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Liquid Exfoliation of Molybdenum Disulfide for Inkjet Printing

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To Hannah, Ralf, Angela & Birgitta
ABSTRACT

Since the discovery of graphene, substantial effort has been put toward the synthesis and production of 2D materials. Developing scalable methods for the production of high-quality exfoliated nanosheets has proved a significant challenge. To date, the most promising scalable method for achieving these materials is through the liquid-based exfoliation (LBE) of nanosheets in solvents. Thin films of nanosheets in dispersion can be modified with additives to produce 2D inks for printed electronics using inkjet printing. This is the most promising method for the deposition of such materials onto any substrate on an industrial production level.

Although well-developed metallic and organic printed electronic inks exist on the market, there is still a need to improve or develop new inks based on semiconductor materials such as transition metal dichalcogenides (TMDs) that are stable, have good jetting conditions and deliver good printing quality.

The inertness and mechanical properties of layered materials such as molybdenum disulfide (MoS$_2$) make them ideally suited for printed electronics and solution processing. In addition, the high electron mobility of the layered semiconductors, make them a candidate to become a high-performance semiconductor material in printed electronics. Together, these features make MoS$_2$ a simple and robust material with good semiconducting properties that is also suitable for solution coating and printing. It is also environmentally safe.

The method described in this thesis could be easily employed to exfoliate many types of 2D materials in liquids. It consists of two exfoliation steps, one based on mechanical exfoliation of the bulk powder utilizing sandpaper, and the other in the liquid dispersion, using probe sonication to liquid-exfoliate the nanosheets. The dispersions, which were prepared in surfactant solution, were decanted, and the supernatant was collected and used for printing tests performed with a Dimatix inkjet printer.

The printing test shows that it is possible to use the MoS$_2$ dispersion as a printed electronics inkjet ink and that optimization for specific printer and substrate combinations should be
Abstract

performed. There should also be advances in ink development, which would improve the drop formation and break-off at the inkjet printing nozzles, the ink jetting and, consequently, the printing quality.

**Key words:** MoS$_2$, TMD, thin films, inkjet printing, industrial printing, 2D inks, liquid exfoliation, cheap flexible electronics, printed electronics, thin films carrier mobility, large-area electronics, graphene analogues, solar cells.
SAMMANFATTNING

Sedan upptäckten av grafen har mycket arbete lagts på framställning och produktion av 2D-material. En viktig uppgift har varit att ta fram skalbara metoder för produktion av högkvalitativa nanosheets via exfoliering. Den mest lovande skalbara metoden hittills har varit vätskebaserad exfoliering av nanosheets i lösningsmedel. Tunna filmer av nanosheets i dispersion kan anpassas med hjälp av tillsatser och användas för tillverkning av halvledare strukturer med inkjet-skrivare, vilket är den mest lovande metoden för på en industriell produktionsnivå belägga den typen av material på substrat.

Även om det finns välutvecklade metalliska och organiska bläck för tryckt elektronik, så finns det fortfarande ett behov av att förbättra eller utveckla nya bläck baserade på halvledarmaterial som t.ex. TMD, som är stabila, har goda bestrykningsegenskaper och ger bra tryckkvalitet. Den inerta naturen tillsammans med de mekaniska egenskaperna som finns hos skiktade material, som t.ex. molybdendisulfid (MoS$_2$), gör dem lämpliga för flexibel elektronik och bearbetning i lösning. Dessutom gör den höga elektronmobilheten i dessa 2D-halvledare dem till en stark kandidat som halvledarmaterial inom tryckt elektronik. Det betyder att MoS$_2$ är ett enkelt och robust material med goda halvledaregenskaper som är lämpligt för bestrykning från lösning och tryck, och är miljömässigt säker.

Den metod som beskrivs här kan med fördel användas för att exfoliera alla typer av 2D-material i lösning. Exfolieringen sker i två steg; först mekanisk exfoliering av torr bulk med sandpapper, därefter används ultraljudsbehandling i lösning för att exfoliera nanosheets. De dispersioner som framställs i lösning med surfaktanter dekanterades och det övre skiktet användes i trycktester med en Dimatix inkjet-skrivare.

Tryckprovet visar att det är möjligt att använda MoS$_2$-dispersion som ett inkjet-bläck och att optimera för särskilda skrivar- och substratkombinationer borde göras, såsom förbättring av bläcksammansättningen med avseende på droppbildning och break-off vid skrivarmunstycket, vilket i sin tur skulle förbättra tryckkvaliteten.
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Viviane Forsberg. September 5, 2016
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<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<td>ALD</td>
<td>atomic layer deposition</td>
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<tr>
<td>CE</td>
<td>chemical exfoliation</td>
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<tr>
<td>CIJ</td>
<td>continuous inkjet</td>
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<tr>
<td>CMC</td>
<td>critical micelle concentration</td>
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<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
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<td>DLS</td>
<td>dynamic light scattering</td>
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<tr>
<td>DLVO</td>
<td>Derjaguin, Landau, Verwey and Overbeek</td>
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<tr>
<td>DMF</td>
<td>dimethylformamide</td>
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<tr>
<td>DMP-2831</td>
<td>Dimatix material printer 2831</td>
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<tr>
<td>DoD</td>
<td>drop-on-demand</td>
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<td>EL</td>
<td>electrochemical lithiation</td>
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<td>EtOH</td>
<td>ethanol</td>
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<td>FET</td>
<td>field effect transistor</td>
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<tr>
<td>FTIR</td>
<td>fourier transform infrared spectroscopy</td>
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<tr>
<td>LBE</td>
<td>liquid-based exfoliation</td>
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<td>LI</td>
<td>lithium intercalation</td>
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<tr>
<td>ME</td>
<td>mechanical exfoliation</td>
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<tr>
<td>MoS₂</td>
<td>molybdenum disulfide</td>
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<tr>
<td>MOSFET</td>
<td>metal oxide semiconductor field effect transistor</td>
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<tr>
<td>NMP</td>
<td>n-methyl pyrrolidone</td>
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Acronyms and Abbreviations

PE polyethylene
PET polyethylene terephthalate
PSD particle size distribution
PVDF poly(vinylidene fluoride)
PZT piezo technology

RFID radio-frequency identification
SDS sodium dodecyl sulfate
SE shear exfoliation
SEM scanning electron microscopy

TEM transmission electron microscopy
TFT thin-film transistor
TIJ thermal inkjet
TMD transition metal dichalcogenide

VMD visual molecular dynamics

XPS x-ray photoelectron spectroscopy
XRD x-ray diffraction

ZP zeta potential
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This thesis is based on the following publications, herein referred to by their Roman numerals:

Paper I

**Exfoliated MoS$_2$ in water without additives**


Paper II

**Liquid exfoliation of layered materials in water for inkjet printing**

Viviane Forsberg, Renyun Zhang, Henrik Andersson, Joakim Bäckström, Christina Dahlström, Magnus Norgren, Britta Andres and Håkan Olin, *Journal of Imaging and Science Technology, 60 (4), 2016* .......................................................... 77

Related papers (not included in this thesis):

**Thermally reduced kaolin-graphene oxide nanocomposites for gas sensing**

Renyun Zhang, Viviane Forsberg, Magnus Hummelgård, Britta Andres, Sven Forsberg, Mattias Andersson and Håkan Olin, *Scientific Reports, 5, 2015.*

**Exfoliated MoS$_2$ for paper based supercapacitors and photodetectors**

Viviane Forsberg, Britta Andres, Renyun Zhang, Magnus Hummelgård, Sven Forsberg, Kenichi Shimizu and Håkan Olin,
List of Papers


Exfoliated Layered Materials for Digital Fabrication

Papers published under the topic of Hybrid Printing (not included in this thesis).
Supervisors: Docent Jonas Örtegren, Dr. Mattias Andersson and Prof. Magnus Norgren.

Hybrid printing - print quality mechanisms when offset and inkjet are combined

Hybrid printing: paper media for combined flexographic and inkjet printing

Flexographic ink film’s resistance to inkjet ink’s solvent flow in Hybrid Printing
INTRODUCTION

1.1 Large-area printed electronics

Printed electronics target simple low-cost devices, for example, radio-frequency identification (RFID) tags or sensors. However, the printing process should also allow for the low-cost production of large-area devices, where substantial need can be seen. In particular a solution is needed that can be used in the production of green energy devices. These energy applications concern both harvesting (solar energy, wind power and thermoelectric generators) and storing energy (supercapacitors and batteries). These devices could be of general use in, for example, the supply and storage of electrical energy for transport systems. They could also serve as end-use-devices for lighting panels or large-area displays.

The requirements for such large-area electronics platforms are hard to meet. We need environmentally friendly materials and processes to develop a substrate suitable for electronics and electronic materials that meet the application requirements. To date, a number of organic [1, 2] and inorganic materials [3, 4] can be employed in the production of large-area electronics. Another important requirement for large-area electronics is the achievement of high electron mobility. However, the low charge carrier mobility of both organic and inorganic materials allows for only low-speed applications. The carrier mobility of organic materials - less than $0.1 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for solution-processed polymers - is several orders lower than that of crystalline silicon [5]. This means that organic transistors are not suitable for high-speed switching, which is necessary, for example, in back-planes that drive large-area displays. Some inorganic materials such as metal oxides are compatible with solution processes, while the silicon variants need vacuum processing. However, both metal oxides and amorphous silicon have only a slightly higher mobility than that of organic semiconductors [3, 4, 6].

Typically, metal nanoparticle inks are employed for conductors, while semiconductor structures are built from organic materials. Flex-
ible substrates vary from polymeric films to photographic papers. There are several printing and coating processes available, including conventional printing methods such as flexography, screen printing, rod coating and inkjet printing. The advantages of using inkjet technology are numerous, but to name a few, the dispersions can be deposited on almost any substrate and at very precise locations because the pattern to be printed is designed digitally, and unlike with conventional techniques, the pattern can be modified easily and printed directly onto the substrate without the need for an intermediate transfer medium [7]. The ink volume used is also significantly smaller than in the conventional printing methods, and the range of substrates that can be printed on is broader.

Another group of materials that might be important in printed electronics is 2D-material, in particular graphene and transition metal dichalcogenide (TMD). One such TMD semiconductor is MoS$_2$, which is an environmentally compatible material suitable for large-scale implementation, as Alharbi et al. [8] show in a comparative analysis to identify abundant and non-toxic binary semiconductor materials. The inertness and mechanical properties of layered materials, including MoS$_2$, might make them ideally suited for flexible electronics and solution processing. Taken together, this means that MoS$_2$ is a simple and robust material with good semiconducting properties that might also be suitable for solution coating and printing. It is also environmentally safe. The higher electron mobility of these TMD materials compared with other printable semiconductors such as the organic ones, make applications using thin films of layered materials such as MoS$_2$ very interesting and promising. Practical applications can be found for these materials in the fields of gas detectors, catalysis, energy storage and solar cells, but so far, the main body of work has focused on single nanosheets [9].

Therefore, the problem is that, although there are well-developed metallic and organic printed electronic inks, there is still a need to improve [10–13] or develop new inks based on semiconductor materials such as TMD, that are stable, have good jetting conditions and deliver good printing quality. To date, the most promising scalable method for achieving this is through the liquid-based exfoliation (LBE) of nanosheets in solvents, which is the first step to obtain thin films
of nanosheets in a dispersion. In some cases, it may be necessary to add additives to improve the printability and jetting performance of those inks. This would open a broad field of research.

Our approach to address these problems was to design dispersions that would allow us to use inkjet printing technology to deposit exfoliated layered material. The TMD used in our studies was the semiconducting MoS$_2$. By successfully achieving this, we could take some steps towards important requirements for the production of large-scale electronics.

Micromechanical cleavage [14] is the simplest exfoliation method to date (i.e., the process used to exfoliate graphene layers from a pristine graphite crystal using Scotch tape). It can also be used to separate the layers from bulk crystals such as MoS$_2$, but the throughput of this method is rather low, limiting its application to devices that employ single nanosheets of 2D materials such as field effect transistor (FET) [15] and fully integrated circuit boards [16]; its application cannot be extended to scalable applications. Scalable exfoliation methods with much higher throughput have emerged [17–20], and with them, prospects for new applications [21]. One type of LBE developed by Coleman et al. [22] and further developments towards higher throughput [19] represent the state-of-the-art technology.

As described in Paper I, to overcome the drawbacks of using organic solvent 2D material dispersions, we used another exfoliation method based on MoS$_2$ dispersions in water. The dispersions achieved were not as good in terms of stability as those obtained in organic solvents, but the quality of the nanosheets was comparable. In our method, bulk MoS$_2$ powder was first pre-processed between sandpapers, and this powder was then dispersed in water by sonication. The sandpaper method might be of interest due to its simple procedure. Additionally because it can be utilized with dry samples, this method should be very fast due to the resulting large shear forces. However, it has been less well investigated than the other methods described in the literature [23]. We believe that the thinning of the bulk powder before sonication makes the process more effective because higher concentrations can be achieved in less sonication time.

In Paper II, we discuss our initial attempt to tune the 2D printed electronic ink. We add surfactants to control the surface tension of the
ink (essential for good jet formation and drop break-off). The addition of a surfactant also improves the stability of the nanosheets in the dispersions and helps avoid the clogging of the printing head nozzles. The tuning of a number of other ink properties is also necessary, and this will be the subject of the continuation of the work presented here in this thesis. Other ink components may also be added, and a study of the quality of the printing results will also constitute a future activity related to the presented work.

1.2 Outline

The main content of each of the nine chapters of this thesis is listed here on this outline.

Chapter One
The overall idea of this thesis and the research questions are presented. Large-area printed electronics and the steps we took to produce inks for inkjet printing are discussed. The motivation for choosing the TMD semiconductor MoS$_2$ is explained and a brief explanation about the two publications from which this thesis resulted is given (both papers are attached in the Appendices).

Chapter Two
Some background information about TMDs is presented.

Chapter Three
Top-down solution exfoliation methods from bulk layered materials are briefly discussed.

Chapter Four
Inkjet printing nozzle technologies and the requirements for favorable jetting and good printability of 2D inks for printed electronics are discussed.
1.2. Outline

Chapter Five
The theory of the stability of colloidal dispersions that is related to 2D dispersions and 2D inks for printed electronics is discussed.

Chapter Six
An overview of substrates for inkjet printing is presented.

Chapter Seven
The preparation of 2D dispersions and 2D inks of MoS$_2$ for printed electronics is discussed. The methods and conditions used to characterize the nanosheets and the dispersions are also listed.

Chapter Eight
The motivation to use sandpapers in order to mechanically exfoliate the MoS$_2$ bulk powder before the LBE step in the preparation of the 2D dispersions and 2D inks is reported. The characterization results for the nanosheets are presented. The results for the stability of the 2D dispersions is presented and compared with the literature. The stability of the 2D inks is discussed. Lastly, the results and conditions used for the test prints of the 2D inks onto polyethylene terephthalate (PET) and resin-coated photo paper using inkjet printing is presented.

Chapter Nine
Finally, the conclusions from this thesis and some outlook is present.
Chapter 2

TRANSITION METAL DICHALCOGENIDES

Novel materials that may be of importance in printed electronics are in the class of semiconducting 2D nanomaterials such as TMDs.

TMDs in their bulk form have been known and studied for decades [24], and with the discovery of graphene [14], such studies been revived in attempts to find materials at the nanoscale that would display properties that lacking in graphene [25].

The electronic properties of TMDs vary, and the band gap decreases the higher the mass of the chalcogen atom (i.e., S to Se to Te) [9]. Here, we focus on the semiconductor MoS$_2$. Bulk MoS$_2$ has an indirect band gap of 1.23 eV [26], and as the number of layers in the material decreases with exfoliation, the indirect band gap increases up to 1.9 eV [27, 28] for single nanosheets, where a transition to a direct band gap semiconductor was observed [28, 29]. This feature was remarkable, as shifting the band gap from the near-infrared to the visible range makes these materials especially interesting for optoelectronics [28, 29], including photovoltaic applications [30].

The transition metal layers (usually Mo or W) are sandwiched between two layers of chalcogen atoms (e.g., S, Se, Te). These intralayers are held together by weak van der Waals’ forces, whereas strong covalent forces hold the individual atomic interlayers together [17, 18]. Depending on the combination of metal and chalcogen atoms, these materials can be insulators, metals or semiconductors.

Electron mobility characterizes how quickly an electron can move through a metal or semiconductor when pulled by an electric field. In semiconductors, there is an analogous quantity for holes, called the hole mobility. The term carrier mobility generally applies to both the electron and hole mobility in semiconductors. It is possible to find out whether the charge carriers in a conductor are positively or negatively charged. We can also measure the number of carriers per unit volume of the conductor using the Hall effect [31]. When an electric field $E$ is applied across a material, the electrons respond by moving with an average velocity called the drift velocity. The electron mobility is defined by the ratio between this velocity and $E$. 
Work on single layers [15] and multilayers [25] of MoS$_2$ have demonstrated a carrier mobility of 200 and 100 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Later, a FETs with a mobility up to 700 cm$^2$ V$^{-1}$ s$^{-1}$ [32], which is comparable to that of nonflexible Silicon-metal oxide semiconductor field effect transistors (MOSFETs), was reported.

This means that even a large degradation of the mobility caused by suboptimal processing conditions, which is expected when printing the materials, still permits the printed production of high speed electronics. Although the main body of work on MoS$_2$ and other TMD has been performed on single-layer flakes, we expect that thin films should not be much less than the bulk value of a carrier mobilities of about 50 cm$^2$ V$^{-1}$ s$^{-1}$ [33]. Using Figure 2.1, one can estimate the position of thin nanosheets of MoS$_2$ as being on the high end of the FET mobility map of semiconductors close to polymorphous silicon, by considering the reported mobilities of this semiconductor in thin films [32] and bulk values [33].

![Figure 2.1: Correlation of the field-effect mobility of thin-film transistor (TFT) and the switching speed of inverter-based ring oscillators. A general trend can be observed across different classes of thin-film semiconductors, despite the large scatter associated with the variation in device attributes, parasitic capacitances and supply voltages. Exfoliated MoS$_2$ is a new semiconductor with the potential to occupy the high-performance corner of the flexible semiconductor material map. Reprinted by permission from Nathan et al. [6] © IEEE, 2011](image-url)
SOLUTION PROCESSING EXFOLIATION
METHODS

The most promising top-down solution processing methods for achieving a high throughput of exfoliated materials may be chemical and liquid-based exfoliation [16, 18–20, 23, 34]. The classical liquid exfoliation method is chemical exfoliation (CE) with lithium intercalation (LI) [35]. Other methods have been employed by Coleman et al. [22]. Their method is based on the use of suitable organic solvents capable of dispersing and stabilizing the nanosheets. This method follows stability theories [36, 37] and acknowledges the mechanical force needed to separate the layers, which they generally apply using ultrasonic energy, as we also do in Paper I and II.

Depending on the liquid media used in direct ultrasonication Niu et al. [23] divided the top-down solution processing methods as follows:

- Organic or low boiling point solvents
- Stabilizer-based exfoliation using ionic or nonionic surfactants, polymers or pyrene derivatives
- Ionic liquid-based exfoliation
- Salt-assisted exfoliation
- Intercalant-assisted exfoliation
- Ion exchange-based exfoliation

Other methods not using sonication that are mentioned by Niu et al. include electrochemical exfoliation and shear exfoliation. Reading this review [23] for more in-depth information on such methods is recommended.
3.1 Chemical exfoliation

Joensen introduced in the 1980s the method called chemical exfoliation (CE) which is an intercalant-assisted exfoliation method with lithium intercalation (LI). This method achieves a relatively high concentration of single nanosheets of MoS$_2$ in acidic conditions. This method with LI is still, to date, the process with the highest yield of MoS$_2$ monolayers [38, 39].

Chemical exfoliation (CE) is the process of intercalating lithium ions into MoS$_2$ powder, and it can be done by dispersing the MoS$_2$ in a 1.6 M n-butyllithium solution in hexane for at least 48 h under inert argon gas conditions (due to the flammability of the lithium source). LBE is then carried out.

Zeng et al. reported a faster LI process, referred to as electrochemical lithiation (EL), a type of electrochemical exfoliation method. The intercalation is controlled via galvanic discharge on an electrochemical cell that uses the bulk layered material in the cathode and a lithium foil in the anode (replacing the expensive n-butyllithium compound).

Some advantages of EL include the prevention of the decomposition of the lithium compounds and the formation of metal nanoparticles [18]. The process can also be carried out in ambient conditions. However, in both processes, structural changes occurred in the crystal from 2H-MoS$_2$ (trigonal prismatic) to 1T-MoS$_2$ (octahedral) due to LI, and a metallic transition was observed [38, 41, 42]. The characteristics of the semiconductor can be restored by mild sintering [43] or ageing [41], but the remaining nanosheets with the metallic phase may be detrimental in some applications. The size range of the nanosheets for the CE method was 300-800 nm [43], while Zeng et al. reported 92% of the monolayers achieved with EL.

3.2 Liquid-based exfoliation

Liquid-based exfoliation (LBE) alone is a relatively simple and scalable process, and although it yields fewer monolayers than other methods such as CE [43] or EL [40], it may be the preferable route for applications in which large quantities of exfoliated nanosheets are desired and monolayers are not necessary.
### Table 3.1: LBE methods for solution processing of MoS₂

Indicating the solvent used, if a surfactant was employed, the final dispersion concentration, exfoliation time and the range or the average lateral nanosheet dimension reported according to AFM or TEM statistical measurements. Adapter from Paper I [44] and Paper II [45]

<table>
<thead>
<tr>
<th>Method</th>
<th>Solvent</th>
<th>Surfactant [Yes/No]</th>
<th>Concentration [g L⁻¹]</th>
<th>Exfoliation time [hour]</th>
<th>Size [nm]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBE</td>
<td>NMP</td>
<td>No</td>
<td>0.3</td>
<td>1</td>
<td>170</td>
<td>[22]</td>
</tr>
<tr>
<td>LBE</td>
<td>NMP</td>
<td>No</td>
<td>7.6</td>
<td>50</td>
<td>700</td>
<td>[39]</td>
</tr>
<tr>
<td>LBE</td>
<td>NMP</td>
<td>No</td>
<td>40</td>
<td>140</td>
<td>200</td>
<td>[39]</td>
</tr>
<tr>
<td>LBE</td>
<td>EtOH/Water</td>
<td>No</td>
<td>0.018</td>
<td>8</td>
<td>100</td>
<td>[46]</td>
</tr>
<tr>
<td>LBE</td>
<td>Water</td>
<td>Yes</td>
<td>0.25</td>
<td>0.5</td>
<td>280</td>
<td>[47]</td>
</tr>
<tr>
<td>SE</td>
<td>Water</td>
<td>Yes</td>
<td>0.4</td>
<td>10</td>
<td>85</td>
<td>[20]</td>
</tr>
<tr>
<td>ME+LBE</td>
<td>Water</td>
<td>Yes</td>
<td>0.8</td>
<td>16</td>
<td>50 − 700</td>
<td>[48]</td>
</tr>
<tr>
<td>ME+LBE</td>
<td>Water</td>
<td>No</td>
<td>0.14</td>
<td>1</td>
<td>242</td>
<td>[44]*</td>
</tr>
<tr>
<td>ME+LBE</td>
<td>Water</td>
<td>Yes</td>
<td>−</td>
<td>1</td>
<td>200</td>
<td>[45]**</td>
</tr>
</tbody>
</table>

Chapter 3. Solution processing exfoliation methods

The nanosheets dispersed in liquid can be easily used in applications such as composites production [49], energy storage and catalysis [17, 18]. Following Coleman’s work [22], a number of liquid-based exfoliation methods have been reported, and those most relevant to the presented work are summarized in Table 3.1.

3.2.1 Ultrasonic exfoliation in liquid

Power, measured in watts, is the measure of electrical energy that is being delivered to a convertor. At the convertor, the electrical energy is transformed into mechanical energy. It does this by exciting the piezoelectric crystals, causing them to vibrate within the convertor in the longitudinal direction. This change from electrical to mechanical energy causes a motion that travels through the horn/probe, causing the tip to vibrate and create pressure waves in the liquid. This action forms millions of microscopic bubbles (cavities) that expand during the negative pressure excursion and implode violently during the positive excursion. This phenomenon, known as cavitation, creates millions of shock waves in the liquid and elevates pressures and temperatures at the implosion sites. Although the cavitational collapse lasts but a few microseconds and the amount of energy released by each individual bubble is minimal, the cumulative effect causes extremely high levels of energy to be released into the liquid.

The larger the probe tip, the larger the volume that can be processed, although at lesser intensity which may impact the exfoliation as suggested by Paton et al. [19]. In other words, simply increasing the volume does not yield higher production. The production rate and the concentration of dispersed nanosheets are inversely proportional to the liquid volume (see Equation 3.1, where $P_R$ is the production rate, $t$ is the production time, $V$ is the liquid volume and $C$ is the concentration).

$$P_R = CV/t$$  \hspace{1cm} (3.1)

The distance of the vibration is called the amplitude. The amplitude and intensity have a direct relationship. If you operate at a low amplitude setting, then you will obtain low-intensity sonication. If you operate at a high amplitude setting, you will have high-intensity
Ultrasonic exfoliation in liquid
sonication. For results to be reproducible, the amplitude setting, temperature, viscosity and volume of the sample must remain constant. The amplitude, not the power, is most critical when trying to reproduce sonication results [50].

Processing with an ultrasonic processor, is significantly faster and more reproducible than a bath sonicator due to the fact that the energy at the probe tip is high (at least 50 times higher than that produced in a bath), focused and adjustable. In a sonication bath the intensity is inconsistent as the water and the temperature both fluctuate. The intensity is also low, fixed and location dependent [50].

O’Neill et al. suggested that optimizing the sonication conditions may lead to a higher concentration and larger nanosheets in terms of lateral size. These authors achieved concentrations of up to 40 g L$^{-1}$, but at the cost of a very high exfoliation time (i.e., 140 h), and the nanosheet lateral size was reduced by more than half due to sonication scission, a process that is more pronounced after 60 h of sonication [39].
The networks of nanosheets can be formed into thin films, which can then be employed in a vast number of applications [21] such as batteries, supercapacitors [51], catalysts [9], sensors [52] and solar cells [53, 54].

After achieving a successful dispersion, the next area of study is typically the dispersion’s application. The main methods of material deposition are rod coating [55], screen printing [56], flexography and inkjet printing. The transfer of the dispersed nanosheets using top-down exfoliation methods such as liquid-based exfoliation (LBE) into different substrates is significantly easier and more straightforward than transfer techniques using bottom-up synthesis methods such as chemical vapor deposition (CVD) [17, 18, 25, 57].

Wang et al. [55] reported a large-scale application of graphene using rod coating, a method that is very promising when the full coverage of a surface is desired. However, when the target of the application is a specific area, printing may be more suitable, with inkjet printing being the preferred method for this, considering the physical properties of the inks such as their low viscosity and low concentration. Only a few studies have been performed on the printing of MoS$_2$ [10, 13]. Finn et al. [13] inkjet printed MoS$_2$ that had been exfoliated using n-methyl pyrrolidone (NMP), resulting in a low-concentration solution. However, by printing each line 30 times, this problem was circumvented. We employed the same method in our printing tests.

Special precautions must be taken when printing with toxic solvents such as NMP and dimethylformamide (DMF). Li et al. [10] used a distillation method for DMF-exfoliated MoS$_2$. In this process, the toxic DMF solvent was exchanged for the nontoxic solvent terpineol. This exchange process also increased the viscosity of the final dispersion from 0.9 cP to approximately 40 cP. A viscosity that is too high may also be detrimental to the inkjet process because a higher onset bias is necessary to jet the drops, creating long filaments and small drops [58]. Therefore, the authors tailored the viscosity to 10 cP using
ethanol. The concentration also increased significantly, which led to the addition of ethyl cellulose to improve the printing quality and shelf-life of the ink.

4.1 Inkjet printing nozzle technologies

Two types of nozzle technologies - thermal inkjet (TIJ) and piezo technology (PZT) - are used for inkjet printing, each differing in how the drops are forced out of the nozzle. Either of these technologies can be used for continuous inkjet (CIJ) or drop-on-demand (DoD) technologies. In continuous inkjet, a continuous stream of drops is produced, and either the drops are recirculated or printed onto the substrate, while in DoD, only the required drops are produced. An illustration of the CIJ and DoD inkjet technologies can be seen in Figure 4.1.

4.1.1 Thermal inkjet

The working principle of TIJ, also known as bubble jet, can be described as follows: a current is applied to the heating element inside the printing head that is in contact with the ink, and the heat applied results in a temperature in the range of 350 - 400 °C. A small bubble of vapor is formed, and based on the higher volume occupied by the vapor than by the liquid, the pressure inside the ink chamber is increased and the ink is ejected from the nozzle. The retracting meniscus breaks the ligament, and a drop is separated. The heating element starts to cool down, and the bubble collapses. The whole process of bubble formation and collapse takes from 2 to 10 µs. The ink must have a volatile component, which is one disadvantage of this technology [59, 60].

4.1.2 Piezo technology

In piezo technology, the ink is ejected by the deformation of the piezo material when an electric field is applied. The deformation of the piezo material causes a change in the ink volume inside the pressure chamber, which generates a pressure wave that propagates
4.1.3. Requirements for printed electronic inks

To be able to print MoS$_2$, suitable inks with the following features are needed [58, 62]:

1. Nontoxic solvents, because printing is usually performed in environments without extensive ventilation;
2. Proper viscosity for the particular printing process used;
3. Surface tension appropriate for the particular printing process used;
4. Optimal concentration, both because it is difficult to evaporate solvents from low-concentration inks and because an overly high concentration may lead to nozzle clogging;
5. Appropriate particle size;
6. Long ink shelf life (stability);
Chapter 4. Deposition Methods

7. The ability to provide good electrical conductivity for the printed pattern;

8. Good ink-substrate interaction to achieve good printability and resolution.
Small particles of one phase dispersed in another are generally called colloidal dispersions, and they are quite different from molecular solutions, in which the solid particles (solute) are totally dissolved in the solvent. To be considered a colloidal dispersion, at least one of the components should have dimensions within the range of 1 nm-1 µm.

To understand the influences of the different ink components on the ink dispersion and the final printing result, one needs first to understand the principles of colloidal stability [63]. In a classical inkjet ink, the colloids are the ink pigments; however, in the printed electronics of 2D materials, the colloids in the inks are the nanosheets.

Figure 5.1: Diagram showing the ionic concentration and potential difference as a function of the distance from the charged surface of a particle suspended in a dispersion medium. Source: Wikipedia
Chapter 5. Stability of colloidal dispersions

5.1 DLVO theory

The Derjaguin, Landau, Verwey and Overbeek (DLVO) theory assumes that a stable colloidal dispersion is one in which the particles resist flocculation or coagulation, which will depend on the attractive forces (i.e., van der Waals’ and dipole-dipole interactions) and repulsive forces (i.e., electrostatic and Coulomb’s laws) that exist between the particles as they approach each other. Van der Waals’ forces will always act to destabilize dispersions. To maintain stability, the repulsive forces should therefore be dominant [64].

This double layer is divided into two regions (see Figure 5.1). One is fixed (stationary), where the counter ions closest to the particle surface are strongly bonded to the surface (also known as the Stern layer) which corresponds to the amount of liquid that moves with the particle. The other region is a diffusion layer, with particles in constant Brownian motion. The difference between these two layers is called the zeta potential, \( \zeta \) [63–65].

The electrical double layers of two particles overlap when these particles approach one another and the particles can move apart. Depending on the magnitude of the force induced when these double layers overlap, the particles may be stabilized against aggregation or a degree of sedimentation or flocculation will occur [63].

Surfactant particles may adhere to and stabilize the nanosheets by a mechanism of semi-micelles, as observed by Manne [66, 67]. Charged surfactants may also influence the net charge density on the particle surface [63], as is the case for the ionic surfactant sodium dodecyl sulfate (SDS) employed in our work in Paper II.

Additionally, adding surfactants is necessary to control the surface tension of the inkjet inks, which is essential during drop formation at the inkjet printing nozzles.

5.2 Electrophoretic mobility (zeta potential)

We evaluate the stability of the 2D inks by estimating the surface charge of the nanosheets through electrophoretic mobility. Electrophoretic mobility is an estimation of the zeta potential. The measurement is performed by evaluating the rate of diffusion of the
5.2. Electrophoretic mobility (zeta potential)

Surface charge when an electric field is applied. This rate of diffusion is dependent upon the strength of the electric field, the net charge at the shear plane close to the surface and the size of the particle. The velocity of the particles moving in the direction of the oppositely charged electrode when an electric field is applied can be measured, and this is the electrophoretic mobility. The electrophoretic mobility measurements employed a laser interferometric technique (Zeta Sizer Nano Series Operating Instructions), which enabled the calculation of the electrophoretic mobility to estimate the zeta potential; such technique is called M3-PALS (Phase Analysis Light Scattering). Once we measured the mobility, the apparent zeta potential could be estimated using the Smoluchowski equation [68], in which \( \zeta \) is the apparent zeta potential, \( \eta \) is the viscosity of the dispersion liquid, \( \mu \) is the electrophoretic mobility and \( \varepsilon \) is the solution permittivity.

\[
\zeta = \frac{\eta \mu}{\varepsilon}
\]  

(5.1)

This method was derived for spherical particles, but it can be used as an estimation for non-spherical particles, as other authors have done [69], to within 20% of the true value [70].
In Paper II we used porous resin-coated composites (also called photo papers) and 100 μm uncoated PET transparent films as substrates. An illustration of a cross-section of a porous resin-coated paper that is similar to that used in Paper II is presented in Figure 6.1. In these types of paper composites, each of the layers has a function. The base paper gives support to the polyethylene (PE) films. On top of the PE films, an inkjet ink-receiving-layer that is applied using a coating method, functions to absorb the ink solvent. This layer is composed of coating pigments such as SiO$_2$ plus a number of other additives like binders and cross-linkers [71]. There are a number of flexible substrates that can be employed for inkjet printing and Figure 6.2 indicates some of them [71].

Figure 6.1: Cross-section SEM image of a resin-coated paper. SEM image at 300x magnification. Image accessed at an acceleration voltage of 15 kV using a Jeol JSM 5600 LV SEM.
Chapter 7

METHODS

7.1 Preparation of the 2D dispersion and 2D ink

We typically prepared 100 mL of the MoS\(_2\) dispersions. For the dispersions in both water and surfactant solution, we aimed to obtain MoS\(_2\) initial concentration, \(C_i = 5\ \text{g L}^{-1}\). The difference was the liquid into which the mechanically exfoliated MoS\(_2\) was dispersed, for which we used pure distilled water (which here in this thesis we refer to as 2D dispersion) or a surfactant solution at \(C_i = 1\ \text{g L}^{-1}\) (2D printed electronic ink, 2D ink). In a few experiments, we used different initial dispersion concentrations (e.g. the concentration of the surfactant stock solutions was varied for the experiments in Paper II).

In Figure 7.1 and Figure 7.2 we illustrate the exfoliation steps involved in a molecular level on the preparation of the 2D dispersion and the 2D ink respectively.

A simplified scheme of the 2D ink production is illustrated in Figure 7.3. In the mechanical exfoliation step, which is Step 1, we used an orbital sander to exfoliate the bulk MoS\(_2\) powder. This thinned powder was then used to prepare the dispersions (Step 2) in surfactant solution using the method of liquid-based exfoliation (LBE). In Figure 7.2, the exfoliated dispersions after Step 2 were left to settle on a bench and decanted in Step 3, and in Step 4 the inkjet printing process was performed using the Dimatix material printer 2831 (DMP-2831).

The LBE was performed using a Sonics Vibracell CV334 750 W ultrasonic probe unit equipped with a 13 mm long step horn tip for volumes of up to 250 mL. The temperature of the dispersion during sonication was controlled by circulating 5 °C water through a 100 mL jacket glass vessel (Ace Glass Incorporated) connected to a heating circulating bath (Polyscience 801 heat circulator). The probe was set to operate for 8 s and standby for 2 s during the 60 min processing time to avoid excessive heating, solvent evaporation and damage to the converter.
Figure 7.1: Exfoliation steps of MoS\textsubscript{2} stacks into nanosheets during the preparation of the 2D dispersion. The illustration of the molecules of MoS\textsubscript{2} were done by Viviane Forsberg using the molecular dynamics simulation software Atomistix ToolKit version 2014.2, QuantumWise A/S [72, 73]
7.1. Preparation of the 2D dispersion and 2D ink

**STEP 1**
Mechanically exfoliated MoS$_2$ powder

**STEP 2**
Add MoS$_2$ to SDS Solution

**STEP 3**
LBE by ultrasonication

**Figure 7.2:** Exfoliation steps of MoS$_2$ stacks into nanosheets during the preparation of the 2D ink. The inset indicates the SDS molecule in (a), the mechanism of semi-micelle surfactant adhesion observed by Manne et al. [67] in (b), and in (c) a simplification of the surfactant adhesion for purpose of illustration employed by us. The illustration of the molecules of MoS$_2$ were done by Viviane Forsberg using the simulation software Atomistix ToolKit version 2014.2, QuantumWise A/S [72, 73] and the SDS molecular docking onto the basal plane of the MoS$_2$ stacked nanosheets was done using the online algorithm [74, 75] from Patch Dock. Some file conversions were done using the VMD software [76].
Figure 7.3: Steps of the preparation of the 2D ink for inkjet printing in (A) and in (B) a simplified illustration at atomic level of the two MoS$_2$ exfoliation steps (i.e. mechanical exfoliation (ME) and liquid-based exfoliation (LBE)). The MoS$_2$ molecules illustrations in (B) were done by Viviane Forsberg using the molecular dynamics simulation software Atomistix ToolKit version 2014.2, QuantumWise A/S [72, 73]
7.2. Characterization of the nanosheets

7.2.1 Atomic force microscopy (AFM)

We performed AFM imaging of the nanosheets deposited on the silicon wafer. The samples were collected from a $C_i = 5 \text{ g L}^{-1}$ dispersion in water (2D dispersion) and in $C_i = 1 \text{ g L}^{-1}$ SDS surfactant solution (2D ink). The dispersions were then centrifuged and decanted. The aliquots were centrifuged once again at 10,000 rpm (Jouan A14) for 2 min to sediment all the particles. We then removed the liquid and re-dispersed the particles in 99.5% ethanol. We washed the remaining surfactant away from the surface of the samples deposited in the silicon wafer for the analysis of the 2D ink’s nanosheets. We used a Dimension 3100 AFM (Digital Instruments) operated in tapping mode for these images.

7.2.2 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) images were accessed using a FEI Nova NanoSEM (450). SEM images of the sample surfaces were acquired in secondary electron imaging mode using 2 kV accelerating voltage and 5 mm working distance. Before image acquisition, the samples were gold sputtered for 20 s to obtain an electrically conductive surface.

7.2.3 Transmission electron microscopy (TEM)

TEM images of MoS$_2$ nanosheets in water were accessed using a JEOL 2000FX operated at 160 kV.

7.2.4 Optical properties (UV-vis spectroscopy)

The optical properties were evaluated by UV-vis absorption measurements using a UV-1800 Shimadzu spectrophotometer. The samples were left to settle on the bench for 30 days before measurement, at which point they were decanted and diluted at a 1:9 ratio.
Chapter 7. Methods

7.2.5 X-ray powder diffraction (XRD)

For the X-ray diffraction analysis, we used a D2 Phaser (BRUKER) X-ray powder-diffraction station. The bulk powder and the exfoliated powder were deposited on a tape or silicon wafer. The 2D dispersion and 2D ink were vacuum filtrated onto poly(vinylidene fluoride) (PVDF) membrane with pore diameter’s of 0.22 µm. The surfactant was washed away from the surface of the 2D ink’s nanosheets using 2 L of distilled water.

7.2.6 Fourier transform infrared (FTIR)

Fourier transform infrared spectroscopy (FTIR) measurements were done using a Nicolet 6700 (Thermo Scientific). These and the SEM measurements were done to complement the XRD analysis. The sample was collected by vacuum filtration of the 2D dispersion onto a cellulose membrane. The nanosheets were then scraped from the surface of the membrane with a spatula. The mechanically exfoliated and bulk powders were measured without additional processing. We have not performed this experiment for the 2D ink’s nanosheets.

7.3 Characterization of the 2D dispersion and 2D ink

7.3.1 Concentration

The final concentration of the 2D dispersion was measured by drying a known volume of the dispersion in a beaker of known mass at 100 °C overnight and determining the remaining mass using a microbalance. The concentration of the 2D ink was not determined.

7.3.2 Viscosity

We measured the viscosity of the 2D ink with a Rheomat RM180 rotational viscometer using spindle set 11, a shear rate of 1108 s⁻¹, a torque of 0.4 mN m and a temperature of 19 °C.
7.3.3 Dispersion Stability

We evaluated the stability of the 2D dispersions in two ways. One way was based on the concentration of the dispersions over time as described in Paper I. The other method was electrophoretic mobility measurements, used to estimate the zeta potential, which we applied for the 2D dispersions and 2D inks mentioned in Paper I and Paper II.

We employed a Zetasizer Nano ZSP (Malvern) for these measurements. For the 2D inks we varied the surfactant concentration around the critical micelle concentration (CMC) of SDS, which is $2 \text{ g L}^{-1}$ [77], and kept the MoS$_2$ concentration constant at $1 \text{ g L}^{-1}$. The minimum concentration of SDS used was $0.2 \text{ g L}^{-1}$, and the maximum surfactant concentration was the CMC of SDS, or $2 \text{ g L}^{-1}$.

We collected samples of the dispersions over time within a period of one month. These dispersions were sonicated for 15 min in a low-power sonication bath before the measurements. We also evaluated the stability of one dispersion with a SDS concentration of $1 \text{ g L}^{-1}$ and a MoS$_2$ concentration of $5 \text{ g L}^{-1}$ six months after initial sample preparation.

7.3.4 Dynamic Light Scattering (DLS)

Because the measurement of the nanosheet’s dimensions using AFM microscopy is a very time-consuming method, we estimate the size of a larger population of particles using the method of dynamic light scattering (DLS), a very accurate method for spherical particles but only an estimation for non-spherical ones [69].

The same dispersion and measurement cell used to measure the electrophoretic mobility was employed to measure the particle size distribution of the samples using the DLS technique.

DLS consisted of an evaluation of the change of light intensity caused by the Brownian motion of the particles in the solvent. The intensity of the light scattered by the particles is measured, and the time-dependent fluctuation in the light intensity is related to the constructive and destructive interference. The Stokes-Einstein equation is then used to determine the hydrodynamic diameter of the scattering objects [63].
RESULTS AND DISCUSSION

8.1 Mechanical exfoliation

The mechanical exfoliation (ME) step with sandpapers might be of interest due to the simple procedure and since it is possible to work on dry samples, the method should be very fast because of the resulting large shear forces. However, it is less well investigated compared to the other exfoliation methods. We used this step on the preparation of both 2D dispersion and 2D ink in Paper I and Paper II respectively.

Not much effort have been dedicated to study the effects of pre-processing the MoS\textsubscript{2} powder before the liquid-based exfoliation (LBE) step, here referred as thinning of the MoS\textsubscript{2}.

Thinning of MoS\textsubscript{2} powder in surfactant solution via ball milling was one of the few studies on the matter [48], but the process was time consuming and would require a post-processing step to remove the residual surfactant.

We believe that thinning of the bulk powder before the sonication makes the process more effective as higher concentrations can be achieved in less sonication time.

Sandpapers have been successfully employed to exfoliate TMD but in a different way [78] from the one proposed in Paper I. There, it was used for thinning the MoS\textsubscript{2} nanosheets using an orbital sander with no intermediate steps.

8.2 Characterization of the nanosheets

8.2.1 Thickness and lateral size

We observed thin single nanosheets in the microscopy images taken of the deposited 2D dispersion (Figure 8.1-A) and 2D ink’ nanosheets (Figure 8.1-C). The thin nanosheets present in the 2D dispersion had a thickness of approximately 1.5 nm, indicating up to two layers of MoS\textsubscript{2} [79]. The thickness of the nanosheets in the 2D ink was slightly - but not significantly - higher, as shown in the thickness profiles (Figure 8.1-B and Figure 8.1-D respectively).
The nanosheets in the 2D ink were slightly smaller in lateral size (200 nm) than the ones in the 2D dispersion (300 nm).

Figure 8.1: AFM images of (A) 2D dispersion’s nanosheets and (C) 2D ink’s nanosheets. Thickness profiles for (B) 2D dispersion’ nanosheets and (D) 2D ink’ nanosheets. Adapted from Papers I and II [44, 45]

Images obtained by TEM indicate very thin nanosheets in the range of the AFM measurements for the 2D dispersion (see Figure 8.2).

Figure 8.2: TEM image of nanosheets in a 2D dispersion. Adapted from Paper I [44]
The PSD of the nanosheets changes significantly as the nanosheets of MoS$_2$ are separated during exfoliation. The initial size of the particles in the bulk powder is approximately 10 times larger than that after exfoliation, as seen by comparing Figure 8.3-A with the measurement of the dispersion before exfoliation and the other images, Figures 8.3-B, C and D.

Sonication, besides separating the layers of the materials, leads to a degree of sonication scission, meaning that the particles break down, especially during prolonged sonication times [39]. We measured a PSD of approximately (126±58) nm for the 2D ink (Paper II) and slightly larger particles for the 2D dispersion (Paper I).

Some sedimentation occurred for the nanosheets in the 2D ink in a period of six months according to the results from Paper II. The PSD dropped from approximately 227 nm to 163 nm and remained constant for a month as can be seen in Figure 8.4.

The surfactant concentration seems to play a role in the stabilization of the larger particles, as seen in Figure 8.3-C and D, because a larger population of larger particles was observed at the higher surfactant concentration.

For the lowest SDS concentration (0.2 g L$^{-1}$), the size of the dispersed nanosheets remained at approximately the same value, which indicated that the amount of surfactant does not greatly impact the PSD as seen in Figure 8.4. The dimensions of the surfactant molecules are significantly smaller than those of the nanosheets (100 times smaller, as seen from Figure 7.2-a) and did not greatly affect the size of the particles. It may have stabilized only the larger particles for a longer period.

8.2.2 Crystal structure and orientation

XRD analysis was performed not only to obtain information about the crystal structure of the exfoliated nanosheets but also to help identify the phases resulting from chemical reactions such as oxidation that may have taken place during the exfoliation process [43].

No shifts in the two-theta values from the nanosheets in 2D dispersion and in 2D ink were observed compared to the bulk powder spectra (see Figure 8.5), so we can say that no changes in the crystalline
Figure 8.3: Particle size distribution of MoS$_2$ nanosheets in water before exfoliation (A) and in 2D dispersion (B) at an initial MoS$_2$ concentration of C$_i$ = 5 g L$^{-1}$. 2D ink at initial MoS$_2$ concentration C$_i$ = 1 g L$^{-1}$ at varied surfactant concentration 2 g L$^{-1}$ and 0.2 g L$^{-1}$ in (C) and (D) respectively. Adapted from Papers I and II [44, 45].

Figure 8.4: Average particle size distribution of nanosheets in 2D ink measured by dynamic light scattering (DLS). Samples taken 3 days, 18 days and 25 days after sample preparation. The legend indicates the surfactant concentration in the solution in which MoS$_2$ was dispersed at an initial concentration of 1 g L$^{-1}$. 
structure occurred during exfoliation. The crystal structure remained 2H-trigonal prismatic.

The pattern obtained for the MoS$_2$ bulk powder indicated a lower intensity 002 peak than the exfoliated sample, as seen in Figure 8.5. It is expected that the more exfoliated the sample, the lower the intensity of the (00l) peaks [35, 81]. The (00l) peaks indicate planes parallel to the basal plane of the MoS$_2$ crystal, which is diminished during exfoliation and therefore should show lower-intensity peaks in the XRD pattern.

The orientation of the crystals during measurement also plays a role in the measured intensity of the (00l) peaks. Therefore, we performed SEM analysis (Figure 8.6). The nanosheets are ordered in the c-axis, pointing upwards in the sample, as illustrated in the SEM image, and therefore more pronounced (00l) peaks should be observed, which is consistent with our findings; the particles are not ordered in the bulk powder, and therefore, a lower intensity 002 peak
Chapter 8. Results and Discussion

Figure 8.6: SEM image of 2D dispersion (A and C) and 2D ink (B and D) deposited onto PVDF membranes by vacuum filtration. The top images are at 30k magnification, and the bottom, at 100k. Adapted from Papers I and II [44, 45]

was measured.

Although the technique should not be relied upon for the purpose of thickness evaluation, the XRD results give an indication of the thickness range of the nanosheets [81]. It is most likely that we obtained predominately more than 5 layers of MoS$_2$. Fewer than 5 layers would result in the absence of the 002 peak that is observed with relatively high intensity in our results.

We did not observe peaks for molybdenum trioxide (MoO$_3$) in any of the exfoliated samples, as seen in Figure 8.5, which we indicated were MoO$_3$ peaks according to database card 1011043; however, for this particular evaluation, x-ray photoelectron spectroscopy (XPS) would have provided a more accurate measurement [43].

In Paper I, FTIR spectra measurements were performed to complement these XRD measurements and to extend the study of the presence of oxides. We performed these analyses on nanosheets of the liquid-based exfoliated dispersions in water, the mechanically exfoliated powder and the bulk MoS$_2$ powders.

The peak at 470 cm$^{-1}$ in the far-infrared region observed in Figure 8.7, which is characteristic of MoS$_2$ [82], was observed for all three measurements, but no peaks for the oxides were observed.
8.2.2. Crystal structure and orientation

Figure 8.7: FTIR spectra for the mechanically exfoliated and bulk MoS$_2$ powders prior to dispersion and vacuum filtered 2D dispersion nanosheets. The data for the measurements are offset on the vertical axis for clarity. Adapted from Paper I [44].

Figure 8.8: Optical properties evaluated by UV-vis measurements for the dispersions in water and in surfactant solution in the left side with the indication of the absorption peaks A and B, and on the right side are pictures of the dispersions. At the bottom of each dispersion image is written the solvent in which the particles were dispersed. The clear dispersions in (a) and (c) are the dispersions before exfoliation 30 days after sample preparation. A 2D dispersion shortly after sample preparation is illustrated in (e). (b) and (d) are the exfoliated samples 30 days after sample preparation and the ones used for the UV-vis measurement. Adapted from Papers I and II [44, 45].
8.2.3 Optical Properties

Due to the presence of surfactant, after sample preparation, two phases were observed for the dispersion described in Paper II. This happened when the samples were decanted or centrifuged. The top phase is the phase with the lower concentration of MoS$_2$, as illustrated in Figure 8.8 and is the phase that constituted the 2D ink used for the printing tests (at the time 6 months after sample preparation). We measured the absorption at both phases. Note that the 2D ink (top phase of dispersion d, see Figure 8.8-d) and the 2D dispersion (dispersion b, see Figure 8.8-b) have very similar curves, which indicates that the concentrations of these two dispersions were very similar.

According to Frey et al. [83], absorption peaks A and B are positioned at 660 nm (1.88 eV) and 602 nm (2.06 eV), respectively, for pristine MoS$_2$. After the exfoliation process, the positions of these peaks are slightly shifted, as we can see in Figure 8.8.

We observed a red shift for these absorption peaks of approximately 14 nm, located at 674 nm (1.84 eV) and 614 nm (2.02 eV), for the top phase of the dispersion in surfactant (see Figure 8.8-d). This red shift is related to the number of layers and not to the particle size and indicates that more than 6 layers are present on the particles [83].

The addition of surfactant could have contributed to this red shift due to the displacement of anions by the surfactant that adsorbed onto the particle surfaces [84], but this shift was similar for the three dispersions measured, including that in water (see Figure 8.8-d), indicating that the surfactant did not influence these measurements in these regions.

For the bottom phase of the dispersion in surfactant, the shift was much smaller, the peaks were much broader and the excitation position values (668 nm and 608 nm) were very similar to the bulk values, indicating that the particles were larger and probably unexfoliated [83], which in a sample without surfactant would result in phase separation (solute/solvent).
8.3 Stability of the 2D dispersion and 2D ink

8.3.1 Stability evaluated by the concentration over time

In Paper I, we applied a first-order reaction equation to data from the literature and to our results [44] to compare the stability (see Equation 8.1, where \( N_0 \) is the initial dispersed concentration and \( N \) is the concentration of exfoliated material in the dispersion after a certain evaluation time \( t \)). \( \lambda \) is the decay rate, and \( t_{1/2} \) is the time at which \( N \) will be half of \( N_0 \).

\[
N = N_0 e^{-\lambda t}
\]  

(8.1)

These data are presented in Table 8.1. The half-life value \( (t_{1/2}) \) for a dispersion prepared with the present method and in the ethanol/water mixture was 23 h, a value that is rather low compared to that of the dispersions prepared in organic solvents but reasonable considering the advantages of employing water as a solvent and using no added agents to increase the stability.

Coleman and co-authors [22] describe a method to measure the stability over time using a home-built apparatus. We refer to these results in the first line of Table 8.1, in which the initial concentration is taken as the concentration after centrifugation. The yield is normally very low for the dispersions of nanosheets, and because we did not measure the stability over time, we cannot directly compare our results to theirs. We then considered the initial concentration that was used to disperse the nanosheets in their work for comparison against our own which was published in Paper I. Nevertheless, the half-time is still higher in organic solvents than in water or water/ethanol mixtures.

The lateral size of the nanosheets produced by solution processing methods was still limited to approximately 300 nm, as seen from the overview presented in Table 3.1, in agreement with our estimation of the lateral size. This size range is partly due to the size of the clusters before exfoliation, which was already in the micrometer range, as we estimated by the DLS measurements presented in Figure 8.3-A, and also due to the sonication process, which tends to break the particles in a process called sonication scission [49].
Table 8.1: A probability decay equation (Equation 8.1) was applied to the stability data reported by other authors in the referenced papers and the stability data from the present work. Adapted from Paper I [44]

<table>
<thead>
<tr>
<th>Method</th>
<th>Solvent</th>
<th>Surfactant</th>
<th>$N_0/N$</th>
<th>Time [hour]</th>
<th>$t_{1/2}$ [hour]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBE</td>
<td>NMP</td>
<td>No</td>
<td>1, 1</td>
<td>600</td>
<td>6028</td>
<td>[22]*</td>
</tr>
<tr>
<td>LBE</td>
<td>NMP</td>
<td>No</td>
<td>27</td>
<td>600</td>
<td>127</td>
<td>[22]</td>
</tr>
<tr>
<td>LBE</td>
<td>EtOH/Water</td>
<td>Yes</td>
<td>167</td>
<td>168</td>
<td>23</td>
<td>[46]</td>
</tr>
<tr>
<td>ME+LBE</td>
<td>Water</td>
<td>No</td>
<td>36</td>
<td>120</td>
<td>23</td>
<td>[44]**</td>
</tr>
</tbody>
</table>

*Initial concentration after centrifugation was considered in this presented data.
** Result published in Paper I

O’Neill reported larger particles based on TEM measurements [49]. The maximum reported concentration [49] achieved in organic solvents (40 g L$^{-1}$) needed a long processing time of 140 h, and a reasonable concentration level can be achieved after 50 h. However, the half-time of the dispersion was not as good as for dispersions at lower initial concentrations [22].

The liquid exfoliation process in organic solvent was the process that achieved the highest concentration and most stable dispersions [20, 22, 39, 47–49]. However, the removal of the solvent after the application may be challenging due to its high boiling point and toxicity. Low-boiling-point organic solvents have been used [46, 49], but the final throughput concentration was rather low.

### 8.3.2 Zeta Potential for the nanosheets in the 2D dispersion and 2D ink

We attributed the stability of the dispersions to the charges created during the LBE step. We identified these charges using electrophoretic mobility measurements. Electrostatic stabilization can be quantified by measurements of the zeta potential, which, for instance, can be estimated by electrophoretic mobility measurements.

If all the particles have a large negative or large positive charge, they will repel each other, and dispersion stability will be obtained. If not, when $|\zeta| = 25$ mV [85], the forces repelling these particles are very small, almost negligible, so they will come in contact, and the
8.3.2. Zeta Potential for the nanosheets in the 2D dispersion and 2D ink dispersion will be unstable.

According to the zeta potential (ZP) distribution in Figure 8.9, most of the particles were in the range of dispersion stability after liquid exfoliation and a small percentage were not, which means that some sedimentation may still occur. During exfoliation, a higher specific surface area was created on the particles, which means that to stabilize the dispersion, more charges are necessary to cover these new surfaces, otherwise, these particles may sediment. The apparent zeta potentials for the exfoliated dispersion (\((-32\pm2)\) mV) and for the non-exfoliated dispersion (\((-39\pm3)\) mV) indicate that charges were present in the systems that accounted for the stability of the dispersions.

For the dispersions using SDS as illustrated in Figure 8.10, we measured a higher zeta potential than for the dispersions in pure water [44]. The higher negativity of the zeta potential values was probably due to the anionic characteristic of the surfactant [64].

The surfactant concentration did not significantly affect the values for the zeta potential, especially when the particles were left to settle for a few days, as can be seen in Figure 8.9. Note also that all measured values were \(|\zeta| > 25\) mV [85], which indicated good dispersion stability. For the sample left to settle for 6 months, the zeta potential was \(-39\pm3\) mV, which was somewhat lower than the values for those measured within a month of sample preparation. The mechanism of stabilization using surfactants can be explained by the DLVO and Hamaker theory [64].

A deviation of approximately 20% of the actual zeta potential for rod-like particles could be observed, as the method employed here, which is based on a combination of electrophoresis and laser Doppler velocimetry techniques, was designed to measure particles with a spherical shape [70], which is not the case for nanosheets.
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Figure 8.9: Average zeta potential of 2D dispersion samples measured before (left image) and 25 days after sample preparation (right image). Adapted from Paper I [44]

Figure 8.10: Average zeta potential for dispersions in surfactant solution at different concentration over a period of 25 days of sample preparation. The legend indicates the surfactant concentration of the stock solution in which MoS$_2$ at a concentration of 1 g L$^{-1}$ was dispersed. Adapted from Paper II [45]

8.4 Test print of 2D ink on flexible substrates

8.4.1 Printing conditions

A MoS$_2$ dispersion in a 1 g L$^{-1}$ surfactant solution was successfully jetted using a Dimatix 2831 piezoelectric materials printer (Fujifilm, USA) with a Dimatix 11610 cartridge with 21 μm printing nozzles, a
8.4.2 Substrates

The substrates used for the test prints were a photo paper (HP Photo Paper Advanced) and a 100 µm thick PET film. The substrates were kept in position by a vacuum plate at the DMP-2831 with a controlled temperature of 30 °C.

8.4.3 Nozzle diameter versus nanosheets size

To be able to print the dispersions and avoid clogging the printing head nozzles, a ratio of 50:1 printing head nozzle to particle size is suggested [88]. The size of the nozzles of the DMP-2831 compared to the maximum range of the particles measured according to the
particle size distribution (PSD) measurements, 500 nm (see Figure 8.3) would give a ratio of approximately 42:1.

### 8.4.4 Visualization of drop formation and drop break-off

Using the drop evaluation tool available for the Dimatix printers, we did not observe from the recorded images captured with the fiducial camera any clogged nozzles during printing. A still image (Figure 8.12) showed a number of nozzles and a few drops that were jetted. The jetting produced uniform drops in general, but they were often broken up, producing satellite drops.

One approach to reduce the formation of satellites is to increase the viscosity. For this, one can increase the concentration, add chemicals such as polymers or perform a solvent exchange to transfer the dispersed nanosheets to a solvent with a higher viscosity [10].

![Image of drop evaluation tool](image)

Figure 8.12: Drop evaluation tool image captured during the inkjet printing of the MoS$_2$ test lines using the DMP-2831. The nozzle spacing is 254 µm. The waveform used was for distilled water, with a 25 volt bias. Adapted from Paper II [45]

The jetting conditions should also be studied more carefully because the applied voltage affects a number of the properties of the droplets such as the droplet break-up from the nozzle, morphology of the drops, drop velocity and size [58, 89], which will eventually impact the printing quality.
8.4.5 Waveform

A scheme of the phases of drop formation and break-off in the DMP-2831 is presented in Figure 8.13 and a print-screen image of the waveform editor showing the phases of the waveform used for the test prints in Paper II is presented in Figure 8.14.

A typical waveform is divided into four phases plus the start, which is actually the continuation of phase four. Each of these phases has three properties: duration, slew rate and level, which can be adjusted in the waveform editor [87] (see Figure 8.14).

Properties of drop formation and break-off:

1. The Level is the percentage of the amplitude relative to the value specified in the cartridge settings waveform screen. It has the most impact on the jetting process.

2. The Slew rate determines how fast the voltage changes. It is the slope of the line in the waveform during the voltage ramps.

3. The Duration is the length of time of the phase. Changing the duration of phase one and slew rate and/or duration of phase two has a strong influence on drop formation.

Two phases for the drop formation and break-off was enough to jet the dispersions we used in Paper II. The drop formation duration was 5.6 µs, and the total pulse duration to jet one droplet was 26.9 µs. This waveform was tuned by the manufacturer to be used to jet distilled water, so we did not adjust the phases ourselves. If we modify the inks in future experiments, we may need to adjust the waveform as well. The non-jetting waveform is to keep the ink nanosheets in Brownian motion to avoid the clogging of the nozzles. The voltage in this case is not high enough to jet a drop.

8.4.6 Test prints results

The test pattern used consisted of an 8 mm-long and 450 µm-wide line between contact pads. We used a 2D ink that was stable for almost a year to print the test lines. Figures 8.15-c and d show printed MoS\(_2\)
Chapter 8. Results and Discussion

Figure 8.13: Drop formation sequence for Dimatix printing heads. Adapted from [87]
test lines consisting of 30 subsequent printed layers on top of each other on the PET film.

The effect of the number of printed layers can be seen when comparing Figures 8.15-c and d, where better coverage of the surface was achieved using 30 printed passes. The printed line contains voids, which is most likely due to the matching of the surface energy of the PET and the MoS$_2$ dispersion. This effect is more visible on the microscopy image in Figure 8.15-b. The edges of the printed lines are shown in Figure 8.15-a. The printed lines with only 6 passes on paper were almost transparent, so we presented only this with 50 passes (Figure 8.15-e).

The presence of stabilizing agents such as surfactants can be detrimental to forming an interconnected phase between the nanosheets because it would form non-conducting layers between the nanosheets that would affect the conductivity [62]. The surfactant particles can be removed by heat treatment, but it was not within the scope of this study to analyze the conductivity of the inks.
Figure 8.15: Inkjet-printed test lines on PET and paper. (a) Microscopy image with 50x magnification of the printed test line with 30 printed passes on PET, the lighter area in the image is the printed one. (b) Same as in (a) but with 100x magnification (c) Test line printed on PET with 30 passes (d) The printing results on PET with 6 passes and (e) the printed results on paper with 50 passes. Adapted from Paper II [45]
CONCLUSION AND OUTLOOK

The method described in this thesis, could be easily employed to exfoliate 2D materials, such as the TMDs MoS$_2$ with good quality nanosheets regarding dimensions, optical properties and crystallinity, comparable to the one reported for dispersions obtained in organic solvents.

Relatively high volumes of 2D inks, sufficient for use in inkjet printing, can be produced with our method, considering the very low drop volumes and consequent ink volume necessary for the deposition of these materials onto substrates. Scalable production of 2D nanomaterials by the shear exfoliation method should be considered in future experiments. This is because simply increasing the solvent volume in direct sonication using the LBE method does not lead to higher dispersed concentration of the nanosheets and because some of the ink properties that we need to improve are concentration and viscosity. The printing test shows that it is possible to use the MoS$_2$ dispersion as an inkjet ink. Optimization for specific printer and substrate combinations should be performed, which would improve the printing quality dramatically.
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