Liquid Phase Exfoliation of Novel 2D Nanomaterials

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To Mum, Dad, Mark and Cahiriona
DECLARATION

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Damien Hanlon
Abstract

Over the past decade, there has been a wealth of research, into two dimensional (2D) layered nanomaterials. These materials have unique properties, that can only be realized when they are reduced to the nanoscale. Following reduction to the nanoscale, these materials have many applications which range from gas sensing, transistor technologies and energy storage devices. Several methods have been developed to produce 2D nanomaterials. Pioneering work from Coleman et al, showed that exfoliation of layered nanomaterials can be achieved using common organic solvents. This liquid base exfoliation technique has been shown to exfoliate layered materials such as; graphene, hexagonal boron nitride and transition metal dichalcogenides (TMDs). Although a wealth of research has been conducted, the extension to new layered nanomaterials had been slow.

Current focus has continued to explore the exfoliation of novel layered materials. Presented in this work, is an extension of the liquid phase exfoliation methodology, as applied to novel layered materials such as; molybdenum trioxide (MoO₃) and black phosphorus (BP). At the outset, MoO₃ was exfoliated in several common solvents, where the Hildebrand solubility parameter was determined to be 21 MPa⁰. Understanding the solubility process is important in order to improve the concentration of nanosheets in solution. To this end, processing parameters such as sonication time (tₛ), initial concentration (Cᵢ) and centrifugation conditions were optimised.

Analysis of optimised dispersions was conducted using AFM and TEM, where the fundamental relationship of the nanosheet size was discovered. Key lateral dimensions were found to follow a simple relation \( \langle L \rangle : \langle w \rangle : \langle t \rangle = 6.6:2.5:1 \), irrespective of the nanosheet size. A significant advantage of 2D materials is a high surface area, useful for several applications. To this end, the charge storage capabilities of three different nanosheet sizes were investigated. Thin films were prepared and tested from nanosheet dispersions; analysis revealed that the nanosheets displayed poor capacitances, \(~ 2 \text{ F/g}\). Such poor capacitance, led to the initial thought, that samples were restricted by the poor electrical conductivity of MoO₃ \( (~10^{-6} \text{ S/m}) \). In order to address this, composite films incorporating a nano-conductor (SWCT), were prepared. Individual samples were designed in dispersion and mixed in solution followed by
vacuum filtration. The conductivities of composite films; increased by 8 orders of magnitude. This facilitated high capacitances of ~ 200 F/g to be realised (10mV/s). In both cases the electrical conductivity and capacitance of the composite films followed percolation behaviour, with a percolation threshold of 3 w.t. %.

The successful exfoliation of MoO₃ validated the strength of LPE. A further extension, of this exfoliation methodology, soon followed into black phosphorus (BP). BP is similar to graphene; both monoatomic layered nanomaterials. However, it was discovered that BP is chemically unstable under ambient conditions. Instability of the material soon became apparent upon exfoliation in some organic solvents. The dispersed nanosheets were noted to deteriorate via a disproportionation reaction mechanism. Optical metrics were developed, to track the rate of reaction and quality of this dispersion over time. Interestingly, the solvation shell of the solvent was found to protect the nanosheets thereby decreasing the rate of reaction. Amide solvents, such as CHP and NMP, showed the greatest stability. Moreover, reaction rate was found to be dependent upon nanosheet size and the quantity of water in a sample (for a given solvent).

The exfoliation of BP has highlighted the pressing need for a qualitative analysis technique, which may be used to investigate samples produced from LPE. Furthermore, optical effect studies may be realised through the exfoliation of molybdenum telluride (MoTe₂), in aqueous surfactant (sodium cholate (SC)). Exfoliation in SC allowed the effect of the surfactant concentration to be analysed using parameters such as; dispersed nanosheet concentration and dispersion stability. It was found that, exfoliation and stabilisation is most efficient around the CMC of the surfactant (6mg/ml). Moreover, an attempt to track different exfoliation behaviour and its relationship to varying populations of mono- and bi-layered species was conducted. This saw the photoluminescence of these species, tracked as a function of the surfactant concentration. The results of which, highlighted an increasing PL with increasing surfactant concentration.
Publications

Aspects of this thesis have been published previously in the following publications. Research containing major contributions from this thesis is indicated with *.


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## Contents

1 Motivation and Thesis Outline........................................................................................................... 9  
   Thesis Outline.................................................................................................................................. 10
2 Materials and Background .................................................................................................................. 12  
   2.1 Introduction.................................................................................................................................. 12  
   2.2 Carbon Nanomaterials.................................................................................................................. 13  
      2.2.1 Properties and Applications of Carbon Nanotubes................................................................. 14  
   2.3 Layered Nanomaterials.................................................................................................................. 15  
   2.4 Inorganic Layered Nanomaterials ................................................................................................. 16  
      2.4.1 Properties of TMDs, Specifically MoTe$_2$.............................................................................. 16  
      2.4.2 Applications of TMDs............................................................................................................ 20  
      2.4.3 Properties of Transition Metal Oxides (TMOs), specifically MoO$_3$.............................. 21  
      2.4.4 Applications of TMOs............................................................................................................ 23  
   2.5 Black Phosphorus-BP .................................................................................................................... 25  
      2.5.1 Properties of BP..................................................................................................................... 25  
      2.5.2 Applications of BP.................................................................................................................. 26  
   2.6 Production Methods of Layered Nanomaterials ......................................................................... 27  
      2.6.1 Liquid Phase Exfoliation (LPE) ............................................................................................ 29  
3 Dispersion Theory............................................................................................................................... 32  
   3.1 Introduction.................................................................................................................................. 32  
   3.2 Solubility Theory........................................................................................................................... 32  
      3.2.1 Solution Thermodynamics .................................................................................................... 33  
      3.2.2 Hansen Solubility Parameters ............................................................................................... 35  
   3.3 Surfactant Stabilisation.................................................................................................................. 37  
      3.3.1 Charged Molecules and Electrostatic Repulsion .................................................................. 38  
4 Characterisation and Methods ............................................................................................................. 40  
   4.1 Introduction.................................................................................................................................. 40  
   4.2 Sample Preparation....................................................................................................................... 41  
   4.3 Sedimentation Methodology......................................................................................................... 42  
   4.4 Absorbance Spectroscopy............................................................................................................ 45  
   4.5 Photoluminescence....................................................................................................................... 49  
   4.6 Raman Spectroscopy..................................................................................................................... 51
4.7 Zeta Potential .................................................................................................................. 54
4.8 Transition Electron Microscopy (TEM) ........................................................................... 55
  4.8.1 Statistical TEM Analysis ............................................................................................... 57
4.9 Scanning Electron Microscopy (SEM) ............................................................................ 58
4.10 Atomic Force Microscopy (AFM) ................................................................................ 60
5 Liquid Phase Exfoliation of Molybdenum Trioxide (MoO$_3$) ............................................ 63
  5.1 Introduction ..................................................................................................................... 63
  5.2 Experimental Procedure ................................................................................................. 63
  5.3 Results and Discussion ................................................................................................... 66
    5.3.1 Optimisation of MoO$_3$ Dispersions ...................................................................... 66
  5.4 Nanosheet Characterisation ........................................................................................... 72
    5.4.1 AFM Characterisation of MoO$_3$ Nanosheets ......................................................... 78
    5.4.2 Solid Sample Characterisation ................................................................................. 80
    5.4.3 Supercapacitor Measurements .................................................................................. 82
  5.5 Conclusions ................................................................................................................... 87
6 Liquid phase exfoliation of Black Phosphorus (BP) ............................................................ 89
  6.1 Introduction ..................................................................................................................... 89
  6.2 Experimental Procedure ................................................................................................. 90
    6.2.1 Sample Preparation ................................................................................................. 90
    6.2.2 Characterisation Methods ....................................................................................... 91
  6.3 Results and Discussion ................................................................................................... 93
    6.3.1 Exfoliation and Basic Characterisation ................................................................... 93
    6.3.2 Nanosheet Size Selection ....................................................................................... 101
    6.3.3 Photoluminescence ............................................................................................... 105
    6.3.4 Nanosheet Stability ............................................................................................... 108
    6.3.5 Size Dependent Stability of BP Nanosheets ........................................................... 111
    6.3.6 Analysis of LPE Nanosheets Under Ambient Conditions ...................................... 115
    6.3.7 Effect of Water on Nanosheet Stability .................................................................... 118
    6.3.8 Effect of Oxygen on Nanosheet Stability ............................................................... 122
    6.3.9 Effect of Solvent Type on Nanosheet Stability ....................................................... 124
  6.4 Conclusions ................................................................................................................... 129
7 Photoluminescence of Molybdenum Telluride Nanosheets in Aqueous Surfactant Solutions ................................................................................................................................. 131
  7.1 Introduction .................................................................................................................... 131
Motivation and Thesis Outline

Over the past decade, there have been significant advances in modern technology, notably; at the forefront has been the development of the transistor. Underpinning such technological advancements is the production of materials with low dimensionality. Richard Feynman’s acclaimed 1959 lecture entitled “there is plenty of room at the bottom” is credited with igniting research and development toward a new field; nanotechnology. This field has grown to become a leading area of research, which encompasses physics, chemistry and engineering. It is focused on developing and implementing materials, which display unique properties at the nanoscale; which in some cases are superior to the bulk. Notable materials such as carbon nanotubes and graphene display unique properties and are all linked by their low dimensionality.

The field has accelerated quickly from graphene, with the discovery of several other 2D classes of materials, displaying a broad palette of properties. These novel materials hold high promise for applications such as gas sensing, hydrogen evolution, and polymer reinforcement. To achieve their full potential; however, the primary challenge is to develop a scalable method to produce large quantities of materials. There are several methods to produce nanoscale materials which can be categorised either as top-down or bottom-up processes. With this in mind, a liquid-phase exfoliation process was developed, which demonstrated that graphene and other bulk layered materials can be exfoliated down to the nanoscale. This methodology offers a simple, low-cost production method for 2D nanomaterials, which is furthermore scalable and thus holds great promise for future applications.

Expansion of this LPE methodology to layered materials beyond graphene, h-BN and TMDs has been slow. Accordingly, this work aims to address this by applying the LPE process
to new layered nanomaterials. Initially, the process will be applied to a novel transition metal oxides (MoO$_3$) and black phosphorus (BP). The effect of exfoliation will be studied by optimising the exfoliation parameters. These parameters will also be compared with those of previously exfoliated nanomaterials, to investigate the fundamental physics of the process. At the time of this work the exfoliation of novel materials was in its infancy, however, a wide range of exotic materials are now being studied, each with their own unique properties. It is hoped that the expansion of the LPE methodology to new materials, will expand the palate of material properties available for device engineers.

**Thesis Outline**

Application of liquid phase exfoliation (LPE) to a transition metal oxide, molybdenum trioxide (MoO$_3$) is investigated during the course of this work. The interaction of MoO$_3$ with a range of organic solvents is studied using Hildebrand solubility parameters. Optimisation of the exfoliation conditions is achieved by subjecting the samples produced to a series of characterisation techniques. Understanding this process allowed for a selection of nanosheet sizes to be filtered onto membranes and undergo investigation for use as supercapacitor electrodes. The storage capabilities of MoO$_3$ nanosheets was inhibited, similar to some TMDs (e.g. MoS$_2$), by their inherent poor electrical conductivity. However, the formation of composite electrodes, with an addition of a small quantity of carbon nanotubes, overcame this problem.

Expansion of LPE technology has spread to new materials where methodologies developed, from the exfoliation of MoO$_3$ were applied to black phosphorus (BP). However, unlike MoO$_3$, the nanosheets produced displayed a chemical instability. This instability was investigated using optical spectroscopy. Fortunately, solvent optimisation was discovered that can shield the nanosheets produced, by encompassing them with a solvation shell. This allowed for a potential metric that predicted stability to be developed.

The chemical interaction at the nanosheet surface is quite complex and difficult to understand. To this end, a study was conducted with Molybdenum telluride (MoTe$_2$) to investigate chemical interaction with surfactant molecules. The chemical environment around the nanosheet was analysed using photoluminescence spectroscopy (PL), which is highly sensitive to chemical change. PL peaks were observed for the mono- and bi-layer nanosheets.
The nanosheet concentration and PL intensity were investigated as a function of surfactant concentration.

It is hoped that the methodologies developed in this thesis, specifically relating to the exfoliation and optical characterisation, can be employed for other nanomaterials. The metrics developed within this work should provide a basis to analyse new nanomaterials which may be unstable, thus yielding a platform from which to advance the characterisation of 2D nanomaterials.
Materials and Background

2.1 Introduction

Nanotechnology arguably defines the current period of research, and holds the key to many future applications. Nanotechnology is the implementation of materials which are defined by a lateral size, the nanometre. Such nanomaterials typically have dimensions between 1 nm and 100 nm. The body of work presented in this thesis can certainly be encompassed under such an umbrella. The key focus of this thesis is directed towards the processing and characterisation of 2D layered nanomaterials in liquid media. 2D materials represent a unique class of nanomaterials, which have generated significant interest over the past decade. However, other nanomaterials, for example 1D carbon nanotubes (CNTs), also display interesting properties.

The following chapter reviews the properties, applications and production methods of selected nanomaterials. Initially, a brief review of carbon-based nanomaterials is considered. While such nanomaterials are employed to a lesser extent in this thesis, it is important to understand the properties and applications of the materials which ignited the 2D field of research. This shall be followed by an in-depth discussion of the materials central to this thesis; molybdenum telluride (MoTe₂), molybdenum trioxide (MoO₃) and black phosphorus (BP). Finally, a comprehensive review of the production methods of 2D layered nanomaterials, specifically focusing on the liquid phase exfoliation (LPE) process, is presented.
2.2 Carbon Nanomaterials

Carbon is the 4\textsuperscript{th} most abundant element in the universe and has been observed since humanities outset in its fundamental forms; charcoal, soot, graphite and diamond. More recently, the discovery of carbon nanotubes and graphene has advanced the study of nanomaterials for the modern age. Although the materials are composed of the same element, they have very different chemical structures (figure 2.1). Structure; however, is not the only difference between the varying forms of carbon; fundamental properties also vary greatly among them. Diamond for instance is a sp\textsuperscript{3} hybridised carbon material which is a poor electrical conductor, but one with excellent thermal conductivity. However, graphene has excellent thermal\textsuperscript{1,2} (~10\textsuperscript{3} W/mK) and electrical conductivity\textsuperscript{3,4} (~10\textsuperscript{4} S/m). The electrical properties of graphene arise due to its structure, which consists of sp\textsuperscript{2} hybridised carbon atoms in hexagonal rings (chicken wire).\textsuperscript{5}

The application of CNTs and graphene is highly dependent upon this unique dimensionality and chemical properties. A brief overview of these properties and applications is given below.

![Figure 1.1: Schematic structure of A) diamond, B) single walled carbon nanotube, C) graphite, D) graphene sheet.](image)

\textsuperscript{2} G. Dresselhaus, Science 1992, 258, 169.
2.2.1 Properties and Applications of Carbon Nanotubes

Carbon nanotubes (CNTs) were first discovered in 1991 by Iijima et al.\textsuperscript{6} from the soot of an arc-discharge experiment. CNTs are composed of a single layer of carbon atoms (graphene) rolled up into a tubular configuration. A CNT can be classified as single (SWCNT) or multiwall (MWCNT). SWCNTs have a single rolled up tube of graphene, while MWCNTs have several concentric cylinders.\textsuperscript{7, 8, 9, 10} The diameters of these tubes can range from 0.4 to 40 nm; however, the length of the nanotubes can in some instances reach up to ~20cm.\textsuperscript{6, 11, 12} The ratio between the width and length creates a 1D nanomaterial. The electrons in CNTs experience quantum confinement in two dimensions; however, they are free to move in the third in this case; the length of the nanotube. The electrical properties of the tubes can range from semiconducting to metallic. The chirality of the CNT dictates the electrical properties which can be described by the translational vector equation (C = na\textsubscript{1} + ma\textsubscript{2}). This equation can be used to predict the electrical behaviour and type of nanotube; armchair, zigzag or chiral.\textsuperscript{6}

CNTs are used throughout this thesis, due to their outstanding electrical properties; mobilities of 10\textsuperscript{5} cm\textsuperscript{2}/Vs.\textsuperscript{13} Their high aspect ratio (length to width) and high electrical conductivity are ideal for making composite electrodes with another active material, which may be electrically poor. Incorporation of these conductive elements into a matrix leads to the provision of a conductive pathway, thereby allowing current to flow in the film. Such properties; however, are only maximised when the CNTs are individualised, which can be achieved through debundling methods, such as liquid phase exfoliation (LPE). The mechanical properties of CNTs also make them attractive to reinforce materials such as plastic\textsuperscript{14} and also to improve composite films, useful for applications as supercapacitors.\textsuperscript{15, 16, 17, 18} In addition to providing electrical enhancement, mixing of CNTs with other nanomaterials can also increase the mechanical properties of a film. CNTs exhibit highly attractive mechanical properties and tensile strengths, their Young’s modulus can vary up to 60 GPa (two orders of magnitude higher than steel).\textsuperscript{19} An atypical application of CNTs is their ability to provide mechanical reinforcement to composite films (as shown in Figure 2.1, composite electrode of MoS\textsubscript{2}/SWCNT). The mechanical properties of CNTs can reinforce these composites and maintain electrical pathways in films which have lost mechanical integrity during testing.
Figure 2.1: SEM image of a composite electrode of MoS$_2$/SWCNT. The SWCNTs (false coloured yellow/green) bridge the crack that has formed to sustain the electrical conductivity of the sample. Scale bar 200 nm

2.3 Layered Nanomaterials

The most famous 2D layered nanomaterial is most certainly graphite. This material can be exfoliated to yield graphene which was isolated in 2004. Graphene is a 2D layered nanomaterial consisting of sp$^2$ hybridised carbon atoms. These atoms are covalently bonded together to form a planar hexagonal structure. Each layer is stacked on top of each other to form the 3D crystal, graphite (figure 1.1 C and D). Unlike CNTs, electrons are free to move in two dimensions. This leads to interesting behaviours not observed in the bulk crystal, with high electrical conductivities and mechanical strength. The production of graphene is achieved through the cleaving of a single layer, from a graphite crystal. There are several processes which have been developed over the past decade to produce graphene layers such as mechanical exfoliation and liquid based processes.
However, graphene is not the only layered nanomaterial; there exists a wide range of layered nanomaterials, each with their own properties and bonding structure. While their chemical nature may change depending on the configuration of different atoms, all of these materials have a common factor, they are composed of individual layers with weak interlayer van der Waals bonding. Recently, research has expanded the range of layered nanomaterials. Discussed below are several which have been studied in this thesis with respect to their structure, chemical properties and applications.

2.4 Inorganic Layered Nanomaterials

Since the isolation of graphene by Geim and Novoselov in 2004,\textsuperscript{20, 25} it has been the subject of continual research, due to its many attractive properties. However, graphene is not the only known layered material; indeed, recent years have seen an explosion of research into the synthesis and characterisation of other 2D materials. Materials such as transition metal dichalcogenides (TMDs),\textsuperscript{26, 27, 28} transition metal oxides (TMOs)\textsuperscript{15} and black phosphorus (BP).\textsuperscript{29, 30, 31, 32, 33} Such materials have a range of chemical and physical properties, which may be employed in a range of promising applications including gas sensing\textsuperscript{15} and hydrogen evolution catalysis.\textsuperscript{34} Development of these nanomaterials for many applications may only be achieved following, exfoliation down to mono- or few-layered nanosheets. The work presented within this thesis is focused on the development of a LPE methodology which is applicable to MoTe\textsubscript{2}, MoO\textsubscript{3} and BP.

2.4.1 Properties of TMDs, Specifically MoTe\textsubscript{2}

TMDs are a well-known class of layered materials, which typically have a MX\textsubscript{2} stoichiometry, where M is a transition metal (Mo, W, Nb, Hf etc.) and X is a chalcogen (S, Se, Te). There are a large variety of TMDs, given the range of transition metals and chalcogens there are 60 possible configurations.\textsuperscript{35} Such structures, depending on the configuration of d orbitals, can produce a wide range of chemical and physical properties from; semiconducting (MoS\textsubscript{2}, WS\textsubscript{2})\textsuperscript{36} to semi-metallic (WTe\textsubscript{2})\textsuperscript{37} to superconducting (NbSe\textsubscript{2}).\textsuperscript{38} Typically the structures of the TMDs follow sandwich geometry, where a transition metal layer is
sandwiched between two chalcogen layers (figure 2.3). Bonding in these materials is quite strong in plane, however, each layer is held together by relatively weak van der Waals bonding out of plane. The variation in stacking, of individual layers on top of each other, leads to different polymorphs. These polymorphs are classified as 2H-hexagonal, 1T-trigonal and 3R-rhombohedral (figure 2.2). The 3R phase is typically found in bulk materials, with mild heating it is seen to relax to the 2H phase.

In addition to their electronic difference, their chemical stability is also different. A transition from the 2H to 1T can be triggered by Li-ion intercalation, where the Li transfers excess charge carriers to the material and induces the phase change. This transition weakens the metal-chalcogen interaction and also the D$_{6h}$ crystal field. This transition from the thermodynamically stable 2H to 1T’ can also be induced by strain as observed for MoTe$_2$, a strain of 0.3-3% is sufficient to induce the transition (figure 2.3A). This methodology is known as strain engineering and is more common practice for electronic applications, where electrical components are required to be either semiconducting or metallic.

![Figure 2.2: Typical geometry for TMDs where purple atoms are transition metals while yellow are chalcogenide atoms. The two structures can be classified into two groups namely 2H and 1T. The 2H polytype exhibits a trigonal prismatic structure while the 1T is octahedral.](image)

The electronic properties of TMDs are quite promising. Depending on the mix of transition metal and chalcogen atom, the electronic behaviour can be changed from semiconducting to metallic. Semiconducting TMDs can be n or p type depending on the atomic
configuration, therefore, making the fabrication of complementary logic devices possible. Transition metals are characterised by their d orbitals, which increase from left to right across the periodic table. The coordination of transition metal directly affects electronic properties. TMDs such as MoS\textsubscript{2} (p-type) and WS\textsubscript{2} (n-type) are both semiconducting, however have different current carriers. Semiconducting TMDs have a defined energy difference between the conduction band minimum and valance band maximum; a band gap.\textsuperscript{28, 41} An increase in the band gap is observed as the bulk material is thinned down to the monolayer. A common behaviour with semiconducting TMDs is the variation of the band gap with layer number. This behaviour arises due to quantum confinement of the electrons. The band structure changes of MoS\textsubscript{2} are shown for reference (figure 2.3 B).

Typically, the transition from valance band to the conduction band is indirect. The minimum of the conduction band and maximum of the valance band do not align. This means for an electron to get promoted a change in momentum is required. Decreasing the layer number from bi- to mono-layer; however, results in transition from an indirect to a direct band gap (figure 2.3 B). This change is most notable by measuring photoluminescence (PL), where the optical transition can be probed. For MoS\textsubscript{2} and WS\textsubscript{2} this transition is only observed for the monolayer species; however, in the case of MoTe\textsubscript{2} the bilayer can also be observed.\textsuperscript{42} A variation in band gap with chalcogen atom can also be achieved, where a change is observed when moving down group 6 (where the bulk $E_g$ of MoTe\textsubscript{2} < MoS\textsubscript{2} < MoSe\textsubscript{2}).

Specifically, the work within this thesis focuses on MoTe\textsubscript{2}. At room temperature the material behaves as a semiconductor; increasing or decreasing its temperature induces structural rearrangement thereby producing metallic or superconducting behaviour respectively.\textsuperscript{43} Nevertheless, the most typical form is the 2H, semiconducting phase. It has an electronic band gap of 0.8 eV in the bulk, increasing to 1.08 eV for the monolayer.\textsuperscript{42} The band gap change is relatively small ~0.2 eV; other TMDs may display a change as high as 0.7 eV on going from monolayer to bulk.\textsuperscript{42, 44, 45} The change in MoTe\textsubscript{2}’s band structure, from indirect to direct occurs for both the mono- and bi-layer. Interestingly, tri-layers have nearly identical direct and indirect band gaps. The transition to direct band gap means, optical techniques, such as PL, tend to be highly beneficial in the study of these materials. Optical excitation, probes the electronic structure, via the emission of a photon. The emitted photon will have a characteristic energy of the band gap of the nanomaterial, which is different for the mono- and bi-layer species. Therefore, this methodology is useful to identify a specific nanosheet thickness by their characteristic photon energy emission.
This is a useful characterisation method which can be employed, for example, to refine the protocol for the exfoliation of such TMDs in solution. This will be discussed in more detail with respect to MoTe$_2$ in chapter 7, where the PL characteristics of monolayer and bilayer nanosheets will be studied, with emphasis on environmental and chemical effects.

Figure 2.3: A) Induced strain in TMDs which produces a change in structure from 2H to 1T, modified from Duerloo et al.$^{46}$ B) Band structure of MoS$_2$ from bulk to monolayer, transition from indirect band gap to direct band gap (1.20-1.90 eV) modified from Duerloo et al.$^{46}$
2.4.2 Applications of TMDs

TMDs are very useful 2D nanomaterials, due to their favourable properties. These materials have been investigated for a wide range of applications including energy storage, transistors, hydrogen evolution among many more. One area where TMDs make a significant impact is within the field of electronics. Once these materials have been exfoliated down to the monolayer, then begin to display band gaps and low level electron mobilities, which are useful for transistor devices. This is the main advantage of TMDs over graphene, which has no band gap and therefore displays poor on/off ratios.

In 2004, the first transistor using a TMD was constructed, tungsten selenide (WSe$_2$), which displayed mobilities, that were half of what was observed for silicon. Indeed, many subsequent studies, have reported the use of such materials as transistors. The performance was quite impressive with on/off ratios of $\sim 10^8$ observed at room temperature for MoS$_2$. One of the main obstacles with the implementation of 2D materials in device fabrication is the connection of these materials with electrical contacts. As the material is scaled from 3D down to 2D, the contacts are found to be lacking a smooth surface, such that effective integration in integrated circuits is problematic. Recently, a study was conducted using MoTe$_2$ as the channel material in a transistor (figure 2.4). A layer of MoTe$_2$ was deposited onto a wafer, the edges were heated using a laser to induce a phase transition from the semiconducting 2H to the metallic 1T'. This allowed metal electrodes to be directly applied to the nanosheet. The band gap of the monolayer is $\sim 1.1$ eV which is quite similar to silicon, which facilitated an easy transition.

![Figure 2.4: Schematic of a MoTe$_2$ nanosheet transistor, which was phase engineered to produce 1T'-metallic MoTe$_2$ to contact with the metal electrodes. Modified from Cho et al.](image-url)
2.4.3 Properties of Transition Metal Oxides (TMOs), specifically MoO$_3$

Transition metal oxides (TMOs) represent a diverse class of materials, with exotic electronic properties ranging from; insulating to semiconducting to metallic.$^{53,54}$ In addition to varying electronic behaviours, there is also a wide range of structural differences between TMOs (TiO$_x$, MnO$_x$, ZnO, RhO$_x$, WO$_x$, MoO$_x$ and many more). Geometries range from brookite to orthorhombic (figure 2.5 A, B and C).$^{55,56,57,58}$ The range of structures makes it difficult to apply LPE; however, there are some layered oxides such as RuO$_2$, MnO$_2$ and MoO$_3$ which hold greater promise. These oxides are similar to TMDs, whereby they are composed of individual layers stacked on top of each other, held together by van der Waals bonding.

It is well known that layered oxides can be exfoliated using ion-exchange based methods.$^{15,53}$ These methodologies are typically employed with TMOs due to their mixed valence. This requires that the structure is balanced by charge balancing counter ions. Tungsten trioxide (WO$_3$) is a common TMO which has been studied for a range of applications from sensing to chromic and photocatalytic applications.$^{59,60,61}$ It has several structural forms; however, when the material is hydrated it forms a layered oxide. It can also undergo structural changes depending on the applied temperature.

The oxide under study within this work is a layered TMO, molybdenum trioxide (MoO$_3$). Typical crystal phases of MoO$_3$ include the thermodynamically stable α-MoO$_3$ and the meta stable β-MoO$_3$.$^{62}$ However, α-MoO$_3$ is the most common form of the oxide. It consists of a series of individual layers stacked on top of each other; covalent bonding is displayed in plane, while out of plane there is weak van der Waals bonding. A single layer is composed two nets of MoO$_6$ octahedra, which are joined together to form one layer in the crystal (figure 2.5 C). The electronic structure of MoO$_3$ is quite important for catalytic activity. Typically, α-MoO$_3$ is a wide band gap semiconductor ($E_g \sim 3.2$eV) displaying n-type behaviour.

Any introduction of oxygen vacancies can significantly affect the electronic behaviour for example; the reduction of MoO$_3$ (orthorhombic) through Magnel phases to MoO$_2$ (monoclinic) alters the material’s electronic behaviour from semiconducting to metallic. This transition to MoO$_2$ can be induced when a sample is subjected to a high-energy electron beam, for example during transition electron microscopy (TEM). An example of this is shown in chapter 5 during the discussion of MoO$_3$ characterisation. The work presented in this thesis is
a systematic approach of the LPE of MoO$_3$. Particular emphasis is placed on the optical and physical characterisation of the nanosheets produced during exfoliation.

*Figure 2.5: A) 3D structure of TiO$_2$ (brookite), B) structure of WO$_3$ (orthorhombic), C) structure of MoO$_3$ (orthorhombic).*
2.4.4 Applications of TMOs

Recently TMOs have attracted a large amount of interest in areas such as; electronics,\textsuperscript{61} electro-chemical energy storage,\textsuperscript{61,63} and gas sensing. TMOs are also being developed for use in electrochemical supercapacitors which holds great promise.\textsuperscript{63,64} Typically these devices have a positive and negative electrode with a solid or liquid electrolyte in between. Charge storage arises from the pseudocapacitance (electrochemical supercapacitor) of fast redox reactions at the surface of the material.\textsuperscript{64} To achieve an efficient device the charge storage needs to be high, while the active material does not deteriorate over the cycle lifetime. One major disadvantage of some TMOs (such as \(\text{WO}_3\) and \(\text{MoO}_3\)) is their poor electrical performance, which ultimately inhibits the fast charge discharge.\textsuperscript{61} \(\text{MoO}_3\) has shown capacitances of \(~9\ F/g\), which can be attributed to this poor electrical behaviour; however, hybrids of zinc oxide (ZnO) and \(\text{MoO}_3\) show higher capacitance of \(~250\ F/g\).\textsuperscript{65} Therefore, overcoming the inherently poor electrical conductivity of these materials produces devices with higher charge storage. To this end, composite formation to address these issues will be discussed further in chapter 5.

Interestingly, a more recent development sees the employment of TMOs, as chemical precursors for CVD growth of layered TMDs.\textsuperscript{66,67} For example \(\text{MoO}_3\) and \(\text{WO}_3\) have been used to seed the growth of \(\text{MoS}_2\), \(\text{WS}_2\) and \(\text{MoSe}_2\) in addition to other TMDs.

A common problem with CVD growth of TMDs is that a large amount of the oxide precursor is often required, typically in powdered form. It has also been shown that it is difficult to control the growth on a substrate.\textsuperscript{68} This makes it difficult to control the process and grow well defined regions of TMDs. The precursor material also cannot be reused which decreases the cost benefit analysis of the process.

Research, in parallel with the work in this thesis into TMOs, shows the use of LPE \(\text{MoO}_3\) nanosheets to seed TMD growth. This approach is highly attractive, as only a small amount of precursor is required. The production method of the precursor, while introducing an extra processing step, ensures a low cost supply due to a recent scale up of exfoliation methodologies. A representation of the reaction mechanism and the nanosheets produced is shown in figure 2.6. Using this method the growth substrate and target substrate are oriented opposite each other to direct the evaporation of the \(\text{MoO}_3\) nanosheets, which react with gaseous sulfur, towards the target. Several works have been published using this methodology.\textsuperscript{69}
Figure 2.6: Schematic representation of the CVD growth of MoSe$_2$ nanosheets from LPE MoO$_3$ precursor. A representative optical image is also shown to represent the growth regions. Modified from O’ Brien et al.$^{66}$
2.5 Black Phosphorus-BP

Recently a theoretical paper published by Tomanek et al\textsuperscript{70} outlined the layered material black phosphorus (BP) and its potential use as a FET with on/off ratios as high as $10^5$. A wealth of research has subsequently been conducted on this material, over the last 18 months. BP nanosheets display attractive properties among which a band gap which is highly attractive for several electronic applications.\textsuperscript{32, 33, 71, 72, 73, 74} Exfoliation methodologies have been developed to produce mono- and few-layer species to test in transistor devices.

2.5.1 Properties of BP

Black phosphorus has been rediscovered in recent research and ignited the field into the production of layered phosphorus. There exist three main polytypes of phosphorus; white, red and black. Each polytype has unique properties; however, most display a high reactivity under ambient conditions. White phosphorous for example, turns yellow in contact with air and is highly pyrophoric. Red phosphorus is an amorphous network of phosphorus atoms and is more stable in an oxygen atmosphere.

Recently, reports on black phosphorus (BP) have suggested that this material has attractive properties for applications in electronics. BP is a layered semiconductor in the bulk, where each individual layer is attracted through van der Waals bonds. It can be exfoliated, using similar techniques used to produce graphene and TMDs, to yield a single layer of phosphorus atoms. Both BP and graphene possess layers of single atoms covalently bonded together, the geometry of a single sheet of BP; however, is not planar. The phosphorus atoms form a puckered orthorhombic structure where each atom is bonded to three others (figure 2.7). This puckering produces highly anisotropic behaviour in the electronic and mechanical properties of BP, where mobilities are an order of magnitude higher in the arm chair compared to the zig-zag direction.\textsuperscript{74} Experimental results show that the band gap of BP scales with the layer number from 0.3 eV in the bulk to 1.8 eV in the monolayer.\textsuperscript{74, 75} This tuneable band gap and high electrical performance make BP quite attractive for electronic devices such as Li-ion batteries, solar cells and field-effect transistors.\textsuperscript{32, 76, 77}
BP does have one major drawback, its chemical stability. Reports have shown that device performance of BP decays over time.\textsuperscript{79} This decay can be attributed to the instability of the nanosheets, which is non ideal. Chemical reactions have shown it to interact with water and oxygen, in a photo catalysed reaction. This reaction produces phosphates which negatively affect the performance of BP.\textsuperscript{75} This is worrying as the inherent properties of BP hold great promise for future technologies. BP device performance, which show great performance over short time periods ($10^5$ on off ratios) are attractive; however, introduction into current technologies require a reliable device.\textsuperscript{33,80} However, recent reports have shown that BP can be shielded by encapsulation of the device using capping layers.\textsuperscript{79} Covering the device with an oxide or graphene coating, encapsulates it and protects it from the atmosphere, thus maintaining peak device performance.

\textbf{2.5.2 Applications of BP}

It is fair to say that while BP has been under some research since the 1960s, significant resurgence has occurred over the last 18 months. Given the attractive properties of BP discussed previously, there have been several reports on applications which range from solar cells to mechanical reinforcement and many more.\textsuperscript{32,71,72,73,76,79} Applications in transistors have attracted considerable interest. BP has displayed ambipolar behaviour in its transport
properties, where the field effect can be observed for both electrons and holes.\textsuperscript{33, 71, 79} Modulation of the drain current achieved values of up to $10^5$, approaching values achieved by MoS\textsubscript{2}.\textsuperscript{33} Attractive mobilities, up to $\sim1000 \text{ cm}^2/\text{Vs}$, were observed and are comparable with MoS\textsubscript{2}. While the mobility’s are less than those of graphene, they are still significantly better than those displayed by the current Si devices ($\sim500 \text{ cm}^2/\text{Vs}$).\textsuperscript{33, 80}

Owing to BP’s attractive band gap it holds great potential for optical and optoelectronic applications. Mobilities and switching values observed for BP are quite similar to MoS\textsubscript{2}. Deviations occur for their band gaps; BP’s has a thickness dependent direct band gap (from 0.3 eV to 2 eV) as opposed to MoS\textsubscript{2} which only displays a direct band gap in the monolayer. This makes BP highly lucrative for photo-detectors, as demonstrated by Engel et al.\textsuperscript{81} A photoresponsivity of $\sim20 \text{ mA/W}$ was obtained with is typically two orders of magnitude higher than values observed for graphene.\textsuperscript{82} Applications to areas beyond electronics are slow; however, the work in this thesis expands the palette of applications where BP can be influential. Advances in production methods may see a surge in some potential applications in other areas. Nevertheless, the inherent properties of BP show great promise for future technologies.

2.6 Production Methods of Layered Nanomaterials

There is a wide variety of methods to produce 2D layered nanomaterials. These methods may be classified into two fields; namely top-down or bottom-up approaches. Bottom-up approaches can involve self-assembly or more commonly chemical vapour deposition (CVD). Self-assembly is a complex production method, typically achieved using a wet chemical process.\textsuperscript{83, 84} Layered materials, such as graphene and TMDs, are commonly produced by CVD-based bottom-up techniques. To produce graphene using CVD, a metal substrate (typically copper) is heated to an elevated temperature ($\sim1000 \, ^\circ\text{C}$), to increase the metal domain size. A carbon based gas (methane) is then passed over the substrate, where it subsequently decomposes due to the elevated temperature and deposits carbon atoms on the surface of the substrate.\textsuperscript{85} The graphene produced by this method is of high quality and is typically low in defects (example displayed in figure 2.8). TMDs can also be produced using similar methods; however, the process is slightly different, where a vapour-phase reaction occurs, using oxide precursors.\textsuperscript{41} This process typically involves heating a precursor metal oxide (MoO\textsubscript{3} or WO\textsubscript{3}) to obtain the required atomic metal followed by treatment using the
desired gaseous chalcogen species e.g. S or Se. (schematic representation shown in figure 2.7).

Top-down techniques span from mechanical cleavage to liquid based methodologies. Mechanical cleavage was the first technique used to produce graphene. While this method does produce high-quality monolayers, it is time consuming and suffers from low throughput. Liquid-based methods include Li-ion intercalation which involves Li ion insertion into bulk crystals to separate the layers thus producing individual layers in solution. This technique produces a large amount of monolayers; however, these nanosheets are highly defective. Other liquid-based techniques, such as LPE, provide a method to produce layered nanosheets in common organic solvents. This methodology was developed by Coleman et al. and is used to produce defect-free mono- and few-layered nanosheets in solution. The choice of production method is governed by the quality and quantity of material required. For example methods such as CVD produce films which are excellent for electronic applications, while LPE is ideal for producing nanosheets for mechanical reinforcement. LPE production methods of layered nanomaterials will be discussed below in greater detail.

![Graphene CVD growth process](image)

**Figure 2.8:** Schematic representation of the graphene CVD growth process on a metal substrate (Cu in this case), identification of graphene growth domains.
2.6.1 Liquid Phase Exfoliation (LPE)

Other production methods of layered nanomaterials have been discussed above. Each method has its own distinct advantages and disadvantages. Some of these methods are quite difficult to scale to industrial levels of production. Liquid-phase exfoliation; however, is a simple technique based upon solubility parameters. Ideally a layered material can be chosen and immersed in a suitable solvent. The solvent is chosen to match the surface energy of the nanomaterial. Energy is added to the system in the form of sonication to overcome the van der Waals cohesive force between the layers of the bulk nanomaterial. Once the energy is sufficient to overcome this binding energy, separation of individual layers begins to occur. After sufficient energy and time has been added to the system, a selection of mono- and few-layer nanosheets are stably dispersed in the solvent. However, solvents are not the only method of stabilisation, surfactant and polymer agents can also be used. In these methods the stabilisation mechanism is different.

The LPE methodology has advanced significantly since its development by Coleman et al in 2008. Originally, graphite was used to produce graphene monolayers stably dispersed in NMP. Surprisingly, the mechanism of exfoliation is still quite poorly understood, but a general mechanism is thought to involve the addition of energy via a sonication probe lowered into the solvent and nanomaterial solution. The high-frequency vibration (>15 kHz) of the probe creates micro cavities which collapse causing a high-energy pulse to emit and shear the layered nanomaterial. A schematic representation of the process is described in figure 2.9 below.

This methodology can be used, not only for graphene, but for any layered nanomaterial. Previous studies have demonstrated the exfoliation of h-BN, TMDs, TMOs and layered III-VI semiconductors. One of the main strengths of this method is that it can produce nanosheets in solution which are then ideal for processing. Film formation and spraying of nanosheet solutions have been demonstrated to develop samples for testing as supercapacitor electrodes and thin films. The main strength is the fact that the process can be scaled to industrial levels to give large quantities of material.

Interestingly, the main drawback with probe sonication is that increasing the volume decreases the effectiveness of the process. A method developed by Paton et al. to use shear mixing to achieve individual nanosheets in solution, allows for the solution processing of
layered nanomaterials to be scaled to large volumes (figure 2.10). It was found that high-speed mixing of a graphene dispersion could induce shear if the rate was above $10^4$ s$^{-1}$. The production rate of nanosheets using shear exfoliation scales with respect to volume as $\sim V^{1.1}$ for solvents and $\sim V^{1.6}$ for surfactants. This means that these methods of production can produce a large amount of material by simply scaling up the volume used during the mixing. Notably this methodology can also be applied to other layered materials such as MoS$_2$.

Exfoliation of TMDs and TMOs has been demonstrated using LPE, where pristine nanosheets of varying sizes were produced. The liquid processing allows for the nanosheet sizes to be selected using centrifugation. Here the dispersion is subjected to accelerated gravitational forces to sediment nanosheets as a function of their mass. It has been shown that nanosheets follow a rule of thumb large and thick, small and thin. Therefore, separation of nanosheets by length can be achieved. A common trend of the resulting dispersion post sonication and size selection is that these samples are stable long term. Some graphene dispersions have shown stability over several years. With the expansion of this technique to new materials, discovery of some chemically unstable materials has arisen.

BP is one of these materials which display chemical instability, as mentioned above. While there is much promise for BP, as a layered semiconductor, there still remains the issue to overcome the nanosheet instability. There have been only three reports using LPE to exfoliate BP nanosheets using common solvents. These solvents are typically amide based which have previously been shown to produce a high concentration for numerous layered nanomaterials. Stability issues have been identified with BP under ambient conditions which may impact on the applicability of LPE. However, this will be discussed in greater detail in chapter 7.
Figure 2.9: LPE process scheme for exfoliation and stabilisation of a 2D layered nanomaterial in a solvent medium.

Figure 2.10: Shear mixing of nanosheet dispersions using a rotor stator. Shown above is the shear mixing of 5L of graphene.
Dispersion Theory

3.1 Introduction

This chapter introduces solubility theory which is used throughout the experimental sections in this thesis. Previous methodologies of solvent exfoliation, pioneered by the initial work of Hernandez et al, are considered in addition to electrostatic stabilising mechanisms. The methods of exfoliation are similar; however, the stabilisation mechanism preventing reaggregation is different. This thesis implements both methodologies, to produce stable dispersions of nanosheets in solution.

3.2 Solubility Theory

Solubility is an inherent property of a solid, liquid or gas. There has been a wealth of research into the solubility theory of polymers; specifically relating to the development of solubility parameters. Solubility parameters are based upon a thermodynamic model which accounts for molecular interactions, through vaporisation energy. Two theories were developed, initially by Hildebrand and then Hansen, to capture the chemistry of mixing using a solubility parameter. Solubility parameters are used in a range of applications from solubility screening to chemical resistance. Previous studies have shown that solubility parameters can be used to investigate the solubility of nanomaterials in certain solvents. Notably, not all solvents can produce a stable dispersion. It is important to correctly match the surface energies of the nanomaterial and solvent. A mismatch of parameters can result in a rapid aggregation of the nanomaterial and ultimately sedimentation. Therefore, the chemical interaction between the solvent and nanosheets is important to understand. The following
subsection discusses the interaction between solvents and nanosheets in terms of solubility parameters and surface energies.\textsuperscript{100, 101}

3.2.1 Solution Thermodynamics

Mechanical exfoliation is a well-known method to produce nanosheets, however, it is a time consuming and tedious process. The use of nanomaterials in applications, such as mechanical reinforcement or batteries, requires a method which can produce large amounts of material. Production methods which are liquid based hold the most promise to meet these exacting needs. Liquid phase exfoliation (LPE) is a solution based process, which exfoliates layered materials via sonication. Sonication is typically done in organic solvents. Therefore, to achieve a stable dispersion of nanosheets in a solvent, solubility theory is investigated. The mixing of two or more chemical compounds produces a change in entropy ($\Delta \bar{S}_{\text{mix}}$) and enthalpy ($\Delta \bar{H}_{\text{mix}}$) in the system and is governed by solution thermodynamics. This interaction can be described by the fundamental principle of Gibbs free energy shown below:\textsuperscript{102}

$$\Delta \bar{G}_{\text{mix}} = \Delta \bar{H}_{\text{mix}} - T \Delta \bar{S}_{\text{mix}}$$

(1)

The Gibbs free energy of mixing ($\Delta \bar{G}_{\text{mix}}$) is a function of the enthalpy ($\Delta \bar{H}_{\text{mix}}$), temperature (T) and entropy ($\Delta \bar{S}_{\text{mix}}$). To achieve a viable dispersion i.e. dissolution, the Gibbs free energy is required to be negative. In an ideal case, large (positive) values of entropy are beneficial to ensure stability. However, two dimensional nanosheets, such as graphene and TMDs, are generally large and rigid, therefore, their entropy is small.\textsuperscript{100, 103} Therefore, to produce a viable dispersion it is advantageous to minimise $\Delta \bar{H}_{\text{mix}}$. To understand the thermodynamics of mixing, it is not sufficient to only consider the interaction between the solute and solvent, the solute-solute and solvent-solvent interactions are also important.

A common rule of thumb in chemical solubility is “like dissolves like”. In a liquid or solid there is a chemical interaction between atoms and molecules. To achieve solubility of a solid in a liquid, the bonds between nearest neighbours needs to be broken. To achieve this, energy needs to be supplied. The total amount of energy to completely separate these molecules is termed the vaporisation energy. This energy represents the van der Waals energy holding the
molecules together. Solubility parameters are derived from this vaporisation energy and are related to the cohesive energy of the solvent. The cohesive energy, by extension, is a representation of the van der Waals energy between molecules in a solvent. Hildebrand recognised this and devised a solubility parameter to accurately describe the system. This parameter is represented by $\delta = \sqrt{E/V}$ (where is $E$ the energy and $V$ is the solvent molar volume) and is defined as the square root of the cohesive energy density. Using these solubility parameters, the Hildebrand-Scratchard equation which can be derived for small molecules as;

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} \approx \Phi(1 - \Phi)(\delta_a - \delta_b)^2$$  \hspace{1cm} (2)

This equation relates the enthalpy of mixing ($\Delta H_{\text{mix}}$) in terms of Hildebrand solubility parameters ($\delta_a$, $\delta_b$ of solvent and solute respectively) and solvent volume fraction $\Phi$. Whist this is an approximate expression due to the approximations in its derivation, it does not dismiss the underlying power in the equation. The expression clearly shows that matching the solubility parameters, $\delta_a$ and $\delta_b$, minimises the enthalpy of mixing.

Relating the Flory-Huggins parameter $\chi$ to $\Delta H_{\text{mix}}$, we obtain an expression that accounts for intermolecular pairwise interactions,$^8,^{104}$

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} = \frac{\chi(1 - \Phi)kT}{v_0}$$  \hspace{1cm} (3)

Here $\Phi$ is the solvent volume fraction while $v_0$ is the solvent molecular volume. The Flory-Huggins parameter was originally developed for polymer systems; however, it can provide a route for control over the dispersion of our nanomaterial. A highly positive $\chi$ indicates a repulsive solute-solvent interaction and subsequently a positive enthalpy of mixing, which if large enough can inhibit the solution process. Furthermore, a negative $\chi$ indicates an attractive interaction and in turn creates a negative enthalpy of mixing which guarantees dissolution. Intermolecular pairwise interactions have been accounted for in the Flory-Huggins parameter($\chi$). It can be expressed in terms of the cohesive energy interactions involved in our system. For non-polar solvents the Flory-Huggins parameter can be expressed as:

$$\chi \approx \frac{v_0}{kT}(\delta_A - \delta_B)$$  \hspace{1cm} (4)
If polar solvents are used a correction term is needed; nevertheless, it is clear that matching of the solvent and nanosheet solubility parameters minimises the enthalpy of mixing. Applying Flory-Huggins theory these nanosheet/solvent interactions can be further understood.

This thermodynamic solubility theory, can accurately describe the interaction of a particle in a solvent. As shown above, careful matching of solubility parameters can be used to produce a stable dispersion free from aggregation effects. Implementation of this theory, to CNT or 2D nanosheets, has been purely empirical. Previous work, conducted in this group derived an equation to accurately represent the enthalpy of mixing for a graphene nanosheet.\textsuperscript{24, 105, 106} This derivation encompasses the above theory accounting for pairwise interactions and the surface energy parameters for solutes and solvents. The energy required to separate all individual layers in the nanomaterial and solvent molecules was modelled. This formulation results in an equation to describe the energy cost per unit volume of mixing\textsuperscript{92}

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} \approx \frac{2}{T_{\text{flake}}} \left( \partial_{\text{nanosheet}} - \partial_{\text{solvent}} \right)^2 \phi$$

(5)

Here $T_{\text{flake}}$ is the thickness of a nanosheet, while $\partial_a = \sqrt{E_{\text{sur}}}$ is the square root of the surface energy relating to phase “a” and $\phi = V_{\text{nanosheet}}/V_{\text{mix}}$ is the nanosheets volume fraction. Therefore, equation (5) shows that solvents which have a surface energy similar to that a nanomaterial will have a high probability of solubility. Typical solvents previously studied, have been amide based, such as NMP and CHP, which have surface energies of \textasciitilde41 mJm\textsuperscript{-2}.\textsuperscript{107}

**3.2.2 Hansen Solubility Parameters**

The interactions between solvent molecules and solutes (nanosheets) can be described using Hildebrand solubility parameters above. However, Charles Hansen identified some shortcomings with the approach, only dispersive forces are considered. There are several types of interactions between solvent molecules and nanosheets. The most important interactions can
be described using the dispersive force (non-polar, $E_D$), polar cohesive energy ($E_P$) and hydrogen bonding ($E_H$). The sum of these interactions represents the total cohesive energy ($E$),

$$E = E_D + E_P + E_H$$  \hspace{1cm} (6)

Larger molecules will have higher cohesive energies and need to be scaled by their volume ($V$). The square root of the respective cohesion energy divided by the molecular volume, ($\delta = \sqrt{E/V}$), is referred to as a Hansen solubility parameter (HSP).\textsuperscript{101,103} The Hildebrand solubility parameter is the sum of the squares of each individual Hansen solubility parameter.

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$  \hspace{1cm} (7)

With this knowledge the Flory-Huggins parameter, $\chi$ can be expressed in terms of each of the energies of interaction,\textsuperscript{104}

$$\chi \approx \frac{\nu z}{kT} \left[ (\delta_{D,A} - \delta_{D,B})^2 + (\delta_{P,A} - \delta_{P,B})^2 + (\delta_{H,A} - \delta_{H,B})^2 \right]$$  \hspace{1cm} (8)

HSP are well known for many solvents and are important when analysing solubility. It is clear that selectively matching these parameters of the solvent and nanosheet will minimise$(\delta_A - \delta_B)^2$. The closer a solvent and nanosheet are with respect to their dispersive, polar and hydrogen bonding energies, the greater the chance of solubility. The implementation of solubility parameters proves to be very attractive; however, not always successful. Complete solubility can be achieved by completely matching the energies of two substances. It has been suggested that the hydrogen bonding component should be subdivided into a Lewis acid and Lewis base component to obtain better accuracy. Nevertheless, this approach provides an accurate model to predict solubility of nanomaterials in solvents. This approach will be used in chapter 5 to assess a series of solvents used to exfoliate a layered nanomaterial.
3.3 Surfactant Stabilisation

In addition to solvent exfoliation, this thesis uses surfactant molecules to aid the dispersion of 2D nanosheets. Surfactants are long chain molecules, which are characterised by a polar head group and a non-polar tail. Due to this amphiphilicity, these molecules tend to adsorb at interfaces. The surfactants orientate themselves where the polar head group is immersed in the polar phase (usually water) while the hydrophobic tail group interacts with the non-polar material such as a nanosheet.\textsuperscript{91,108} There are many types of surfactants; anionic, cationic and non-ionic. Typically with ionic surfactants, an increase in surfactant molecules at the air/solution interface with increasing surfactant concentration is observed. Surfactant molecules can interact with not only the solvent medium but also themselves, to form aggregates in solution.

These aggregates can accumulate to reduce the energy in solution, by orientating the polar head groups out to the solvent medium, while the hydrophobic tail groups are directed into the centre of a surfactant sphere (fig 3.1). This configuration minimises the interaction between the non-polar tail groups and the solvent.\textsuperscript{108} These aggregates are called micelles and are formed at a specific concentration for each surfactant known as the critical micelle concentration (CMC). The geometry of the micelles is dependent upon the type of surfactant used, however, observed geometries include a sphere, ellipsoid, cylinder or even an inverted micelle. The micelle size is also dependent upon effects such as temperature and solution pH.

![Figure 3.1: A) Illustration of a typical surfactant molecule with characteristic hydrophobic tail group and the hydrophilic head group. B) Scheme of surfactants in solution.](image)
A monolayer of molecules forms on the surface where the non-polar tail groups are directed above the surface of solvent while free surfactant molecules are randomly dispersed in solution. This occurs when the concentration of surfactant \( C_{\text{surf}} \) is below the CMC. Once the concentration of surfactant increases to the CMC we observe the formation of micelles \( C_{\text{surf}} > C_{\text{CMC}} \).

### 3.3.1 Charged Molecules and Electrostatic Repulsion

A common method to stabilise a nanosheet in solution is to use surfactants to coat the surface. Typically ionic surfactants, such as sodium cholate SC, are used and impart a local charge on the nanosheet. This charge is balanced by a counter ion in solution. The counter ion is influenced by Brownian motion and is deflected away from the polar head of the surfactant. As the polar head group and counter ion are separated in solution, a charge is imparted on the surface of the nanosheet. If a sufficient charge is imparted on the nanosheets they are stabilised from aggregation. The varying charge distribution around the nanosheet produces a potential difference; the electrical double layer (EDL).\(^\text{108}\)

![Illustration of a surfactant molecule, identifying the regions of tightly and loosely bound counter ions. The potential drop is also identified over the respective regions.](image)

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\(^\text{108}\)
The EDL was first modelled by Helmholtz in the late 19\textsuperscript{th} century, where he investigated the distribution of ions close to a charged surface. Naturally to maintain balance the net charge and magnitude must be equal. The model proposed that the potential should fall to zero a short distance away from the charged surface; however, his model was insufficient to account for a high charge density very close to the surface. It was proposed by Stern, to divide the local environment into two regions, an area adjacent to the particle which has the highest density of tightly bound ions (referred to as the Stern layer) and a section further away composed of loosely bound ions (figure 3.2). The potential drop across this model is rapid for the stern layer, which is quite close to the charged surface.\textsuperscript{109} The Debye-Huckel equation, where the Debye length ($\kappa^{-1}$) is the characteristic decay of the potential, can be used to describe the interaction.\textsuperscript{109, 110} When the electrical energy is low, with potentials below 25mV, the Debye length can be described as

$$\kappa = \sqrt{\frac{\sum e^2 n_i z_i^2}{\varepsilon_r \varepsilon_0 kT}} \quad (12)$$

The Debye length ($\kappa^{-1}$) is a measure of the “thickness” of the EDL, and is largely dependent upon the properties of the liquid such as the number (n) and relative permittivity ($\varepsilon_r$). The limit of this diffuse layer is defined as the slipping plane. This plane represents the limit of particle stability, moreover, when the charged particle moves under the force of gravity or Brownian motion; particles within this defined limit also move. The potential energy of the slipping plane is known as the zeta potential ($\zeta$) and is used to gauge the stability of a colloid. A sufficient electrostatic repulsion is needed to overcome the van der Waals attractive potential between nanosheets. Typically the measure for a stable colloid is $10 < \zeta < -10$. The sign of the potential is indicative of the type of surfactant used whether cationic or anionic.\textsuperscript{108, 110, 111} Zeta potential is used in chapter 7 to investigate the stability of nanosheets in solution. The effect of surfactant concentration on the nanosheet stability will be further discussed there.
Characterisation and Methods

4.1 Introduction

The aim of this chapter is to discuss the main characterisation techniques employed in this thesis. This work focuses on the preparation and characterisation of 2D-layered nanomaterials, processed in dispersion through LPE. A mixture of nanomaterial and solvent or surfactant solution are combined and then subjected to ultrasonication. Post sonication the dispersion is highly polydisperse; therefore, size selection must be performed using controlled centrifugation. This centrifugation step plays a key role in selecting the size and thickness of nanosheets, in addition to removing any unexfoliated material. Optimisation of this process is explained in the following chapters. After centrifugation the supernatant is decanted and then initially subjected to absorbance/extinction spectroscopy. The absorbance/extinction spectra are essential to determine not only the dispersed concentration but also the size and thickness of the nanosheets in dispersion. Once the basic characterisation is completed more advanced techniques such as zeta potential, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) are used to determine the quality and stability of the exfoliated material. The sample is typically analysed using multiple microscopy methods such as; transition electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) where statistical analysis is performed to assess the quality and dimensionality of the nanosheets present. The range of techniques described above, are employed not only in the production of 2D nanosheets but also to assess the geometry and quality of the material. These will be discussed in further detail below.
4.2 Sample Preparation

Layered crystals are necessary for LPE, due to weak van der Waals between layers. The principle behind LPE is to provide an energy source to overcome these weak bonds out of plane to produce individual and few layer nanosheets. Throughout this work, this is achieved through ultrasonication, although other techniques can in principle be applied. Ultrasonication supplies energy to the system through the conversion of an electrical signal into a mechanical vibration carried by a metal probe which is lowered into the liquid. The cavitation energy is controlled by altering the amplitude of the vibration. The physical vibration creates micro cavities which collapse and release a high energy cavitation field. Any material in the local cavitation field will be subject to high shear forces which will exfoliate the material. This methodology has been proven to exfoliate not only 2D layered materials such as graphene and TMD’s but it is also suitable for 1D system’s such as carbon nanotubes. The shearing of the layers of sheets or individual nanotubes is only the initial step, without a suitable stabilising medium the material will re-aggregate and sediment. Stabilisation can occur, as previously discussed in chapter 3, via electrostatic/ steric or energetically favourable solution interactions.

Here a sonication tip as opposed to a sonication bath is used because while both can exfoliate a layered material the efficiencies of the two differ substantially. Firstly a sonication bath typically operates with a power output ~ 25W, whilst a sonication probe has an output of ~750W. The difference in power ultimately means that exfoliation in a sonication bath is less efficient and thus, will take longer to achieve the same degree of exfoliation. As has been previously shown the concentration of dispersed nanomaterial follows a power law relationship, with time scaling as \( t^{1/2} \). Therefore, the sonication probe is a more efficient process.

Another downfall of using a sonication bath is that the modulation of exfoliation in the bath varies from one position to another; this has a significant impact on the reproducibility of samples. A rotor system could be used to rotate a number of samples around a given axial point thus ensuring that all samples achieve the same degree of exfoliation. Most of the materials discussed in this thesis are new to liquid phase exfoliation (chapter 5 and 6) it was; therefore, prudent to use the more reproducible method of probe sonication. Bath sonication was only
used in this work to homogenise composite dispersions, where two individual components were originally probe sonicated and mixed in given wt. % ratios in the sonication bath.

4.3 Sedimentation Methodology

Following exfoliation, the resulting dispersion is quite poly-dispersed (i.e. there are a number of stable and unstable species in solution). The stable phases consist of small and large nanosheets which are stabilised by the respective solvent or surfactant mechanism; the unstable components consist of unexfoliated material and aggregated nanosheets in the liquid. These unstable components will gradually sediment over time. The sedimentation process however, can be accelerated through centrifugation.

Assisted centrifugation is not a trivial pursuit, as it involves complex system dynamics and balancing of environmental forces. Any particle in solution experiences three forces; the force due to gravity ($F_g$), the force due to buoyancy ($F_B$) and the force due to viscous drag ($F_D$) (figure 4.1).

\[ F_g = m \cdot g \]  

*Figure 4.1: Forces acting on a particle in solution.*

The force experienced by a particle in solution due to gravity can be expressed using Newton’s third law of motion:
Where \( m \), is the nanosheet mass and \( g \) is the acceleration due to gravity. Re-expressing the equation (1) in parameters more suitable for a fine scale measurement such as centrifugation of nanosheets, we can re-express it in terms of the density and volume of the particle, yielding:

\[
F_g = \frac{4}{3} \pi r^3 \rho_{ns} g
\]

(2)

where \( r \), is the radius of the particle which we assume to be a sphere and \( \rho_{ns} \) is the density of the particle.\(^{125}\) The buoyancy force exerted on each particle is defined as; the weight of the fluid displaced by the volume of each particle when immersed in the liquid. Again, we assume a spherical particle which yields:

\[
F_B = \frac{4}{3} \pi r^3 \rho_s g
\]

(3)

a similar expression, as equation 2, describing force exerted on the particle is obtained. The density of the fluid displaced (\( \rho_s \)), not the density of the particle, needs to be taken into account.\(^{125}\) Finally, the force exerted on particles moving through a fluid can be modelled by Stokes law where; the particle has to expend energy in shearing the fluid that passes by it, which yields:

\[
F_D = 6\pi r \eta v
\]

(4)

This equation accounts for the viscosity of the fluid (\( \eta \)); the medium the particles are moving in and the velocity of the sheet itself (\( v \)). Viscosity in this instance is a measure of the resistance to the flow of a liquid and is quite important for the exfoliation process. This will be discussed in more detail in chapter 5.\(^{126,127}\) Combing the net forces experienced by a particle in solution we can obtain an equation for the motion of sedimentation:

\[
\frac{4}{3} \pi r^3 (\rho_{ns} - \rho_s) g = 6\pi r \eta v_t
\]

(5)

When a particle is in a liquid, it will immediately experience a force downward due to gravity and a subsequent force upwards due to buoyancy.\(^{128}\) If we assume that the particle’s density is
greater than that of the solvent, the particle will begin to fall to the bottom of the vial. Once the particle begins to move it will generate a drag force which will oppose the movement, the faster the movement, the greater the drag force will become until the particle reaches terminal velocity \( v_t \). The value of the terminal velocity can be obtained from rearrangement of equation (5), however, we are more interested in the time taken for the particle to sediment \( T_{sed} = 1/v_t \), where \( v_t \) is the terminal velocity and \( l \) is the length of the vial): \(^{125}\)

\[
T_{sed} = \frac{9\eta}{2r^2(\rho_{ns} - \rho_s)g}
\]  \( (6) \)

The time for the particle to reach the bottom of the vial is dependent upon the viscosity and density of the fluid as well as, the density of the material. Therefore, the rate of sedimentation is specifically related to the system in which the particles are dispersed; this shall be discussed in more detail in chapter 5 when referring to, achieving a stable dispersion and choosing a suitable solvent. It can also be shown that using centrifugation accelerates this process (replacing \( g \) with \( \omega^2 r \), where \( \omega \), is the angular velocity of the centrifuge and \( r \), is the radius) by increasing the force exerted on the particles due to gravity. \(^{125, 128}\) It is important to note that the sedimentation theory, described above, is strictly applicable to spherical particles only. To a first approximation, it can be applied to 2D nanosheets in solution; however, very little is known about nanosheet sedimentation during centrifugation as buoyancy and friction are shape dependent. If the concentration of nanosheets is too high in the sample then hindered settling becomes important. In practice, centrifugation can be used successfully to separate nanosheets by mass. \(^{129, 130, 131}\)

Centrifugation work in this thesis employs the use of sedimentation theory to achieve a stable dispersion where, the nanosheets do not sediment over time. This is achieved by using decay time constants. Typically, nanosheet systems contain three dominant species; firstly we have unexfoliated material, which will sediment fast therefore having a short time constant. Secondly, we have stable exfoliated nanosheets; these can be subdivided into two groups; small nanosheets (~100nm) which remain in the dispersion as they are stabilised through buoyancy and solvent interaction and larger sheets which are exfoliated and stabilised in the liquid; however, sediment slowly due to their large mass. Large nanosheets, while somewhat stable, eventually decay over time. To model this behaviour we undertake a series of different
centrifugation steps at varying speed (RPM) and time and subsequently measure the dispersed nanosheets using absorbance spectroscopy. The methodology employed in this process will be discussed in further detail in chapter 5. However, the observed behaviour can be modelled using an exponential decay function:

\[ A = A_{\text{stable}} + A_{\text{semi-stable}} e^{-t/\tau_1} + A_{\text{unstable}} e^{-t/\tau_2} \]  

(7)

Fitting this equation to the data enables the time constants for each unstable component to be determination.\(^{132}\) The speed or for how long we need to centrifuge to achieve a dispersion with only stable nanosheets can be identified. This methodology is quite important and is heavily used in chapters 5 and 6 and used to a lesser extent in chapter 7. The use of decay constants is also applied to the chemical stability of nanosheets in dispersion rather than in terms of sedimentation as outlined above. This advancement is discussed with respect to Black Phosphorus in chapter 6.

4.4 Absorbance Spectroscopy

The interaction of light with matter is a fundamental process which has been under investigation for centuries. The propagation of light from one medium to another, with different densities, leads to a bending of the beam as the speed of the traveling wave changes, this phenomenon is called refraction. This work however, is focused on the interaction of light with nanosheets species dispersed in a solvent or surfactant system. Two main events happen when a light beam propagates through a liquid sample containing particles; the beam is partially scattered or absorbed by the particles. When a light beam passes through a sample, the intensity of the beam will be decreased due to absorption or scattering effects. This variation in intensity is explained by the Beer-Lambert law.\(^{133}\) A reduction in intensity is proportional to the initial intensity before the beam interacted with the sample and is given by,

\[ dI = -\beta I C dl \]  

(8)

The change in intensity (dI) is dependent upon the sample concentration (C), the path length (l), and a constant (\(\beta\)). The expression needs to be integrated for the length of the entire path.
length; therefore, we integrate the intensity (I) over the range from the starting and final intensity:

\[ \int_{I_0}^{I} \frac{dI}{I} = -\beta \int_{0}^{C} dl \]  

(9)

which can be further simplified to:

\[ \ln \left( \frac{I}{I_0} \right) = -\beta C \]  

(10)

introducing a constant \( \alpha \) and change to base 10; the familiar Beer-Lambert equation is obtained:

\[ \log_{10} \left( \frac{I}{I_0} \right) = -\alpha C \]  

(11)

\[ I = I_0 10^{-\alpha C} \]  

(12)

Here, alpha (\( \alpha \)), is the absorbance coefficient (units \( \text{L.g}^{-1}\text{m}^{-1} \)) and can be used to determine the concentration of a dispersion. The transmittance is given by the ratio of the final intensity to the initial intensity (\( I/I_0 \)) therefore, we can convert the above equation into the more useful form in terms of absorbance (\( A = -\log_{10} T \)),

\[ A = \alpha C \]  

(13)

This is the form of the Beer-Lambert equation which will be discussed and used in this work (figure 4.2 A).\textsuperscript{133} It can be used to determine the concentration of the dispersed nanosheets in solution once the absorbance coefficient (\( \alpha \)), of the material is known. The spectral region under study in this work is primarily in the UV-vis range (UV-100-400nm, vis-400-700nm); we expect to see an absorption peak of the materials under study t, when the frequency of the light beam matches an electronic transition in our materials.
Whilst the discussion so far has been in relation to absorption spectroscopy, the term absorption should not be used in the case of nanomaterial dispersions as, depending on particle size, the spectra acquired in transmission may contain a non-trivial contribution from light scattering. The term extinction is more appropriate. For molecules, even when self-aggregated in solution, the absorbance spectrum is identical to the extinction spectrum. The same cannot be said for 2D-nanosheets, which can have a broad range of lateral size distributions from 50-1000nm. In LPE samples, there is a distribution of Rayleigh and Mie scattering events, dependent upon the spectral position and the size of the nanosheets (figure 4.2 B).\textsuperscript{134}

In order to acquire absorbance spectra, we needed to overcome the scattering present in the samples; therefore, the optical properties were measured in an integrating sphere. The sphere itself is approximately 150mm in diameter and the internal walls are covered with a diffuse white reflective coating. The coating is to insure that there is maximum internal reflectance of the beam. A schematic diagram of the process is shown below (figure 4.3).
Figure 4.3: Geometric representation of integration sphere measurements and the positioning of the cuvette in the centre of the sphere.

The beam enters through the front port where it directly interacts with the sample, here the beam is split into absorbance from the material, scattering due to the geometry of the nanosheets and then the transmission of the beam (lower intensity). The difference between the integrating sphere and an ordinary spectrophotometer is that in an ordinary spectrometer, the scattered light is lost after it leaves the sample; this can be incorrectly attributed to absorbance of a material. In the case of an integrating sphere the scattered light is captured by the coating and then re-scattered multiple times inside the sphere. The multiple scattering events cause the intensity level inside to reach a steady state. Therefore, we obtain a uniform coverage inside the sphere. The intensity levels are captured in the sphere radiant flux (L). This equation is essentially separated into two quantities; the first part is approximately equal to the flux of the radiance on a diffuse surface. The second part of the equation is a unitless quantity. This quantity is known as the sphere multiplier and accounts for the multiple scattering events inside the sphere.\textsuperscript{135,136}

\[
L = \frac{\phi}{\pi A_s} \times \frac{\rho}{1 - \rho(1 - f)}
\]  
(14)

The radiance (L), is defined in terms of the radiant flux (\(\phi\)), the reflectance (\(\rho\)), the surface area of the sphere (\(A_s\)) and the port fraction (\(f\)), which is a term introduced to calculate the area.
of the ports which light can escape. The sphere multiplier (second term) is an important quantity as it accounts for the specific geometry of the sphere in use. Accounting for this geometry setup, the sphere is able to obtain the real absorbance value unlike a normal spectrometer. Furthermore, by determining the real absorbance spectra in the integrating sphere, in addition to an extinction measurement, we can obtain scattering spectra through the simple relationship between extinction $\varepsilon(\lambda)$, absorbance $\alpha(\lambda)$ and scattering $\sigma(\lambda)$, \( (\varepsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda)) \).\(^{136}\) This is a powerful technique as the different spectral responses from our nanosheets systems can be deconvoluted. This in turn will allow us to determine the scattering exponent of our samples and relate this exponent to a lateral length. This methodology will be discussed in more detail in chapter 6 with respect to size selection and optical metrics.

Probing 2D layered nanomaterials optically is quite important. When excited by the beam, an electron may get promoted from the valance band to the conduction band which can create a bound state, where the promoted electron and hole are attracted to each other by Coulomb forces. This attraction of the electron and positively charged hole forms an exciton, where the attraction provides a stabilising energy balance.\(^{137}\) The optical absorbance and extinction spectra for 2D materials are predominantly dominated by excitonic features where, absorption of light occurs with their excitation. It has been shown that excitons can be influenced by temperature and by the thickness of the nanosheet.\(^{138, 139}\) These excitonic transitions are more dominant at lower temperature as they have a typical binding energy of a few meV; however, at room temperature this increases substantially for 2D materials, (~ 900meV).\(^{140}\)

### 4.5 Photoluminescence

Photoluminescence (PL) is the spontaneous emission of light from a material which has been optically excited. PL incorporates the emission of light via fluorescence (fast ~ ns) and phosphorescence (slow ~ ms). In the simplest case, at room temperature, most molecules populate the ground state of their energy levels. Excitation with an appropriate laser provides sufficient energy to promote an electron from the valance band to a vibrational level of the conduction band. The excited state loses its vibrational energy through collisions and falls to the lowest energy level of the excited state. From here, the electrons can either decay back
down to the ground state via non radiative processes, or by emitting a photon which is characteristic of the optical energy gap (fluorescence) (figure 4.4)

**Figure 4.4: Schematic of the luminescence process.**

PL is a non-invasive characterisation tool which requires no electrical contacts or junctions to be applied to the material. A sample can be measured in solid or liquid form. The local environment surrounding the material can have a significant effect on the intensity of the luminescence signal obtained. This effect is known as quenching, and results in a decrease in the PL intensity due to the deactivation of the excited state via non radiative processes. The transitions probed using PL, with respect to 2D layered nanomaterials, are predominantly excitonic; therefore, the role of solvent and surfactant molecules will influence the quantifiable PL. PL probes the discrete electronic states of a material, making it extremely sensitive to any form of defects and surface modification of a material. With this in mind, it has been rigorously employed to investigate the purity of samples and functionalization of materials. Any introduction of defects can have an effect on materials intrinsic properties, these effects can be comprehensively studied using PL spectroscopy. Introduction of defects into a material can
introduce sub band states which can form emission centres. These defects can cause a shift or even generate luminescence peaks.\textsuperscript{143, 144}

In this thesis PL is used to characterise 2D-nanosheets in solution. These layered nanomaterials in most cases, only become luminescent in the monolayer form due to the transition from indirect to direct semiconductors transition.\textsuperscript{42, 145} Therefore, the primary role of PL is to determine the presence of luminescent species in dispersion.

### 4.6 Raman Spectroscopy

Raman spectroscopy is one of the most important analytical tools for analysing chemical species, with applications in research areas ranging from; pharmaceuticals to semiconductor thin films.\textsuperscript{146} The technique itself is based on light scattering and was developed by Venkata C. Raman in 1928. In its simplest form, the process involves a photon of light interacting with samples to produce scattered radiation with a different frequency. The resulting change in wavelength yields a variety of information about the sample such as; chemical identification, chemical bonding and environmental effects such as; stress and strain. This technique became common practise in the mid 1990’s due to advances in instrumentation, which yielded smaller more compact devices, which utilised new lasers and detectors.

This technique involves shining a monochromatic light (typically a laser of known wavelength) upon a sample, the light may then be absorbed, reflected or scattered. The scattering of incident light in the Raman process can yield crucial information about the molecular structure of the sample.\textsuperscript{147} Analysis of this scattered light yields not only the incident wavelength (Rayleigh scattering is an elastic process) but also light which was scattered at other wavelengths. This conversion of the wavelengths can be classified as stokes and anti-stokes scattering.
Furthermore, we have three forms of scattering possible in our sample, Rayleigh scattering, Stokes scattering and anti-Stokes scattering (Figure 4.5). The observed frequency change of the scattered light depends on the vibrational state of the molecule. The dominant process is Stokes scattering, where the observed scatter is lower in energy. The measurement is typically done at room temperature where the population state of the molecule is mainly in the ground state configuration, which makes Stokes scatter more probable. While the molecule will be principally in the ground state there will be a small population in the excited state; therefore, excitation leads to an increase in the observed energy of the scattering photon giving rise to anti-Stokes scattering. These processes can be observed in the Jablonski diagram below (figure 4.6).

![Jablonski diagram of Raman processes of scattering energy levels.](image)

Figure 4.5: Illustration of the experimental setup and Raman process for scattering of light.

Figure 4.6: Jablonski diagram of Raman processes of scattering energy levels.
Incident photons will interact with the sample and depending on the local geometry of the molecules the energy change is characteristic of the local bonds. The vibrational states are dependent upon the nature of the bond where shorter bonds are harder to polarise than longer ones; however, environmental factors such as temperature can also influence the frequency. It is also important to identify the resonant mode of operation of the Raman. Unlike the non-resonant mode, where an increase in energy of the sample excites electrons to a virtual state followed by immediate decay, in resonant Raman the sample is excited at a frequency close the frequency of an electronic transition (schematic in figure 4.7). This coincidence of frequencies allows for a greater Raman signal intensity and analysis of samples at lower concentrations (typically $10^{-8}$M). Therefore PL is more likely when the Raman is operated in the resonant mode.

![Diagram](image-url)

**Figure 4.7:** Schematic representation of the different processes for resonant and non-resonant Raman spectroscopy.
4.7 Zeta Potential

Particles in a colloidal system carry a charge as discussed in chapter 3. Work in this thesis employs the use of an ionic surfactant to help stabilise and disperse nanosheets in solution which in turn, imparts a surface charge and local diffuse charge in the vicinity of these nanosheets. One of the most reliable methods to measure surface charge is Zeta potential. This method involves applying an electric field to a solution containing nanosheets with a surfactant coating and measuring how fast the nanosheets move. The movement of the nanosheets under an applied electric field is known as electrophoresis. Stability limits for zeta potential measurement are typically given by $10 < \zeta < -10$ mV. If particles have a potential outside of the defined limits, the repulsive electrostatic forces are usually sufficient to prevent reaggregation.

It should be noted; however, that in the Zeta potential measurement we do not observe all of the charge. The applied electric field is pulling the nanosheets in one direction while simultaneously pulling the counter-ions in the opposite direction. However, not all counter ions will move against the nanosheets, those within very close proximity will in fact move with the nanosheets. This limit is known as the slip surface. It is this potential that is measured when one determines the Zeta potential. The mobility of the particle ($\mu$), is also related to the applied electric field ($E$), and the drift velocity ($v$), via the following equation $v = \mu E$. Using the Henry equation for spherical particles we can determine that the relationship between zeta potential and particle mobility is given by,

$$\zeta = \frac{3\eta\mu}{2\varepsilon\varepsilon_0 f(\kappa a)}$$

(15)

It is clear that the zeta potential ($\zeta$), depends upon the viscosity ($\eta$), mobility ($\mu$), permativity ($\varepsilon\varepsilon_0$), and Henry’s function ($f(\kappa a)$), where $\kappa$ and $a$ are the Debye length and the particle radius respectively.

To measure this potential we employ laser Doppler velocimetry. This technique involves passing two beams through the solution under applied bias. One beam is a reference beam, which can be passed through the cell without being scattered while the incident beam is passed through the solution (figure 4.8). The two beams are coincided beyond the sample where there is a frequency difference due to constructive and deconstructive interference, which leads to a Doppler shift in frequency.
Figure 4.8: Schematic representation of the experimental setup for the measurement of the Zeta potential via electrophoretic mobility of the particles in an applied electric field.

4.8 Transition Electron Microscopy (TEM)

Transition electron microscopy (TEM) is an important tool used to investigate the morphology and quality of nanomaterials. The work in this thesis relies on the use of bright field TEM to assess and quantify the nanosheets produced using LPE. TEM has previously been used to characterise nanosheet dispersions for a number of years, where the lateral dimensions and sample quality can be determined quite easily. 8, 24, 106, 113, 118, 138, 151

TEM employs the use of an electron beam, which is projected down a column to interact with a sample. The interaction between the sample and electrons results in the scattering of the beam, which is analysed using a charge-coupled device (CCD) camera. The configuration of the microscope is displayed in figure 4.9 A.

A TEM microscope uses an electron beam to create an image of the sample. This beam is generated at the top of the column via an electron gun. The electron guns are usually of two types; field emission (Schottky, Cold FEG) or thermionic (W, LaB₆). For high performance TEM, a high spatial resolution and small source size is required. Field emission guns out perform their thermionic cousins, in this department, where the beam size is up to 1,000 times smaller and 100 times brighter. Therefore, in this work all low resolution TEM was conducted on an Joel 2100 operated at 200kV using a LaB₆ filament while high resolution TEM (HRTEM) was conducted on a field emission FEI-Titan operating at 300kV.
In the simplest case, an electron beam travels down the column and interacts with the sample which results in some electrons being scattered at a given angle, relative to the normal incident beam. The electron beam is mainly undisturbed while some electrons are scattered elastically and in-elastically (figure 4.9 B). Given the average distance between electrons at 100kV, typically 0.15mm, it is safe to assume the interaction between the beam and sample is a one electron event. The use of the selective area aperture post sample imaging plane, is crucial to refocus the electron beam. Depending on where the focal plane is taken post beam/sample interaction, the TEM can operate in diffraction or imaging mode. Using the back focal plane of the intermediate and projector lens, a diffraction pattern is produced. This can be used to investigate samples to determine whether they’re crystalline or amorphous. Successful exfoliation of the nanomaterial will result in a thin crystalline material which should give characteristic diffraction spots; however, if there are contaminates or non-crystalline material present we will observe a diffuse cloud. Diffraction patterns can also be used to detect monolayer nanosheets via their theoretical diffraction patterns as demonstrated in the case of graphene.\cite{1, 152, 153}
4.8.1 Statistical TEM Analysis.

Low resolution TEM has been used to analyse the quality of the nanosheet dispersion produced by LPE. In this work, we employ similar techniques previously developed in this group to statistically quantify the mean length and width distributions of our samples. A sample is produced by separating different sizes of nanosheets by mass, using a centrifuge. This approach is similar to previous methods; however, here an RPM trapping method is used. This methodology implements a series of centrifugation speeds where, the supernatant after one speed is taken and centrifuged at a higher one. The sediment is redispersed in fresh solvent and subjected to analysis, while the supernatant is moved onto the next step, centrifugation at a higher speed. Once the nanosheet size of interest has been isolated the sample is deposited onto a TEM grid. The choice of TEM grid used in the statistical analysis is quite important and is dependent upon the size of nanosheets that are assumed to be in the dispersion. For example, if a low RPM is used the majority of the nanosheets are assumed to be quite large; therefore, the sample can be deposited onto a holey carbon TEM grid. An example of this type of grid is given in figure 4.10 A, which consists of a stretched layer of carbon, pulled over a support structure which enables the solvent to wick through the holes in the grid and the nanosheets to be deposited on the surface. This type of grid is better for imaging large nanosheets as the smaller ones can pass through the holes. However, if the sample is predominantly composed of small nanosheets then a continuous carbon film is used. This captures all sizes of nanosheets; however, care needs to be taken in the deposition process to avoid aggregation or washing away of the nanosheets.

Once the sample has been appropriately deposited onto the TEM grid, using a statistical analysis, the mean length and width of the sample can be determined. This is achieved by randomly moving around the grid and imaging the nanosheets. It is important to image a fair representation of both small and large flakes, with this type of sample; there is a bias to larger flakes due to the fact that small flakes can be difficult to see on the surface of the TEM grid. Therefore, the count of nanosheets is greater for larger than smaller flakes. This can be avoided through experience. Once a random selection of nanosheets has been imaged the statistical analysis can be performed. To generate length and width statistics of the sample a line is drawn to encompass the longest axis of the nanosheet and denoted “length”. Another line is then drawn perpendicular to the length and denoted “width”. An example of this methodology is
given in 4.10 B. This methodology is repeated for a large number of flakes (>150) to reduce any errors occurred in measuring.

![Figure 4.10: A) TEM image of the holey carbon and continuous film TEM grids respectively, B) Image representation of the assignment of the length and width of nanosheets.](image)

The use of TEM in this thesis is quite important as it allows us to determine the mean geometry of the nanosheets. This information can be used to relate it to how the scattering exponent scales as a function of nanosheets length. In addition this data can be used to correlate AFM statistics. Such analysis of this statistical data will be discussed further in chapters 5, 6 and 7.

### 4.9 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a widely used technique to image the surface of nanostructures. Similar to TEM it relies on the use of an electron beam to generate a signal which can be converted into an image. An electron beam is focused onto the samples by electromagnetic lenses (figure 4.11 A). The accelerating voltage typically used is between 2 and 10 eV. The interaction of the beam and the surface of the sample generates a tear drop shaped interaction volume (figure 4.11 B).
SEM uses backscattered electrons (BSE) and secondary electrons (SE) to generate an image. Rastering the beam across the surface generates multiple BSE and SE which are collected in the BSE or SE detectors. The energy of SE is typically between 3-5 eV; therefore, these electrons have quite a low escape depth, in the order of nm. BSE are higher in energy as they are inelastically scattered. The escape depth of BSE’s is typically a micron. Therefore, we have two different escape depths of these electrons to characterise our sample. BSE are highly sensitive to element type as it is a function of the atomic number. Higher atomic number elements have a greater proportion of back scattered electrons, SE are generated closer to the surface thus, are more sensitive to surface morphology. One main advantage of SEM is the ease at which samples can be measured. Within 5 mins of preparation, the sample can be inside the microscope and undergoing analysis. One fundamental problem, when analysing most 2D materials, is the effect of surface charge. In this work, the samples used in SEM were coated with a 3nm layer of Pt/Pd to improve the efficiency of charge dissipation. Without this coating, a charge would build up on the surface and distort the image. This coating does not impede any analysis for this work as SEM was only used to characterise the lateral dimensions of the nanosheets. If compositional analysis of the sample was needed to be undertaken then no coating was applied. All SEM work in this thesis was performed on a Zeiss Ultra plus SEM with a LaB$_6$ electron gun.
4.10 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is an important characterisation tool for a variety of materials from nanotubes to 2D layered nanomaterials. This technique gives information about the sample geometry in addition to the quality of samples that can be produced. Unlike traditional microscopes, the AFM does not rely on electromagnetic radiation to create an image rather it measures the vertical displacement of a tip head, as it is rastered across the sample. This generates a topographical profile of the nanomaterial (figure 4.12). The resolution of the method is sub nanometre in certain configurations.\textsuperscript{155, 156}

![Figure 4.12: Schematic representation of the topography process and line profile generation.](image)

The movement of the tip across the surface is detected by a laser which is reflected on the back side of the cantilever and then focused on a photodiode. The technique has two modes of operation, contact mode (directly related to topography) and non-contact mode (due to oscillation of cantilever). The choice of operation mode depends on the properties of the sample, for instance if the sample is quite soft then contact mode may cause the sample to compress and thus lead to a spurious height measurement.\textsuperscript{155}

The interaction between the tip and sample is described by the Lenard Jones potential (figure 4.13). Here we can see the interaction is a function of the tip sample distance. In the contact region the cantilever is typically less than a few angstroms from the surface of the sample. The main force between the cantilever and the surface is repulsive; the tip is rastered across the surface directly following the topography of the surface.
In the non-contact mode; however, the cantilever is held further away from the surface, (tens or hundreds of angstroms) where the interatomic force is attractive. Intermittent contact is characterised by the tapping mode, whereby the tip oscillates at its resonant frequency and slowly profiles the surface as it moves across. Moving from right to left on this potential curve, the atoms are weakly attracted to each other. As the separation between the tip and surface is decreased, this attraction increases. When the separation is sufficiently close the electron clouds begin to overlap and repel each other.\textsuperscript{155,157} Any further decrease in the separation will result in sample deformation due to a positive van der Waals force.\textsuperscript{157} During this process the changes in the deflection or oscillation of the cantilever due to attractive or repulsive interactions, are converted into topographic information about the sample.

This method was used to determine information relating to the geometry of the dispersed nanosheets, in this thesis. The samples were prepared by depositing a small volume of dispersion (~60µl), onto pre heated silicon water. The sample then began to evaporate and left the deposited nanosheets on the wafer in a coffee ring formation. The location of the analysis of the dropcast sample is not arbitrary; a suitable region of the substrate surface needs to be investigated, in order to avoid aggregation effects. Analysis of a region with a density which is too high, impedes an accurate determination of the length (L), width (W) and thickness.

\textbf{Figure 4.13: Schematic representation of the 3 modes of AFM measurements and the Lenard Jones potential for the interaction of the AFM and sample.}
(N). A low density area is ideal as reliable statistics of the nanosheets can be obtained.\textsuperscript{15, 138} Building this information up over an entire sample, one can obtain mean distributions for the size of nanosheets. Such information can be used to plot surface area as a function of nanosheet height to obtain greater insights into the sonication process. These relations will be further discussed in chapter 5.

One serious issue with measuring samples under ambient conditions is the presence of a water layer on top of the nanosheets. It is, therefore, imperative to measure in the correct mode to minimise these effects. In this work intermittent tapping mode is used where the tip is oscillated at its resonance frequency $\sim 300$kHz. It is also important to measure the samples soon after deposition. In our case we not only have to deal with water adsorbed on top of the nanosheets, we will also have residual solvent which can also contribute to an inaccurate height analysis. It is crucial in the case of surfactant samples to repeatedly wash the wafer to remove excess surfactant, as this will inhibit the accurate analysis of the lateral dimensions and the height of the nanosheets. It is important to account for these effects in the analysis of the data obtained; however, this will be further discussed in chapters 5, 6 and 7.
Liquid Phase Exfoliation of Molybdenum Trioxide (MoO$_3$)

5.1 Introduction

The role of 2D materials in future technologies remains of high importance. While materials such as graphene, BN and TMDs have been successfully used in devices there remain other layered materials for example oxides, III-VI and double hydroxides which hold great potential. Previous work has shown that when exfoliated down to mono or few layers, nanomaterials are useful for applications in polymer reinforcement, gas sensors and transistors. Demonstration of LPE to a new layered material will open up a greater selection of materials available to device engineers. There is a broad palate of layered materials yet to be investigated; however, at the beginning of this research extension of the LPE process to new materials had been slow. Therefore, this chapter assess the applicability of LPE, to layered oxides, namely molybdenum trioxide (MoO$_3$). This work presents the exfoliation of MoO$_3$ in a range of organic solvents. The nanosheets produced are subjected to a selection of characterisation techniques, such as TEM, AFM, PL and Raman spectroscopy, to assess the quality of material. Finally, the suitability of these nanosheets for use in supercapacitor electrodes will be investigated with varying nanosheet size and scan rate.

5.2 Experimental Procedure

MoO$_3$ powder (99.98%, CAS 1313-27-5) and all solvents used were purchased from Sigma Aldrich at the highest available purity. P3-single wall carbon nanotubes (SWNTs) were purchased from Carbon Solutions Inc. Previous solubility studies were used to determine appropriate solvent selection for investigation. A typical solvent screening experiment required 1 g/L MoO$_3$ sonicated in 10 mL of solvent for 15 min at 25% amplitude with a horn
probe sonication tip while ice-cooling the dispersion. The resulting dispersion was centrifuged for 50 min at 1,500 rpm (~240 g) in a Hettich Mikro 220R centrifuge. The supernatant was decanted and subjected to absorbance spectroscopy. The centrifugation parameters used in the solvent screening were established using a methodology to minimise the effects of solvent viscosity. The most viscous solvent in the screening study was N-Cyclohexyl-2-pyrrolidone (CHP, $\eta=11.5$ mPa.s); therefore, CHP required the longest centrifugation time (at a given rate) for the nanosheets to reach a steady state concentration. CHP was used to obtain the limit of centrifugation parameters which can subsequently applied to other solvents without the need to obtain these for each solvent. The following solvents were used for the screening: CHP, N,N'-dimethyl-N,N'-trimethyleneurea (DMPU), cyclohexanone, 2-propanol (IPA), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), tetrahydrofurane (THF), chloroform, toluene, heptane, pentane and methanol.

Preparation of a standard MoO$_3$ stock dispersion involved adding molybdenum trioxide powder (30 g) to 2-propanol (100 mL) in a 140 mL open top, flat bottomed beaker. The beaker was connected to an external cooling system that allowed for cooled water (5°C) to flow around the dispersion during sonication. The dispersion was sonicated using a horn probe sonication tip for 5 h, pulsed for 9s on and 2 s off.

Centrifugation parameters were optimised using the above dispersion procedure with an initial concentration of 50 g/L. Aliquots of 30 mL were centrifuged in a Hettich Mikro 220R centrifuge for varying time periods (10 min to 250 min) and rotation rates (f; 500-2,000 rpm, 26 g-430 g). The top 20 mL was decanted from the vial and diluted to perform absorption spectroscopy in a 1 cm optical grade quartz cuvette using a Cary 6000i. The concentration study entailed varying the initial concentration of MoO$_3$ in 100 mL IPA and determining the resultant absorbance at 375 nm as a measure for the concentration. The sonication time study experiments began with an initial concentration of 300 g/L. During the experiment, 5 mL aliquots were removed at given time intervals and immediately centrifuged at 1,500 rpm (~240g) for 110 min. The supernatant was again decanted and analysed using absorption spectroscopy.

Nanosheet size selection is achieved using centrifugation. The times for centrifugation were obtained using sedimentation time constants, $\tau$, as discussed in chapter 4. They are identified by employing sedimentation theory and fitting experimental data to decay constants. Very small (vs-) MoO$_3$- Aliquots of stock dispersion described above were centrifuged at 5
krpm (2600 g) for 120 min. The supernatant was subsequently decanted and characterised as vs-MoO$_3$. Small (s-) MoO$_3$- Aliquots of stock dispersion were centrifuged at 1.5 krpm (~240 g) for 110 min (3τ$_2$ as described in the results and discussion section). The supernatant was decanted from the vial and characterised as s-MoO$_3$. Large (l-) MoO$_3$- Aliquots of stock dispersion were centrifuged at 1 krpm (~100 g) for 30 mins (3τ$_1$) to remove any large unexfoliated material. The supernatant was decanted from the vials and further centrifuged at 1 krpm for 105 mins (>τ$_2$). The supernatant was decanted and discarded while the sediment was redispersed in fresh IPA.

P3-SWNTs are functionalised (carbocyclic acid) single walled carbon nanotubes. They are used in this work to increase the electrical properties of composite electrodes. 5 mg of P3 CNT’s were dispersed in IPA (50 mL) at a concentration of 0.1 g/L. This solution was then sonicated for 30 min in a horn probe sonication tip, followed by sonication for one hour in a sonication bath and an additional 30 min in the horn probe tip. This dispersion was then mixed with a predetermined concentration of MoO$_3$ dispersion, described above, to form a composite of known wt.%. The concentration of MoO$_3$ dispersion was obtained from accurate weighing of an alumina membrane (pore size 25 nm) before and after filtration.

To investigate MoO$_3$ for use as a supercapacitor, dispersions were filtered onto nitrocellulose membranes and dried at room temperature. These films were subsequently transferred onto an aluminium electrode coated in an adhesive polymer ( polyethylenimine (PEI)) using the transfer method of Wu et al.\textsuperscript{13} The electrochemical electrode was cut out of this larger aluminium electrode using a circular (18mm diameter) punch. The sample was then placed in an electrochemical cell (EL-cell combi) in a half-cell configuration using a Li-ion based electrolyte (1 M LiClO$_4$ in propylene carbonate). Electrochemical testing was performed using a Reference 600/EIS300 Gamry potentiostat. Capacitance was calculated from the cyclic voltammogram (CV) curve by integrating the negative portion of current over time (as calculated from voltage using scan rate) to give the charge stored. This was divided by the voltage range used (2V). The capacitance was normalised to the mass of the electrode material (MoO$_3$ + SWCNT, typically ~0.7 mg). Electrical conductivity was calculated using a four probe method with a Keithley 2400 source metre. Silver electrodes were used where the electrode spacing was typically on the order of a millimetre.
5.3 Results and Discussion

5.3.1 Optimisation of MoO$_3$ Dispersions

While a number of distinct liquid exfoliation technologies exist\cite{151}, probably the simplest is LPE which involves sonating the layered crystals in certain stabilising liquids.\cite{24, 47, 106, 151} The energy during sonication tends to exfoliate\cite{113} the crystals to give nanosheets stabilised against aggregation through interaction with the liquid.\cite{106} The stabilising liquids can be certain solvents\cite{7, 8, 24, 47, 106, 118, 166}, solvent blends\cite{101, 122}, aqueous surfactant solutions\cite{90, 91, 117, 120} or polymer solutions.\cite{114, 167} In this work MoO$_3$ powder was dispersed in a number of common solvents to test the applicability of LPE to this layered material, to yield mono and few layer species.

The structure of MoO$_3$ consists of molybdenum atoms in an octahedral position surrounded by oxygen atoms, making up one individual layer.\cite{168} These individual layers are stacked on top of each other, held together by weak van der Waals forces (figure 5.1 A).\cite{169, 170} To investigate the possibility of solvent exfoliation of layered oxides, MoO$_3$ powder was sonicated (sonication time, $t_s = 15$ mins, initial MoO$_3$ concentration, $C_i = 1$ g/L) in a range of common solvents. The centrifugation regime is crucially important and must be carefully chosen to avoid effects due to variation of viscosity among solvents (centrifugation (CF) time, $t_{CF} = 50$ min, centrifugation rate = 1.5 krpm, i.e. ~240 g). TEM performed on the dispersions showed they were rich in 2D nanosheets as shown in figure 5.1 B. To measure the dispersed concentration in each solvent optical absorbance spectroscopy was performed. Here the extinction per unit path length ($\text{ext}/L$) at 375 nm was taken as a metric for the dispersed concentration. The concentration ($\text{ext}/L$) was found to vary over 3-4 orders of magnitude for the solvents studied. A plot of $\text{ext}/L$ versus the Hildebrand solubility parameter of each solvent ($\delta_s$) shows a well-defined peak (figure 5.1 C). This parameter is defined as the square root of the solvent cohesive energy density\cite{171} and is well known to influence solubility for both molecular\cite{171, 172, 173} and nanoscale solutes.\cite{47} The best performing solvents were N-Cyclohexyl-2-pyrrolidone (CHP) and N-methyl-2-pyrrolidone (NMP). Previous studies on graphene and TMDs have also shown these amide solvents to give the highest concentrations of nanosheets.\cite{24, 118}
In the simplest case classical solution thermodynamics shows that the concentration of 2D solutes in a solvent is given by:

\[ C \propto \exp \left(-\frac{v_{NS}}{3kT}(\delta_s - \delta_{NS})^2\right) \]  

(10)

where \( \delta_{NS} \) represents the Hildebrand parameter of the 2D solute, \( v_{NS} \) represents the molecular volume of the solute and the factor of three stems from the solute dimensionality. It is important to note that this equation is not strictly applicable to nanoscale solutes such as graphene or MoO\(_3\) due to its simplicity. The model’s main weakness is the fact that the width of the concentration vs \( \delta_s \) peak rarely agrees with theoretical values. Moreover, there are other models such as Hansen solubility parameters which are more appropriate; however, Hildebrand solubility parameters provide a solid framework to predict nanosheet solubility. Nevertheless, fitting equation (10) to the data in figure 5.1 C, results in a good fit with \( \delta_{NS} = 20.7 \) MPa\(^{1/2}\) for MoO\(_3\). The maximum of the plot is similar to previously exfoliated layered materials such as graphene, BN and the TMDs which solubility maximum in the range of 21-
22.5 MPa\textsuperscript{1/2}. This confirms that MoO\textsubscript{3} behaves similarly to other layered materials. The choice of solvent, however, is not only important in obtaining the maximum concentration of dispersed nanosheets but also in the consideration of toxicology and ease of processing. Bearing this in mind, the study was continued using 2-propanol (IPA) as the solvent to disperse MoO\textsubscript{3}. IPA, in comparison to amide solvents such as NMP and CHP, yielded \~25% less dispersed nanosheets. IPA was chosen as it gave a relatively high concentration of dispersed nanosheets while its low toxicity and boiling point make it useful for film formation. Subsequently, it has also been shown that layered III-VI semiconductors, such as gallium sulphide (GaS), indium selenide (InSe), and double layered hydroxides can also be exfoliated using the LPE methodology.

To assess the quality and demonstrate control over the nanosheet dispersion, a series of parameters were investigated; namely centrifugation speed, starting concentration and the effect of sonication time. Firstly dispersions of MoO\textsubscript{3} were prepared with a longer sonication time (t\textsubscript{s} = 2 h, C\textsubscript{i} = 50 g/L) than for the solubility study and were subsequently centrifuged at different speeds (expressed as rotation rate, f) and times. Similar to the solvent study the extinction at 375nm was used as a metric for the dispersed concentration of the nanosheets and the effect of varying the rotation rate at a fixed time (65min) was investigated.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.2.png}
\caption{A) Optical extinction spectra as a function of centrifugation speed (f), B) optical extinction spectra for fixed speed as a function of centrifugation time (t\textsubscript{CF}).}
\end{figure}
As shown in figure 5.2 A, optical extinction spectra depend strongly on the centrifugation speed (for fixed CF time, $t_{CF} = 65$ min). At low rotation rate, the spectral features are superimposed on a broad background generally attributed to light scattering.$^{47, 175}$ When increasing the centrifugation velocities, both scattering background and concentration are reduced as larger aggregates are removed from the dispersion. Similar behaviour (figure 5.2 B) can be observed for dispersions centrifuged at a fixed rate for various times with the background decreasing as CF time is increased. This behaviour can be summarized by plotting the extinction (at 375 nm) versus CF time, for different CF rates in figure 5.3.

![Graph showing extinction as a function of centrifugation time for two fixed speeds 500 and 1500 rpm. The data is fitted to a bi exponential decay where the time constants are shown inset.](image)

**Figure 5.3:** Extinction as a function of centrifugation time ($t_{CF}$) for two fixed speeds 500 and 1500 rpm. The data is fitted to a bi exponential decay where the time constants are shown inset.

Similar to the behaviour previously observed for sedimentation of graphite/graphene dispersions, these curves can be fitted with a bi-exponential decay,$^{128}$ where the decaying components represent two unstable species in the system in addition to a stable component. The unstable species can be separated into a slow sedimenting phase and a fast sedimenting phase.$^{113}$ These can be defined as large, unexfoliated grains of powder which sediment quickly and mid-sized exfoliated nanosheets which sediment more slowly.$^{113, 121}$ Within this scheme, the absorbance decays with time as$^{128}$.
\[ \left( \frac{A}{l} \right) = \left( \frac{A}{l} \right)_0 + \left( \frac{A}{l} \right)_1 e^{t/\tau_1} + \left( \frac{A}{l} \right)_2 e^{t/\tau_2} \]  

Here, \((A/l)_0\) represents the absorbance, normalised by path length, of any stable phase while \((A/l)_1\) and \((A/l)_2\) represent the initial absorbance of the fast and slow sedimenting phases, respectively. Furthermore \(\tau_1\) and \(\tau_2\) represent the sedimentation time constants of these phases, respectively. The short and long time constants are in the range of 2-10 and 10-100 min (figure 5.3.13 inset). Empirically, the time constants decrease roughly as \(\tau \propto f^{-2}\), equivalent to \(\tau \propto F^{-1}\) where \(F\) is the centrifugal force during centrifugation (where \(f\) is the centrifugation speed). The time constants are important information relating to the stability of the nanosheet dispersions. Once the time constants are known, the optimal centrifugation time can be investigated. For example, if one wanted to remove all unexfoliated powder but retain all dispersed nanosheets (stable and unstable i.e. phases 0 and 1), then the required centrifugation time would be \(t_{CF} \geq 3\tau_2\) (where 3 time constants is the time taken for the exponential to decay by 95\%). In addition, one must choose a CF rate that gives a good balance between the concentration of the final dispersion and the CF time required. This is necessary to produce stable dispersions of MoO\(_3\) nanosheets, a combination of 1.5 krpm (~240 g) and \(t_{CF}=110\) min was chosen. This resulted in a stable concentration characterised by \(A/l= 109\) m\(^{-1}\).

After centrifugation conditions had been optimised to enable the choice between a high concentration and a stable dispersion, the effect of the initial concentration of the dispersion on the final nanosheet concentration post centrifugation was investigated. A sample was sonicated for 2h and then centrifuged at the optimum conditions, as determined above to be 1.5 krpm for 110 min, to isolate only the stable nanosheets. A plot of the extinction versus \(C_i\) is shown in figure 5.4 A. The dispersed concentration of nanosheets increases for an increase in starting concentration up to 100 mg/ml beyond which the dispersed concentration begins to taper off. The IPA begins to become saturated beyond this limit and the amount of material stably dispersed decreases. The concentration for the remainder of the study was fixed at 300 mg/ml. While it is important to investigate the amount of material dispersed it is crucial to also determine the optimum sonication time to facilitate maximum throughput. This was achieved by investigating the dispersed concentration of nanosheets as a function of the sonication time (figure 5.4 B).
Figure 5.4: A) Extinction plotted as a function of initial concentration of MoO₃, B) extinction as a function of sonication time (tₛ), C) Nanosheet length as a function of tₛ.

Here, similarly to the initial concentration, an increase in the dispersed nanosheets with increasing sonication time is observed. This is a non-linear increase following a power law where the dispersed nanosheet concentration increases with the sonication time to the power of a half. This behaviour has been previous reported for other nanosheet systems. ⁸⁸, ¹¹³, ¹²¹

It is not expected that solvent used, initial concentration or centrifugation time (so long as only stable nanosheets are retained - t₀ CF ≥ 3τ₂) have any significant effect on the nanosheet size. However, the lateral size of the nanosheets will certainly depend on the sonication time and the centrifugation rate. To assess this, TEM analysis was performed on dispersions prepared, while independently varying sonication time and CF rate. In order to probe whether nanosheet size changed with increasing sonication times, as a result of potential sonication induced scission, the mean flake lengths were measured for a number of sonication times (figure 5.4 C). A minor reduction in flake size was recorded up to sonication times of 8 h, suggesting that sonication induced scission¹⁷⁶ may occur over the range of sonication times studied. The mean flake length, L, was measured for a number of CF rates (figure 5.5 A). The flake length decreased from ~100 nm to ~40 nm as the rate was increased from 1.5 to 10 krpm (~240 g to 10500 g). Moreover, the nanosheet length falls off as \( f^{-1/2} \). This allows a working metric to predict the mean size of the nanosheets attainable at a given CF rate. Shown in figure 5.5 B is a TEM image of a typical MoO₃ nanosheet (3 krpm, ~950 g) where a distribution of nanosheet sizes from 200 to 60nm in lateral sizes is observed.
Figure 5.5: A) Nanosheet length as a function of CF rate, B) Representative image of the nanosheet sizes at 3 krpm.

The nanosheets obtained in this work are smaller in size than those obtained for solvent-exfoliated graphene and MoS$_2$ nanosheets. Pervious work has produced nanosheets with mean lengths of ~1 µm and ~0.3 µm.$^{47,88}$

5.4 Nanosheet Characterisation

The optimisation of the dispersion process was thoroughly investigated as discussed above. It is clear that the MoO$_3$ powder can be successfully exfoliated to give nanosheets of varying lateral dimensions. The rest of the investigations in this work will be based upon a stock dispersion which was prepared at an initial concentration of 300 g/L sonicated for 5 h. While the successful exfoliation of the material is promising, further characterisation is required to investigate the quality of nanosheets produced. To this end three nanosheet sizes will be investigated to study quality as a function of nanosheet sizes. The optimised procedure above yielded exfoliated nanosheets with typical lateral dimensions of 100 nm × 40 nm. This is denoted as s-MoO$_3$. However, as shown in figure 5.5, even smaller flakes can be obtained
by centrifugation at higher rates. Very small nanosheets were prepared by centrifugation at 5000 rpm (~2600g) which were also characterised in detail. These are denoted vs-MoO$_3$. Alternatively, larger flakes can be prepared by a controlled centrifugation procedure.\textsuperscript{175,177} The size selection procedure for larger flakes involves a short initial centrifugation at low rpm to first remove unexfoliated powder in the sediment. The supernatant is then subjected to a second longer (or faster) centrifugation step to precipitate exfoliated material of larger sizes (while keeping the smaller exfoliated flakes – s-MoO$_3$ - in the supernatant). The sediment can then be redispersed in fresh solvent yielding a dispersion of larger flakes (l-MoO$_3$). These three nanosheet sizes will be characterised and discussed in further detail below.

\textbf{A}

\textbf{B}

\textbf{VS} \hspace{1cm} \textbf{S} \hspace{1cm} \textbf{L}

\textbf{Figure 5.6: A) Photograph of the three nanosheet dispersion from left to right, vs, s and l. B) Temporal stability of the nanosheets in dispersion as a function of time.}

Shown in figure 5.6 A is a photograph of dispersions of vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ in IPA. These dispersions are visually different: while the large nanosheet dispersion resembles a colour similar to that of the initial white powder, the small nanosheets yield a faint blue colour in dispersion and the very small nanosheets exhibit a weak blue colour. As the preparation procedure was designed to remove all unstable material ($t_{\text{CF}} > 3t_2$), the s-MoO$_3$ and vs-MoO$_3$ dispersions are expected to be stable. However, the large nanosheets were produced by centrifugation of the nanomaterial at 1,000 rpm (~100 g), and it was therefore expected that the dispersions of l-MoO$_3$ would be less stable. To test this, a sedimentation analysis was performed. This analysis involved measuring the dispersion absorbance as a function of time over 300 h in a purpose built sedimentation apparatus.\textsuperscript{128} The data presented in figure 5.6 B
shows s-MoO$_3$ to be relatively stable with only 8% of dispersed material sedimenting over the time frame. Surprisingly, the vs-MoO3 was slightly less stable with ~20% sedimentation over 300 h. Conversely, the l-MoO$_3$ was unstable with ~75% sedimentation over 300 h. However, this sedimentation is still slow enough to allow further processing, for example in film formation.

To investigate the quality of nanosheets produced in this process and assess the lateral dimensions of the three characterised nanosheet sizes, statistical TEM analysis was performed. To deposit the nanosheets on a TEM grid, a few drops were drop cast and excess solvent was wicked away using filter paper. In all cases a large number of quasi-2D nanosheets were observed, however, it was quickly evident that the nanosheets were unstable for long periods under the direct electron beam. Overexposure of the nanosheets resulted in defect and hole formation. Examples of these holes can be seen in the representative images (both bright field and dark field) in figures 5.7 and 5.8 respectively.
Figure 5.7: Bright field image of MoO₃ nanosheet with increasing exposure time to the electron beam from right to left. Evident are holes due to the induction of oxygen defects in the crystal lattice.

Figure 5.8: Dark field TEM images of a MoO₃ nanosheet with increasing magnification from left to right showing clear evidence of defect induction (holes).
It is evident from the bright and dark field images that defects were introduced into the crystal lattice of the MoO$_3$ nanosheets. This introduction of defects was caused by the interaction of the electron beam with the MoO$_3$ structure, creating vacancies. This phenomenon is not new and has been extensively reported where the beam causes the MoO$_3$ to be reduced through a series of reduction steps, called Magneli phases, to MoO$_2$. The introduction of these defects, in this work, was only observed when the nanosheets are exposed to the electron beam for a long period of time (>10 min). Therefore, if the images are taken quite quickly then the introduction of defects should be minimal. This strategy was employed in the imaging of the three characteristic sizes of nanosheets in this work. Low resolution imaging was performed on the vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ nanosheets as well as HRTEM (figure 5.9, A-C and D-F respectively). The low resolution images show the nanosheets to be electron transparent which directly correlates to the thickness of the quasi 2D nanosheets. The characteristic sizes were also observed to be different. The HRTEM images clearly reveal the MoO$_3$ crystal lattice, indicating the exfoliated material to be of high structural quality. Analysing each Fast Fourier Transform (FFT) confirmed the structure to be consistent with the layered alpha phase of MoO$_3$. 178, 179, 180

![Figure 5.9: A-C) Low resolution images of vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ respectively, D-F) HRTEM images of vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ with their corresponding FFT image inset.](image-url)
From the low resolution TEM images, the length (L) and width (w) of ~100 nanosheets per sample was measured. This data is plotted in figure 5.10 A, which clearly shows the length scaling approximately linearly with the width, suggesting a well-defined L/w ratio. In addition, it confirmed that the lateral sizes scale as expected, with vs-MoO₃ < s-MoO₃ < l-MoO₃. From this data the mean lengths and widths were calculated and are plotted in figure 5.10 B. The mean nanosheet lengths were 61 nm, 108 nm and 378 nm for vs-MoO₃, s-MoO₃ and l-MoO₃, respectively. The mean width was perfectly proportional to the mean length giving a mean L/w ratio of 2.7, independent of nanosheet size. This well-defined L/w ratio can be attributed to the structure of individual MoO₃ monolayers. The nanosheet structure, consists of two strata of MoO₆ octahedra stacked vertically in the [010] direction to form a 2D monolayer. Bonding in the plane of each monolayer is through edge sharing oxygen bonds in the [100] and [001] directions, while inter-strata bonding is through an axial oxygen bond in the [010] direction. The octahedral bilayers contain three types of crystallographically inequivalent oxygen sites; namely singly (in [010] direction), doubly (in [100] direction), and tertiary (in [001] direction) coordinated oxygen atoms. These crystallographically inequivalent sites are reflected in varying Mo-O bond lengths, ranging from 1.67 Å to 2.33 Å. Moreover, sonication-induced scission is expected to result in a breakage of in-plane Mo-O bonds, with the weakest and longest bond of the tertiary coordinated oxygen in [001] direction being cleaved preferentially over the other Mo-O bonds. This yields nanosheets which are shorter in the [001] direction relative to the [100] direction resulting in a well-defined aspect ratio.

Figure 5.10: A) Nanosheet length plotted as a function of its corresponding width, B) The mean length for the respective size as a function of mean width.
5.4.1 AFM Characterisation of MoO₃ Nanosheets

While TEM is quite useful in determining the lateral dimensions and surface area of nanosheets, it is more difficult to accurately determine nanosheet thickness. Therefore, the thickness of the nanosheets was assessed using AFM. The exfoliation of MoO₃ in IPA is ideal for this analysis technique as the low boiling point ensures a rapid evaporation of the solvent. The sample was deposited onto a 300nm, SiO₂/Si wafer for analysis. While solvent choice aids film deposition, it does not prevent aggregation during drying. A new methodology was implemented to reduce this effect. The wafer was preheated to 100 °C and a low volume of the dispersion was dropped onto the wafer. The preheated surface allowed for rapid evaporation of the solvent and minimised aggregation effects. The formation of a coffee ring structure on the surface was visually evident post deposition; however, these areas were avoided for statistical analysis as the nanosheets were too densely packed to allow for reliable statistics. Areas such as those in figure 5.11 A, shows regions which were typically imaged where the packing density is quite low and reliable determination of the nanosheet edges can be achieved.

A large number of nanosheets (~100) had their characteristic L, w and thickness (t), measured for each nanosheet size dispersion. Firstly, the mean AFM lateral size (i.e. \( \langle L \rangle \) or \( \langle w \rangle \)) was plotted against the equivalent value measured by TEM, shown in figure 5.11 B. The agreement between the two techniques was found to be almost perfect (where perfect agreement is indicated by a dotted line). However, fitting showed the AFM sizes to be ~20 nm larger than those from TEM (solid line). The overestimation for the AFM values is consistent with broadening due to tip-convolution effects, as the sample was measured in ambient where there was undoubtedly adsorbed moisture on the surface of the sample. The interaction between the sample surface and the tip is slightly hindered due to the adsorbed layer of moisture. This layer can influence the measured step height of the nanosheets, thus introducing an error. This error is minimal for large nanosheets but becomes important when the size is reduced, as shown in the comparison to the TEM statistical data (figure 5.11 B). In any case, this implies the samples analysed by AFM to be free of aggregation effects, (or at least that the TEM and AFM samples suffered the same degree of aggregation).
As the TEM data above, showed a correlation between $\langle L \rangle$ and $\langle w \rangle$, the nanosheet thickness was also investigated as a function of length, as shown in figure 5.11 C. Firstly, it was clear that the nanosheet thickness scales with vs-MoO$_3$ < s-MoO$_3$ < l-MoO$_3$, with mean thicknesses of 14 nm, 21 nm and 80 nm respectively. The thinnest nanosheets were observed in the vs-MoO$_3$ dispersion with a thickness of 3 nm, consistent with that of a few stacked monolayers. For the larger sizes, the thinnest nanosheets observed were 7.4 and 14 nm for s-MoO$_3$ and l-MoO$_3$ respectively. Furthermore, it was clear that there was a correlation between thickness and the length of the nanosheets suggesting a well-defined L/t ratio with a
mean value of 6.6 (figure 5.4.1 C). With this well-defined ratio, the mean dimensions of the nanosheets can be determined to scale as $L:w:t=6.6:2.5:1$.

The nanosheet length, scaling as a function of thickness, is most likely not a fundamental relationship. Rather, the thickness is likely related to the surface area of the nanosheets ($A=L.w$). In the LPE process the energy required to exfoliate a MoO$_3$ crystallite is expected to scale linearly with its area. Moreover, for a given amount of energy, it is more likely for a large crystallite to be exfoliated to yield smaller nanosheets than a smaller nanosheet to be exfoliated yielding even smaller ones. To investigate this theory, the nanosheet thickness is plotted in figure 5.4.1.1 D not as a function of either the length or width but as a function of their product, yielding the surface area ($A$), where $A=L.w$. Here a clear relationship can be observed which is consistent with $t \propto \sqrt{A}$.

5.4.2 Solid Sample Characterisation.

While a wealth of characterisation techniques can be performed directly on the liquid dispersions, there remains a need to investigate the solid samples made from these dispersions. To this end, formation of films of vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ were undertaken through filtration of the respective dispersions onto alumina membranes (figure 5.12 A-C).

Figure 5.12: A-C) Filtered membranes and D-F) representative SEM images of vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ respectively (all SEM scale bars 500nm).
In addition to the size differences previously determined from TEM and AFM, a colour difference was also observed in the filtered films (figure 5.12 A-C). The surface morphologies of these films was analysed using SEM. At higher magnifications the films consisted of a disordered array of 2D nanosheets (figure 5.12 D-F). Thin films such as those achieved here by vacuum filtration are ideal for a number of spectroscopic techniques such as Raman and photoluminescence spectroscopy. These films were characterised firstly by Raman spectroscopy ($\lambda_{ex}=532$ nm) where the characteristic spectra are shown in figure 5.13.

![Raman Spectra](image)

**Figure 5.13:** Representative Raman spectra for the starting powder of MoO$_3$ and the three nanosheet sizes investigated (vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$).

It has long been known that the Raman spectrum of MoO$_3$ is rich in information, providing insight into phase, crystallite size, content of oxygen vacancies and stoichiometry of the material.$^{181}$ All MoO$_3$ spectra in figure 5.13 display the characteristic peaks expected for the layered orthorhombic alpha-phase MoO$_3$.\textsuperscript{56,168} According to Dieterle et al., the ratio of the intensities of the 285 cm$^{-1}$ peak to that at 295 cm$^{-1}$ can provide a measure of the true stoichiometry of the material.$^{181}$ Applying this to the samples investigated here yields a stoichiometric ratio of the starting powder as MoO$_{2.96}$, slightly below that of the ideal ratio of MoO$_3$. Furthermore, applying this to the nanosheet sizes investigated, the stoichiometry of the
very small, small and large nanosheets can be found to be at slightly lower stoichiometries of \( \text{MoO}_2.94 \), \( \text{MoO}_2.95 \), \( \text{MoO}_2.95 \), respectively. The slightly lower stoichiometries, between the processed nanosheets and the raw powder, are most likely due to the reduction in nanosheet size due to shearing. It is known that defects such as oxygen vacancies accumulate at the edges of the nanosheets. Therefore when the exfoliation process is carried out, smaller nanosheets than the bulk powder are acquired. These smaller nanosheets have a higher edge to basal plane ratio which may account for the slightly lower stoichiometry. The M=O stretching vibration at 996 cm\(^{-1}\) can be used to determine, via the presence of additional peaks in the region, the level of oxygen vacancies present in the sample. The presence of side bands cannot be observed in the sample, which confirms minimal oxygen defects present. Therefore it can be concluded that the LPE process does not introduce substantial oxygen vacancies in the \( \text{MoO}_3 \) nanosheets.

5.4.3 Supercapacitor Measurements

A number of studies have previously shown that \( \text{MoO}_3 \) nano-rods and platelets are useful as electrodes in supercapacitors.\(^{16,182,183}\) The nanosheets produced in this work may be quite promising in this area due to their ease of processing and the ability to generate high concentrations quite easily. Another distinct advantage with solution processing is the ease of film formation which is highly relevant for the formation of electrodes to test a material’s energy storage capabilities. Previous work has also shown, that 2D materials have a high surface area which results in high capacitances.\(^{184}\)

The charge storage properties of \( \text{MoO}_3 \) nanosheets were investigated in a Li-ion based electrolyte (1 M LiClO\(_4\) in propylene carbonate). This analysis was performed in a half-cell configuration using Li sheets as reference and counter electrodes. The three characteristic sizes of nanosheets (vs-\( \text{MoO}_3 \), s-\( \text{MoO}_3 \) and l-\( \text{MoO}_3 \)) were filtered onto a nitrocellulose membrane to form highly porous films, as shown in figure 5.14 A (s-\( \text{MoO}_3 \) film is shown). These films were then transferred onto aluminium foil to form a conducting back electrode to contact the entire film. The charge storage ability of these films was tested and the resulting cyclic voltammograms (CVs) are shown in figure 5.14 B. All three electrodes performed quite poorly achieving capacitances of \( \sim \) 2 F/g (dV/dt=10 mV/s). While the measured capacitances of the films were quite poor, this did not necessarily reflect poor capacitance capabilities in the films. For example, it is not uncommon for layered semiconductors to exhibit poor electrical
In this case, MoO$_3$ is a wide band gap semiconductor which has electrical conductivity of the order of $\sigma \sim 10^{-6}$ S/m (for 1 $\mu$m thickness). Therefore it was considered that the electrodes were inhibited by the poor conductivity of MoO$_3$, which would affect the charge-discharge rate, manifesting in a limited storage capability. To overcome such limitations highly conductive carbon nanotubes were mixed with dispersions of the MoO$_3$ nanosheets and filtered to form composite films.

Figure 5.14: A) SEM of a typical MoO$_3$ electrode, B) Characteristic CV curves of the vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$ nanosheets.

These composite films were transferred onto aluminium foil and their charge storage capabilities tested. 2D nanosheets/carbon nanotube composites are known to retain properties of the 2D matrix while displaying conductivities varying over 9 orders of magnitude. The use of carbon nanotubes in 2D nanosheet composite films has been previously shown to improve the performance of MoS$_2$-Li-ion battery electrodes. In figure 5.15, a representative SEM image of a 15% SWCNT MoO$_3$ film is shown which was used for electrochemical testing. The representative image shows excellent mixing of the 2D MoO$_3$ nanosheets and the SWCNTs. The films also have a high degree of mesoporosity which is essential to allow the electrolyte access to the internal surface of the nanosheets.
As demonstrated above, the electrochemical storage performance of MoO$_3$-only films was quite poor and possibly limited by the electrical conductivity. To investigate this, the new SWCNT-MoO$_3$ composites were tested electrically with increasing nanotube content to determine if an increase in the electrical conductivity could be observed (figure 5.16 A).

It is clear that increasing the mass fraction ($M_f$) of the nanotubes does not initially increase the electrical conductivity substantially. Above a certain mass fraction ($M_f$) the electrical conductivity of the composite dramatically increases by 8 orders of magnitude, up to
~1000 S/m for 25 w.t.% nanotubes. This dramatic increase in the conductivity occurred above a value of $M_f = 3$ wt.%. The behaviour displayed here is consistent with percolation theory; the sharp increase is associated with the formation of the first conducting paths of networked nanotubes which extend through the film. This percolative behaviour has also been previously observed for composite films such as graphene/MoS$_2$ and SWCNT/MoS$_2$. The nanotubes in this case act as the electrical conductor. Increasing the loading level until the first conducting path appears spanning the network is known as the percolation threshold ($M_{fc}$). Beyond this threshold, the electrical conductivity scales as

$$\sigma \propto (M_f - M_{fc})^t$$ (13)

Here, $t$ is the percolation exponent which is often observed close to 2.0. While the data is expressed as a mass fraction, it should technically be in terms of volume fraction; however this expression holds reasonably well up $M_f \sim 30$ wt.%. To see if the data model shows a percolative exponent close to 2.0, this function was fit to the data shown in figure 5.16. A. Shown in red is the fitted function (13) with exponent of 2.0 which fits the data quite well with a percolation threshold of $M_{fc} = 3$ wt.%. This result is consistent with other SWCNT/MoS$_2$ composites.

The electrical conductivities of the composite films were promising, and therefore electrodes were prepared with mass fractions of nanotubes ranging from 1-25 wt.%. Figure 5.16 B shows CVs for an electrode with 15 wt.% nanotubes. The dramatic increase in the charge storage can be clearly observed for all three size composites (vs-MoO$_3$, s-MoO$_3$ and l-MoO$_3$/ SWCNT) showing a capacitance of ~200 F/g. This represents a 100-fold increase in the charge storage capabilities of the composite films compared to pure MoO$_3$ films. Accordingly, a series of composites were prepared to investigate the capacitance change with nanotube content ranging from 0-25 wt.%. (Figure 5.17 A)
Figure 5.17: A) Specific capacitance as a function of SWCNT mass fraction, B) Specific capacitance as a function of scan rate.

The capacitance increase observed is similar for all three characteristic MoO$_3$ nanosheet sizes (figure 5.17 A, B). A low capacitance is observed for mass fractions below the percolation threshold (~1-6 F/g at 10 dV/dt). Above the threshold, a dramatic increase is seen in the capacitance, as high as 200 F/g at a scan rate of 10 dV/dt. It is clear that the capacitance increase occurs at the same threshold as the electrical conductivity of the composite films. The capacitance capabilities of the films are, therefore, clearly linked to the electrical conductivity of the MoO$_3$ nanosheets. It should also be noted that the increase in capacitance cannot simply be attributed to the contribution of the nanotubes, which are found to have a capacitance of 2 F/g at 10dV/dt. If this behaviour could be described by rule of mixtures, the capacitance contribution from the nanotubes would remain constant at 2 F/g for all nanotube contents. Clearly what is observed here is quite different and most accurately described by an increase in capacitance being facilitated by improved charge transport via the nanotubes to the MoO$_3$ active sites. The capacitance achieved, for a high loading of nanotubes, is quite comparable to other reports where the values are in the region of 349 F/g for α-MoO$_3$ nanobelts (CV, 0.1 mV/s), and 303 F/g for mesoporous α-MoO$_3$ (CV, 1 mV/s). The cycle stability was also increases with SWCNT loading; one possibility is that the nanotubes prevent the electrode from mechanical failure.
5.5 Conclusions

In conclusion, this work clearly enhances and enables numerous possibilities for liquid exfoliation technologies. MoO$_3$ powder has been successfully exfoliated to produce nanosheets. Solubility of MoO$_3$ in several common organic solvents was investigated using Hildebrand solubility parameters. The observed Gaussian peak was centered close to 21 MPa$^{1/2}$ which was similar to previous studies on other layered systems such as graphene and TMDs. Furthermore, control over the dispersion process was demonstrated where the effect of initial concentration, centrifugation rates and sonication time were all investigated. The concentration of the nanosheets was found to scale as a function of sonication time as $\sim t^{0.5}$. Optimisation of these conditions allowed for the determination of the nanosheet size and stability by careful selection of processing parameters. Control over centrifugation conditions allowed for the size selection of nanosheets ranging from 400-50 nm. It was also observed that only nanosheets below 200-300 nm had long term stability in solution.

Characterisation of the nanosheets via TEM and AFM yielded a clear relationship between the lateral dimensions of the nanosheets, where $\langle L \rangle : \langle W \rangle : \langle T \rangle = 6.6:2.5:1$ held for all sizes. This relationship can be attributed to the bonding scheme within the nanosheets themselves, coupled with the scaling of exfoliation energy required for a given flake area. Raman spectroscopy was performed on filtered films, of three characteristic sizes of nanosheets, allowing the defect levels to be determined. In all cases the reduction in oxygen stoichiometry was negligible with respect to the starting powder, therefore, indicating that the nanosheets are not damage during the LPE process.

MoO$_3$ dispersions were filtered onto filter membranes and were investigated for use as a supercapacitor electrode. Here, poor energy storage of $\sim 2$ F/g was initially observed which was determined to be related to low electrical conductivities ($\sim 10^{-6}$ S/m). Inclusion of a conductive additive in the form of SWCNT increased the conductivity by 8 orders of magnitude. Determination of capacitance of MoO$_3$/SWCNT composites yielded a significant increase in the specific capacitance with values as high as $\sim 350$ F/g (0.1 mV/s) achieved. Interestingly, a percolative behaviour was observed in both the capacitance and electrical conductivity of the MoO$_3$/SWCNT composites where in both cases the percolation threshold was found to be 3 wt% of nanotubes.
This work clearly underlines, that solvent exfoliation can be applied to materials beyond the accepted group comprising graphene, BN and TMDs. Control over the exfoliation parameters allowed insights into the process for new materials. The dimensions of the nanosheets produced followed an inherent relationship which may be similar for other 2D materials. It is hoped that the conditions refined here will assist in future work.
6.1 Introduction

It has been over a decade since the discovery of graphene, a monoatomic layered material. Graphene’s main exfoliation methodologies such as mechanical cleavage and liquid phase exfoliation have extended of late, to other layered structures such as BN and TMD’s. Over the years, BN and TMD’s have been investigated for many applications in the areas of electronics, reinforcement and supercapacitors.\textsuperscript{50, 84, 162}

In the past year however a new 2-dimensional material has been generating considerable excitement in the research community.\textsuperscript{1, 20, 41, 159, 189, 190} This material known as phosphorene (black phosphorus), which is comprised of monoatomic layers that are stacked vertically and held through van der Waals bonding is similar to graphene. Calculations show that black phosphorus has a direct band gap which increases from \(~2.3\) to \(1.5\) eV from bulk to monolayer.\textsuperscript{77} In contrast graphene exhibits no band gap. This makes BP an extremely attractive material to study as tuning the layer number will change the band gap of the material. As a result a lot of research into devices such as transistors,\textsuperscript{33, 71, 79} photodetectors\textsuperscript{191} and solar cells\textsuperscript{72} that takes advantage of this tuning has been undertaken.

In order to realise their full potential, nanosheets need to be isolated from the bulk crystal. It has been shown that mono and a few layered species have been isolated through mechanical exfoliation. However, this is useful only for certain applications and is not scalable. Theoretically calculations predict that BP shows promise for applications in the thermoelectric\textsuperscript{192} and gas sensing areas\textsuperscript{163}, however they require a large amount of material to test. Previous LPE methodologies that have been applied to graphene and TMD’s have been
proven to yield large amounts of high quality nanosheets in solution. These nanosheets are ideal, as they may be prepared to make films and electrodes for testing in numerous real world applications. BP nanosheets have been shown to be quite unstable, degrading via reactions with water and oxygen. While LPE has proven historically to be somewhat problematic requiring exfoliation in ambient conditions and typically in wet solvents, if overcome then LPE would be a lucrative technique to produce large quantities of BP.116,193

The work in this chapter demonstrates the exfoliation of BP in common solvents to yield large quantities of few layer nanosheets. It is demonstrated that if a suitable solvent is chosen such as N-cyclohexyl-2-pyrrolidone (CHP), then the rate of oxidation can be reduced, thereby allowing for the processing and fabrication of devices in ambient conditions. Key control over centrifugation conditions yields a selection of stably dispersed nanosheets from 100nm up to 1µm. These nanosheets display direct gap photoluminescence, thereby verifying the presence of few layer nanosheets that are stably dispersed in solution. Furthermore the relationship between nanosheet size and oxidation rate is probed, where there is a clear relationship showing that the reaction occurs at the edge. This shall be discussed in further detail below.

6.2 Experimental Procedure

6.2.1 Sample Preparation

Black phosphorus (BP) crystals were purchased from Smart Elements (purity 99.998%); all other materials were purchased from Sigma Aldrich and used as received. BP was lightly ground with a pestle and mortar and immersed in CHP (concentration 2 g/L). The dispersion was sonicated for 5 hours at 60% amplitude with a horn-probe sonication tip (VibraCell CVX, 750W) under cooling, yielding a stock dispersion. Aliquots of this dispersion were centrifuged at 1,000 rpm (106 g) for time periods varying from 5 to 240 min in a Hettich Mikro 220R centrifuge equipped with a fixed-angle rotor. The supernatant was decanted and subjected to absorbance spectroscopy. The supernatant was centrifuged at 1,000 rpm for 180 min and was denoted the standard sample (std-BP). The std-BP was subsequently separated into small and large stable nanosheets. For this purpose, aliquots of std-BP dispersion were subjected to an additional centrifugation of 5 krpm (2,660 g) for 120 min. The supernatant (containing small flakes) was decanted and characterised as S-BP while the sediment (containing large flakes) was re-dispersed in fresh CHP and characterised as L-BP. Alternatively, size selected
nanosheets can be obtained through controlled centrifugation. A series of samples were prepared with different centrifugation conditions. A sample was centrifuged at 2 krpm (426 g, 2 h). The sediment was discarded, while the supernatant was subjected to further centrifugation at 3 krpm (958 g, 2 h). The sediment was collected and redispersed in fresh solvent, while the supernatant was subjected to further centrifugation at 4 krpm (1,702 g, 2 h). This procedure was repeated for 5 krpm (2,660 g, 2 h), 10 krpm (10,170 g, 2 h) and 16 krpm (25,000 g, 2 h) to yield samples with decreasing sizes in the respective sediments.

Degradation studies and PL measurements were conducted in an argon-filled glovebox (O<sub>2</sub> < 0.1 ppm; H<sub>2</sub>O < 0.1 ppm), in pump-freeze deoxygenated and dry CHP with a water content of 29 ppm. A sample was prepared under these dry conditions using similar sonication parameters as above. The resultant dispersions were transferred into centrifugation vials, which were sealed and centrifuged for 3 h at 100 g to obtain the std-BP GB sample. To increase the population of few-layered species for the PL measurement, this std-BP GB sample was centrifuged for 16 h at 25 g. The sediment was discarded and the supernatant centrifuged again at 710 g for 180 min. All solvent transfer was carried out in the glovebox under inert gas conditions.

6.2.2 Characterisation Methods

Optical extinction and absorbance was measured on a Perkin Elmer 650 spectrometer in quartz cuvettes. To distinguish between contributions from scattering and absorbance to the extinction spectra, dispersions were measured in an integrating sphere, using a home-built sample holder to place the cuvette in the centre of the sphere. The absorbance spectrum is obtained from the measurement inside the sphere. A second measurement on each sample was performed outside the sphere, to obtain the extinction spectrum. This allows for the calculation of the scattering spectrum. Experiments to track both water and BP degradations were performed on a Perkin Elmer Lambda 1050 spectrometer in extinction.

Bright field TEM was performed by depositing some of the dispersion on grids. The sample was then baked in vacuum at 120°C for several hours and imaged on the day they were deposited, termed Day 1. For stability studies the same flake was then imaged on Day 3 and 16 respectively. No changes in nanosheet structure or morphology were observed between Day 1 and Day 3. At Day 16 a combination of reaction products and water adsorption, results in a liquid layer on the flake. This layer can be removed with the beam and comparison of the shape of the flakes between Day 1 and Day 16 was analysed.
AFM was conducted on several samples. A drop of the dispersion, transferred to IPA, was deposited on a pre-heated (150 °C) Si/SiO$_2$ wafer with an oxide layer of 300 nm. Raman spectroscopy on individual flakes was performed on deposited wafers and filtered films with 633 nm excitation laser in air under ambient conditions. X-ray Photoelectron Spectroscopy was performed under ultra-high vacuum conditions (<5×10$^{-10}$ mbar), using monochromated Al Kα X-rays (1486.6 eV) from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. Core-level regions were recorded at an analyser pass energy of 15 eV and with slit widths of 6 mm (entry) and 3 mm × 10 mm (exit), resulting in an instrumental resolution of 0.48 eV. After subtraction of a Shirley background, the core-level spectra were fitted with Gaussian-Lorentzian line shapes and using Marquardt’s algorithm.

Photoluminescence in dispersion was acquired on a Horiba Scientific Fluorolog-3 system equipped with 450 W Xe halogen lamp and a nitrogen cooled InGaS diode array detector (Symphony iHR 320). Spectra were obtained at 5°C using appropriate cut-off filters.
6.3 Results and Discussion

6.3.1 Exfoliation and Basic Characterisation

A similar methodology, as shown previously in chapter 5, was employed to exfoliate Black phosphorus (BP). BP (2g/L) was probe sonicated in cyclohexyl pyrrolidone (CHP), which shows the highest dispersions of nanomaterials in previous studies. The mixture of BP and CHP was sonicated for 5 hours. Following sonication, the solution turned dark brown, as shown in figure 6.1 A. To remove any unexfoliated material the dispersion was centrifuged, at 1,000 rpm (106 g) for time periods varying from 5 to 240 min. The supernatant was decanted and subjected to absorbance spectroscopy. The samples were measured in an integrating sphere, which removes the scattering, to measure the real absorbance of the material. Following this, the sample is measured outside of the sphere where the extinction spectrum is measured. The scattering spectrum therefore, can be determined using the following relationship $\varepsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda)$. Here $\varepsilon(\lambda)$, $\alpha(\lambda)$, $\sigma(\lambda)$ are the extinction, absorbance and scattering coefficients, respectively. Representative spectra are shown in figure 6.1 B. The absorbance coefficient through, accurate filtration and weighing, was determined to be $\alpha(\lambda=465\text{nm}) = 15 \text{ L g}^{-1}\text{cm}^{-1}$. This was then used to determine the concentration of all subsequent FL-BP dispersions.

![Figure 6.1: A) Optical image of the BP/CHP dispersion, B) Extinction absorbance and scattering spectra of sample after 1krpm for 180 mins, C) Absorbance at 465nm as a function of CF time at fixed rotations (1krpm).](image-url)
To produce a stable dispersion, free from sedimentation, the sample was centrifuged for varying times (at fixed speed). Analysis of absorbance spectra at 465nm over these time periods yielded an exponential decay, similar to previous work in chapter 5 \( A = A_{\text{initial}} + A_{\text{res}} e^{-t/\tau} \). Fitting this curve allows the stable time constant to be determined. This time constant (\( \tau \)) was determined to be 86 min (figure 6.1 C). Therefore, to obtain a dispersion where the nanosheets are stable times > 2\( \tau \) have to be used.\(^{15,34}\) This insures any unexfoliated nanomaterial is removed from the dispersion.

The quality of nanosheets dispersed in solution was investigated using TEM analysis. In all cases, the grids were covered with a large amount of electron transparent nanosheets, with varying lengths, as shown by the selection of images in figure 6.2 A-F. Lateral dimensions, up to 3\( \mu \)m, were observed.

To further characterise the quality of nanosheets produced, HRTEM was conducted (figure 6.3 A, B). One difficulty with using CHP as a solvent is its high boiling point, which makes it difficult to remove from the nanosheets. This makes imaging in high resolution, to investigate the lattice, difficult. An overnight high temperature bake was used to remove as much of the CHP as possible, however, it is still difficult to observe the lattice. To overcome this, the BP crystal was exfoliated in IPA, a lower boiling point solvent which has been proven to successfully exfoliate a number of other layered materials.\(^{15,34}\) This dispersion was investigated using scanning transmission electron microscopy (STEM) and high-angle annular dark field (HAADF), where the lattice can be observed (figure 6.3 C, D respectively). It is clear that lattice is free from defects over large regions of our nanosheets.
Figure 6.2: A-F) representative TEM images of BP nanosheets in dispersion.
Figure 6.3: A, B) HRTEM images of std-BP nanosheets exfoliated in CHP, C, D) STEM and HAADF image of std-BP exfoliated in IPA.

Statistical TEM analysis was performed on the std-BP sample dispersed from CHP. The length of ~200 nanosheets, were measured and analysed to produce a mean length of the sample, shown in figure 6.4 A. There are two peak distributions of the nanosheets centred at ~100nm and ~3µm. This means that for the std-BP sample there are both small and large nanosheets stably dispersed. Interestingly, the mean sizes produced for BP are considerably larger than those reported for other layered 2D nanosheets (TMD’s and TMO’s) which are typically below 1µm.15,138 The larger nanosheet size can be attributed to the large size of the starting crystal. The starting material, unlike previous work, is a crystal which was lightly ground to produce chunks. These chunks are on the millimetre scale.

To investigate the effect of sonication time on the resulting concentration of std-BP, aliquots of dispersion (~2ml) were taken out and subject to the centrifugation conditions to remove any unstable material. As shown in figure 6.4 B, the concentration of std-BP increases
sub linearly as a function of sonication time \((t_s \sim 0.4)\). This is a similar behaviour as reported for other layered materials such as graphene and molybdenum trioxide (chapter 5).\(^{15,34}\)

![Graph](image)

**Figure 6.4:** A) Statistical TEM analysis of std-BP dispersion showing a bimodal distribution at \(\sim 100\text{nm} \) and \(3\mu\text{m}\). B) Sonication time study where the absorbance of std-BP increases as \(t_s \sim 0.4\).

AFM analysis was performed on the std-BP dispersion to obtain an accurate measurement of the nanosheet thickness. CHPs’ high boiling point inhibited an efficient deposition onto a wafer for analysis. Similar to the HRTEM analysis, the sample was sonicated in CHP and transferred into IPA. The transfer into IPA is crucial for the deposition of the dispersion onto a Si wafer to undergo AFM analysis due to its low boiling point and therefore, ease of evaporation. A small amount of the std-BP (in IPA) was deposited onto a preheated wafer. Upon evaporation of the solvent, a typical coffee ring stain was left on the wafer. For imaging the nanosheets, areas outside these “coffee rings” were chosen as there was a lower loading density. This significantly reduces the risk of aggregation effects. A selection of representative images is shown in figure 6.5B. The apparent height of the nanosheets was measured, where it was shown to be 27nm (figure 6.5 A). It is difficult to actually attribute this mean thickness of 27nm to an actual real height due to several effects which are inherent in this analysis from samples produced by LPE. Firstly measuring accurate heights in the AFM on these samples is challenging due to contributions form capillary and adhesion forces.\(^{44,95}\) When the samples are deposited and measured under ambient conditions there is always adsorbed water on the surface of both the nanosheets and wafer surface.\(^{37,194}\)
The adsorbed water may not be uniform, in thickness, across these components due to the chemical difference between the Si surface and the surface of the BP nanosheets. This leads to an inaccurate measurement of the thickness, typically for 2D nanosheets the thickness is overestimated. An accurate determination of the height was achieved by using step height analysis. This is an advanced technique, which involves conversion of the measured height into a number of layers. This approach has been previously demonstrated in the case of MoS$_2$ nanosheets, where a careful measurement of incomplete edges and steps allows for the determination of the apparent height of one layer of the material. An example of one analysis of the step height is given in figure 6.6 A. A series of steps are evident on the edge of the nanosheet. Analysis of this region in the topography profile displays a series of steps. Plotting the apparent height of as a function of step number we see a clear trend, with an associated step height of 2nm (figure 6.6 B). This step height is also observed for MoS$_2$ nanosheets (~1.9nm). This means that one layer of BP appears to be 2nm in height in the AFM, even though the real thickness is ~0.7nm. Moreover, this correlation can be used to convert the apparent height of the nanosheets into a number of layers.

The statistical AFM counts from the std-BP sample, have been converted into a number of layers (figure 6.7 A). The mean thickness in the sample is $\langle N \rangle = 9.7 \pm 1.3$, averaged over 150 nanosheets. This mean thickness is influenced by some large nanosheets. As reported in chapter 5, larger nanosheets are usually thicker than smaller ones. TEM has confirmed that lengths up to 5µm are observed. These nanosheets have a considerable effect on the mean thickness.
value. To investigate this, the relationship between thickness and surface area, similar to chapter 5, is shown in figure 6.7 B. Approximately 70% of the nanosheets in the dispersion have N≤10. The thickness of the nanosheets follows a power law with respect to the surface area of the nanosheet, where $N \sim A^{0.5}$.

![Figure 6.6: A) apparent height measure across an edge of nanosheet as a function of position, B) Apparent height plotted as a function of step number where there is a clear step height of 2nm.](image)

It is well known that BP is unstable in air; therefore, to assess the quality of nanosheets produced by LPE, X-ray photoelectron spectroscopy (XPS) was performed. The characteristic P2p$_{1/2}$ and P2p$_{3/2}$ species of the std-BP sample are observed, where there is a contribution from a P$_x$O$_y$ species (figure 6.8). These phosphate species present in the sample account for $\sim$15%. These species are formed due to the oxidation of the BP nanosheets under ambient conditions. The oxidation of the nanosheets will be discussed below in greater detail in the nanosheet stability section; however, it should be noted that freshly prepared nanosheets exhibit oxidation levels consistent with other layered materials such as MoS$_2$ (typically observe levels between 10-15%), even with CVD MoS$_2$.195
Figure 6.7: A) mean number of layers in the std-BP dispersion, B) the number of layers as a function of nanosheet surface area, $N \sim A^{1/2}$.

Figure 6.8: XPS spectra of the std-BP sample, showing the characteristic P peaks and the highlighted oxide ($P,O_x$) species. Oxidation level is $\sim$15%.
### 6.3.2 Nanosheet Size Selection

A range of nanosheet sizes can be obtained using controlled centrifugation conditions. The ability to control the size of nanosheets is quite important, as some applications, for example hydrogen evolution, require small nanosheets, as in the case of gallium sulphide (GaS) where the reaction occurs at the edge. In the case of BP, a stepped centrifugation was employed; the nanosheets were trapped between sequential rpm’s. The dispersion was centrifuged at 2 krpm (424 g) for 2 h where the supernatant was decanted, while the sediment is discarded. In this case the sediment is removed, as it is composed of primarily unexfoliated nanosheets. The supernatant is subjected to another centrifugation at 3 krpm (958 g) for 2 h. Again, the supernatant is decanted and moved to the next centrifugation step at higher rpm. The sediment is redispersed in fresh solvent by mild agitation. The process of decanting the supernatant and redispersing the sediment in fresh solvent is employed through multiple steps to achieve varying size distributions of nanosheets in the respective preparations. Repeating this procedure yields multiple dispersions, where the lateral dimensions of the nanosheets decrease with increasing centrifugation speed. The centrifugation speeds and steps are indicated in figure 6.9. Statistical TEM analysis was performed on all size selected samples, showing mean lateral dimensions from 150-620 nm (figure 6.10).

![Schematic representation of the stepped centrifugation.](image)
The nanosheet histograms are also displayed in figure 6.10. At high rpm’s the inset highlights the narrow distribution of small nanosheets. It is clearly evident that increasing the centrifugation speed decreases the mean nanosheet length. It should also be noted the narrower the distributions with increasing speed, an added benefit of the trapping between different centrifugation speeds. This means that variation of centrifugation speeds can produce samples of a given mean length, with a narrow size distribution. In addition to statistical TEM analysis the samples were also subjected to absorbance spectroscopy. For each sample the extinction, absorbance and scattering spectra were measured as shown in figure 6.11 A-C respectively.
Figure 6.11: A, B, C) extinction, absorbance and scattering spectra for varying nanosheet sizes.

It is clearly evident that the spectral shape changes dramatically as a function of the nanosheet size. These changes are primarily due to the fact that in each dispersion there is a different mean size of nanosheet, which in turn contributes differently to the respective extinction, absorption and scattering spectra. Not only does the size of the nanosheets give rise to such profound effects, as evident in the spectra, the nanosheets become smaller. Therefore, we may see a greater contribution from the edges.\textsuperscript{138, 197, 198} The spectral changes can be investigated by plotting the ratio of optical extinction coefficient at two wavelengths $\varepsilon_{600\text{nm}} / \varepsilon_{340\text{nm}}$, versus nanosheet length, $\langle L \rangle$, as shown in figure 6.12 A. This ratio depends on nanosheet length in a well-defined way. The absorbance spectra also display a similar trend (figure 6.11 B). In both cases we see a pronounced effect where small nanosheets do not seem to absorb strongly in the higher wavelength regions. A clear relationship, between intensity ratios, can be used to determine the nanosheet length in solution (figure 6.12 A, B).
Furthermore, the scattering spectra shown in figure 6.11 C also vary strongly with nanosheet length. Previous work has shown that in the high wavelength regime, low absorbance from nanosheets, the scattering exponent scales as a power law with wavelength: $\sigma \propto \lambda^{-n}$. The scattering exponent $n$ is known to be sensitive to nanosheet length. Therefore, by fitting the curves in the range 700-800 nm the scattering component can be related to a nanosheet size. The resultant values of $n$ are plotted versus inverse nanosheet length (figure 6.13). This data can be used to generate metrics, which allow the estimation of $\langle L \rangle$ from the optical spectra. For example using this data, a potential metric can be obtained to show that $L(\mu m) \approx 0.42/n$. This expression is extremely useful as it can be used to determine the nanosheet length, in situ via optical spectroscopy without the need for expensive and time consuming TEM or AFM.
6.3.3 Photoluminescence

The dispersed BP nanosheets were analysed using PL, which is a highly useful technique for layered semiconductors. PL can be used to determine the layer number of the nanosheets by their characteristic energy. This technique involves exciting a material over a range of energies to probe the optical band gap of the material. In this case, PL was measured in solution. The influence of solvent molecules, due to chemical interaction with the nanosheets, may affect the PL. The main benefit of measuring PL in solution is that a large amount of nanosheets can be probed simultaneously. This technique is quite powerful, a representative analysis of the system is obtained. Unlike other 2D materials such as MoS₂ which only exhibits PL in the monolayer, BP luminesces for a large range of layer numbers. This means we can see PL across a large number of layers. Furthermore, the PL energy is characteristic of each layer i.e. transition from bulk to monolayer sees the optical gap change from 0.3eV to 1.8eV. Using this technique, the type of nanosheet in the sample can be determined.

To achieve the most pristine sample, BP was exfoliated under inert conditions. Given BP’s known instability this precaution should produce a pristine sample with minimal levels of oxidation. The sonication conditions were similar as those above to prepare a std-BP sample. An extra centrifugation step was used to remove any large nanosheets which will not display PL but may contribute to self quenching. Emission-excitation contour maps for few layer BP
were obtained (figure 6.14 A, B). A strong luminescence signal, where very clear emission lines can be seen at ~ 600nm and ~900nm. Weaker features can also be seen at ~1150, 1260 and 1325 nm. These spectral features can be associated with the optical band gap of 1-5 layer BP species respectively. The detection of PL was surprising in CHP, as this solvent can typically quench any PL intensity, as observed for CNT dispersions.\textsuperscript{8}

![Figure 6.14](image)

**Figure 6.14**: A, B) Photoluminescence excitation/emission contour maps of few-layer BP dispersion with the layer numbers identified by a white line, C) A photoluminescence line spectrum excited at 510 with indicated extinction spectrum (dotted line), D) the line spectrum at 510 fitted using Gaussian line representing the 1,2,3,4 and 5 layer species detected in solution.

A single line spectrum which was excited at 510nm is shown in figure 6.14 C. Here, the PL is shown in addition to the extinction spectrum. Fitting this spectrum using Gaussian functions gives quite good fits for 1, 2, 3, 4 and 5 layer BP species (figure 6.14 D). The sample investigated confirmed that LPE of BP produced mono and few layer species. Comparison of
these results with other reports is analysed. It is quite important to note that the PL is influenced by the surrounding environment. In this case the sample was prepared in CHP a solvent with a high dielectric constant, which results in a low exciton binding energy. The energy, therefore, of the transitions are very close to the optical band gap of BP, however, are slightly higher than those from micromechanically cleaved samples (Appendix figure 9.1). This deviation can be accounted for due to different chemically interacting mediums. Nevertheless, an intense PL signal from the mono and bilayer species, is observed. PL intensity is dependent upon factors such as, the relative internal PL quantum yield (PLQY), concentration of the sample, which may induce self-quenching and the population of the respective layers in solution.

To determine the mean distribution of layer number in sample, a statistical AFM analysis was used. The population by layer number is represented in figure 6.15 A, where a representative AFM image is shown (figure 6.15 B). The statistical analysis was performed on ~300 nanosheets, where the subsequent length and width was measured. It is necessary to measure a large amount of nanosheets, to compile an accurate description of the population thickness. The mean thickness was determined to be 8.2 layers. The population of layer numbers, present in the sample, is shown in table 6.1. Interestingly, the population of nanosheets scales with the layer number.

![Figure 6.15: A) mean number of layers measured by statistical AFM, B) Number of layers plotted as a function of nanosheet surface area. C, D) representative images of nanosheets.](image-url)
Table 6.1: Volume fractions of 1-5 layered nanosheets in dispersion measured by AFM statistical analysis.

<table>
<thead>
<tr>
<th>layer number</th>
<th>volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L</td>
<td>0.5 %</td>
</tr>
<tr>
<td>2L</td>
<td>2.2 %</td>
</tr>
<tr>
<td>3L</td>
<td>5.1 %</td>
</tr>
<tr>
<td>4L</td>
<td>6.1 %</td>
</tr>
<tr>
<td>5L</td>
<td>6.4 %</td>
</tr>
</tbody>
</table>

6.3.4 Nanosheet Stability

Literature reports, from mechanically exfoliated and LPE BP have identified issues with nanosheet stability as a function of time.\textsuperscript{71,191,201} These reports are focused on exfoliation of BP and testing in applications such as transistors. It was noted that device performance suffered over relatively short time periods (~1 week), however, no extensive study had been undertaken to investigate the degradation, at the time of this work. Recently, encapsulation of the devices after fabrication, using a capping oxide layer, maintains device performance over prolonged periods of time.\textsuperscript{76} A chemical reaction has been suggested for the instability, which involves water and oxygen.\textsuperscript{75} Therefore, the capping layer shields the nanosheets from an interaction with oxygen and water. LPE, therefore, may not be an ideal process to produce these nanosheets, as it is usually done in ambient conditions, where there is ample supply of oxygen and water available. In addition to the moisture present in the atmosphere there is also dissolved water in the solvents.

Nevertheless the analysis above has shown that high quality samples can be achieved by LPE methods. This section aims to investigate the stability of the nanosheets in dispersion as a function of time. Absorbance spectroscopy of an inorganic sample can be used to determine the concentration of dispersed nanosheets in solution. Therefore, this is an ideal optical characterisation technique to investigate stability. The stability the std-BP dispersion was measured, at defined intervals, over a period of ~300 hrs (figure 6.16 A). Interestingly, there is a decrease in the absorbance of the sample over time. Optimisation of the centrifugation conditions in the experimental section above should prevent any nanosheets sedimenting over time. The sample was shaken before each measurement however; there was also no evidence
of any sediment at the bottom of the vial. A visible change in the colour of the sample was also noted, a transition from yellow to transparent. The reaction products in the proposed disproportionation reaction should not be dominant in the spectra, in the range of the BP due to the fact they should be molecules and have large HOMO-LUMO gaps.  

It is unknown what effect the chemical reaction products will have on the extinction spectra and if they will interfere with the concentration measurements. To investigate this, a std-BP sample was prepared and subjected to a similar study as the absorbance, a series of measurements up to ~300hrs. A decrease in the extinction intensity was observed, similar to the absorbance data (figure 6.16 B).

To quantify the decrease in the absorbance and extinction over time, the intensity at 465nm was chosen to act as a metric for the dispersed concentration of BP. This will allow the concentration of the BP nanosheets to be tracked over time (figure 6.16 C). Here we observe a continuous decrease in the concentration of nanosheets over time which follows a single exponential decay. This decay curve fitted to figure 6.16 C (shown in inset), shows that in our system we have two components; unreacted and reacted nanosheets. The reacted nanosheets follow an exponential decay with a time constant of 187 hrs. Unlike absorbance spectroscopy, where the real absorbance is measured using an integrating sphere, extinction spectroscopy is complex for 2D nanosheets due to the non-negligible light scattering. Interestingly the extinction intensity also decays via a single exponential decay. Both the std-BP sample, measured using extinction (blue) and absorbance (black) over 300hrs, decay on the same curve with similar time constants 173 and 187 hrs respectively. After three days the sample has decreased in intensity by 8%.

This work proposes a reaction scheme involving water and oxygen and phosphorus which may result in the degradation of the nanosheets via a disproportionation reaction mechanism. The products of this reaction are typically phosphates, following reaction at edge sites. This study will investigate the effect water and oxygen (proposed reaction components) has on the decrease in absorbance/extinction as a function of time to gauge their impact on the reaction:

$$\text{BP} + 3\text{H}_2\text{O} \rightarrow \text{BP}_{2\text{VAC}} + \text{PH}_3 + \text{H}_3\text{PO}_3$$  \hspace{1cm} (6.1)
Figure 6.16: A) Absorbance spectra over time with 465nm indicated, B) extinction spectra of std-CHP sample measured over ~300 hrs, C) extinction/absorbance tracked over time, both data sets fitted to single exponential decays.
6.3.5 Size Dependent Stability of BP Nanosheets

The BP nanosheets have been shown to degrade over time, as evident from the optical absorbance and extinction spectra. This analysis was conducted on the std-BP sample which is composed of both small and large nanosheets. A size selection was employed using the std-BP dispersion as the starting point. Centrifugation procedures were used to separate the large and small nanosheets. This process and centrifugation conditions are summarised in figure 6.17. This procedure produces three characteristic nanosheet dispersions; std-BP (composed of small and large nanosheets), small nanosheets (s-BP) and large nanosheets (l-BP).

Figure 6.17: Schematic representation of nanosheet size selection of the three characteristic sizes s-BP, std-BP and l-BP.
TEM statistical analysis was used to determine the mean statistical length of the nanosheets in the size selected dispersions. The length of the nanosheets scaled as l-BP > std-BP > s-BP, with lengths of 2.26 ± 1µm, 1 ± 1.4 µm and 130 ± 111 nm respectively. These three nanosheet dispersions were also investigated using absorbance spectroscopy (figure 6.18 A). The absorbance spectra were normalised to 300nm, where the difference in spectral shape between the samples can be seen. This shape difference is directly related to the nanosheet sizes, similar to previous studies.34 Dispersions of the three sizes of nanosheets were filtered onto alumina membranes and analysed using Raman spectroscopy (6.18 B). All three samples display the characteristic, $A_g^1$, $B_{2g}$ and $A_g^2$ phonons of FL-BP.75 It has been shown by Martel et al, that the intensity ratio of $A_g^1 / A_g^2$ can be used to determine the oxidation levels of the nanosheets. Analysis of >100 spectra yielded a ratio > 0.6 which is suggestive of minimal oxidation of the basal plane.75

![Figure 6.18: A) absorbance spectra and B) Raman spectra for the three characteristic dispersions s-BP, std-BP and l-BP.](image)

Employing a similar stability metric, as shown above with the std-BP sample, it is clear that the absorbance intensity decrease occurs as a function of nanosheet size (figure 6.19 A). The l-BP nanosheets seem to be the most stable followed by the std-BP and s-BP samples. The time constants (τ) for the l-BP; std-BP and s-BP are 233, 187 and 114 hrs respectively (figure 6.19 B). It is evident that the rate of dissolution is affected by the size of the nanosheets, which
is indicative of an edge driven reaction. The percentage decrease in intensity of the l-BP, std-BP and s-BP after three days is 2, 8 and 10% respectively. While this is certainly not ideal, it is sufficient time to characterise the samples to obtain information for optical and structural properties.

Figure 6.19: A) absorbance taken at 465nm plotted as a function of time over ~300 hrs, B) fitting the decay curves to single exponential decay curves yields time constants which are plotted as a function of nanosheet length.

A relationship between the decay time constants ($\tau$) and the nanosheet length can be represented by the formula $\tau = 107 \times 10^{0.241}$ and can be used to estimate the mean nanosheet length. The use of time constants is ideal for a basic comparison, however, a more appropriate method is to determine the ratio of unreacted nanosheets to the total nanosheets in dispersion is needed (reacted and unreacted). This can be achieved through the fitting of the data with the single exponential decays. The functional form of the fit is $A = A_{UnRe} + A_{Re}e^{-t/\tau}$, where $A_{UnRe}$ represents the unreacted component of nanosheets in dispersion while $A_{Re}$ represents the reacted component. The ratio therefore of $A_{Re}/(A_{UnRe} + A_{Re})$ will determine the proportion nanosheets with have undergone degradation in our dispersion. Shown in table 6.2 is the parameters obtained from the l-BP, std-BP and s-BP dispersions.
Accordingly, to establish a metric to measure the stability of a dispersion a plot of the decay time constant ($\tau$) against the ratio of $A_{Re}/(A_{UnRe} + A_{Re})$ is shown in figure 6.20. Ideally the most stable sample would populate the top left hand side of this plot (green box) where it would have a large time constant (slow decay rate) and a low amount of material reacted. It is clear in our case that the large nanosheets are the most stable due to the small amount of edge sites in proportion to the basal plane, while the small nanosheets have the largest ratio of edge to basal plane therefore, reacting the quickest. The std-BP dispersion has both large and small nanosheets; therefore, is in-between the behaviour of the large and small.

Figure 6.20: Plot of time constants against the amount of unreacted nanosheets in dispersion.

It is important to note that a similar methodology has recently been employed by Martel et al.\textsuperscript{75} to mechanically cleaved BP. Reaction rates in this study (100 hrs), are considerably slowly than those observed by Martel et al (1 hr).\textsuperscript{75} One explanation for the difference in reaction

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Table 6.2: The kinetic degradation data for l-BP, std-BP and s-BP dispersions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L (NM)</th>
<th>$A_{Re}/(A_{UnRe} + A_{Re})$</th>
<th>$\tau$ (H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-BP</td>
<td>2300</td>
<td>0.19</td>
<td>233</td>
</tr>
<tr>
<td>Std-BP</td>
<td>1000</td>
<td>0.26</td>
<td>187</td>
</tr>
<tr>
<td>S-BP</td>
<td>130</td>
<td>0.27</td>
<td>114</td>
</tr>
</tbody>
</table>
rates may be the production methods of the nanosheets. Faster rates were observed for nanosheets prepared via mechanical exfoliation than LPE samples. This may be attributed to the solvation shell of the solvent in LPE samples inhibiting the reaction.

6.3.6 Analysis of LPE Nanosheets Under Ambient Conditions

The stability of nanosheets in CHP has been demonstrated, where the reaction rate was found to vary as a function of nanosheet size. Recent studies by Martel et al, on mechanically exfoliated BP, showed an increased rate, possibly suggesting a different mechanism. To investigate the stability of LPE nanosheets in air, a sample was deposited onto substrates and analysed using AFM and TEM. These samples were then left exposed to the ambient. The topography of the nanosheets was tracked over time using AFM. Images of a region on the wafer is shown in figure 6.21 A. The same region was relocated after 4 and 11 days. It is clear that there is some adsorption on the surface of the nanosheets.

![Image of AFM topography profiles](image)

**Figure 6.21:** A) AFM topography profiles for fresh, 3 and 11 days, B) Thickness measurement of the line profile in A as a function of time.
A line profile is taken (white line) across a nanosheet on the top left of the relief map. The freshly measured (within 3 hours) sample in figure 6.21 B has a sharp onset to the nanosheet edge and also on the opposite side when the tip has returned to the substrate. With increasing time, however, the height profile becomes higher and broadens. At 11 days the thickness of the nanosheet has almost tripled and the length has increased, due to water adsorption onto the surface of the nanosheet. This water thickness is also most likely composed of reactant products from the disproportionation reaction.

Similar to the AFM analysis over time, a TEM analysis was also conducted. Here several nanosheets were imaged also over a 16 day period. The same nanosheet was relocated each time. Initially, the nanosheet exhibited sharp edges and was free from any holes or bubbling regions. As time progressed, the nanosheet begins to adsorb water from the atmosphere. Unlike AFM where it is quite difficult to remove the adsorbed layer the electron beam; however, can remove this to reveal the extent of the damage. This was achieved by focusing the electron beam on the nanosheet, to evaporate the water off, leaving the images shown in figure 6.22. Here we see that the flakes are pristine when measured fresh and degrade over time, where visible holes are seen to form in the lattice of the nanosheet. The edges are also softened compared to the fresh image taken.

![Representative TEM images taken over 16 days showing damage to nanosheets.](image)

*Figure 6.22: Representative TEM images taken over 16 days showing damage to nanosheets.*
The combination of AFM and TEM data clearly shows that the BP nanosheet degrade over time when exposed to the atmosphere. Clear holes in the nanosheets are observed, in addition to water adsorption. To characterise the degradation products, XPS was conducted on a freshly prepared std-BP film. Analysis of the phosphorus core peaks are shown after 1 and 3 days (figure 6.23 A and B respectively). The presence of a phosphorus oxide (P\textsubscript{x}O\textsubscript{y}) species is detected in addition to the BP phosphorus peaks. An oxide level ((P\textsubscript{x}O\textsubscript{y}) was determined to be \textasciitilde15%. However, after 3 days aging in dispersion a second film was prepared and subjected to XPS. The P\textsubscript{x}O\textsubscript{y} species subsequently increased to 24%. The increased percentage of P\textsubscript{x}O\textsubscript{y} species is consistent with the 8 % loss of material in the std-BP after 3 days monitored by absorbance spectroscopy (figure 6.23 A).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure623.png}
\caption{A) XPS spectrum of std-BP film freshly prepared showing 15\% P\textsubscript{x}O\textsubscript{y} species, B) aged std-BP dispersion in CHP where the P\textsubscript{x}O\textsubscript{y} species increased to 24\% similar to that determined from the absorbance spectroscopy.}
\end{figure}
6.3.7 Effect of Water on Nanosheet Stability

Analysis has shown that BP nanosheets do in fact degrade over time in both solution and when deposited on substrates. A similar reaction mechanism to the one presented here, has been proposed by Martel et al, which involves a photo oxidation reaction involving water and oxygen. One of the main benefits of LPE is the low tech processing of samples, where exfoliation can be achieved using kitchen blenders.\(^95,97\) Therefore, the presence of oxygen is difficult to avoid for potential scale up. However, the effect of water was investigated on the reaction rate of BP nanosheets. Controlled amounts of water, up to 50 vol. % in some cases, were added to std-BP dispersion (figure 6.24 and 6.25 A). The effect on the absorbance intensity was investigated over ~300hrs. Interestingly, the rate reaction increases with increasing water addition. A similar behaviour is also observed for the s-BP and l-BP samples (figure 6.25 B and C). The decrease in absorbance saturates for water additions above 10% for s-BP and std-BP, while the l-BP still shows an increased stability for water additions up to 50%.

![Absorbance vs Time Plot](image)

*Figure 6.24: Absorbance (λ_{465nm}) plotted as function of time for the std-BP sample with 0.3 and 5% water additions.*
Figure 6.25: A, B, C) Absorbance normalised to initial value for water additions to std-BP, s-BP and l-BP respectively.
The increased stability for larger nanosheets can be attributed to the large ratio of edge to basal plane. This behaviour was previously shown above (figure 6.20), where the rate of reaction was shown to follow a well-defined ratio with respect to nanosheet size. Therefore, the reaction is believed to be edge driven. The l-BP dispersion is predominantly composed of quite large nanosheets, in some cases up to 3µm, therefore, it has a large basal plane to edge ratio. The time constants (τ) and stability ratio (\(A_{Re}/(A_{UnRe} + A_{Re})\)) are shown in the appendix table 9.1 for all additions of water. A clear trend is observed where the time constants decrease and the stability ratio increases with increasing additions of water. Moreover this metric, poses as a suitable guide to determine the dependence of the stability of the nanosheets as a function of water additions. To determine the effect of water content on the time constants and metric, a plot of how these parameters vary as a function of volume fraction is shown in figure 6.26 A and B respectively. We see that for the s-BP and std-BP nanosheets that after 5% water addition, the reacted nanosheets saturates where further addition of water will not affect the metric (figure 6.26 B). A different trend however, is observed for the large nanosheets where we see a slow increase of reacted nanosheets as a function of water which indicates that the reaction rate is indeed slower for larger flakes.

![Figure 6.26](image-url)

*Figure 6.26: A) time constants for all three dispersions with varying water content, B) metric ratio of reacted nanosheets plotted as a function of volume fraction of water added.*
One possibility for the observed trends may be due to the kinetics of the reaction and availability of the reactant species. Nevertheless we observe a clear difference in reaction rate depending upon the size of the nanosheets in dispersion. If the data for varying water additions as a function of nanosheet size is plotted using our metric for stability (i.e. $\tau$ vs $A_{Re}/(A_{Re} + A_{UnRe})$) we observe a well-defined relationship between the stability of the nanosheets as a function of size and water additions. Firstly we can see that the entire data set spans linearly from low reacted amount of large time constant, down towards high reacted amount of nanosheets and low time constant. It is clear that the most stable dispersion is in the top left quadrant of this graph where it will have a small reacted component of nanosheets with a large decay time constant. Moreover it is clear that the stability of the l-BP > std-BP > s-BP, also scales with the nanosheet size. Additions of water in all cases regardless of size, shifts the data point toward the bottom right quadrant increasing the amount of nanosheets reacted and lowering the decay time constant. This metric, is very useful as it allows one to investigate the stability of your dispersion in comparison with other samples. It should also be noted that increasing the water addition of the sample, shifts it further to the right showing that the water content in the sample, is directly related to the stability of the nanosheets (figure 6.27).

![Graph showing the relationship between stability and water addition](image)

*Figure 6.27: Time constant of decay curves plotted as a function of the reacted component of nanosheets.*
6.3.8 Effect of Oxygen on Nanosheet Stability

All of the previous samples have been prepared under ambient conditions, where during the process; there is water vapour and oxygen present. To try and quantify the effect of oxygen on the reaction process a std-BP sample was prepared in a glove box, under inert conditions, where there is <0.1ppm of oxygen and water present. CHP solvent was dried to remove excess water. Interestingly, upon introducing the dried solvent into the glovebox, there was no increase of the water or oxygen content which is common for other solvents. Even during sonication of the ground BP crystal in CHP inside the glove box there was no increase in water or oxygen content. This would suggest that the water and oxygen contents in the glove box sample are indeed minimal.

The sample was prepared in the glove box and then aliquots were removed periodically to measure the optical spectra. Again, these were used to determine a decay curve, as shown in figure 6.28 A. We can see that the curve for the glove box std-BP sample is more stable than that of the std-BP produced in the ambient conditions. It is important to note that the std-BP sample prepared in the glove box does degrade due to residual water present in the solvent ~30ppm as determined by Karl fisher titration.

Additionally, the three sizes of nanosheets were prepared in a glove box to minimise the level of oxygen and water and then they were removed. The samples were bubbled with oxygen, for 10 min’s. While some samples will have water and oxygen purposely added, there will be a baseline level of these components in the atmosphere. Nevertheless, this study investigates the difference between samples with an excess of oxygen. Unfortunately, there was no discernible difference between the samples with oxygen bubbled through and the ones which didn’t (figure 6.28 B). It is most likely that leaving the samples exposed to ambient conditions, allowed for sufficient oxygen and water vapour for the reaction to proceed. Certainly there is sufficient oxygen also dissolved, in the water which was added to the samples, to complete the disproportionation reaction. Additional decay curves are plotted in appendix figure 9.1 A, B and C.
In any case, it can be seen that the reaction of the samples in ambient conditions has sufficient amounts of water and oxygen to complete the degradation process. Furthermore, it is difficult for us to track the role of oxygen due to the difficulty measuring in an oxygen free environment, however, as reported by Martel et al.\textsuperscript{75} oxygen is involved in the reaction.

The effect of water and oxygen, on the stability of BP, has been investigated. The stability of nanosheets is dependent upon the nanosheets size thus indicating that the reaction is edge driven. Water was determined to increase the rate of reaction of the BP nanosheets, however, the role of oxygen was difficult to determine conclusively. A wealth of information about the stability of the nanosheets has been determined, however, the effect of the solvent is still unknown. The interaction, between the nanosheets and the solvent, needs to be strong to
disperse the nanosheets and prevent aggregation. Typically amide solvents provides the most stable samples, however, other solvents such as IPA can be used. The effect of the solvent on the nanosheet stability, therefore, warrants investigation.

6.3.9 Effect of Solvent Type on Nanosheet Stability

The discussion of nanosheet stability has been systematically investigated to analyse the effect of several parameters. The focus thus far has been solely based upon a sample exfoliated in CHP. This section extends this investigation to other common solvents such as NMP and IPA. A similar approach will be taken to analyse the absorbance as a function of time and investigate these solvents using time constants and the solubility metric. To begin a sample was prepared in IPA, and investigated using TEM to gauge the quality of nanosheets produced. A representative image is shown in figure 6.29, of a nanosheet exfoliated in IPA. Similar to the approach employed previously, the nanosheet was revisited after 5 days. Interestingly, the nanosheet exfoliated in IPA showed greater damage after 5 days than the nanosheet, from CHP, after 16 days. It is well known that CHP is difficult to remove from nanosheets upon deposition due to its high boiling point. IPA however, has a low boiling point and can evaporate easily. Upon deposition and drying of the two solvents, the CHP may leave a residual layer on top of the nanosheets which may partially shield them from reacting with oxygen and water in the atmosphere.

Nevertheless, the initial sample produced from IPA yielded high quality nanosheets. The stability over time may be affected by different solvents. Exfoliation was extended to NMP and then an optical absorption analysis was performed (figure 6.30). The dispersion stability is compared between the std-BP sample in CHP, IPA and NMP. A sample produced under atmospheric conditions in CHP and NMP appear to decay at similar rates while IPA shows an increased rate of reaction. The time constant changing solvent from CHP to IPA decreases from ~190hrs to 57hrs. NMP has a similar time constant as CHP, ~187 hrs. This indicates that the choice of solvent, used to exfoliate the BP crystal, directly impacts the stability of the resulting nanosheets. The solvation shell of CHP and NMP partially shields the nanosheets thus decreasing the rate of reaction.
Figure 6.29: TEM of BP nanosheets produced from CHP and IPA after time periods indicated on top left of TEM image.

Figure 6.30: Absorbance metric for the std-BP dispersion in varying dispersive solvents.
It has been shown that water significantly affects the stability of the BP nanosheets. Therefore, when exfoliating in different solvents it is important to account for any deviations, in this case water content. The observed difference in behaviour between the solvents may be due to varying water contents. In order to accurately attribute any observed behaviour to solvent nanosheet interaction, the solvent water content was determined. To accurately measure the water content in solvents a Karl Fisher titration was performed, where a known mass was analysed over a period of ~150 hrs. As shown in figure 6.31 the results are indeed surprising, where the water content in the IPA and CHP are similar while NMP is the lowest over the period. Typical water contents over the week period range from ~400ppm to ~800ppm in the case of NMP and even higher ~1100ppm for CHP and IPA. The observed water contents of the solvents does not directly correlate to the stability of the nanosheets in dispersion, as CHP has almost twice the amount of residual water when compared to NMP. Nevertheless, both solvents have similar decay time constants of ~190hrs. Furthermore, the stability of the nanosheets must indeed, be related to the interaction between the solvent shell of the solvent and the nanosheets.

Figure 6.31: water content of CHP, NMP and IPA measured using the Karl Fisher titration method over a period of ~150 hrs.

Aliquots of water were also added to the respective solvents, to investigate the effect of excess water (appendix figure (9.2 A, B, C)). In the case of IPA, more water in dispersion
decreased the stability of the nanosheets similar to that of the CHP samples, however, NMP showed a different behaviour than that of the other two solvents. In the case of NMP additions of water did not seem to influence the reaction rate of the BP, all samples decayed with similar time constants for additions up to 10%. This behaviour is certainly unusual as a similar behaviour between the two amide based solvents was expected. Therefore the interaction with excess water is certainly more effective for shielding using NMP however if the samples do not have water purposefully added then both CHP and NMP perform similarly (figure 6.32).

![Graph showing reaction time constants as a function of the stability metric formula for different solvents.]

*Figure 6.32: reaction time constants as a function of the stability metric formula for different solvents.*

Applying the metric formula, to the different solvents, showed an expected behaviour where CHP and NMP are similar. However, IPA performs poorly (figure 6.32). It is clear from the water content experiment that the solvent with the highest water percentage is not necessarily the most unstable, therefore, highlighting the effective solvent shell as the stabilising mechanism. This metric reinforces what we observe for the analysis in the TEM from the initial quality and also the aging study where the solvents which are lower on this scale exhibit a higher proportion of damage to the nanosheets over time (IPA). The interaction
between the solvent and nanosheets, therefore, has a profound effect on the reaction rate and stability of the dispersion.

The interaction of the surrounding medium has been shown to have a substantial influence on the reaction of BP. Exfoliation in organic solvents is the most popular method; however, it has been demonstrated previous surfactant and polymers can also be used. Aggregation in solution is prevented in surfactant and polymer systems, by electrostatic and steric forces respectively. These methods were used to exfoliate BP to produce the std-BP dispersion. A common anionic surfactant (sodium cholate, SC) has been used previously to exfoliate graphene and TMD’s.\textsuperscript{90, 91, 138, 203} An absorbance decay curve was measured over a period of ~200 hrs (appendix figure 9.3). As expected samples prepared in SC/H\textsubscript{2}O are less stable than their solvent counterparts. This reduction in stability is most likely attributed to the fact that the solvent is H\textsubscript{2}O which was shown to decrease the stability of the nanosheets. Fitting the SC data set to the stability metric shows that the most unstable system as expected is indeed the water surfactant (figure 6.33). While the surfactant does shied the nanosheets to some extent the system is saturated with an abundance of water thus driving the disproportion reaction.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{image.png}
\caption{reaction time constants as a function of stability metric where water surfactant was added and shown to be the most unstable.}
\end{figure}
6.4 Conclusions

LPE of BP nanosheets in an organic solvent is presented in this chapter. A dispersion was produced in an amide solvent, CHP, which has been used successfully in previous studies. A standard dispersion was identified through careful control over the centrifugation conditions, where a sedimentation time constant ($\tau$) was found to be 86mins. The quality of the nanosheets produced was investigated using TEM and AFM, which yielded the mean length and thickness to be $<L> = 1.0 \pm 1.4 \mu$m and $<N> = 9.4 \pm 1.3$nm respectively. The effect of sonication time was investigated, where the concentration of nanosheets showed a sub linear dependence $\sim t^{0.5}$, similar to previous studies. Size selection methodologies enabled lateral dimensions from $\sim200$nm up to 2$\mu$m to be obtained. The absorbance, extinction and scattering spectra of different sizes were found to vary as a function of nanosheet length. The scattering spectra were also used to develop a metric, to determine mean length from the scattering exponent $n$, $L \sim 0.42/n$. In addition, the std-BP sample was found to contain few layer nanosheets ($<N>=1-5$) as determined from PL spectroscopy. The population of these species increased as a function of the layer number, from 0.5% for one layer to 6.5% for 5.

The dispersed nanosheets were found to be unstable, displaying a decrease in the absorbance/extinction intensity over time. Interestingly, the intensity of absorption (and extinction) spectra was observed to follow a single exponential decay over a time period of $\sim300$hrs. Fitting these decay curves, allowed the determination of the decay time constant and development of a stability metric ($A_{Re}/(A_{UnRe} + A_{Re})$). It was found that, the ratio of the time constants versus the stability metric ($A_{Re}/(A_{UnRe} + A_{Re})$), scale with the nanosheet length. Many parameters, such as water, oxygen and solvent type were investigated using this metric. Moreover, the concentration of water and oxygen were determined to have a negative effect on the stability of the nanosheets over time. The solvation shell was found to have a profound effect on the reaction rate. Ultimately the stability can be enhanced by a clever choice of solvent. Amide solvents such as CHP and NMP were found to display greater stability than IPA. This is not surprising as it is well known that the amide solvents provide the most concentrated dispersions, therefore, have a strong interaction with the nanosheet surface. Over a 3 day time period, the decay of the dispersion was determined to be $\sim10\%$ in good solvents (CHP, NMP) while a poor solvent (IPA) can have as much as $\sim25\%$ of the material lost.

Accordingly, the BP nanosheets are determined to follow a disproportionation reaction due to the decrease in the nanosheet stability with water. The reaction products were
determined to be phosphates from analysis of XPS in conjunction with a decrease in the pH of the dispersions. The reaction rate was determined to scale with the flake length which is indicative with a predominant edge driven reaction. This is in contrary with a basal plane reaction proposed by Martel et al.\textsuperscript{75}

The work presented in this chapter significantly advances the characterisation methodologies of samples produced from LPE. It is hoped the methodologies developed can be applied to other materials which may display some instability. With the expansion of new materials under investigation it is believed nanosheet stability will become important. The development of optical metrics is imperative as they provide a simple route to analyse a sample. To this end, the future work section will discuss this topic further.
Photoluminescence of Molybdenum Telluride Nanosheets in Aqueous Surfactant Solutions

7.1 Introduction

The work presented in this thesis, thus far, has been concentrated on the LPE process and its extension to new layered nanomaterials (MoO$_3$ and BP). The characterisation of these nanomaterials has focused on refining exfoliation parameters for example, the effect of sonication time ($t_s$), initial concentration ($C_i$) and centrifugation conditions on the resulting dispersion. Data has been presented on the PL of BP; however, it is difficult to fully understand the production of mono- and few-layer species with such novel materials, as suitable spectroscopic metrics are lacking.

Exfoliation throughout this work was typically conducted in a solvent medium, as previously shown in chapters 5 and 6. The toxicity of some solvents, specifically NMP and DMF, requires special handling procedures and high boiling points also limit the processability to some extent. Therefore, a low toxicity solvent is sought-after. Water is one of the most abundant solvents; however, by itself it cannot be used to exfoliate most nanomaterials, due to its high surface tension. Previous work has shown that, nanomaterials such as graphene, TMDs and h-BN, can be successfully exfoliated in a water surfactant mixture, yielding high degrees of exfoliation in a low toxicity liquid. $^{91, 204}$

Recently, literature has seen numerous reports on PL properties of TMDs from a variety of production methods, such as mechanical cleavage and LPE. $^{42, 44, 205, 206}$ In typical group VI TMDs, PL is only observed in monolayered nanosheets which are direct gap semiconductors, opposed to the indirect gap few-layered or bulk material. This makes the
monolayer the most attractive species for optoelectronic applications. In addition, it is well known that PL is highly sensitive to the local environment; which may enhance or quench a materials’ PL signal.\textsuperscript{140,207} This makes PL an ideal characterisation technique to test the quality of a material and its interaction with the local environment, for example chemical doping.\textsuperscript{208,209,210} In this chapter, the photoluminescence of surfactant-exfoliated MoTe\textsubscript{2} nanosheets is used to gain further insights into the nanosheets produced using LPE. It should be noted that MoTe\textsubscript{2} was chosen as a rather uncommon model TMD, as tellurides are the least studied of the group VI TMDs. Until very recently, for example, the direct gap nature of the monolayer had not been experimentally confirmed.\textsuperscript{211}

7.2: Experimental Procedure

7.2.1: Pre-treatment of Raw Powder

Molybdenum Telluride (MoTe\textsubscript{2}) powder was purchased from American Elements (purity 99.9\%) and sodium cholate (SC) was purchased from Sigma Aldrich. Initial dispersions of MoTe\textsubscript{2} showed poor stability. Therefore, to remove impurities in the MoTe\textsubscript{2} raw powder a pre-treatment method was used. The raw powder was immersed in a solution of H\textsubscript{2}O (concentration 5 g/L in 80 mL volume of H\textsubscript{2}O) and was sonicated for 5 hours at 60\% amplitude, while being pulsed (for 6s on 2s off) in a horn-probe sonication tip (VibraCell CVX, 750 W), under cooling. The resulting stock dispersion was centrifuged at 4.5 krpm (2100 g) for two hrs and the supernatant (containing most of the impurities) was discarded. This process was repeated multiple times to yield sediment, which was then lightly dried on a hot plate. This pre-treated powder was used for the duration of the study.

7.2.2: Sample Preparation

A sample of MoTe\textsubscript{2} (5g/L) in SC/H\textsubscript{2}O (6g/L) was prepared using similar sonication conditions as indicated above. This sample was sonicated for 1.5 hrs at 60\% amplitude. The resulting dispersion was centrifuged at 4.5 krpm (2100 g) for 2 hrs. The supernatant was decanted and subjected to absorbance/extinction spectroscopy, to determine the nanosheet concentration. The centrifugation conditions were chosen from reference to previous studies, which show decrease of thick nanosheets at these speeds.\textsuperscript{138} Analysis of the dispersions, using PL spectroscopy, displayed very weak signals for the mono- and bi-layer nanosheets. To
improve the PL intensity, the supernatant, was centrifuged at 4.5 krpm (2150 g) for 2 hrs and was centrifuged again at 10 krpm (10,170 g) for one hour. The sediment was re-dispersed in a solution of SC and water (SC/H2O) (6 g/L), while the supernatant was discarded. The additional centrifugations removed both, larger and thicker, as well as very small nanosheets, which improved the signal to noise ratio in the PL measurements. The effect of surfactant concentration was investigated, by preparing a series of samples with SC concentrations ranging from 1-25 g/L. These samples were also subjected to similar centrifugation conditions as stated above and analysed using absorbance/extinction and PL spectroscopy.

7.2.3: Sample Characterisation

Optical extinction and absorbance spectroscopy was performed using a quartz cuvette in a Perkin Elmer 650 spectrometer (0.4cm path length). To distinguish between the contributions of scattering and absorbance, to the extinction spectra, dispersions were measured in an integrating sphere. The absorbance spectrum of the sample was obtained from the measurement inside the sphere. The sample was then removed and the extinction performed outside the sphere. The scattering spectrum can be obtained using the simple relation, \( \epsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda) \) where \( \epsilon \), \( \alpha \) and \( \sigma \) are the extinction, absorbance and scattering components, respectively.

PL measurements were performed in a NS2 Nanospectralyzer from Applied Nanofluorescence, using a 683 nm excitation laser line. Three spectral lines were initially investigated; 638nm, 683nm and 785nm (appendix figure 9.6). The highest PL intensity was observed from 683nm; therefore, the follow study was conducted using this laser line. The PL spectra presented here were obtained using a reduced volume quartz cuvette (0.4 cm, 1.5 mL). The optical densities were in all cases below 70 m\(^{-1}\), above this considerable reabsorption and self-quenching occurs (see appendix figure 9.4). Owing to the low PL intensity, the measurements were left to accumulate for long time periods. Samples were measured using an acquisition time of 4 s per scan and accumulated over 750 spectra. The spectra were then baseline corrected and fitted on the eV scale. The spectra should typically be fitted using lorentzian functions; however, this provided a poor fit. Therefore, the spectra were fitted using three Gaussian functions, which suggests inhomogeneous broadening is dominant.\(^{212}\) A third component is blueshifted with respect to the monolayer species and is most likely an artefact of the instrument or weak PL from SC.
Bright-field transition electron microscopy (TEM) was performed using a JEOL 2100 operated at 200 kV. Samples were prepared for analysis by depositing aliquots of dispersion onto continuous carbon film grids. These grids were placed on top of filter membranes, which allowed excess fluid to wick off. Following several drops of dispersion, the TEM grids were baked in vacuum at 120 °C for 12 hrs, to remove excess solvent. Atomic force microscopy (AFM) was conducted using a Veeco Nanoscope-IIIa (Digital Instruments) system equipped with an E-head (13 μm scanner) in tapping mode, following depositing a drop on a pre-heated (150 °C) SiO₂/Si wafer. Following deposition, the wafer was soaked in water to remove excess surfactant from the surface. It was important to remove the excess surfactant as it inhibits statistical analysis which is used to determine mean height of the nanosheets. Statistical analysis (both AFM and TEM) was performed on the nanosheets by measuring the longest axis of the nanosheet and assigning it “length”, then measuring an axis perpendicular to this, at its widest point, and assigning it “width”. Raman spectroscopy was performed using a WITec alpha 300 with a 532 nm excitation laser and a laser power of < 1 mW. In all cases spectra shown are an average from a line scan consisting of 25 discrete point spectra.

7.3 Results and Discussion

7.3.1 The Dispersion and Characterisation of MoTe₂ Nanosheets

In chapter 5 and 6, the exfoliation process in solvents was refined by optimising the exfoliation conditions. These parameters are important, for multiple materials, and have shown some fundamental relationships for example; the concentration of nanosheets scaling as a function of sonication time ~ t₀.⁵.¹⁵ While optimisation of exfoliation conditions is important, the main focus of this work is to investigate the photoluminescence of MoTe₂ nanosheets in solution. Therefore, sonication conditions were chosen which are similar to those used in previous sections. To aid throughput of samples, the sonication time was chosen to be 1.5 hrs. To remove any large and thick nanosheets a common centrifugation of 4.5 krpm (2100 g) for 2 hrs was employed, similar to previous studies.¹³⁸

The exfoliation was conducted in water surfactant dispersions, which has been proven for materials such as graphene and many TMDs, to produce mono- and few-layer species.⁹⁰,⁹¹ Backes et al. showed that MoS₂ could be successfully exfoliated in surfactants and that the dispersions produced displayed PL characteristic of monolayer species.¹³⁸ Therefore, there is
no doubt that high quality dispersions can be produced in water surfactant mixtures. However, little is known about the actual nanosheet surfactant interaction or surfactant packing densities. In this work, MoTe$_2$ powder was exfoliated in SC, a common anionic surfactant. The concentration was initially chosen at the critical micelle concentration (CMC) value, which should yield a highly concentrated dispersion. For SC, this is 6 g/L. A pre-exfoliation and washing step using water, in the absence of surfactant, was introduced for the raw powder (as described in the experimental section). This step removed the un-exfoliated material, which sedimented to the bottom of the vial, while the impurities remained in the supernatant. The supernatant was then discarded and the sediment was collected. This sludge was slowly dried to yield a new starting powder, which improved the consistency of experimental results.

Accordingly, a standard dispersion (std-MoTe$_2$) was prepared using the treated stock powder. The sample was then centrifuged at 4.5krpm (2100 g) for 2hrs in order to remove any large and thick nanosheets. A typical dispersion is shown in figure 7.1 A. To analyse the nanosheet length and thickness, statistical TEM and AFM were used. This analysis involves measuring $>100$ nanosheets, to determine the mean length and thickness after deposition of a drop on TEM grids and Si/SiO$_2$ wafers, respectively as previously described for surfactant exfoliated MoS$_2$. Representative TEM and AFM images are shown in figure 7.1 B and C. Analysis of the images, determined the mean length, L, and thickness, N, of the nanosheets to be $<L> = 66 \pm 2$nm and $<N> = 4$, respectively (figure 7.1 D and E). The mean length observed is consistent with other studies for few and monolayer TMD species.

The std-MoTe$_2$ dispersion was characterised using absorbance spectroscopy. Similar to other TMDs there are some discernible features. However, probably the most interesting feature is the A exciton peak which is associated with the transition at the direct gap. Unfortunately, it cannot be detected in the setup used, as it is located at 1,150 nm. The extinction spectrum ($\varepsilon$) is shown in figure 7.2 A. The extinction spectra of 2D materials typically also contain a contribution from size dependent scattering of the nanosheets. To overcome this, an integrating sphere (similar to studies in chapter 6) was used to separate the extinction spectrum ($\varepsilon$) into its absorbance ($\alpha$) and scattering ($\sigma$) components, as shown in figure 2 A (Note $\varepsilon (\lambda) = \alpha (\lambda) + \sigma (\lambda)$). The contribution from scattering to the measured extinction is minor in this case, as nanosheet lateral sizes are rather small (70 nm in length). However, since this work analyses photoluminescence of the MoTe$_2$ dispersions further down below, it is important to compare concentrations as accurately as possibly. Therefore, absorbance spectra were used for the remainder of the study.
Figure 7.1: A) Photograph of std-MoTe\textsubscript{2} dispersion B, C) Representative TEM and AFM images of the MoTe\textsubscript{2} nanosheets, respectively D, E) Statistical TEM and AFM analysis.

Figure 7.2: A) Extinction (\(\varepsilon\)), absorbance (\(\alpha\)) and scattering (\(\sigma\)) spectra of std-MoTe\textsubscript{2}. B) Raman spectra for the raw powder, pre-treated and exfoliated std-MoTe\textsubscript{2} samples.

To determine the quality and structural integrity of the nanosheets produced, the std-MoTe\textsubscript{2} sample was filtered onto alumina membranes and subjected to Raman spectroscopy
(figure 7.2 B). In addition to the processed, std-MoTe$_2$ sample, the raw powder and pre-treated powder were also investigated. The characteristic Raman modes for MoTe$_2$ are observed for all three samples (as indicated in spectra).\textsuperscript{213, 214} The raw powder shows some sign of oxidation with the presence of an oxide peak around 148 cm$^{-1}$.\textsuperscript{215, 216} This peak; however, can also be seen in the pre-treated and exfoliated powder samples. The width of the Raman modes present, in both the pre-treated and exfoliated nanosheets, is narrower than the raw powder, suggesting that these samples are more crystalline than the starting powder. Neither the use of a pre-treatment step, nor the exfoliation itself, introduces any additional oxide peaks. This suggests that the majority of oxides present in the samples are in the starting powder to begin with. In addition, it should be noted that it has previously been shown for micromechanically cleaved MoTe$_2$ that the B$_{12g}$ mode is only active in nanosheets with 2-5 layers.\textsuperscript{211} The appearance of this peak in the surfactant-processed sample also confirms the successful exfoliation.

However, since little is known about exfoliation of MoTe$_2$ in the liquid, it is important to further analyse the sample quality and quantify the extent of the oxidation present. With this in mind, the std-MoTe$_2$ sample, which was used for the Raman analysis above, was subjected to XPS. This technique has been used in the previous chapters to identify the level of oxidation of nanosheets. The Mo and Te core level spectra are presented in figure 7.3 A and B, respectively. In both cases, there is oxidation present in the form of MoO$_3$, MoO$_2$ and TeO$_2$. The extent of oxidation present is between 13 and 20%. This is a considerable level of oxidation; however, it is typically in line with oxide levels of other nanomaterials which have been prepared by LPE.\textsuperscript{138}

![Figure 7.3](image)

\textit{Figure 7.3: Fitted XPS core level spectra of A) Mo and B) Te with levels of oxidation indicated. The fit components and respective percentages are indicated in the figure legend.}
7.3.2 Effect of Surfactant Concentration on Exfoliation and Optical Properties

The standard dispersions of MoTe$_2$ characterised above were prepared using the CMC value for SC, 6 g/L. This is the minimum concentration, above which any further addition of surfactant initiates the formation of micelles. Initially, the effect of the SC concentration on the amount of nanosheets dispersed in a given sample was investigated. A series of samples were prepared with concentrations of SC ranging from 0.5 to 25 g/L. Absorbance spectroscopy was used to investigate the change in dispersed nanosheet concentration. To investigate if there is any change in spectra shape with varying surfactant the spectra were normalised to 265 nm, this can be seen in figure 7.4. Notably, there is a slight shift between the samples, in addition to an intensity change, over the spectral range. This is rather important, as it has previously been shown for other liquid exfoliated TMDs that the absorbance spectra change with nanosheet size and thickness due to edge and confinement effects as will also be further illustrated down below.$^{138}$ This suggests that not only nanosheet concentration, but also sizes change with the surfactant concentration as has previously been shown for surfactant exfoliated MoS$_2$ produced from turbulence assisted shear mixing.$^{97,203}$

![Figure 7.4: Absorbance spectra of MoTe$_2$ dispersions for varying surfactant concentrations as indicated in the figure legend (pre-treated powder used after a long drying time).](image-url)
To track the nanosheet concentration, the intensity change (at 545 nm) was plotted as a function of surfactant concentration as shown in figure 7.5 A. It should be noted that there are two plots in the figure, a short and a long dry. This refers to the amount of time the pre-treated stock powder (pre-treated to remove impurities) was dried at the initial step of the process. Clearly, the drying time has a significant effect on the concentration of the nanosheets produced, across the range of SC concentrations. The shorter drying time gives a higher concentration of nanosheets; however, there is greater scatter in the data. The only explanation for this is that the powder from the shorter drying time still contained traces of water contributing to the mass when weighing the powder to prepare the dispersions. This can well be responsible for the greater scatter in the data. However, it is difficult to rationalise why traces of water in the starting powder would improve the exfoliation and yield and higher concentration. Nevertheless, the remainder of the study was conducted using the long-dry, pre-treated powder which gave the cleaner data.

Since the spectral shape changes with the surfactant concentration (figure 7.4), it is important to test whether the wavelength chosen to track the nanosheet concentration is independent from changes in spectral shape. To do this, two different wavelengths (345 nm and 545 nm, respectively) were plotted as a function of surfactant concentration as shown in figure 7.5 B. Both samples, significantly, display the same qualitative trend. Changes in spectral shape are usually indicative of a change in the distribution of nanosheet size and thickness in the sample. In both cases, a clear trend is observed: an initial increase in the concentration of the dispersed nanosheets with increasing surfactant concentration. This linear increase is observed up to the CMC of SC (6 g/L). However, beyond the CMC the concentration begins to decrease with increasing SC concentration (i.e. SC > 6 g/L). Interestingly, the dispersed concentration of nanosheets is lower for higher concentrations (>15 g/L) of SC, than for low concentrations (1-2 g/L). This trend is most likely related to charge screening and depletion interactions between the nanosheets. This interaction typically occurs beyond the CMC concentration of the surfactant, where the concentration of micelles grows. The increase in micelles decreases the coating of surfactant on the nanosheets, ultimately leading to aggregation and a lower concentration of dispersed nanosheets. In addition, the increased pool of counterions can reduce the negative net charge on the nanosheet surface. To further shine light on this behaviour, zeta potential measurements were conducted as described below.
Colloidal particles, that are coated by surfactant, are stabilised by repulsive inter-particle interactions due to the combination of an adsorbed layer of the ionic surfactant and a diffuse cloud of counter ions.\cite{217,218} This so called electrical double layer results in a repulsive electric field which prevents aggregation of nearby particles. We can characterise this repulsion via the zeta potential\cite{217,218} of the surfactant-coated nanosheets\cite{219,220} which is generally a measure for colloidal stability.\cite{90,204}

In general, a colloid is considered to be stable if there is a Zeta potential of $|\zeta| > 10 \text{ mV}$.\cite{111,221} Therefore, investigating the Zeta potential as a function of the concentration of surfactant used to exfoliate the nanomaterial, will determine the optimum concentration of SC (figure 7.6). Interestingly, the plot follows the plot of dispersed nanosheet concentration versus surfactant concentration exactly. The stability of the nanosheets in solution, reaches a maximum at the CMC (6 g/L). Beyond 6 mg/mL, the stability of the dispersion decreases similar to the absorbance behaviour (figure 7.5). Excellent stability is observed at the CMC value of SC where the zeta potential reaches ~ 55 mV.
Accordingly, the dispersed concentration plot, shown in figure 7.5 B, can be rationalised as follows. Below the CMC of the surfactant, the surfactant packing density on the nanosheets is not maximised. Hence, as the surfactant concentration is initially increased, the surface coverage and therefore inter-nanosheet potential barrier is increased also giving a higher nanosheet concentration. As the surfactant concentration is increased above the CMC, destabilisation of the surfactant coated nanosheets occurs due to depletion interaction and charge screening.\(^9\)

![Figure 7.6: Zeta potential measured as a function of the concentration of SC the MoTe\(_2\) was exfoliated in.](image)

As evident from extinction spectra and Zeta potential, the most concentrated and stable nanosheets are those which are exfoliated at the CMC, presumably due to an interplay of surfactant coverage and destabilisation by depletion interaction.\(^9\) Accordingly, it is very attractive to analyse how PL responds to these changes in the nanosheets’ dielectric environment. The PL response with excitation, at 683 nm, was subsequently measured for the MoTe\(_2\) dispersions exfoliated in SC of different concentration (3 laser wavelengths; 638nm, 683nm and 785nm are shown in appendix figure 9.5). MoTe\(_2\) is a direct band gap semiconductor in the mono- and bi-layer form and has an optical band gap of \(\sim 1\) eV; therefore,
nIR luminescence is expected for these species.\textsuperscript{42, 211} Shown in figure 7.7 is a typical PL spectrum of a std-MoTe\textsubscript{2} sample. There are two clear peaks centred at 1.09 eV and 1.04 eV, which are consistent with the mono- and bi-layer components of MoTe\textsubscript{2}, respectively. The observed band gaps are consistent with theoretical calculations and previous studies.\textsuperscript{211, 214}

The identification of these PL peaks is quite important as it confirms that the LPE process produces mono- and bilayers.\textsuperscript{211} A baseline subtraction was performed and the spectra were fitted using two components which yielded a poor fit (example of a spectrum before baseline subtraction is shown in appendix figure 9.6). Fitting to 3 components yielded an excellent fit to the data. The third component (blue) is blueshifted with respect to the monolayer peak (1.12 eV). Given the trion of MoTe\textsubscript{2} is typically only observed at low temperatures, it is most likely an artefact of the spectrometer or a contribution from SC.\textsuperscript{42} Therefore, the main focus of this work will be investigating the mono- and bi-layer spectra.

![Figure 7.7: PL spectrum of std-MoTe\textsubscript{2} excited using a 683nm laser. The peak is fitted using 3 Gaussian fits. The mono and bilayer components are identified with a green and red fit respectively. A third component, in blue, is most likely attributed to luminescence from SC.](image-url)

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*Figure 7.7: PL spectrum of std-MoTe\textsubscript{2} excited using a 683nm laser. The peak is fitted using 3 Gaussian fits. The mono and bilayer components are identified with a green and red fit respectively. A third component, in blue, is most likely attributed to luminescence from SC.*
In the following, the PL response for both mono and bilayer nanosheets is studied as a function of SC concentration as shown in figure 7.8 A. It is clear that the intensity varies as a function of the concentration of surfactant where a peak is centred at the CMC. The same behaviour is observed for mono- and bilayer species. The observed trend in PL intensity also follows the same behaviour as the concentration and zeta stability. The peak in the concentration, zeta potential and PL intensity may be attributed to a greater efficiency of the exfoliation process at the CMC and hence also a larger population of very thin mono and bilayer species at the CMC. This would imply that the trends observed in this work are solely due to a greater efficiency of the exfoliation process, which varies with surfactant concentration.

However, the PL intensity is also sensitive to the dielectric environment of the nanosheets. As suggested by the zeta potential measurements, the surfactant coverage is lower below the CMC. This can lead to different levels of nanosheet doping, due to a change in relative concentrations of water and surfactant in the vicinity of the nanosheets. Such variations in nanosheet doping strongly influence PL intensity, widths and position. To investigate the possible doping effect of SC on the MoTe$_2$ nanosheets, the peak positions and width were also investigated (figure 7.8 B and C).

Increasing the surfactant concentration does not have any noticeable effect on the mean peak position of the mono- and bi-layer nanosheets. Previous reports have shown that a change of the dielectric constant can induce a blueshift of ~40 meV in the case of some TMDs. The mono- and bi-layer components display minor blue shifts of ~ 8meV; however, this is most certainly within the error of the equipment. The mean width of the peaks seems to bounce around somewhat. Generally the bilayer has a slightly higher associated peak width, but again all within error of the instrument. To this end, the energy peak positions and widths are constant over the range of SC concentrations indicating solvatochromism is not effecting emission.
Figure 7.8: A) PL intensity normalised to the optical density, for exfoliation of nanosheet dispersion in varying amount of surfactant, plotted as a function of SC concentration, B, C) peak energy positions and energy widths of the mono- and bi-layer components with increasing SC concentration.
To test whether the changes in MoTe$_2$ PL intensity are due to a different population of mono- and bi-layered nanosheets, when MoTe$_2$ is exfoliated in surfactant with varying concentration, a reference experiment was performed where the surfactant concentration was varied from the same sample. To achieve this, a sample was sonicated at the CMC and subjected to the standard centrifugation conditions. The dispersion was then centrifuged at a high centrifugation rate to sediment all of the nanosheets. This sediment was re-dispersed in different SC/H$_2$O with varying surfactant concentrations by mild bath sonication. The samples were then measured using absorbance spectroscopy and subjected to PL measurements. Interestingly, a different trend appears to be observed, where increasing surfactant increases the PL intensity (figure 7.9). This suggests that the variation of the PL intensity observed, when MoTe$_2$ is exfoliated in SC of different concentrations, is likely due to different mono—and bilayer population. However, redispersion of the same sample gives an increased PL intensity with increasing surfactant due to an effect of the different dielectric environment around the nanosheets.\textsuperscript{140}

![Figure: 7.9: PL intensity measured as a function of dispersion SC concentration. Initial sample was sonicated in 6mg/ml centrifuged and redispersed in varying concentrations of SC/H$_2$O.](image-url)
The peak position and widths of the samples, redispersed in different Sc/H$_2$O, do not change with increasing surfactant concentration. (appendix figure 9.7 A and B respectively). This is a similar trend as previously observed, where exfoliation was conducted on different samples in different surfactant concentrations (figure 7.8 A). Moreover, it is evident that these two methods of investigation do not indicate that the surfactant is chemically doping the nanosheets, as the peak position would be expected to shift. Chemical enhancement and quenching of PL have been reported in the literature for nanomaterials such as CNTs and ZnO nanoparticles. However, these effects typically occur with a peak shift.\textsuperscript{206, 207}

To correlate the two behaviours the mono- and bi-layer components are overlain in figure 7.10. It can be seen that the PL intensity, as a function of the surfactant concentration, increases for increasing surfactant concentration, for both mono- and bi-layer PL. The trend in both methods appears to agree (within scatter); a similar PL intensity up to \(\sim 2.5\text{g/l}\) followed by an enhancement in the intensity. It should be noted that the intensity of the monolayer PL is higher than that of the bilayer PL (approximately twice as high).

The mechanism of PL enhancement with surfactant concentration is certainly not straightforward. The data which was sonicated in a series of samples of different surfactant concentration appears to follow a trend which shows a peak at the CMC; however, within error it may be fair to argue that both methods agree with each other. It is difficult to separate the possible effects of population density of mono- and bi-layers and a changing dielectric environment with surfactant concentration. Nevertheless, a clear dependence upon surfactant concentration is shown and warrants further investigation.
Figure 7.10: A, B) Mono- and bi-layer PL intensity plotted as a function of increasing surfactant concentration, indicated are the two sample preparation methods for comparison. Initially all samples have been individually exfoliated in varied amounts of surfactant (solid data points). The second is where one sample was exfoliated at the CMC, centrifuged at high RPM and redispersed in varying amounts of surfactant (open data points)
7.4 Conclusions

The work presented in this chapter has demonstrated that SC can be used to exfoliate MoTe$_2$. Statistical TEM and AFM analysis determined the length and thickness to be $66 \pm 2$ nm and $\langle N \rangle = 4$, respectively under the chosen centrifugation conditions. Raman and XPS confirmed the exfoliated nanosheets to be of reasonable structural quality and integrity. The dispersed nanosheet concentration and zeta potential were investigated as a function of SC concentration during the exfoliation. In both cases, a peak at the CMC of SC (6 g/L) was observed, suggesting that exfoliation and stabilisation is most efficient around the CMC of the surfactant.

For the first time, it was also attempted to track whether different exfoliation behaviour, would coincide with different populations of monolayered species. For this purpose, the photoluminescence response of the mono-and bi-layered species was tracked as function of surfactant concentration. An increase in PL intensity with increasing surfactant concentration was observed. However, unfortunately, it is not yet conclusive whether this is due to different population of mono-and bilayer or due to changes in the dielectric constant around the nanosheets, which were also shown to have a similar impact on the PL intensity. Certainly this behaviour warrants further investigation.

This work enhances the field of LPE, with improvement to the processing and optical characterisation. Moreover, PL has been implemented to directly characterise the mono- and bi-layer species in dispersion. This technique will be discussed further in the future work section in this thesis.
Conclusions and Future Work

8.1 Conclusions

The aim of this thesis was to expand liquid-phase exfoliation technology to new layered materials. The exfoliation quality of the samples produced was investigated using a range of optical techniques. Previous studies have shown that LPE can be used effectively to exfoliate graphite, BN, and TMDs; however, extension to other layered nanomaterials has been slow.

The extension of LPE technology to a TMO, molybdenum trioxide (MoO₃), was initially studied through investigation of exfoliation parameters. Dispersion of MoO₃ in a solvent medium was investigated using Hildebrand solubility parameters, where the optimal solvent was at the peak of a Gaussian function centred at 21 MPa¹/². This peak position is typically observed for other layered materials, such as graphene and TMDs, and it indicates that amide solvents, such as NMP and CHP, are ideal for exfoliation of the nanomaterial. In the case of this work; however, these solvents were not chosen due to their high toxicity and high boiling points. A high boiling point solvent makes it difficult to process the nanosheets in solution. Therefore, IPA was identified as a suitable low boiling point alternative, which yielded high-quality dispersions. Statistical TEM and AFM analysis allowed the lateral dimensions and thickness of the nanosheets to be determined. Interestingly, the exfoliation of MoO₃ was found to shear with respect to the lateral bond lengths in the nanosheets. A distinct ratio between the l: w: t, of exfoliated nanosheets, was found to be 6.6:2.5:1. Moreover, the lateral dimensions of the exfoliated nanosheets depend on the properties and structure of the material. The suitability of MoO₃ nanosheets as the charge-storing component of
supercapacitors was assessed. The energy storage of the MoO$_3$ nanosheets was found to be limited by their inherently poor electrical conductivity.\textsuperscript{37, 118, 166} The addition of a conductive element, SWCNT, allows for the full potential of the MoO$_3$ active material to be achieved. Capacitances of $\sim 200$ F/g were observed for composite films. Interestingly, the capacitance, upon addition of SWCNTs, followed percolation behaviour. The percolation threshold was determined to be 3 wt.\%.

Methodologies developed when working with MoO$_3$ were applied to BP, where the concentration of nanosheets was found to vary as a power law with sonication time ($\sim t^{0.5}$) in addition the number of layers were found to scale as $<N> \sim \text{area}^{0.5} (A^{0.5})$. Modification of previous centrifugation techniques allowed for the isolation of nanosheets with dimensions which range from 200 nm up to 3 $\mu$m. This enabled the formulation of a quantitative spectroscopic length metric from absorbance and scattering spectra, whereby nanosheet length is related to the scattering exponent via $L \sim 0.42/n$.

Interestingly, the absorbance (and extinction) spectra decrease, in intensity over time. This is highly unusual for layered nanomaterials and suggests chemical degradation. Analysis of the decrease in intensity, in different solvent systems, yielded insights into the chemical degradation of BP. This clearly showed that some solvents can exfoliate BP whilst simultaneously shielding the nanosheets from water and oxygen, hence significantly slowing down the reaction rate. This is crucial as it allows further processing and testing of the nanosheets in a number of applications. Furthermore, optimisation of the process allows for the exfoliation of BP nanosheets down to monolayers as confirmed through PL spectroscopy.

It has been shown in related studies, partly conducted in parallel to this thesis, that the luminescence characterisation of nanosheet dispersions can yield crucial information about the nature of the dispersion.\textsuperscript{44, 205} However, many factors can influence the observed PL such as the local environment, as well as the degree of exfoliation (due to a typical indirect to direct transition from few layers to monolayer).\textsuperscript{140, 206} To investigate the effect of these parameters on the observed luminescence, MoTe$_2$ was chosen as a model compound. While exfoliation of MoTe$_2$ has, in principle, been shown previously,\textsuperscript{42, 211} it is probably one of the least studied TMDs. Therefore, it is an excellent choice as optical properties and improvement of the sample quality can be tackled in parallel. The aim of this work was primarily to investigate the effect of the local environment on the PL intensity. In this regard, the use of surfactants rather than solvents is beneficial, as similar degrees of exfoliation can be obtained, while at the same time
varying the chemical environment. The dispersible nanosheet concentration showed a non-linear behaviour as a function of the surfactant concentration with a peak centred at the CMC. The effect on PL of the exfoliation and redispersion in varying surfactant concentration was investigated. A complex behaviour was observed where the PL increases with increasing surfactant concentration. Unfortunately these two behaviours could not be separated and further research is warranted. Nevertheless, in conjunction with the concentration and stability study this work yields crucial insight into the variation in nanosheet behaviour with surfactant concentration.

The work presented in this thesis advances understanding in the field of LPE by extending such methodologies to new layered materials. While this work is important, further investigation into the chemical stability of the nanosheets is warranted. Many layered materials are expected to degrade under ambient conditions. The methodologies established in this work will provide a solid platform to characterise and potentially address stability issues through optimisation of the dispersion parameters. It has also been shown that the local environment has a substantial effect on the luminescence which can, in turn, be used to quantify sample quality.

8.2 Ongoing and Future Work

This section introduces the ongoing research built on the foundation of the work presented in this thesis. The main aims going forward are to investigate the stability of 2D dispersed nanomaterials from their optical absorbance spectra and also from their luminescence properties. As shown in chapters 6 and 7, optical properties are highly sensitive to the nanosheets’ local environment, which is ideal for tracking potential degradation. While this work is currently in its infancy, there is clear evidence that potential metrics, such as those discussed in this thesis, are also applicable to other layered nanomaterials. These materials include WS$_2$, which is expected to be highly stable in terms of chemical degradation and NbS$_2$, which is known to degrade.

The methodology presented in chapter 6, where the BP nanosheet absorbance response was found to be time dependent, was applied to NbS$_2$. Analysis of a standard dispersion of NbS$_2$ in CHP was produced using similar exfoliation and centrifugation conditions as those
used for BP. Similar to BP, the extinction intensity decreases over time. A decrease in the extinction spectra was observed (figure 8.1A). An intensity ratio was plotted as a function of time, where the data followed a single exponential decay (figure 8.1B). The std-NbS$_2$ sample decayed faster than that of the std-BP (indicated with olive curve), where a substantial increase in the reaction rate was observed for additions of water $> 6\%$. For a given addition of water; however, the reaction rate does not increase as quickly as observed for BP, which may indicate a different reaction mechanism. This will need to be further investigated, however, it is clear that the experimental methodology to track chemical changes is useful for other materials.

Figure 8.1: A) Decrease in absorbance over time of std-NbS$_2$, B) Intensity of NbS$_2$ at 465nm as a function of time.

The strength of measuring a sample using absorbance spectroscopy is that a large number of nanosheets are probed thus making the technique quite robust. While this is a great advantage, in some cases a more refined analysis, with the potential to specifically probe certain nanosheet sizes or thicknesses, is desired. For instance, with the absorbance measurement there is a range of distributions of size and thickness of nanosheets in the sample. In turn, it is difficult to specifically identify the rate of one component or thickness of nanosheet. In addition, changes are only observed when the material is actually consumed in the reaction. For materials that are believed to be stable, a different approach should be taken. With this in mind, an analysis of the PL over time was initiated. The aim was to track the change of the nanosheets’ PL over time. An initial approach is to measure the PL of WS$_2$ using a Raman spectrometer. This technique has been recently developed in the group in parallel to the work conducted within this thesis. A drop of the dispersion was deposited onto a glass slide.
and a Raman spectrum was acquired under resonant excitation at 532 nm over a wide spectral region. In addition to the Raman modes of the nanosheets, the PL from monolayers is clearly discernible at high Raman shifts (figure 8.2 A). If a ratio could be developed to determine the variation over time it would provide an insight into potential degradation or reaggregation of monolayered WS$_2$. It should be noted that, in contrast to PL measurement in a PL spectrometer, the PL intensity, when measured in a Raman spectrometer, is strongly dependent on the focus of the laser within the drop. However, this effect can be avoided by normalising the spectra to the Raman mode of the WS$_2$. The intensity ratio of Raman/PL hence provides a good metric for changes in monolayered WS$_2$.

Plotting this intensity ratio as a function of time shows a decay curve which is similar to that obtained from BP and NbS$_2$ (figure 8.2B). The curve begins to saturate after 20 days with a ~10% decrease in WS$_2$ PL observed after 7 days. This decay curve, however, unlike that form the optical absorbance, tracks the change in only the monolayer component of the sample. These preliminary results emphasize that optical fingerprints can indeed be used to track nanosheet degradation, even in cases where the material is expected to be stable. However, much more research will be necessary to elucidate whether this is a result of chemical degradation or reaggregation of monolayers into few-layered material.

![Figure 8.2](image)

**Figure 8.2:** A) Raman spectra of WS$_2$ dispersed in SC/H$_2$O measured at 4 and 8 days respectively, B) here the ratio of the PL peak at 2,439 cm$^{-1}$ (~2 eV) to the Raman mode at 359 cm$^{-1}$ is plotted as a function of time showing a decay curve and a decrease in the PL intensity.
Appendix

9.1 PL Intensity of BP Nanosheets in CHP

Figure 9.1: A) BP nanosheets PL peak position measured as a function of layer number, B) PL width measured as a function of
### 9.2 Effect of Water on Stability of BP Nanosheets

*Table 9.1: Stability metric and time constants for additions of water to BP nanosheets samples; std-BP, s-BP and l-BP.*

<table>
<thead>
<tr>
<th>sample</th>
<th>$A_{Re}/(A_{UnRe} + A_{Re})$</th>
<th>$\tau$ (h)</th>
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<tr>
<td>Std-BP 1%</td>
<td>0.23</td>
<td>155</td>
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<tr>
<td>Std-BP 3%</td>
<td>0.5</td>
<td>67</td>
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<tr>
<td>Std-BP 5%</td>
<td>0.89</td>
<td>40</td>
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<td>Std-BP 10%</td>
<td>0.7</td>
<td>30</td>
</tr>
<tr>
<td>Std-BP 12.5%</td>
<td>0.93</td>
<td>36</td>
</tr>
<tr>
<td>Std-BP 25%</td>
<td>0.93</td>
<td>25</td>
</tr>
<tr>
<td>Std-BP 50%</td>
<td>0.92</td>
<td>30</td>
</tr>
<tr>
<td>s-BP 1%</td>
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<td>150</td>
</tr>
<tr>
<td>s-BP 3%</td>
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<td>62</td>
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<tr>
<td>s-BP 5%</td>
<td>0.87</td>
<td>30</td>
</tr>
<tr>
<td>s-BP 10%</td>
<td>0.82</td>
<td>30</td>
</tr>
<tr>
<td>s-BP 12.5%</td>
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<tr>
<td>s-BP 50%</td>
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<tr>
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<tr>
<td>L-BP 50%</td>
<td>0.15</td>
<td>53</td>
</tr>
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</table>
9.3 Effect of Oxygen on Stability of BP Nanosheets

Figure 9.2: Extinction spectra for additions of oxygen and water to std-BP dispersion measured as a function of time.
9.4 Effect of Different Solvents of Stability of BP Nanosheets

Figure 9.3: Absorbance spectra measured over time for different solvents. Water additions up to 10vol% are also shown.
Figure 9.4: Absorbance measured as a function of time for BP nanosheets dispersed in SC/H$_2$O.
Figure 9.5: A) PL intensity for a range of optical densities. With decreasing concentration of the nanosheet dispersion, the PL also decreases. B) PL intensity versus dispersion optical density. With increasing optical density the nanosheets begin to self-quench.
Figure 9.6 Three laser lines initially used to investigate PL from MoTe$_2$ nanosheets. The 683nm line shows the highest intensity, which was used for the majority of the work presented in chapter 7. The 785nm line shows a contribution from the overcompensation of the Raman OH of water.

Figure 9.7 Raw spectra of std-MoTe$_2$ sample (683nm), sitting on a broad background.
Figure 9.8: A sample of MoTe$_2$ sonicated at CMC of SC (6g/l) and redispersed in varying surfactant concentrations. A, B) Peak energy and width measured as a function of surfactant concentration, for mono- and bi-layer components.
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