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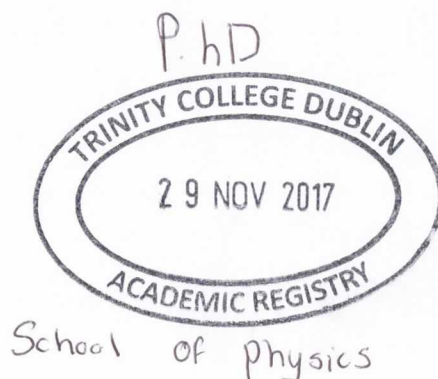
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Abstract

Over the last decade, there has been a large push towards making two dimensional (2D) nanomaterials a more realistic component of industrial applications. One of the main limiting factors to this point has been the ability to produce these materials in large quantities. In 2008, it was demonstrated by Coleman *et al* that liquid phase exfoliation (LPE) could be utilised as a production method of large quantities of 2D nanosheets. This method was first performed on graphene and transition metal dichalcogenides, such as MoS₂ and WS₂.

A recent move has been to try to exfoliate new materials such as molybdenum trioxide and black phosphorus but the extension to newer materials has been slow. Presented in this thesis is the continuation of this via the exfoliation of novel layered materials, such as gallium sulphide (GaS) and layered double hydroxides (LDHs). Initially this technique was applied to GaS where the production of large quantities of nanosheets by liquid exfoliation of layered GaS powder was demonstrated.

The exfoliation was achieved by sonication of the powder in suitable solvents. The variation of dispersed concentration with solvent was consistent with classical solution thermodynamics and showed successful solvents to be those with Hildebrand solubility parameters close to 21.5 MPa^{1/2}. In this way, nanosheets could be produced at concentrations of up to $\sim 0.2 \text{ g L}^{-1}$ with lateral sizes and thicknesses of 50 – 1000 nm and 3 – 80 layers, respectively. Using controlled centrifugation techniques, it was possible to prepare dispersions containing size-selected nanosheets. Spectroscopic measurements showed the optical properties of the dispersions to vary strongly with nanosheet size, allowing the elucidation of spectroscopic metrics for in situ estimation of nanosheet size and thickness.

Another layered family that, to this point, had been untapped by LPE are the LDHs. Although, LDHs have a different crystal structure to other layered materials such as the TMDS. It is demonstrated that liquid phase exfoliation can be used to convert layered crystals of nickel hydroxide into Ni(OH)₂ nanosheets in relatively large quantities and without the need for ion intercalation. While other procedures require harsh synthesis conditions and multiple reaction steps, this method involves ultrasonication of commercially available powders in aqueous surfactant solutions and so is relatively mild and potentially scalable. TEM, AFM, XPS and Raman spectroscopy show the exfoliated nanosheets to be relatively

thin (mean 10 monolayers thick) and of good quality. Size selection by liquid cascade centrifugation allowed the production of samples with mean nanosheet lengths ranging from 55 to 195 nm. Optical measurements on dispersions showed the optical absorption coefficient spectra to be relatively invariant with nanosheet size while the scattering coefficient spectra varied strongly with size. The resultant size-dependence allows the extinction spectra to be used to estimate nanosheet size as well as concentration.

Liquid phase exfoliation (LPE) has proven to be a versatile technique to produce uncharged 2D nanosheets from layered crystals. However, almost all studied starting materials consist of pure powder or crystals purchased from chemical suppliers. To test the true versatility of this process, the procedure has been subjected to three starting materials with varying degrees of purity and composition. These include talcum powder (principle component, the layered compound talc), Fuller's earth cat litter (known to contain layered silicate compounds, most notably palygorskite and bentonite) and beach sand (suspected to contain small amounts of layered clays). In all cases, dispersions containing large quantities of nanosheets with almost all non-nanosheet material removed by the centrifugation step were produced. Powder x-ray diffraction identified the nanosheets produced to be talc, a bentonite/palygorskite mixture and mica for the three starting materials respectively. Particularly interesting is the fact that bentonite, palygorskite and mica sheets are charged and are always accompanied by charge balancing counterions.

The optical characterisation of GaS and the LDHs has highlighted a pressing need for further quantitative analysis of the effect that the scattering background has on optical extinction spectra for LPE samples. This was demonstrated through the exfoliation of boron nitride and five TMDS where the scattering spectra were plotted as a function of flake length. It was found that for flake lengths down to 150 nm it was possible to use previously determined analytical methods to quantify the scattering spectra through Mie and Rayleigh scattering.

List of Keywords:

Layered Materials, 2D Nanosheets, Liquid Phase Exfoliation, Gallium Sulphide, III-VI metal chalcogenide, Layered Double Hydroxide, Transistion Metal Dichalcogenides

List of Publications

- 1) Harvey, A.; Backes, C.; Gholamvand, Z.; Hanlon, D.; McAteer, D.; Nerl, H. C.; McGuire, E.; Seral-Ascaso, A.; Ramasse, Q. M.; McEvoy, N.; Winters, S.; Berner, N. C.; McCloskey, D.; Donegan, J. F.; Duesberg, G. S.; Nicolosi, V.; Coleman, J. N., Preparation of Gallium sulphide Nanosheets by Liquid Exfoliation and Their Application As Hydrogen Evolution Catalysts. *Chem Mater* 2015, 27, 3483-3493.
- 2) Harvey, A.; He, X. Y.; Godwin, I. J.; Backes, C.; McAteer, D.; Berner, N. C.; McEvoy, N.; Ferguson, A.; Shmeliov, A.; Lyons, M. E. G.; Nicolosi, V.; Duesberg, G. S.; Donegan, J. F.; Coleman, J. N., Production of Ni(OH)₂ nanosheets by liquid phase exfoliation: from optical properties to electrochemical applications. *Journal of Materials Chemistry A* 2016, 4, 11046-11059.
- 3) Harvey, A.; Boland, J.; Godwin, I.; Murtaza, G.; Lewis, D.; O'Brien, P.; Coleman, J.; Exploring the versatility of liquid phase exfoliation: Producing nanosheets from talcum powder, cat litter and beach sand
- 4) Backes, C.; Szydłowska, B. M.; Harvey, A.; Yuan, S.; Vega-Mayoral, V.; Davies, B. R.; Zhao, P. L.; Hanlon, D.; Santos, E.; Katsnelson, M. I.; Blau, W. J.; Gadermaier, C.; Coleman, J. N., Production of Highly Monolayer Enriched Dispersions of Liquid-Exfoliated Nanosheets by Liquid Cascade Centrifugation. *ACS Nano* 2016, in press.
- 5) Gholamvand, Z.; McAteer, D.; Harvey, A.; Backes, C.; Coleman, J. N.; *Chem. Mater.*, 2016, 28, 2641-2651.
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- 7) Varrla, E.; Paton, K. R.; Backes, C.; Harvey, A.; Smith, R. J.; McCauley, J.; Coleman, J. N.; *Nanoscale*, 2014, 6, 11810–11819.
- 8) Varrla, E.; Backes, C.; Paton, K. R.; Harvey, A.; Gholamvand, Z.; McCauley, J.; Coleman, J. N.; *Chem. Mater.*, 2015, 27, 1129–1139.
- 9) Ferguson, A.; Harvey, A.; Godwin, I. J.; Bergin, S. D.; Coleman, J. N.; The dependence of the measured surface energy of graphene on nanosheet size *2D Materials* 4 (1), 015040
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- 11) Backes, C.; Hanlon, D.; Szydłowska, B. M.; Harvey, A.; Smith, R. J.; Higgins, T. M.; Preparation of Liquid-exfoliated Transition Metal Dichalcogenide Nanosheets with Controlled Size and Thickness: A State of the Art Protocol *JoVE (Journal of Visualized Experiments)*, e54806-e54806
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I see now that the circumstances of one's birth are irrelevant. It is what you do with life
that determines who you are - Myūtsū
It is important to draw wisdom from different places. If you take it from only one place
it becomes rigid and stale - General Iroh

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Chapter 1

Motivation & Thesis Outline

Throughout history, materials have been the driving force behind most technological advances. From the discovery of bronze by combining copper and tin, to use for tools and weapons, to the use of silicon in many communication based technologies, materials have been a defining feature in human advancement. The control of the properties of the material is the determining factor for the range of its application. With the trend of technological devices getting smaller and more powerful it is necessary to find a material that can have great physical properties but also be able to be reduced to a size in the order of nanometers. This led to the discovery of graphene, a one atom thick monolayer of graphite which sparked interest due to its great electrical mobility and strength.

This field has accelerated quickly with many other 2D materials, also showing exciting properties, being discovered. These materials hold high promise for applications such as gas sensing, hydrogen evolution, and polymer reinforcement. One of the main limitations for their use in industrial applications has been the lack of effective production methods. This method, needs to be cheap, simple, scalable and most importantly be able to produce large quantities of high quality nanosheets. There are several methods that have been used to this point but none have been able to achieve all of these feats. With this in mind a liquid phase method was developed which has been successfully used on a number of materials to reduce them to the nanoscale. This methodology offers a simple, low-cost production method for 2D nanomaterials, which, furthermore, is scalable and thus holds great promise for future applications.

Expansion of this method to other materials apart from graphene, hBN and TMDs has

been slow. Accordingly, this work aims to help with this problem by exfoliating a number of families of materials using liquid phase exfoliation. Initially this will be applied to a member of the III-VI metal chalcogenide family and layered double hydroxides in both solvent and surfactant respectively. The exfoliation parameters will be optimised and compared to previously exfoliated nanomaterials, to investigate the fundamental physics of the process. From here the true versatility of the method will be tested by exfoliating a number of unconventional materials, talcum powder, beach sand and cat litter. Thus, demonstrating that LPE can be used on raw materials as well as synthesised powders. Finally, a detailed look will be given to the optical properties of some TMDs with emphasis given to the scattering coefficient of the materials.

Thesis Outline

Chapter 2: Background Theory

An overview of carbon materials, transition metal dichalcogenides, III-VI metal chalcogenides and layered double hydroxides. The history and physical properties of each family of materials is discussed in detail as well as available exfoliation methods and applications. Some exfoliation techniques are discussed with emphasis given to liquid phase exfoliation. The basic concepts of dispersion theory are introduced, mainly focusing on the thermodynamics of stabilisation of particles in suspension and DLVO theory and how they can be used to stabilise two dimensional nanosheets in aqueous environments.

Chapter 3: Materials & Methods

The sourcing of materials and all experimental techniques used in this thesis are outlined and discussed. The theory behind all characterisation methods is also described in detail.

Chapter 4: Exfoliation of Gallium sulphide

Possibility of exfoliating gallium sulphide powder into nanosheets in solvents is tested. The exfoliation parameters are optimised and an ideal solvent is determined. The nanosheets are size selected using a new method and the effect flake length has on the materials absorption properties are discussed. Four separate size metrics are found for concentration, mean length and mean thickness.

Chapter 5: Exfoliation of Layered Double Hydroxide

Possibility of exfoliating nickel hydroxide powder into nanosheets in surfactant is tested. Surfactant concentration, as well as other parameters are optimised. The phase of the material is measured, confirming that β - $\text{Ni}(\text{OH})_2$ can be exfoliated without treatment to the powder. Size metrics are determined including a concentration metric that can be used from just an extinction spectra despite scattering effects. These exfoliation parameters are extended to four other layered hydroxides and a comparison of their performance as catalysts in evolution reactions are analysed.

Chapter 6: Testing the Versatility of Liquid Phase Exfoliation

The versatility of liquid phase exfoliation is investigated as the method is applied to three impure starting materials, talcum powder, clay from a beach and cat litter bought in Aldi. The possibility of exfoliating crystals with charged surfaces as well as a method to only remove exfoliated material is determined.

Chapter 7: Effects of nanosheet size on the absorption spectra of 2D materials

Five different semiconducting TMDs and hBN are size selected using the method described in chapter 4. The extinction, absorption and scattering are measured for the six materials and the effects of this on absorption coefficient, excitation position and excitation intensity ratio are analysed. For the first time a full study on the effect of nanosheet length for 2D nanosheets on the scattering of light is determined.

Chapter 8: Conclusion and Future Work

A full conclusion is given for the four results chapters is given as well as a brief overview on work that is still ongoing and future work. This includes the expansion of these exfoliation methods to new materials as well as comparing chapter 4's methods on other III-VI metal chalcogenides.

Chapter 2

Background Theory

2.1 Introduction

Within this chapter is a discussion on the selected families of materials used in this thesis, which include the III-VI metal chalcogenides, layered double hydroxides and transition metal dichalcogenides. As well as a brief consideration of the materials that lead to this research topic being of interest. This will include points on both the physical and optical properties of nanomaterials as well their use in current and future applications in nanotechnology.

Nanotechnology is one of, if not the most defining research areas being conducted in modern times, and holds the key to many future applications such as printed and transparent electronics. The materials that this industry is based around are known as nanomaterials, i.e. having a lateral size of the order of nanometers. Although there is no definitive definition for a nanomaterial, it is generally accepted that they are materials with at least one of their dimensions fewer than 100 nms. Of primary interest in this work is that of 2D materials, nanomaterials that are large in the x and y direction but are atomically thin in the z direction, with special consideration on the different production and exfoliation methods. Finally, there will be a comprehensive review of liquid phase exfoliation, a method used to remove 2D nanosheets from bulk crystals in liquid. This will lead to a discussion on the concept of dispersion theory, the mechanism that prevents reaggregation of nanosheets in the liquid phase.

2.2 Carbon Materials

Carbon is one of the most abundant and important elements in the world. Due to its four valence electrons it possesses great versatility in forming chemical bonds, which has made it pivotal to all known life on Earth. This allows it to form bonds with other carbon atoms and a wide range of other elements as well as existing in many different allotropes such as charcoal, soot, graphite, fullerene and diamonds (Figure 2.1). More recently the discoveries of carbon nanotubes and graphene have advanced the study of this material into the modern age. Despite all these compounds being comprised entirely of the same element they are all packed differently. For example, diamond is composed of sp^3 hybridised atoms tetragonally arranged to give a three dimensional crystal structure, making it a poor electrical conductor.

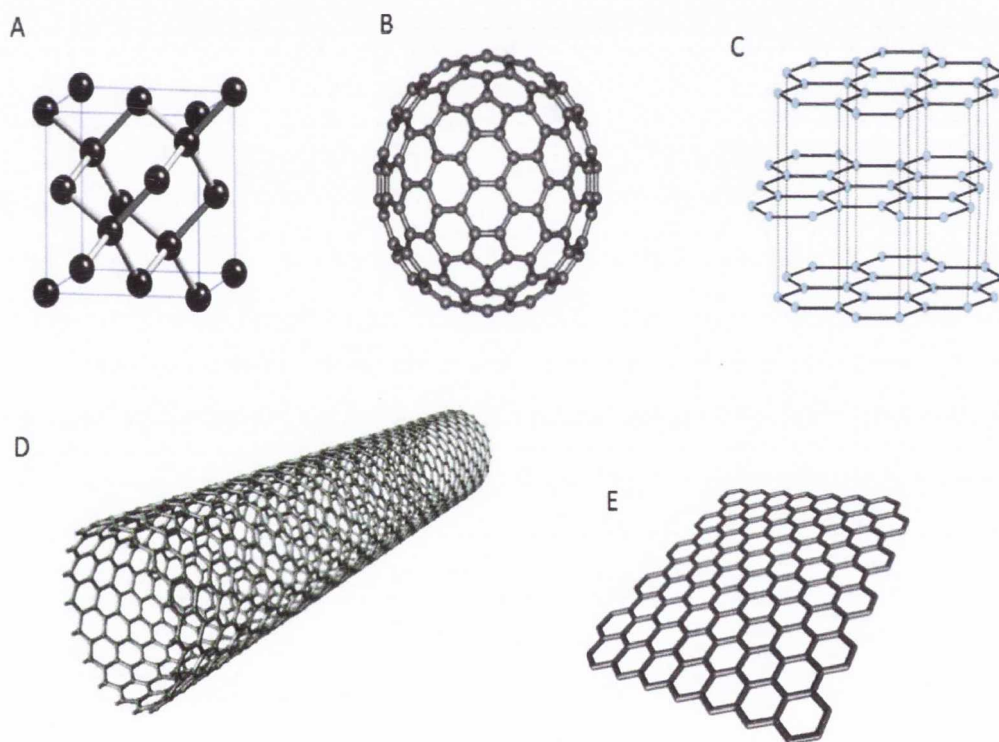


Figure 2.1: Atomic structure of (A) diamond, (B) fullerene, (C) graphite, (D) 1-D carbon nanotubes and (E) 2-D graphene sheet.[1]

In contrast, the sp^2 hybridised atoms in graphene are arranged in hexagonal rings allowing for very high theoretical electrical conductivity ($\sim 10^8$ S/m) when doped[2, 3].

Carbon nanotubes and graphene are very commonly used in modern research areas due to their excellent properties. This is discussed below.

2.2.1 Carbon Nanotubes (CNTs)

Carbon nanotubes were first discovered in 1991 by Iijima *et al* in material produced by an arc-discharge experiment[4]. CNTs, as with graphene, are comprised of sp^2 hybridised atoms in hexagonal rings that have been rolled into a tubular configuration. They can exist in the form of single wall (SWNTs) or multi-wall (MWNTs) which comprise of several concentric cylinders[5, 6, 7, 8]. The diameters of these CNTs can range from 1 nm to 2 nm and 10 nm to 30 nm respectively but the lengths of CNTs can range up to ~ 20 cm[4, 9]. This aspect ratio creates what are known as 1D nanomaterials. This creates a quantum effect where the electrons within the CNTs experience quantum confinement in two directions leading to very interesting properties, namely outstanding electrical properties with mobilities of 10^5 cm^2/Vs [10].

In addition, CNTs can range from being semiconducting to metallic. This is dictated by the chirality of the nanotube which can be described by the translational vector equation ($C = na_1 + ma_2$). This equation can be used to predict the electrical behaviour and type of nanotube; armchair or zigzag, which are both metallic, or chiral, which is semiconducting[4]. As well as impressive electrical properties, CNTs exhibit outstanding mechanical properties with their Young's modulus ranging from 60 GPa to 1 TPa, two orders of magnitude higher than steel[11].

CNTs have been used for a range of applications such as a transistor or in energy storage, while the addition of small amounts of CNTs to metals and plastics can also improve the tensile strength. 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 or mechanically poor.[12, 13] Incorporation of these elements into a matrix leads to the provision of nanotube networks, once the number of nanotubes reaches a certain point (known as the percolation threshold) this allows for conductive pathways, thereby allowing current to flow in the film or mechanical reinforcement.

2.3 Layered Materials & Graphene

Where 1D materials are exfoliated from fibres in their bulk form, 2D materials are exfoliated from layered crystals. These materials consist of weakly bound layers that are attracted by Van der Waals interactions out of plane but are strongly bound in plane by chemical bonds. The most famous example of these kind of materials is graphite, which is comprised of layers of the 2D material graphene stacked on top of each other to make a 3D crystal. This is the simple definition of graphene, more specifically graphene is a mono-atomically thick sheet of sp^2 hybridised carbon atoms, arranged in a honeycomb lattice. As a result of the weak Van der Waals bonds, with a binding energy of 10 mJ/mol, the graphene layers can be removed from the graphite crystal by exfoliation[14]. This was first demonstrated in 2004 by Geim *et al*, where they performed micromechanical exfoliation using scotch tape to 'peel' off the layers[14]. There have been several other methods developed over the past decade to produce graphene nanosheets such as micromechanical exfoliation as well as liquid based processes[15, 16]. Here, due to the fact the nanosheets are atomically thin, the electrons are confined in one dimension but are free to move in the other two dimensions within the graphene nanosheet. This leads to interesting behaviours not observed in the bulk crystal, with improved properties such as electrical conductivities and mechanical strength[14, 17].

2.3.1 Materials beyond Graphene

Although there has been a lot of time and money put into the research of graphene since its isolation in 2004 there are many other layered materials that also deserve attention. In recent years, there has been an explosion of research into the synthesis and characterisation of other 2D materials such as boron nitride (BN)[18], transition metal dichalcogenides (TMDs)[19, 20, 21], transition metal oxides (TMOs)[13], and black phosphorus (BP)[22, 23, 24]. Boron nitride is a structural analogue of graphite consisting of stacked sp^2 bonded sheets where, instead of carbon atoms, there are alternating boron and nitrogen atoms existing in a honeycomb structure[25]. Hexagonal boron nitride (hBN) is different to graphene as it is an electrical insulator; as a result the applications available are vastly different to graphene[25].

BP has a different structure to BN and graphene, where the phosphorus atoms form a puckered orthorhombic structure where each atom is bonded to three others, as shown in Figure 2.2. 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[26]. Of significant interest is the presence of a band gap, which scales with the layer number from 0.3 eV in the bulk to 1.8 eV in the monolayer[26, 27]. This tuneable band gap and reported high performance in some electrical applications make BP quite attractive for electronic devices such as Li-ion batteries, photodetectors and field-effect transistors[28, 29].

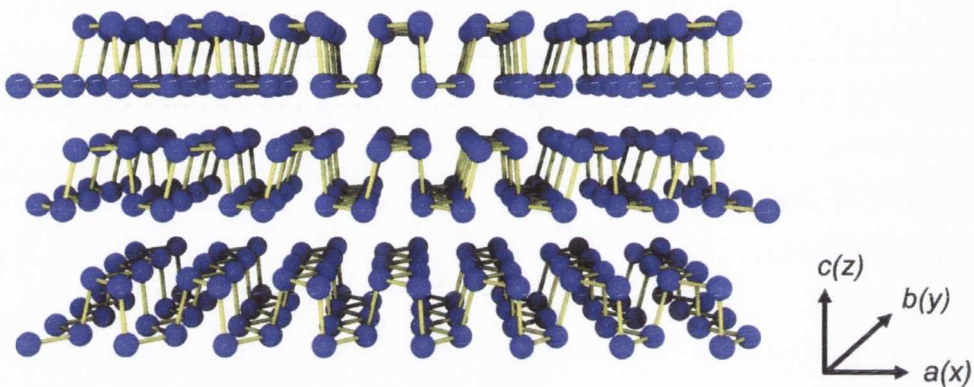


Figure 2.2: *3D structure of black phosphorus*[30].

TMDs have received large levels of interest in research. First studied in the 1960s, they have recently experienced an academic renaissance and become a largely prominent topic of research[31, 32]. This follows on from the experimental isolation of 2D NbSe₂ in 2005[33], and the resulting demonstration of the material's electronic, optical, electrochemical and mechanical properties.[32, 34, 35] Similarly TMDs also exhibit fascinating and highly beneficial changes to their properties once thinned to a monolayer[18, 36]. Work within this thesis includes research on the optical properties of some TMDs and will be discussed in the following section. The difference in structures between materials such as graphene, BP and TMDs show that there are many applications available depending on what material is used.

2.4 Transition Metal Dichalcogenides (TMDs)

TMDs consist of a family of materials that generally have a stoichiometry of MX_2 , where M is a transition metal (Mo, W, Ti, V etc) and X is a chalcogen (S, Se and Te). Due to the number of transition metals there is a large number of possible TMDs, with up to 60 possible configurations (Figure 2.3), of which two thirds form graphite-like layered structures with thickness' in the range of 6-7 Å; in contrast to graphene's thickness of 3.5 Å[31].

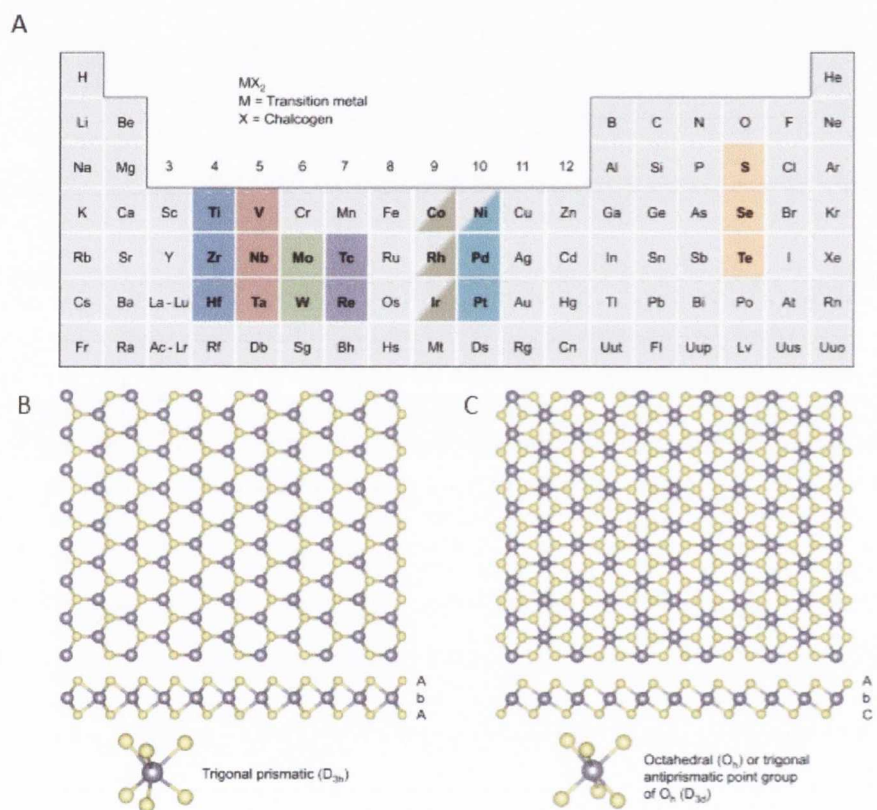


Figure 2.3: Periodic table highlighting elements in transition metal dichalcogenides. Top and side views of generic monolayer TMD with (b) trigonal prismatic and (c) octahedral coordinations[18].

The individual sheets consist of metal atoms being sandwiched between two layers of chalcogen atoms in a X-M-X structure. Like with graphene and graphite, these layers stack on top of each other to form 3D crystals that are bound by Van der Waals bonds.

Although conversely, different polymorphs can exist depending on the stacking of the layers, with the two most common being 1T and 2H.

The electronic properties of these materials are diverse and depend on the configuration of the d orbitals of the transition metal, resulting in a wide variety of types including semiconducting (MoS_2 , WS_2)[32], semimetals (WTe_2 , TiSe_2)[37, 38] and metallic (NbSe_2 , VSe_2)[33, 39]. Additionally, their chemical stability is different. A phase change can be induced via alkali metal intercalation where, for example, 2H polymorphs are transitioned to 1T by Li-ion intercalation[40]. During lithium intercalation, there is an electron transfer from the Li to the structure of TMDs and thus the electron density of the d orbital of the transition metal increases. The semiconducting 2H phase is then destabilised, favouring the phase transition to the metallic 1T phase.

The electronic and optical properties depend strongly on the number of layers of the TMD, especially when there are fewer than five layers[41]. In the cases of MoS_2 and WS_2 the optical bandgap can be varied from 1.2 eV to 1.9 eV and 1.3 eV to 2.1 eV respectively when going from the bulk to the monolayer[18]. The bulk crystals of these materials exist as indirect band gap semiconductors, whereas they become a direct band gap semiconductor when thinned down to a monolayer. For MoS_2 , this is due to the quantum confinement and the resulting change in hybridisation between p_z orbitals on S atoms and d orbitals on Mo atoms[36]. This change from indirect to direct bandgap can be clearly observed by the photoluminescence quantum yield which increases by four orders of magnitude and in the absorption spectra of materials where the A-exciton can shift by up to 30 nm[36, 42, 43]. The band structure of both bulk and monolayer MoS_2 and WS_2 are shown below in Figure 2.4.

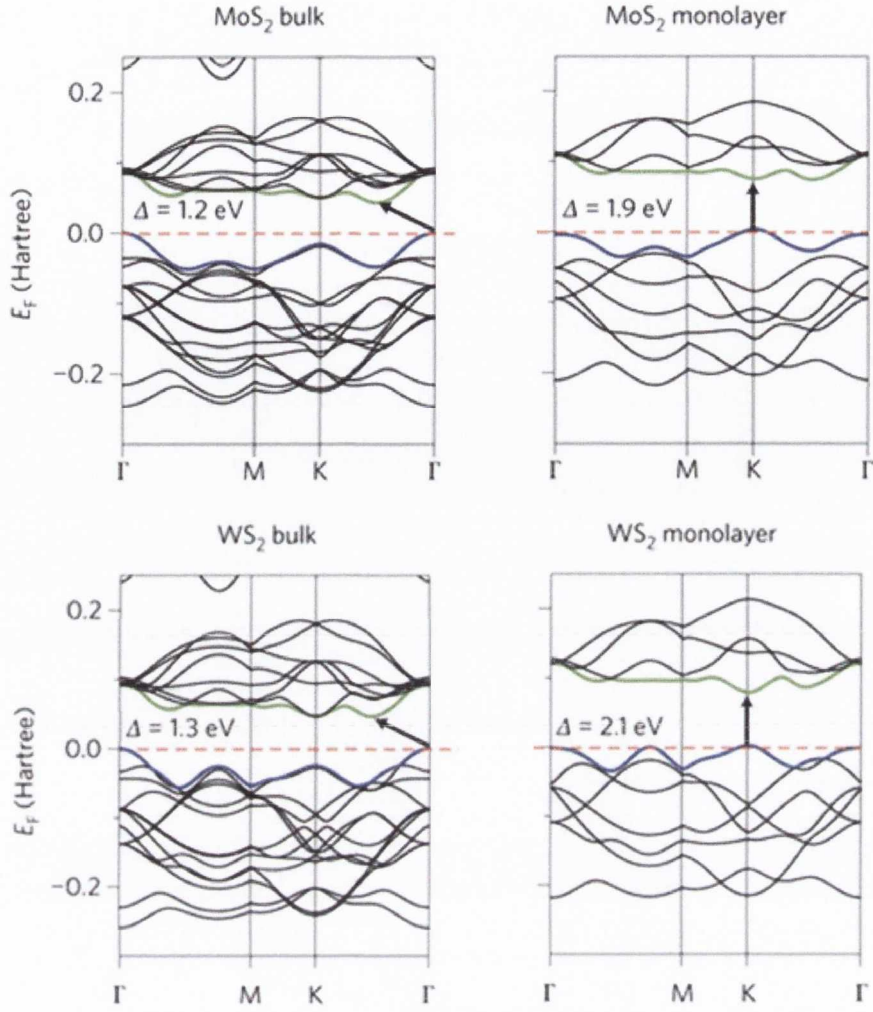


Figure 2.4: Band structure of both MoS_2 and WS_2 bulk crystal and monolayer demonstrating how they change when exfoliated[18].

2.4.1 Size Dependence of Absorption Spectra in TMDs

Not only does the change in layer number have an effect on the optical properties, specifically the absorption spectra, but the lateral dimensions of the nanosheets also play an important role[42, 43, 44]. These effects were shown qualitatively on nanosheets in colloidal systems multiple times before being quantified by Backes *et al* for MoS_2 [42]. With subsequent work done on WS_2 and graphene[43, 45]. The length dependence is determined by the effect of flake edges on the local electronic structure, density of states and thus the local optical absorption coefficient of the nanosheets. The observed absorption spectra will then be the sum of edge and core contributions[42]. Thus, the population of edge to

centre atoms increases with decreasing nanosheet size, causing the spectral shape to be size dependent (as indicated in Figure 2.5). This can be seen by a changing extinction coefficient as well as change in relative intensity of absorption peaks.

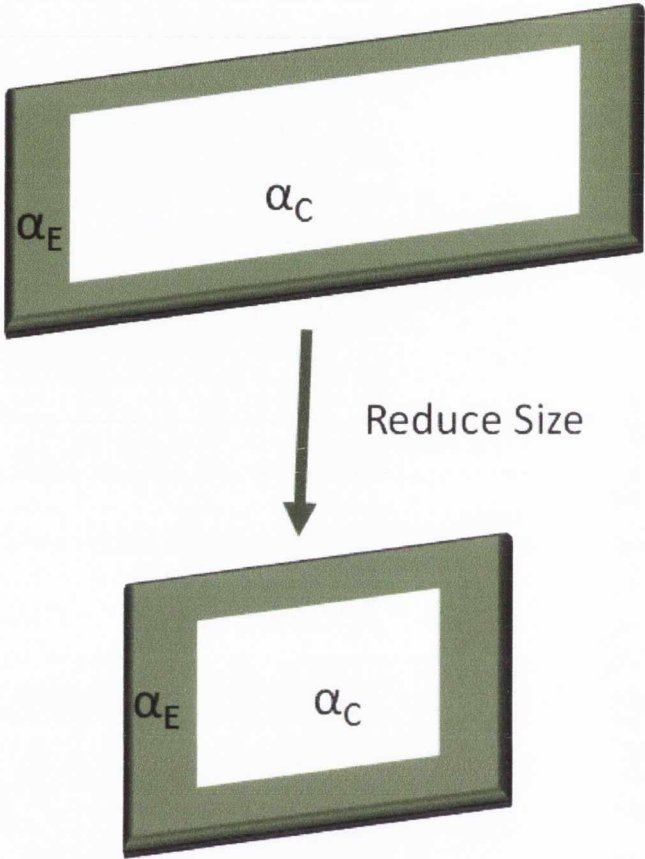


Figure 2.5: Representation of the ratio of the absorption coefficient at the edges of a nanosheet (α_E) versus in the core (α_C) changing as the size of the nanosheet changes.

As mentioned previously, by reducing the nanosheet thickness the band gap increases due to confinement effects. This happens as a result of a phenomenon where electrons and holes are squeezed into a dimension that approaches a critical quantum measurement, called the exciton Bohr radius. This causes a blueshift in the position of the A-exciton for 2D nanosheets when the number of layers decreases. These changes will be demonstrated in chapter 7.

2.5 III-VI Metal Chalcogenides (MCs)

III-VI metal chalcogenides are a family of materials that usually exist in the form MX ($M = \text{Ga, In, X} = \text{S, Se, Te}$) but have been observed in the forms M_2X_3 , M_3X_4 , M_4X_5 , M_5X_6 and M_6X_7 [44, 46]. These stoichiometries can be dependent on the crystal symmetries, for example, β , γ and ϵ phases for InSe and α , β , γ , δ , and κ phases for In_2Se_3 [47, 48]. Typically, taking InSe as an example; monolayer hexagonal InSe consists of planar quaternary layers, in which close-packed Se–In–In–Se sheets pile up along the c-axis (Figure 2.6). The separate layers are bonded together by Van der Waals interactions, with strong covalent bonding within each layer[49]. Studies of MCs began in the 1950s and their anisotropic mechanical, optical and electronic characteristics were the subject of investigation in the 1970s, with key interest being taken on their non-linear optical properties[50, 51, 52], photovoltaic applications[53, 54] and terahertz generation capabilities[55].

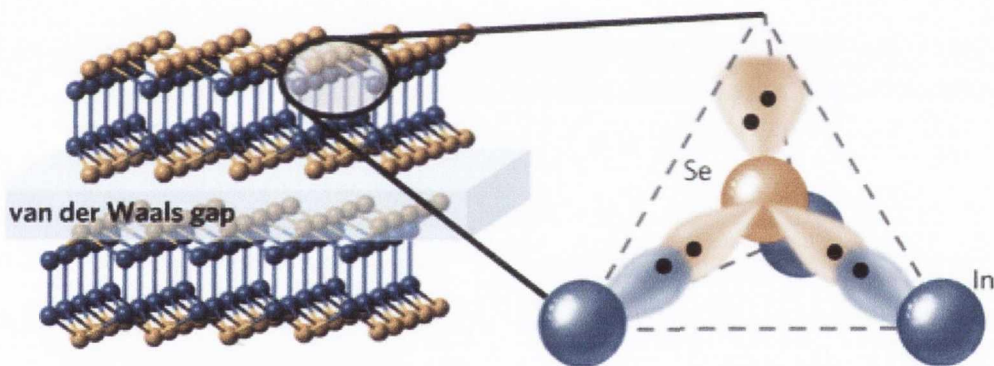


Figure 2.6: Structure of typical III-VI metal chalcogenide with a zoomed in image demonstrating the trigonal structure[56].

Since the discovery of stable 2D crystals, research on MC nanosheets has thus far focussed mainly on the metal monochalcogenide (i.e., GaS, GaSe, GaTe and InSe) with the exception of In_2Se_3 . In contrast to the intensely studied TMDs group, the III-VI semiconducting crystals of InSe, In_2Se_3 and GaTe are reported to hold a direct band gap in bulk and few-layer form, a promising feature for the development of efficient optoelectronic miniaturised devices.[57, 58] Many reports state that bulk and few layer GaSe and GaS

are indirect semiconductors; however, a recent report on exfoliated GaSe on sp^2 carbon reports GaSe to have a direct band gap with photoluminescence centred around $h\nu \sim 2$ eV[57, 58].

Similar to TMDs, MC are used in a range of applications that have been attracting increasing interest recently. MC possess some of the merits of TMDs but also have some more advantageous properties, such as higher carrier mobility, direct band gap electronic structure in some compounds for all thicknesses, rare p-type electronic behaviours and high charge density, to name a few[59]. For example, the room-temperature electron mobility of InSe FETs can reach as high as $1055 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [59], much larger than that of MoS_2 , WSe_2 , etc. Nanosheet InSe photodetectors were broad spectra responsive from UV-visible to near infrared. The photoresponsivity and photodetectivity of InSe photodetectors were 104 AW^{-1} and 1013 Jones respectively, much higher than 1×10^{-3} and $7.5 \times 10^{-3} \text{ AW}^{-1}$ for graphene and MoS_2 respectively[60, 61]. These unique characteristics and high performances greatly motivate the use of 2D MC materials for practical device applications in electronics, optoelectronics, and optics in the future as well as in some electrochemical applications.

2.5.1 Gallium (II) Sulphide

A typical representative example of this family is gallium sulphide (GaS). This material is most commonly found as layered crystal but it also exists in a variety of structures such as nanobelts and nanotubes[62]. GaS is particularly attractive due to its relatively low cost. In its layered form it is comprised of S-Ga-Ga-S repeating units stacked along the c-axis in a hexagonal structure with a monolayer thickness of 0.75 nm and a van der Waal gap of 0.24 nm. GaS first started generating interest in the 1970's due to its interesting optical properties[63, 64]. This was continued through the 1990's and although a number of papers have studied the layered form of GaS, work on its exfoliation to give nanosheets is in the very early stages[65]. Exfoliation has, to this point, only been achieved by micromechanical cleavage, which suffers from low throughput and can only produce material quantities suitable for fundamental studies, and atomic layer deposition, which is limited by cost and the need for complicated chemical procedures[66, 67, 68].

Like with other 2D materials it is clear that the properties of exfoliated gallium sulphide

differ from the bulk form. It is these changing properties that have led to increased interest in its use for some applications[66, 67, 68]. For example, exfoliated nanosheets of GaS have been used to fabricate sensitive photodetectors exhibiting a photoresponsivity of 19.2 AW^{-1} under light irradiation of 254 nm[66, 67]. In addition, it is likely that GaS will be useful in applications beyond optoelectronics. Gallium sulphide produced by atomic layer deposition has been combined with carbon nanotubes to produce high performance anodes in Li ion batteries[69]. However, for such materials to be competitive in applications such as battery electrodes, large quantities would be needed. Applications such as this highlight the need to develop a scalable method to produce nanosheets of gallium sulphide and related materials. These issues will be addressed in chapter 4.

2.6 Layered Double Hydroxides (LDHs)

Layered double hydroxides (LDHs) are a class of ionic layered compounds that are made up of positively charged layers with an interlayer region containing charge compensating anions and solvation molecules[70]. They exist in the form

$[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{\frac{x}{n}}^{n-}]^{n-} \bullet H_2O$ ($M^{2+} = \text{Mg, Ni, Co etc}$; $M^{3+} = \text{Ga, Fe, Al etc}$) where the metal cations occupy the centres of edge sharing octahedra, whose vertexes contain hydroxide ions forming a 2D sheet[70]. These sheets then stack on top of each other to create 3D crystals (Figure 2.7). There are also cases where $x = 0$ giving more simplified compounds of $M^{2+}(\text{OH})_2$ [71]. The chemistry of LDHs is now a large topic of research with applications such as fire retardant additives[72], catalysts in gas evolution reactions[73], supercapacitors[74] and as precursors for preparing CO_2 adsorbents[75].

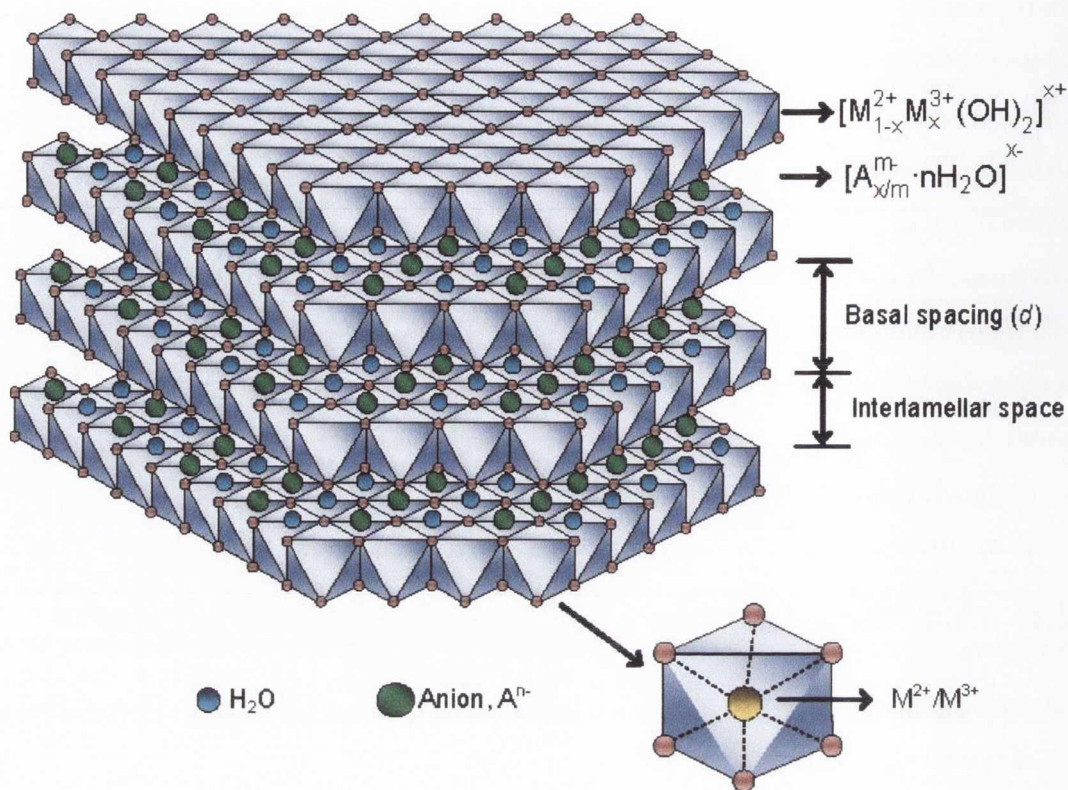


Figure 2.7: Schematic representation of the LDH structure[76].

As well as the previously mentioned applications, there are a wide variety of others that have been successfully researched for LDHs across many disciplines such as catalyst precursors, anion exchangers, bioactive nanocomposites and electroactive and photoactive materials[70]. A limitation to these applications is due to the inaccessibility to the inner surfaces of the host layers[77]. A solution to this problem is through exfoliating the individual layers of the materials producing nanosheets[71, 78, 79]. To this point LDH nanosheets have been produced through both bottom up and top down methods[71, 78, 79]. The bottom up method mainly consists of using synthesis to make the material. Here, an aqueous co-precipitation system is introduced into an oil phase with dodecyl sulphate (DDS) as surfactant and 1-butanol as co-surfactant. The reverse micelles act as nanoreactors, in which LDH single layers can be formed due to limited space and reagents[80].

Top down methods are much more frequently used with 'top-down' synthesis being the most common, despite this being difficult due to the charge density of LDHs being

significantly higher than that of other layered materials. This method requires modification of the LDH inter-layer environment and then selection of an appropriate solvent system, for example, ion-exchange intercalation of the LDH with anionic surfactant such as DDS[81]. Both these methods give largely monolayer nanosheets in reasonable quantities but suffer from the disadvantage that all involve multistep chemical processes and are quite time consuming. These issues will be addressed in chapter 5.

2.6.1 Nickel Hydroxide

Nickel hydroxide ($\text{Ni}(\text{OH})_2$) is an example of a LDH where $x = 0$ in the chemical formula in section 2.6 and thus exists in the form of $\text{M}(\text{OH})_2$ [82]. $\text{Ni}(\text{OH})_2$ has been a very well researched material that has origins in the 1950s and 60s[83, 84]. Originally there was an interest in the water/hydroxyl/oxyhydroxy content of thin/bulk nickel oxide films, leading to concepts such as bound water, water of composition, structural water and adsorbed water, and their importance for corrosion and battery performance[85]. This has been continued into modern day with more interest on 2D $\text{Ni}(\text{OH})_2$ as opposed to its bulk form[86].

There are two main polymorphs of $\text{Ni}(\text{OH})_2$, α and β , where the β phase is isostructural with brucite, i.e. $\text{Mg}(\text{OH})_2$ and occurs naturally as the mineral theophrastrite. α - $\text{Ni}(\text{OH})_2$ consists of layers of the beta form orientated parallel to the crystallographic ab-plane, i.e. the layers are not parallel, intercalated by water molecules. Both of these forms are layered and thus, in theory, can be exfoliated to produce one layer thick nanosheets[87, 88].

Similar to other LDHs, $\text{Ni}(\text{OH})_2$ has been mainly exfoliated using chemical synthesis methods and through ion exchange[77, 89]. A drawback of this is that it only works for the alpha phase as it requires intercalated ions within the layers or specially synthesised powders[82]. This occurs as the material requires intercalated anions in its interlayer space. The intercalated anions can be ion-exchanged with other anions of larger size which weaken the attraction between layers. This leads to exfoliation within a polar solvent where the solvent replaces the interlayer water molecules and weakens the strong hydrogen-bonding network, thus inducing the exfoliation. However, for β - $\text{Ni}(\text{OH})_2$ other methods are required as there is no interlayer ion that can be exchanged[90].

2.6.2 Applications of LDHs

As mentioned previously, research into the applications of LDHs nanosheets is a vibrant area of research. In 2007 Wang *et al.* fabricated the first thin film supercapacitor electrode from LDH nanosheets consisting of Co-Al hydroxide which had been exfoliated in formamide[91]. This led to a high specific capacitance of up to 2000 F/cm^3 (667 F/g), a good electrochemical stability, and a high-rate capability[91]. This impressive electrochemical behaviour was attributed to the special microstructure of the thin-film electrode and a more comprehensive investigation proved that the partial isomorphous substitution of Co^{2+} by Al^{3+} is the key factor in the electrochemical behaviour. This implies the need for two different metal ions but this application has also shown to be effective for single metal LDHs such as Ni(OH)_2 with specific capacitances of 1715 F/g [92]. As well as this, LDHs have been used in composite electrodes with carbon based materials to improve performance[93, 94, 95]. Carbon materials have high power densities and long life cycles but the small double layer capacitance limits its application[93]. LDHs have relatively higher capacitance and fast redox kinetics while the relatively low mechanical stability and cycle life are the major limitations[93].

LDHs have also shown excellent performance as catalysts for the oxygen evolution reaction. Currently, the state of the art materials are IrO_2 and RuO_2 but are limited by high cost[96, 97]. Monolayer nanosheets prepared from NiFe and NiCo LDHs have been shown to exhibit similarly high catalytic activity[73]. By exfoliating the nanosheets it is also possible to access the edge-sharing MO_6 octahedral layers, the putative active surface in metal oxides and hydroxides, detached from the bulk materials[70]. Unlike with electrodes for supercapacitors, where the enhancement of activity is due to an electrochemical surface area, improvement in oxygen evolution reaction (OER) activity from bulk to nanosheet is believed to be due to an increase in the number of edge sites and to higher electronic conductivity[73].

As the starting material for the synthesis of LDHs is cheap and readily available LPE is a very applicable exfoliation technique for this families use in applications, especially for single valence layered hydroxides such as Ni(OH)_2 or Co(OH)_2 where no synthesis is required.

2.7 Exfoliation of Layered Materials

The production of two dimensional nanosheets is the key component of 2D nanotech research[98]. This can be achieved through both 'bottom up' methods such as chemical vapour deposition and atomic layer deposition or 'top down' such as mechanical exfoliation and ion intercalation[14, 21, 33, 99, 100, 101]. The ability to be able to control the lateral size and thickness, the material shape, the morphology and the quantity whilst keeping the production costs cheap has been a major part of research in the field. However, no one technique has been able to combine all these points with specific approaches chosen based on the application being tested. For example, for detailed intrinsic characteristics of a material, material quality is of the utmost importance and so low yield methods such as mechanical exfoliation are used[14]. For circuitry or logic applications required for processing information, precise growth techniques such as epitaxy or CVD are viable options, but for applications where material quality constraints are relaxed but large quantities and low cost are important, liquid methods are more popular such as chemical exfoliation, ion intercalation and LPE.

2.7.1 Mechanical Exfoliation

Mechanical exfoliation of 2D materials was first used by Frindt in 1963 on MoS_2 , but most famously used by Geim and Novosolov in 2004 to exfoliate graphene from graphite[14, 102]. This is a simple method where a piece of scotch tape is adhered onto the surface of the graphite powder. A schematic of this is shown in Figure 2.8. It is then pulled away, removing graphene as the adhesive force of the tape is enough to overcome the Van der Waals bonds between the layers. These graphene layers can then be transferred onto a substrate such as ITO or Si/SiO_2 . In 2005 this method was extended to MoS_2 and NbSe_2 [33]. The nanosheets produced by this method are usually of very high quality, creating monolayers with lateral dimensions of 10s of microns. However the drawback of this exfoliation technique is that it is very slow and tedious with no scope for scale up, thus leading to a very poor yield.

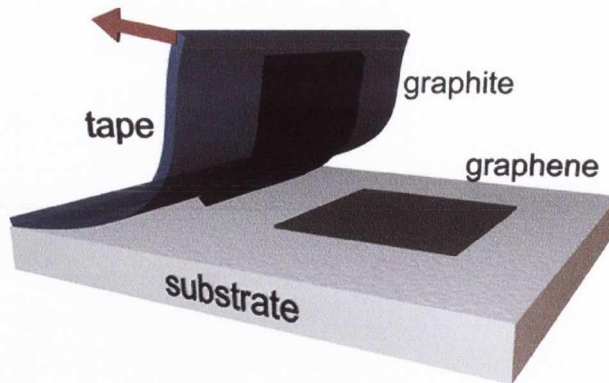


Figure 2.8: *Graphic demonstrating the mechanical exfoliation process.*

2.7.2 Chemical Vapour Deposition

2D materials, such as graphene and TMDs, are commonly produced by chemical vapour deposition (CVD)[99, 100]. Typically, the wafer (substrate) is exposed to one or more volatile precursors such as selenium vapour, which react and/or decompose on the substrate surface to produce the desired deposit. To produce graphene using CVD, a metal substrate (typically copper) is heated to an elevated temperature ($\sim 1000^{\circ}\text{C}$), 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. This method produces high quality graphene that is low in defects, while it is also possible to control the dimensions of the nanosheet[103]. Subsequently it has also been shown that TMDs can be produced using very similar methods; however, the process is slightly different, where a vapour-phase reaction occurs, using oxide precursors[104]. This process typically involves heating a precursor metal oxide (MoO_3 or WO_3) to obtain the required atomic metal followed by treatment using the desired gaseous chalcogen species e.g. S or Se (Figure 2.9)[105, 106].

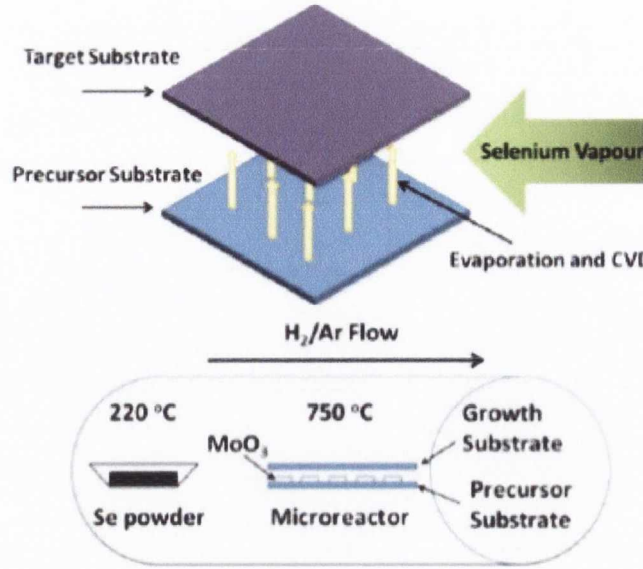


Figure 2.9: *Graphic demonstrating nanomaterial growth through chemical vapour deposition*[106].

2.7.3 Ion Intercalation

Ion intercalation is a method that has been used to delaminate nanosheets since the 1970s[107]. It works on the principle that layered materials can strongly adsorb guest molecules into the spacing between layers, creating what are called inclusion complexes. This method has been used on many of the layered materials such as graphite, TMDs and TMOs[104, 108, 109, 110, 111, 112]. The intercalation process weakens the bonding between planes by increasing the distance between them, thus reducing the energy required to separate the sheets, which is achieved through thermal shock or ultrasonication[77]. A schematic of this is shown in Figure 2.10. This can create large monolayers but there are limitations resulting from adsorbed ions that are sensitive to ambient conditions as well as difficulties in removing the ions from the nanosheets. This method is similar to ion exchange where ions that already exist between the layers of a crystal are exchanged with bulkier ions, thus weakening the interlayer bonds.

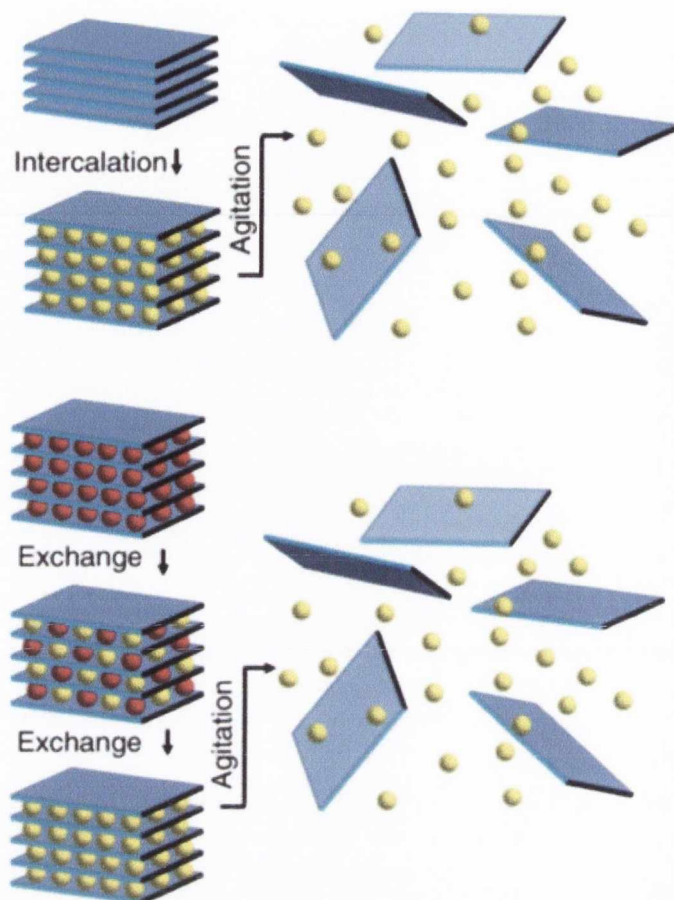


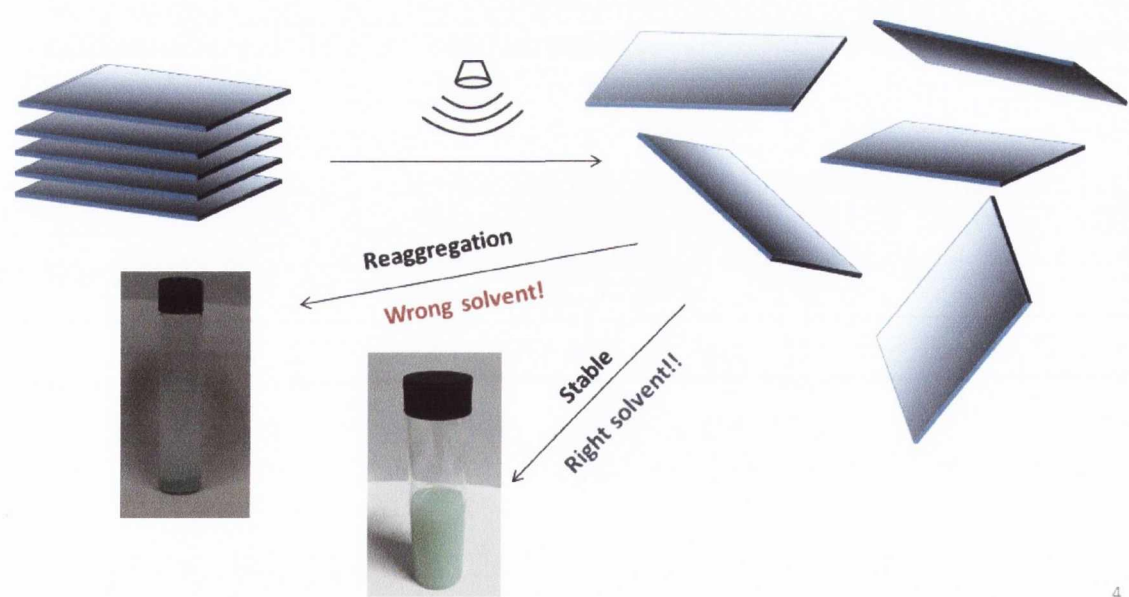
Figure 2.10: *Graphic demonstrating exfoliation of nanosheets through ion intercalation and ion exchange*[113].

2.8 Liquid Phase Exfoliation (LPE)

The methods mentioned above all have advantages and disadvantages with most centred around low throughput, difficulty of process and remaining contaminants. A relatively new method that addresses these issues, called liquid phase exfoliation, has been developed to exfoliate uncharged layered crystals into nanosheets[16]. LPE was first demonstrated in 2008 by Coleman *et al* when they exfoliated graphene from graphite through ultrasonication. The graphene nanosheets were then prevented from reaggregation through solvent-nanosheet thermodynamics (section 2.9) using NMP as a solvent[16]. Since this time, the methodology has drastically progressed and extended to several layered families such as hBN[114], TMDs[20, 115], TMOs[13] and black phosphorus[22]. Despite this there is still

a lot of advancements that can be made, such as extending the families exfoliated as well as improving its throughput.

In a perfect scenario a layered crystal is chosen and submerged in a suitably picked solvent and energy is added to the system, either in the form of ultrasonication or shear forces. If the energy is enough to overcome the Van der Waals bonds' cohesive force between the layers within the crystal, separation of individual layers will occur. After sufficient energy and time has been added to the system, a selection of mono- and multi-layer nanosheets ranging from two to twenty layers are stably dispersed in the solvent. However, solvents are not the only method of stabilisation, surfactant and polymer agents have also been shown to stabilise against reaggregation but for these methods the stabilisation mechanism is different. A schematic demonstrating this is shown in Figure 2.11. Unfortunately there is more to achieving a successful dispersion, it requires a careful selection of solvent or surfactant depending on the Hildebrand solubility parameter of the material, which is a measure of the degree of interaction between solute and solvent[13, 20, 44]. Also, to achieve the ideal throughput it is important to optimise the exfoliation parameters such as starting powder concentration and sonication time[13, 44].



4

Figure 2.11: Graphic demonstrating exfoliation of nanosheets through liquid phase exfoliation illustrating the effects of a good and bad solvent.

It should be noted that despite ultrasonication assisted LPE providing a relatively high throughput it is still unsuitable for industrial applications as increasing the volume of the dispersions decreases the exfoliation yield, this is due to the energy density decreasing. A solution to this was provided by Paton *et al.* in 2014 where shear mixing was used instead of ultrasonication[116]. Here a shear mixer induces high-shear laminar flow or localised turbulence causing the Van der Waals bonds to be broken which leads to delamination of the nanosheets (Figure 2.12). This method demonstrated that 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.



Figure 2.12: *Graphic demonstrating exfoliation of nanosheets through shear exfoliation.*

Interestingly, this work also showed that all that is needed for exfoliation is a minimum shear rate. Thus, any device that can provide this shear rate can exfoliate a layered material. This was demonstrated by using a kitchen blender[117].

One of the main advantages of LPE is that the production of nanosheets occurs in liquid. This is ideal for further processing such as film formation, spraying and ink-jet deposition to create supercapacitor electrodes and thin-films[12, 118]. This also makes them easily analysable using liquid based characterisation methods, where dimensional based metrics can be determined such as with MoS₂ using UV-vis spectroscopy[42].

2.9 Dispersion Theory

Dispersion theory is a key component of liquid phase exfoliation as it describes the physics and chemistry of the stabilisation process. Within this, two of the key methodologies of exfoliation are considered. Solvent exfoliation, pioneered by the initial work of Coleman *et al*, as well as electrostatic stabilising mechanisms, or surfactant exfoliation. The methods of exfoliation between the two are similar; however, the stabilisation mechanism preventing reaggregation is different. This thesis implements both methodologies to produce stable dispersions of nanosheets in solution.

2.9.1 Solvent Stabilisation

Solubility parameters are based upon a thermodynamic model which accounts for molecular interactions through vapourisation energy. The theory was initially developed by Hildebrand and then improved upon by Hansen, to capture the chemistry of mixing using a solubility parameter. It has been shown that by matching Hildebrand solubility parameters of a solvent and solute it is possible to stabilise a colloidal dispersion of nanomaterials[13, 20, 44]. This can be applied to LPE where it has been shown that different solvents can stabilise nanosheets with differing success. In the case of a nanomaterial having a vastly different Hildebrand solubility parameter to the solvent that it is dispersed in the nanomaterial will rapidly reaggregate causing sedimentation. Conversely if the parameters are the same or very close the nanosheets will be suspended and become a stable dispersion. The interaction is best understood via the Gibbs free energy, ΔG_{MIX} , which is the difference in the given free energy between a mixture of two components and the two components in their unmixed form and can be written as[119]:

$$\Delta G_{MIX} = \Delta H_{MIX} - T\Delta S_{MIX} \quad (2.1)$$

Where ΔH_{MIX} is the enthalpy of mixing, ΔS_{MIX} is the entropy of mixing and T is the temperature. For favourable mixing, Eq. 1 needs to be negative, thus ΔS_{MIX} needs to be large or ΔH_{MIX} needs to be small. For mixtures containing small molecules the entropy contribution can be very large but as a result of the nanosheets being big and rigid the entropy will be low and therefore it is necessary to minimise ΔH_{MIX} . To achieve this, it is first necessary to be aware of what it is comprised of [120, 121]:

$$\frac{\Delta H_{MIX}}{V_{mix}} = \frac{\chi\varphi(1-\varphi)kT}{\nu_0} \quad (2.2)$$

Where φ is the solute volume fraction, ν_0 is the volume of one molecule and χ is the Flory-Higgins parameter and is defined as [6, 122]:

$$\chi = -\frac{z}{2} \frac{(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})}{kT} \quad (2.3)$$

Where z is the coordination number of both solvent and solute and ϵ represents the strength of the inter-molecule pairwise interaction energy. The subscripts A and B represent the solute and solvent respectively. χ is a very important parameter and provides a method for controlling the dissolution of the nanosheets. From equation 2.2 and equation 2.3 it can be seen that as well as solvent-solute interactions, both solute-solute and solvent-solvent interactions must be accounted for also. Also, it can be seen that if $\chi < 0$, solute - solvent interactions are dominant, while if $\chi > 0$, the solute molecules (nanosheets) are attracted to each other. Thus, the smaller χ is, the stronger the attractive interaction between the solute and solvent, leading to a smaller ΔH_{mix} and more favourable mixing.

Intermolecular pairwise interactions are a difficult parameter to work with and thus it is more common work to with the cohesive energy, where ΔE_C can be defined as:

$$(\Delta E_C)_A = \frac{-z\epsilon_{AA}/2}{\nu_0} \quad (2.4)$$

The Hildebrand solubility parameter (δ) can be linked to this equation when it is taken into account that $\delta = \sqrt{(\Delta E_C)/V}$. Using this definition of the Hildebrand solubility

parameter and subbing equation 2.4 into equation 2.3, equation 2.3 becomes:

$$\chi = \frac{\nu_0}{kT}(\delta_A - \delta_B)^2 \quad (2.5)$$

Despite this being quite a nice result it doesn't show the whole picture as it only takes dispersive contributions into account. In reality there are also contributions from polar and hydrogen bonding interactions. Nevertheless, it is clear that matching of the solvent and nanosheet solubility parameter minimises the enthalpy of mixing. Applying this theory to CNTs or 2D nanosheets has shown good initial results but has mostly been empirical. In 2012, Hughes et. al derived an equation to describe the enthalpy of mixing for a graphene nanosheet[121, 123]. This derivation was modelled by accounting for the energy required to separate all individual nanomaterial layers and solvent molecules and combining this with the above theory. This resulted in an equation to describe the energy cost per unit volume of mixing[123].

$$\frac{\Delta H_{MIX}}{V_{mix}} \approx \frac{2}{T_{flake}} (\gamma_{nanosheet} - \gamma_{solvent})^2 \varphi \quad (2.6)$$

Where T_{flake} is the thickness of the nanosheet and $\gamma = \sqrt{E_{sur}^a}$ is the square root of the surface energy, or the energy required to form a unit area of surface at the interface, of a given phase 'a' and $\varphi = \frac{V_{nanosheet}}{V_{mix}}$. Therefore, equations 2.5 and 2.6 show that solvents having a surface energy or Hildebrand solubility parameter similar to a given 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 $\sim 41 \text{ mJ m}^{-2}$ [124]

As previously mentioned, equation 2.5 doesn't take into account the polar or hydrogen bonding contributions. The sum of the squares of these three contributions are equal to the square of the total Hildebrand solubility parameter (δ_T) and individually are known as Hansen solubility parameters, named after Charles Hansen who originally noted the limitations in Hildebrand's method[125]. Such that:

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (2.7)$$

Where δ_D , δ_P , δ_H are the dispersive, polar, and hydrogen bonding solubility parameters

respectively. Subbing this into equation 2.5:

$$\chi = -\frac{\nu_0}{kT}[(\delta_{D,A} - \delta_{D,B})^2 + (\delta_{P,A} - \delta_{P,B})^2 + (\delta_{H,A} - \delta_{H,B})^2] \quad (2.8)$$

This equation now gives a way to quantify the stability of the nanosheets versus different solvents. Where by matching different Hansen solubility parameters will minimise $(\delta_A - \delta_B)^2$ and ultimately minimise the enthalpy of mixing resulting in a stable dispersion. With the knowledge behind this stabilisation method, other materials such as TMDs and TMOs have been exfoliated using liquid phase exfoliation[20, 13]. There is still a range of materials that can be exfoliated such as III-VI metal chalcogenides. This approach is used in chapter 4 to provide a solvent screening process for a layered material.

2.9.2 Surfactant Stabilisation

The second exfoliation method used in this thesis is through surfactant stabilisation. A surfactant is a long chain molecule that contains an amphipathic structure where there is a polar head group and a non-polar tail group. As surfactant exfoliation is performed in water it could also be characterised as having a hydrophilic head group and hydrophobic tail group, as shown in Figure 2.13. Thus, in liquid phase exfoliation, the head group is attracted to the non-polar material, in this case the nanosheet, and the tail group orients itself with the polar phase[115, 126].

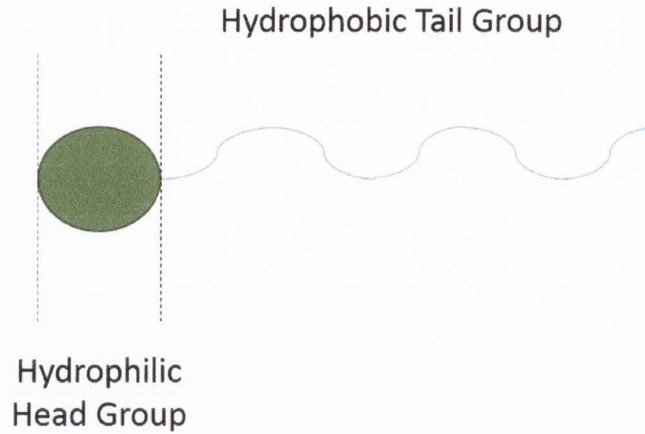


Figure 2.13: *Reconstruction of a standard surfactant chain with hydrophobic tail group and hydrophilic head group.*

When surfactants are dissolved in water the non-polar tail group disrupts the structure of the liquid, increasing the free energy of the system. The system then responds in order to minimise contact between the hydrophobic tail and the water by breaking down the hydrogen bonds between the water molecules. As a result of this, some of the surfactant molecules accumulate at the interface of the system causing a single layer of surfactant molecules along the surface of the water[126]. Due to the hydrophilic group the surfactants won't be completely expelled from the liquid. As the surfactant concentration increases the molecules that haven't been expelled to the surface, to reduce the energy in the solution, accumulate together by orienting the head groups into the centre of a surfactant sphere surrounded by tail groups. When these aggregates are fully formed they are known as micelles and occur at the critical micelle concentration of a surfactant (CMC).

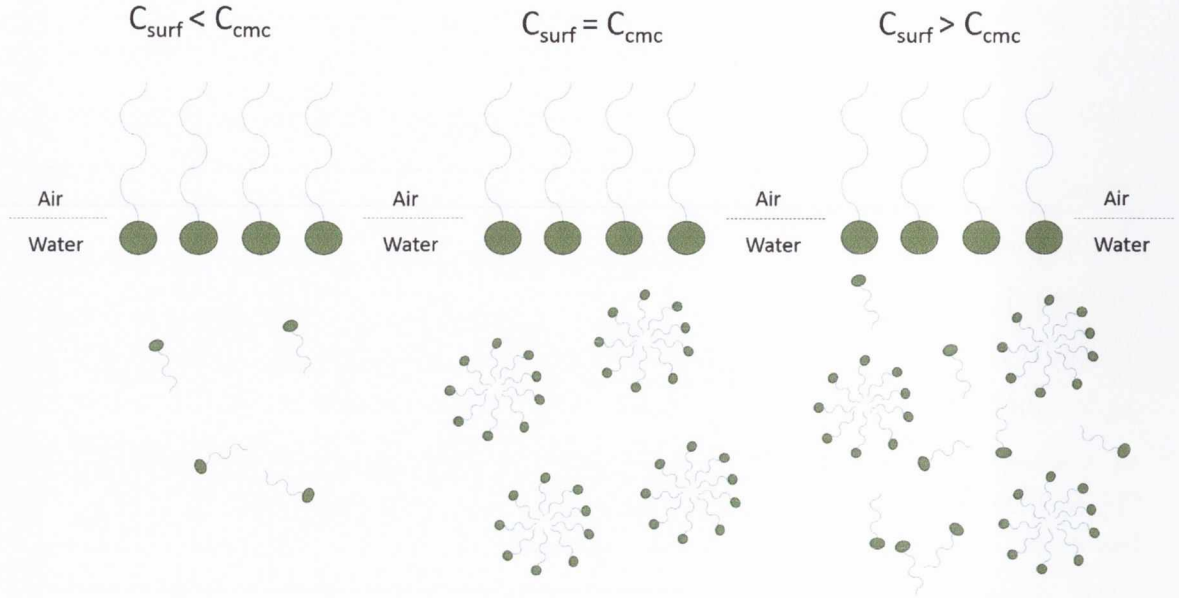


Figure 2.14: Demonstration of the orientation of surfactant molecules in water in the examples of $C_{surf} < C_{CMC}$ where the molecule orientate themselves to the surface with some excess surfactant in the liquid, $C_{surf} = C_{CMC}$ where the molecules orientate themselves to the surface with excess surfactant molecules creating micelles and $C_{surf} > C_{CMC}$ where the situation is the same as $C_{surf} = C_{CMC}$ but there are also excess molecules.

However, when the concentration of the surfactant is increased beyond the CMC there are charge screening effects and depletion interactions between the molecules, thus making the CMC the ideal concentration[127]. This is shown in Figure 2.14. The surfactant concentration at which the CMC occurs changes for all surfactants as well as being dependent on properties such as temperature and pH[126].

Surfactants are very commonly used to stabilise nanosheets against reaggregation. The tail bonds to the nanosheet as it is more attracted to the material than it is to the liquid. As most surfactants used in LPE are ionic such as sodium cholate (SC) or sodium dodecyl benzenesulfonate (SDBS) this creates a charge on the nanosheet. This charge is balanced by a counter ion of the tail group which is pushed away by Brownian motion but stopped from completely separating by the electrostatic attraction, thus creating a charge around the nanosheet. If this charge is large enough it will successfully repel the nanosheets from each other and prevent reaggregation. This charge distribution around the nanosheet produces a potential difference; the electrical double layer (EDL)[126].

The physics of the double layer was studied by Derjaguin and Landau and indepen-

dently by Verwey and Overbeek and is known as DLVO theory. They theorised that for dispersed spherical particles, assuming a balance between repulsive and attractive potential energies, that the attractive force is due to Van der Waals interactions and the repulsive force is due to the EDL. Thus, to disperse the particles the repulsive force must be greater than the attractive force[128]. The total potential energy of attraction, V is the sum of the the potential energy of attraction, V_A and repulsion, V_R

$$V = V_A + V_R \quad (2.9)$$

V_A in a vacuum for two spheres, radius r , at a distance D apart can be given as

$$V_A = -\frac{Ar}{12D} \quad (2.10)$$

Where A is the Hamaker constant.

V_R depends on the size and shape of the dispersed particles, the distance between them, the Zeta potential, ζ , the dielectric constant of the dispersing liquid, ϵ_r , and the effective thickness of the electrical double layer known as the Debye screening length, κ^{-1} where[128]

$$\kappa^{-1} = \left[\frac{\epsilon_r \epsilon_0 kT}{2e^2 n_0} \right]^{1/2} \quad (2.11)$$

and n_0 is the number of surfactant molecules per volume. For two small particles of radius r when $\kappa r \ll 1$

$$V_R = \frac{\epsilon_0 \epsilon_r r^2 \zeta^2}{D} e^{-\kappa D} \quad (2.12)$$

Substituting equation 2.9 and 2.11 into this equation gives

$$V = \frac{\epsilon_0 \epsilon_r r^2 \zeta^2}{D} e^{-\kappa D} - \frac{Ar}{12D} \quad (2.13)$$

Therefore, for a stable dispersion the zeta potential must be high in order to prevent reaggregation. Typically values of $-30mV < \zeta < 30mV$ are necessary to prevent reaggregation. The sign just indicates whether the surfactant is anionic or cationic.

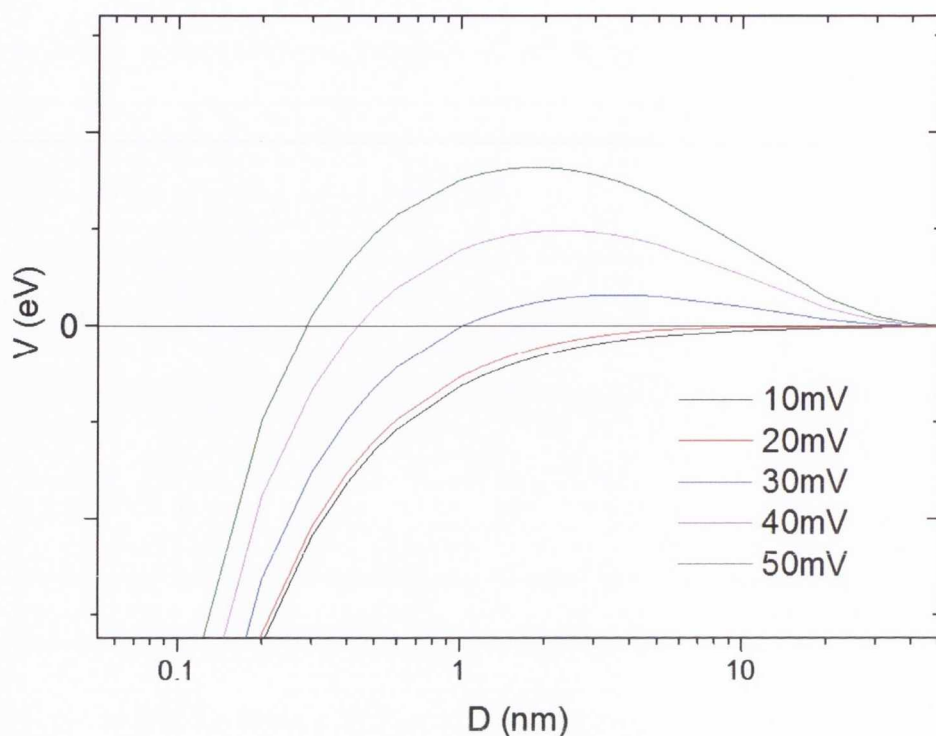


Figure 2.15: A plot of total potential energy (both attractive and repulsive forces) vs separation.

When V is plotted against the separation D , as can be seen in Figure 2.15, there is a deep potential well for small values of D that decreases in energy for decreasing values of zeta potential. If the particles overcome this barrier the attractive force dominates and the particles bond together. For $\zeta < 30\text{mV}$ the potential well disappears thus making it far easier for reaggregation to occur due to steric hindrance where the surfactant molecules become too close together. Although this model is only for spherical particles and not planar objects, whose repulsive term will change depending on orientation, it still gives a general idea on the physics behind the process. This theory is used in chapter 5 and 6 to exfoliate layered double hydroxides as well as for three 'unconventional' materials.

Chapter 3

Materials & Methods

3.1 Introduction

Discussed in this chapter is the sourcing of the materials used in this thesis, as well as the methods used to exfoliate and characterise them. The work throughout is mainly on the production of 2D nanosheets, which is achieved by exfoliating layered crystals in a liquid using sonic energy or shear forces. The resultant nanosheets are then stabilised by an appropriate solvent or by surfactant. The solution is highly polydisperse, with nanosheets ranging from less than 50 nm to greater than 1 μm . These nanosheets can either be size selected using a controlled centrifugation regime or the non-exfoliated materials can be removed using a simple centrifugation process to produce a 'standard' dispersion. The resulting dispersions are then decanted and characterised using a variety of methods, the fastest and most used is absorption spectroscopy that can be used to determine concentration, thickness, and lateral length. Microscopic techniques can also be used such as transmission electron microscopy or scanning electron microscopy for statistical and qualitative analysis.

3.2 Materials

A number of materials were used for this project and were mostly purchased from Sigma Aldrich. Initially, they were bought at the highest available purity but for the latter part of the thesis a washing method was developed that obviated the need for very high quality

powder. All surfactants and solvents were purchased from Sigma Aldrich.

3.3 Production of 2D Nanosheets

2D materials have been shown to exhibit vastly superior properties to their bulk counterparts [129]. For example, graphene has incredible physical characteristics such as high strength and electrical conductivity but graphite, which is comprised of stacked layers of graphene, only has moderate physical characteristics[2, 14, 130, 131, 132]. Thus, it is necessary to exfoliate layered materials into nanosheets by breaking the weak, out of plane van der Waals bonds. In this work, ultrasonication in an aqueous medium is used to accomplish this but it can also be achieved through other methods such as micro-mechanical exfoliation[14, 102]. During sonication, the sonic energy is transmitted through the liquid by ultrasound waves, which as they cross the medium will cause the molecules in the liquid to oscillate about their mean position. When the negative pressure caused by an ultrasonic wave crossing a liquid is large enough, the distance between the molecules of the liquid exceeds the maximum molecular distance required to hold the liquid intact, causing voids or cavitations to be formed (i.e. bubbles). These bubbles expand through a few acoustic cycles before violently collapsing on compression, causing a high energy cavitation field, as demonstrated in Figure 3.1. Any material in the area of this field will be subject to high shear forces which will exfoliate the material, producing nanosheets. These nanosheets or nanotubes are then stabilised against reaggregation via electrostatic or energetically favourable solution interactions (as mentioned in section 2.7)[6, 15, 16, 19, 104, 121, 125, 130, 131, 133, 134, 135].

This method has been shown to work on a range of materials both 1D and 2D[5, 6, 13, 16, 20, 22, 44, 90, 115, 136, 137]. In practice, this method is achieved by mixing the powder in an appropriate solvent or surfactant and then sonicating for a fixed length of time using an ultrasonic tip or bath. Centrifugation is then used to remove the unexfoliated nanosheets which sediment much faster. The supernatant, which is usually a deep colour, is then decanted and kept for further analysis.

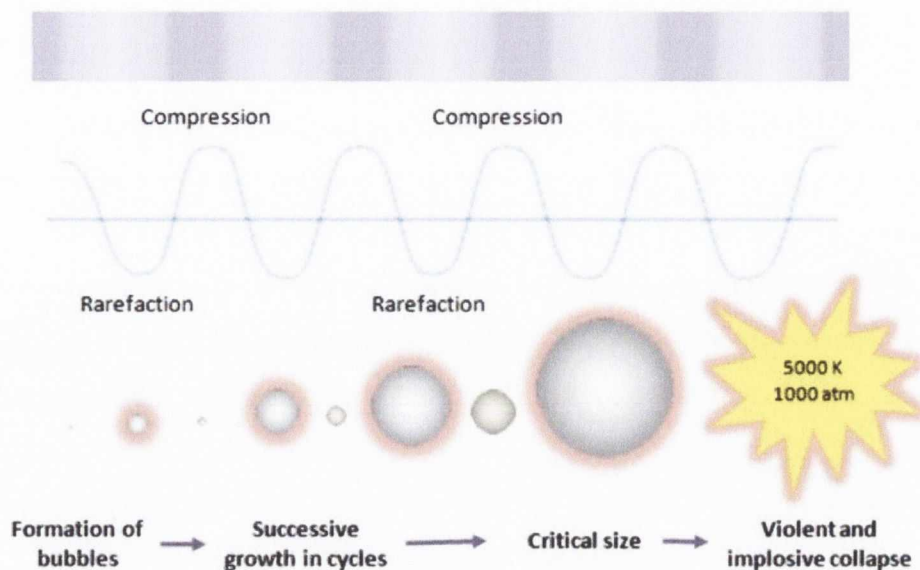


Figure 3.1: *Representation of the cavitation bubbles increasing before implosion.*

Although both bath and tip sonication can be used, tip sonication is a far more effective method as it operates at 750 W versus 25 W - 100 W, thus it will take less time to achieve the same degree of exfoliation. Also, the power output for a bath varies with position due to localised hot spots, thus making the position of the sample in the bath a large impact on reproducibility. In this thesis this impact is reduced by applying a rotor system that rotates a number of samples around a given axial point thus ensuring that all samples achieve the same degree of exfoliation.

3.3.1 Centrifugation Regime

After sonication, the exfoliated nanosheets are comprised of a range of lateral sizes and thicknesses. As well as this, the dispersion is quite polydispersed as all the material won't have been exfoliated. These particles will sediment at different rates due to different buoyancy, drag and gravitational forces acting on them[138]. This is governed by the equation

$$T_{sed} = \frac{9L\eta}{2r^2 (\rho_{ns} - \rho_s) g} \quad (3.1)$$

Where, T_{sed} is the time it takes for the particle to sediment, L is the length of the vial, η is the viscosity of the fluid, r is the radius of the particle and ρ is the density of the solvent or the particle (nanosheet). The time for the particle to sediment to the bottom of the vial is determined by the density of the particle and the viscosity of the solvent. It is important to note here that that this theory is derived for spherical particles but can still be used to separated 2D nanosheets by mass.

There are three distinct phases of nanosheets, consisting of unexfoliated material, partially exfoliated material which consists of large, thick nanosheets, and well exfoliated thin nanosheets which won't sediment. These species will sediment at different rates with the unexfoliated material sedimenting quickly, the exfoliated material not sedimenting at all, and the partially exfoliated material sedimenting slowly due to their large mass. These sedimentation rates can be controlled by being aware of the time constants that govern the process and can be modelled as:

$$A = A_{stable} + A_{quasi-stable}e^{-\frac{t}{\tau_1}} + A_{unstable}e^{-\frac{t}{\tau_2}} \quad (3.2)$$

Where τ_1 is the time constant belonging to the quasi stable material and will be quite long and τ_2 is the time constant belonging to the unstable material and will be very short. The stable material doesn't have a time constant as it is prevented from sedimentation through buoyancy and solvent or surfactant interaction depending on the type of dispersion. Thus, to only remove unexfoliated material it is only necessary to wait a short time but to obtain a dispersion with well exfoliated nanosheets it requires a much longer time[13].

Allowing the nanosheets within a dispersion to sediment is a slow process and doesn't allow a lot of control. Centrifugation is a method that overcomes both of these issues. Centrifugation involves rotating a liquid sample about a fixed axis, with the centripetal force being applied perpendicular to the axis. It is possible to model equation 3.2 to centrifugation by undertaking a series of different centrifugation steps at varying speed (RPM) and time and subsequently measure the dispersed nanosheet concentration[139]. This methodology is used in chapter 4 to obtain a stable dispersion of gallium sulphide.

As RPM is a relative measure to individual centrifuges and is dependent on the rotor size it is useful to convert it to relative centrifugal force (RCF) as it can be used across rotors of differing radii. During centrifugation a centripetal force is applied where the

acceleration due to this force is measured in multiples of g, giving a dimensionless quality

$$RCF = \frac{\omega^2 r}{g} \quad (3.3)$$

or more simply

$$RCF = 1.118 \times R \times \left(\frac{RPM}{1000} \right)^2 \quad (3.4)$$

Where R is the radius of the rotor and is in mm.

3.4 UV-vis Spectroscopy

3.4.1 Extinction Spectroscopy

Light interacts with matter in a multitude of ways and is one of the fundamental processes in physics. Of interest in this work is the interaction of light with suspended nanosheets in solution, and most notably the absorption and scattering of light. Both scattering and absorption remove energy from a beam of light traversing through a medium[140]. This attenuation is known as extinction. When a light beam is passed through a sample, the intensity of the beam will be decreased due to absorption or scattering effects[141]. This is the basis of UV-vis spectroscopy where a cuvette containing a dispersion is placed into a holder within the spectrometer and is exposed to light of different wavelengths. This can cause two phenomena within the sample, photon absorption, which occurs at different energies by exciting an electronic transition within the material or light scattering[140, 142]. The light that passes through the sample is then collected and the difference in irradiance is detected and measured as an increase in absorption.

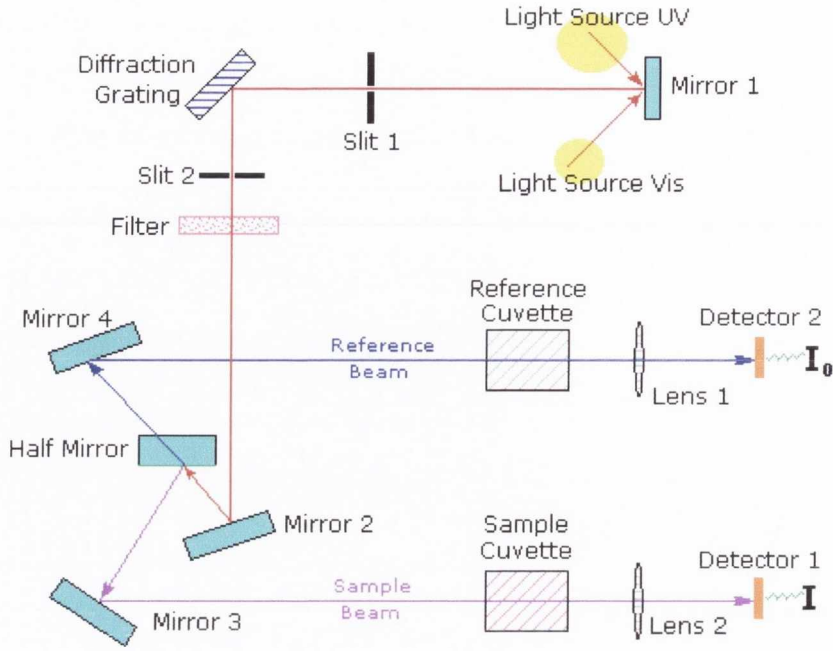


Figure 3.2: A schematic of a standard UV-vis spectrometer.

A schematic of a typical UV-vis spectrophotometer is shown above in Figure 3.2. The physics behind the operation of this device is best described by the Beer-Lambert Law[143], where, if the intensity of the light passing through a medium is reduced by dI on passing through a sample length dl (Figure 3.3):

$$dI = -\rho I C dl \quad (3.5)$$

Where ρ is a constant and is dependent on the material and C is the concentration of the sample. Integrating over the length of the sample

$$\int \frac{dI}{I} = -\rho \int C dl \quad (3.6)$$

$$\ln \left(\frac{I}{I_0} \right) = -\rho C l$$

This can be simplified further by defining $\rho = \epsilon \ln(10)$ and rewriting in $\log_{10}$

$$\log_{10} \left(\frac{I}{I_0} \right) = -\epsilon C l$$

Where ϵ is the extinction coefficient of the material. This can be converted to absorbance A using $A = -\log_{10}(T) = \log_{10}\left(\frac{I_0}{I}\right)$ giving the more useful Beer-Lambert equation

$$A = \epsilon CL$$

This is a very useful equation as it can be used to determine the concentration of a dispersion when the extinction coefficient is known.

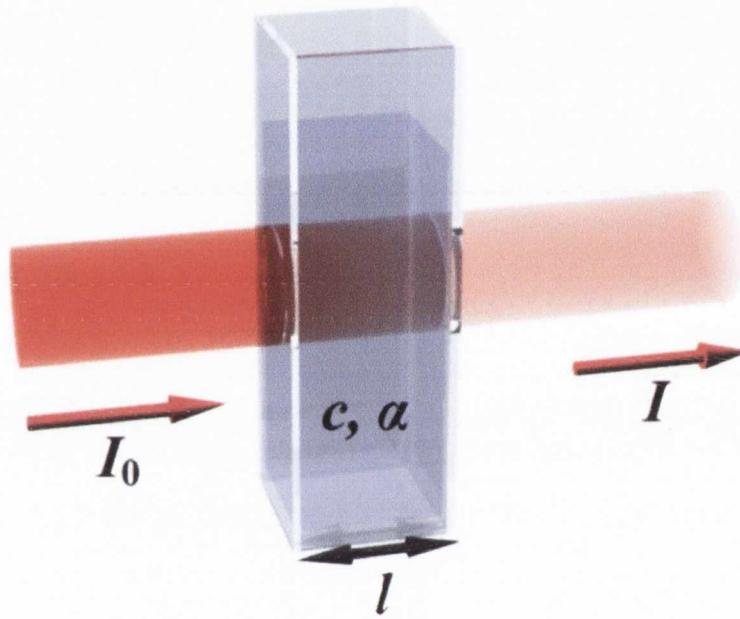


Figure 3.3: Schematic representation of the Beer-Lambert law process where the intensity of the light decreases with increasing cuvette path-length.

Extinction spectroscopy is a very useful tool as it can be applied to many different cases. As mentioned previously it can be used to determine the concentration of a dispersion but can also be used to develop metrics to determine the size of the nanosheets[42, 43]. These methods are used in all results chapters of this thesis.

3.4.2 Absorption Spectroscopy

As mentioned previously extinction spectroscopy accounts for both absorption of photons by the material as well as the photons that have been scattered. In most instances this isn't

an issue as a lot of UV-vis spectroscopy is performed on molecules in liquid samples that don't scatter incident light. As a result, the terms extinction and absorption spectroscopy can be used interchangeably but for the case of colloidal dispersions such as nanosheets suspended in solution it is important to differentiate between the two. This is achieved by using a simple equation

$$\epsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda) \tag{3.7}$$

Where $\epsilon(\lambda)$ is extinction, $\alpha(\lambda)$ is absorption and $\sigma(\lambda)$ is scattering. This is an important distinction as depending on particle size, the spectra for any given nanomaterial can change drastically, especially for materials such as BN that don't absorb any light between 300 nm and 800 nm but has a very bright white colour due to the photons being scattered[144].

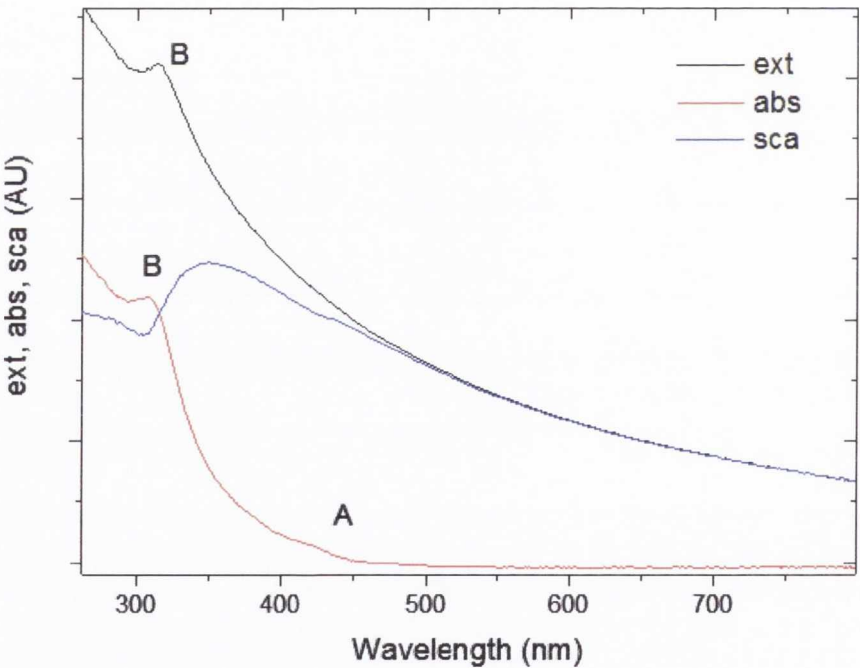


Figure 3.4: Plot of extinction, absorption, scattering spectra for gallium sulphide showing the effect that scattering has on the extinction spectra.

As can be seen in Figure 3.4 there is a noticeable difference between extinction and

absorption, where the peak due to the B exciton is visible in both but the A exciton has been completely superimposed by scattering in the extinction spectrum as well as there being no absorption between 450 nm and 800 nm. In order to overcome this issue and remove the scattering contribution from the extinction spectra it is necessary to use an integrating sphere attachment with a UV-vis spectrophotometer. The sphere itself is approximately 150 mm in diameter and the internal walls are covered with a diffuse white reflective coating. The coating acts as a way to insure that there is a maximum internal reflectance of the beam. A schematic is shown below in Figure 3.5

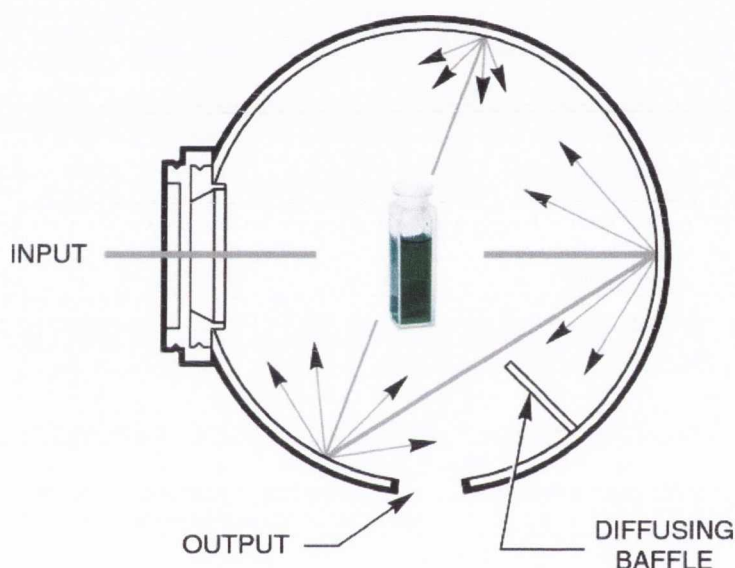


Figure 3.5: Schematic representation of an integrating sphere with cuvette in centre where the scattered light is reflected within the sphere and is detected as transmitted light.

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 and the transmission of the beam (lower intensity). The advantage of the integrating sphere over a standard UV-vis spectrophotometer is that the UV-vis only measures a change in intensity of the beam, thus all scattered light is measured as absorbance as it is lost after leaving the sample. In the case of an integrating sphere the scattered light is reflected by the coating on the inside of the sphere. The reflectance causes the intensity level to reach a steady state

(A diffusing baffle is used to stop direct light entering the detector before this happens). Therefore, reflectance is uniform 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 unit less quantity. This quantity is known as the sphere multiplier and accounts for the multiple scattering events inside the sphere[145].

$$L = \left(\frac{\Phi}{\pi A_s} \right) \left(\frac{\rho}{1 - \rho(1 - f)} \right) \quad (3.8)$$

Where (L), is defined in terms of the radiant flux (Φ), the reflectance (ρ), 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.

By using the integrating sphere it is possible to measure pure absorption as shown in Figure 3.4. This can be used for more exotic excitonic measurements and can be used for metric based measurements, as well as this it can be used as a more accurate measure of concentration as the extinction coefficient is very size dependent for certain materials such as the layered double hydroxides and can make exact measurements tricky.

3.4.3 Scattering Spectroscopy

The third variable of equation 3.7 is the scattering component. Up to this point, extinction, and to a lesser degree absorption spectroscopy, have been used successfully to characterise 2D nanosheets in solution. The third component, scattering is a far less well known characteristic for 2D nanosheets and can give a lot of important information about the nanosheets[42]. In LPE samples there are two distinctive scattering effects that can occur, Rayleigh scattering and Mie scattering[42, 44]. Rayleigh scattering is the elastic scattering of light particles much smaller than the wavelength of the incident light ($<1/10$ wavelength) and scatters light equally in all directions. It was first described by Lord Rayleigh in 1881 and can be given as

$$\sigma_s = \frac{2\pi}{3} \frac{d^6}{\lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (3.9)$$

Where σ_s is the Rayleigh scattering cross section, d is the diameter of the spherical particle, n is the refractive index of the material and λ is the wavelength of the light. It is clear that for σ_s to be high λ must be low i.e. short wavelengths scatter more light than long wavelengths. A real life example of this is the colour of our sky, where the small particles in the atmosphere scatter more blue light ($\lambda \sim 350$ nm) which are detected by our eyes than red light ($\lambda \sim 650$ nm).

Mie scattering is dominant for larger particles where the size of the particle is approximately that of or greater than the wavelength of the incident lights. Unlike Rayleigh scattering, Mie scattering isn't largely particle size dependent with the exception that larger particles will scatter more light in the forward direction, as shown in Figure 3.6.

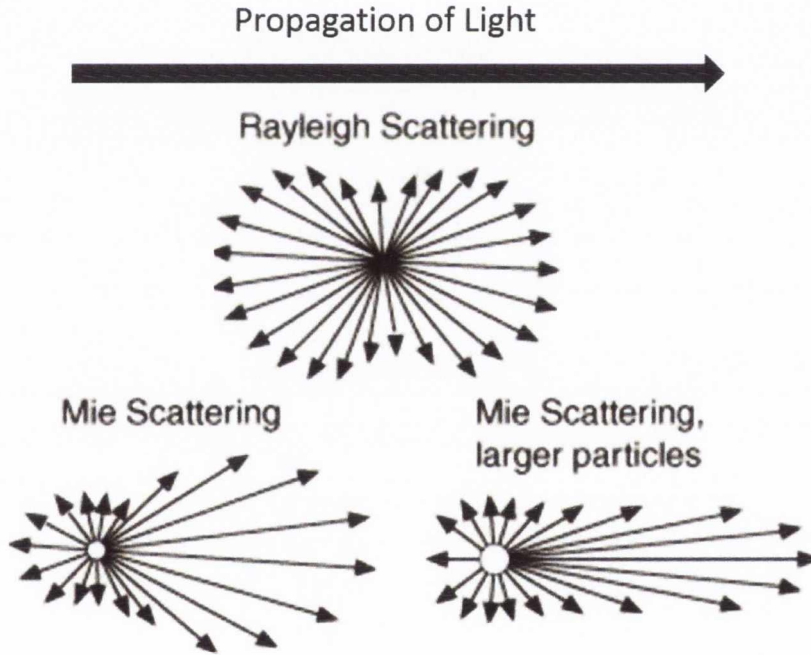


Figure 3.6: *Scattering effects of particles as dictated by Mie and Rayleigh theory.*

In LPE samples there is a contribution from both Rayleigh and Mie scattering depending upon the spectral position and the size of the nanosheets. This can be easily seen in the

scattering spectra of medium sized nanosheets, 200 nm - 600 nm, for most materials where the scattering exponent, which is expected to be 4 for Rayleigh scattering, is between 1-4. This range of values make it possible to determine lateral metrics for the nanosheets.

3.5 Raman Spectroscopy

Raman spectroscopy was first developed by Venkata C. Raman in 1928, the physics of which was awarded a Nobel prize in 1930. It has since become one of the most important characteristic techniques for chemical species[146]. Where Rayleigh scattering is an elastic phenomenon, Raman spectroscopy is based on the inelastic scattering of photons, where the photon of incident light interacts with a sample producing 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. In regards to LPE it is also possible to discern the level of damage done to the nanosheets during exfoliation as well as the proportion of defects within the nanosheets[13, 16, 22, 44, 147].

This technique involves shining a monochromatic light upon a sample which can be either absorbed, reflected or scattered. If the photon is scattered it has been absorbed by the material and reemitted and thus has interacted with either the electron cloud or a nucleus within the material, potentially causing an energy change. If only electron cloud distortion is involved in the scattering process the scattering will be elastic, as with Rayleigh scattering, due to the relatively light electrons but if lattice vibrations are induced, energy will be transferred either from the incident photon to the molecule or from the molecule to the scattered photon. This is an inelastic process and is Raman scattering. The Rayleigh scattered light is filtered and not detected so that the Raman scattered light can be detected and analysed[148].

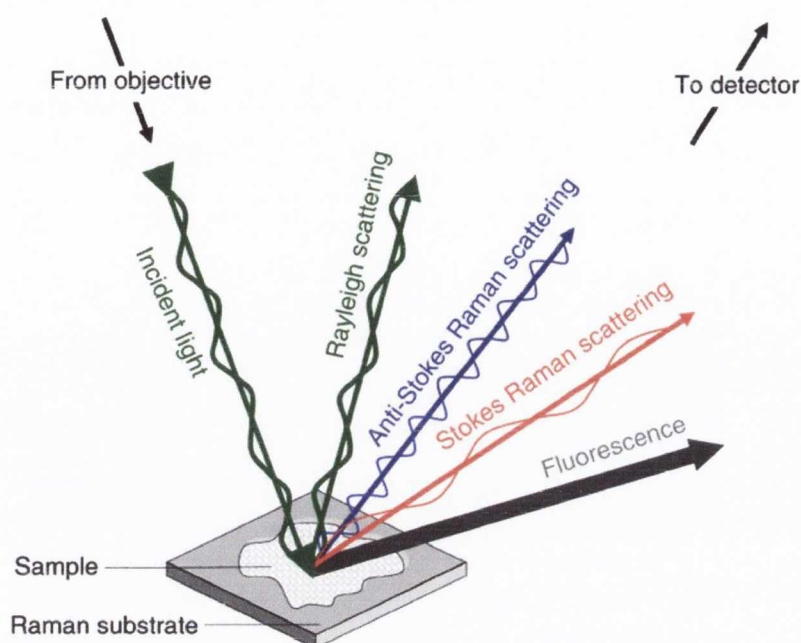


Figure 3.7: *Light interacting with a sample and exhibiting Raman scattering.*

There are two principle types of Raman scattering, Stokes and Anti-Stokes scattering, as shown in Figure 3.7.[148]. The most common of these is Stokes scattering which is where the molecule is excited from the ground state to a higher energy excited state and relaxes to a higher vibration state than the ground state causing a decrease in energy for the scattered photon. However, due to thermal energy, some molecules exist in an excited state, scattering from these states to the ground state causes an energy transfer to the photon giving rise to anti-Stokes scattering[148]. These process can be observed in the Jablonski diagram below (Figure 3.8).

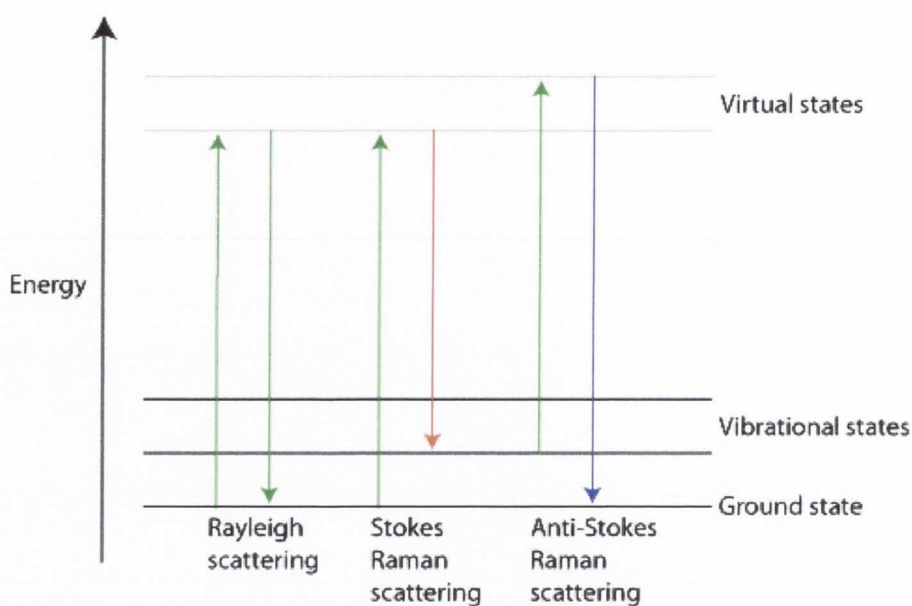


Figure 3.8: *Jablonski diagram demonstrating Stokes and Anti-Stokes scattering.*

3.6 X-ray Photoelectron Spectroscopy (XPS)

Similar to Raman spectroscopy, XPS is a very useful tool to determine the elemental composition of a material as well performing stoichiometric analysis on a compound[22, 149]. XPS is commonly used as a surface science technique where the composition of the surface of a material can be found to determine quality of the film, purity and oxygen content[44]. For this thesis it is most commonly used to determine the level of oxidation in the material as well as discovering any other impurities and to get quantitative information on the stoichiometry of the sample.

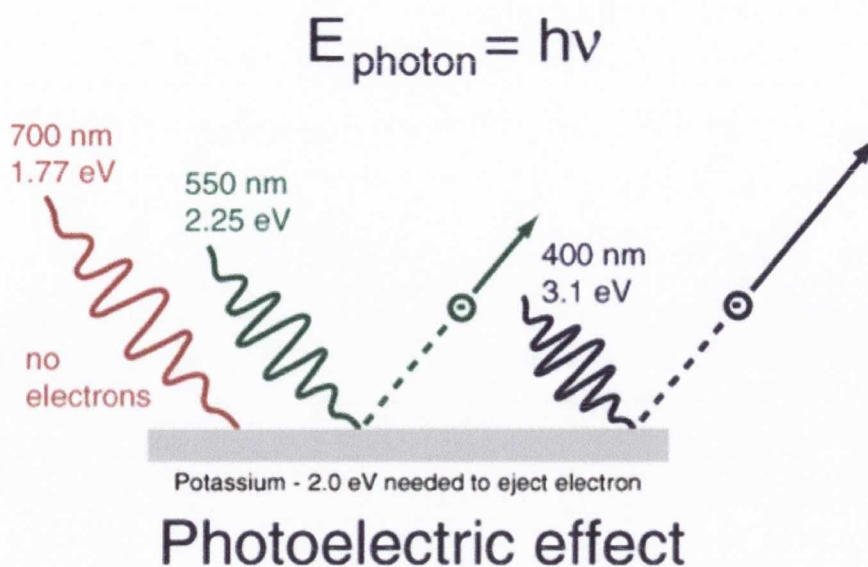


Figure 3.9: *Diagram of the photoelectric effect, the basis of XPS.*

The principle behind XPS is the photoelectric effect, where if light is shone onto a material the energy transfer from the photon to the electron causes the electron to escape from the material as a free electron, as shown above in Figure 3.9. This electron then has a kinetic energy depending on the energy of the incident photon, the binding energy and the work function of the material as given by:

$$E_k = hf - (\Phi + E_B) \quad (3.10)$$

Where E_k is the kinetic energy, hf is the photon energy, Φ is the work function and E_B is the binding energy[150]. As the work function and the binding energy of the electron will be dependent on the material, thus by measuring the kinetic energy of the electron the material composition can be discovered.

An XPS operates by shining X-rays onto a material in vacuum. When an X-ray photon hits and transfers this energy to a core-level electron, the electron is emitted from its initial state with a kinetic energy dependent on the incident X-ray and binding energy of the atomic orbital from which it originated. The energy and intensity of the emitted photoelectrons are analysed to identify and determine the concentrations of the elements present. These photoelectrons originate from a depth of < 10 nm therefore the informa-

tion obtained is from within this depth[150].

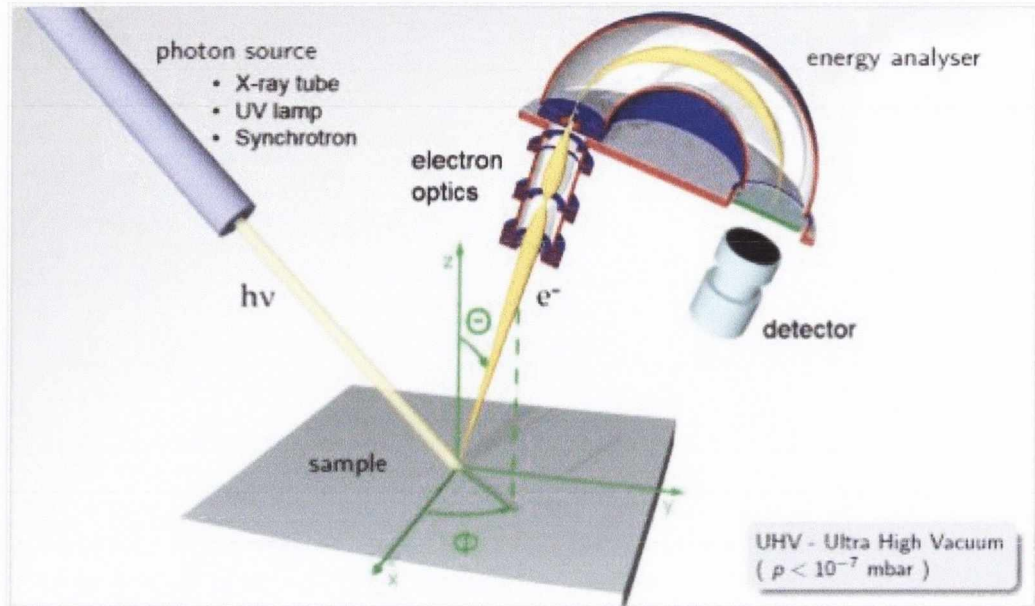


Figure 3.10: *Schematic of an XPS spectrometer.*

This penetration depth depends on electron interaction with matter characterised by the energy dependent inelastic mean free path λ as given by the equation

$$I = I_0 e^{-\frac{x}{\lambda}} \quad (3.11)$$

Generally for XPS, 3λ is used as a penetration depth as this ensures that 95% of all photoelectrons have been scattered before reaching the surface. By correlating λ and the kinetic energy of the electron this gives very good information of the species being irradiated[150]. A schematic of an XPS is shown above Figure 3.10.

3.7 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a very important tool for LPE samples as it gives visual information on the quality of the nanosheets after exfoliation[13, 16, 20, 22, 44, 90, 98, 115, 134]. 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. The work in this thesis was done using bright field low resolution imaging but there are many other methods available when using TEM.

The resolution of an optical microscope is limited by the wavelength of visible light which can only give a resolution of 200 nm - 400 nm which is far too large for most nanomaterials. In 1927 De Broglie theorised that electrons exhibited wave like behaviour and this was individually confirmed by Davisson and Germer, and Thomson and Reid through electron diffraction experiments. This led to the belief that instead of photons, electrons could be used for microscopy as the wavelength of an e^- is given as

$$\lambda = \frac{1.22}{E^{1/2}} \quad (3.12)$$

where λ is the electron wavelength and E is the electron energy. From equation 3.12 it is possible to work out that for a 100 keV electron, a wavelength of 1.4 pm (0.004 nm) and a resolution of 2 pm is possible, which is much smaller than the diameter of an atom. This resolution has yet to be achieved though, with values of 0.1 nm much more realistic but still much superior resolution than optical microscopes.

TEM operates by projecting an electron beam through a column of electromagnetic lenses onto a sample. These electrons then interact with the sample and can produce many secondary signals such as auger electrons, secondary electrons, backscattered electrons etc. More importantly to TEM, the electron can also, either be completely transmitted through the sample or transmitted through the sample whilst being scattered, elastically or inelastically (Figure 3.11). The electrons that are transmitted by the specimen are then detected by a CCD camera and converted to an image[151].

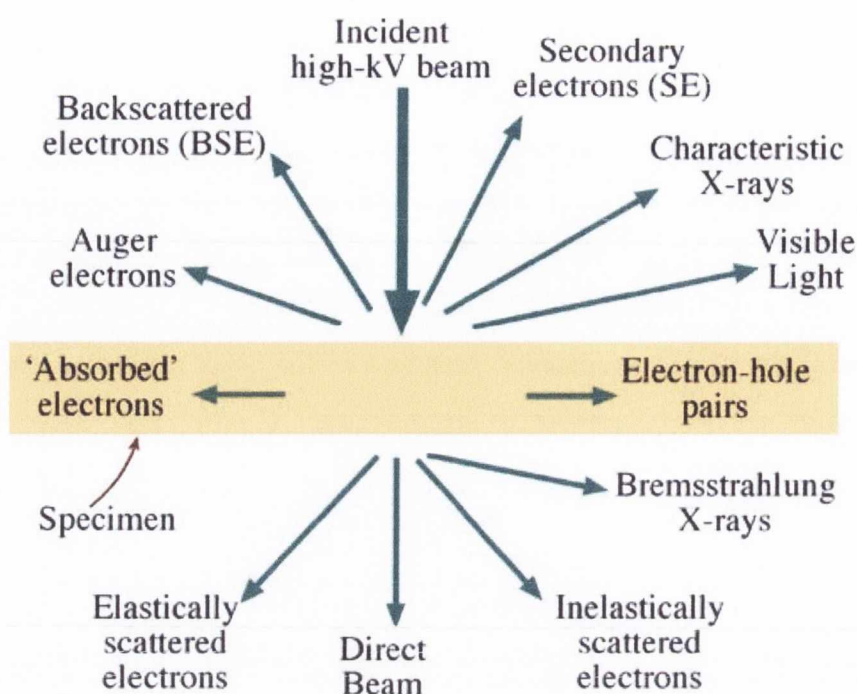


Figure 3.11: Possibilities of the outcome of electrons incident on a material.

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)[151]. 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 can be up to 1,000 times smaller and 100 times brighter. In this work, all low resolution TEM was conducted on a Joel 2100 operated at 200 kV using a LaB₆ filament while high resolution TEM (HRTEM) was conducted on a field emission FEI-Titan operating at 300kV. The beam is then passed through a condenser lens where it is focused on the sample. Here, the beam is scattered and passes through an aperture, where only a certain fraction of the electrons are permitted through. Finally, the beam is focused by a projector lens and focused onto a screen or CCD[151]. A schematic is shown below in Figure 3.12.

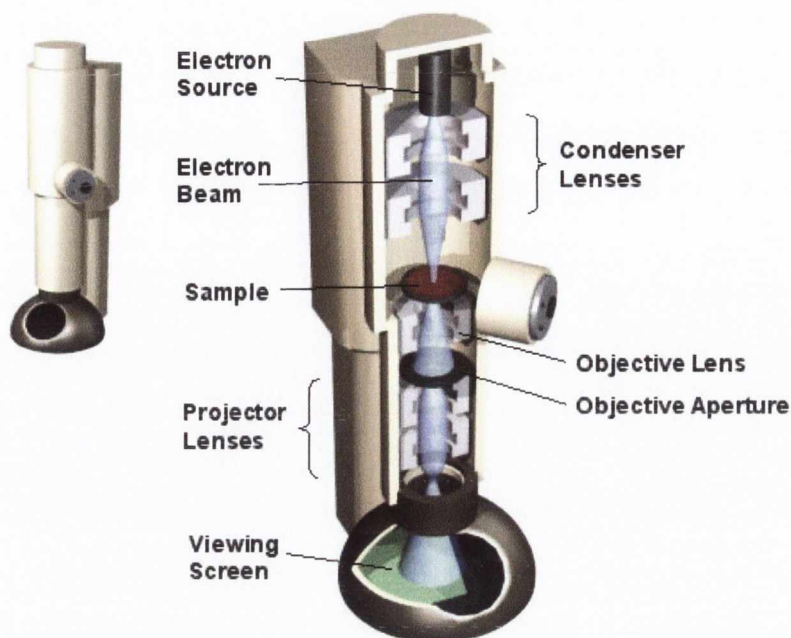


Figure 3.12: *Schematic of a typical transmission electron microscope.*

Depending on the size of the aperture differing amounts of electrons are detected and thus give you different levels of information. In the case of 2D nanosheets on a carbon substrate, if a small aperture is used only a small number of electrons are detected. This creates a large contrast between the nanosheets and the substrate that they are on as the substrate is mostly electron transparent. This is useful for very thin nanosheets as they would otherwise be difficult to image. conversely, a large aperture leads to most of the electrons being detected. This helps for materials with a large atomic number, as this is the main contributor to electron scattering, and thicker samples.

3.7.1 Quantitative Analysis

Low resolution TEM isn't only used for qualitative analysis on the appearance of the nanosheets but also for statistical analysis to assess flake dimensions. In this work, similar methods are employed which have been previously developed in this group to statistically quantify the mean length and width distributions of our samples[20, 42, 44, 134].

This has become of greater interest since the development of liquid cascade centrifugation where the ability to produce size selected samples has been simplified and thus the need to measure the dimensions of the nanosheets increased. To achieve this the sample is

deposited onto a TEM grid and dried to remove all residual solvent. The choice of TEM grid used in the statistical analysis is quite important. The preferred grid is dependent upon the size of nanosheets that are thought to be in the dispersion. For example, if a low RPM is used to produce the dispersion the majority of the nanosheets are expected 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 3.13 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 as well as ensuring that all solvent is removed. The different types of grids are shown in Figure 3.13.

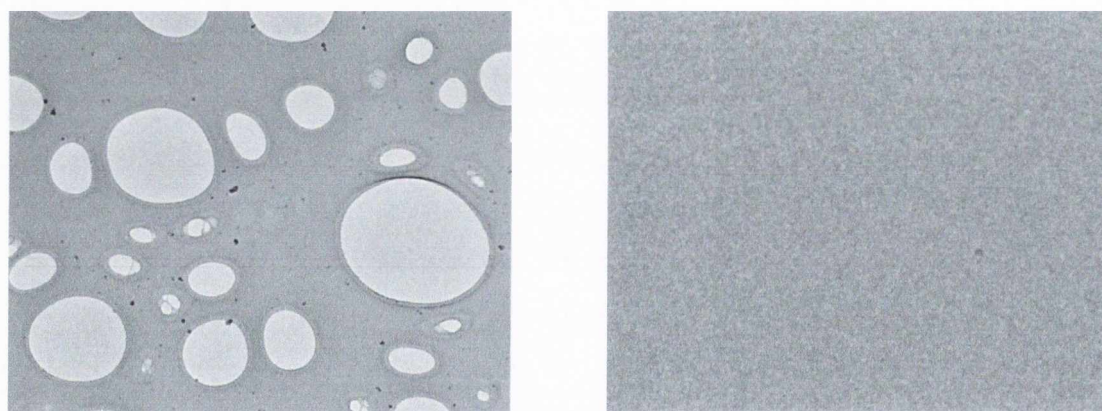


Figure 3.13: *Typical TEM images of (A) a holey carbon grid and (B) a continuous carbon film.*

Once the sample has been appropriately dropped and prepared it is possible to image the nanosheets and apply statistical analysis to obtain mean length and width measurements of the sample. This is achieved by randomly moving around the grid and imaging the nanosheets which are observed. It is important to image a fair representation of both small and large flakes. With these 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 flakes 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 Figure 3.14 A. This methodology is repeated for a large number of flakes (>150) to reduce any errors occurred in measuring. As a result of large counts being needed it is also important to try and obtain as many flakes within an image as possible without causing the flakes to reaggregate. An example is shown in Figure 3.14 B.

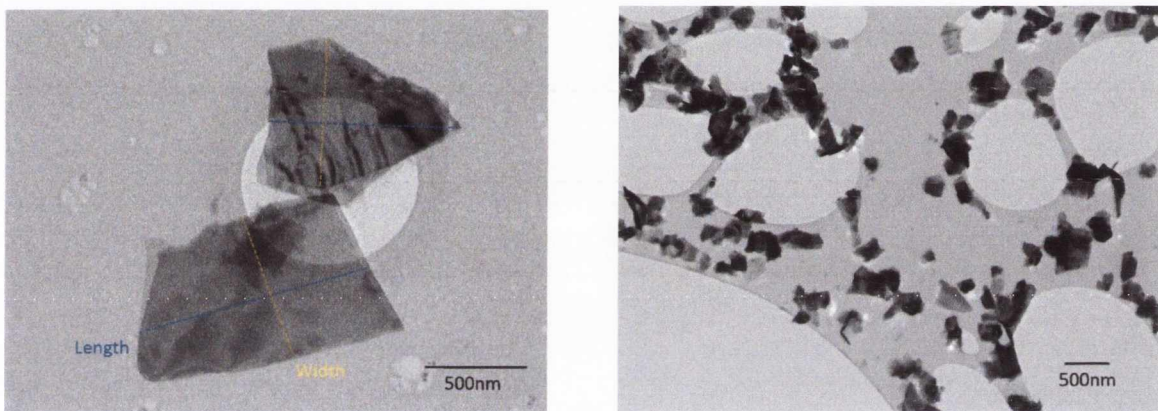


Figure 3.14: *TEM image demonstrating (A) length and width measuring and (B) a typical image for flake counting for statistics.*

Statistical TEM is used throughout this thesis. It is used to obtain length stats of standard dispersions as well as to develop length distributions for different average length dispersions to create metrics. In addition, this data can be used to correlate AFM statistics. Such analysis of this statistical data will be discussed further in chapters 4, 5, 6 and 7.

3.8 Atomic Force Microscopy (AFM)

For 2D materials it is very important to know the thickness of the nanosheets. This can be achieved through a variety of methods but the easiest and most common is atomic force microscopy (AFM). This method gives information of the sample geometry and the quality of the dispersed nanosheets[42, 43]. Unlike the other microscopes used in this thesis the

AFM doesn't operate through the use of scattered electrons but instead uses a cantilever with a very sharp tip (atoms thick) that is scanned over a sample surface. This generates a topographical profile of the nanomaterial being imaged. Similarly to TEM, an AFM can image at sub nanometer resolution. A schematic is shown in below in Figure 3.15[152].

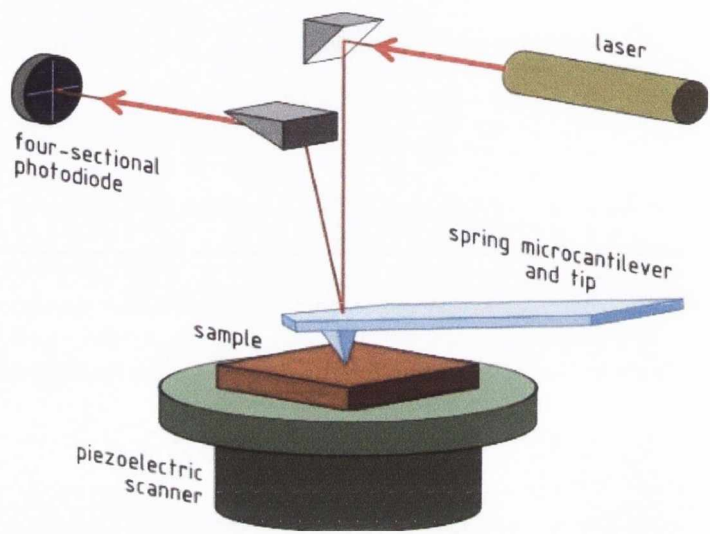


Figure 3.15: *An animated reconstruction of the schematic for an atomic force microscope.*

The typical operation of an AFM consists of directing a laser onto a spring cantilever which is reflected to a split photodiode. The cantilever is then moved along a surface where a piezoelectric scanner moves the tip relative to the sample in a 3D pattern causing the tip to be displaced. The displacement causes the laser beam reflection to change position which is detected by the photodiode. This is then converted from raw data into an image by the AFM. This technique has three modes of operation. Contact, non-contact and tapping mode[152, 153].

All these modes are governed by the Lennard Jones potential which describes the attraction and repulsion of objects as they get closer to each other. In contact mode, the cantilever is held as close to the sample as possible (2-3 angstroms) and is rastered across the surface. When the tip approaches an object the large force required, as governed by Pauli repulsion, for the atoms of the tip to come into contact with the sample cause it

be repulsed and rise over the sample while still remaining within a few angstroms[152, 153].

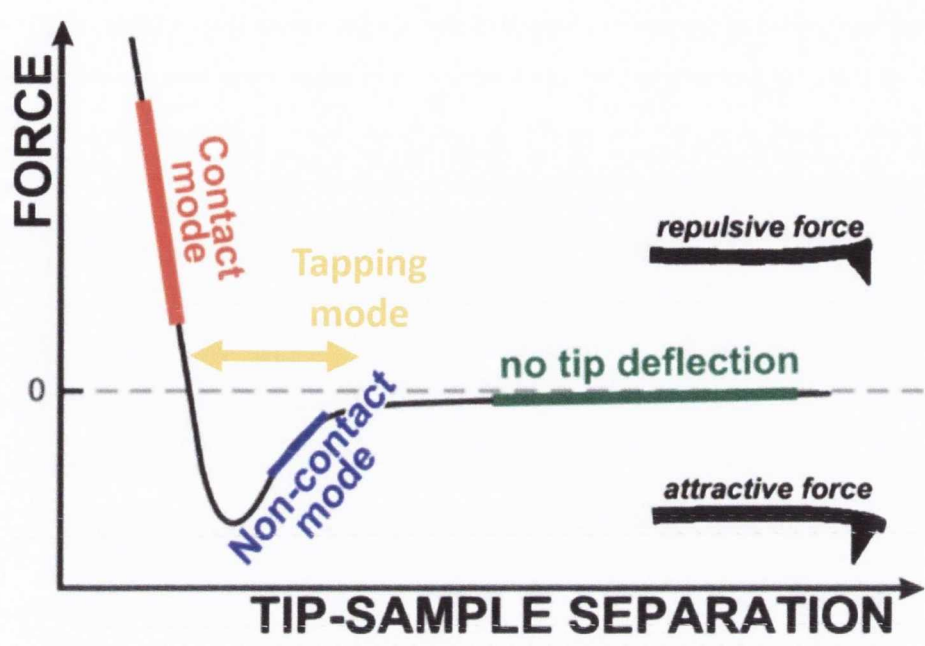


Figure 3.16: Schematic representation of the 3 modes of AFM measurements and the Lenard Jones potential for the interaction of the AFM and sample.

Non-contact mode operates with the tip higher than for contact mode, usually nms above the surface. When the tip passes above an object, the attractive Van der Waals force causes the tip to move towards the sample, causing the cantilever to bend and the direction of the beam reflection to change. In Figure 3.16, a graph of force versus tip-sample seperation is shown demonstrating this. Both contact and non-contact modes have flaws though, as contact mode can cause loosely attached objects to be dislodged and can cause the cantilever to break easily due to high frictional forces. For non-contact mode these problems are avoided but there is a significant decrease in lateral resolution as well as being affected more affected by water on the surface. As a compromise, tapping mode is frequently used. In this mode the cantilever oscillates at its resonant frequency and slowly profiles the surface. By doing this it eliminates frictional forces by intermittently contacting the surface and oscillating with sufficient amplitude to prevent the tip from being trapped by adhesive meniscus forces from the contaminant layer, such as solvent or water[42, 43, 152, 153].

AFM is used in this thesis to determine the nanosheet thickness for different sets of

dispersed nanosheets. This involves depositing a small volume of dispersion on to a silicon wafer. The wafer is heated using a hot plate to approximately 180 °C, boiling off the solvent leaving just the nanosheets on the wafer. In the case of surfactant dispersions the wafer is then washed with water to remove any residual surfactant. When measuring the sample a suitable region of the substrate surface needs to be investigated, in order to avoid aggregation effects. Where a reaggregated area will appear as very large nanosheets with no discernible way to assess thickness. Analysis of a region with a density which is too high, impedes an accurate determination of the length (L), width (W) and thickness (t). A low density area is ideal as reliable statistics of the nanosheets can be obtained. To separate the number of layers (N) from t step height analysis is used, where the increase in nanosheet thickness with each step is used to determine the thickness of one layer i.e. if every increase of thickness is a multiple of 2nm, the thickness of one layer is 2 nm. This method is used in chapters 4, 5 and 6.

3.9 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a widely used technique to image the surface of nanostructures as well as powders of layered materials[13, 22, 44, 90, 115, 152]. As mentioned in section 3.7, when an electron beam is incident on a sample some electrons can be back scattered (BSE) or cause the emission of secondary electrons (SE). It is these electrons that are of interest in SEM. Similar to TEM, an electron beam is used to generate a signal that is converted to an image, although the accelerating voltage in this instance is between 2 and 10 eV as opposed to 100 keV. A schematic of a typical SEM is shown in Figure 3.17.

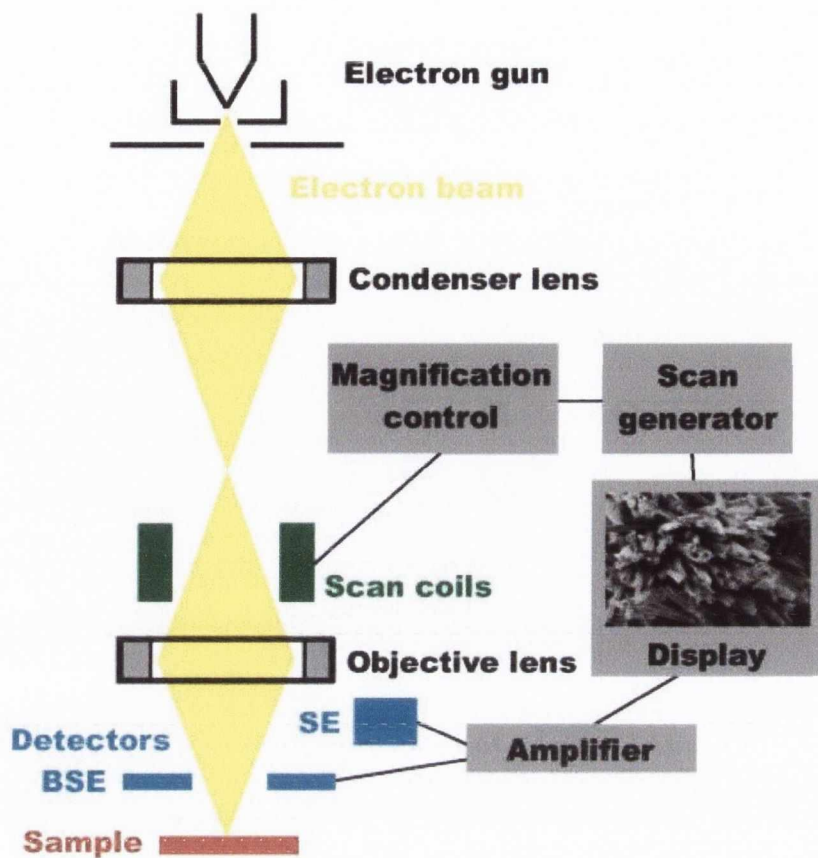


Figure 3.17: A schematic representation of a scanning electron microscope.

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 than SE and come from much deeper within the sample after being either elastically or inelastically scattered. The escape depth of BSE are typically in the order of a micron. Therefore, there are two different escape depths for these electrons to characterise our sample. BSE are highly sensitive to element type as it is a function of the atomic number, thus higher atomic number elements have a greater proportion of back scattered electrons[151]. This makes them more useful for detecting contrast between areas of different chemical composition. SE are generated closer to the surface thus, are more sensitive to surface morphology[152, 154]. Also, characteristic x-rays are emitted when the electron beam removes core shell electrons from the sample which are filled by an electron from a higher shell. These x-rays can be used for generating data on chemical composition.

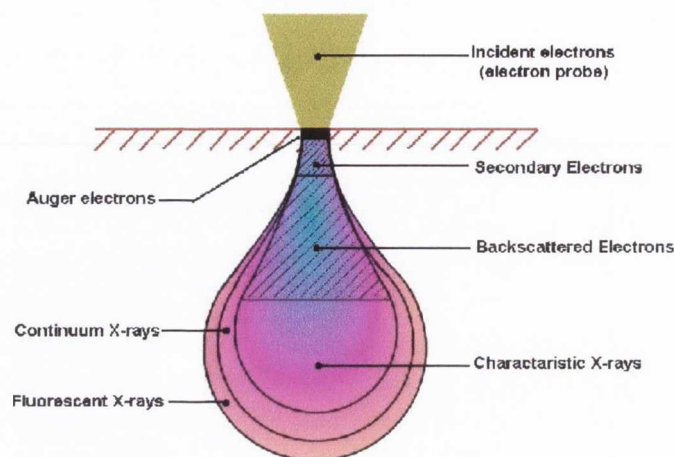


Figure 3.18: *Teardrop shaped interaction volume for electrons involved in SEM imaging.*

The image resolution of a SEM is typically limited to a few nm due to the electron spot and the interaction volume of the beam and the sample. The interaction volume is teardrop shaped and large in relation to the beam spot size, the size of which depends on the atomic number of the sample as well as its density and the electron acceleration energy[152, 154]. A representation of this is shown in Figure 3.18.

3.10 Zeta Potential

As mentioned in section 2.7.2 surfactant dispersions are colloidal systems consisting of nanosheets carrying a charge suspended in a liquid dispersion. This stabilises the nanosheets in the solution which in turn, imparts a surface charge and local diffuse charge in the vicinity of these nanosheets. One of the main governing variables in this stabilisation process is the zeta potential existing in the electrical double layer around the nanosheets. For a stable dispersion $-30 \text{ meV} < \zeta < 30 \text{ meV}$ is necessary, if the nanosheets have a potential outside of this limit, the repulsive electrostatic forces are usually sufficient to prevent reaggregation. The most common measurement method involves applying an electric field to a solution containing nanosheets with a surfactant coating, which causes movement of the charged ions in oppositely charged directions, and measuring the how fast the nanosheets 'move'. This movement is known as electrophoresis and is shown in Figure 3.19[155, 156].

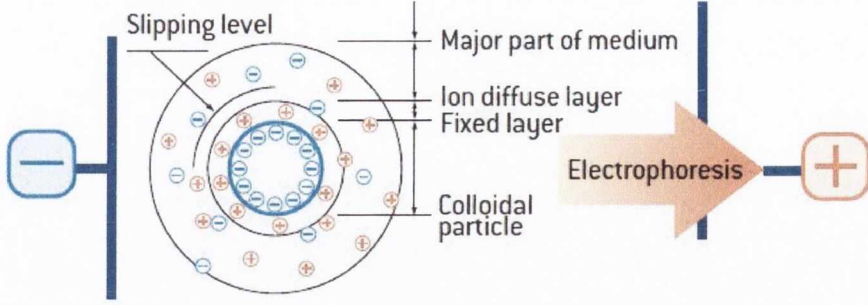


Figure 3.19: Schematic showing the movement of ions due to electrophoresis.

Not all counter ions move against the nanosheets, those within very close proximity will in fact move with the nanosheets. This limit is known as the slip surface and it is this potential that is measured to determine the Zeta potential.

This electrophoretic mobility is most commonly measured using laser Doppler velocimetry where two beams are passed through the solution under applied bias. One beam uses a reference beam, which can be passed through the cell without being scattered while the incident beam is passed through the solution. Small frequency shifts then arise owing to the movement of particles in an applied electric field. The frequency shift Δf is equal to [157]

$$\Delta f = \frac{2v \sin\left(\frac{\theta}{2}\right)}{\lambda} \quad (3.13)$$

where v is the particle velocity, λ is the laser wavelength and θ is the scattering angle. The measured electrophoretic mobility (U_E) is converted into zeta potential (ζ) through Henry's equation

$$U_E = \frac{2\epsilon\zeta F(\kappa a)}{3\eta} \quad (3.14)$$

where ϵ is the dielectric constant of the dispersant, $F(\kappa a)$ is the Henry function and η is the viscosity. These two equations are related via $v = U_E E$. A typical Zeta potential cell is shown in Figure 3.20.

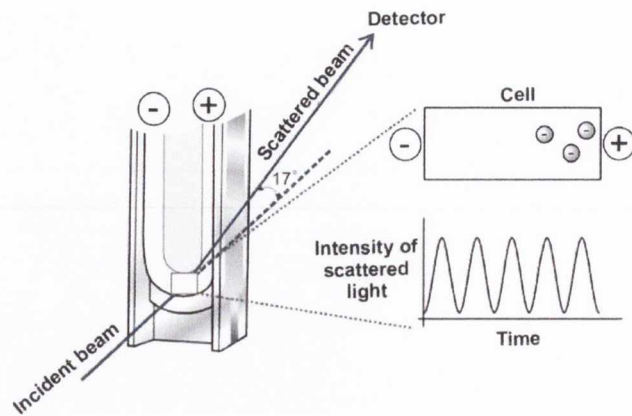


Figure 3.20: Schematic representation of a cell where the Zeta potential is measured through electrophoretic mobility of the particles in an applied electric field.

Chapter 4

Exfoliation of Gallium sulphide

4.1 Introduction

2D materials play a hugely important role in many applications such as technology and energy storage. While materials such as graphene, BN and TMDs have been successfully used in devices, there remain other layered materials for example transition metal oxides (TMOs), black phosphorus and III-VI metal chalcogenides[13, 22, 44, 66, 77, 114]. By expanding the method of LPE to other materials, it broadens the options for certain applications. For example, III-VI metal chalcogenides exhibit great properties as photodetectors and photodiodes but until now all research has been done through micro-mechanical exfoliation or atomic layer deposition but these methods are limited by scalability and complicated procedures, thus it would be beneficial to attempt exfoliation through LPE methods[49, 66, 67].

In this chapter, a procedure to exfoliate a III–VI metal chalcogenide, gallium sulphide, in solvents by bath sonication is demonstrated. The nanosheets produced are subjected to a selection of characterisation techniques, such as TEM, AFM, and Raman spectroscopy, to assess the quality of material. In addition, the spectroscopic properties are tested versus flake length, thickness and dispersion concentration. This facilitates the production of dispersions with well-defined nanosheet sizes and specific properties. Finally, the suitability of these nanosheets for use as a catalyst in the hydrogen evolution reaction is tested.

4.2 Experimental Procedure

4.2.1 Materials

Gallium sulphide powder (99.999 % GaS-05-P) was purchased from American Elements. All solvents were purchased from Sigma-Aldrich at the highest available purity, with all being >99 %.

4.2.2 Sample Preparation

Gallium sulphide powder was sonicated in a solvent using an ultrasonic bath (P30 H Ultrasonic from Fischer scientific). The sonication was performed with an amplitude of 100 % and a frequency of 37 kHz in 50 mL plastic centrifuge tubes. The water in the sonic bath was cooled by a water cooling system to 20–30 °C (depending on length of sonication) enabled by cold water being pumped through piping that was wrapped around the interior of the bath. Once sonicated, the dispersion was centrifuged in a Hettich Mikro 220R centrifuge with a fixed angle rotor 1060 (NB: For this centrifuge, rpm are related to g force via $RCF = 106.4f^2$, where f is the rotation rate in krpm). The top 60 % of the supernatant was then taken from the centrifuged dispersion for analysis and the sediment was discarded.

Centrifugation parameters were optimised using the above sonication parameters in the solvent N-cyclohexyl-2-pyrrolidone (CHP). Aliquots of 10 ml were centrifuged for varying time periods (5 min to 240 min) and for varying rotation rates (500 RPM-10000 RPM, 28 g-1086 g). The supernatant was decanted and the extinction was measured in a 0.4 cm path length cuvette using a PerkinElmer Lambda 650 spectrometer (details section 4.3) at 420 nm as a measure of the concentration.

For the solvent screening, 1 g/L of GaS was sonicated in 20 mL of each solvent for 6 h and centrifuged for 180 min at 2.5 krpm. The following solvents were used: isopropanol ($\delta_T = 23.6 \text{ MPa}^{1/2}$), N-methyl-2-pyrrolidone ($\delta_T = 23 \text{ MPa}^{1/2}$), methanol ($\delta_T = 29.6 \text{ MPa}^{1/2}$), chloroform ($\delta_T = 19 \text{ MPa}^{1/2}$), N-cyclohexyl-2-pyrrolidone ($\delta_T = 20.5 \text{ MPa}^{1/2}$), dimethylformamide ($\delta_T = 24.9 \text{ MPa}^{1/2}$), cyclopentane ($\delta_T = 16.5 \text{ MPa}^{1/2}$), heptane ($\delta_T = 15.3 \text{ MPa}^{1/2}$), hexane ($\delta_T = 14.9 \text{ MPa}^{1/2}$), pentane ($\delta_T = 14.4 \text{ MPa}^{1/2}$), acetone ($\delta_T = 19.9 \text{ MPa}^{1/2}$), acetonitrile ($\delta_T = 24.3 \text{ MPa}^{1/2}$), 1,3-dioxolane ($\delta_T = 21.4 \text{ MPa}^{1/2}$), ben-

zonitrile ($\delta_T = 22.5 \text{ MPa}^{1/2}$), isopropoxyethanol ($\delta_T = 21.4 \text{ MPa}^{1/2}$). The final, optimised exfoliation was performed as follows: 45 g/L of GaS was sonicated for 6 h in isopropanol (IPA) in 20 mL vials and then centrifuged for 180 min at 2.5 krpm. The sonication time study experiments began with an initial concentration of 45 g/L. During the experiment, 5 mL aliquots were removed at given time intervals and immediately centrifuged at 2.5 krpm ($\sim 240 \text{ g}$) for 180 min. The supernatant was again decanted and analysed using extinction spectroscopy.

To size select the nanosheets, a controlled centrifugation regime was carried out. Initially, 10 mg/ml GaS in 90 mls of IPA was sonicated for 6 hours. This dispersion was then centrifuged at 0.5 kRPM for 60 mins with the supernatant being retained and the sediment being discarded. This supernatant was centrifuged again at 1 kRPM for 60 mins and the sediment redispersed in fresh IPA producing the size, which will be referred to as XL. The sample centrifuged at 1 kRPM was decanted and the supernatant was centrifuged at 1.5 kRPM for 60 mins. Again the sediment was redispersed in fresh IPA, producing the L size. These steps were repeated in increments of 0.5 kRPM up to 3 kRPM, thus producing 5 sizes.

4.2.3 Sample Characterisation

Low-resolution bright field transmission electron microscopy imaging was performed using a JEOL 2100, operated at 200 keV. Holey carbon grids (400 mesh) were purchased from Agar Scientific and prepared by diluting a dispersion to a low concentration and drop casting onto a grid placed on a filter membrane to wick away excess solvent. Statistical analysis was performed of the flake dimensions by measuring the longest axis of the nanosheet and assigning it as “length”, L. Atomic force microscopy (AFM) was carried out on a Veeco Nanoscope-IIIa (Digital Instruments) system equipped with a E-head (13 μm scanner) in tapping mode after depositing a drop of the dispersion (10 μL) on a preheated (120 $^\circ\text{C}$) Si/ SiO₂ wafer with an oxide layer of 300 nm. Typical image sizes were 3–10 μm taken at scan rates of 0.4–0.6 Hz. The high concentration dispersion was diluted with IPA immediately prior to deposition to yield a pale colloidal dispersion. After deposition, the wafer was rinsed with 5 mL of water and 5 mL of isopropanol. Typical image sizes were 2x2 mm² at scan rates of 0.8 - 1.0 Hz with 512 lines per image. The apparent thickness

was converted to number of layers using previously developed step-height analysis.[42]

Raman spectroscopy was performed using a WITec alpha 300 with 532 nm excitation laser in air under ambient conditions. The Raman emission was collected by an Olympus 100 $\times$ objective (N.A. = 0.8) and dispersed by 600 lines mm⁻¹ gratings. The laser energy was kept below 0.2 mW. The mean of 20 spectra is displayed.

X-ray Photoelectron Spectroscopy was performed under ultrahigh vacuum conditions (<5 $\times$ 10⁻¹⁰ mbar) using monochromated Al K α X-rays from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. The analyser pass energy was set to 100 eV for survey and 20 eV for core-level spectra, yielding a maximum energy resolution of 0.65 eV. An electron flood gun was used for charge compensation and the binding energy scale was referenced to the adventitious carbon 1s core-level at 284.8 eV. After subtraction of a Shirley background, the core-level spectra were fitted with Gaussian–Lorentzian line shapes. Samples were prepared by vacuum-filtering the dispersions using porous cellulose filter membranes (MF-Millipore membrane, mixed cellulose esters, hydrophilic, 0.025 μ m, 47 mm) to give thin films.

4.3 Optimisation of Exfoliation Parameters

Gallium sulphide crystals consist of monolayers of gallium atoms in a hexagonal arrangement surrounded by sulfur atoms in a S-Ga-Ga-S stack. These layers are stacked on top of each other, held together by weak Van der Waals forces, making it a suitable candidate for liquid phase exfoliation[63].

Before any proper analysis can be made, it is necessary to ensure that the prepared dispersions are stable. This can be achieved by tailoring the centrifuge regime to remove any nanosheets that will sediment over time[13]. To achieve this, 10 g/L of GaS powder was sonicated in 3 x 30 ml of cyclohexyl-2-pyrrolidone (CHP) for 6 hours using an ultrasonic bath. These were then centrifuged for one hour at a range of different RPMs with the supernatant being retained. The concentration of these dispersions was measured using optical extinction spectroscopy ($T = 10^{-ext}$) via the Beer-Lambert law, where the absorbance of a material sample is proportional to the concentration of the material in a liquid sample[115, 116]. This is then repeated with a constant RPM (2.5 kRPM) for a

range of times. The concentrations are plotted against RPM and time with the UV-vis spectra inset as shown below.

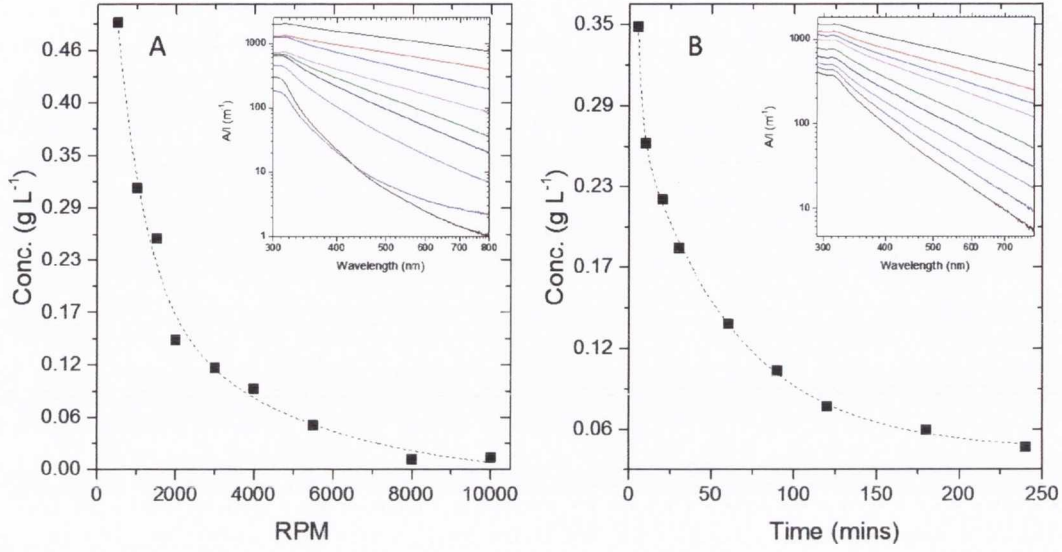


Figure 4.1: A) *Conc. vs RPM with extinction spectrum on a log-log plot inset.* B) *Plot of Conc. vs centrifugation time with absorption spectrum on a log-log plot inset.*

As can be seen in Figure 4.1 A and B the concentration goes as a double exponential which can be fitted as:

$$A/l = A/l_0 + A/l_1 e^{-\frac{t}{\tau_1}} + A/l_2 e^{-\frac{t}{\tau_2}} \quad (4.1)$$

Where A/l is the absorbance normalised to the path length of the cuvette, A/l_0 is the stable state absorbance A/l_1 and A/l_2 are the absorbances after τ_1 and τ_2 , which are the decay constants. A single exponential can not be fitted due to there being two separate unstable phases; a fast-sedimenting phase and a slow-sedimenting phase[13, 139]. The fast-sedimenting phase is associated with large, unexfoliated powder in the dispersion and the slow-sedimenting phase is due to larger quasi-exfoliated sheets that are not completely stable[19]. The time constants were found to be $2.6 \text{ mins} \pm 0.7 \text{ mins}$ and $60.6 \text{ mins} \pm 3.8 \text{ mins}$ for the time study, and $733.63 \text{ RPM} \pm 50 \text{ RPM}$ and $4204 \text{ RPM} \pm 900 \text{ RPM}$ for the RPM study. Once these time constants are known it is then possible to determine an

appropriate time and RPM for centrifugation. As $t_{cf} = 3t_1$ (i.e. the time taken for 95 % of the unstable material to sediment), for future studies t_{cf} and f were chosen to be 180 mins and 2500 RPM respectively. The solvent choice is important, as a very viscous liquid is required. The correct selection here ensures that if complete stability has been achieved from these centrifugation steps using a high viscous solvent then complete stability will be achieved for all solvents, with a lower viscosity, in future studies. This is because the flakes will take a longer length of time to sediment in a high viscosity solvent than a low viscosity solvent. Thus CHP, with $\eta = 11.5$ Pas, was selected.

From the UV-vis spectra (Figure 4.1 inset), it can be seen that there are significant contributions from scattering as the spectra show a near monotonic increase with decreasing wavelength with no features of note, except a small peak at 315 nm corresponding to the A exciton. This is due to these dispersions acting as colloidal systems where the nanosheets scatter light according to Mie and Rayleigh theory. Thus, the UV-vis is measuring extinction and not simply pure absorption. This has been shown for many other 2D materials in the same system and thus extinction and absorption must be treated separately where $\text{ext}(\lambda) = \text{abs}(\lambda) + \text{sca}(\lambda)$. This has led to the use of extinction spectra to estimate dispersed concentration being complicated by the recent realisation that both absorbance and scattering coefficients are generally dependent on nanosheet size[42]. The wavelength used has to be chosen with care and requires an understanding of the size-dependent extinction coefficients as discussed below in section 4.5.1. In the case of GaS, it was found that the extinction coefficient at 365 nm is relatively nanosheet-size-independent (for nanosheet sizes of <300 nm) with a value of $\varepsilon \approx 3654 \text{ Lg}^{-1}\text{m}^{-1}$ (shown in section 4.5.1). This allows the estimation of the dispersed nanosheet concentration, C , using $\text{Ext}_{365\text{nm}} = \varepsilon_{365\text{nm}}Cl$ (C is concentration and l is the cell length)[44].

4.3.1 Solvent Screening

For liquid-phase exfoliation, it has been shown that the solvent plays a major role in the production of nanosheets, where, depending on the Hildebrand solubility parameter, it is possible to produce concentrations that differ by orders of magnitude[13, 16, 19, 44]. To test this, GaS was exfoliated in a range of different solvents, each with differing Hildebrand solubility parameters ($C_i = 1 \text{ mg/ml}$, $t_{\text{sonic}} = 6 \text{ hours}$, $\text{RPM} = 2.5 \text{ kRPM}$, $t_{cf} = 180$

mins). Figure 4.2 A is a graph of conc vs. Hildebrand solubility parameter (δ_T), where δ_T is defined as the square of the cohesive energy, which shows the values of A/l ranging over 3 orders of magnitude. A simple model according to classical thermodynamics shows that:

$$Conc \propto \exp\left(\frac{-\nu_{ns}}{3kT}(\delta_s - \delta_{NS})^2\right) \tag{4.2}$$

where δ_{NS} is the Hildebrand parameter of the solute and ν_{NS} is the molecular volume of the solute. Equation 4.2 was fitted to Figure 4.2 A (dashed line) and shows a very good fit confirming the validity of the use of thermodynamics for these systems. It was found that the best solvents were ones with $\delta_T= 21.5 \text{ MPa}^{1/2}$ close to values of 23, ~ 22.5 , 22, 21 $\text{MPa}^{1/2}$ as reported recently for graphene, BN, MoS_2 , and MoO_3 [13, 121, 158, 159]. Good solvents include CHP, NMP, and IPA. IPA was chosen for further studies due to its low toxicity, low boiling point, and ease of use for device fabrication.

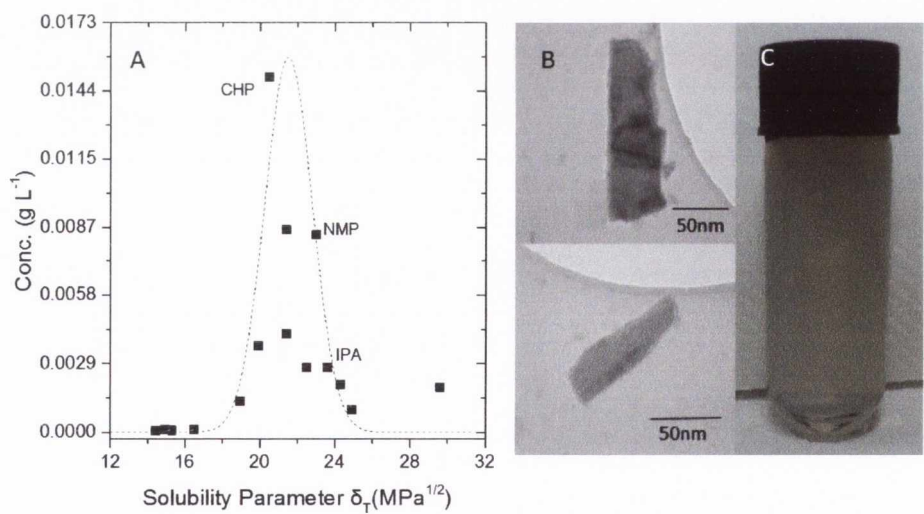


Figure 4.2: A) *Conc. vs Hildebrand solubility parameter for 15 solvents*, B) *TEM images of standard sample nanosheets, showing well exfoliated flakes*, C) *GaS standard sample dispersion*.

To ensure that exfoliation is occurring, transmission Electron Microscopy (TEM) was performed on the IPA dispersion by dropping a few drops (ideally 0.1mg) onto carbon holey TEM grids with images shown in Figure 4.2 B. These measurements showed all

dispersions tested to contain large quantities of electron-transparent 2D nanosheets with well defined edges. Figure 4.2 C shows a yellow liquid, which is a dispersion of gallium sulphide in IPA.

4.3.2 Optimisation of Sonication Time and Initial Concentration

Once the centrifugation parameters and solvent choice have been optimised it is possible to achieve the highest throughput of exfoliated GaS nanosheets by controlling both the sonication time as well as the initial concentration of GaS powder (C_i). This was achieved by firstly determining the best sonication time by sonicating GaS powder, at a fixed initial concentration (C_i) for a range of times in IPA and centrifuging using the previously mentioned centrifugation parameters. To achieve the optimal initial concentration, GaS was sonicated for a fix time ($t_{sonic} = 6$ hrs) for a range of initial concentrations. As before, the concentration was found using UV-vis and plotted against time and C_i .

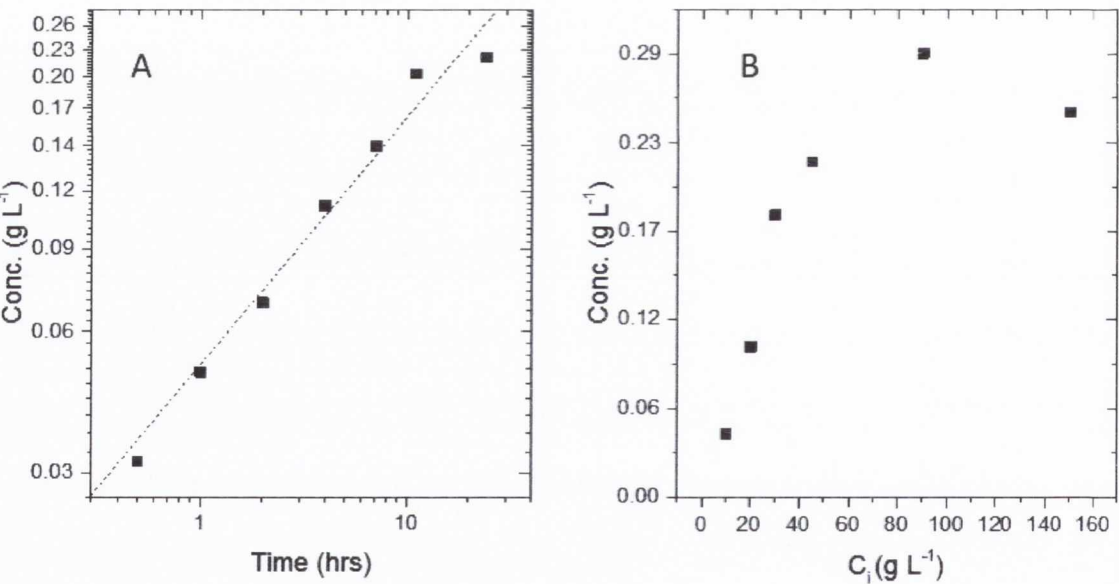


Figure 4.3: A) *Conc. vs sonication time on log-log plot.* B) *Conc. vs initial gallium sulphide concentration.*

As can be seen in Figure 4.3 A, nanosheet concentration scales as $t_{sonic}^{1/2}$. This is consistent with other materials exfoliated with this method such as Graphene, MoS₂ and MoO₃[13, 160, 161]. When varying the initial concentration of powder, the concentration of exfoliated

nanosheets increases, and then begins to plateau at approximately 45 g/L (Figure 4.3 B). This is due to the energy provided by the ultrasonication not being able to access all the powder beyond 45 g/L[160]. Thus, to achieve an optimum concentration of GaS and a completely stable dispersion, requires parameters of initial GaS concentration $C_i = 45$ g/L (due to higher yield than 75 g/L), sonication time $t_{sonic} = 6$ hrs, centrifugation rate $f = 2.5$ krpm (equivalent to 665 g), centrifugation time $t_{CF} = 180$ min. This protocol, produces dispersions with concentrations of $C = 0.22$ g/L of GaS nanosheets.

4.4 Nanosheet Characterisation

It is necessary to provide appropriate confirmation that the material has been successfully exfoliated with no defects during the sonication process, as well as checking for oxidation in the GaS starting powder using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). GaS dispersions were filtered onto nitrocellulose membranes and the films were analysed using both Raman spectroscopy and XPS.

A Raman spectrum for GaS is shown (Figure 4.4 A) and displays typical features for GaS with Raman modes at 195.2 cm^{-1} , 300.7 cm^{-1} , and 367.9 cm^{-1} . These match the values for GaS powder as well as mechanically exfoliated GaS nanosheets[66, 162, 163]. Interestingly, there was also a peak at 243.2 cm^{-1} which was also seen for the GaS powder, which is attributed as the $\nu_1(A_1)$ mode of the GaS_4 molecular unit as typically found in Ga_2S_3 [164]. In Figure 4.4 B is a standard SEM image for a GaS dispersion showing clearly exfoliated nanosheets, stacked on top of each other as is common for vacuum filtration.

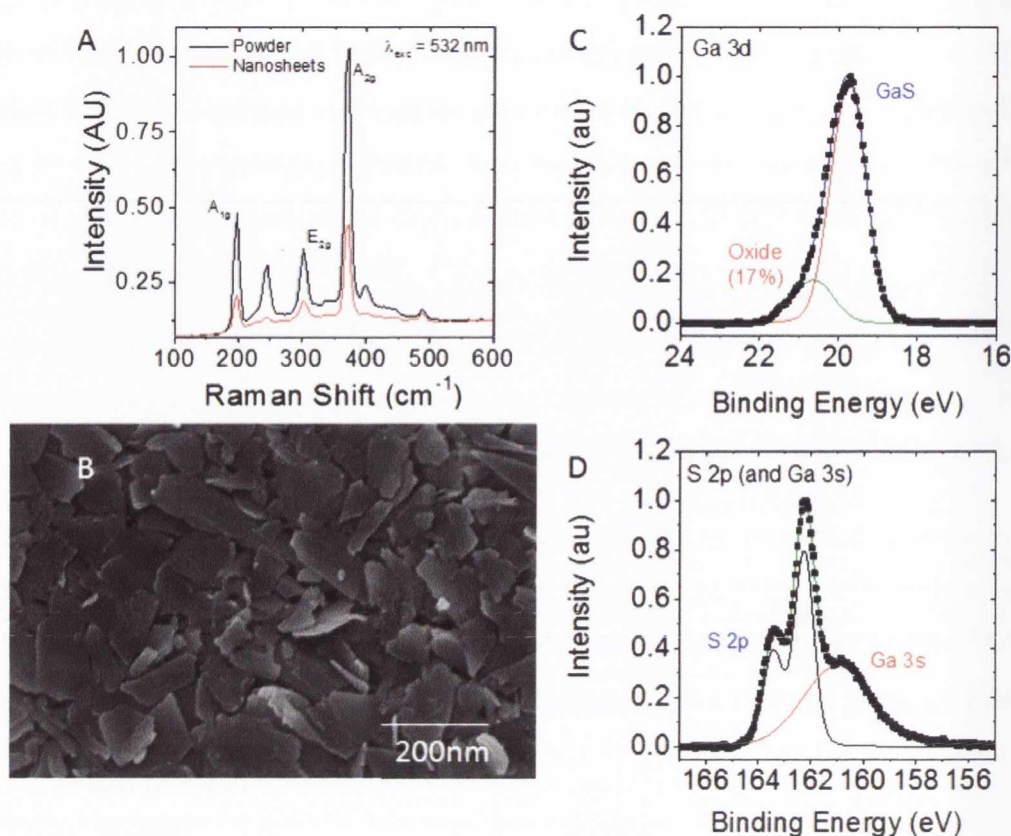


Figure 4.4: A) Raman spectrum of the filtered standard dispersion showing the characteristic resonant modes. B) SEM image of thin film of GaS. C, D) Fitted XPS Ga3d and S2p core level spectra of a filtered dispersion confirming the chemical nature of the nanosheets.

XPS measurements of the Ga 3d, Ga 3s and S 2s core levels (Figure 4.4 C and D) shows that there is small amount of oxidation with 17% Ga_2O_3 . The expected components of the powder are also roughly in the correct stoichiometry with the ratio 1:1.25. The oxidation was also found in the raw powder showing that it is not due to the exfoliation procedure. In addition, all XPS peaks in the starting powder are significantly broadened in terms of full width at half maximum of the fit components suggesting a lower degree of order and/or purity in the starting powder compared to the exfoliated material. This shows that the sonication and centrifugation partially purifies the material. This can be understood in terms of the presence of significant amounts of Ga_2S_3 in the starting powder. Since Ga_2S_3 is not layered, it is not exfoliated in the sonication step and therefore removed during centrifugation.

4.5 Size Selection of GaS Nanosheets

A significant advantage of liquid-phase exfoliation is that nanosheets can be size-selected using well established techniques by controlled centrifugation. In this section, a procedure to produce size selected nanosheets is discussed as well as a quantifiable method to determine length, thickness, and concentration from the absorption spectra of the material. This is necessary as the average nanosheet length produced by the optimised parameters was 90 nm[13, 22, 42, 43].

Although small nanosheets are good for certain applications, eg as catalysts, it is advantageous to produce flakes over a wider range of sizes[165]. To achieve this, a method known as liquid cascade centrifugation was employed where the supernatant is subjected to successive centrifugation. To begin, the dispersion is centrifuged at 0.5 krpm (26.6 g) for 1 h and the supernatant is decanted while the sediment is discarded. In this case the sediment is removed, as it is composed primarily of unexfoliated nanosheets. The supernatant is subjected to another centrifugation at 1 krpm (106.4 g) for 1 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 through multiple steps to achieves a variety of size distributions of nanosheets in the respective dispersions. Repeating this procedure yields multiple dispersions, where the lateral dimensions of the nanosheets decrease with increasing centrifugation speed. This is shown in the schematic below in Figure 4.5.

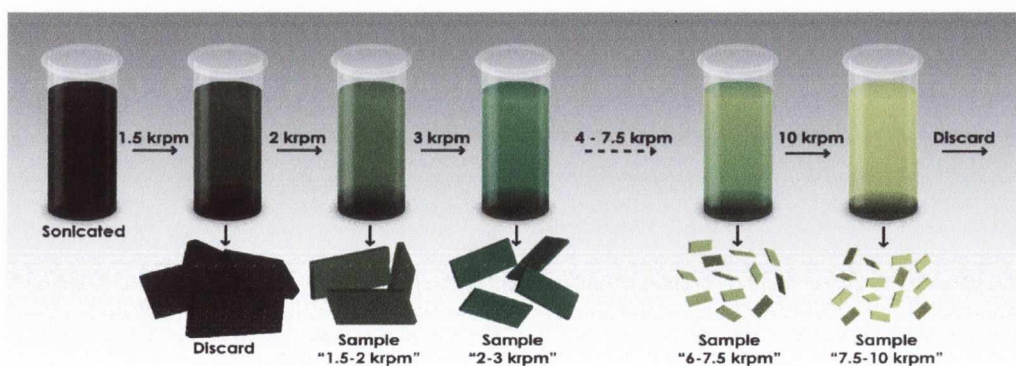


Figure 4.5: *Schematic of liquid cascade centrifugation.*

Size-selection was performed via this controlled centrifugation (see methods for specific

RPMs). By this procedure, five different sizes were produced and subjected to detailed characterisation. Henceforth, the sizes will be referred to as XL, L, M, S, and XS going from largest to smallest. To confirm the success of the size selection method, both TEM and AFM were performed on the nanosheets.

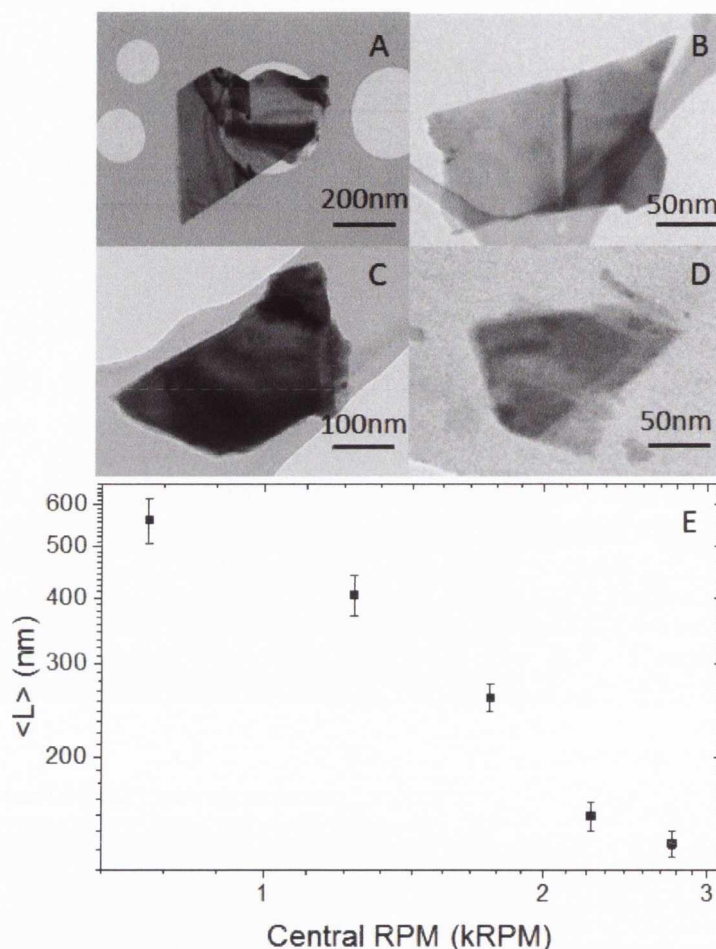


Figure 4.6: A-D) Representative TEM image for the four largest sizes. E) $\langle L \rangle$ vs central RPM.

TEM was performed on the five dispersions using the same method as before and the average length of each was found by measuring the longest dimension of 100 nanosheets from the dispersions using ImageJ software. Shown in Figure 4.6 A-D are representative images of four of the nanosheet sizes. $\langle L \rangle$ was found to be 561 nm, 405 nm, 260 nm, 154 nm, and 137 nm for the five sizes. A graph of $\langle L \rangle$ against central RPM was plotted (Figure 4.6 E), showing a clear trend where the material follows a trend of L decreasing

as rpm^{-1} as predicted by theory.

In all instances, the TEM images showed that the nanosheets were well exfoliated and electron transparent. TEM is a good tool for measuring the lateral dimensions of these nanosheets but is only useful for a qualitative analysis of thickness, especially for thicker samples where methods such as layer counting are impractical. For quantifiable measurements, an atomic force microscope (AFM) was used on the five samples. This was achieved by depositing several drops of dispersion onto a SiO_2 substrate.

Similar to the TEM images, the AFM images showed well exfoliated nanosheets with very similar lateral dimensions as well as matching $\langle L \rangle$ measurements (Figure 4.7 A) but unfortunately, no isolated monolayers were found. As a result of the lack of monolayers, converting thickness from nanometers to number of layers becomes challenging. To resolve this, the fact that incompletely exfoliated nanosheets often display terraces separated by steps associated with flake edges was taken advantage of (Figure 4.7 C)[42, 116].

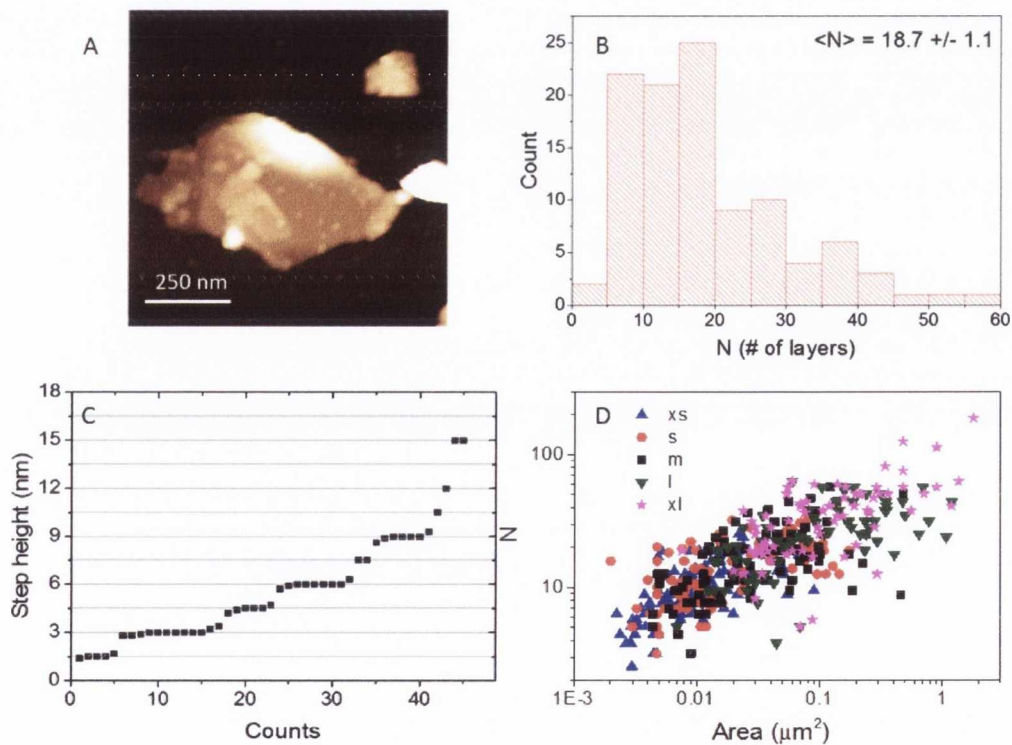


Figure 4.7: A) Representative AFM image of a nanosheet from the medium size. B) Histogram of number of layers of medium size. C) Number of layers vs nanosheet area showing obvious trend. D) Step height analysis of medium size.

By analysing the apparent AFM height on a large number of steps over many flakes and plotting the step height in ascending order, it is clear that the step height is always a multiple of 1.5 nm.

A trend was also observed that showed a direct relationship between the surface area of the flake and the thickness of the flake with $t \propto A^{1/2}$ (Figure 4.7 D)[13]. As mentioned previously, no isolated monolayers were found with $\langle N \rangle$ being 18 and 10 for M and XS respectively with the thinnest flake being 3 layers (Figure 4.7 B). From the previous result, this would imply that smaller flakes are needed to produce monolayers which would be possible to do but in that case the flake would be a nanodot as opposed to a nanosheet.

It has been previously reported that optical extinction changes as a function of size, thus the five separate dispersions were measured using a UV-vis spectrometer with an integrating sphere extension (Figure 4.8 A)[42]. As in section 4.3, it can be seen clearly that the spectra are largely influenced by scattering effects.

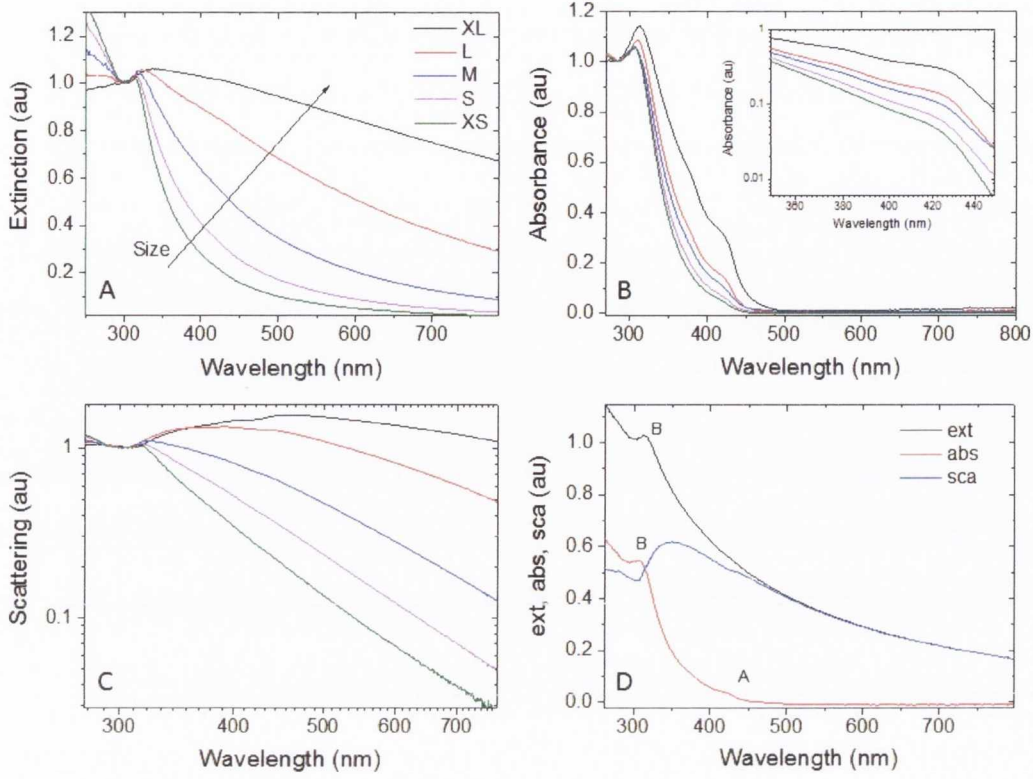


Figure 4.8: A, B, C) Normalised A/l vs wavelength of the extinction, absorbance, and scattering spectra of five sizes ranging from 150nm-600nm showing a clear size dependence on the spectra. D) Extinction, absorbance, and scattering of the m size showing the effect of scattering on the spectra.

Thus, it is necessary to use an integrating sphere which measures pure absorbance by removing scattering from an extinction spectra[42]. To avoid confusion, extinction and absorbance henceforth will be referred to as ext and abs respectively.

The abs and ext spectra were normalised to the local minima at 290 nm as this point doesn't red or blue shift with size. It can be clearly seen in Figure 4.8 A and B that the size of the nanosheets has a direct impact on the shape and features of the ext and abs spectra. Of note is the abs spectra, GaS is known to display excitonic transitions at ~ 410 nm (A-exciton, direct transition at the Γ -point) and ~ 315 nm (B-exciton, transition at the M-point). This isn't noticeable in the ext spectra but it can now be seen in the abs spectra (Figure 4.8 A) that there is a peak at 410 nm that was previously hidden by light scattering in the ext spectra as well as the b exciton at 310 nm. The A exciton is shown in Figure 4.8 B inset showing how the intensity increases with increasing length. Also of note is that λ_B blueshifts with decreasing size. By measuring both abs and ext

it is possible to get the scattering spectra, which can give information about the flakes (Figure 4.8 C). This is achieved by subtracting the abs spectrum from the ext spectrum i.e. $\sigma(\lambda) = \epsilon(\lambda) - \alpha(\lambda)$, where ϵ , α , and σ are the extinction, absorption, and scattering coefficient respectively. It can be seen that the slope of each scattering spectra (log-log plot) changes dramatically depending on size, i.e. for the size L the spectra is far more shallow than for the size S which is far steeper. This is because the scattering for these dispersions goes as a power law i.e. $\text{abs} = \lambda^{-n}$, where n is the scattering exponent which is heavily size dependent[115].

Finally, in Figure 4.8 D, is a plot of ext, abs and sca for the size L. This shows clearly how much scattering affects the extinction spectra as there is zero absorbance until $\sim 450\text{nm}$ as well as the A exciton being suppressed. The peaks at 420 nm and 310 nm have been labelled as the A and B exciton respectively.

4.6 Length, Concentration and Thickness Metrics

4.6.1 Scattering Exponent

It has been shown previously that the scattering of light by nanosheets follows a power law $\approx \lambda^{-n}$ where n is the scattering exponent[115]. As can be seen in Figure 4.8 C, this scattering exponent clearly depends on the size of the nanosheets. The scattering exponent was found for each of the five sizes by fitting a linear function between 550 nm and 750 nm for a log - log plot of the scattering spectra, as demonstrated in Figure 4.9 A. This region was selected as it is the range of the spectra with zero absorption. Also, as this is a zero absorption region, it is assumed that all contributions in extinction are due to scattering and thus, n was found from the extinction spectra as well. This value, n , ranged from 0.78 ($L = 588\text{ nm}$) to 3.8 ($L = 140\text{ nm}$) and when plotted against L (Figure 4.9 B) there is a clear linear trend yielding a fit of:

$$L(\mu\text{m}) = 0.67 - 0.14n \quad (4.3)$$

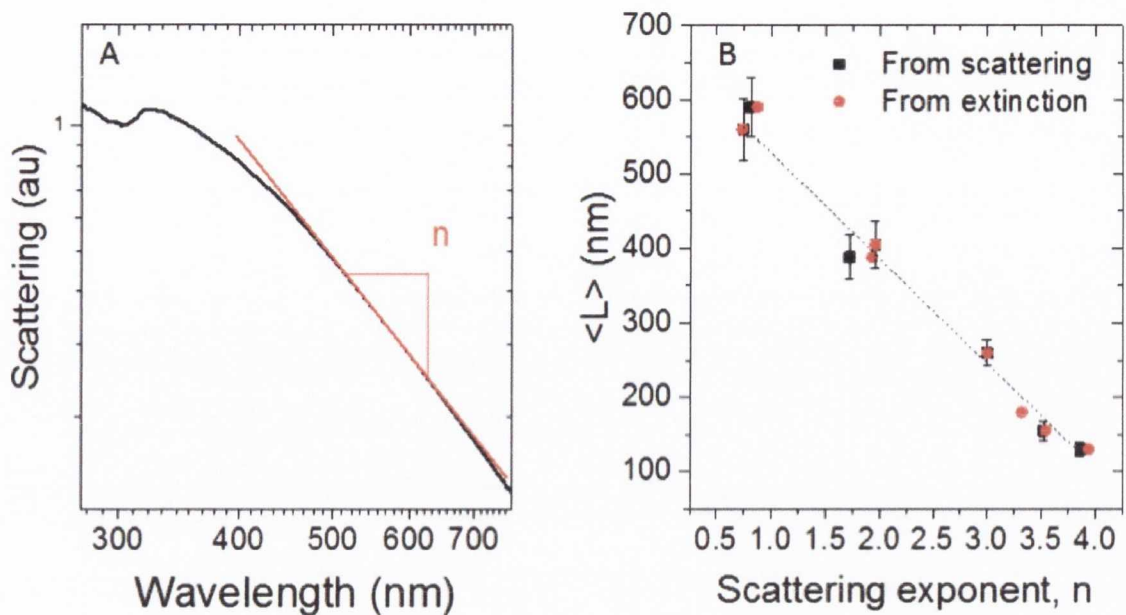


Figure 4.9: A) Log-Log plot of a scattering spectra demonstrating how the scattering exponent, n is obtained. B) $\langle L \rangle$ vs n for both extinction and scattering.

The range of values here make a lot of sense as this process is limited by Rayleigh scattering and thus should have a maximum value of 4. Despite this result, there are still some misgivings in the findings as when a linear fit is plotted the trendline crosses the y-axis at 661 nm implying that the largest flakes either don't scatter light or the largest flakes that can be produced are that length. Neither of these statements are true, what is the most likely scenario is that as the flakes get very large, $> 650\text{nm}$, the graph becomes asymptotic.

4.6.2 Ratio of Absorption Peaks:

As previously shown with MoS_2 and WS_2 , the intensity ratio of the absorption peaks is dependent on nanosheet size[42, 43]. For GaS , when the absorption spectrum is normalised to the local minimum at 290 nm, it is clear that the intensity of the A exciton peak is affected by the $\langle L \rangle$ of the nanosheets. This change in peak ratio comes from the absorption coefficient, α , having a different value at the edges than for the bulk[42, 43].

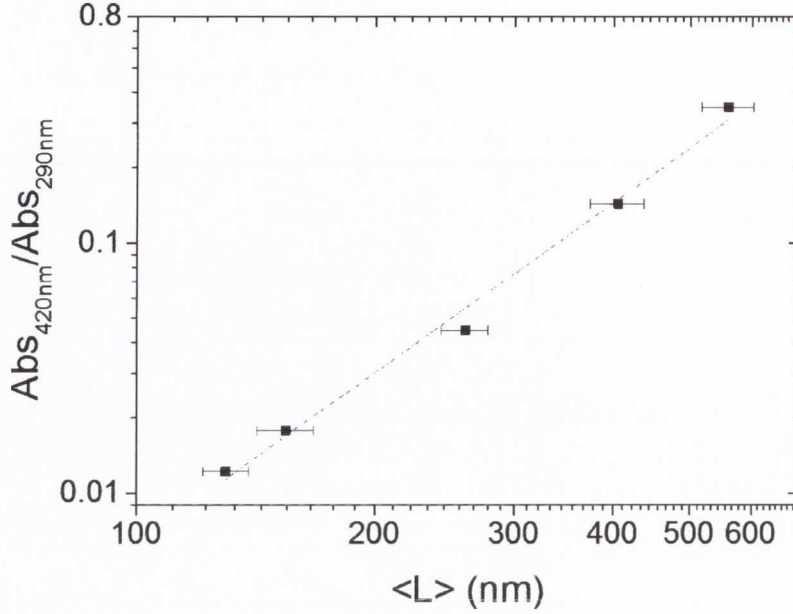


Figure 4.10: Ratio of absorbance at 420 nm to that at 290 nm, Abs_{420nm}/Abs_{290nm} plotted versus $\langle L \rangle$.

When the flakes get smaller, edge effects begin to play a major role due to the decreasing ratio of $\alpha_{core} / \alpha_{edge}$. A graph of A_{420nm}/A_{290nm} vs L was plotted (Figure 4.10) on a log-log plot and fitted to the equation:

$$L(\mu m) = 0.93(A_{420nm}/A_{290nm})^{0.44} \quad (4.4)$$

This is a useful result but it is noted that obtaining length from the scattering exponent is much easier.

4.6.3 Ext Coefficients to Determine Dispersion Concentration:

While the determination of $\langle L \rangle$ is useful, it is critical to control concentration/mass of the nanosheets, for most applications. An accurate determination of the extinction/absorbance coefficient is therefore required. As mentioned previously, the absorption coefficient (and thus extinction and scattering) changes with size, as observed for MoS_2 [42]. Therefore, extinction ϵ , absorbance α and scattering σ coefficient spectra were also analysed for the determined sizes. The GaS nanosheet concentration in each case was determined by fil-

tration and weighing. The coefficient was then found using the Beer Lambert law, where the extinction, absorption and scattering spectra were measured at a range of different dilutions. Depending on the wavelength, the coefficients vary more or less strongly as a function of nanosheet size (Figure 4.11 A).

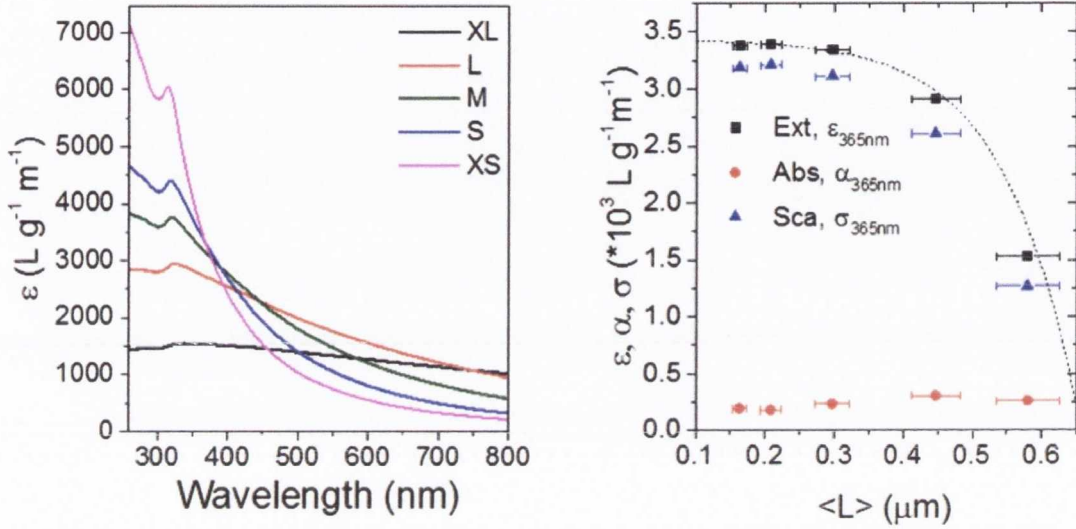


Figure 4.11: A) Extinction coefficient spectra plotted vs wavelength. B) Extinction, absorbance, and scattering coefficients as a function of L .

Empirically, it was observed that there is an invariance of extinction and absorbance coefficients at 365 nm over a wide range of size from 100 nm - 350 nm (Figure 4.11 B) making this an ideal wavelength for a rough determination of the concentration from the extinction spectra. In case a more accurate determination of the concentration is required, the equation below can be used (where $\langle L \rangle$ can be determined by equation 2 or 3):

$$\epsilon = 3464 - 21.18e^{(0.0078\langle L(\mu\text{m}) \rangle)} \quad (4.5)$$

4.6.4 $\langle N \rangle$ from λ_B

In addition to the determination of length and concentration from the optical spectra, it would also be useful to have a metric to assess the mean number of layers. In the case of MoS_2 , the energy/wavelength of the A-exciton provided such a metric due to quantum confinement effects[42]. The same effects are seen for GaS, thus N was plotted as a func-

tion of the peak position of the B-exciton from the absorbance spectra, λ^b (Figure 4.12).

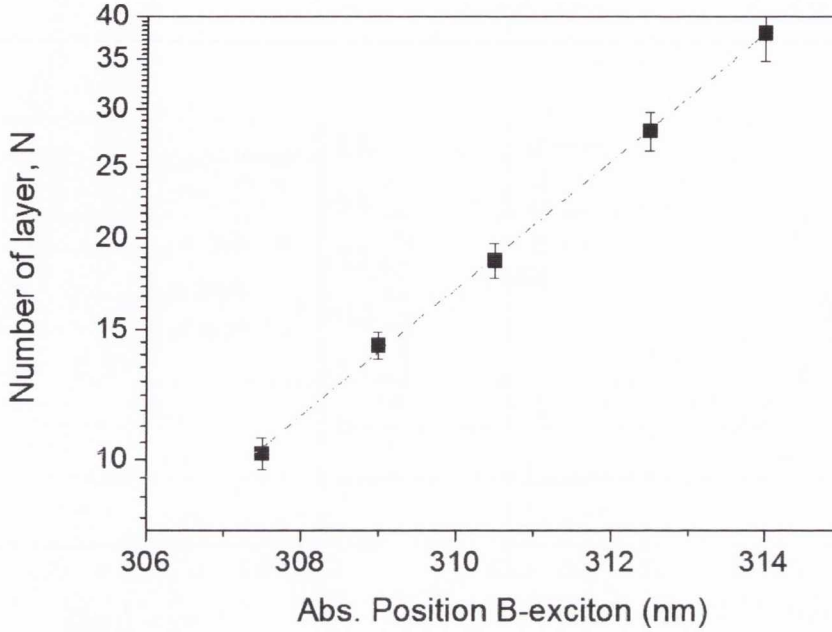


Figure 4.12: *Number of monolayers per nanosheet, N (determined from AFM) plotted versus position of the B-exciton, λ^b (measured from the absorbance spectra). The relation can be used as metric to determine N .*

To find N , step height analysis was used with the previously described method in section 4.5. The B-exciton was used rather than the A-exciton in this case, as the intensity of the A-exciton is comparatively weak for all GaS sizes. It is necessary to note that, in the case of GaS it was found that the peak positions in absorbance spectra give a more reliable measure than extinction spectra, as artificial peak shifts are introduced in the extinction due to the scattering background. $\langle N \rangle$ of GaS nanosheets can be determined from the peak position of the B-exciton in the absorbance spectra:

$$N = 10^{-25.65+0.0867\lambda_B(nm)} \quad (4.6)$$

The presented quantitative in situ spectroscopic metrics to determine $\langle L \rangle$, $\langle N \rangle$ and concentration of liquid exfoliated GaS underline the strength of LPE, as these will be extremely useful to prepare dispersions with known dimensions and concentrations to test

in applications.

4.7 Conclusion

In conclusion, it was demonstrated that layered III-VI semiconductors such as GaS can be exfoliated in appropriate solvents by sonication. Dispersibility can be well described in the framework of solution thermodynamics. Although a number of solvents can be used to exfoliate GaS, isopropanol was focused on due to its low toxicity and boiling point. Sonication and centrifugation parameters were optimised to yield stable dispersions with typical concentrations of 0.2 g/L. Raman, XPS, and TEM imaging show the exfoliated nanosheets to be widely structurally perfect and free of defects except for some oxygen content.

The advantage of liquid exfoliation techniques was utilised to perform size-selection by controlled centrifugation. This allowed the production of liquid-exfoliated GaS nanosheet dispersions with mean lateral dimensions ranging from ~ 100 nm to > 600 nm and mean number of layers from 10 to 40 as quantified by statistical TEM and AFM analysis. Importantly, it was found that optical extinction, absorbance, and scattering spectra to vary strongly as a function of size and thickness. This enabled the establishment of quantitative spectroscopic metrics to accurately determine mean length, thickness, and concentration of the dispersion.

These results are general and thus, it should be possible to transfer these procedures almost exactly for the exfoliation of other III-VI metal chalcogenides such as InS and GaSe. This will open up this whole family of 2D materials for exploitation. In addition, it is important to note that this paper describes using LPE to exfoliate a member (GaS) of yet another family of layered compounds (III-VI metal chalcogenides). This underlines the generality and versatility of this method, which should lead to many as yet untested layered materials will be exfoliated using such procedures.

Chapter 5

Exfoliation of Layered Double Hydroxides

5.1 Introduction

The variety of layered materials is an advantage that hasn't been fully profited from. It will be important to continually increase the number of families of layered compounds that can be exfoliated. By doing this it opens up a number of new applications such as oxygen evolution or sensing[70, 82]. A promising class of materials is the family known as the layered double hydroxides. The LDHs are a family of layered compounds with monolayers having the general chemical formula:

$$[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{\frac{x}{n}}^{n-}]^{n-} \bullet H_2O \quad (5.1)$$

where A^{n-} represent charge balancing anions which can reside between the layers and M^{2+} and M^{3+} are divalent and trivalent metal ions ($M^{2+} = Mg^{2+}, Fe^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}$ etc. and $M^{3+} = Al^{3+}, Fe^{3+}, Co^{3+}$ etc)[70]. Each layer is comprised of a central layer of metal ions sandwiched between layers of OH- groups. These materials tend to differ from the more well known families of layered materials as the monolayers are commonly charged and accompanied by charge balancing anions[70]. These crystals have been exfoliated using ion exchange where the charge balancing ion is replaced by a bulkier ion such as

dodecyl sulphate, this increases the space between the layers and thus reduces the van der Waal interaction making delamination easier[77]. These swelled crystals are then exfoliated in solvents such as formamide but these methods can be quite time consuming and cumbersome due to the need for multistep chemical processes[70].

Fortunately a subset of this family are considerably less complicated and exist in the form $M(OH)_2$, where $x = 0$ from equation 5.1, with $Ni(OH)_2$, $Co(OH)_2$ and $Mg(OH)_2$ being common examples[82, 166]. To date, these materials have only been exfoliated using ion intercalation[77, 89]. However, it would be advantageous to investigate the ability of LPE to produce dispersions of these materials as it would facilitate many applications which use spray deposition and inkjet printing[118]. As well as this, these materials can exhibit interesting optical properties despite all containing wide band gaps making it possible to devise statistical metrics, such as in chapter 4. This is due to d-d transitions within the metal ion of each LDH[90].

In this chapter a method for exfoliating a layered double hydroxide, $Ni(OH)_2$, will be demonstrated as well as a comprehensive size selection process whereas nanosheets of controlled lengths can be used for application such as catalysis. The dependence of the optical properties of the dispersions on nanosheet size are characterised, leading to metrics which allow the estimation of not only nanosheet concentration but also lateral size from extinction spectra. These methods will then be expanded to other members of the LDH family, $Co(OH)_2$, $Mg(OH)_2$, $Cu(OH)_2$ and $Zn(OH)_2$.

5.2 Experimental Procedure

5.2.1 Materials

Nickel (>95 % item no. 283662), Cobalt (>95 % item no. 342440), Magnesium (>99 % item no. 63081), Zinc (>95 %) and Copper hydroxide (>95 % item no. 289787) powder and sodium cholate (SC, item no. C1254) were purchased from Sigma Aldrich. De-ionized water was prepared in house and all solvents used were purchased with the highest available purity.

5.2.2 Sample Preparation

To remove potential impurities that may arise due to low cost, the hydroxide powder was pre-treated by sonication using a sonic tip in de-ionized water for 2 h. The dispersion was then centrifuged at 4.5 krpm (2150 g) for 1 h and the supernatant decanted with the sediment being retained and dried at 60 °C. Pre-treated Ni(OH)_2 was sonicated in surfactant and de-ionized water solution using a sonic tip. The sonication was performed using a solid flat head tip (Sonics VX-750) at 60 % amplitude with a 6 s on 2 s off pulse rate in an 80 mL metal cup. Mostly ice cooling was used except for the sonication time study, in this instance water cooling was used where a chiller pumps water around the metal cup maintaining a temperature of 15 °C. Once sonicated, the dispersion was centrifuged in a Hettich Mikro 220R centrifuge with a fixed-angle rotor 1060 (N.B.: for this centrifuge, rpm are related to g-force via $\text{RCF} = 106.4f^2$, where f is the rotation rate in krpm). The top 60% was then taken from the centrifuged (supernatant) for analysis and the sediment was discarded.

The surfactant concentration study entailed sonicating 10 g L^{-1} Ni(OH)_2 powder in 50 mL in increments of 1 g L^{-1} - 12 g L^{-1} of SC and de-ionized water for 1 h and centrifuging for 120 min at 1.5 krpm (240g) with the supernatant being decanted and analysed. The initial Ni(OH)_2 concentration experiments comprised of sonicating increments of 0.1 g L^{-1} to 75 g L^{-1} Ni(OH)_2 powder in 9 g L^{-1} of surfactant solution for 1 h and centrifuging for 120 min at 1.5 krpm (240g) with the supernatant being decanted. The sonication time study was carried out using water cooling, as overnight sonicating was required. 20 g L^{-1} of Ni(OH)_2 powder was sonicated in 9 g L^{-1} SC surfactant solution for 24 h with 4 s on 4 s off and 60% amplitude and centrifuging for 120 min at 1.5 krpm (240g) with the supernatant being decanted. In all cases, the supernatant was decanted and the absorption and extinction were measured in a 4 mm path length cuvette using a PerkinElmer Lambda 650 spectrometer (see below). The final optimized conditions were performed as follows: 20 g L^{-1} of X(OH)_2 were sonicated for 4 h in 9 g L^{-1} of SC and then centrifuged for 120 min at 1.5 krpm (240g).

Liquid cascade centrifugation was used with subsequently increasing rotation speeds as previously reported. 20 g L^{-1} Ni(OH)_2 in 80 mL of 9 g L^{-1} SC was sonicated for 4 h with a 6 s on 2 s off pulse rate. The 80 mL of sonicated dispersion was centrifuged at 0.5

krpm (27g) for 60 min. The sediment was discarded and the supernatant was centrifuged at 1 krpm (100g) for 60 min. The sediment after this centrifugation step was redispersed in fresh surfactant solution ($C_{SC} = 9gL^{-1}$, 25 mL) by 5 min bath sonication producing the largest size. The supernatant after the 1 krpm centrifugation step was centrifuged at 1.5 krpm (240g) for 60 min, producing the second largest size in the redispersed sediment. These steps were repeated in further increments of 2 krpm (425 g), 2.5 krpm (665g), and 3 krpm (950 g). In total five sizes were produced.

5.2.3 Characterisation Methods

Low-resolution bright field transmission electron microscopy imaging was performed using a JEOL 2100, operated at 200 kV. Holey carbon grids (400 mesh) were purchased from Agar Scientific and prepared by dropcasting a dispersion, of low concentration dispersion, onto a holey carbon tem grid which was placed ontop of a filter membrane to wick away excess solvent. The grid was placed at an elevated temp under vacuum to remove any residual solvent. Statistical analysis was performed of the flake dimensions by measuring the longest axis of the nanosheet and assigning it as “length”, L .

Atomic force microscopy (AFM) was carried out on a Veeco Nanoscope-IIIa (Digital Instruments) system equipped with a E-head (13 μm scanner) in tapping mode after depositing a drop of the dispersion (10 μL) on a preheated (120 $^{\circ}C$) Si/ SiO₂ wafer with an oxide layer of 300 nm. Typical image sizes were 3–10 μm at scan rates of 0.4–0.6 Hz. The high concentration dispersion was diluted with IPA immediately prior to deposition to yield a pale colloidal dispersion. After deposition, the wafer was rinsed with 5 mL of water and 5 mL of isopropanol. Typical image sizes were 2x2 mm² at scan rates of 0.8 - 1.0 Hz with 512 lines per image. The apparent thickness was converted to number of layers using previously developed step-height analysis[42].

Raman spectroscopy was performed using a WITec alpha 300 with 532 nm excitation laser in air under ambient conditions. The Raman emission was collected by an Olympus 100 $\times$ objective (N.A. = 0.8) and dispersed by 600 lines mm⁻¹ gratings. The laser energy was kept below 0.2 mW to reduce damage to the sample. 20 spectra were measured over a 4 μm line scan and averaged to obtain a rep spectra of the material.

X-ray Photoelectron Spectroscopy (XPS) was performed under ultrahigh vacuum con-

ditions ($<5 \times 10^{-10}$ mbar) using monochromated Al K α X-rays from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. The analyser pass energy was set to 100 eV for survey and 20 eV for core-level spectra, yielding a maximum energy resolution of 0.65 eV. An electron flood gun was used for charge compensation and the binding energy scale was referenced to the adventitious carbon 1s core-level at 284.8 eV. After subtraction of a Shirley background, the core-level spectra were fitted with Gaussian–Lorentzian line shapes. Samples were prepared by vacuum-filtering the dispersions using porous cellulose filter membranes (MF-Millipore membrane, mixed cellulose esters, hydrophilic, 0.025 μm , 47 mm) to give thin films.

5.3 Analysis of Ni(OH)₂ Powder

The layered form of Ni(OH)₂ was purchased as a powder from Sigma Aldrich (cost 27 c/g). The crystal structure is shown in Figure 5.1 A,B. When purchased at low cost it is possible that such powders contain non-negligible quantities of impurity material, the presence of which can negatively affect the exfoliation procedure[130]. In an attempt to remove some of these impurities, a pre-treatment procedure was employed which involved sonicating 3 g of powder for 2 hours in 80 ml water followed by a centrifugation step (1 h at 4500 rpm) to separate the solubilised and unstable components. Here the sediment contained the treated Ni(OH)₂ crystallites while the supernatant contained the impurity material. The sediment was then dried under vacuum at a low temperature to give a pre-treated powder. It is noted that, in addition to removing water-soluble impurities, such a procedure generally improves the yield of any subsequent exfoliation process as the crystal gets broken up into nanosheets which then reaggregate during this step[130]. To determine if any morphological changes had occurred scanning electron microscopy was performed on both the starting powder and the water treated powder (Figure 5.1 C,D).

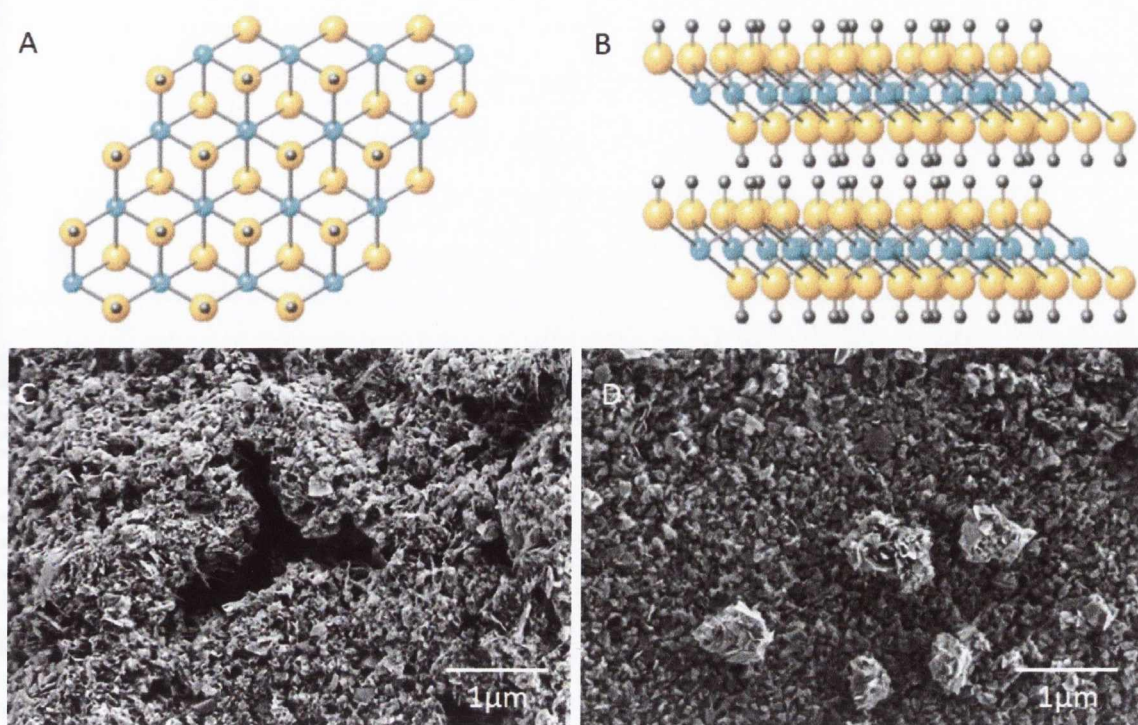


Figure 5.1: A,B) Top and side view of the structure of Ni(OH)_2 . Blue, Ni; yellow, O; silver, H. SEM image of the bulk powder (C) and the pretreated powder (D).

As can be seen there are few physical differences that can be observed from the SEM between the starting powder and the pretreated powder in relation to morphology although there is a clear difference in the orientation of the material. In Figure 5.1 C the crystal comprises of tightly packed nanosheets whereas in Figure 5.1 D the nanosheets have sedimented and are loosely packed which is easier to re-exfoliate back into nanosheets, thus producing larger concentrations[130].

Both starting material and pretreated powder were analysed by XRD to determine their structure (Figure 5.2). The XRD patterns of both bulk and pre-treated Ni(OH)_2 were consistent with single phase $\beta\text{-Ni(OH)}_2$ with the expected crystalline hexagonal structure ($a = 0.3126 \text{ nm}$, $c = 0.4605 \text{ nm}$), although there were two extra weak peaks in the bulk sample that are most likely due to removed impurities[82]. As no peaks from other phases are found, this suggests the layered material to consist of only one phase and contain only single valence Ni^{2+} [82]. This is important as the absence of the -balancing counter ions which are often found in LDHs will make LPE much more straightforward.

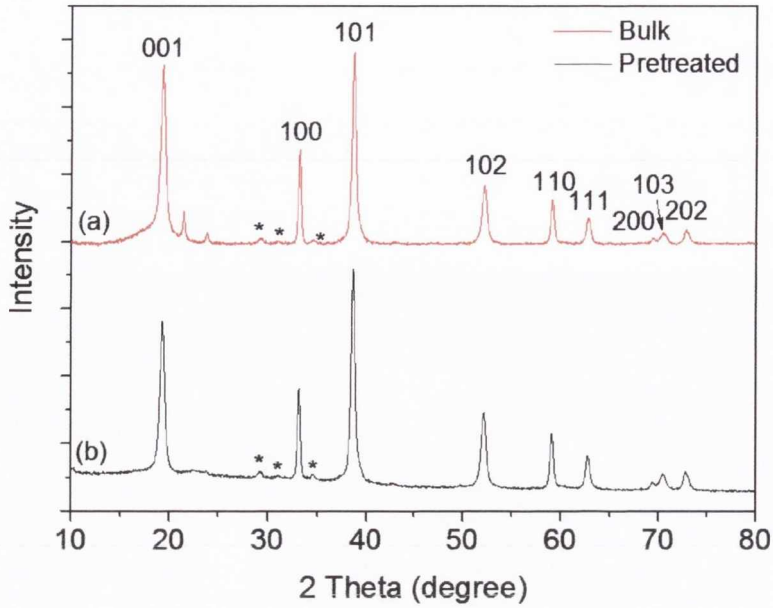


Figure 5.2: XRD spectra of bulk and pretreated $\text{Ni}(\text{OH})_2$ powder.

5.4 Exfoliation of $\text{Ni}(\text{OH})_2$

Contrarily to GaS, surfactant exfoliation was used to produce $\text{Ni}(\text{OH})_2$ nanosheets, rather than solvent exfoliation as it has been shown to produce smaller, thinner nanosheets[42]. For some applications it is advantageous to use larger nanosheets but for certain applications, such as catalysts in the HER or as a supercapacitor electrode, it is necessary to use smaller nanosheets[73, 165]. To demonstrate this 20 mg/ml of pre-treated $\text{Ni}(\text{OH})_2$ was sonicated in 9 mg/ml sodium cholate and water solution. The resultant dispersion was then centrifuged at 1.5 kRPM (240 g) and the supernatant decanted and retained resulting in a milky green liquid (Figure 5.3 A) and is referred to as the standard sample. To assess the quality of the exfoliation as well as to analyse the contents of the nanosheets, low-res TEM was performed on the dispersion. Large quantities of exfoliated 2D nanosheets that were electron transparent with well defined edges were found (Figure 5.3 B). Statistical analysis showed that the nanosheets had a mean length of $126 \text{ nm} \pm 4 \text{ nm}$ (Figure 5.3 C).

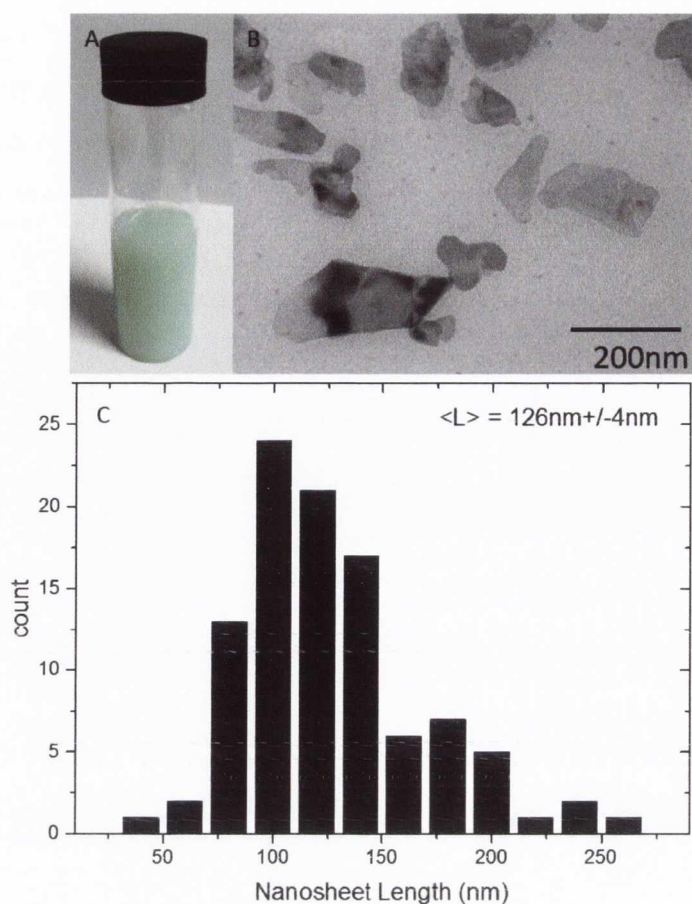


Figure 5.3: A) Photograph of typical $\text{Ni}(\text{OH})_2$ dispersion in surfactant solution. B) Representative low resolution TEM image of $\text{Ni}(\text{OH})_2$ nanosheets. C) Histogram of nanosheet length, $\langle L \rangle$, as measured by TEM.

To fully optimise the exfoliation process it is necessary to assess the mass produced within an individual dispersion by determining the concentration of nanosheets within the liquid. This is usually achieved by measuring the extinction of a dispersion through optical spectroscopy. Unfortunately for materials such as $\text{Ni}(\text{OH})_2$ this is not obvious, as the measured optical extinction, ext , is not just dictated by the absorption of light but also contains contributions from scattering effects. The scattering component varies with size which make concentration measurements unreliable[44, 90]. To address this, the ext , abs and sca spectra were converted to their respective coefficient spectra for the standard sample (using $\text{Ext} = \epsilon Cl$, where C and l are concentration and cell length respectively), as shown in Figure 5.4. This was performed following careful measurements of the dispersed nanosheet concentration, where the concentration is obtained by mass weighing through

vacuum filtration. The ext, abs, sca spectra were obtained using an UV - vis spectrometer with an integrating sphere attachment to separate abs from ext. From these spectra it is clear that the extinction is dominated by scattering effects with a very weak contribution from the absorption. The absorption coefficient spectrum displays a band edge at ~ 300 nm (~ 4.1 eV) as well as absorption peaks associated with the Ni^{2+} ions at 386 nm and 654 nm. This will be discussed further in section 5.6.

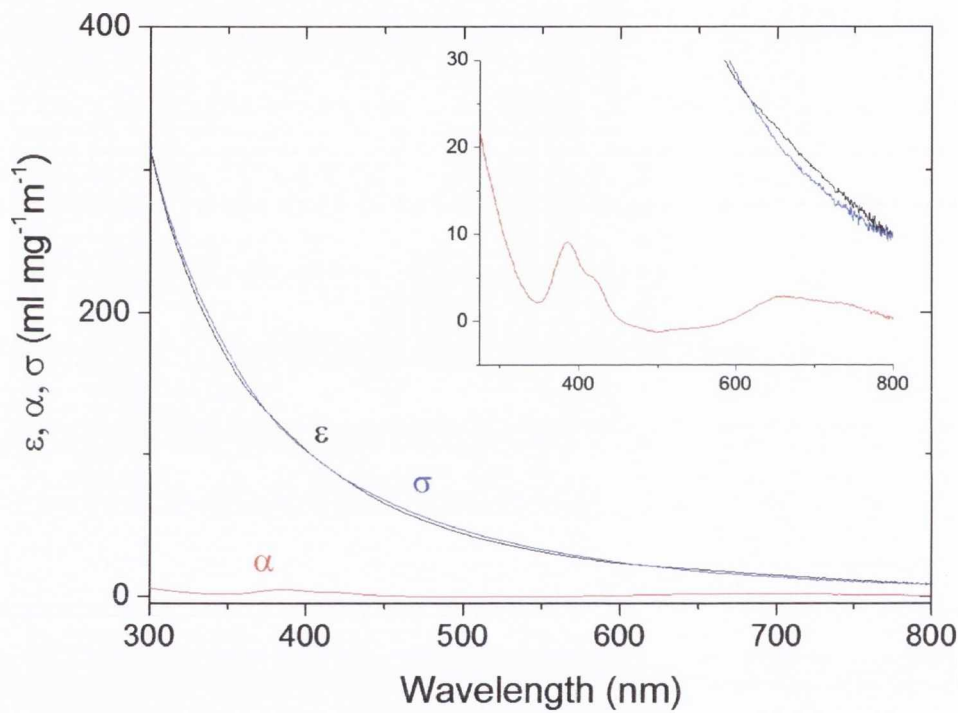


Figure 5.4: Optical extinction, absorption, and scattering spectra of $\text{Ni}(\text{OH})_2$. Inset: magnified view showing absorption spectrum.

As can be seen in the inset of Figure 5.4 the absorption coefficient at 386 nm is $\sim 10 \text{ mlmg}^{-1}\text{m}^{-1}$. This can be used to determine the nanosheet concentration from the absorbance (abs) via $\text{Abs}_{386\text{nm}} = \alpha_{386\text{nm}}Cl$. However, as an integrating sphere is not a standard piece of equipment and not readily available for most researchers, it is also useful to use the extinction coefficient to obtain the concentration. As well as this, the value obtained is very low relative to the extinction and thus is liable to have high error. This

can be achieved by using careful analysis of the extinction spectra and will be discussed in section 5.6.

5.4.1 Optimisation of Exfoliation Parameters

Similar to GaS, it is necessary to optimise the exfoliation conditions as to achieve the highest concentration, high quality dispersion within a reasonable time frame. The first parameter that is necessary to optimise is the surfactant concentration.

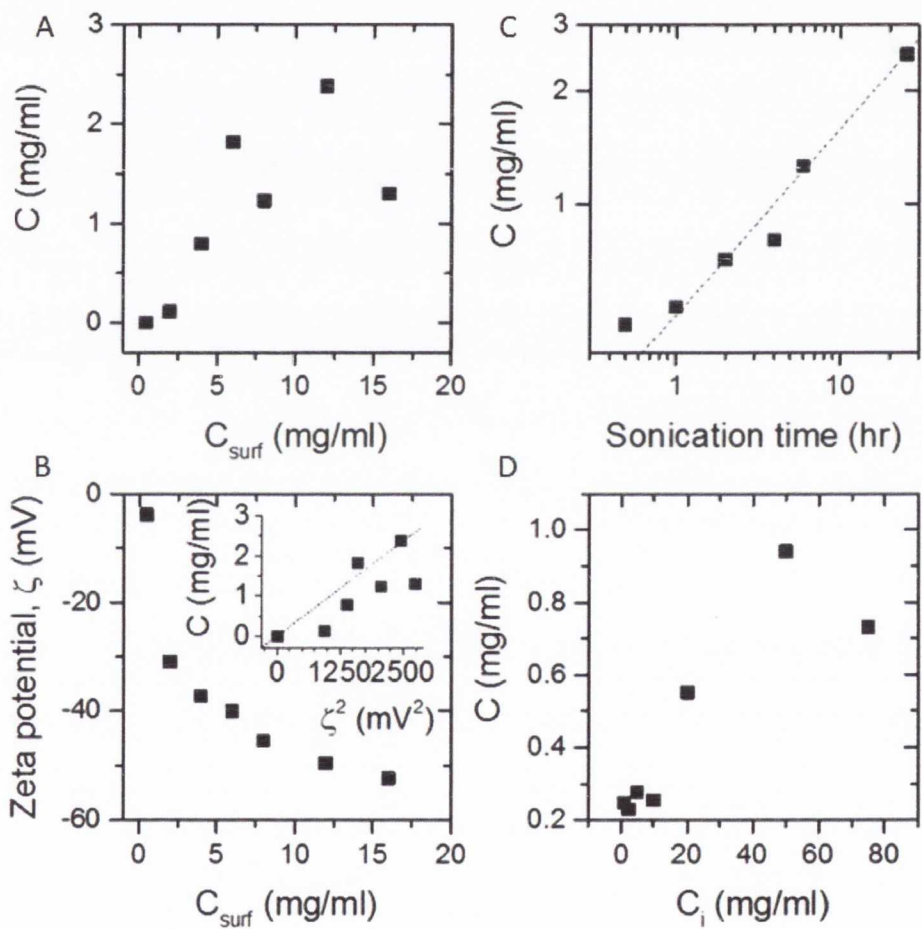


Figure 5.5: (A) Final Ni(OH)_2 nanosheet concentration plotted against surfactant concentration showing a peak at 9 g/L of sodium cholate. (B) Zeta potential plotted against surfactant concentration of dispersions from 1F. (C) Final concentration of Ni(OH)_2 plotted against sonication time indicating a square root dependence (dashed line). (D) Final concentration of Ni(OH)_2 nanosheets plotted vs. initial bulk Ni(OH)_2 concentration.

To achieve this 10 mg/ml of $\text{Ni}(\text{OH})_2$ powder was sonicated with varying amounts of surfactant concentration and centrifuged as described in section 5.2. The $\text{Ni}(\text{OH})_2$ concentration of these dispersions were then measured using the coefficients found in the previous section and plotted against surfactant concentration, as shown in Figure 5.5 A.

As can be seen there is a distinctive peak at ~ 9 mg/ml which is reasonably close to the critical micelle concentration (CMC) of sodium cholate[167], although this could show that there are small amounts of charge balancing ions on the surface of the nanosheets. In Figure 5.5 B, the absolute value of the zeta potential showed a steady increase with surfactant concentration which correlates to increasing nanosheet coverage and thus stability[115]. Secondly, the concentration of both material and surfactant were kept constant and the sonication time was varied (Figure 5.5 C). This lead to a square root dependence for final concentration versus sonication time, as has been shown for other 2D materials[13, 160, 161]. Finally, the initial powder concentration was varied while keeping the surfactant concentration consistent (Figure 5.5 D). Initial conc was then plotted against final concentration where there is a clear linear trend as expected, with a plateau at about 20 g l^{-1} [13, 44]. Combining these optimised conditions produces parameters of $C_i = 20 \text{ mg/ml}$, $C_{surf} = 9 \text{ mg/ml}$, $t_{sonic} = 4 \text{ hrs}$. These parameters combined with centrifuge conditions of $cf_{RPM} = 1.5 \text{ kRPM}$ and $cf_{time} = 2 \text{ hrs}$ yields a final concentration of 3 mg/ml which compares to the 2 mg/ml and 1 mg/ml found for graphene and MoS_2 respectively[160, 161].

5.5 Characterisation of $\text{Ni}(\text{OH})_2$ Nanosheets

Once the $\text{Ni}(\text{OH})_2$ nanosheets have been dispersed in the liquid phase, it is possible to perform more detailed characterisation techniques. To achieve this the dispersions were filtered onto nitrocellulose membranes using vacuum filtration, creating thin films of nanosheets stacked on top of each other. Scanning electron microscopy was performed on these films, as shown in Figure 5.6A inset, showing exfoliated nanosheets existing in disordered arrays, appearing structurally similar to films of other nanosheets types produced by LPE, such as GaS, as demonstrated in chapter 4.

To confirm that the film comprised of $\text{Ni}(\text{OH})_2$ nanosheets and to show that the exfoliation method didn't induce defects, Raman spectroscopy ($\lambda = 532 \text{ nm}$) was performed on

the film and the pre-treated powder (Figure 5.6). Both spectra show three distinct peaks at 324 cm^{-1} , 458 cm^{-1} and at 3583 cm^{-1} . The peak at 3583 corresponds to the internal stretching of the O-H bond, whereas 324 and 458 corresponds to the E_g and A_{1g} lattice modes respectively[82].

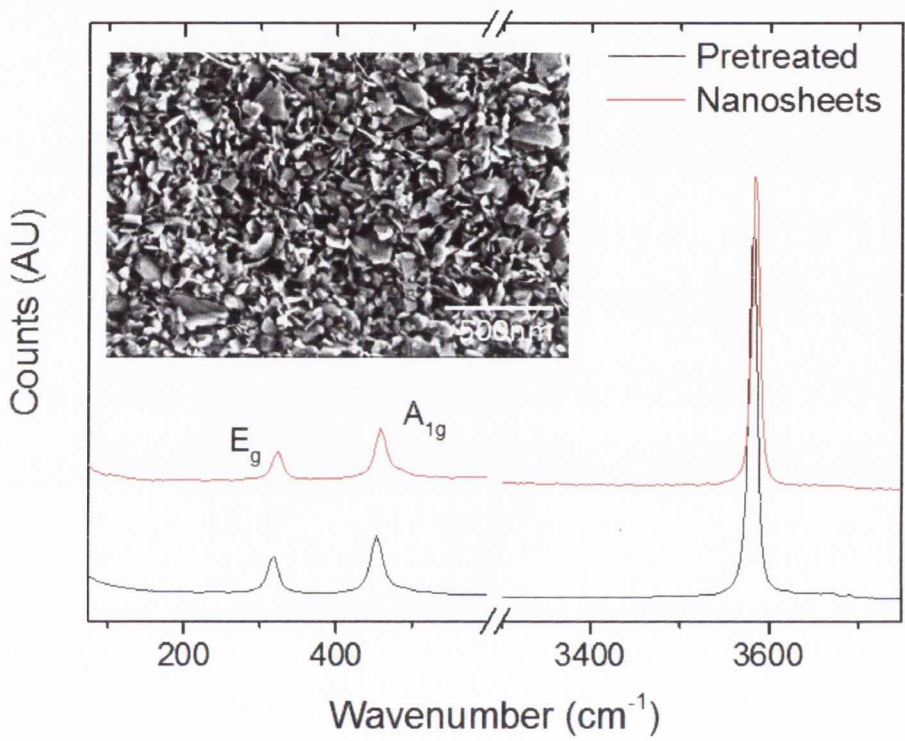


Figure 5.6: Raman spectrum (excitation wavelength = 532 nm, mean of 20 spectra) of standard film and pre-treated powder showing characteristic phonons of the Ni(OH)_2 with Representative SEM image of a film made with the filtered standard dispersion inset.

As demonstrated with GaS, XPS is a very powerful and useful tool to characterise 2D nanosheets through monitoring of the surface chemistry and chemical compositions. Shown in Figure 5.7 are Ni 2p and O 1s XPS core level spectra measured on both the pre treated powder and the exfoliated Ni(OH)_2 . The complex metal core level spectra of the Ni 2p core-level were fitted using the parameters established by Biesinger *et al*[168]. Fitting revealed both the pre-treated sample and exfoliated samples to consist almost exclusively of Ni(OH)_2 [168]. Although this data does not allow accurate differentiation between α , β

and γ $\text{Ni}(\text{OH})_2$, it can be concluded that the samples contain virtually no NiO or NiOOH and $<1\%$ Ni metal[82]. The corresponding $\text{O } 1s$ core-level spectra mainly show the expected $\text{Ni}(\text{OH})_2$ contribution at ~ 531 eV (red). There is also as a broad component on the high binding energy shoulder (blue), which contributes $\sim 30\%$ for the pre-treated sample and $\sim 23\%$ for the nanosheets. This is attributed to organic impurities remaining in the pre-treated sample and sodium cholate in the exfoliated sample, as well as residual nitrate from the synthesis. It is noted that sonication during the exfoliation process did not result in an increased NiO_x content as shown by the $\text{Ni } 2p$ and $\text{O } 1s$ core level spectra of the pre-treated and processed $\text{Ni}(\text{OH})_2$ (Figure 5.7).

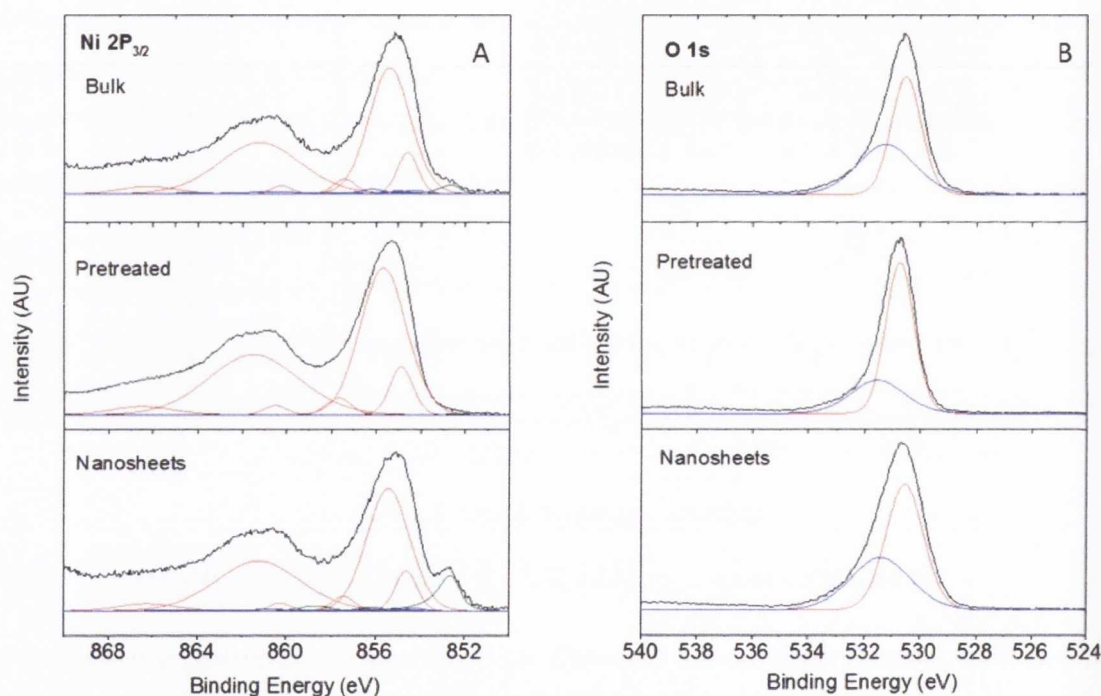


Figure 5.7: A,B) Fitted XPS core level spectra of pre-treated powder and a film of reaggregated, exfoliated nanosheets. (A) $\text{Ni } 2P_{3/2}$ core level spectra. (B) $\text{O } 1s$ core level spectra.

5.6 Size selection and Optical Characterisation of $\text{Ni}(\text{OH})_2$ Nanosheets

As mentioned previously, LPE has a significant advantage over other exfoliation procedures as it is possible to readily size select the nanosheets[13, 42]. This can be achieved

through a number of methods but in this section it was accomplished using liquid cascade centrifugation (LCC), where a number of sequential size selection steps are used to isolate nanosheets in different size ranges[43]. Using this method, five sizes were obtained XL, L, M, S and XS. Before the optical characterisation was performed it was necessary to ensure that the size selection procedure had worked, thus TEM was utilised. Both the statistical analysis showed a clear reduction in size from XL to XS with the mean length reducing from 195 nm to 87 nm (Figure 5.8).

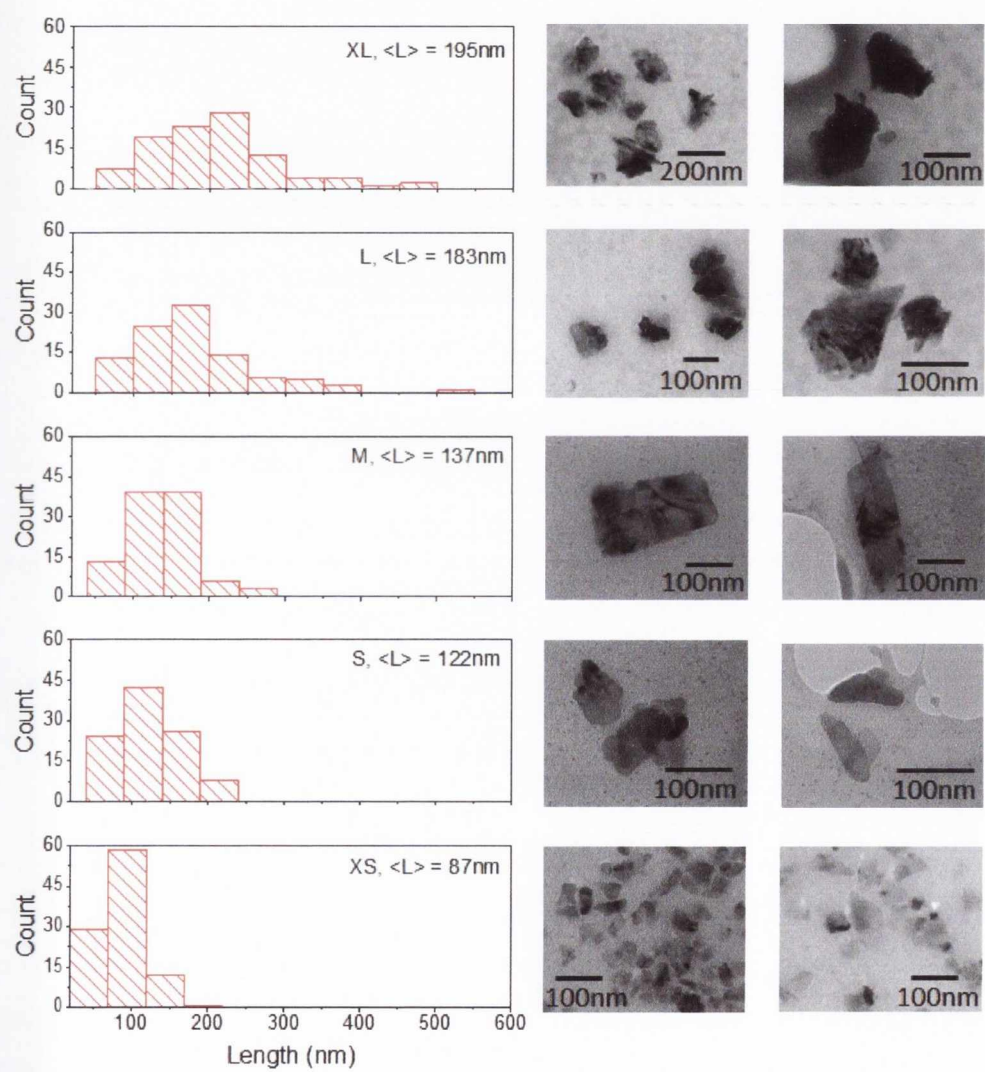


Figure 5.8: A-E) Histogram of nanosheet length, $\langle L \rangle$ for XL, L, M, S, XS respectively. F-K) Representative TEM images for XL, L, M, S, XS respectively.

The nanosheet length of a colloidal dispersion has a range of distinct effects on the

optical properties[42, 43]. As a result, the extinction, absorption and scattering coefficient spectra were measured for each (as shown in Figure 5.9). It is clear from this data that the extinction coefficient is very sensitive to nanosheet size with ϵ increasingly strongly with $\langle L \rangle$ for all wavelengths. Also, the extinction spectra and scattering spectra look almost identical due to a very small contribution from light absorption.

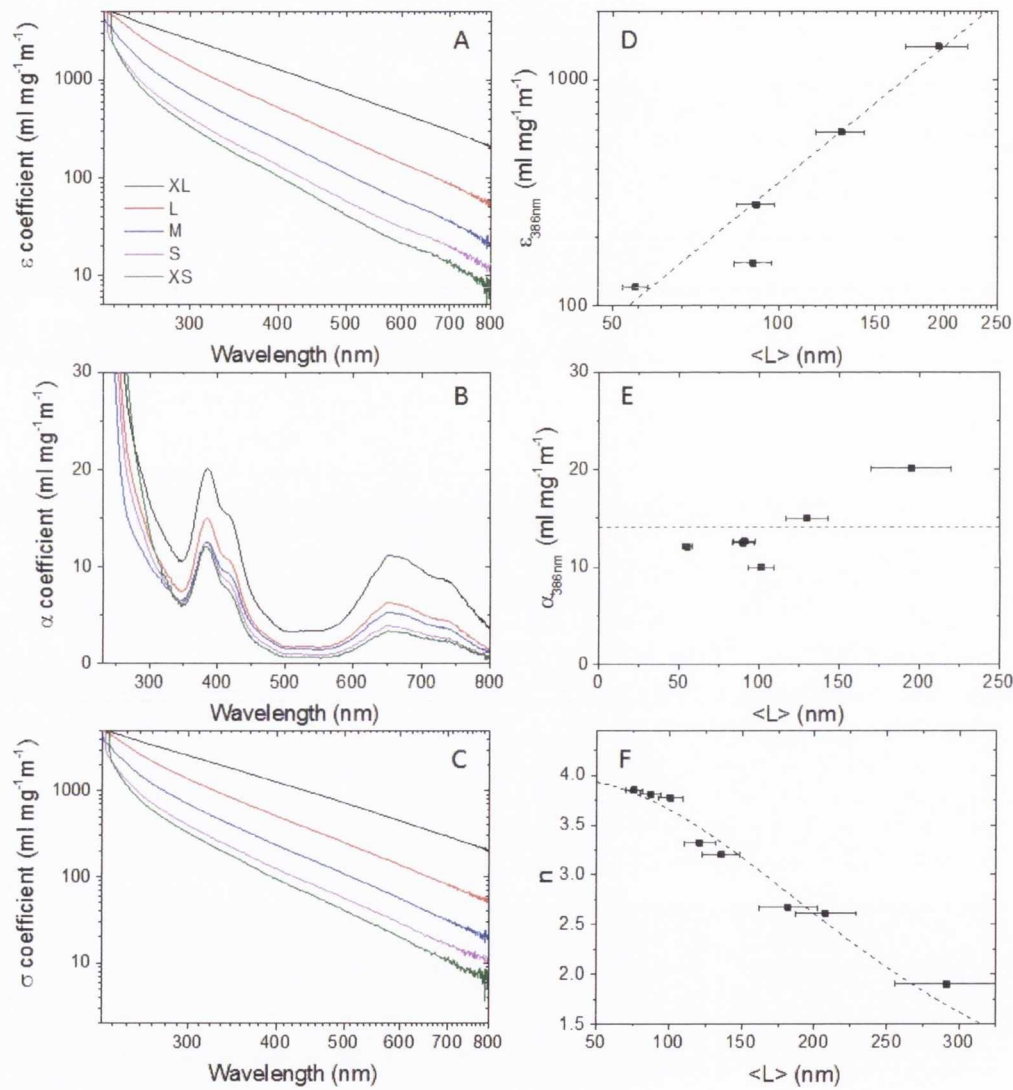


Figure 5.9: A-C) Extinction (A), absorption (B) and scattering (C) coefficient spectra for all five sizes. (D) Extinction coefficients ($\lambda = 387$ nm) as a function of $\langle L \rangle$. (E) Absorption coefficients ($\lambda = 387$ nm) as a function of $\langle L \rangle$. (F) Long wavelength scattering exponent, n , measured from scattering (or extinction) spectra, plotted versus TEM $\langle L \rangle$.

As shown in Figure 5.9 B, the absorption spectra doesn't change much with size. The slight difference for XL most likely being due to slight error in removing the absorption from the extinction spectra by the device. The peaks at 386 nm and 654 nm don't shift with nanosheet size due to the fact that they are caused by absorption within the Ni^{2+} ions which are much smaller than the size of the nanosheets[90]. The peaks at 700 nm and 400 nm are due to the $^3\text{A}_2 \rightarrow ^3\text{T}_1(3\text{f})$ and $^3\text{A}_2 \rightarrow ^3\text{T}_1(3\text{P})$ transitions respectively. These transitions are all associated with Ni^{2+} in an octahedral symmetry and are assigned on the basis of the d^8 system with the local crystal field altering the free ion levels[169].

The scattering spectra are characterised by a power law decay, $\sigma \propto \lambda^{-n}$, which holds for $\lambda > 300$ nm. This value, n , is known as the scattering exponent and is size dependent as can be seen in Figure 5.9 F. The extinction and absorption coefficient at 386 nm are plotted against $\langle L \rangle$ in Figure 5.9 D. The extinction coefficient at 386 nm, $\epsilon_{386\text{nm}}$, is very similar to the scattering coefficient, with the values being almost the same for the same flake length. This is due to the contribution from absorption being very low as $\alpha_{386\text{nm}} = 14 \text{ Lg}^{-1}\text{m}^{-1}$. In Figure 5.9 E it appears that $\alpha_{386\text{nm}}$ increase with $\langle L \rangle$, this is most likely due to scatter in the data that has arisen from the use of an integrating sphere to extract a value of α so small. It is expected that $\alpha_{386\text{nm}}$ is independent of $\langle L \rangle$ and is controlled by the number of Ni^{2+} ions per volume. This is not the case for the extinction coefficient as it increases strongly with nanosheet length in a manner which can be described empirically by

$$\epsilon_{386\text{nm}} \approx \sigma_{386\text{nm}} = 0.035 \langle L^2 \rangle \quad (5.2)$$

Where $\langle L \rangle$ is in nm. This equation is valid for materials where $\sigma \gg \alpha$ and the behaviour is essentially a manifestation of the length dependence of the scattering coefficient and can be described by Mie theory, in principle[141]. Although, this can become incredibly complex as there are no theoretical studies which predict the size dependence of the scattering coefficient of ensembles of nanoscale discs which would allow validation of eq. 5.2.

As mentioned previously the scattering coefficient scales with the wavelength as λ^{-n} . This has been demonstrated for other 2D materials such as MoS_2 , BN and GaS and is

consistent with Mie scattering[42, 44, 98]. From the scattering spectra the scattering exponent, n , has been taken by measuring the slope of the curve and has been plotted against $\langle L \rangle$. This graph shows an increase in n from 2 to almost 4. This isn't an unexpected result because for the very small particles with $L \ll \lambda$, it is expected that the light would be scattered via Rayleigh scattering which is characterised by a scattering exponent of $n = 4$ [141]. For larger nanosheets Mie scattering becomes dominant as the light is scattered across all wavelengths. Using an empirical relationship to fit this data

$$n = [1 + (\frac{\langle L \rangle}{257})^{-2.5}] \quad (5.3)$$

Where $\langle L \rangle$ is in nm. This equation can also be expressed in terms of $\langle L \rangle$

$$\langle L \rangle = 257[\frac{4}{n} - 1]^{0.4} \quad (5.4)$$

As discussed in section 5.4 it is useful to be able to obtain the concentration of a dispersion by using extinction spectroscopy instead of absorption spectroscopy due to the availability of the equipment[42]. It is possible to obtain the concentration of a dispersion using α but this isn't ideal as it requires the use of an integrating sphere, thus it is more feasible to use ϵ . A downside to this is that $\langle L \rangle$ changes so drastically with ϵ , thus it is necessary to obtain a size dependent metric for ϵ . By combining equation 5.2 and 5.4 this is attainable.

$$\epsilon_{386nm} = 2312[\frac{4}{n} - 1]^{0.8} \quad (5.5)$$

Where ϵ_{386nm} is in $Lg^{-1}m^{-1}$. By obtaining n from the extinction coefficient spectrum equation 5.5 can be used to obtain the extinction coefficient at 386 nm. This can be used to obtain the concentration using the Beer Lambert Law

$$C = \frac{Ext_{386nm}}{2312l}[\frac{4}{n} - 1]^{-0.8} \quad (5.6)$$

Where l is the path length of the cuvette and C is the concentration in gL^{-1} . This equation allows for the concentration of a given dispersion to be obtained using a simple ext spectroscopy measurement and avoids the need for expensive and time consuming statistical TEM.

5.7 Expansion to other Layered Double Hydroxides

$Ni(OH)_2$ is only one of many layered double hydroxides. Four more examples of this family are $Co(OH)_2$, $Cu(OH)_2$, $Mg(OH)_2$ and $Zn(OH)_2$, none of which to this point have been exfoliated using liquid phase exfoliation. All five layered double hydroxides studied in this work have identical structures (Figure 5.1A) which mimic that of the 1T polytype of MoS_2 . All contain only single valence metal ions (M^{2+}) meaning the monolayers are nominally uncharged while in all cases the surfaces consist of OH^- groups implying that each material should display similar surface chemistry[90]. Because liquid exfoliation relies on stabilisers (i.e. solvent, surfactant or polymer molecules) binding to the nanosheet surface, this similarity in surface chemistry suggests that any exfoliation route that works for one of the materials should work for all five[115].

5.7.1 Initial Exfoliation

All five materials were exfoliated using the optimised conditions obtained from section 5.4 with the same sonication and centrifugation parameters, resulting in four deeply coloured dispersions with nickel, copper and cobalt hydroxide being green, blue and pink respectively and both magnesium and zinc hydroxide being white as expected based off the colours of the powders (Figure 5.10 A).

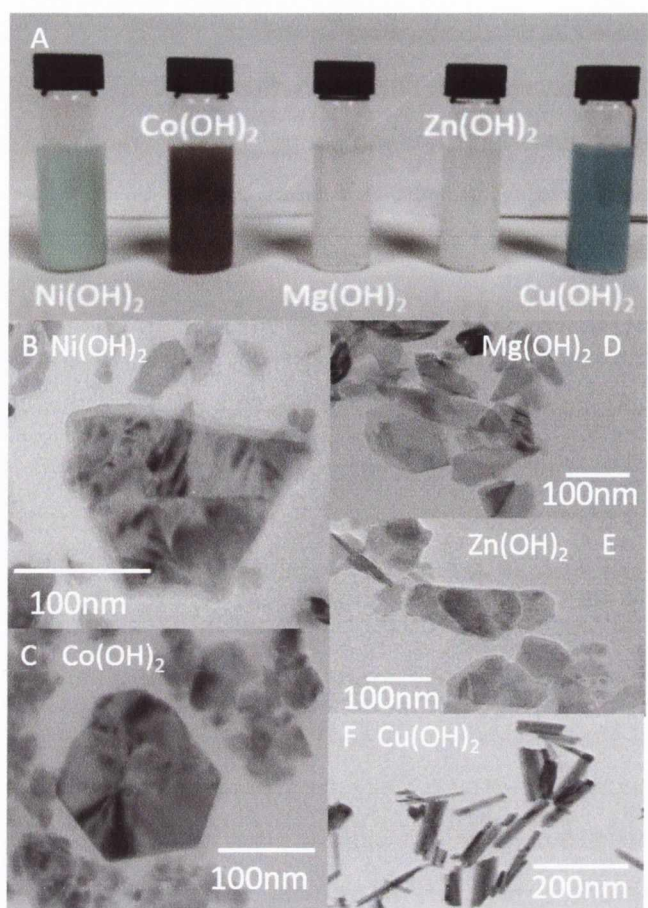


Figure 5.10: A) Photograph of dispersions of LDHs produced by a “standard” exfoliation procedure. B-F) Representative TEM images of few-layer LDH nanosheets of each type.

To ensure successful exfoliation, transmission electron microscopy was performed on all five standard samples typical images shown in Figure 5.10 B-F. In all cases except Cu(OH)_2 , the exfoliated product consisted of 2-dimensional nanosheets. As is usually found in the case of LPE, these nanosheets are not exclusively monolayers but generally consist of few-layer nanosheets with a broad thickness distribution[42, 116, 117]. For example, Ni(OH)_2 nanosheets exfoliated by LPE displayed thicknesses varying from 1-25 monolayers with a mean thickness of 10 monolayers[90]. While such thickness polydispersity is clearly a disadvantage over ion-exchange based methods of LDH exfoliation, it is believed for this to be an acceptable downside when compared to the speed and ease associated with LPE. While most of the materials studied here conform to the normal shape usually observed for nanosheets produced by LPE[13, 42, 116, 170], the exfoliation

product for the $\text{Cu}(\text{OH})_2$ sample was clearly different (Figure 5.10 F), displaying a more belt-like structure. While the length/width aspect ratio for the other four materials was close to 1.5, the $\text{Cu}(\text{OH})_2$ nanosheets displayed $< 3.83/1 >$. Although the nature of this difference is not clear, it is noted that MoO_3 nanosheets exfoliated by LPE displayed $\langle \text{length/width} \rangle = 2.6$, which is higher than is normally found[13]. While in that case the unusual aspect ratio was related to atomic structure of MoO_3 , this is unlikely to be the case here.

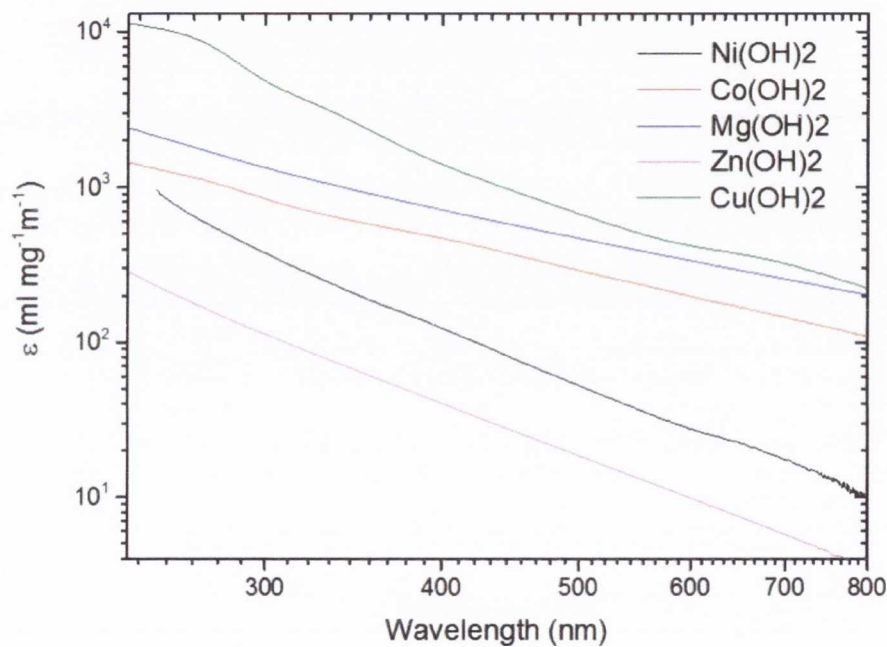


Figure 5.11: *Optical extinction spectra of dispersions of LDH nanosheets produced by the “standard” procedure.*

To further characterise the materials the extinction coefficient spectra were obtained for each hydroxide. This was achieved using previously described methods used throughout this thesis with the dispersion concentration measured by filtration and weighing. As can be seen from Figure 5.11 all the spectra are effectively featureless due to large contributions by light scattering and thus give little material information. Despite three of the materials having distinctive colours this is to be expected as all four materials are insulators with

bandgaps larger than 3 eV with only small absorption contributions from the metal ion, as described in section 5.6. The absorption features of each material are explained in greater detail in section 5.9.

5.8 Characterisation of LDHs

Once the nanosheets were dispersed in the liquid phase it is possible to perform more detailed characterisation. To achieve this, thin films are prepared through vacuum filtration. Raman spectroscopy ($\lambda = 532 \text{ nm}$) was used to examine the dispersed nanosheets for each hydroxide (Figure 5.12). In four cases (Ni, Co, Cu and $\text{Mg}(\text{OH})_2$) the Raman spectroscopy is as expected.

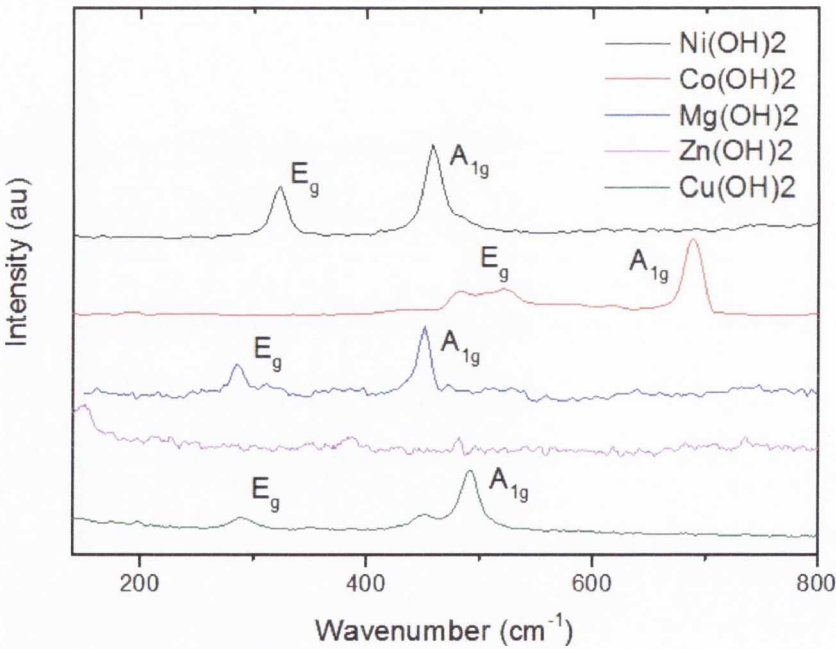


Figure 5.12: Raman spectra, measured on films prepared by filtration of dispersions of LDH nanosheets produced by the “standard” procedure.

For $\text{Ni}(\text{OH})_2$, as previously reported, there are distinct peaks at 324 and 458 cm^{-1} corresponding to the E_g and A_{1g} Raman-active transitions characteristic for $\beta\text{-Ni}(\text{OH})_2$ [82].

This is very similar to magnesium and copper hydroxide whose equivalent modes correspond to 281 cm^{-1} and 445 cm^{-1} and 288 cm^{-1} and 491 cm^{-1} respectively[171, 172]. For $\text{Co}(\text{OH})_2$ the modes are shifted as they correspond to 479 cm^{-1} and 686 cm^{-1} for the E_g and A_{1g} [173, 174]. This is likely due to the $\text{Co}(\text{OH})_2$ being more tightly packed within the lattice and thus will have higher vibrational frequencies. For $\text{Zn}(\text{OH})_2$ no measurable spectra has been appropriately achieved although the most Raman active spectra has been attached. In the cases of $\text{Co}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ there are also additional features at 515 cm^{-1} and 450 cm^{-1} respectively which correspond to the A_u modes. For the four materials described this matches with previously reported Raman spectra[82, 171, 172, 173, 174].

5.9 Optical characterisation of Size Selected LDHs

Similar to previous work, the dispersions produced by LPE have a broad distribution of nanosheet length and thicknesses, this means that they can be readily size selected. Again, this work uses the method referred to as liquid cascade centrifugation (LCC), a method that involves a number of sequential centrifugation steps, to isolate nanosheets in different size ranges (see Methods). Here five size-selected dispersions are produced for each of the five materials. They were labelled in order of decreasing size as XL, L, M, S, XS.

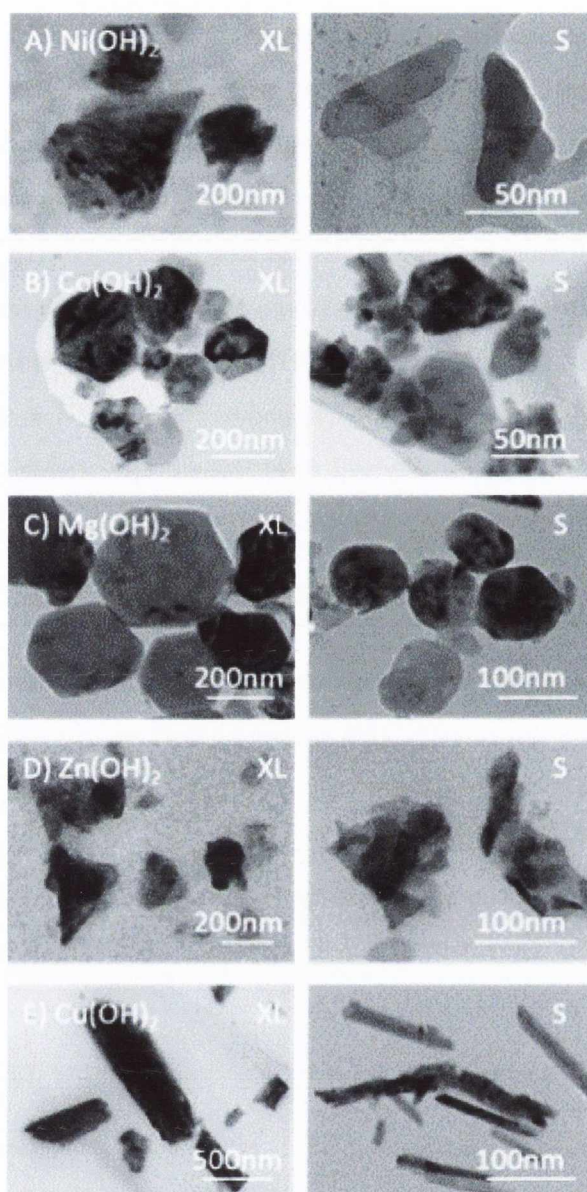


Figure 5.13: *Size selection of LDHs. A-E) TEM images of nanosheets separated into the extra-large (XL, left) and small (S, right) fractions for each of the five nanosheet types.*

For each material, TEM was performed on each size and analysed as described previously. Shown in Figure 5.13 A-E are representative images of the XL and S sizes. Statistical analysis was performed on each of the nanosheet lengths. In all instances the nanosheets and nanobelts were well exfoliated for all sizes and there was an obvious decrease in average size going from XL to XS. With changes in size ranging from 223 nm to 65.67 nm, 194 nm to 39nm, 470 nm to 205 nm, 234 nm to 77 nm for Ni(OH)_2 , Co(OH)_2 ,

Mg(OH)₂, Zn(OH)₂ and Cu(OH)₂ respectively.

In Figure 5.14 A is a plot of the mean length $\langle L \rangle$ against Central RPM where the materials follow a trend of L decreasing as rpm^{-1} as predicted by theory with Cu(OH)₂ having the longest nanosheets ranging from 946 nm to 267 nm and Co(OH)₂ having the shortest. For Cu(OH)₂ this makes sense, as the nanosheets are nanobelts they will have much larger $\langle L \rangle$ while having a similar surface area. For Co(OH)₂ the nanosheets are similar in length to Ni(OH)₂ and Zn(OH)₂ but all three are much smaller than Mg(OH)₂. The chosen centrifugation method separates the material by mass as smaller lighter nanosheets need a higher centripetal force to cause them to sediment. Thus, for these materials, the length at a given rpm scales roughly inversely with density in the order: Mg(OH)₂ > Zn(OH)₂ > Ni(OH)₂ > Co(OH)₂.

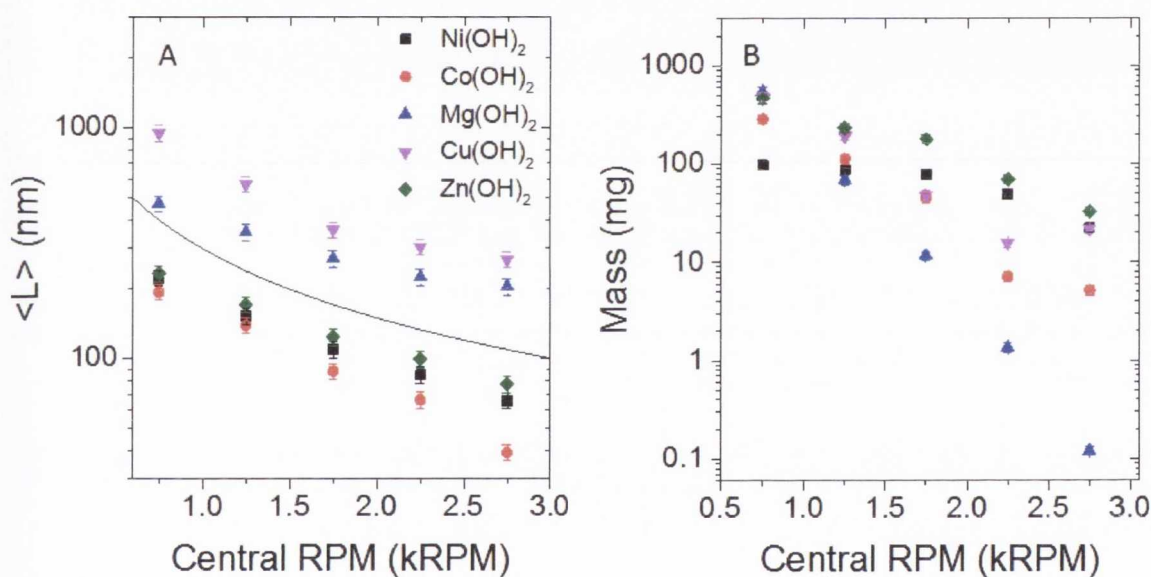


Figure 5.14: A-B) Mean nanosheet length (A) and mass of nanosheets collected (B) for each fraction, plotted as a function of the central centrifugation speed used to collect each fraction.

As well as being able to control the lengths of the nanosheets using LCC it is also possible to produce and control large masses of each given size. To demonstrate this the concentration of each dispersion was found using previous methodologies. As the volume is known during the redispersion step it is possible to convert concentration into mass produced. This is shown in Figure 5.14 B where mass collected is plotted against central

RPM. This graph shows a very obvious trend with a lot of mass for the large sizes that decreases with decreasing nanosheet size due to the small nanosheets being collected at most steps. Thus, the amount will decrease with increasing RPM as well as this, all the larger nanosheets are collected in earlier steps. For $\text{Mg}(\text{OH})_2$ the drop in mass is most dramatic. This is most likely due to there being fewer small particles in the starting powder.

As previously reported, as well as being shown in this thesis, the optical properties of nanosheets change drastically with size[42, 43]. This was demonstrated by measuring the extinction, scattering and absorption spectra for all sizes of all five hydroxides. Shown in Figure 5.15 are the respective spectra of $\text{Zn}(\text{OH})_2$, $\text{Co}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$, chosen as three materials with distinctive colours and thus, spectra. The spectra of $\text{Ni}(\text{OH})_2$ has been shown previously and $\text{Mg}(\text{OH})_2$ is shown in the appendix. As can be seen, the extinction and scattering spectra are very similar due to the absorption spectra being mainly featureless and most of the contribution to extinction being due to scattering effects.

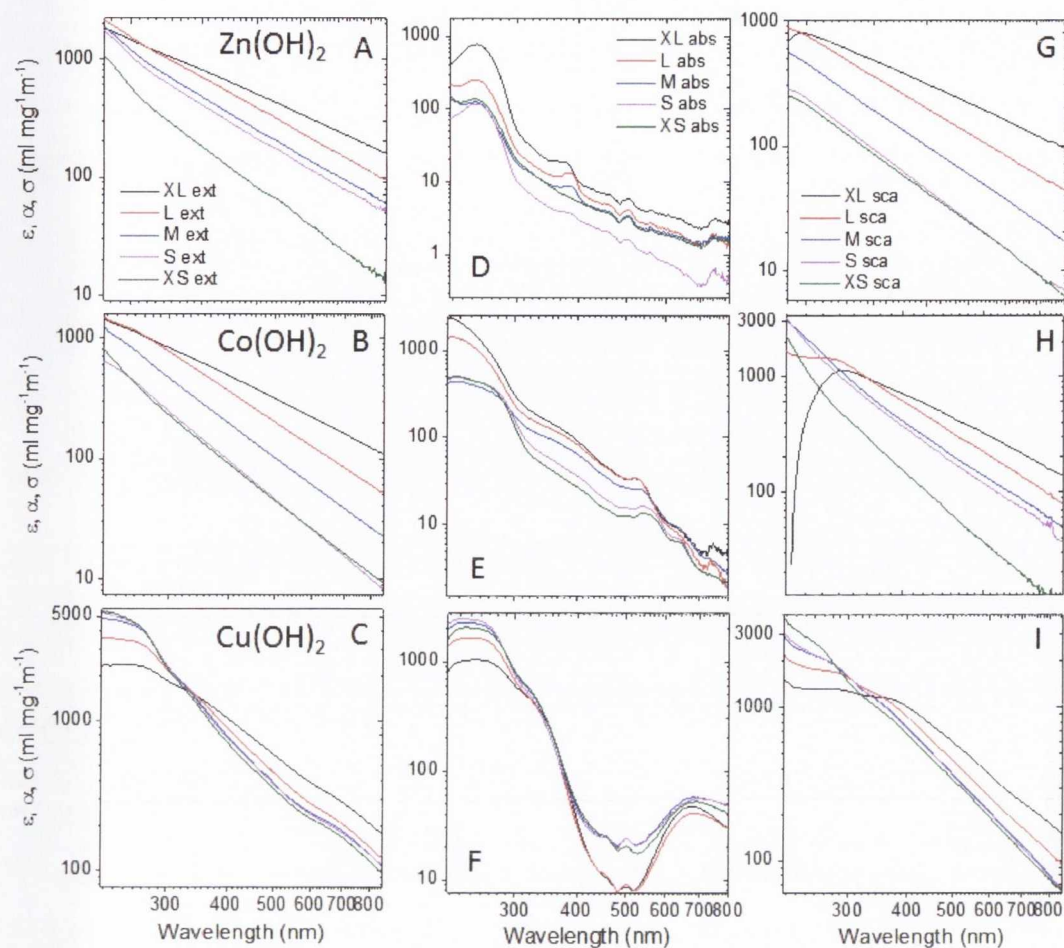


Figure 5.15: A-C) Optical extinction (A-C), absorption (D-F) and scattering (G-I) coefficient spectra measured for five different fractions (different sizes) of Zn(OH)_2 , Co(OH)_2 and Cu(OH)_2 nanosheets respectively.

It can be seen clearly that the absorption spectra for size selected Zn(OH)_2 are mainly featureless as it is a white material that absorbs close to zero light until approximately 400 nm with a bandedge at approximately 280 nm. For both Co(OH)_2 and Cu(OH)_2 the spectra doesn't appear to be largely size dependent but the intensity does increase slightly with increasing length. The absorption spectra for both cobalt and copper hydroxide (as well as nickel hydroxide) are quite interesting as unlike many layered materials such as the TMD's the absorption isn't due to the entire compound but just due to the metal ion within the hydroxide. To demonstrate this, the absorption spectra of the five materials of approximately the same length were plotted together. This is shown below in Figure 5.16.

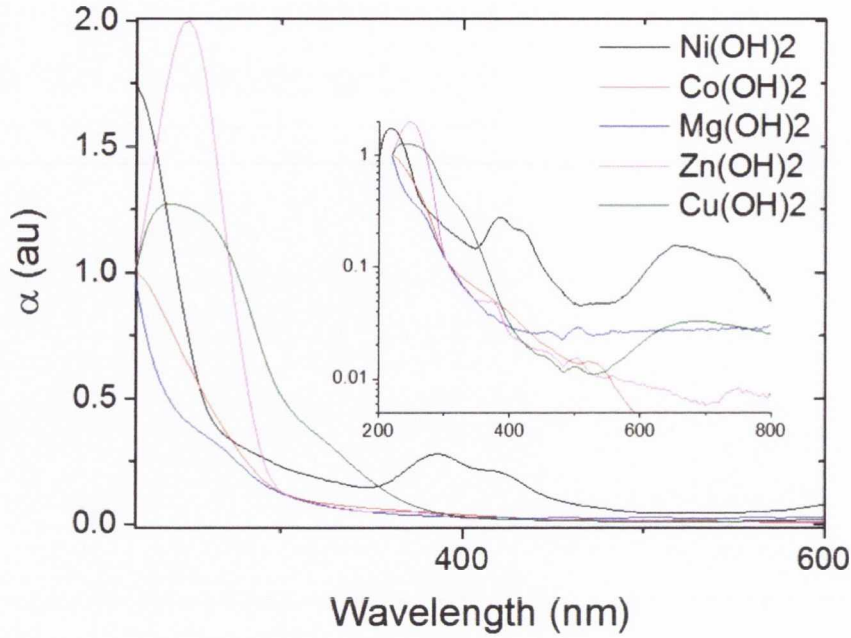


Figure 5.16: Normalised absorption spectra for each material (250nm). The data shown represent the XL fractions for Ni(OH)₂, Co(OH)₂ and Zn(OH)₂ samples but the XS fractions for the Mg(OH)₂ and Cu(OH)₂ samples. These fractions were chosen to ensure a similar size range ($\langle L \rangle \sim 200\text{-}250$ nm) for each material. Inset: semi-log plot.

For the example of Ni(OH)₂ the peaks at 700 nm and 400 nm are due to the $^3A_2 > ^3T_1$ (3F) and $^3A_2 > ^3T_1$ (3P) transitions respectively (there is also a peak at ≈ 1100 nm which is due to the $^3A_2 / ^3T_2$ (3F) transition) as described in section 5.6[175]. For both Mg(OH)₂ and Zn(OH)₂ there are no features of interest before 300 nm where they both have a bandedge at < 220 nm and 250 nm corresponding to > 5.6 eV and 5 eV. The absorption in Co(OH)₂ and Cu(OH)₂ is due to d-d transitions within the band gap. For Co(OH)₂, in the absence of spin-orbit coupling, only the $^4A_2(^4F) > ^4T_1(^4P)$ transition is allowed in the visible spectrum, accounting for the peak at 600 nm. In Cu(OH)₂ the observed absorption band at 700 nm is due to the overlap of $^2B_{1g} > ^2A_{1g}$ and $^2B_{1g} > ^2B_{1g}$ [176, 177, 178].

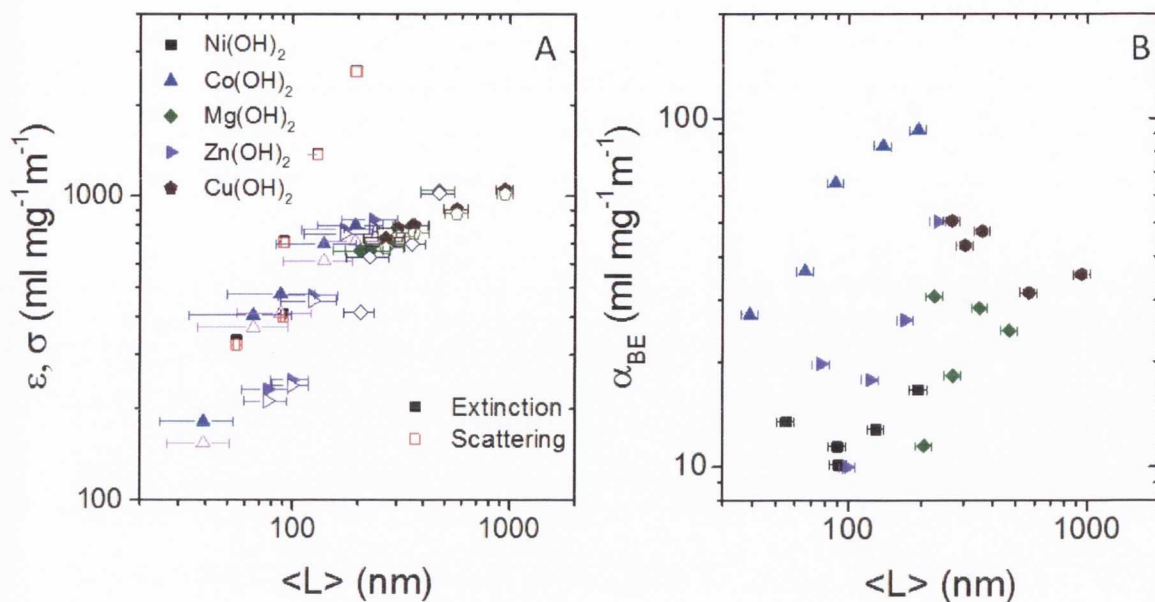


Figure 5.17: Extinction and scattering (A), absorption (B) coefficients measured close to the bandedge for each material plotted versus mean nanosheet length. The wavelengths where the coefficients were taken at 300 nm for Ni(OH)_2 , Mg(OH)_2 , Zn(OH)_2 and 400 nm for Co(OH)_2 , Cu(OH)_2 .

To determine the effects that length have on the ext, sca, and abs coefficients the nanosheet $\langle L \rangle$ was plotted against the three parameters for a specific wavelength just below the material bandedge (Figure 5.17 A,B). As expected ϵ and σ increase with increasing $\langle L \rangle$, also, all four materials show a very similar trend with the exception of Ni(OH)_2 which increases at a greater rate. α also increases with $\langle L \rangle$ although with different absolute values for the different materials. ϵ and σ are plotted together as they are very similar.

It has been shown that the scattering exponent of a material can be used to obtain $\langle L \rangle$ for 2D nanosheets. The scattering exponent, n , can be extracted from the scattering spectra by measuring the slope of the spectra in a region with zero absorption. This value n is plotted against $\langle L \rangle$ for the five materials in Figure 5.18. The graph shows n to be very close to 4 for very small nanosheets and to increase to approximately 1 - 2 for larger nanosheets. This is due to the contributions from Rayleigh scattering which is predicted for $L \ll \lambda$ and is characterised by a scattering exponent of $n = 4$ [44, 141]. For larger nanosheets, Mie scattering becomes predominant, resulting in a reduction of n .

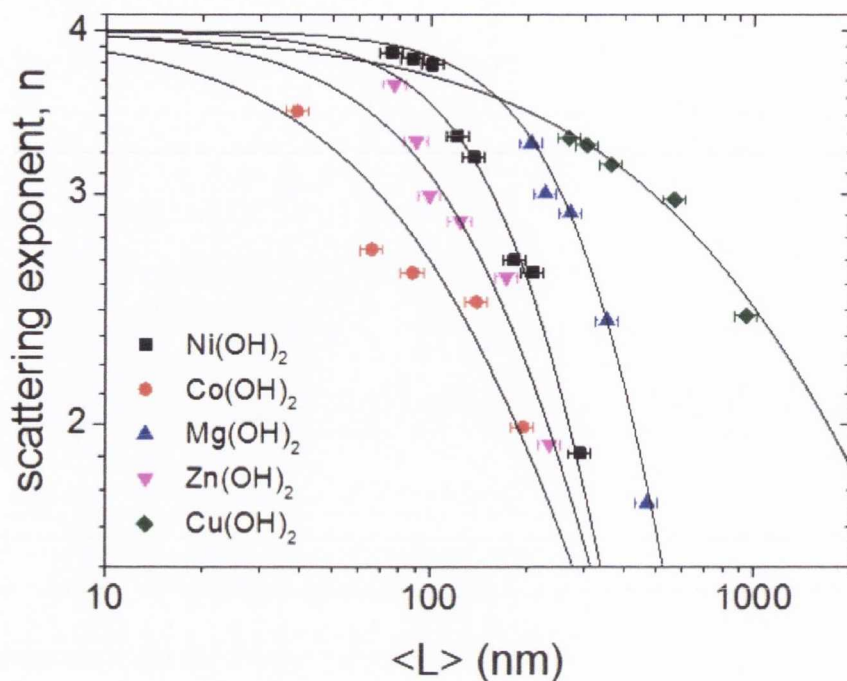


Figure 5.18: *Scattering exponents plotted versus mean nanosheet length for each material. The lines are fits to equation.*

All five curves were fitted using an empirical function that is described in detail in chapter 7 that has previously been published for $\text{Ni}(\text{OH})_2$ with differing variables[90]. These fits can then be used to obtain $\langle L \rangle$ from n and prevent the need for statistical TEM. The specific fits are given in the appendix. Four of the five materials exhibit similar trends with the exception of copper hydroxide, this is most likely due to the nanobelt geometry of the $\text{Cu}(\text{OH})_2$ nanosheets as scattering effects are due to the complete size of the nanosheets and not a simple length effect.

5.10 Conclusions

In conclusion, it was demonstrated that liquid phase exfoliation can be used to exfoliate layered $\text{Ni}(\text{OH})_2$ crystals from commercially available powder to give liquid dispersions of few layer $\text{Ni}(\text{OH})_2$ nanosheets with the identity of the dispersed material being characterised by SEM, Raman and XPS. This process yields nanosheets in a broad size range at

reasonably high concentrations and with production rates which compare well to graphene production by LPE. This process allows the nanosheets to be size-selected in a simple and efficient manner. It was found that the optical extinction of the dispersions to vary strongly with nanosheet size. Detailed studies showed the nanosheet absorbance to be roughly size invariant but the optical scattering spectra to depend strongly on nanosheet length.

LPE results in nanosheet dispersions which are solution-processable and can be easily formed into structures such as films. This makes it easy to characterise the material using such methods as SEM, XPS and Raman spectroscopy which showed no damage had been done to the nanosheets during exfoliation. As well as this the resulting nanosheets were mostly free of contaminants and had approximately the correct stoichiometry.

This work has extended LPE to a new class of materials, the layered hydroxides, and further demonstrates the versatility of this method. It is possible to view Ni(OH)_2 as a model system which has been used to demonstrate LPE. This was shown for four other hydroxide materials, Co(OH)_2 , Mg(OH)_2 , Zn(OH)_2 and Cu(OH)_2 , where these methods produced high quality nanomaterials in all instances. As well as this, the four other materials were size selected and their size dependent optical properties were demonstrated.

Chapter 6

Testing the Versatility of Liquid Phase-Exfoliation

6.1 Introduction

As mentioned previously LPE has been used for a variety of families of layered materials from graphene, BN, black phosphorus to TMDs and TMOs[13, 16, 20, 22, 115]. Within this thesis, this method has been successfully expanded to III-VI metal chalcogenides and layered double hydroxides but in all these instances the materials are synthesised in a lab and are purchased at high purity. This doesn't fully demonstrate the versatility of this method. Here it is shown that materials such as layered silicates found in nature can also be exfoliated by this method, showing that LPE isn't just suitable for the purest materials but that any layered material, regardless of purity, can be exfoliated and isolated from their non-layered impurities.

Three examples of these natural or 'unconventional' materials are talcum powder which is made up mostly of the layered material talc[179], clay dug up from a beach, which from its texture was suspected to be a layered compound and cat litter, a mined clay known as Fuller's earth which primarily consists of layered hydrous aluminium silicates such as bentonite and kaolinite[180, 181, 182]. In all cases, the materials contain a high number of non-layered materials such as magnesium carbonate and zinc oxide in the case of the talc and calcite and quartz for the cat litter[180]. For the beach clay, it is unknown what the contaminants are but the clay was surrounded by sand.

In this chapter, the versatility of liquid-phase exfoliation is demonstrated where these three materials are exfoliated to yield nanosheet dispersions. It is demonstrated that by using appropriate cleaning techniques that the nanosheets within the materials can be isolated and used for future characterisation. In line with previous results, it is anticipated that the ultrasound would remove few-layer nanosheets from the layered materials present. However, it was not clear whether the resultant nanosheets would be stable in water or require the presence of a surfactant to stabilise them against aggregation. This would be ascertained by centrifugation to remove any nanosheets which were not stably dispersed, as well as any non-nanosheet material. This shall be discussed in greater detail below.

6.2 Experimental Method

6.2.1 Materials

Talcum powder and cat litter were both purchased from Tesco and Lidl respectively. The clay was extracted from a beach in Parknasilla, Co. Kerry. Sodium cholate (SC, item no. C1254) and all solvents were purchased from Sigma Aldrich and the highest available purity.

6.2.2 Preparation of Nanosheets

As these materials have mixed composition and contain many impurities, it is necessary to introduce a treatment step to purify the powders. The materials were initially sonicated in chloroform for one hour, then centrifuged for one hour at 4.5 kRPM with the supernatant being decanted and discarded with the sediment being retained. This was then repeated with acetone, then with deionised water. The powders were then dried at 60 °C in a vacuum oven. The pre-treated powders were sonicated in surfactant and water solution using a solid flat head sonic tip (Sonics VX-750) at 60% amplitude (6s on/ 2s off) for 4 hrs. To prevent the sonic tip from overheating and potentially damaging the samples or boiling off the solvent, ice cooling was used. After sonication, the dispersions were centrifuged in a Hettich Mikro 220R centrifuge with a fixed-angle rotor 1060). Finally, the top 75% of the dispersions were taken and kept for further analysis and characterisation.

6.2.3 Characterisation and Equipment

Optical extinction and absorbance were measured on a PerkinElmer 650 spectrometer in 0.4 cm path length quartz cuvettes. To differentiate 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 (N.B. cuvettes need to be transparent to all sides and correct/reproducible positioning is important). The absorbance spectrum is obtained from the measurement inside the sphere. A second measurement on each dispersion was performed outside the sphere in the standard configuration to obtain the extinction spectrum. This allows calculation of the scattering spectrum (extinction minus absorbance). Low-Resolution bright field transmission electron microscopy imaging was performed using a JEOL 2100, operated at 200kV. Holey carbon grids (400mesh) were purchased from Agar Scientific and prepared by diluting a dispersion to a low concentration and drop casting onto a grid placed on a filter membrane to wick away excess solvent. Statistical analysis was performed of the flake dimensions by measuring the longest axis of the flake dimensions by measuring the longest axis of the nanosheet and assigning it as 'length', L . Scanning electron microscopy was performed with a Carl Zeiss Ultra SEM operating at 2kV. Images were acquired using the secondary electron detector. X-ray diffraction patterns were measured using a Bruker D8 Advance diffractometer using a copper K_{α} X-ray source (40 kV, 1.5406 Å), with a step size (2θ) of 0.04° and a dwell time of 6 s. X'Pert HighScore software (v.2.0, PANalytical BV, Netherlands) was used to match the powder patterns to known materials from the ICDD database.

6.3 Exfoliation of Materials

6.3.1 Pretreatment Method

Talcum powder was purchased from Tesco while a Fuller's earth-based cat litter was purchased from Lidl. A sandy clay was collected from a beach at Parknasilla, near Sneem in Co. Kerry, Ireland. SEM analysis (Figure 6.1 A-C) showed the talcum powder contain large quantities of platelet-like materials, presumably layered crystallites. The morphol-

ogy of the cat litter sample was less clear showing particulates of a range of sizes which may or may not have been layered. SEM images of the clay showed large numbers of small platelet-like structures that appeared to sit on large continuous structures. It is likely that these represent a mixture of layered clay particles mixed with small stones or sand.

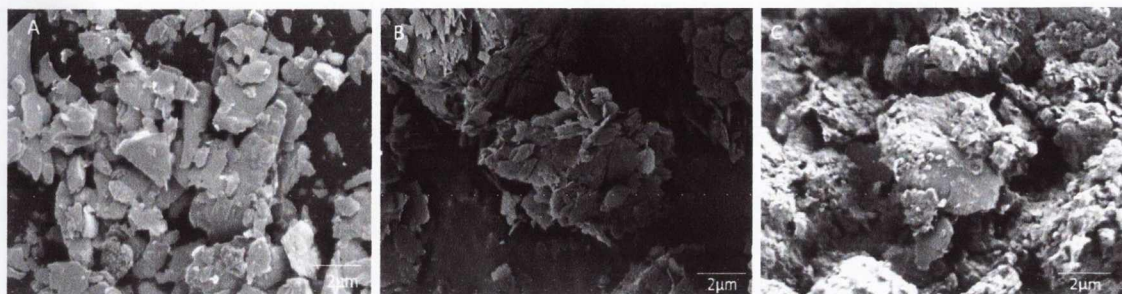


Figure 6.1: *A-C) SEM images of the microstructure of the starting materials: A) talcum powder, B) clay and C) cat litter.*

To remove molecular impurities, a washing step that had not been used in the previous chapters and described in the methods section was introduced resulting in three dried powders.

6.3.2 Exfoliation into Nanosheets

To test if these materials could be exfoliated using LPE, the treated powders (1.6 g) were sonicated as described in the methods section. The surfactant-stabilised dispersions were completely stable as shown in Figure 6.2. To determine the stability of the dispersions, the zeta potential of the sample was measured immediately after centrifugation and was found to be $\zeta = -34 \text{ mV}$, $\zeta = -23 \text{ mV}$, $\zeta = -29 \text{ mV}$ for talc, cat litter and clay respectively. Although, these values are not particularly high, they were high enough to impart stability on the dispersed nanosheets.

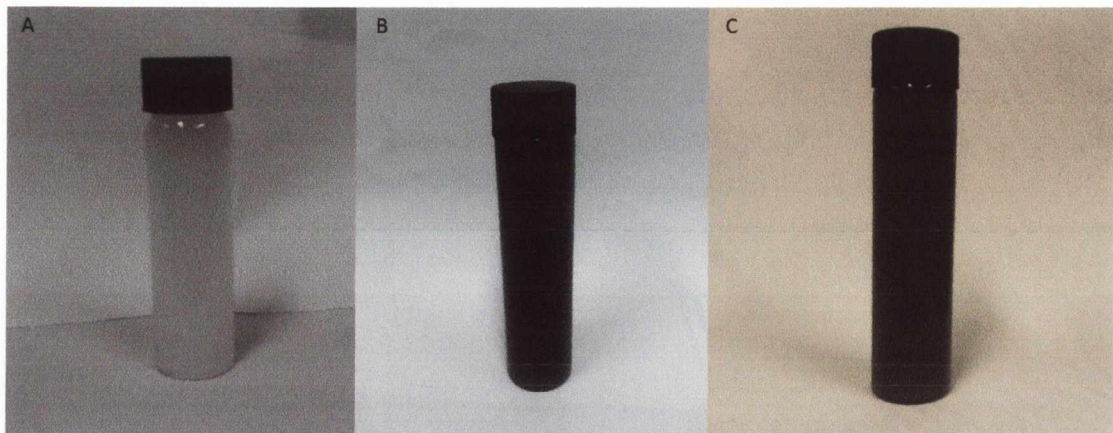


Figure 6.2: A-C) Photographs of dispersions (after centrifugation) of - A) talcum powder, B) clay and C) cat litter, all in water and stabilised by the surfactant sodium cholate ($C_{surf}=6$ mg/ml).

While the talc dispersion was a milky white in colour, the cat litter and clay dispersions were much darker in colour and thus of interest for UV-vis measurements. The optical extinction coefficient (ϵ) spectra of the three nanosheet dispersions were measured, as shown in Figure 6.3 A (concentration was measured by filtration and weighing). These spectra are broad and featureless, as is usually found for nanostructured insulators due to the presence of light scattering[42, 44]. To account for this, the absorption coefficient (α) spectra (Figure 6.3 B) was also measured using an integrating sphere. For talc and cat-litter, these spectra are mainly featureless and show bandedges at 3 - 3.5 eV (350-400 nm), consistent with insulating behaviour but perhaps somewhat lower than expected than the values of ~ 3.5 eV for talc and > 5 eV normally found for layered silicates[183, 184]. However, for clay the absorption coefficient never reached zero, even at high wavelength, implying the presence of metallic impurities. As mentioned previously, subtracting the absorption from the extinction spectra gives the scattering coefficient (σ) spectra as shown in Figure 6.3B yielding power-law behaviour in the high wavelength regime as expected (Figure 6.3 C).

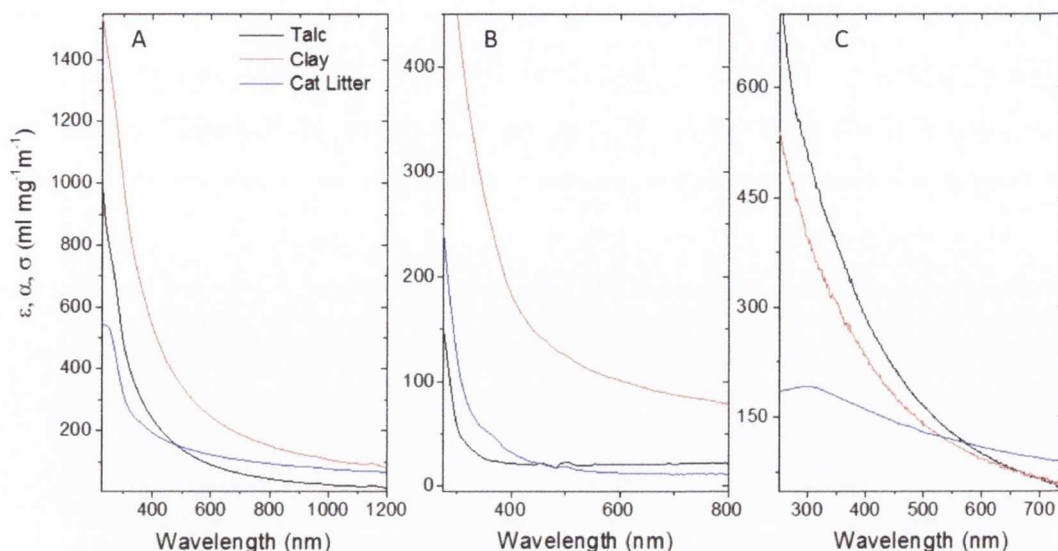


Figure 6.3: A-C) Optical spectra for exfoliated dispersions of talc, clay and cat litter showing A) extinction, B) absorption and C) scattering coefficient spectra.

In order to estimate the mass of nanosheets exfoliated, a known volume of the dispersions were filtered onto alumina membranes using vacuum filtration. As the nanosheets were coated with sodium cholate the films were washed with 250 ml of water to remove most of the surfactant. The films were then dried in a vacuum oven, removing any residual sodium cholate and weighed. This led to the estimation of dispersed concentrations of ~ 0.1 mg/ml, ~ 8 mg/ml and ~ 1.2 mg/ml for talc, cat litter and clay respectively. For both the cat litter and the clay, these values compare very well with other 2D materials such as graphene, MoS_2 [161] and $\text{Ni}(\text{OH})_2$ [90] with values of 2 mg/ml, >1 mg/ml and 2-3 mg/ml respectively. The concentration of the talc is quite low but compares to values found for BN in IPA of 0.06 mg/ml[98].

To observe the quality of the nanosheets, images were taken using TEM where a few drops of each dispersion were pipetted onto separate holey carbon grids. TEM images (inset of Figure 6.4A-C) showed the presence of large quantities of 2D nanosheets in each case, with very little to no evidence of larger 3D objects. This is a particularly interesting result in the case of both the cat litter and the clay as it shows that LPE is capable of extracting only the nanosheets from an inhomogeneous starting material while rejecting the larger, 3D objects. This 3D/2D separation is most likely due to simple mass separation where the 2D nanosheets are smaller and lighter than their 3D counterparts. However 2D

objects moving in a fluid feel a resistance force which increases with aspect ratio[185]. The length of the imaged nanosheets were measured (defined as the longest dimension) with histograms shown in Figure 6.4 A-C. As is generally found for LPE, roughly lognormal length distributions were observed, with means of 600 nm, 370 nm and 315 nm for talc, clay and cat litter respectively.

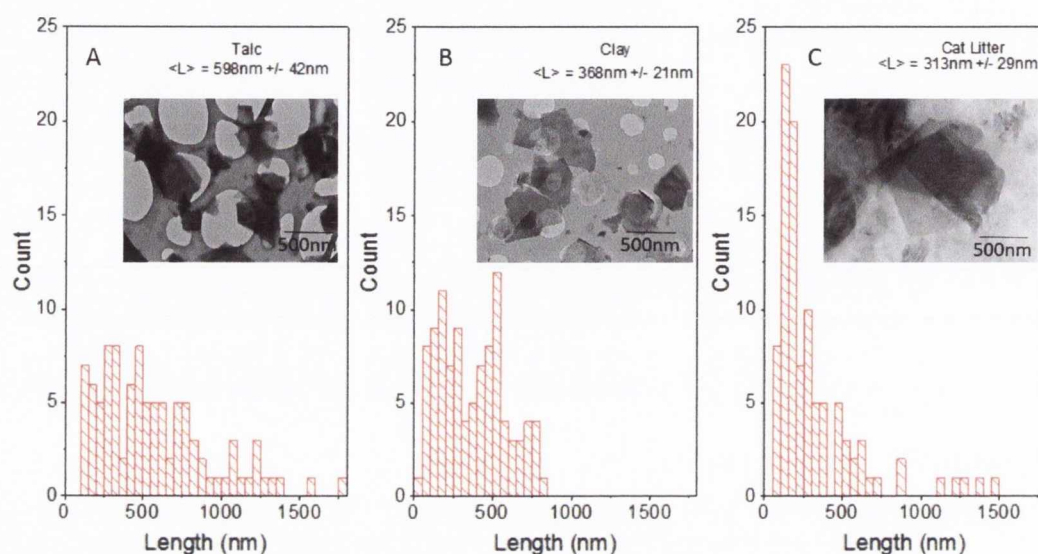


Figure 6.4: A-C) Histograms showing nanosheet length (i.e. the longest dimension) distribution for A) talc, B) clay and C) cat litter. Inset are representative TEM images.

It was of interest whether water could act as a stabiliser by itself or if it would require surfactant as the nanosheets may have charged surfaces. To test this, multiple washing steps were introduced after which the Zeta potential and an extinction spectra were measured. The washing step comprised of centrifuging the dispersion at 5 kRPM for 2 hours to sediment all the nanosheets, decanting all of the supernatant and redispersing the sediment with water. This was performed four times to ensure that all of the surfactant had been removed. Shown in Figure 6.5 are graphs of normalised scattering exponent and Zeta potential vs number of washes. In all instances, the Zeta potential decreased to approximately -15 mV, a value far too low to stabilise the nanosheets, and sedimentation of all dispersed nanosheets. Although it suggests the presence of a double layer of charged nanosheets and charge balancing counter ions[186].

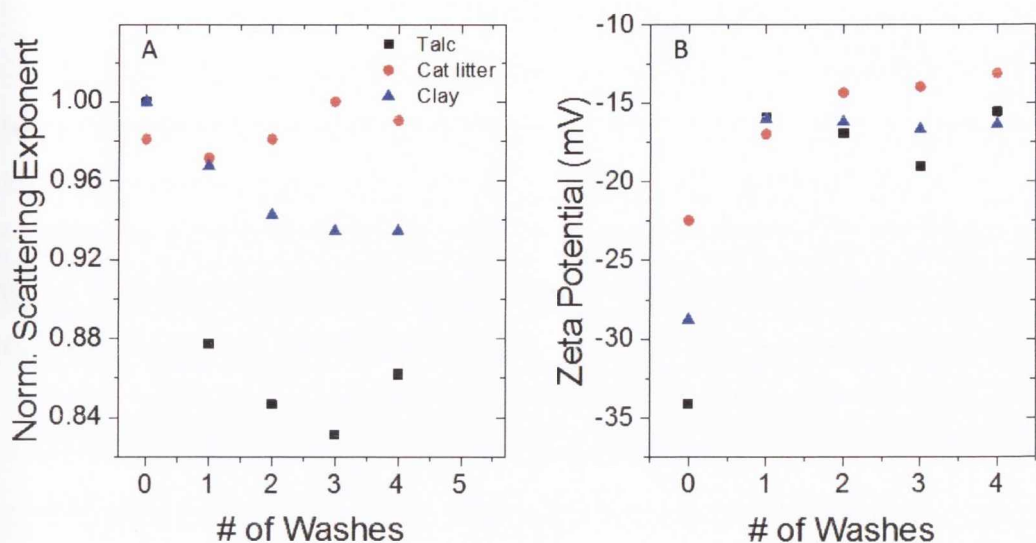


Figure 6.5: A) Scattering exponent normalised to largest value obtained from extinction spectra for talc, cat litter and clay vs number of washes. B) Zeta potential vs number of washes of each of three standard samples.

As mentioned previously, the scattering exponent measures the degree of light being scattered with a large number implying small nanosheets and a small number implying large nanosheets. Up to this point in this thesis, it has been used as a measure of length but more realistically it is a measure of the area of the nanosheets[141]. This is due to photons being scattered by all dimensions of the nanosheets or a cluster of reaggregated particles. Thus, if the scattering exponent for a dispersion decreases, it implies that the nanosheets are reaggregating and forming particulates. This shown in Figure 6.5 B, where for both clay and talc the scattering exponent decreases. This is due to the surfactant being removed from the nanosheets which is causing the nanosheets to reaggregate[187]. As both the scattering exponent and zeta potential are decreasing as the surfactant is being removed, it shows that the nanosheets are not effectively stabilised by charge balancing ions.

6.4 Material Characterisation

6.4.1 X-Ray Diffraction

It is of interest to unambiguously identify the nanosheets extracted from the three starting materials. X-ray diffraction was employed with the aim of achieving this goal and fully characterising the 2D materials produced by LPE. Powder X-ray diffraction (pXRD) was performed on both starting and exfoliated materials for talcum powder, clay and cat litter, with the aim of deducing any crystalline phases present (Figure 6.6). The nanosheets were extracted from liquid by evaporating all solvent using a vacuum oven.

The pre-treated talcum powder sample (Figure 6.6 A) gave intense reflections at $2\theta \sim 19^\circ$ and 29° with smaller peaks at a number of other angles. The pattern could be fully indexed to talc-2M (magnesium silicate hydroxide, ICDD # 00-019-0770, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$). There was no apparent change in this diffraction pattern in the post-exfoliation samples, suggesting the exfoliated material to be of the same crystalline phase as the bulk (i.e. talc nanosheets).

The pXRD results for the clay before and after exfoliation (Figure 6.6 B) are extremely interesting. The pXRD pattern of the pre-exfoliation, bulk material (Figure 6.6 B) was indexed to hexagonal quartz (ICDD # 01-087-2096), which is typical for clay samples. This implies that the starting material was dominated by sand with only small amounts of other materials. However, post-exfoliation, the picture is very different; The pXRD pattern of the material (Figure 6.6 B) can be indexed to muscovite-2M (ICDD # 00-046-1311, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$), also known as mica, a well-known layered material[188]. This result is significant as it means that the exfoliation procedure employed also selects between crystalline layered structures and non-layered structures.

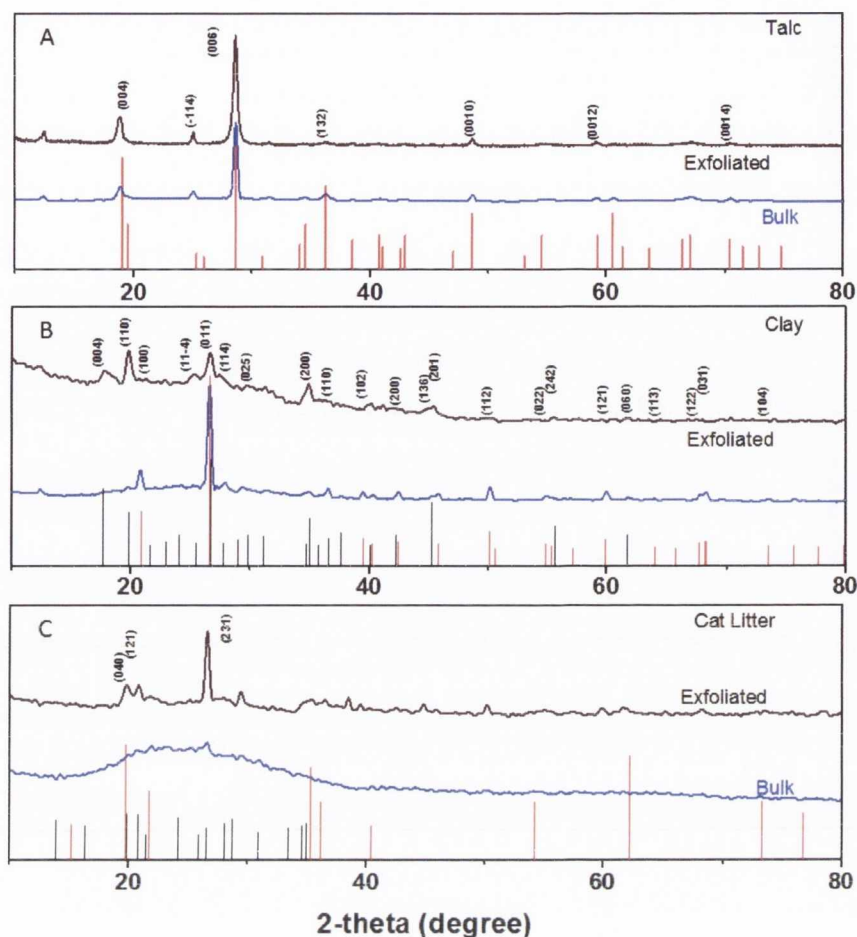


Figure 6.6: A): pXRD patterns of talcum powder and exfoliated talc nanosheet. B): pXRD patterns of clay from Parknasilla, near Sneem in Kerry, Ireland. C): pXRD patterns of: Coshida cat litter and exfoliated nanosheets extracted from Coshida cat litter.

A similarly striking purification effect was noted with the cat litter sample (Figure 5=6.6 C). The pXRD data of the starting material shows virtually no Bragg reflections in the pattern, suggesting it is mainly amorphous. However, when the material post exfoliation was examined, a number of reflections were observed with well-defined pair of peaks at $2\theta \sim 20^\circ$ and 21° and an intense peak at $2\theta = 27^\circ$. The pair are assigned to the (040) and (121) planes of bentonite (ICDD # 00-003-0019), a layered clay which consists mainly of bentonite $[(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and is commonly found in cat litter. The latter intense peak can be assigned to the (231) plane of palygorskite (ICDD # 00-031-0783), again a common component of cat litter $[(\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_4(\text{H}_2\text{O})]$. These results are important as they show that LPE can extract exfoliated nanosheets

from a mixed system, while rejecting any unexfoliated layered compounds and amorphous material.

It is clear from the pXRD results that this procedure employed ‘selects’ and purifies crystalline nanosheets from layered bulk materials. I hypothesise that it is possible to use this exfoliation procedure on rather impure, even amorphous, ores to produce few-layer crystalline nanosheets from the layered materials within these ‘ores’. This would be consistent with recent work showing that MoS₂ nanosheets can be extracted from molybdenite ore by LPE[189]. It is clear that a wide range of naturally occurring materials and minerals could be targets for further exploration and thus exploitation.

6.4.2 X-ray Photoelectron Spectroscopy

As these samples aren’t synthesised and are found in nature, it is important to be aware of what contaminants could be in the nanosheets post exfoliation. To determine this, XPS was performed on the nanosheets that had been dried into a powder consisting of reaggregated exfoliated material. A survey scan was performed on each of the materials and the elemental compositions were extracted and plotted as histograms (as shown in Figure 6.7).

For all three samples carbon and sodium are detected. This is from the sodium cholate that remains as residual surfactant. The XPS data for the talcum powder shows that there are high levels of oxygen, magnesium and silicon. This is to be expected as the layered material within talcum powder is talc whose chemical structure is $Mg_3Si_4O_{10}(OH)_2$ or $Mg_3Si_4O_{12}$, as the XPS doesn’t detect hydrogen, which is very comparable to our composition of $Mg_{3.1}Si_{3.2}O_{13.3}$. There was also detected iron and aluminium but both were less than 1% of the total mass. Similarly for clay, the XPS data showed very little contamination from metal ions with sodium, iron and magnesium being detected but again with values fewer than 2% of the total mass. From the XRD of the clay, the exfoliated nanosheets were shown to mainly comprise of the material known as mica. From the XPS data the material was found to be mainly made of potassium, aluminium, silicon and oxygen with Mica’s chemical structure being $KAl_2(AlSi_3O_{10})(F,OH)_2$. Again these data sets work very well with each other.

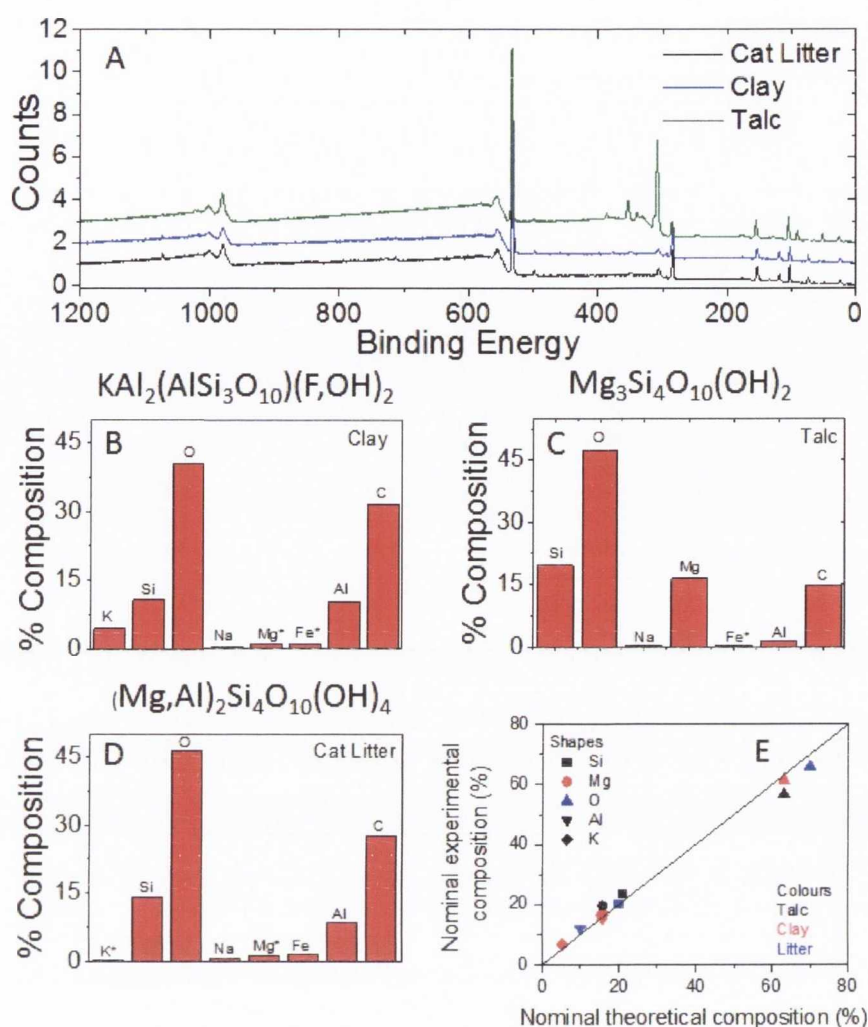


Figure 6.7: A) XPS survey of talc, cat litter and talc. B-D) Histograms containing elemental compositions for B) talc, C) clay and D) cat litter. E) Nominal experimental composition (excluding sodium and carbon) from XPS vs nominal theoretical composition.

Finally, the cat litter was a slightly more complicated story as it was found to be comprised of two materials, bentonite and palygorskite but the XPS showed that sodium, aluminium, magnesium, silicon and oxygen, which are the components of both these layered compounds. There were also very low contributions from potassium and iron.

It is interesting to see if the experimental compositions match with the theoretical compositions of the materials detected using XRD. This is shown in Figure 6.7 E, where the x axis represents the amount of each element detected by XPS divided by the total amount of other atoms from structural formula (i.e. ignore impurities and Na and C). The $y = x$ behaviour shows the proportions observed by XPS are consistent with XRD.

6.5 Conclusion

It is clear that liquid-phase exfoliation is an extremely versatile technique to produce nanosheets from layered precursors. Here, it has been shown that it is possible to process naturally occurring materials such as talc, Fuller's earth cat litter and a clay/sand mix using LPE and obtain purified nanosheets while rejecting any unwanted non-2D material. Using a simple pretreatment method, the materials were cleaned of inorganic and organic impurities that may have been on the nanosheets. The materials were then exfoliated into nanosheets, the quality of which were identified with TEM, finding that $\langle L \rangle$ of 600 ± 42 nm, 315 ± 29 nm and 370 ± 21 nm for talcum powder, clay and cat litter respectively. Zeta potential measurements were also used to confirm if the nanosheets consisted of charged layers and it was found that they exhibited potentials with an absolute value of 14 - 15 mV confirming this to be true but the values are not high enough to stabilise the nanosheets.

To investigate the materials that had been exfoliated, XRD and XPS were both used. XRD confirmed that only layered materials were remaining in the final dispersions with talcum powder remaining mainly unchanged, clay being exfoliated from sand and mica to just mica, and the cat litter dispersion to just be comprised of bentonite and palygorskite, two layered materials. XPS showed that there are very few elemental impurities remaining in the dispersions.

The work conducted in this chapter shows the true ability of liquid-phase exfoliation to only remove the layered material from a compound and exfoliate them into nanosheets. Where after centrifugation the supernatant consisted of mostly 2D nanosheets and the sediment consisted of 3D materials that had been 'rejected' during the exfoliation process. It is particularly surprising that the bentonite and palygorskite layered crystals contained in the cat litter as well as the mica in the beach sand could be exfoliated by LPE, despite consisting of charged layers with charge-balancing counter ions.

Chapter 7

Size Dependent Optical Response of 2D TMDs

7.1 Introduction

The work presented in the previous chapters investigates the exfoliation of layered crystals to 2D nanosheets as well as basic characterisation of these nanosheets. Being more focused on refining the exfoliation and centrifugation properties of these materials such as determining the Hildebrand solubility parameter and discovering the time decay constants during the sedimentation process. In both chapter four and chapter five some work was done on characterising the scattering spectra of GaS and LDH nanosheets as well as determining the optical response to changing nanosheet size but not in great detail.

Previous work pioneered by Backes *et al* investigated the optical properties of 2D TMD's where the extinction spectra were correlated directly to the lateral dimensions of the 2D nanosheets[42, 43]. This allowed the optimization and refinement of the exfoliation process to selectively produce close to monodispersed nanosheets. The work presented in this chapter will build on the work of Backes *et al* and extend these methods to other TMDs. Also there will be an investigation on the light scattering caused by 2D nanomaterials to attempt to determine length based metrics similar to what has been done for nanoparticles[42, 190].

In this chapter, the size dependence on the optical spectra of five TMDs and BN are investigated. By analysing the optical response, metrics were derived to determine the

concentration and mean length of a dispersion for all six materials from their extinction spectra, continuing on the work of Backes *et al* in 2014 and 2015. Finally, the scattering spectra are analysed and investigated for potential length based metrics.

7.2 Experimental methods

7.2.1 Materials.

BN powder, MoS₂ powder, MoSe₂ powder, MoTe₂, WS₂, WSe₂, sodium cholate and D₂O were purchased from Sigma Aldrich. De-ionized water was prepared in house and all solvents used were purchased with the highest available purity.

7.2.2 Production of 2D Nanosheets

For each material, 1.6g of powder was pre-treated by sonication using a sonic tip in de-ionized water for 1 hr. The dispersion was then centrifuged at 4.5kRPM (*2150g*) for 1 hr and decanted with the sediment being retained and dried. The pre-treated material was then sonicated in 2 mg/ml of sodium cholate and de-ionized water solution using a flat head tip (Sonics VX-750) with 60% amplitude and 4s on/ 4s off for 6 hours. To prevent solvent evaporation, temperature control was performed using ice cooling. Once sonicated the dispersion was centrifuged in a Hettich Mikro 220R centrifuge with a fixed-angle rotor 1016) at 0.5 kRPM for 2 hours (NB: For this centrifuge, rpm are related to *g-force* via $RCF = 106.4f^2$, where *f* is the rotation rate in krpm). The top 60% was then taken from the centrifuged sample for analysis and the sediment was discarded. The absorption and extinction were measured in a 4mm path length cuvette using a PerkinElmer Lambda 650 spectrometer (details below).

7.2.3 Size Selection

Liquid cascade centrifugation was used with subsequently increasing rotation speeds as previously reported. The dispersion was centrifuged at 1 krpm for 120mins. The sediment was retained and the supernatant was centrifuged at 2 krpm for 120 mins. The sediment after both these centrifugation steps were redispersed in fresh surfactant solution (1 hr

bath sonication) producing the two largest sizes. The supernatant after the 1 krpm centrifugation step was centrifuged at 2 krpm for 120 mins, producing the third largest size in the redispersed sediment. These steps were repeated in further increments of 3 krpm, 4 krpm, 5 krpm and 10 krpm thus producing six sizes. These dispersions are named using the same nomenclature as in previous chapters.

7.2.4 Characterization and Equipment

Optical extinction and absorbance was measured on a PerkinElmer 650 spectrometer in quartz cuvettes with a path length of 0.4 cm. 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 center of the sphere. If a photon is scattered multiple times in the sample, it may eventually get reabsorbed before exiting the cuvette. This in turn would lead to a slightly reduced scattering intensity, while at the same time, increasing the absorbance intensity. Thus, the cuvettes need to be transparent on all sides and correct positioning is important. The absorbance spectrum is obtained from the measurement inside the sphere. A second measurement on each dispersion was performed outside the sphere in the standard configuration to obtain the extinction spectrum. This allows calculation of the scattering spectrum (extinction minus absorbance). Low-resolution bright field transmission electron microscopy imaging was performed using a JEOL 2100, operated at 200 kV. Holey carbon grids (400 mesh) were purchased from Agar Scientific and prepared by diluting a dispersion to a low concentration and drop casting onto a grid placed on a filter membrane to wick away excess solvent. Statistical analysis was performed of the flake dimensions by measuring the longest axis of the nanosheet and assigning it as “length”, L .

7.3 Exfoliation and Size Selection of Nanosheets

7.3.1 Determination of Appropriate Exfoliation Media

As the ultimate goal of this chapter requires the measurement of ε , almost importantly σ spectra of a range of materials, it is necessary to measure the spectra hundreds of nanome-

ters before the band edge. This is to remove any effects that absorption could play on the scattering spectra. Of the six materials chosen all but BN require the measured wavelength range to go beyond 800 nm, with MoTe₂ being the most extreme example of this as the A-exciton is at approximately at 1150 nm[36, 191, 192, 193, 194]. Unfortunately most solvents, especially water, strongly absorb at wavelengths in the nIR[195]. Thus, the solvent choice is of particular importance. To test for the best solvent, the absorption spectra were measured for a range of solvents.

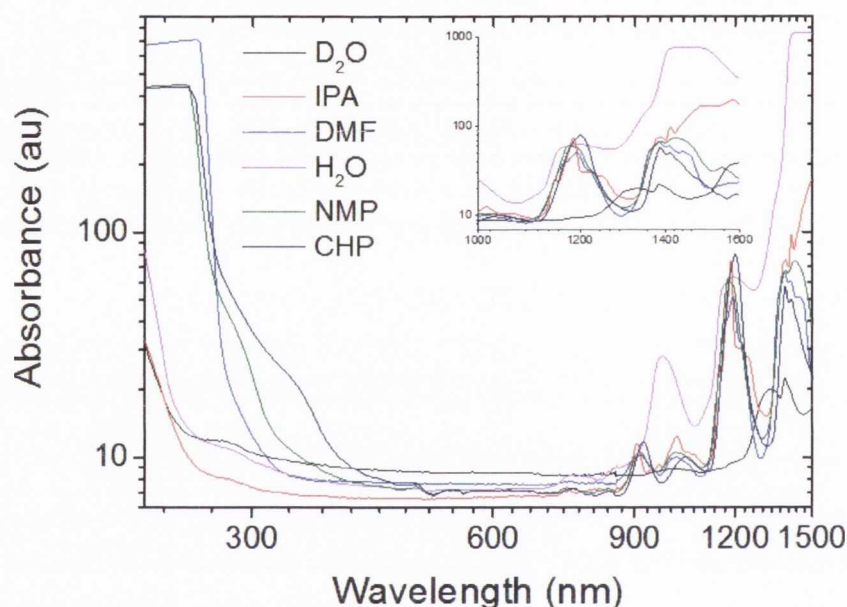


Figure 7.1: Absorption spectra for a range of solvents between 220nm and 1500nm with a zoom in of 1000nm to 1600nm inset.

As can be seen in Figure 7.1, there is very little absorption, for all solvents, between 300 nm and 800 nm but beyond 1000 nm in the nIR regime there is a lot more. The highest absorbing solvent is water where the peak at 1400 nm saturates the detector, this instantly rules it out as a possible solvent as it will be impossible to get accurate spectra for any material at those wavelengths. IPA, DMF, NMP and CHP are all better but it has been shown that it has much harder to obtain smaller nanosheets using these solvents[42]. Also, DMF, CHP and NMP absorb too strongly beyond 300 nm, affecting the analysis of materials such as WS₂ with important absorbance features at high energy[43]. By far the

best choice is D₂O with little absorbance across the entire spectral region of interest and which is compatible with surfactant exfoliation giving access to small nanosheets. Thus, D₂O and a surfactant (SC) are used as the solvent for exfoliation for the project.

7.3.2 Size Selection of 2D Nanosheets

To produce length based metrics from UV - vis spectroscopy, dispersions with various size distributions are required. To achieve this, 20 mg/ml of powder was sonicated in water for one hour and centrifuged at 4.5 kRPM for one hour. This removed most impurities from the powder. This pre-treated powder was then sonicated in 2 mg/ml D₂O/SC surfactant solution for 6 hours, and centrifuged using LCC, as described before, with slightly varied centrifugation parameters to the previous chapters (specific RPMs in section 7.2.3).

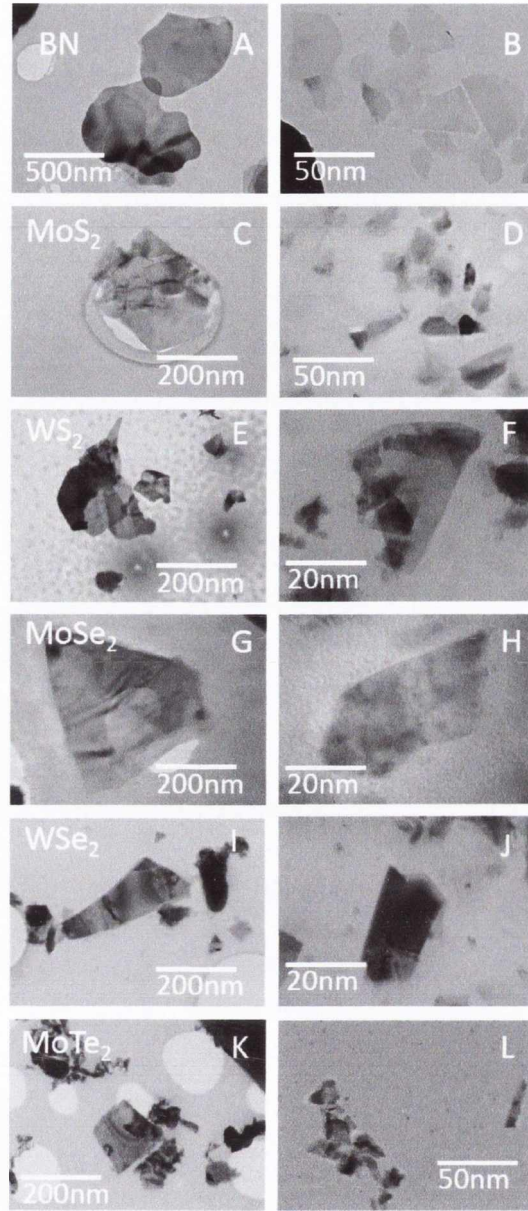


Figure 7.2: Representative TEM images of the XL and S size for (A-B) BN, (C-D) MoS₂, (E-F) WS₂, (G-H) MoSe₂, (I-J) WSe₂ and (K-L) MoTe₂.

Two of the six materials, MoS₂ and WS₂, have length and thickness metrics in the literature. However, to obtain $\langle L \rangle$ for the others it is necessary to use statistical TEM[42, 43]. At the same time, TEM confirms the quality of the exfoliation and the successful size selection by the centrifugation method. Thus, following exfoliation, the dispersions were subjected to TEM. Here, a few drops of dispersion were pipetted onto holey carbon TEM grids, images were taken and the length of 100 nanosheets measured. Similar to chapter 4

and chapter 5 the LCC method has clearly worked and has produced nanosheets of varying length, as shown in Figure 7.2 and 7.3. For the five TMDs the nanosheets look as expected with most of the flakes being rectangular and triangular in shape. The BN, however, is circular or disc shape, in agreement with previous reports on LPE BN nanosheets[115]. From the length distribution histograms of each size of the six materials, the mean lateral size was determined.

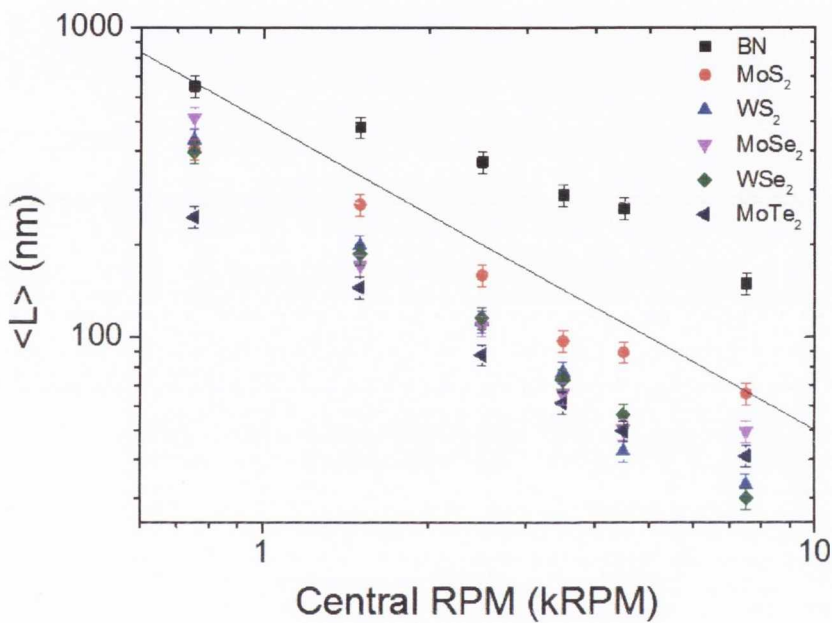


Figure 7.3: Log-log plot of the mean length $\langle L \rangle$ plotted vs central RPM from each trapping step with a RPM^{-1} fit for the 6 materials.

It is important that the nanosheets produced are of similar lengths, thus making them more comparable when plotted against certain variables, such as scattering exponent. To show that this was the case, $\langle L \rangle$ was plotted vs central RPM for all materials. As can be seen from Figure 7.3 there is a wide distribution of sizes for each material with all the materials having similar flake lengths for the same RPMs, with ranges of ~ 400 nm to 50 nm. The exception to this is BN, where the nanosheets range from 650 nm to 180 nm. This is due to the BN flakes being thinner for a given length as well as being a lighter material than the TMDs. Thus, as centrifugation separates by mass, it will have larger nanosheets for any given centrifugation parameters. Figure 7.3 also shows that the mean

length $\langle L \rangle$ when plotted against Central RPM follows a trend of L decreasing as rpm^{-1} as predicted by theory.

7.3.3 Determination of Optical Coefficients and $\langle L \rangle$ Metrics

Due to the issues of solvent absorbance in the nIR region as discussed above, materials with absorbance features at high energy are more convenient to work with. For this reason, initially the work was started with BN, MoS_2 and WS_2 .

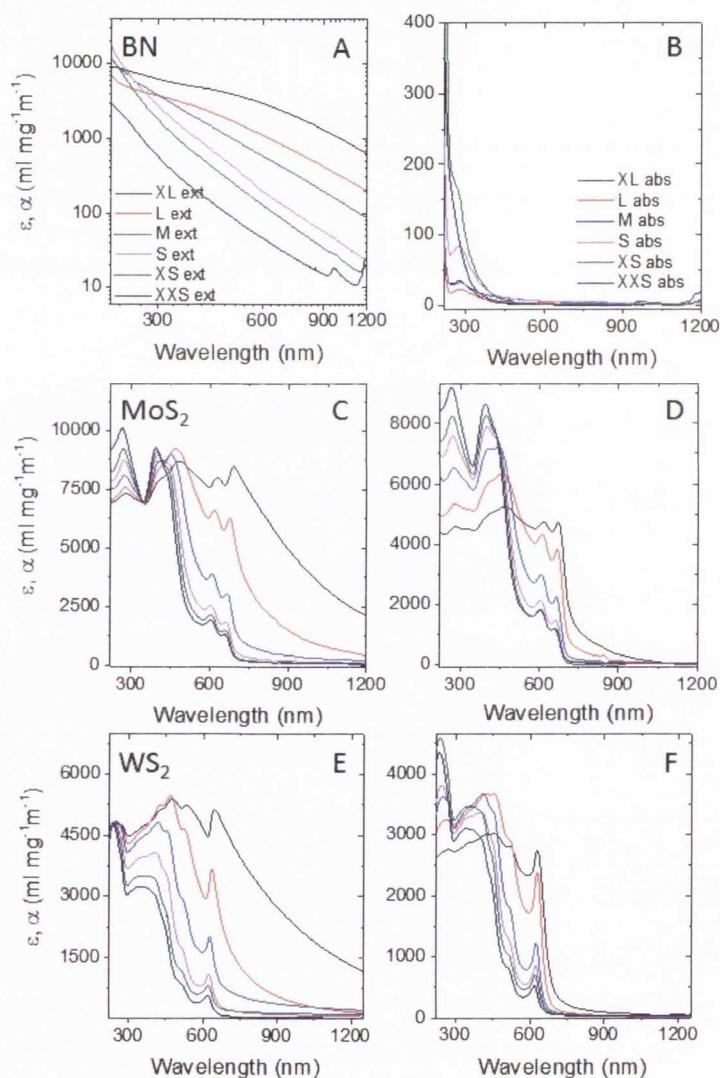


Figure 7.4: Optical extinction and absorption coefficient spectra measured for five different fractions (different sizes) of BN (A-B), MoS_2 (C-D) and WS_2 (E-F) nanosheets.

To extract the scattering exponent, first the extinction and absorption spectra of each dispersion are measured. The scattering spectrum is obtained by subtracting the absorption from the extinction spectra[42].

To achieve this each dispersion was diluted with fresh solvent to avoid detector saturation and measured using a UV-vis spectrometer with an integrating sphere accessory. The concentration of each dispersion was also determined using vacuum filtration and mass weighing and the spectra were then converted to coefficient spectra (Figure 7.4).

From Figure 7.4 B it is possible to see that for BN, an insulator, there is no absorbance for wavelengths above ~ 300 nm, with the extinction spectra being dominated by scattering effects[196]. In addition, a clear dependence of the extinction spectra on the nanosheet size can be observed for all wavelengths. This is to be expected for BN, as the optical properties are dominated by scattering effects[197]. For MoS₂ and WS₂, two materials that are not dominated by scattering effects, the spectra are rich in excitonic features thus making the scattering spectra more complicated. An important feature in the absorbance spectra is the lowest energy transition referred to as A-exciton which is associated with the transition from valence band to conduction band edge at the K point. The A-exciton appears at 650 nm - 700 nm for MoS₂ and 600 nm - 647 nm for WS₂ but both blue shift with decreasing size. For wavelengths larger than these it can clearly be seen that the absorbance drops to zero[42, 43]. Also, even though the extinction coefficients at a given spectral position for these two materials does change with size there are points in each that are size invariant. This can be seen for MoS₂ at 345 nm and 235 nm for WS₂. This makes it possible to obtain the concentration for these two materials for a range of sizes through the Beer - Lambert law using UV-vis spectroscopy.

Due to well defined changes in the extinction spectra with size it is possible to determine metrics. For BN, there are no absorption peaks from which to derive metrics, with the exception of a peak at ~ 300 nm which is in a region where there are large contributions from the solvent thus making the values unreliable, it is still possible to obtain a concentration metric by plotting the extinction coefficient at a particular wavelength vs $\langle L \rangle$.

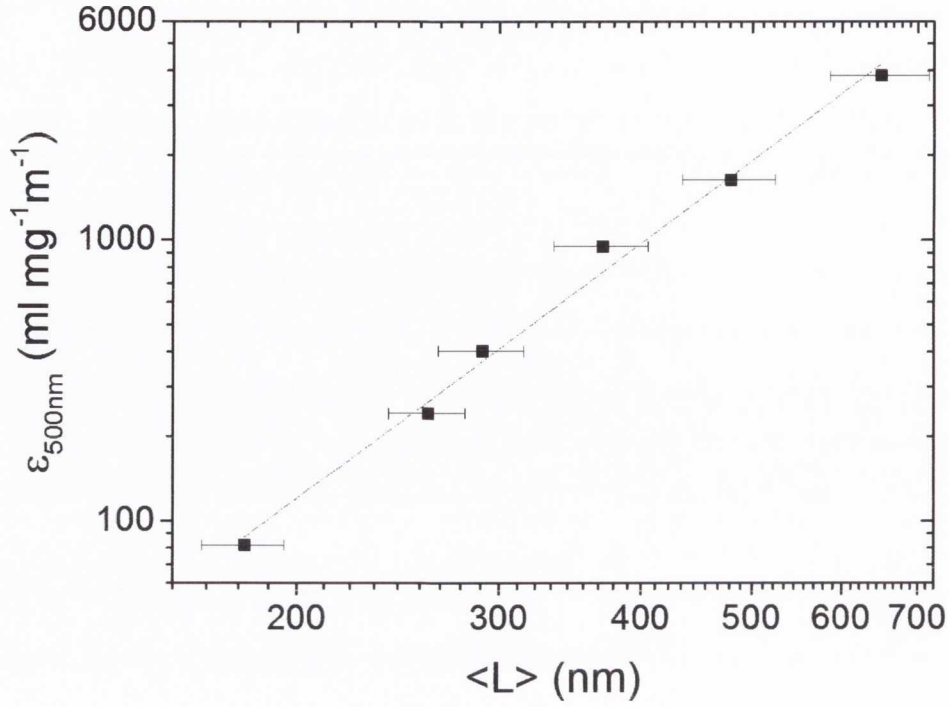


Figure 7.5: Extinction coefficient at 500 nm vs $\langle L \rangle$ for BN.

This is shown in Figure 7.5 where there is a clear trend with the extinction coefficient at 500 nm increasing as the average nanosheet length increases. When this data is fitted it yields an equation of :

$$\epsilon_{500nm} = 1.36 \times 10^{-5} (\langle L \rangle)^3 \quad (7.1)$$

Where $\langle L \rangle$ is in nm. When $\langle L \rangle$ is related to the scattering exponent, n in section 7.4 it will be possible to obtain a relation similar to the one obtained in chapter 5 where the extinction is related to n .

For MoS_2 and WS_2 these relationships have already been obtained and published by Backes *et al* in 2014 and 2016 respectively and have metrics for $\langle L \rangle$ and concentration [42, 43]:

$$\langle L (\mu m) \rangle = \frac{3.5 \left(\frac{Ext_B}{Ext_{345nm}} \right) - 0.14}{11.5 - \left(\frac{Ext_B}{Ext_{345nm}} \right)} \quad (7.2)$$

$$\epsilon_{345nm} = 6900 \text{ ml mg}^{-1} \text{ m}^{-1} \quad (7.3)$$

for MoS₂ where $\text{Ext}_B/\text{Ext}_{345nm}$ is the ratio of extinction intensity at the B exciton versus at the extinction intensity at 345 nm. For WS₂ they are:

$$\langle L \text{ (}\mu\text{m)} \rangle = \frac{2.3 - \left(\frac{\text{Ext}_{235nm}}{\text{Ext}_{290nm}} \right)}{0.02 \left(\frac{\text{Ext}_{235nm}}{\text{Ext}_{290nm}} \right) - 0.0185} \quad (7.4)$$

$$\epsilon_{235} = 4770 \text{ ml mg}^{-1} \text{ m}^{-1} \quad (7.5)$$

These changes in extinction can be viewed as two different principles between BN and the two TMDs. For BN, the change in extinction coefficient is just a different way to express the change in scattering coefficient. This is determined by the size dependent scattering exponent. This has been shown in chapters 4 and 5 in this thesis for GaS and the LDHs. For TMDs, peak intensity ratios are chosen in the resonant regime where the extinction spectra are dominated by absorbance. In this case, the change in extinction coefficient is due to intrinsic material properties where the extinction coefficient is different in the basal plane compared to the edges as a result of the increasing roll of edge effects for smaller nanosheets[42, 43]. Therefore, as mentioned above, the extinction coefficient at a certain wavelength is dependent on $\langle L \rangle$ and this governs that peak intensity ratios in the resonant regime can be used to determine $\langle L \rangle$.

These relations make it possible to obtain the mean length and concentration of a nanosheet dispersion by just using the UV-vis spectrum of a material. It would be advantageous to be able to derive these relations for the other TMDs in this study that, to this point, do not have published metrics from the extinction spectra. These metrics are obtained by plotting the extinction coefficient at a specific wavelength or ratio of extinction peaks vs. $\langle L \rangle$ for a range of nanosheet sizes and fitting an empirical function. Thus, the extinction and absorption spectra of each size of the MoSe₂, WSe₂ and MoTe₂ were measured (Figure 7.6).

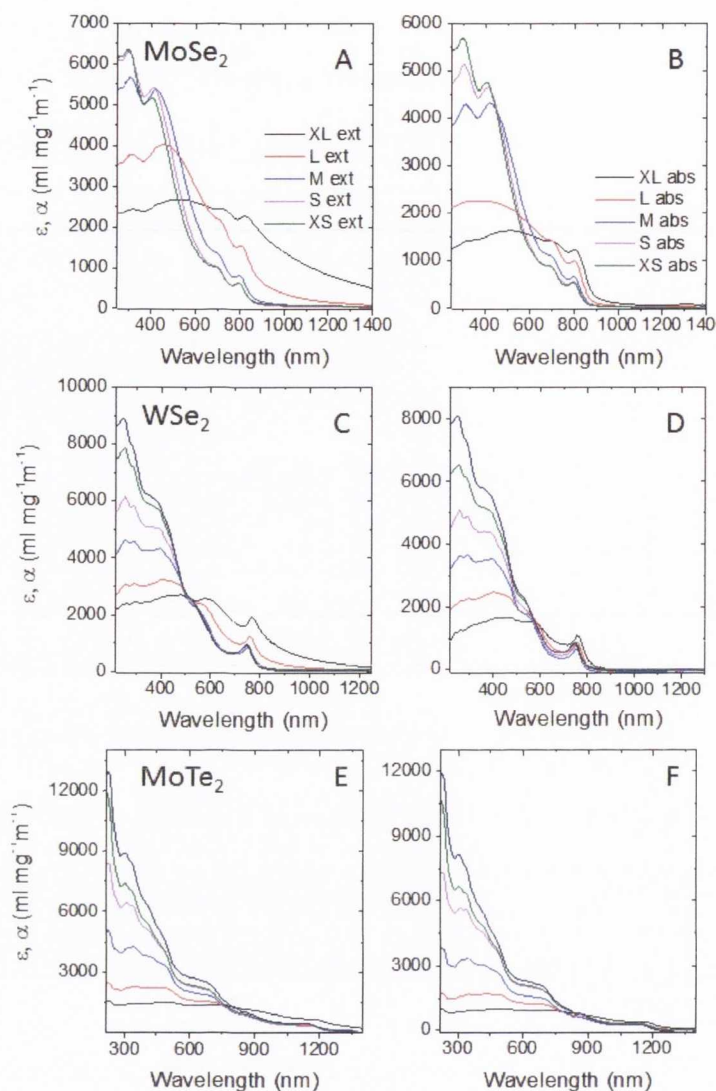


Figure 7.6: Optical extinction and absorption coefficient spectra measured for five different fractions (different sizes) of MoSe_2 (A-B), WSe_2 (C-D) and MoTe_2 (E-F) nanosheets respectively.

Similar to MoS_2 and WS_2 , it can be seen that the spectral profile of the optical extinction and absorption spectra of these three materials strongly depend on the nanosheet dimensions due to edge and confinement effects. For MoSe_2 , WSe_2 and MoTe_2 the A excitation was found to occur at 800 - 826 nm, 758 nm - 765 nm and 1151 nm - 1180 nm respectively and blue shifts for decreasing nanosheet size. This can make it difficult to measure the regions of zero absorption but as shown in Figure 7.6 B, D, F these regions are still obvious due to the use of D_2O .

To test if it is possible to obtain concentration and length metrics, it is advantageous

to determine positions where the extinction coefficient is most invariant with length. For MoSe_2 , WSe_2 and MoTe_2 , these points are 650 nm, 486 nm and 750 nm respectively. The extinction coefficient of these positions were then plotted against $\langle L \rangle$ for each. In addition, the extinction coefficient at 300 nm is plotted as function of $\langle L \rangle$ for each material which shows a strong size-dependence.

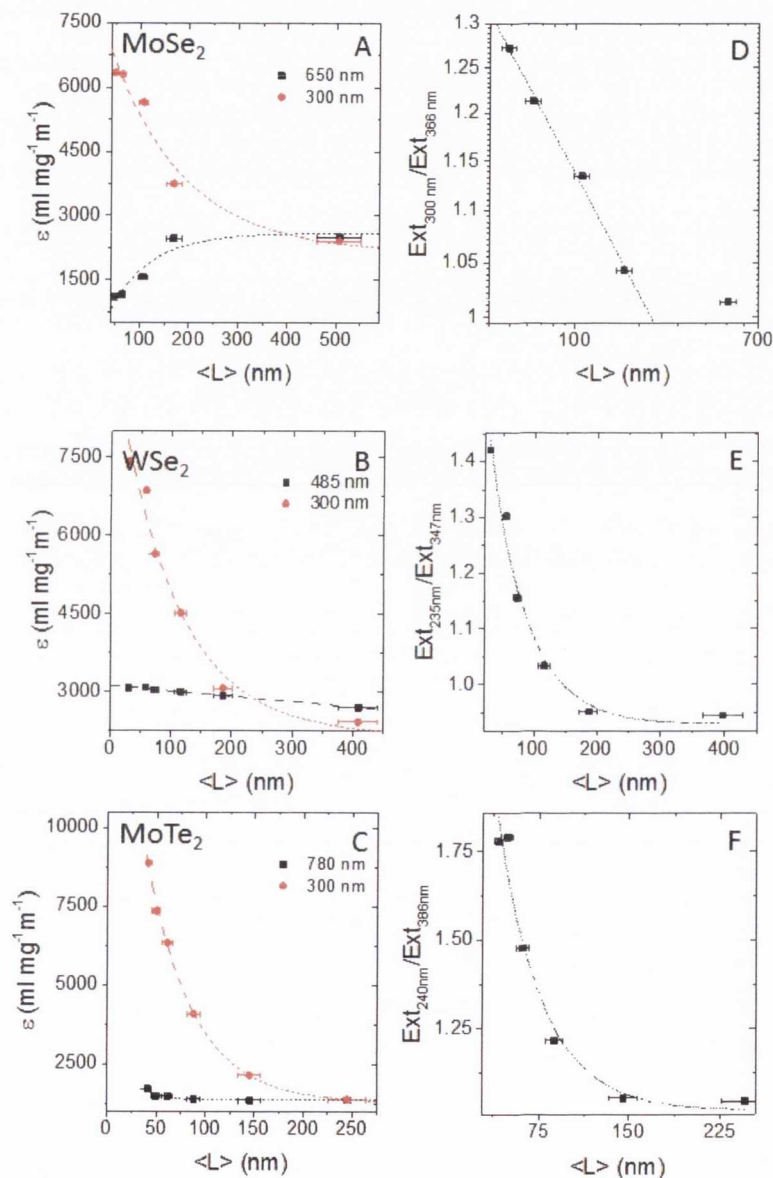


Figure 7.7: A-C) Extinction coefficient at 300 nm and most invariant wavelength versus $\langle L \rangle$ for (A) MoSe_2 , (B) WSe_2 and (C) MoTe_2 . (D-F) Ratio of extinction intensities versus $\langle L \rangle$ for (E) MoSe_2 , (F) WSe_2 and (G) MoTe_2 .

In Figure 7.7 A-C it can be seen that there is a clear change in extinction coefficient with changing nanosheet size. For MoSe₂ at 550 nm this can be seen as a plateau value of 2600 ml mg⁻¹m⁻¹ for <L> greater than 150 nm, then a decrease to ~1200 ml mg⁻¹m⁻¹ for values of <L> smaller than 50 nm. A similar effect is also seen with WSe₂ and MoTe₂ with widely invariant values of 3100 mg⁻¹m⁻¹ at 486 nm and 1400 mg⁻¹m⁻¹ at 750 nm for a range of sizes. This makes it very simple to obtain the nanosheet concentration through an extinction measurement. Alternatively, the strongly size dependent extinction at 300 nm can be used to determine a metric to extract the extinction coefficient and hence nanosheet concentration. This follows an exponential decrease in the extinction coefficient with increasing <L>. This is beneficial for a material such as MoSe₂ where the extinction coefficient isn't invariant for all <L> and thus will need to be calculated in the future. To obtain the length dependent ϵ it is necessary to use the empirically found equations that are shown below:

MoSe₂:

$$\epsilon_{300nm} = 2140 + 6201.02e^{-\left(\frac{\langle L \rangle (nm)}{149-88}\right)} \quad (7.6)$$

WSe₂:

$$\epsilon_{300nm} = 2172 + 7416.42e^{-\left(\frac{\langle L \rangle (nm)}{100.6}\right)} \quad (7.7)$$

MoTe₂:

$$\epsilon_{300nm} = 1287.61 + 17657.04e^{-\left(\frac{\langle L \rangle (nm)}{48.03}\right)} \quad (7.8)$$

While it is beneficial to look for the positions with minimal changes of the extinction coefficient with nanosheet size for the determination of the concentration, a robust length metric is obtained where spectral changes with nanosheet size are maximised, which are shown in Figure 7.7 D-F against <L>[42]. The changing ratio of peak intensities caused by the changing ratio of core and edge absorption coefficient can be clearly seen for all three materials (Figure 7.7 D-F). There is a clear change between 50 nm and 200 nm, after which a saturation point appears, where either bulk properties or edge effects dominate.

In the instance of MoSe₂, where there is a clear change, this can be fitted and thus yield a metric relating $\langle L \rangle$ and intensity ratio. With WSe₂ and MoTe₂ these relations can be fitted as exponentials. For the three materials these equations are:

MoSe₂:

$$\langle L \rangle = 230.93 \left(\frac{Ext_{300nm}}{Ext_{366nm}} \right)^{-6.37} \quad (7.9)$$

WSe₂:

$$\langle L \rangle = -59 \left(\ln \left(\frac{\frac{Ext_{235nm}}{Ext_{347nm}} - 0.93}{0.85} \right) \right) \quad (7.10)$$

MoTe₂:

$$\langle L \rangle = -36.9 \left(\ln \left(\frac{\frac{Ext_{240nm}}{Ext_{385nm}} - 1.02}{2.52} \right) \right) \quad (7.11)$$

Where $\langle L \rangle$ is in nm for all equations.

7.4 Scattering Exponent as a Function of Nanosheet Size

In addition to length metrics obtained from extinction peak intensity ratios in the resonant regime, it is expected that the scattering in the nonresonant regime of the extinction spectra is also size dependent. It is possible to obtain the scattering coefficient spectra from the scattering spectra which are obtained by subtracting the absorption spectra from the extinction spectra. This was performed for each material and the scattering coefficient spectra (σ) are plotted for each size (Figure 7.8).

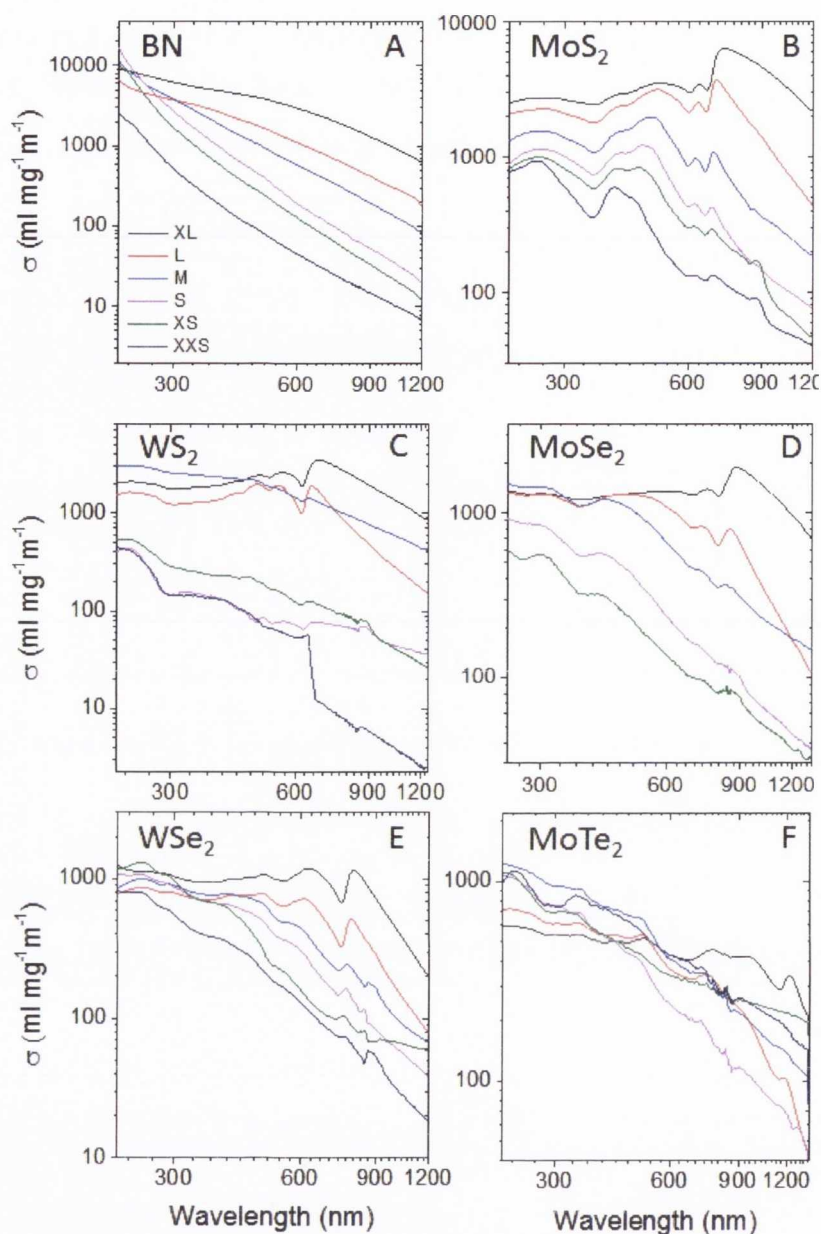


Figure 7.8: Scattering coefficient spectra for (A) BN, (B) MoS_2 , (C) WS_2 , (D) MoSe_2 , (E) WSe_2 and (F) MoTe_2 .

As expected for BN, due to their being no absorption contributing to the extinction spectra, the scattering spectra are entirely featureless with a clear change in shape of the spectra depending on nanosheets size. For the other five materials the spectra have numerous features caused by resonant scattering, all of which occur for wavelengths shorter than the position of the A-exciton. In the zero to low absorbance area at high wavelengths it is possible to obtain the scattering exponent, n for all of these materials, as well as for

BN. It has been suggested that the scattering exponent is size dependent and can be used for metrics to determine the average length of a nanosheet dispersion[42, 198]. Thus, n was plotted against $\langle L \rangle$ for all sizes of the six materials and is shown in Figure 7.9.

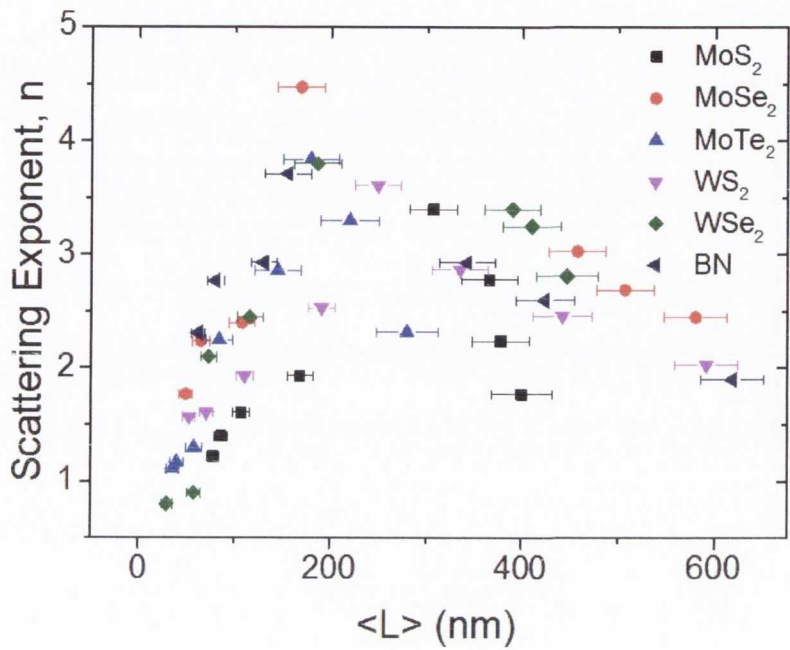


Figure 7.9: $\langle L \rangle$ vs n for BN, MoS₂, WS₂, MoSe₂, WSe₂ and MoTe₂.

As the length decreases from ~ 700 nm down to 150nm, the scattering exponent increases from ~ 2 - ~ 4 which has been previously reported for other layered 2D nanosheets[22, 44, 90]. What is very surprising is that the value for n doesn't saturate at 4 but continues to decrease to a value of ~ 1 for smaller nanosheets. This behaviour isn't consistent with Rayleigh scattering, as for very small particles, the value of n should saturate at 4[141]. Interestingly, the point where the saturation occurs appears to be similar for all the materials. This indicates that 2D nanomaterials have an intrinsic characteristic that when their length is reduced beyond a critical point the scattering exponent decreases. This mechanism is not straightforward and could be due to a number of reasons such as the refractive index of the materials changing dramatically beyond a critical length.

Despite the scattering exponent decreasing for very small nanosheets, it is still possible to achieve metrics for sizes larger than ~ 150 nm in length which can still be useful.

In chapter 5 an equation was determined for fitting the scattering exponent of differing materials as a function of length. This was repeated for these materials (Figure 7.10).

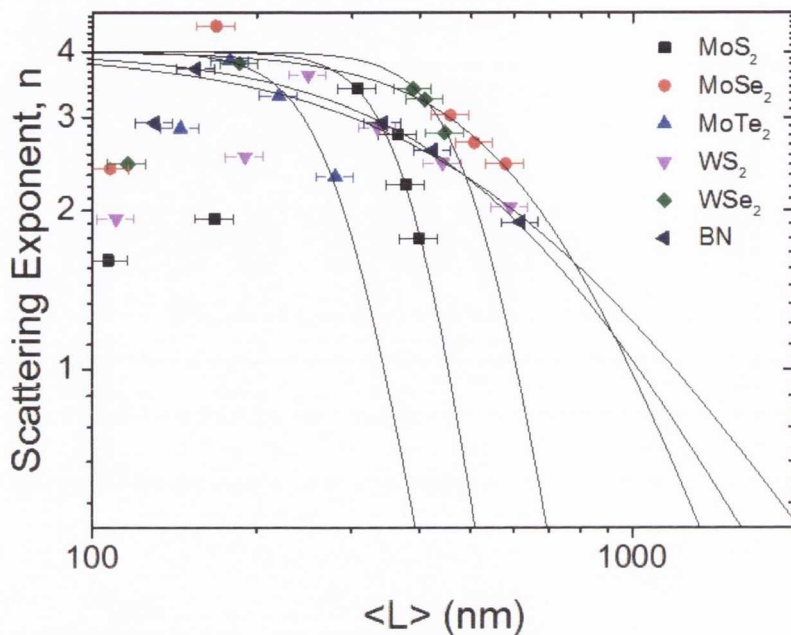


Figure 7.10: *Scattering exponents plotted versus mean nanosheet length for each material. The lines are fits to equation 7.12.*

Similar to the hydroxides in chapter 5 this equation 7.12 can be fitted well for nanosheets greater than 150 nm. By rearranging the equation it is possible to obtain $\langle L \rangle$ as a function of n as shown below:

$$\langle L \rangle = L_0 \left(\frac{4}{n} - 1 \right)^{\frac{1}{c}} \quad (7.12)$$

Where L_0 and c are two constants that are material dependent with a table of each value for each material shown below.

2D Material	L_0	c
BN	577.89	1.92
MoS ₂	394.57	7.23
WS ₂	599.58	1.59
MoSe ₂	671.04	2.83
WSe ₂	513.24	6.48
MoTe ₂	289.95	6.35

Figure 7.11: Table showing L_0 and c for each of the six materials.

By substituting these values into equation 7.12, this equation can be used to determine values for $\langle L \rangle$ by obtaining the scattering exponent as with GaS and Ni(OH)₂.

As mentioned previously, when the scattering coefficient is plotted against λ , it follows a power law $\propto \lambda^{-n}$ at high wavelengths or in regions with no contributions due to absorption[115]. When this is fitted, the complete relationship can be given as:

$$\sigma = K\lambda^{-n} \tag{7.13}$$

Where σ is the scattering coefficient, λ is the wavelength of light, n is the scattering exponent and K is a size dependent variable, for a given nanosheet length and is related to the refractive index of the material[198]. This value can also be obtained when obtaining the scattering exponent and thus is plotted against $\langle L \rangle$.

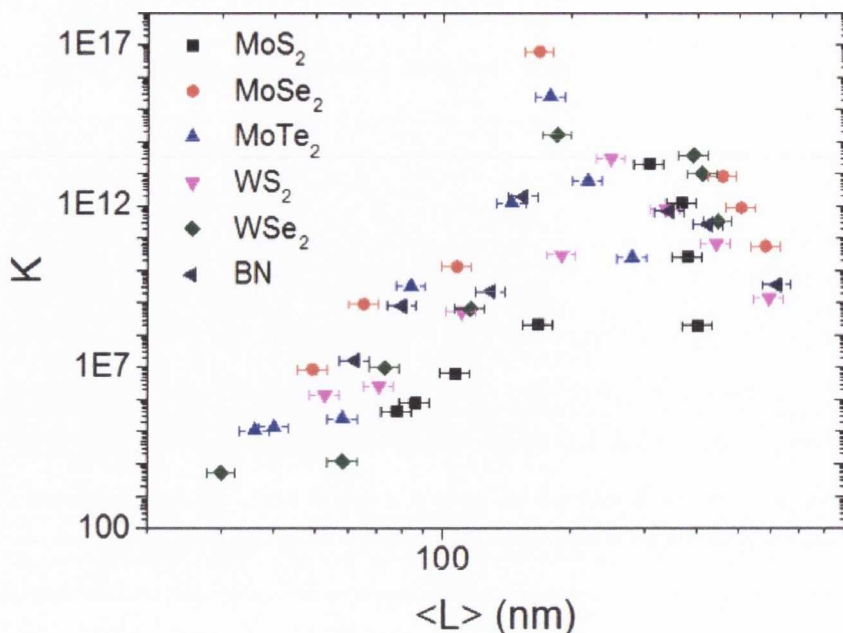


Figure 7.12: K plotted versus mean nanosheet length for each material.

As can be seen in Figure 7.12 the length dependence of the variable K is very similar to that of the scattering exponent n , with an increase up to a value of $\sim 1 \times 10^{14}$ for values of $\langle L \rangle$ up to about 200 nm, then a decrease to ~ 5000 for the smallest nanosheets. As expected this shows that larger nanosheets scatter more light but the fact that there is a turnover point is still not fully understood. As K is dependent on the refractive index of the material, this turnover could show a change in refractive index and thus, this could be the reason for the decrease in both K and the scattering exponent for decreasing $\langle L \rangle$ but requires further studies.

7.5 Conclusion

The work presented in this chapter has demonstrated the success of liquid cascade centrifugation to reliably produce nanosheet dispersions with different size and thickness distributions for a range of materials. This has led to a range of sizes of 650 nm to 30 nm for BN, MoS₂, WS₂, MoSe₂, WSe₂ and MoTe₂. The optical response (extinction,

absorbance, scattering) of these dispersions was analysed. It is important to choose the appropriate solvent to investigate the optical properties of 2D materials. Thus, D₂O was chosen, as it is possible to measure optical responses for materials, such as MoTe₂ in liquid that otherwise cannot be measured at high or small wavelengths, respectively. It was then possible to quantify the extinction coefficient for a range of materials as well as determining dimensional metrics by identifying length variant and invariant ranges of the spectra in the resonant regime. This facilitated the development of optical metrics which can be used to determine the $\langle L \rangle$, with this being achieved for the first time for four of these materials.

For the first time, the effect that lateral dimensions of a nanosheet dispersion produced by liquid phase exfoliation was investigated for a range of materials across a wide length range also covering the non-resonant regime where spectra are dominated by scattering. This initially lead to the expected result that the scattering exponent, n increases to a value of approximately 4 for decreasing nanosheet length. However, for small nanosheets, an unusual result was obtained, as n then began to decrease for continuously decreasing $\langle L \rangle$. This can not be explained by Mie or Rayleigh theory and could be due to the refractive index of the materials changing for smaller nanosheets compared to larger nanosheets. Finally the scattering spectra were used to determine metrics to yield $\langle L \rangle$ for nanosheet dispersions of six different material for $\langle L \rangle > 150$ nm..

This work is of great importance for the emerging field of liquid exfoliation, as the obtained metrics and insights into the optical properties can be used to improve sample processing and provide an in depth understanding of the optical response. Moreover, extinction and scattering spectra have been implemented to directly determine the lateral dimension and concentrations of dispersions produced by LPE.

Chapter 8

Conclusions & Future Work

The aim of this thesis was to expand liquid phase exfoliation to new families of layered materials and to characterise the exfoliated materials using optical methods. These methods have already successfully been used on graphene, BN, TMDs and TMOs but there is still a lot more scope for further expansion.

LPE was initially used on the material gallium sulphide (GaS), a member of the III-VI metal chalcogenide family, using solvent exfoliation techniques. It was demonstrated that layered III-VI semiconductors such as GaS can be exfoliated in appropriate solvents, such as CHP and NMP by sonication. Dispersibility can be well described in the framework of solution thermodynamics. Although a number of solvents can be used to exfoliate GaS, isopropanol was focused on due to its low toxicity and boiling point. Sonication and centrifugation parameters were optimised to yield stable dispersions with typical concentrations of 0.2 g/L. Raman, XPS, and TEM imaging show the exfoliated nanosheets to be widely structurally perfect and free of defects except for some oxygen content.

The advantage of liquid exfoliation techniques was utilised to perform size-selection by controlled centrifugation. This allowed the produce liquid-exfoliated GaS nanosheet dispersions with mean lateral dimensions ranging from ~ 100 nm to >400 nm and mean number of layers from 10 to 40 as quantified by statistical TEM and AFM analysis. Importantly, it was found that optical extinction, absorbance, and scattering spectra to vary strongly as a function of size and thickness. This enabled the establishment of quantitative spectroscopic metrics to accurately determine mean length, thickness, and concentration of the dispersion.

These results are general and thus, it should be possible to transfer these procedures almost exactly for the exfoliation of other III-VI metal chalcogenides such as InS and GaSe. This will open up this whole family of 2D materials for exploitation. In addition, it is important to note that this paper describes using LPE to exfoliate a member (GaS) of yet another family of layered compounds (III-VI metal chalcogenides). This underlines the generality and versatility of this method, which should lead to many as yet untested layered materials will be exfoliated using such procedures.

Similar methodologies that were used on GaS were applied to the layered double hydroxide family with particular interest being placed on Ni(OH)_2 , with the exception that surfactant stabilisation was used rather than solvent exfoliation. It was demonstrated that liquid phase exfoliation can be used to exfoliate layered Ni(OH)_2 crystals from commercially available powder to give liquid dispersions of few layer Ni(OH)_2 nanosheets with the identity of the dispersed material being characterised by SEM, Raman and XPS. This process yields nanosheets in a broad size range at reasonably high concentrations and with production rates which compare well to graphene production by LPE. This process allows the nanosheets to be size-selected in a simple and efficient manner. It was found that the optical extinction of the dispersions to vary strongly with nanosheet size. Detailed studies showed the nanosheet absorbance to be roughly size invariant but the optical scattering spectra to depend strongly on nanosheet length.

LPE results in nanosheet dispersions which are solution - processable and can be easily formed into structures such as films. This makes it easy to characterise the material using such methods as SEM, XPS and Raman spectroscopy which showed no damage had been done to the nanosheets during exfoliation. As well as this the resulting nanosheets were mostly free of contaminants and had approximately the correct stoichiometry.

This work has extended LPE to a new class of materials, the layered hydroxides, and further demonstrates the versatility of this method. It is possible to view Ni(OH)_2 as a model system which has been used to demonstrate LPE. This was shown for four other hydroxide materials, Co(OH)_2 , Mg(OH)_2 , Zn(OH)_2 and Cu(OH)_2 , where these methods produced high quality nanomaterials in all instances. As well as this, the four other materials were size selected and their size dependent optical properties were demonstrated.

It is clear that LPE is an extremely versatile technique to produce nanosheets from

layered precursors. Here, it has been shown that it is possible to process naturally occurring materials such as talc, Fuller's earth cat litter and a clay/sand mix using LPE and obtain purified nanosheets while rejecting any unwanted non-2D material. Using a simple pretreatments method the materials were cleaned of inorganic and organic impurities that may have been on the nanosheets. The materials were then exfoliated into nanosheets, the quality of which were identified with TEM, finding that $\langle L \rangle$ of 600 ± 42 nm, 315 ± 29 nm and 370 ± 21 nm for talcum powder, clay and cat litter respectively. Zeta potential measurements were also used to confirm if the nanosheets consisted of charged layers and it was found that they exhibited potentials of 14 - 15 mV confirming this to be true but the values not high enough to stabilise the nanosheets.

To investigate the materials that had been exfoliated XRD and XPS were both used. XRD confirmed that only layered materials were remaining in the final dispersions with talcum powder remaining mainly unchanged, clay being exfoliated from sand and mica to just mica, and the cat litter dispersion to just be comprised of bentonite and palygorskite, two layered materials. The XPS showed that there very few elemental impurities remaining in the dispersions.

The work conducted in this chapter shows the true ability of liquid phase exfoliation to only remove the layered material from a compound and exfoliate them into nanosheets. Also it is particularly surprising is that the bentonite and palygorskite layered crystals contained in the cat litter as well as the mica in the beach sand should both consist of charged layers with charge-balancing counter ions, yet could still be exfoliated by LPE.

The work presented in this chapter has demonstrated the success of liquid cascade centrifugation by selectively screening differing average nanosheet length in a dispersion for a range of materials. This has led to a range of sizes of 650 nm to 30 nm for BN, MoS₂, WS₂, MoSe₂, WSe₂ and MoTe₂. It is possible to measure optical responses for materials, such as MoTe₂ in liquid that otherwise can't be measured at certain wavelengths by selective choosing of an appropriate solvent. By achieving this it is then possible to quantify the extinction coefficient for a range of materials as well as determining dimensional metrics for the same materials by determining length invariant ranges of the spectra. This lead to length metrics for all six materials, with this being achieved for the first time for four of these materials.

For the first time, the effect that lateral dimensions of a nanosheet dispersion produced by liquid phase exfoliation was investigated for a range of materials across a wide length range. This initially lead to the expected result that scattering exponent, n increases to a value of approximately 4 for decreasing nanosheet length but then to an unusual result where n then began to decrease for continuously decreasing $\langle L \rangle$. This isn't explained by Mie or Rayleigh theory and could be due to the refractive index of the materials changing for smaller nanosheets compared to larger nanosheets. Finally the scattering spectra were used to determine metrics to yield $\langle L \rangle$ for nanosheet dispersions.

This work enhances the field of LPE, with improvement to the processing and optical characterisation. Moreover, extinction and scattering spectra have been implemented to directly determine the lateral dimension and concentrations of dispersions produced by LPE.

8.1 Ongoing and Future Work

This section demonstrates the research that is still on going that has stemmed from this thesis. This mainly includes expanding these methods to more materials within the same families. In chapter 4 LPE was used on GaS, a III-VI metal chalcogenide but there are other materials in this family that can still be exfoliated using the same conditions, similar to the methods shown in chapter 5. Also, work on another family of materials, known as the metal diborides, has begun using liquid phase exfoliation to isolate nanosheets.

8.1.1 Comparison of III-VI Metal Chalcogenides

It was shown to optimise the exfoliation parameters of GaS it is necessary to use conditions of $C_i = 45 \text{ gL}^{-1}$, $t_{sonic} = 6 \text{ hours}$, solvent = IPA, $cf_{time} = 180 \text{ mins}$ and $cf_{rpm} = 2.5 \text{ kRPM}$ but as just one member of this family persumably it is possible to exfoliate others with the same conditions. Thus, these parameters were used to exfoliate GaSe, GaTe and InSe. This resulted in three brown liquids of different shades (Figure 8.1A). To confirm exfoliation TEM was used on the four standard dispersions.

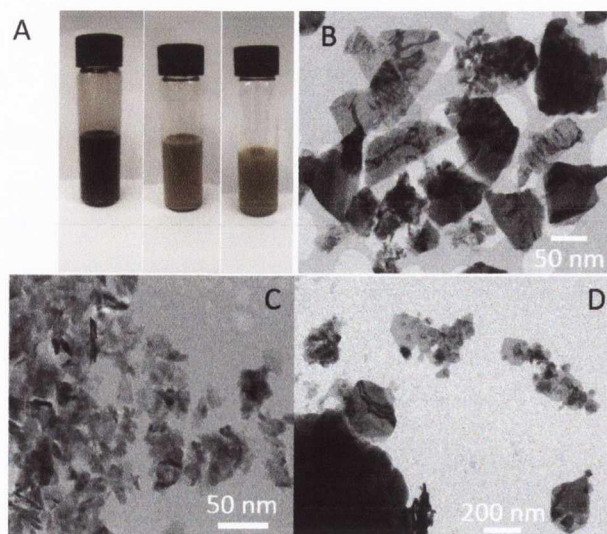


Figure 8.1: A) Photos of the dispersions of GaSe, GaTe and InSe (left to right). Representative TEM images of the 'standard' dispersion for (B) GaSe, (C) GaTe and (D) InSe.

As can be seen in Figure 8.1B-D this method has produced similar nanosheets to that of GaS. As well as this they are well exfoliated showing electron transparency and distinctive edges with similar dimensions.

The UV-vis spectra of gallium sulphide is quite interesting depending on whether you measure the extinction or absorption spectra. This is due to a scattering background supressing some of the features of the absorption spectra. Thus, it is of interesting to compare this to the other three materials. To achieve this measurements of the ext, sca and abs were made on the standard dispersions, as shown in Figure 8.2. It can be clearly seen that as with GaS there are clear scattering effects, as for all the materials there are zero absorbance regimes in the abs spectra but not the extinction spectra. Also of note are the exciton positions specifically the b exciton as there are clear shifts in position for each material.

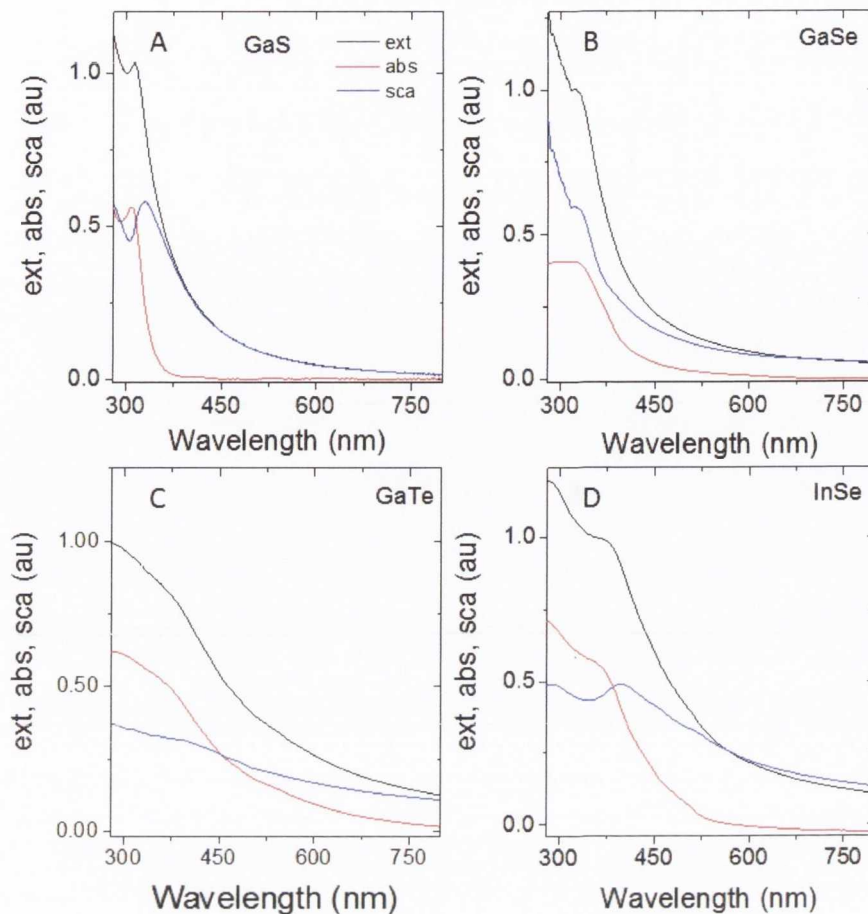


Figure 8.2: Normalised extinction, absorption and scattering spectra for (A) GaS, (B) GaSe, (C) GaTe and (D) InSe.

This isn't surprising as these materials have a wide distribution in terms of band gaps, ranging from 3.05 eV to 1.26 eV. Unfortunately the A-exciton isn't largely obvious in any of the spectra but this is due to the nanosheets being quite small. This leads to the intensity being quite low as shown in section 4.5 where the intensity ratio between peaks rapidly decreases as $\langle L \rangle$ decreases.

It was shown that GaS exhibits changing optical properties depending on the size of the nanosheets and thus, it would be interesting if similar effects happen with these materials. Thus GaSe, GaTe and InSe dispersions were all size selected using LCC with the same parameters that were used on GaS. Ext, abs, and sca spectra were then performed on all the materials (Figure 8.3).

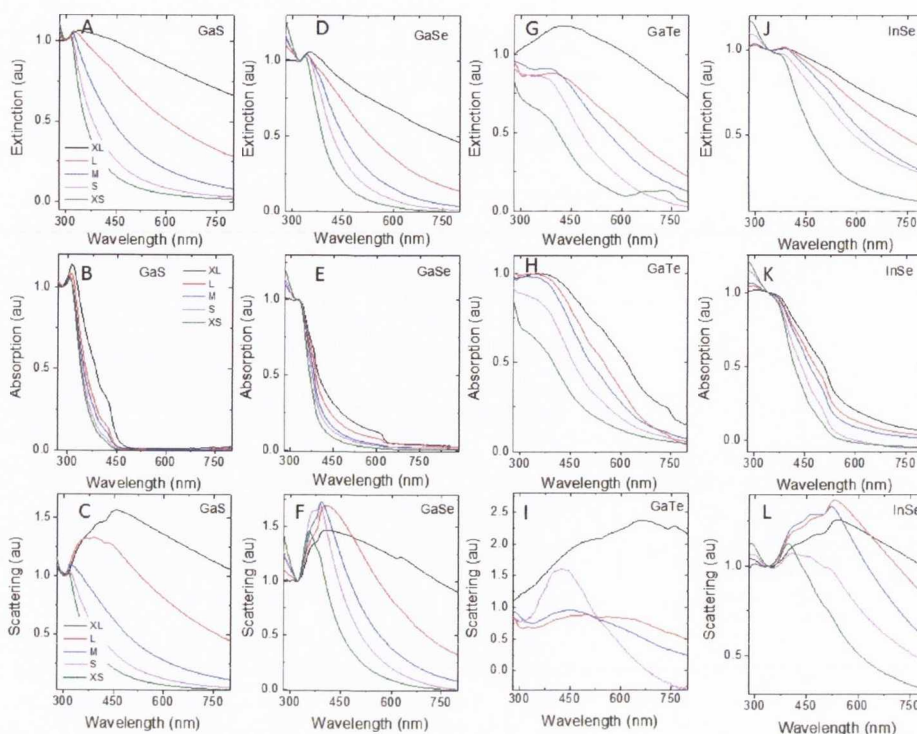


Figure 8.3: Normalised extinction, absorption and scattering spectra for size selected (A-C) GaS, (D-F) GaSe, (G-I) GaTe, (J-L) InSe.

As with GaS, the extinction spectra for GaSe, GaTe and InSe are heavily affected by scattering with a power law background seen for all sizes. Although despite this the B exciton is still observable at approximately nm, nm, and nm respectively. Of more interest is the absorption spectra where it is now possible to view the A exciton for all the materials. Like with GaS the ratio of the peaks is dependent on size, as well as this it appears that the A-exciton blue or red shifts. In regards to the scattering spectra, the scattering exponent, n also is determined by nanosheet size. These three properties could be of note to investigate further in future studies to determine optical based metrics for the three other materials similar to GaS.

8.1.2 Exfoliation of Metal Diborides in Aqueous Media

As mentioned throughout this thesis there are still many families of materials that can be exfoliated. This includes the metal diboride family, specifically TiB_2 and ZrB_2 . Preliminary exfoliation work has been started on these materials, including exfoliation with PVA being used as a binder in water instead of using surfactants. This is due to the fact

that one of these materials most promising applications is to be used to reinforce certain polymers, such as poly vinyl alcohol (PVA). This is aided if the nanosheets are already coated in the same polymer whilst in suspension.

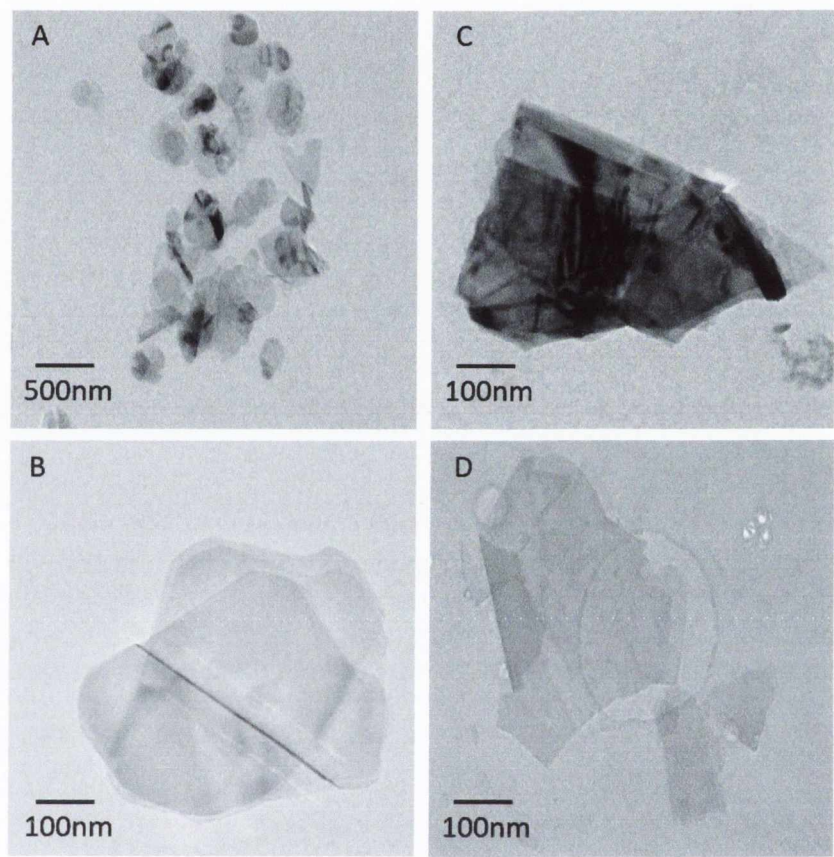


Figure 8.4: TEM images of the 'standard' sample of (A-B) TiB_2 and (C-D) ZrB_2 .

This exfoliation technique was demonstrated by sonicating 20 mg/ml of the respective material in 20 mg/ml of PVA/water solution for 4 hrs. These dispersions were then subjected to one step of LCC between 500 RPM and 1000 RPM with the sediment being retained and redispersed in water. This resulted in two dispersions that were deeply black/grey in colour.

To ensure the existence of nanosheets TEM was performed with the images being shown below in Figure 8.4, where it can be seen that there are large numbers of well exfoliated nanosheets with $\langle L \rangle = 795.42 \text{ nm}$ and 406.27 nm for TiB_2 and ZrB_2 respectively. There is a large difference in the average length but this could be simply due to a larger number

of quite small flakes existing in the ZrB_2 dispersion reducing the average length.

As these nanosheets are mainly going to be used for future applications, as opposed to in depth characterisation studies, it is important to obtain the optical coefficients of the material for easy concentration calculations. This was performed using the previously described methods (chapter 4 - 7) by measuring the ext, abs and sca spectra and obtaining the concentration of the dispersions through mass weighing, which were found to be 1.41 mg/ml and 0.34 mg/ml for TiB_2 and ZrB_2 respectively. In Figure 8.5 are the spectra for both materials.

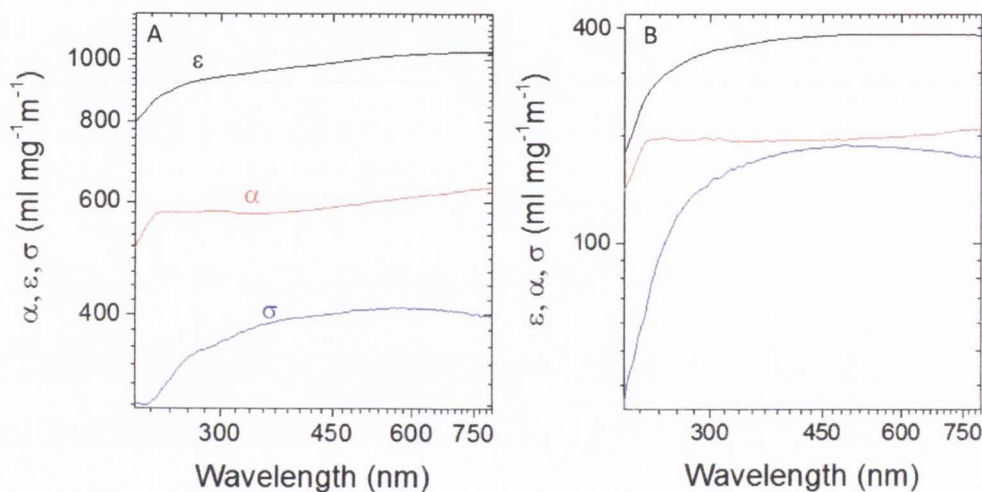


Figure 8.5: Extinction (ϵ), absorption (α) and scattering (σ) coefficient spectra for (A) TiB_2 and (B) ZrB_2 .

Although, these are featureless spectra they're different to all the previously measured materials as they are semi-metals as opposed to semiconductors or insulators. This leads to light being absorbed across all wavelengths and has also led to smaller contributions from light scattering making it much easier to assess dispersion concentration from both the extinction and absorption spectra.

This exfoliation work is only in its infancy but is of interest primarily expanding the available nanomaterials but also due to it being a rare case of a non semiconductor material being exfoliated also as it has been exfoliated in polymer as opposed to solvent or surfactant. Also due to the material being a semi-metal it could be useful for some electrical based applications where semiconductors are limited by their electrical conductivity.

Chapter 9

Appendix

9.1 Extinction, Absorption and Scattering of $\text{Mg}(\text{OH})_2$

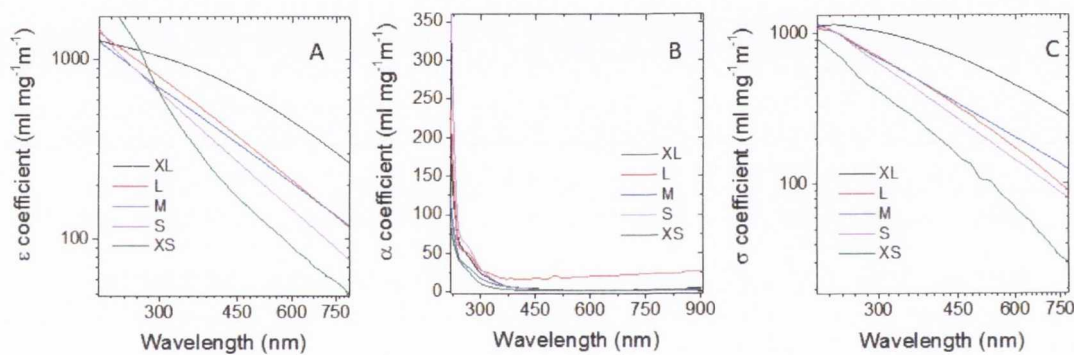


Figure 9.1: *Extinction (A), absorption (B) and scattering (C) coefficient spectra for all five sizes of $\text{Mg}(\text{OH})_2$*

9.2 AFM for Talc, Clay and Cat Litter

AFM was performed on the three materials from chapter 6 using the same methods as in chapter 4.

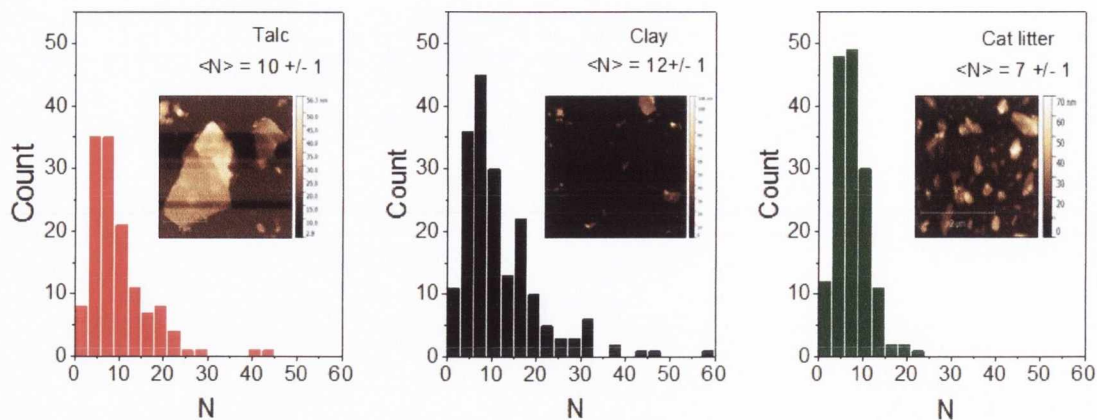


Figure 9.2: AFM histograms for exfoliated (A) talcum powder, (B) clay and (C) cat litter.

9.3 Scattering Exponent Fits for LDHs

As shown in chapter 7. It is possible to obtain $\langle L \rangle$ as a function of scattering exponent, n as shown below:

$$\langle L \rangle = L_0 \left(\frac{4}{n} - 1 \right)^{\frac{1}{c}}$$

Where L_0 and c are two constants that are material dependent with a table of each value for each material shown below.

2D Material	L_0	c
$\text{Ni}(\text{OH})_2$	257	2.5
$\text{Co}(\text{OH})_2$	185	1.12
$\text{Mg}(\text{OH})_2$	425	2.13
$\text{Zn}(\text{OH})_2$	231	1.47
$\text{Cu}(\text{OH})_2$	1689	0.88

Figure 9.3: Table showing L_0 and c for each of the five LDHs.

9.4 Scattering Exponent vs $\langle L \rangle$ for all materials

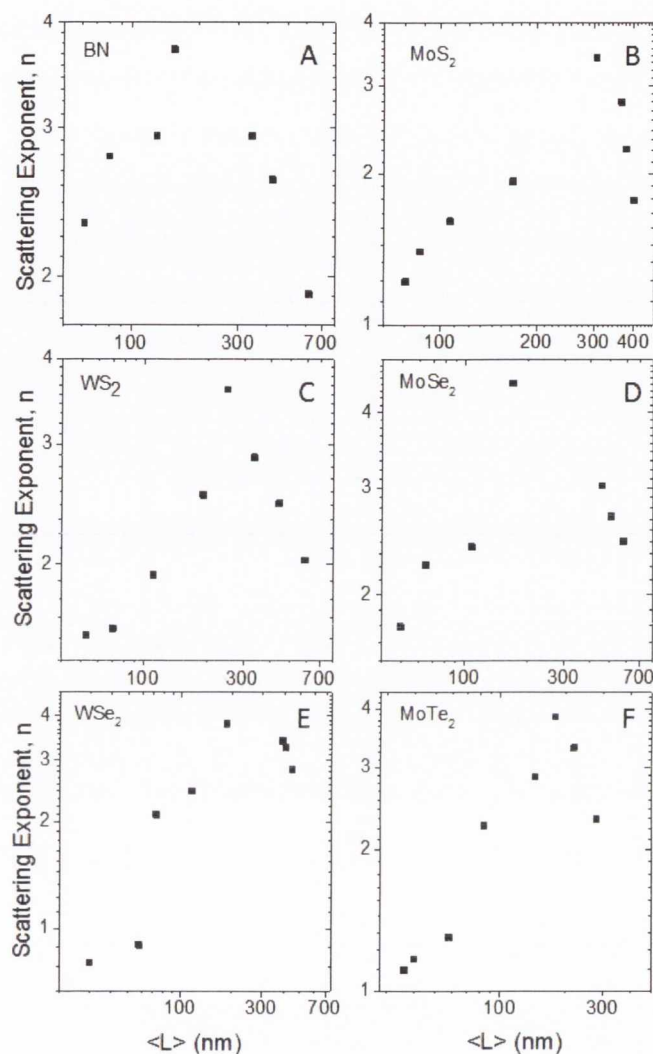


Figure 9.4: *Scattering Exponent vs $\langle L \rangle$ for all materials*

9.5 Scattering exponent vs $\langle L \rangle$, $\langle A \rangle$, $\langle V \rangle$

As shown in chapter 7, when the scattering exponent is plotted against $\langle L \rangle$ there is general trend where n increases to a value of 4 for $\langle L \rangle$ of 600 nm to 150 nm then decreases. There is some scatter in this data though, which could be due to only one dimension of the nanosheets being taken into account. To address this, the mean nanosheet area ($\langle A \rangle$)

and mean nanosheet volume ($\langle V \rangle$) were also found. To discover which parameter is best suited to be plotted against n , the log of the scattering exponent was plotted against the log of each parameter. These plots were then fitted with a parabola fit (as each describe parabola like behaviour) and the R^2 values found. As can be seen in Figure 9.4 $\text{Ln}(n)$ vs $\text{Ln}(\langle A \rangle)$ yields the best fit. This is as a result of the light scattering off the entire nanosheet and not just one plane with potential differences of 100s of nm between different sides of the nanosheet. The volume of the nanosheet doesn't affect this as the thickness, due to being 2D materials, are much smaller than the length or the width of the nanosheets.

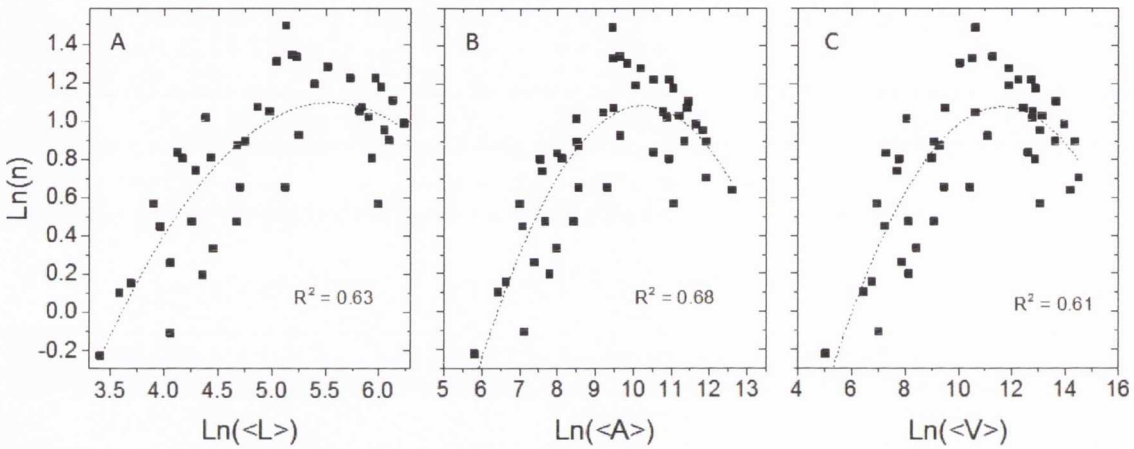


Figure 9.5: *Fitted curves of n vs $\langle L \rangle$, $\langle A \rangle$, $\langle V \rangle$*

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