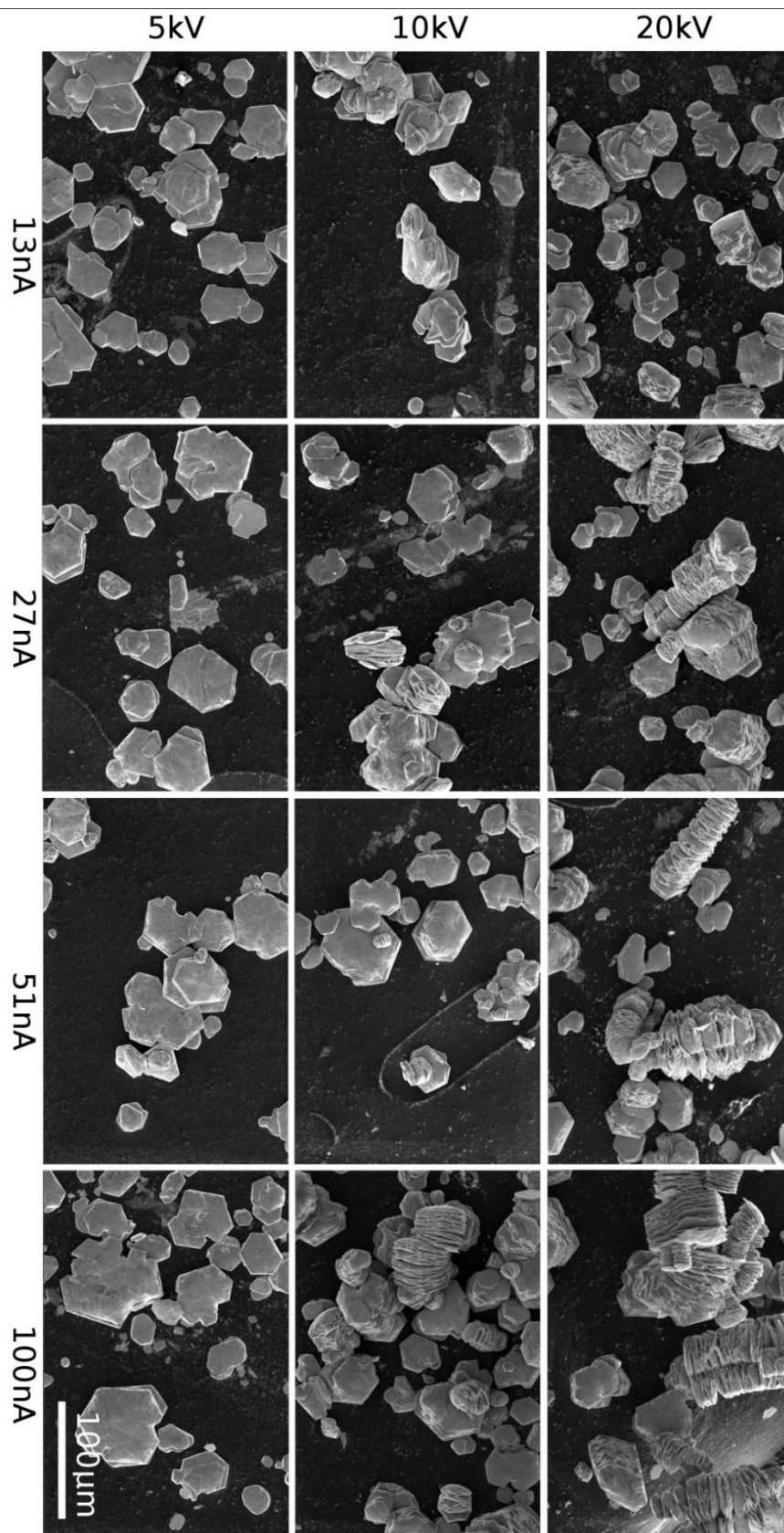


Figure 3.27: Final expansion of MoS<sub>2</sub> crystals at different accelerating voltages and current in SEM.

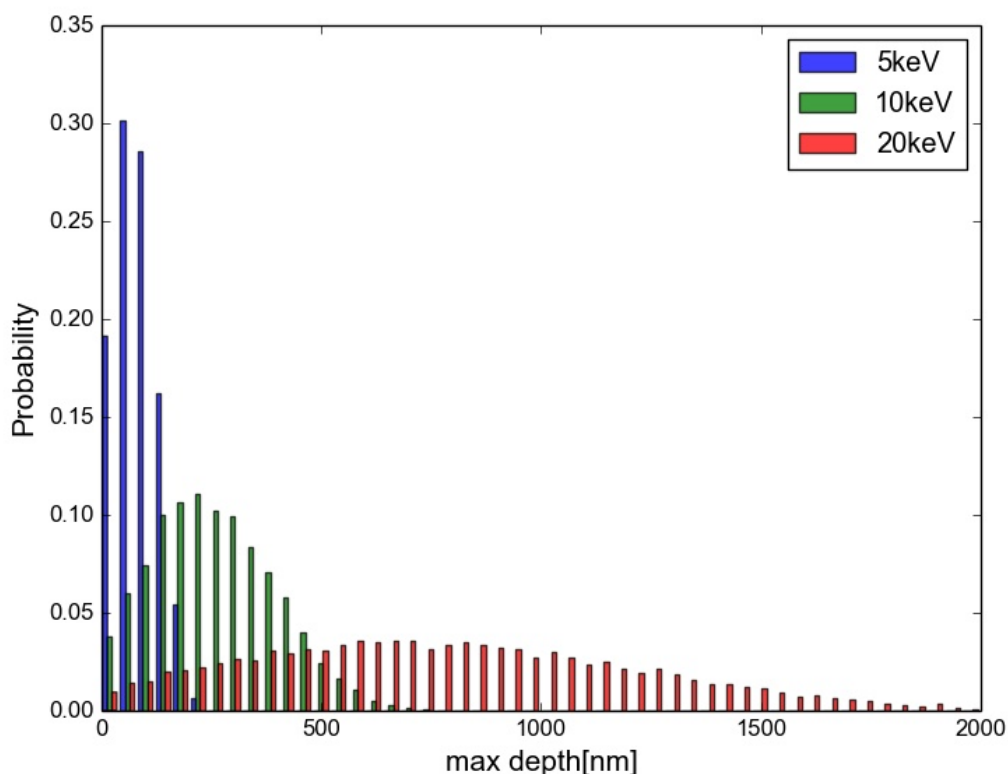


Figure 3.28 Maximum electron penetration depth depending on accelerating voltage.

In order to probe possible charge transfer, XPS spectra were recorded. Figure 3.29 shows Mo 3d spectra. The Mo 3d<sub>5/2</sub> peak before intercalation is at 229.17 eV, whereas the peak after intercalation, heating and electron radiation are at 229.55 eV. We attribute the energy shift of 0.38 eV to higher binding energies to doping of MoS<sub>2</sub> and a change of the Fermi energy position in the valence band [118]. We should mention that there was no change in shape of the Mo 3d and S 2p spectra for different processing steps, which means that there was no variation in chemical environment of MoS<sub>2</sub> like oxidation or reduction of MoS<sub>2</sub> [119,120]. From the XPS spectra also follows that the Mo/S ratio remains the same during each processing step. It has been recently shown that hydrazine reduces MoS<sub>2</sub> while changing its stoichiometry [121]; our EDX investigation, however, showed no significant change of the atomic ratio in any of our samples, possibly due to lower reaction temperatures.

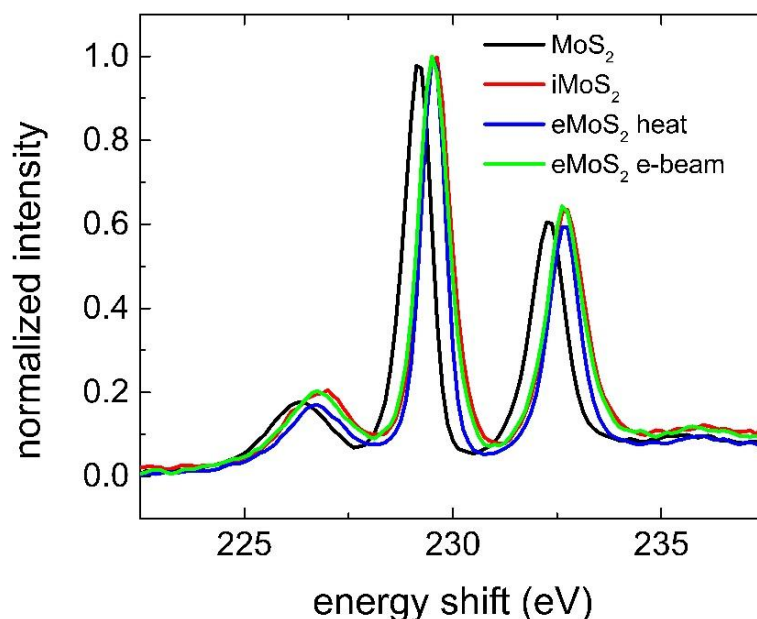


Figure 3.29: XPS spectra of MoS<sub>2</sub> (black), iMoS<sub>2</sub> (red) and eMoS<sub>2</sub> expanded by both heating (blue) and e-beam (green).

### 3.3.1 E-beam expansion-different intercalants

We also tested whether the expansion with an electron beam follows the same pattern as expansion by heating, regarding the co-intercalated molecules. The samples used in 3.1 were irradiated with an electron beam until the expansion ceased. At that point a micrograph was recorded and a comparison is presented in Figure 3.30. We see that the results match those from the previous chapter.

TBAOH was again found to be the most efficient intercalant for MoS<sub>2</sub> expansion. This result would seemingly strengthen the hypotheses that the e-beam expansion process is in fact expansion by heating. However, it could also mean that the quaternary ammonium (QA) salts are similarly susceptible to electron radiation damage. The strong correlation between electron and heat expandability – regardless of the intercalant used – does however encourage us to use the e-beam expansion as an indicator of crystal expandability by heating.

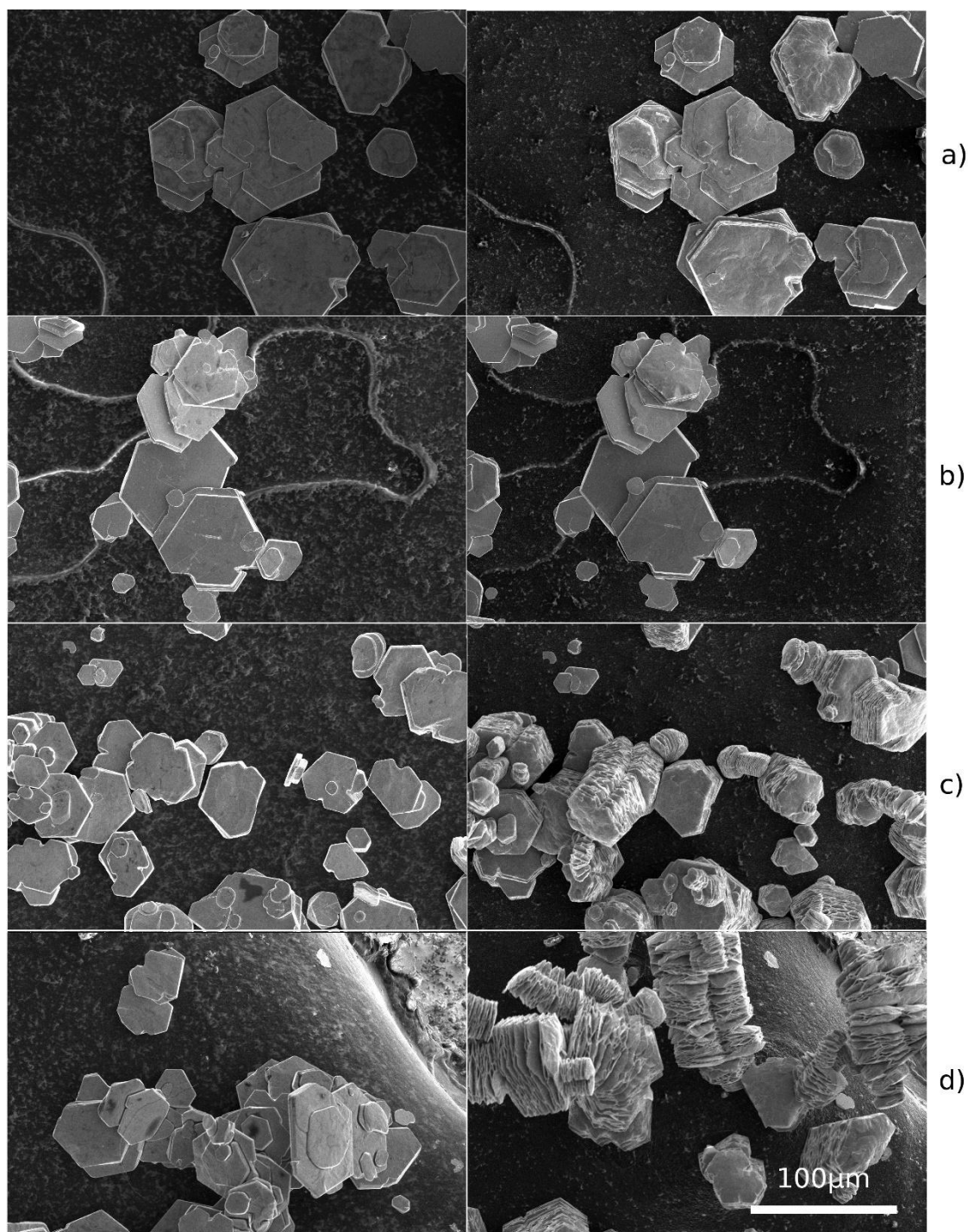


Figure 3.30: SEM expanded MoS<sub>2</sub> intercalated with different molecules. TBAI (a), choline (b), CTAB (c) and TBAOH (d). Left: before expansion, right: after expansion.

### 3.4 Optimisation of Intercalation Reaction Conditions

Since MoS<sub>2</sub> is available in bulk quantities and we implied in the introduction that the intercalation/expansion methods presented in this work can be used on large scale in analogy to EG, we proceeded to investigate how to decrease the amount of reactants. Additionally, we recognize that hydrazine hydrate is a highly toxic substance, use of which should be minimised as much as possible.

Therefore we prepared a series of reaction mixtures decreasing both TBAOH and hydrazine hydrate relative to MoS<sub>2</sub>. In order to check whether particular reaction mixtures resulted in expandable crystals, we took a small amount of intercalated MoS<sub>2</sub> powder, put it on a carbon tape, dried it and irradiated it by an electron beam in an SEM. In this way we could omit an extra step of expansion by heating, and could work with small amounts of MoS<sub>2</sub>, since e-beam expansion can be done on individual crystals. The resulting expanded crystals are presented in Figure 3.31. Apparently, expansion is not strongly dependent on the amount of intercalant, but will not take place at too low amounts of hydrazine. This is in accordance with our previous observation that MoS<sub>2</sub> is not intercalated with insufficiently high hydrazine concentrations (aided by adding NaOH). We also notice that the crystals treated with 100μl TBAOH and 100μl hydrazine solution expand a bit less than those treated with lesser amounts of TBAOH solution. This can be explained by dilution of the hydrazine mixture, since TBAOH is heavily hydrated.

A weak influence of lowering the TBAOH amount on expandability is to be expected, since the ratio of TBAOH/ MoS<sub>2</sub> is still below 0.15 even in samples with the least TBAOH. According to the TGA (Figure 3.7) the highest intercalated mass percentage is around 10%, and since MS spectra show that there is a significant amount of water co-intercalated, we can conclude that the amount of TBAOH in reaction mixtures remains well above what gets intercalated in the crystals.

Finally, the question remains whether we could decrease reactants relative to MoS<sub>2</sub> even further. While we have not reached the turning point, the amount of reactants is so small that the MoS<sub>2</sub> powder remains hardly wetted. Decreasing them further would result in inhomogeneous reaction products. While in principle this problem could be overcome by dilution, this would inhibit the reaction due to reasons stated in the previous paragraph.

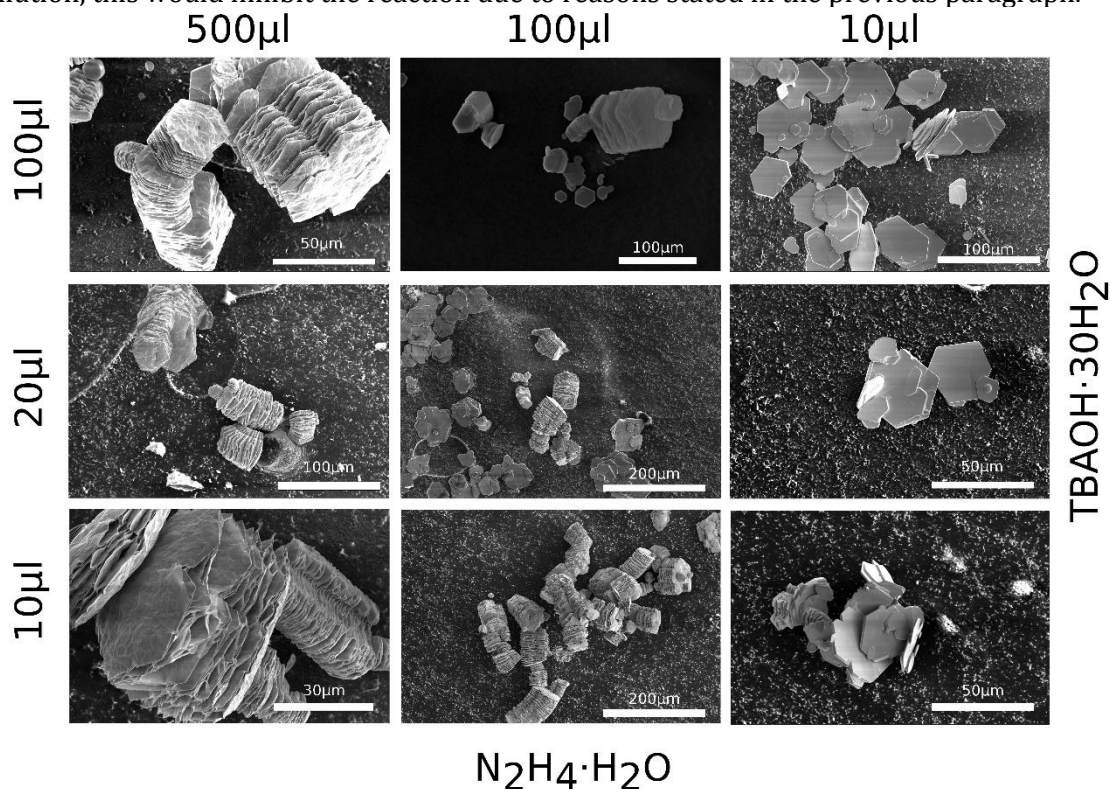


Figure 3.31: E-beam expanded MoS<sub>2</sub> crystals by different amounts of TBAOH and N<sub>2</sub>H<sub>4</sub>.

### 3.5 Formation of Flexible MoS<sub>2</sub> Foils

We tested if it is possible to compress eMoS<sub>2</sub> into flexible sheets. This was achieved by compacting different amounts of eMoS<sub>2</sub> with a hydraulic press. An example of the foil is

presented in Figure 3.32. In comparison, it is impossible to press foils from unexpanded  $\text{MoS}_2$ . However, we must note that the foils we manufactured are still quite brittle. They can be bent to some degree, as seen in the figure, but will break upon repeated deformation. We believe this is a consequence of rather small expansion of  $\text{eMoS}_2$ . It was reported that in order to construct good quality EG foils, the particle expansion in the c axis should be at least by a factor 80 [122]. However, for hot plate expanded  $\text{MoS}_2$  this ratio remains closer to 10.

Similarly, in EG higher expansion volumes have been correlated with stronger pressed foils as well as other factors ranging from intercalants to expansion temperatures [123] that have not been investigated in our study.

As discussed in the previous chapter, the aspect ratio varies depending on the method of expansion and is relatively low for hot plate expanded flakes that were used for foil construction, since this was the only method useful for production of  $\text{eMoS}_2$  in significant amounts.

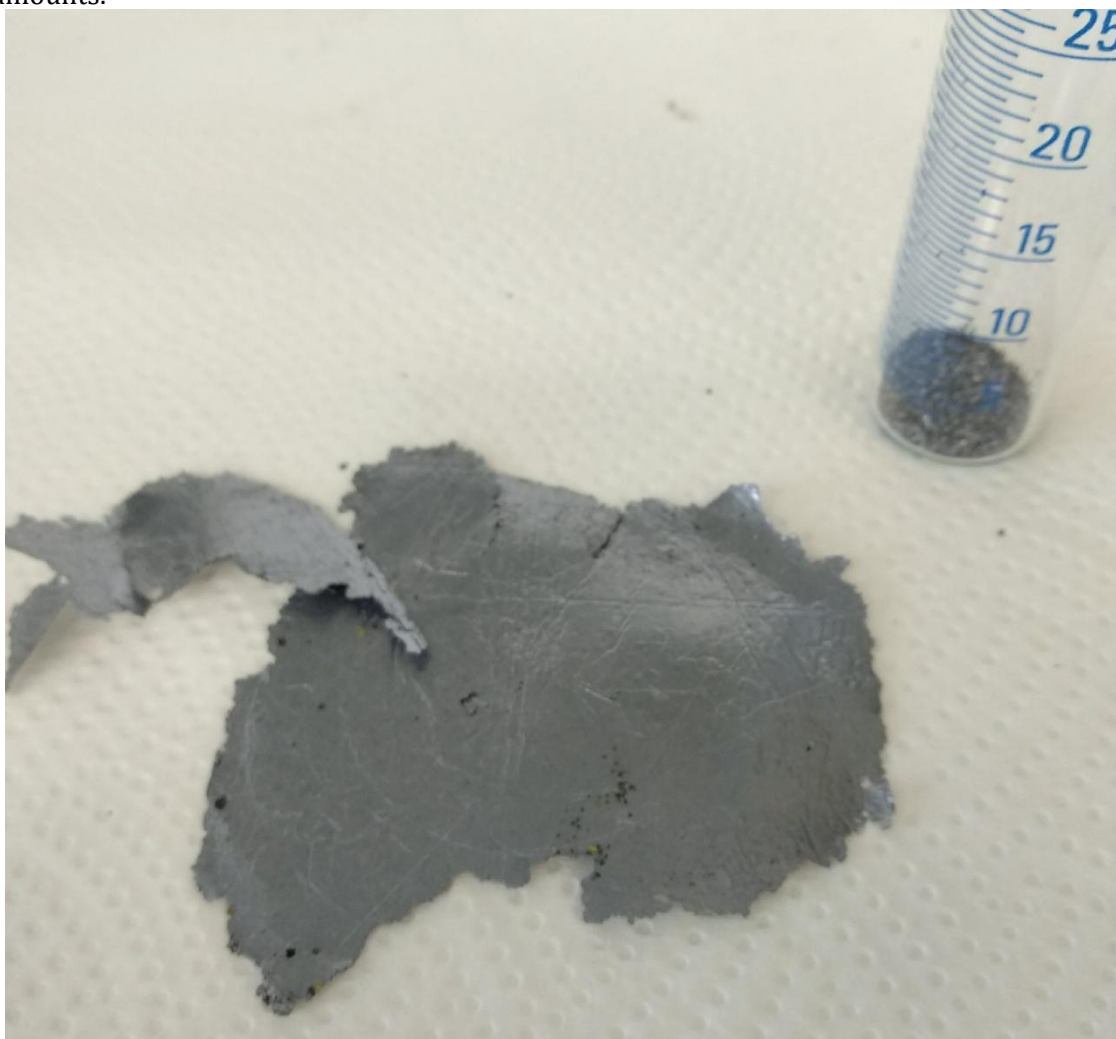
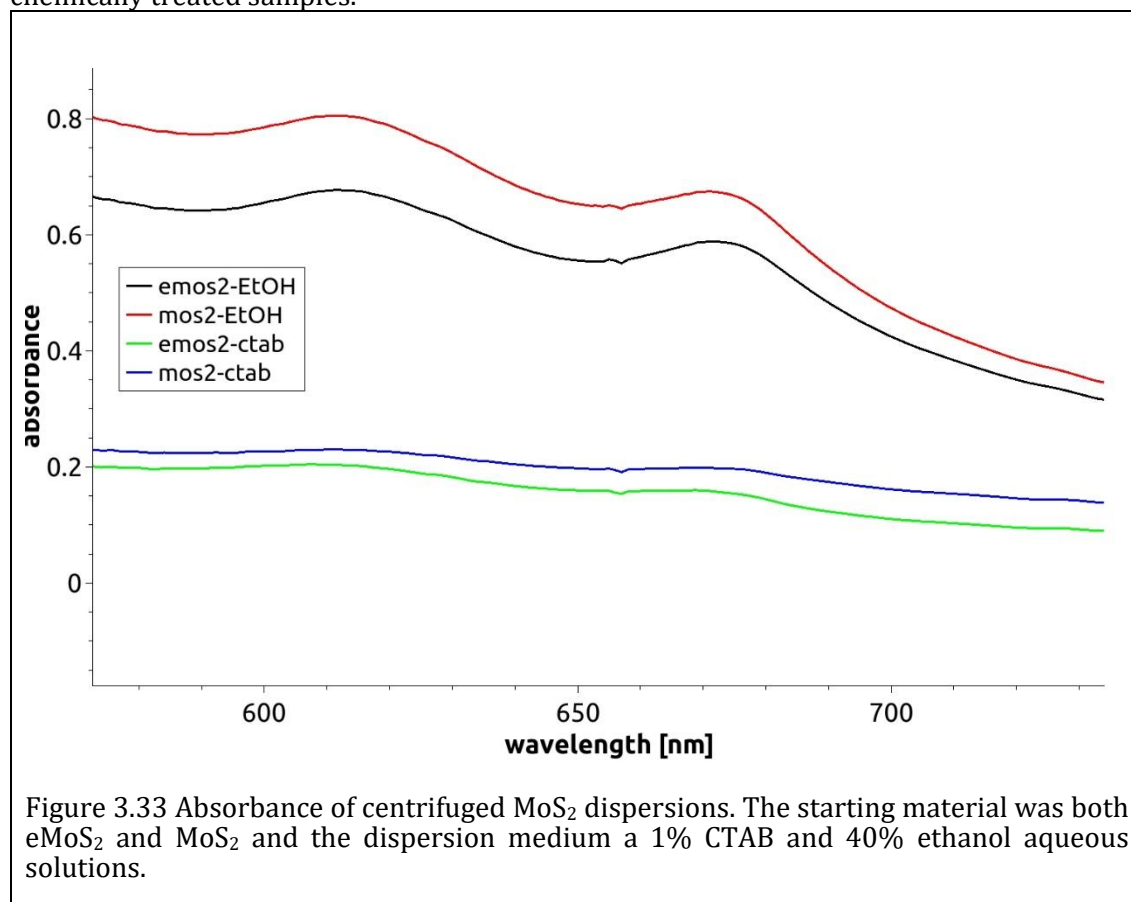


Figure 3.32: Thin foil prepared from expanded  $\text{MoS}_2$  with the same amount of unexpanded  $\text{MoS}_2$  in the cylinder.

### 3.6 Exfoliation and Film Deposition

We tested how  $\text{eMoS}_2$  fared as a precursor in liquid exfoliation. To this end, equal amounts of  $\text{MoS}_2$  and  $\text{eMoS}_2$  were each mixed with 1% CTAB water or a 40% vol. ethanol solution and sonicated for an hour in an ultrasonication cleaning bath. The resulting suspensions were centrifuged at 4000 rpm and UV-vis spectra were recorded. In both cases the

absorbance is comparable and is actually a bit lower for the expanded sample (Figure 3.33). This is counterintuitive but can be explained by possible chemical changes on the MoS<sub>2</sub> surface. Since the procedures used are optimised for native MoS<sub>2</sub>, they might not work for chemically treated samples.



### 3.6.1 Deposition of MoS<sub>2</sub> thin films from a liquid/liquid interface

Nanoparticles can be concentrated at a nonpolar/polar liquid/liquid interface by introduction of a suitable promoter chemical. In the case of MoS<sub>2</sub>, this can be done by introducing alcohol (ethanol or isopropyl alcohol) to the liquid/liquid system and shaking. After the hexane droplets in water coalesce, a visible film of nanoparticles is seen at the liquid/liquid interface.

As described in the introduction, there are a few ways reported of deposition from such an interface [94], [98], [103], [124], [125]. However, we note that the procedures described to date can be simplified and made more scalable by a small change that is film transfer and concentration by a pipette. There are several reasons to utilise this method:

#### *-Separation of sequestration and deposition receptacles*

In liquid-liquid nanoparticle systems receptacle hydrophobicity/hydrophilicity is very important. For separation of the nanoparticles a hydrophobic receptacle (we used a centrifuge tube) is preferred. In this case the meniscus will point downwards, as will the film climbing in the same direction. This concentrates the film in the lower part of the receptacle and if sufficient subphase is removed, folds are formed on the liquid/liquid interface. These are easily transferred as shown in the next section.

The deposition receptacle should be hydrophilic. In this case the meniscus climbs upward, however if the walls have not been wetted, the film does not climb the interface. A series of time lapse photographs is presented in Figure 3.34 and a scheme of the process in Figure 3.35.

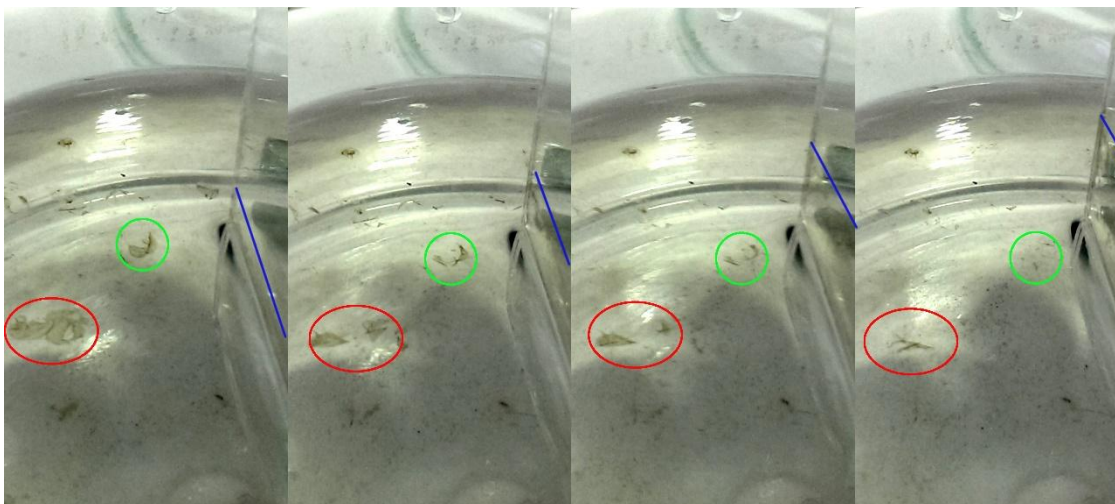


Figure 3.34: MoS<sub>2</sub> film deposition from the liquid/liquid interface. Red and green circles mark two of the folds in the film, while the blue line marks the height of the deposited film.

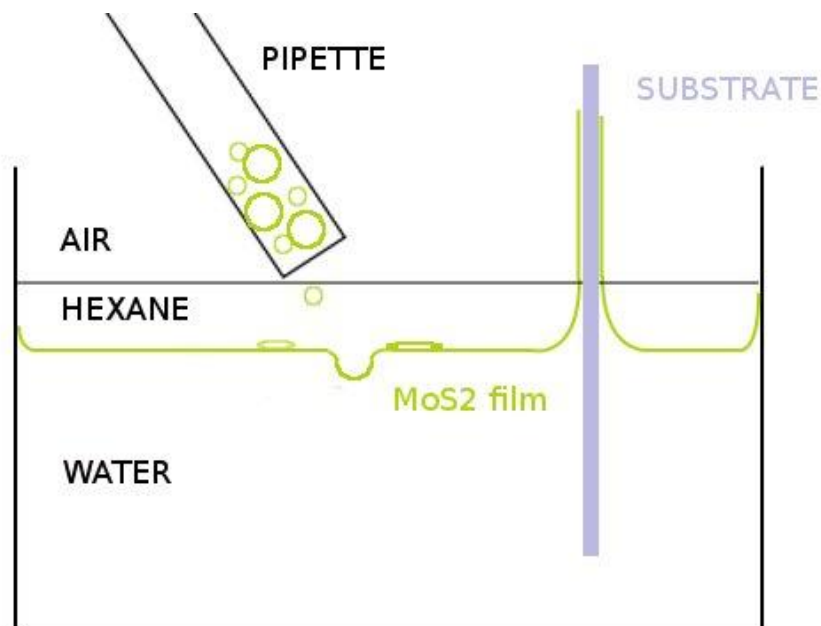


Figure 3.35: Scheme of film transfer to a deposition receptacle.

*-Careful tuning of the deposition medium*

Sometimes it is desirable to change the medium due to the constraints set by the deposition process. For example, the substrate might be reactive to water (a popular dispersion medium). One such example are sacrificial salt wafers used for annealing and film transfer used in the next section. Another example are substrates coated with water sensitive materials.

With this method it is possible to deposit thin (Figure 3.36) films of MoS<sub>2</sub> to various hydrophilic substrates (Figure 3.37) in a time-efficient manner.

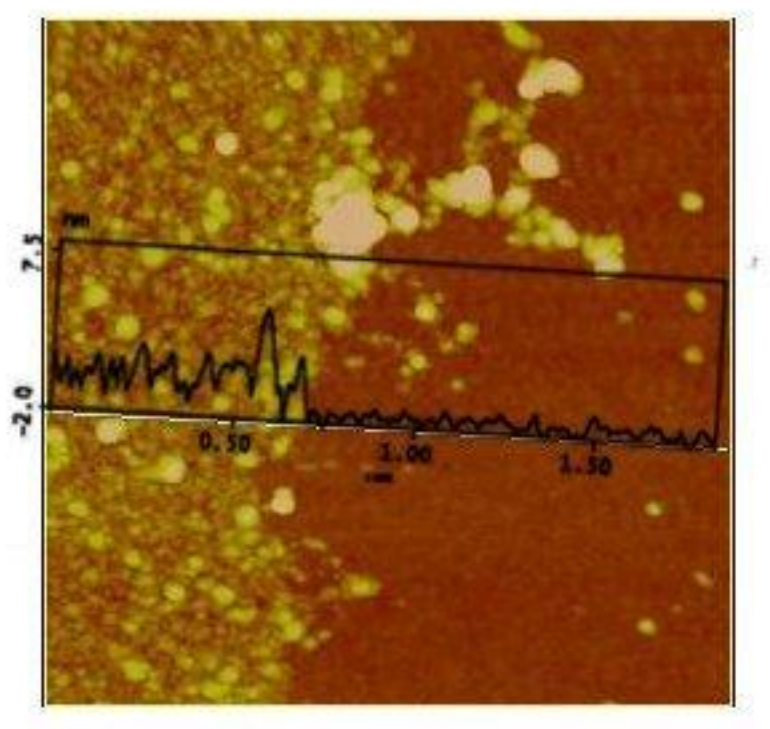


Figure 3.36: Thin MoS<sub>2</sub> film deposited on a silicon wafer from a liquid/liquid interface.

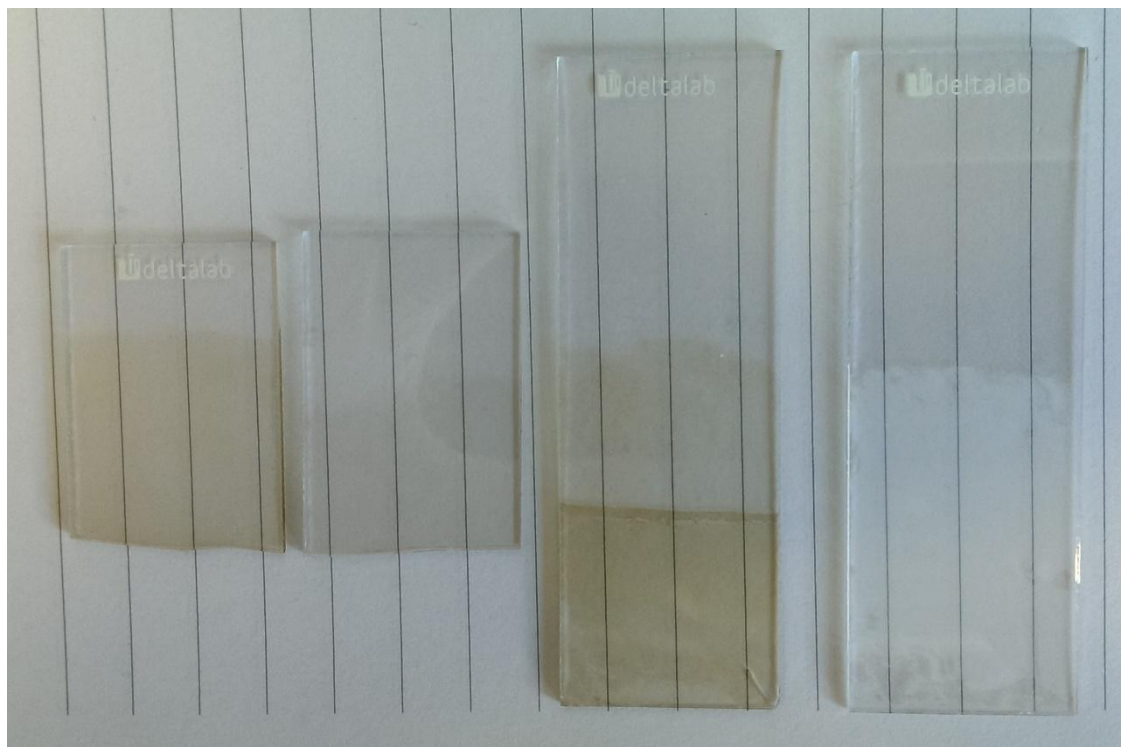


Figure 3.37: Thin MoS<sub>2</sub> films deposited on glass slides. Background ruled paper, line spacing 7 mm approximately.

### 3.6.2 Deposition of MoS<sub>2</sub> films on sacrificial NaCl wafers

We used the method described in chapter 1.1.6 to deposit compact MoS<sub>2</sub> films on NaCl wafers. In order to prevent the dissolution of the wafers, acetonitrile was used instead of water as a subphase. MoS<sub>2</sub> was exfoliated by a previously reported method of mixed solvents with 40% vol. Ethanol in water and was centrifuged at 4000 rpm for an hour to remove unexfoliated material. The films were then brought to the liquid/liquid interface by mixing the supernatant dispersions with hexane, isopropyl alcohol, and by shaking in a centrifuge flask (Figure 3.38). The films were then transported (concentrated) by pipette to an acetonitrile/hexane interface in a beaker. This transfer was repeated to further minimise the water content in the acetonitrile phase (Figure 3.39). After that the films can be deposited by simply lifting the substrates from acetonitrile through the interface. The photographs and micrographs of the wafers after the deposition can be seen in Figure 3.40: and Figure 3.41 respectively. The wafer surface remains undissolved with crystal edges still visible in figure after the deposition and a homogeneous film is deposited. On the contrary it is impossible to form films from an aqueous subphase, due to water dissolution of the wafers.

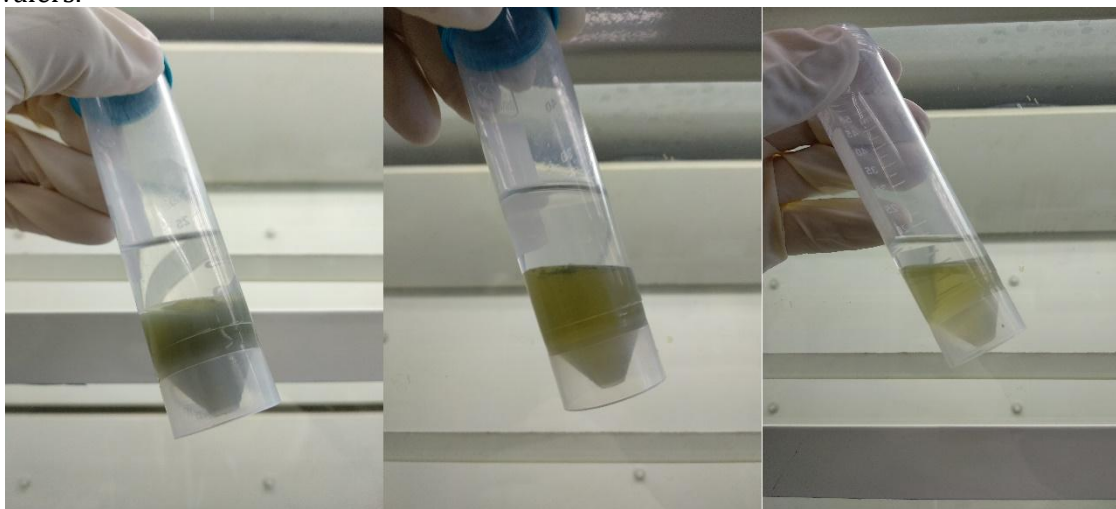


Figure 3.38: MoS<sub>2</sub> nanoparticle film aggregating to water/hexane interface. The process is facilitated by introduction of a few drops of isopropyl alcohol.

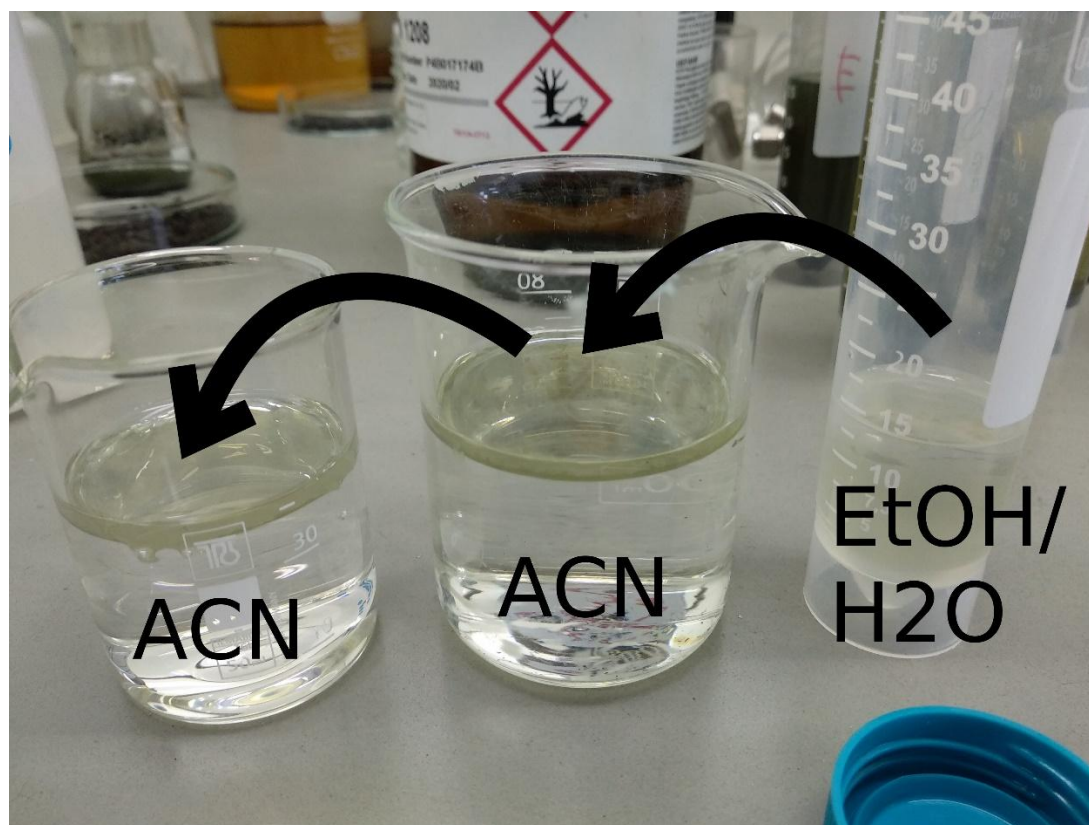


Figure 3.39: MoS<sub>2</sub> nanoparticle film transfer. The film (green) is lifted from one beaker to another with a pipette. In order to reduce the water concentration in the subphase the process is repeated.

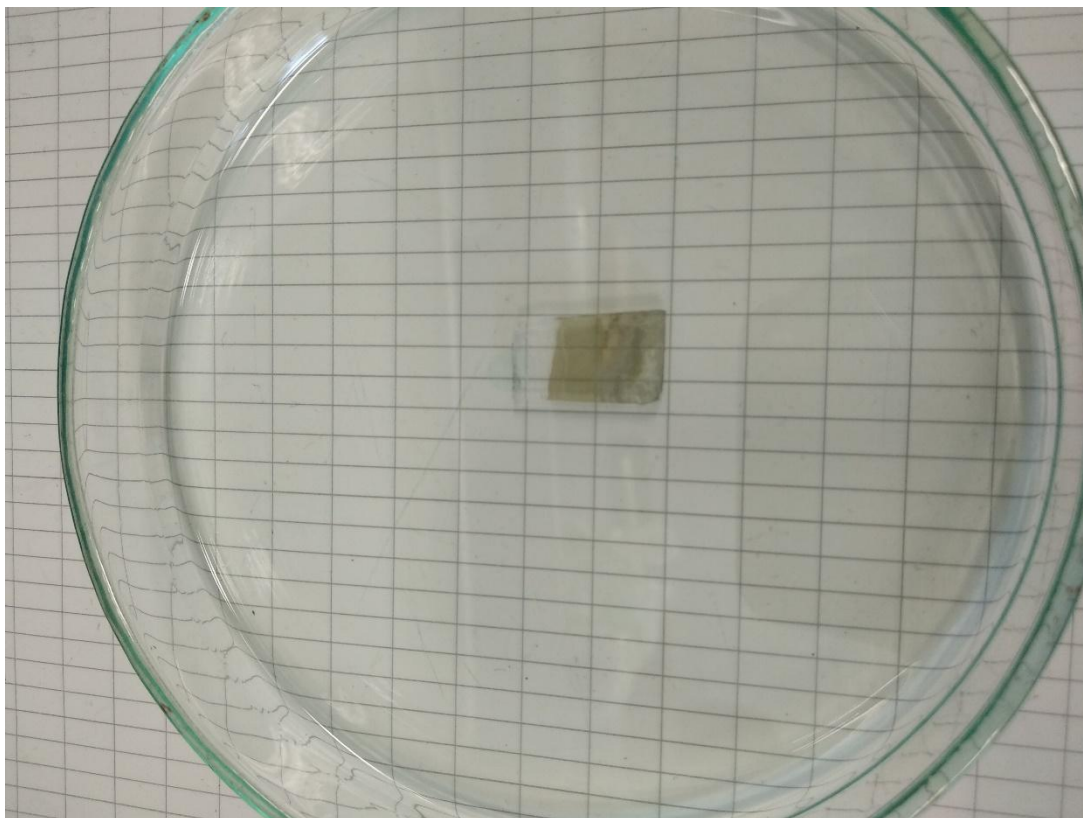


Figure 3.40: MoS<sub>2</sub> film deposited on a NaCl wafer.

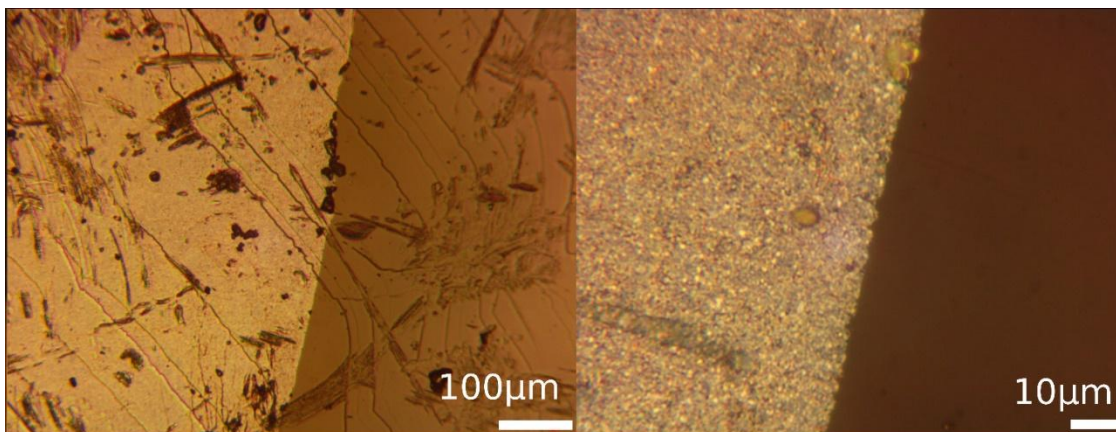


Figure 3.41: Optical micrograph of a MoS<sub>2</sub> film on a NaCl wafer. The micrographs show the same film edge in different magnification.

The films deposited on sacrificial wafers can be annealed at high temperatures (NaCl only melts at 801 °C) or chemically treated, and can be subsequently easily deposited on water surface by dissolution of the NaCl substrate and transferred on a substrate of choice.

### 3.7 Oxidation of Expanded MoS<sub>2</sub>

MoO<sub>3</sub> is an oxide of molybdenum that has been studied in detail for its potential application as electrodes [126] charge transport layer in LEDs and solar cells, [127], catalysts. etc. It can be synthesised by simply heating molybdenum powder in the air at 600 °C [128].

After confirming the expansion did not significantly alter the physical properties of the MoS<sub>2</sub> crystals (chapter 3.2 and 3.3), we proceeded with expansion at higher temperatures. The

goal of these experiments was to determine whether the crystals – which we expected to oxidise – would keep the characteristic accordion shape. We chose to investigate the expansion at 600 °C, since at higher temperatures MoO<sub>3</sub> becomes increasingly volatile, and destruction of the eMoS<sub>2</sub> structure was expected. The iMoS<sub>2</sub> samples were prepared as described in previous chapters. They were intercalated by 1:6 molar mixture of NaOH/hydrazine hydrate and TBAOH in excess amount and left to react for 24h. After that the samples were washed with deionised water and dried for 12h.

The iMoS<sub>2</sub> was then introduced into a furnace heated to 600 °C and left to react with the air for different periods of time. The resulting crystals were investigated by SEM (Figure 3.42) and Raman Spectroscopy (Figure 3.43).

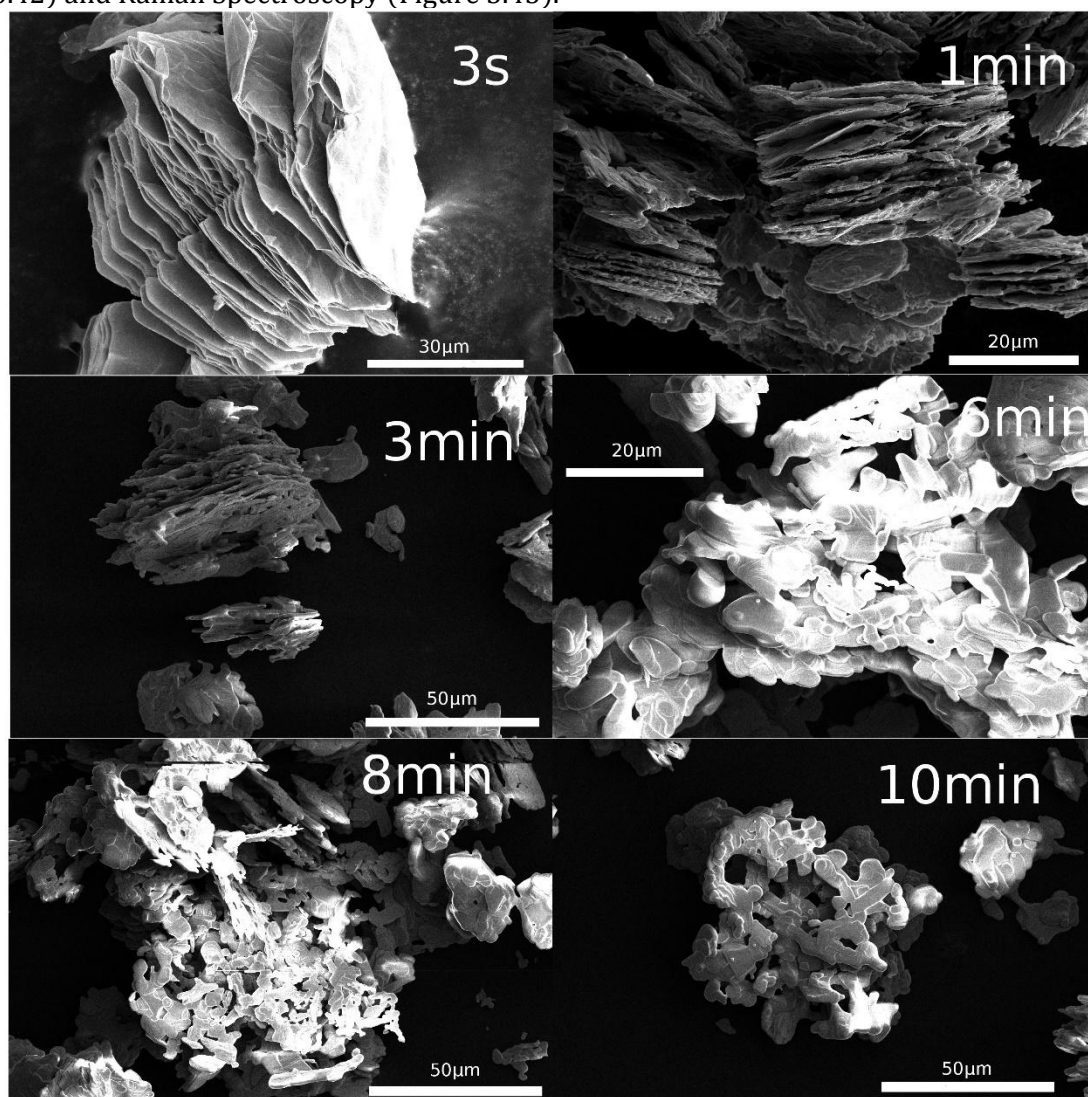
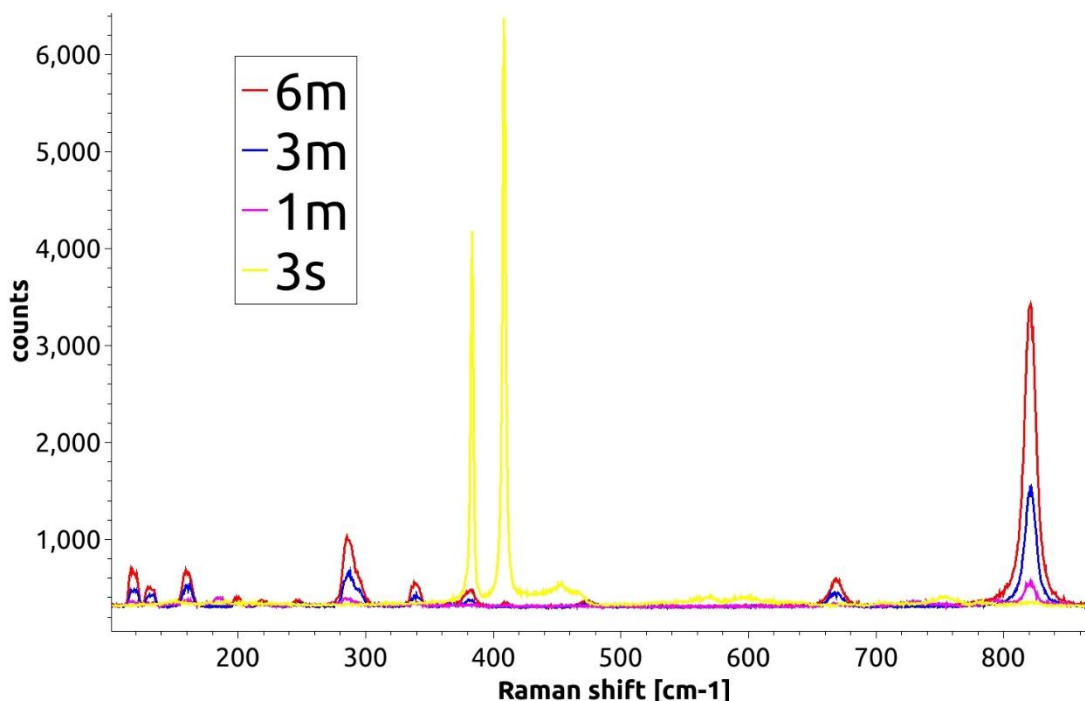


Figure 3.42: iMoS<sub>2</sub> expanded at 600 °C for different periods of time.

Figure 3.43: Raman spectra of oxidised eMoS<sub>2</sub>.

The results depicted in the figure confirm that the samples become increasingly oxidised. The peaks in the Raman spectra assigned to MoO<sub>x</sub> [128] become increasingly pronounced as the characteristic MoS<sub>2</sub> peaks disappear. Interestingly, a fast expansion of 3s still produces non-oxidised eMoS<sub>2</sub>, however in a minute no MoS<sub>2</sub> signal remains and the oxide signal is becoming increasingly stronger.

SEM micrographs show that the low density/high surface area structure remains preserved at lower oxidation times (even up to a few minutes), however, eventually the structure disappears.

We conclude that the iMoS<sub>2</sub> can be transformed to a low density/high surface material by a fast, cheap and scalable reaction in a furnace. The expanded material retains the shape of its parent compound - eMoS<sub>2</sub> - if the reaction time is kept short enough, and the results also show that it is possible to find a reaction time at which the material is completely oxidised, yet it retains its high surface area structure. This is a completely novel morphology in Molybdenum oxide, and we expect it to be of importance in various applications. We also note that partially oxidised MoS<sub>2</sub> has already been shown as a candidate in various applications as well. Finally, this simple reaction also testifies to versatile uses of expandable MoS<sub>2</sub>.



## Chapter 4

### Expansion of $\text{TiS}_2$ and $\text{TaS}_2$

$\text{TiS}_2$  and  $\text{TaS}_2$  have been reported to intercalate hydrazine as well as various other amines [44]. However, in our preliminary experiments we noticed that both materials expand spontaneously when in contact with aqueous hydrazine. Due to the similarity of their reactions with hydrazine they are discussed together in this chapter. A rapid expansion is depicted in a sequence of time lapse photographs (Figure 4.1) and Video 4.1.

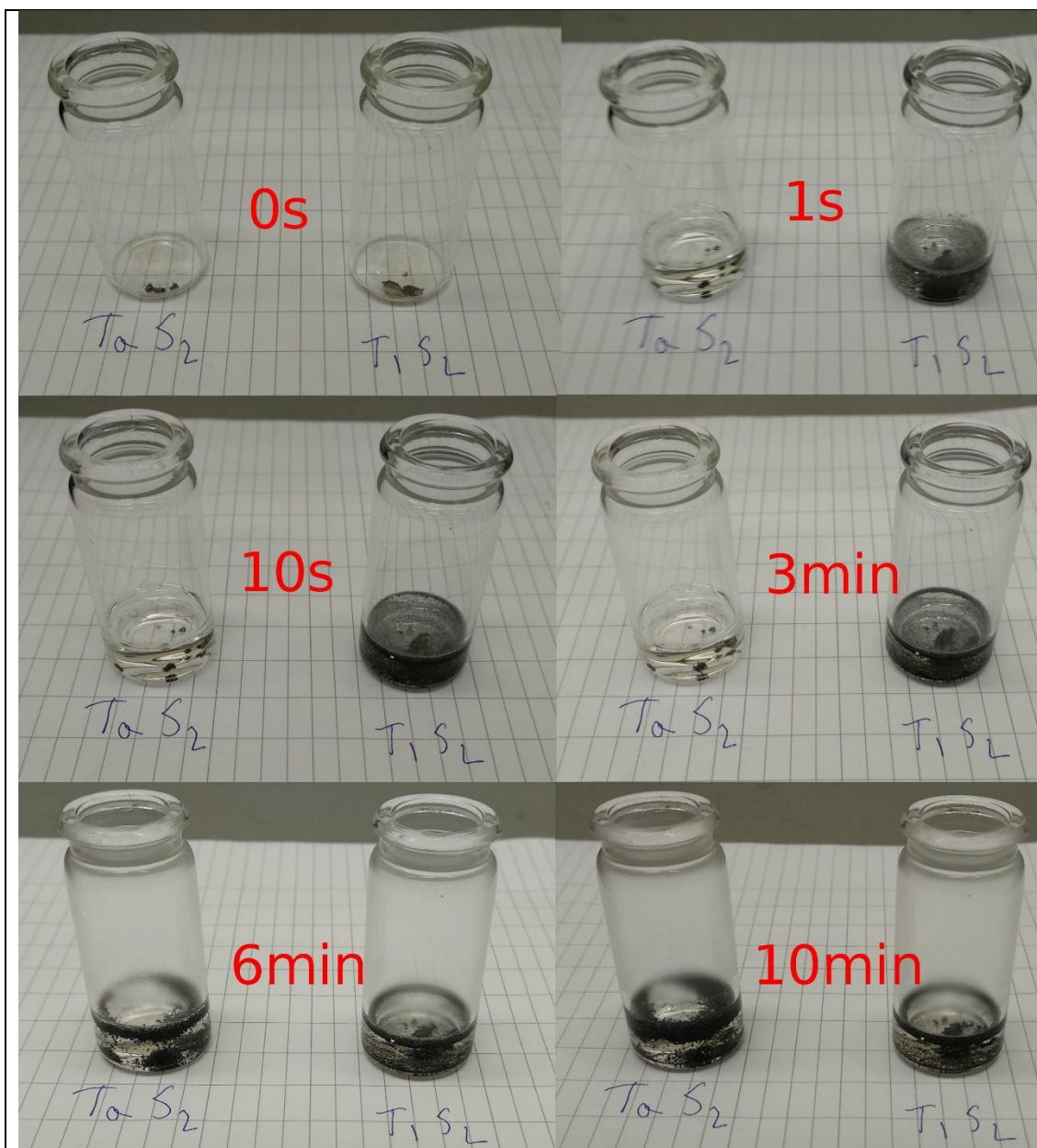


Figure 4.1: Time-lapse of  $\text{TaS}_2/\text{TiS}_2$  expansion in hydrazine hydrate.

From Video 4.1 and Figure 4.1 it is clearly visible that the reaction of  $\text{TaS}_2$  in the case begins slowly and subsequently to accelerate, which is accompanied by breaking of larger crystals. After this phase the expansion slows down, and after a few minutes no further expansion is visible. Gas formation in the form of bubbles also indicates that the room temperature reaction follows a similar path to that of  $\text{MoS}_2$  upon heating.  $\text{TiS}_2$ , on the other hand, expands more rapidly, and the reaction is completed in a few seconds. Upon contact with hydrazine both compounds change their colour from golden to black. This change of colour is reversible after washing and drying in line with previous observations [44].

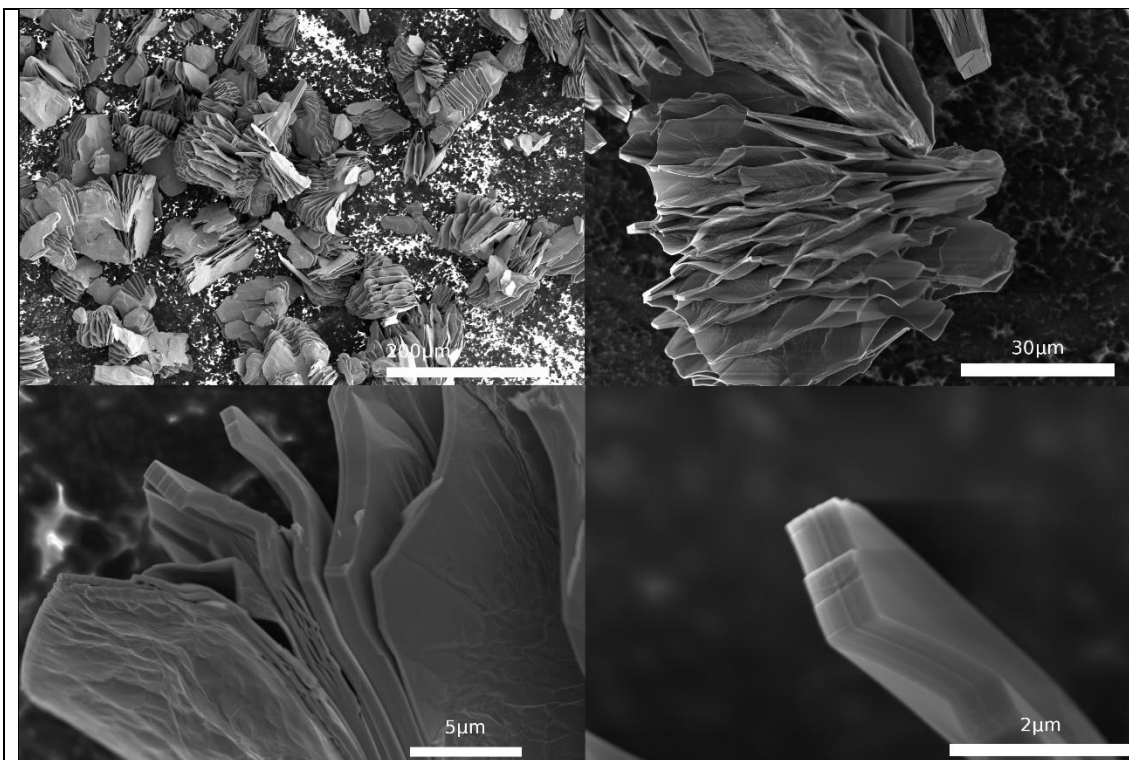


Figure 4.2: Hydrazine-expanded  $\text{TiS}_2$  crystals under progressively bigger magnification (in order from left to right, top to bottom).

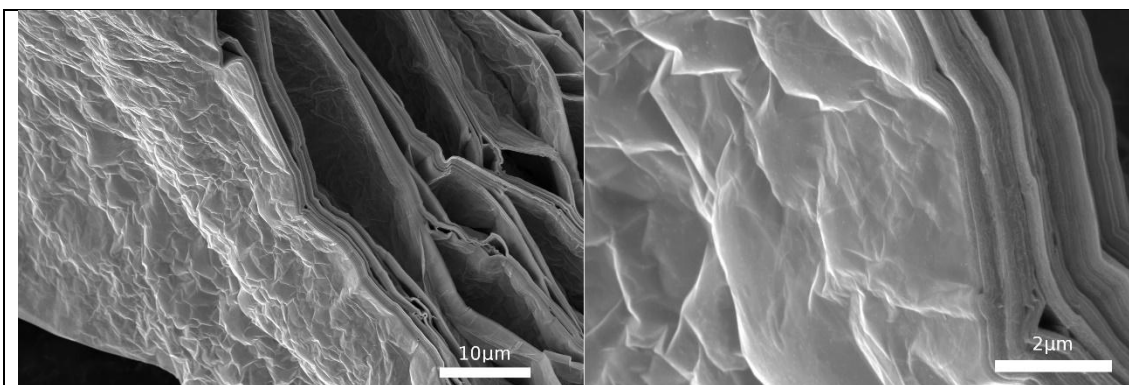


Figure 4.3: Hydrazine-expanded  $\text{TaS}_2$  in two magnifications.

The expanded flakes (after no further expansion takes place) were further characterised by SEM microscopy. The flakes are presented in Figure 4.2 and Figure 4.3. Although the  $\text{TiS}_2$  and  $\text{TaS}_2$  expanded crystals show some features of similar morphology as expanded  $\text{MoS}_2$ , they are expanded to a lesser degree than expanded  $\text{MoS}_2$ . This is probably due to the difference in expansion reaction kinetics; while intercalated  $\text{MoS}_2$  is expanded rapidly in a few seconds, the  $\text{TiS}_2$  and  $\text{TaS}_2$  expansion reaction takes longer (several minutes). We also notice that the crystals shrink to some extent after the washing and drying process – this does not seem to be the case with  $\text{MoS}_2$ .

## 4.1 Exfoliation of $\text{TiS}_2/\text{TaS}_2$

In order to evaluate the effect of hydrazine on the efficiency of exfoliation, we firstly repeated liquid phase exfoliation of  $\text{TaS}_2$  by standard procedures [55]. All the samples were sonicated for an hour in an ultrasonic bath and were frequently rotated since sonic baths

have hot spots, points of high intensity, and we wanted to prevent systematic errors due to different conditions of exfoliation. After the exfoliation, the samples were centrifuged first at 2000 rpm for 15 min in order to remove large non-exfoliated material and then at 4500 rpm for 30 min in order to select thinner nanoflakes. The resulting suspensions before (left) and after (right) the second centrifugation step can be seen in Figure 4.4.

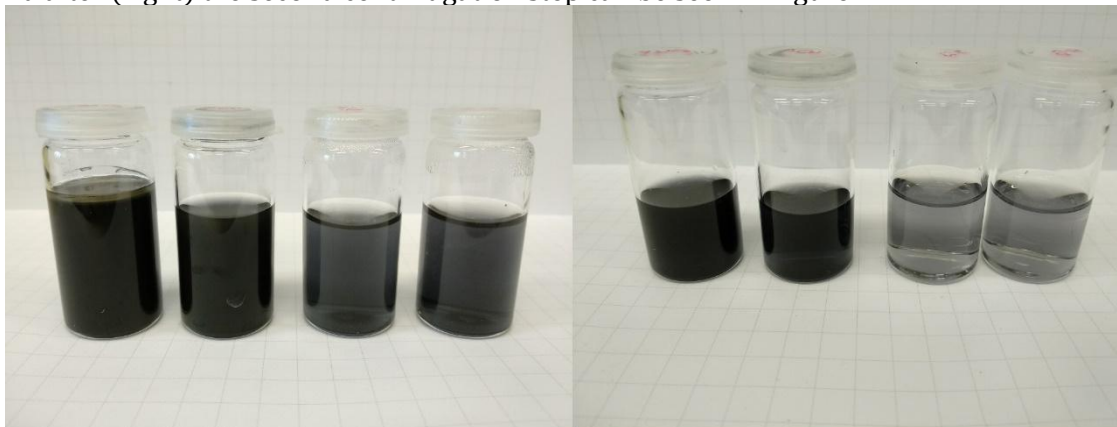


Figure 4.4: Exfoliated TaS<sub>2</sub> suspension in different solvents before (left) and after (right) two centrifugation steps, solvents from left to right (in both photos): saturated aqueous solution of n-butanol, acetonitrile, 5% vol. aqueous solution of isopropyl alcohol, water.

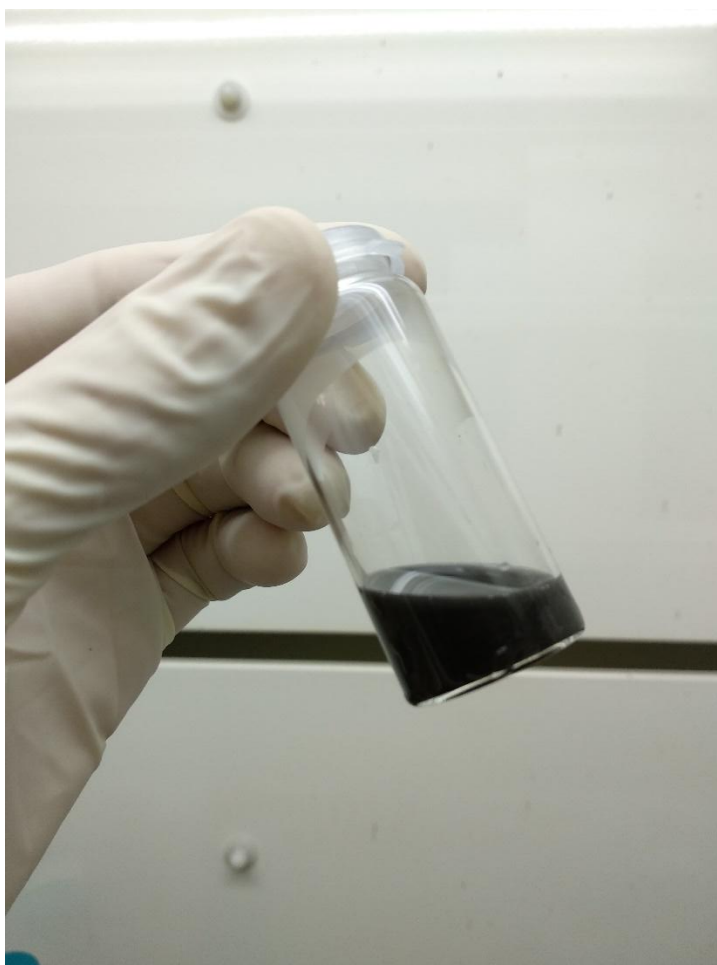


Figure 4.5: Dispersion of TaS<sub>2</sub> sonicated in hydrazine hydrate.

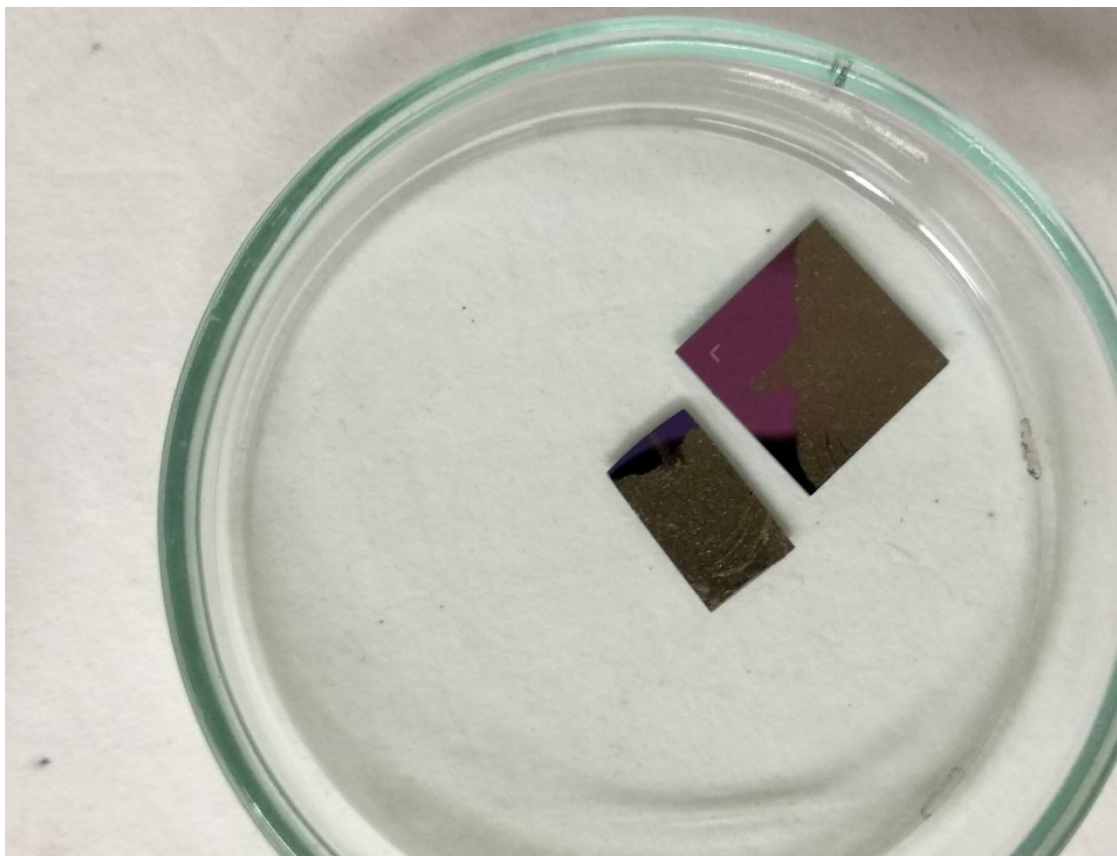


Figure 4.6:  $\text{TaS}_2$  films deposited on silica wafers.

Although the expanded  $\text{TaS}_2$  proved harder to exfoliate into nanoflakes than native materials, it does easily delaminate to thicker flakes if the crystals are briefly sonicated while expanding in hydrazine (Figure 4.5). The resulting flakes were deposited on silica wafers (Figure 4.6) and were investigated by AFM. The majority of flakes produced by this method are around 100 layers thick (50-100nm) and microns in lateral dimension (Figure 4.7) with a smaller number of thinner flakes (<5nm) are presented in Figure 4.8.

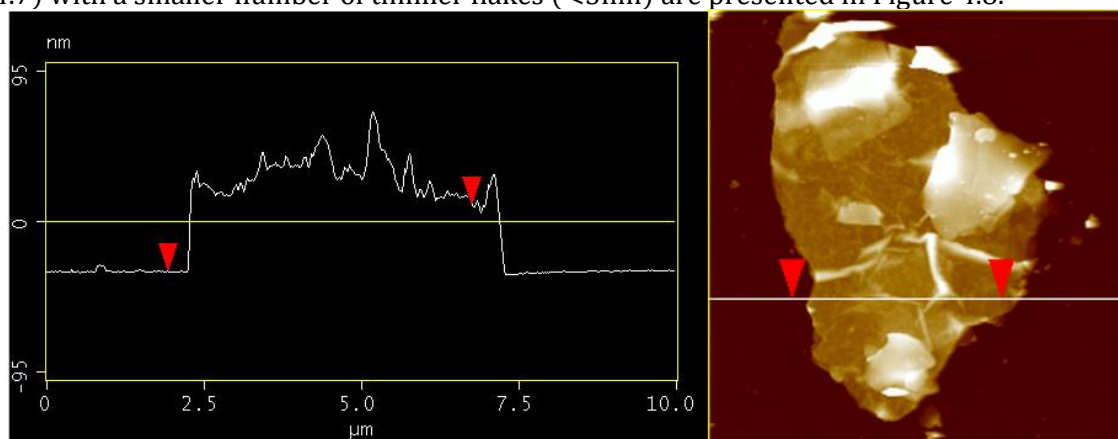


Figure 4.7: Thicker and larger  $\text{TaS}_2$  flakes produced by sonicating hydrazine expanded  $\text{TaS}_2$ .

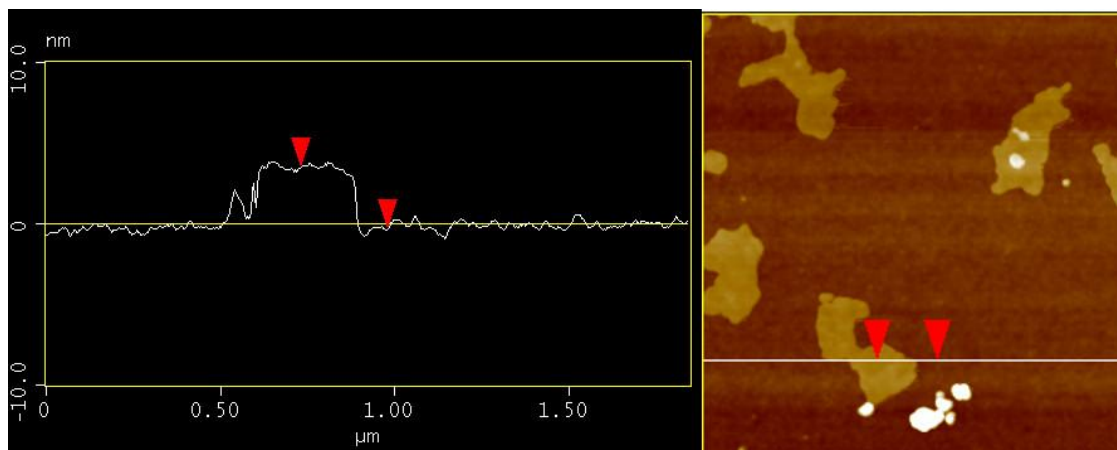


Figure 4.8: Thinner  $\text{TaS}_2$  flakes produced by sonicating hydrazine expanded  $\text{TaS}_2$ .

In conclusion both  $\text{TiS}_2$  and  $\text{TaS}_2$  crystals were shown to be highly reactive in hydrazine hydrate, and expand in the  $c$  direction. However, the expansion was slower and to a lesser degree compared to the rapid thermal expansion of intercalated  $\text{MoS}_2$ , with  $\text{TaS}_2$  expanding slower and to a lesser degree than with  $\text{TiS}_2$ . We assume that this is a consequence of a relatively slower reaction comparing to  $\text{iMoS}_2$  expansion.

Unlike  $\text{MoS}_2$ , both expanded  $\text{TaS}_2$  and expanded  $\text{TiS}_2$  contract to some degree when they are washed with water and left to dry in air atmosphere. This result is to be expected since  $\text{TiS}_2$  and  $\text{TaS}_2$  reportedly intercalate hydrazine reversibly [47] with water co-intercalating in the interplanar space. After the washing, some percentage of intercalated hydrazine leaves the crystals along with co-intercalated water and this leads to observable shrinkage. While the crystals expand partially due to gas formation – visible in  $\text{MoS}_2$ ,  $\text{TiS}_2$  and  $\text{TaS}_2$ , this reversible swelling is observed only in the latter two.

Although the expansion in aqueous hydrazine failed to improve the exfoliation efficiency into dispersible nanoflakes, it has proved practical in providing a fast route to exfoliating larger and thicker (100 nm to 1 μm) flakes. These were deposited on silicon dioxide wafers from a liquid-liquid interface as described in chapter 3.6 and may be useful for different applications where a very low layer number is not necessary, if not outright undesirable. Two such applications might be the production of thicker  $\text{TiS}_2$  electrodes and the manufacture of devices based on  $\text{TaS}_2$  as the active (phase change memory) material, which require thicker flakes to avoid the influence of the substrate.

We suspect that the reason for our inability to improve the exfoliation efficiency lies in the fact that crystals are not fully expanded after the reaction with hydrazine. In fact, SEM micrographs reveal thicker slabs (hundreds of nanometers thick) still relatively intact after the expansion, and the majority of flakes (visible in AFM micrographs) also fall into this category. In particular, for  $\text{TaS}_2$ , a large fraction of the gas formed upon intercalation seems to leave the crystals again before it can contribute effectively to the expansion.

## Chapter 5

# Conclusions

The present thesis presents several pathways towards expanding different TMD compounds with softer methods than reported previously. For MoS<sub>2</sub>, a representative of the semiconducting group 6 TMDs, this treatment consisted in the intercalation (from several hours to several days) with quaternary ammonium salts in a hydrazine hydrate/NaOH solution. The dried intercalated compounds expand within seconds upon heating to 300 °C, the temperature that rapidly decomposes the QA salts, but not MoS<sub>2</sub>. To efficiently expand the crystallites, the formation of the gases from the decomposition of the organic intercalants must be faster than their diffusion out of the crystals. This puts a lower limit to the size of the crystallites that can be expanded, since at some crystal dimension the paths that the gas molecules must travel to escape the crystal will get so small, that virtually all of the molecules will manage to escape before there is a chance for the pressure to build up and inflate the crystals. For MoS<sub>2</sub> reacting with hydrazine this limits the expansion to crystals larger than 100 µm. Among the QA salts tested, TBAOH proved to be the most effective. It results in accordion-shaped expanded material with a surface area of 2.6 m<sup>2</sup>/g, corresponding to the surface of 200 nm thick MoS<sub>2</sub>, with pore sizes limited to above 100 nm. The expansion does not appreciably change the chemical composition compared to the starting material before intercalation, but due to the expansion the average crystallite size decreases by roughly the factor 2. The synthesis of expandable MoS<sub>2</sub> is important since the material is a true analogue of expandable graphite - a material used on industrial scale. The analogy is even more complete since MoS<sub>2</sub> - like graphite - is a mineral available in bulk quantities. The methods we developed are fast, require minimal equipment and small amounts of chemicals, making eMoS<sub>2</sub> an intriguing material for applications currently using expanded graphite.

Expansion of TBAOH intercalated MoS<sub>2</sub> can be induced not only via heating, but also via e-beam irradiation. The somewhat serendipitous observation during the study of iMoS<sub>2</sub> in an SEM presents both an alternative pathway for expansion as well as an opportunity to study the expansion process in more detail. In particular, the expansion occurs only in the restricted volume that receives a sufficient flux of electrons. This volume depends superlinearly on the energy of the electrons, as confirmed not only by the observed expansion at different accelerating voltages in the SEM, but also by Monte Carlo simulations of the electron propagation. The penetration depth depends also on the angle of incidence of the electron beam relatively to the crystal plane. When a crystallite, which usually has its (001) crystal planes oriented parallel to the substrate, starts expanding at the top, the expansion speed is typically non-uniform across the circumference, leading to tilting, which in turn accelerates the expansion by facilitating electron penetration from the sides. We believe this is the first recorded observation of expansion of layered materials by electron irradiation, and although an expansion in SEM seems impractical, comparable and higher flux densities and accelerating voltages can be achieved in a simple electron gun – like in old cathode ray tube monitors. We believe that the construction of a simple e-beam expansion setup would make it possible to further investigate the e-beam expansion of MoS<sub>2</sub> and analogous layered materials.

Another advantage of expansion in the SEM, especially for research purposes, is that it only requires small amounts of material. We used it to test the expandability of compounds resulting from the use of different amounts of hydrazine hydrate and TBAOH to establish the lowest threshold quantity necessary, in order to minimise the use of hydrazine and its many hazards.

To assess possible applications of expanded MoS<sub>2</sub>, we pressed it into flexible sheets and used it as precursor material for liquid exfoliation, and expanded iMoS<sub>2</sub> at 600 °C in the air to yield MoO<sub>3</sub> of the same accordion-like morphology as eMoS<sub>2</sub>. This is a novel morphology of MoO<sub>3</sub> with possible application in electrodes and batteries – a field where high specific surface materials are desirable.

Although we did not achieve higher concentrations of dispersed MoS<sub>2</sub> nanoparticles when dispersing eMoS<sub>2</sub> compared to MoS<sub>2</sub>, we believe this could be due to slight chemical changes of eMoS<sub>2</sub>, rendering existing exfoliation methods less efficient. We believe that this problem could be addressed by investigating other solvents or surfactants in the future.

Besides expanding MoS<sub>2</sub>, we also improved an existing method for deposition from liquid dispersion, based on the concentration of flakes at the interface between two immiscible liquids. Separating the sequestration and deposition receptacles by film transfer with a pipette allows to independently choose the deposition liquids for their respective purpose. As a proof of concept, we showed high-quality film deposition on several hydrophilic substrates, including sacrificial NaCl substrates that we subsequently dissolved in water, which is an important step towards free-standing TMD films. This was only achievable by film transfer from the exfoliation medium (aqueous solution) to pure acetonitrile by several subsequent film transfers. We believe our modifications make this deposition method even more versatile.

Contrary to MoS<sub>2</sub>, TiS<sub>2</sub> and TaS<sub>2</sub> expand spontaneously upon contact with hydrazine hydrate at room temperature. However, compared to separate intercalation and expansion steps, the simultaneous action of both processes results in a less effective expansion. Nevertheless, such expanded material can be more easily cleaved into sub-100-nm flakes via very short ultrasonication compared to unexpanded starting material. This type of flakes is advantageous for use as electrodes (in the case of TiS<sub>2</sub>) or as the active material for fast phase change memories (TaS<sub>2</sub>). Interestingly, the expansion by hydrazine did not help to increase the concentration of TiS<sub>2</sub>/TaS<sub>2</sub> nanoflakes after prolonged sonication. This might be a consequence of chemical change in the materials, since hydrazine is known to partially reduce the TiS<sub>2</sub>/TaS<sub>2</sub>. Consequently, the standard exfoliation media proved ineffective. We believe that it might be possible to circumvent this problem by exploring a wider array of possible solvents that might be more suitable for exfoliation and stabilisation of reduced TiS<sub>2</sub>/TaS<sub>2</sub>.

## Appendix A

# Other Dichalcogenides

### A.1 MoSe<sub>2</sub>, WS<sub>2</sub>, SnS<sub>2</sub>

In order to broaden the scope of the study we also tried to intercalate two other widely investigated group 6 transition metal dichalcogenides (MoSe<sub>2</sub> and WS<sub>2</sub>), and a poor metal dichalcogenide (SnS<sub>2</sub>)

The MoS<sub>2</sub> analogues were treated in same conditions as MoS<sub>2</sub>, described in chapter 3.1. The first observation was the obvious absence of bubbles, indicating less vigorous reaction with hydrazine in alkaline conditions relative to the reaction with MoS<sub>2</sub> in the same conditions. After the reaction time of one day the crystals were washed and dried, and were investigated for expansion under SEM. Micrographs for MoSe<sub>2</sub> and WS<sub>2</sub> observed before and after irradiation are seen in Figure A.5.1 and Figure 5.2, respectively. The materials failed to expand indicating an unsuccessful intercalation.

Tin disulphide was also treated in the same manner as MoS<sub>2</sub>, however the compound does not seem to react in the same way, and hence no gas bubbles are observed. A greater hindrance however is the fact that the compound slowly dissolves in alkaline conditions.

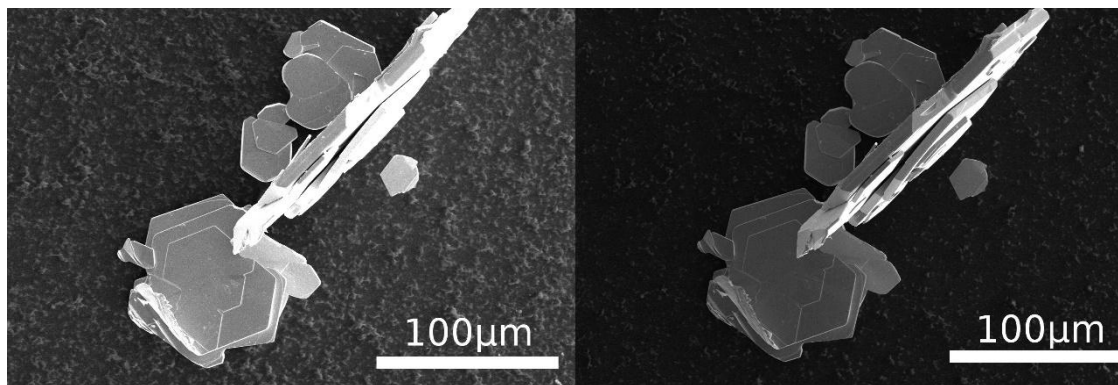


Figure A.5.1: Intercalated MoSe<sub>2</sub> before and after e-beam irradiation.

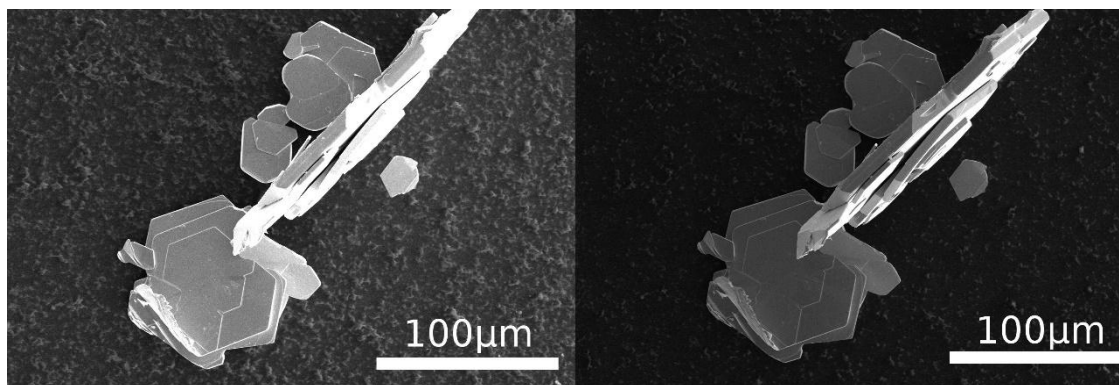


Figure A.5.2: Intercalated MoSe<sub>2</sub> before and after e-beam irradiation.

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## Publications Related to the Thesis

Matej Prijatelj, Nataša Čelan Korošin, Tomaž Skapin, Victor Vega-Mayoral, Daniele Vella, Janez Kovač, Dragan Mihailović, Christoph Gadermaier, "Preparation of air-stable expandable MoS<sub>2</sub> and rapid expansion by low temperature heating and electron beam irradiation" *Materials Letters*, vol. 218, str. 229-232, 2018

## Journal Articles

Victor Vega Mayoral, Tetiana Borzda, Daniele Vella, Matej Prijatelj, Eva Arianna Aurelia Pogna, Claudia Backes, Jonathan N. Coleman, Giulio Cerullo, Dragan Mihailović, Christoph Gadermaier, "Charge trapping and coalescence dynamics in few layer MoS<sub>2</sub>", *2D materials*, vol. 5, no. 1, str. 015011-1-015011-8, 2018

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# Biography

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