

Optimization of Junction Resistance in Solution-Processed 2D Nanosheet Networks



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Declaration

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Oran Cassidy

ABSTRACT

Networks of solution-processed two-dimensional (2D) nanosheets are a promising materials platform for printable and flexible electronics, combining the unique physicochemical properties of atomically thin crystals with scalable processing into large-area films. Such networks can retain electrical performance under repeated strain, making them attractive for wearable and implantable technologies. However, their electrical conductivity is typically reduced by several orders of magnitude relative to that of individual nanosheets due to the presence of inter-nanosheet junctions. Charge transport across these junctions proceeds by charge hopping, giving rise to a so-called junction resistance that forms the principal bottleneck in network conductivity. Lowering this resistance is therefore a central challenge for realizing functional nanosheet network devices.

This thesis explores strategies to reduce junction resistance through three complementary approaches: (i) preparation of high aspect ratio nanosheets by electrochemical exfoliation (EE), (ii) assembly of aligned and homogeneous networks by liquid interface deposition (LID), and (iii) modelling of network charge transport in the AC regime to extract junction resistance and determine its dependence on nanosheet dimensions.

Cathodic EE using alkylammonium intercalants was shown to yield large-area, thin TMD nanosheets (MoS_2 , WS_2 , and WSe_2) while preserving their desirable semiconducting 2H phase. Compared to shear exfoliation, EE produced nanosheets with an order of magnitude higher aspect ratio (~ 100 vs. ~ 15), directly addressing the requirement for conformal sheets to form conductive junctions. Networks of these nanosheets, assembled by LID, were incorporated into TFTs electrolytically gated with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) as the ionic liquid dielectric. The resulting devices exhibited average mobilities of $10.7 \pm 0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (MoS_2), $9.1 \pm 2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (WS_2), and $2.0 \pm 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (WSe_2) with on/off ratios of $(2.6 \pm 0.4) \times 10^3$, $(3.4 \pm 0.6) \times 10^3$,

and $(4.2 \pm 1.8) \times 10^4$, respectively. These figures of merit are competitive with alternative semiconducting material systems, such as carbon nanotubes and metal oxides. Importantly, device performance was retained on a flexible polyethylene terephthalate (PET) substrate, with a WSe₂ TFT on PET maintaining high mobility ($1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and on/off ratio ($\sim 3 \times 10^3$) over 1000 bending cycles.

To refine the LID technique, a procedure was established to optimise single nanosheet layer deposition by varying nanosheet ink concentration and interfacial areal mass load. Using electrochemically exfoliated (EE) graphene as a reference system, several figures of merit for film quality were defined. Optimal deposition was identified at low ink concentration (0.02 g L^{-1}) and high areal mass load (21 mg m^{-2}). These parameters were then applied to assemble multilayer films by sequential deposition of monolayer-enriched EE graphene onto glass. Conductivity-thickness data for these films was fitted using a novel percolative scaling model, yielding a high bulk conductivity ($\sigma_B = 1.4 \times 10^5 \text{ S m}^{-1}$) and low bulk transition thickness ($t_x = 12 \text{ nm}$). As transparent conductors, these networks compared favourably with graphene nanosheet films in the literature, with a representative sample combining 85% optical transmission and sheet resistance of $4.1 \text{ k}\Omega \square^{-1}$. Finally, analogous EE graphene films were fabricated on Kapton to realise a flexible transparent conductor. Although the device maintained conductivity ($\sim 3.5 \times 10^3 \text{ S m}^{-1}$) over hundreds of bending cycles, the sheet resistance ($15.7 \text{ k}\Omega \square^{-1}$) was higher and the transmission ($\sim 50\%$) much lower than the films on glass, likely due to the reduced post-processing temperature required by the polymer substrate.

Finally, a model linking junction resistance to nanosheet dimensions was hypothesised and tested. To enable this, a liquid cascade centrifugation protocol was developed that could selectively isolate fractions of EE MoS₂ with distinct thickness distributions, including populations of substantially thick nanosheets. These size-selected dispersions were then

deposited into films by both LID and spray coating, and they were electrically characterized by impedance spectroscopy to extract junction resistance. While a clear correlation between junction resistance and nanosheet thickness was not established, the results revealed that networks assembled by LID consistently exhibited substantially lower junction resistance than those prepared by spray coating, reinforcing its suitability for producing low junction resistance networks and hence high-performance nanosheet network devices.

List of Publications

1. T. Carey, **O. Cassidy**, K. Synnatschke, E. Caffrey, J. Garcia, S. Liu, H. Kaur, A. Kelly, J.M. Munuera, C. Gabbett, D. O'Suillabjain, J.N. Coleman. (2023). High-Mobility Flexible Transistors with Low-Temperature Solution-Processed Tungsten Dichalcogenides. *ACS Nano*, 17 2912–2922.
[Basis for Chapter 6]
2. K. Synnatschke, A. Müller, C. Gabbett, M.J. Mohn, A. Kelly, K. Mosina, B. Wu, E. Caffrey, **O. Cassidy**, C. Backes, Z. Sofer, U. Kaiser, J.N. Coleman. (2024). Inert Liquid Exfoliation and Langmuir-Type Thin Film Deposition of Semimetallic Metal Diborides, *ACS Nano*, 18 28596–28608.
3. J. Neilson, E. Caffrey, **O. Cassidy**, C. Gabbett, K. Synnatschke, E. Scheneider, J.M. Munuera, T. Carey, M. Rimmer, Z. Sofer, J. Maultzsch, S.J. Haigh, J.N. Coleman. (2024). Production of Ultrathin and High-Quality Nanosheet Networks via Layer-by-Layer Assembly at Liquid-Liquid Interfaces, *ACS Nano*, 18 32589–32601.
4. E. Caffrey, T. Carey, L. Doolan, A. Dawson, E. Coleman, Z. Sofer, **O. Cassidy**, C. Gabbett, J.N. Coleman. (2024). Using Electrical Impedance Spectroscopy to Separately Quantify the Effect of Strain on Nanosheet and Junction Resistance in Printed Nanosheet Networks, *Small*, 21, 2406864.
5. **O. Cassidy**, K. Synnatschke, J.M. Munuera, C. Gabbett, T. Carey, L. Doolan, E. Caffrey, J.N. Coleman. (2025). Layer-by-layer assembly yields thin graphene films with near theoretical conductivity, *npj 2D Materials and Applications*, 9 2.
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6. L. Doolan, Y. Sozen, E. Caffrey, E. Coleman, T. Carey, A. Dawson, C. Gabbett, **O. Cassidy**, J. K. Vij, Z. Sofer, A. Castellanos-Gomez, J. N. Coleman. (2025). The

electrical and morphological characteristics of mechanically exfoliated nanosheets, *Small Science*, 5 12.

7. T. Nowack, L. Bastonero, T. Knickrehm, T. Carey, **O. Cassidy**, J.N. Coleman, Z. Sofer, K. Synnatschke, N. Marzari, C. Backes. (2025). Assessing quality and purity of MoS₂ nanosheets by diffuse reflectance IR spectroscopy, *2D Materials*, 12 045021.

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Table of Contents

1	Introduction & Outline	1
2	2D Materials Properties & Applications.....	5
2.1	Graphene	7
2.1.1	Graphene Applications	9
2.2	Transition Metal Dichalcogenides	11
2.2.1	TMD Applications	16
2.3	Flexible Electronics.....	18
3	Nanosheet Synthesis	20
3.1	Solution Processing.....	22
3.1.1	Liquid Phase Exfoliation.....	23
3.1.2	Chemical Exfoliation	24
3.1.3	Electrochemical Exfoliation	26
3.1.4	Solvent & Surfactant Stabilization.....	32
3.2	Size Selection.....	34
4	Deposition & Characterization Techniques	37
4.1	Spray Coating	38
4.2	Liquid Interface Deposition.....	40
4.3	Characterization	43
4.3.1	Atomic Force Microscopy	43
4.3.2	Ultraviolet-Visible Spectroscopy	45
4.3.3	Raman Spectroscopy	48
4.3.4	Electron Microscopy	52
4.4	Camera Film Scanning.....	54
4.4.1	Image Processing	54
4.5	Electrical Characterization	57
4.5.1	Two-Probe Measurements.....	58
4.5.2	Impedance Spectroscopy	60

5 Charge Transport in Nanosheet Networks	63
5.1 Percolation	64
5.1.1 Percolation Modelling.....	67
5.2 Junction Resistance in Nanosheet Networks	70
5.2.1 DC Network Model.....	71
5.2.2 AC Network Model.....	73
5.3 Interpreting Impedance Spectroscopy	75
5.3.1 Limitations of Ideal Network Model	78
5.4 Network Properties	79
5.4.1 Overlap Area & Conformality	80
5.4.2 Nanosheet Alignment.....	82
5.4.3 Interfacial Impurities.....	82
5.4.4 Junction Regimes	84
5.5 Applications.....	85
5.5.1 Transistors	86
5.5.2 Electrolytic Gating.....	90
6 Electrochemical Exfoliation of Transition Metal Dichalcogenides for 2D Thin Film Transistors	92
6.1 Procedure	94
6.1.1 EE of TMDs	94
6.1.2 Shear Exfoliation of MoS ₂	95
6.1.3 Size Selection & Solvent Washing.....	96
6.1.4 Nanosheet Characterization.....	97
6.1.5 Film Deposition	98
6.1.6 TFT Measurements.....	100
6.1.7 Microscopy	101
6.2 Results & Discussion	101
6.2.1 Size-Selected Shear & EE Comparison AFM Statistics.....	101

6.2.2	Other TMD AFM Statistics	104
6.2.3	Size-Selected Shear & EE Comparison Characterization	105
6.2.4	Other TMD Characterization	108
6.2.5	Different TMD TFTs	109
6.2.6	Size-Selected EE MoS ₂ TFTs	111
6.2.7	Flexible TFT	112
6.3	Conclusions	114
7	Development of Liquid Interface Deposition for Low Junction Resistance Nanosheet Networks	116
7.1	Procedure	119
7.1.1	Graphene Ink Preparation	119
7.1.2	Nanosheet Ink Characterization	119
7.1.3	Optimization Study Film Deposition.....	120
7.1.4	Optimization Film Characterization	121
7.1.5	Layer-by-Layer Film Deposition	125
7.1.6	Flexible Device Deposition & Characterization.....	127
7.2	Results and Discussion.....	128
7.2.1	Graphene Characterization	128
7.2.2	Deposition Optimization	129
7.2.3	Layer by Layer Films.....	132
7.2.4	Flexible TCF	137
7.3	Conclusions.....	139
8	Thickness Dependence of Junction Resistance.....	140
8.1	Procedure	143
8.1.1	Thickness Selection.....	143
8.1.2	UV-Vis Spectroscopy	144
8.1.3	AFM.....	144
8.1.4	Substrate Preparation.....	145

8.1.5	Liquid Interface Deposition	145
8.1.6	Spray Coating.....	145
8.1.7	Film Thickness Measurement	146
8.1.8	Impedance Spectroscopy	146
8.1.9	Optical Microscopy	147
8.2	Results & Discussion	147
8.2.1	UV-Vis Spectroscopy	147
8.2.2	AFM Statistics	148
8.2.3	Impedance Spectroscopy	150
8.3	R _j Versus Nanosheet Dimensions.....	151
8.4	Conclusions	154
9	Conclusions & Future Work	156
A	Appendix A.....	163
A.1	Theory Chapter 5	163
A.1.1	Percolation Derivation.....	163
A.1.2	DC Network Derivation	164
A.1.3	AC Network Derivation	169
A.1.4	Randles Equivalent Circuit Modelling.....	169
A.2	Experimental 1	172
A.2.1	AFM Flake Counting.....	172
A.2.2	Size-Selection Histograms.....	173
A.2.3	Film Thickness AFM Measurements	174
A.2.4	Cyclic Voltammetry	175
A.2.5	Full TFT Measurements.....	176
A.2.6	Size-Selected TFT Measurement	177
A.3	Experimental 2	178
A.3.1	AFM Measurements.....	178
A.3.2	Optimization Study Deposition Setup	179

A.3.3	KOH Glass Treatment & Mask	180
A.3.4	Scanner Calibration	181
A.3.5	Scan Analysis.....	183
A.3.6	Electrical Measurements	186
A.3.7	Layer-by-Layer Deposition.....	188
A.3.8	Fitting of Neilson et al. Data.....	192
A.3.9	EEG Extinction Measurement	193
A.3.10	Concentration Limits for Interfacial Film Formation	195
A.3.11	TCF Literature Comparison.....	196
A.4	Experimental 3	198
A.4.1	AFM of MoS ₂ Nanosheets.....	198
A.4.2	Phase Shift Interferometry	199
A.4.3	AFM Measurements	201
A.4.4	Impedance Measurements.....	201
A.4.5	Optical Microscopy.....	204
B	Appendix B	207
B.1	Processing for $\langle \text{Ext} \rangle_{\text{film}}$, $\Delta \text{Ext}_{\text{film}}$, & Σ_{film}	207
B.2	Relative Film Perimeter Length	210
B.3	Measurement of EEG Extinction Coefficient.....	214
B.4	Conductivity Measurement.....	216
B.5	Multilayer Deposition Code	219
	Bibliography	226

List of Figures

Figure	Title
Figure 2.1	2D Materials & Their Applications
Figure 2.2	Graphene Structure
Figure 2.3	Graphene Properties & Applications
Figure 2.4	Transition Metal Dichalcogenides Composition & Structure
Figure 2.5	Transition Metal Dichalcogenides Polymorphism & Density of States
Figure 2.6	Transition Metal Dichalcogenides Band Structure
Figure 2.7	Transition Metal Dichalcogenides Applications
Figure 3.1	Chemical Vapour Deposition & Micromechanical Exfoliation
Figure 3.2	Liquid Phase Exfoliation
Figure 3.3	Chemical Exfoliation
Figure 3.4	Electrochemical Exfoliation
Figure 3.5	Alkylammonium Cations
Figure 3.6	Exfoliation Solvent Stabilization
Figure 3.7	Liquid Cascade Centrifugation
Figure 4.1	Spray Coating
Figure 4.2	Liquid Interface Deposition
Figure 4.3	Atomic Force Microscopy
Figure 4.4	Ultraviolet-Visible Spectroscopy
Figure 4.5	Raman Spectroscopy
Figure 4.6	Scanning Electron Microscopy
Figure 4.7	Camera Film Scanning & Processing
Figure 4.8	2-Probe Measurements
Figure 4.9	Impedance Spectroscopy

Figure 5.1	SEM Images of Nanosheet Networks & Inter-Nanosheet Junctions
Figure 5.2	Percolation in Nanosheet Networks
Figure 5.3	1-D Model of a Rough Thin Film
Figure 5.4	Fit of Percolation Model
Figure 5.5	Nanosheet Network DC Resistor Model
Figure 5.6	Randles Equivalent Circuits
Figure 5.7	Impedance spectra and Nyquist Plots, Modified Randles Circuit
Figure 5.8	Network & Nanosheet Properties that Influence Junction Resistance
Figure 5.9	Different Junction Resistance Regimes in MoS ₂ Nanosheet Networks
Figure 5.10	MOSFET Schematic & Transfer Curves
Figure 5.11	Electrolytic Gating
Figure 6.1	Electrochemical Exfoliation Setup
Figure 6.2	Shear Exfoliation Setup
Figure 6.3	Liquid Interface Deposition Setup and Device Schematic
Figure 6.4	AFM Size Statistics of MoS ₂ for Electrochemical & Shear Exfoliation
Figure 6.5	Comparison of Aspect Ratio for Different Exfoliation Techniques
Figure 6.6	AFM Statistics of WS ₂ & WSe ₂
Figure 6.7	Raman & UV-vis Characterization of MoS ₂
Figure 6.8	Raman & UV-vis Spectra of WS ₂ & WSe ₂
Figure 6.9	Representative Electrical Characteristics of EE TMD TFTs
Figure 6.10	Device Mobility Scaling with Lateral Size in EE MoS ₂
Figure 6.11	Flexible WSe ₂ TFT
Figure 7.1	Optimization Deposition Setup
Figure 7.2	Transmission Scan Characterization
Figure 7.3	Multilayer Deposition Setup

Figure 7.4	Electrochemically Exfoliated Graphene Characterization
Figure 7.5	Deposition Optimization Results
Figure 7.6	Multilayer Deposition Results
Figure 7.7	Comparison of the Rigid TCFs Produced with Existing Literature
Figure 7.8	Flexible EE-Graphene Transparent Conducting Film
Figure 8.1	Schematic of Junction Conduction Model
Figure 8.2	Drill Centrifugation Setup
Figure 8.3	Thickness Selection UV-vis Spectra
Figure 8.4	AFM Statistics for Thickness Selected Dispersions
Figure 8.5	Centrifugation Theory Plots for Inferring Dispersion Statistics
Figure 8.6	Impedance Spectra
Figure 8.7	Plots of Junction Resistance versus Sheet Dimensions
Figure 8.8	Optical Microscopy Images Comparing Deposition Techniques

In memory of my late grandfather, Cathal Cassidy

1935 - 2022

"Do the best you can, when you can, if you can."

"I am indebted to my father for living, but to my teacher for living well"

Alexander the Great

Chapter 1

Introduction & Outline

For as long as humanity has sought to harness the forces of nature, progress has been inseparable from advancement in materials. Flint blades and woodworking gave early humans leverage over their environment, laying the foundations of survival. Clay pottery made it possible to store surplus food and express ornamental art. The alloying of copper and tin into bronze produced durable tools and weapons, supporting the rise of the first complex societies. Ironworking supplied a cheap and abundant metal, turning swords and ploughshares from elite possessions into instruments of mass armament and agricultural expansion. The industrial manufacture of Portland cement and Bessemer steel built the foundations of modern infrastructure. Most recently, the advent of silicon integrated circuits and synthetic polymers ushered in the present digital and modern ages. At every stage, the horizons of human life have been defined by materials science. From the demands of daily survival to the grand scope of civilizational ambition, it is material technology that makes all advancement possible.

At the forefront of this long trajectory lies the development of nanomaterials. Despite their modern connotations, nanomaterials are not new. Carbon nanoparticles in soot have been used as pigments for makeup and art since prehistory¹; metallic colloids have coloured glass since early antiquity², most famously in the colour-changing Lycurgus cup³; and medieval Damascus steel, prized for producing high-quality swords, has been shown to contain cementite nanowires and carbon nanotubes inadvertently formed through high-temperature processing⁴. Only with modern microscopy and characterization techniques, however, could such structures be identified and purposefully engineered, giving rise to nanoscience as a distinct subdiscipline of materials science.

The scientific study of nanomaterials began with nanoparticles, notably Faraday's isolation of gold nanoparticles and characterization of their optical behaviour in 1859⁵. The discovery of fullerenes and carbon nanotubes followed in the late 20th century^{6, 7}. The true turning point, however, came with Geim and Novoselov's isolation of graphene by peeling off individual layers of graphite using scotch tape⁸, which revealed the remarkable physics of atomically thin lattices. Subsequent studies extended this paradigm to a wide family of layered crystals⁹, opening the field of 2D materials as the emblematic frontier of nanoscience.

As addressed in Chapter 2, 2D materials exhibit unique physics with potential applications in neuromorphic computing, quantum information systems, and supercapacitors, to name but a few examples. In this thesis, the focus is on thin films composed of many 2D nanosheets, or nanosheet networks, and their use in flexible electronic devices. Emphasis is placed on process challenges involved in scaling these applications to commercialisation.

Chapter 3 discusses the preparation of 2D materials, with a focus on scalable solution-processing methods for exfoliating layered crystals into nanosheets. Liquid-phase exfoliation and electrochemical exfoliation are compared, with the latter identified as the

material preparation method of choice in this work due to its ability to yield high-quality nanosheets in solution, which can be readily formulated into inks.

Following ink formulation, the properties of the constituent nanosheets must be characterized. Chapter 4 introduces the microscopic and spectroscopic methods for doing this, which are used throughout this work. The deposition of nanosheet inks into films is also considered, with spray coating and liquid interface deposition examined in detail. Liquid interface deposition is shown to yield highly aligned, homogeneous networks and was therefore used as the deposition method of choice in this work. Finally, the methods of electrical characterization of these networks are presented, using measurements in both DC and AC modes.

Chapter 5 addresses charge transport in nanosheet networks. It begins by treating these systems as disordered ensembles of current paths and introducing their percolation behaviour, which can be modelled by various approaches. While individual nanosheets can exhibit excellent electrical performance, the conductivity of a network is substantially reduced by the resistance of inter-nanosheet junctions. This junction resistance, arising from charge hopping between adjacent sheets, limits the performance of nanosheet network devices. To quantify it, models of network electrical properties in both DC and AC regimes are introduced, providing a means of extracting junction resistance from measurable nanosheet and network parameters. The reduction of junction resistance, through both material preparation and deposition strategy, forms a central aim of this work.

Transition metal dichalcogenides (TMDs), a class of semiconducting 2D materials, are of particular interest for thin-film transistors (TFTs). Chapter 6 demonstrates the preparation of TMD nanosheet inks by electrochemical exfoliation, their deposition by liquid interface deposition, and the fabrication of TFTs that exhibit competitive performance when compared with other nanomaterial systems such as carbon nanotubes and metal oxides.

Such devices are then transferred onto flexible substrates and shown to maintain performance under repeated strain, highlighting their suitability for flexible electronics.

Refinements to liquid interface deposition are presented in Chapter 7, where a reproducible method for depositing electrochemically exfoliated graphene films with controlled thickness by repeated layer by layer depositions is developed. Such networks were modelled by a novel approach for describing percolation behaviour, and their junction resistances were quantified using the DC charge transport model. The deposition technique is then used to deposit the electrochemically exfoliated graphene onto a flexible substrate, demonstrating a flexible transparent conducting film.

Finally, Chapter 8 investigates the dependence of junction resistance on nanosheet dimensions, and compares networks fabricated by spray coating and liquid interface deposition. Electrochemically exfoliated MoS₂ dispersions were used to prepare films deposited by both methods, which were then characterised by impedance spectroscopy. The AC charge transport model was used to extract junction resistances, which were plotted against nanosheet dimensions to test a model of junction conduction and to evaluate which deposition strategy offers reduced junction resistance.

*"And even your atom, my dear mechanists and physicists –
how much error, how much rudimentary psychology is still
residual in your atom!"*

Friedrich Nietzsche

Chapter 2

2D Materials Properties & Applications

A 2D material is any crystal structure in which one lattice dimension is both sufficiently small compared to the other two and comparable to the de Broglie wavelength of the crystal's charge carriers. In such solids, charge carriers are spatially confined in a 2D plane, giving rise to so-called quantum confinement. Energy levels are no longer continuous, and instead become discrete, which leads to exotic optoelectronic properties that are absent in their bulk crystal counterparts¹⁰.

The emblematic class of 2D materials are the layered crystals. Such crystals are characterized by a strong intralayer covalent bonding, while the layers are weakly held together by van der Waal's (vdW) force. Early investigations were focused on naturally derived layered crystals, represented by graphite. As the layers are chemically and mechanically stable individually, it is possible to delaminate few or single layers of material into free-standing 2D nanosheets. Chemical approaches nowadays can synthesize artificial

2D materials, such as metallic platelets, polymers, immobilised adlayers, etc. In the 2D configuration, materials exhibit vastly different and tuneable physiochemical properties, establishing them as a frontier of materials science.

Emerging as the premier scientific advancements of the 21st century, 2D materials derived from layered crystals present a rich and varied platform for the development of emerging advanced technologies. In the timeframe since graphene's first successful isolation in 2004⁸, many new 2D material systems beyond graphene have been isolated from layered crystals and studied. Examples include hexagonal boron nitride h-BN¹¹, the Transition Metal Dichalcogenides¹², Transition Metal Oxides¹³, and Black Phosphorous¹⁴, and MXenes¹⁵ to name but a few in an ever-growing library.

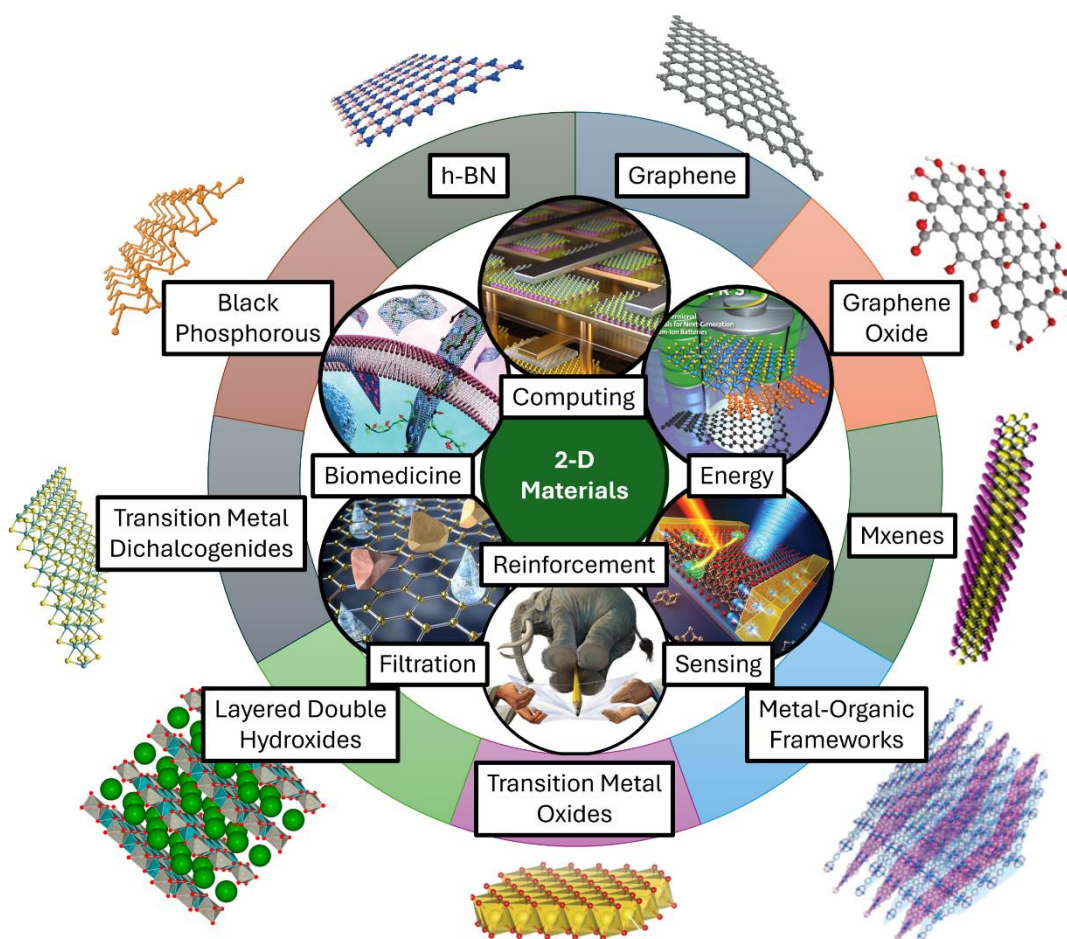


Figure 2.1: 2D Materials & Their Applications. Summary of a range of isolated layered crystal 2D materials and examples of application spaces that exists in the literature. Adapted from refs¹⁶⁻²⁷.

The versatility, performance, and potential cheap abundance of these materials presents an enticing target for research groups of all varieties. Indeed, at least 10 of the top 100 accessed papers published in Nature Scientific Reports in 2024 involve 2D materials²⁸. Among these 10 a great diversity of 2D materials is now represented: graphene²⁹⁻³¹, reduced graphene oxide³², graphene oxide^{33, 34}, layered-double hydroxides^{35, 36}, MXenes^{37, 38} and MoSe₂³⁸, for a wide variety of applications: flexible iontronics²⁹, supercapacitors³¹, biosensing³², hydrophobic textiles³³, battery anode materials^{34, 38}, fuel cells^{35, 36}, and solar cells³⁷ – all of which illustrate how the field has branched out into various material systems and technologies in the past 20 years. A range of isolated 2D materials and their potential applications are summarized in a graphic in Figure 2.1.

2 types of 2D material will be focused on in this work – graphene, and the transition metal dichalcogenides (TMDs), specifically MoS₂. However, it must be noted that techniques for preparation and deposition of these 2D materials are broadly applicable to most 2D material systems if desired to exploit various other physiochemical properties.

2.1 GRAPHENE

The prototypical 2D material, graphene consists of a planar honeycomb lattice of carbon atoms with sp² hybridized bonding to each 3 neighbouring atoms extending out in a near-infinite plane, as shown in Figure 2.2A. The bonding forms 2 bands – a filled deep valence σ band, which is responsible for the mechanical robustness of a graphene monolayer, and a π band, which is half occupied by the remaining valence electron uninvolved in bonding³⁹. It is this unbonded electron in the π band which gives rise to the high carrier concentration observed in graphene (up to 10¹³ cm⁻³)⁴⁰.

Prior to its isolation from graphite in 2004 by Geim and Novoselov⁸, it was hypothesized that a single layer of carbon atoms could not be thermodynamically stable, however it was subsequently shown that isolated graphene monolayers maintain stability via a “ripple”

mechanism⁴¹. Prior work on graphite led to theoretical insight into graphene's properties, including P. R. Wallace's prediction of its electronic structure⁴², which were later validated by experiment.

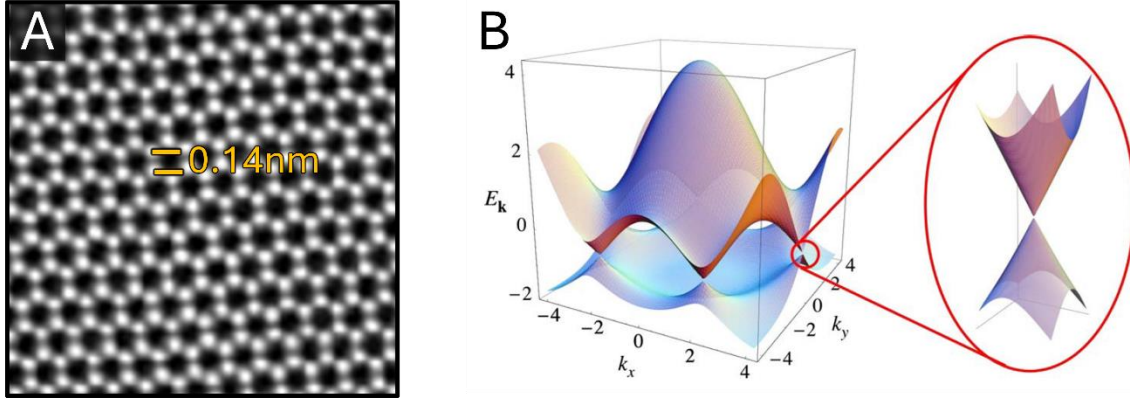


Figure 2.2: Graphene Structure. A – HR-STEM image of graphene, showing the honeycomb lattice structure and the 0.14 nm carbon-carbon bond length. Adapted from ref⁴³. B – Dispersion relation in the hexagonal unit cell of graphene, with inset showing the Dirac point zoomed in where the dispersion relation is approximately linear for small excitations. Adapted from ref³⁹.

Graphene's mechanical properties are among the best of any known material. Its sp^2 bonding and planar geometry give it a Young's modulus of 1.0 ± 0.1 TPa and intrinsic strength of 130 GPa, measured by nanoindentation studies⁴⁴. Its failure strain is also remarkably high, shown to be 25%⁴⁴. Just as the bonding confers these superior mechanical properties, it also makes graphene an ideal thermal conductor, with in-plane thermal conductivities of up to 5000 W mK^{-1} reported⁴⁵. However, these superlative properties degrade substantially by the presence of defects and "crumpling" in the sheet⁴⁶. While pristine monolayer graphene is centrosymmetric and thus not piezoelectric, asymmetry introduced by defects can enable measurable piezoelectric and triboelectric effects⁴⁷.

Electronically, graphene is a zero-bandgap semi-metal. This arises due to the zero-bandgap structure of its electronic bands at the vertices of its hexagonal Brillouin zone, shown in Figure 2.2B. For any small excitation of charge carriers at these points, the dispersion relation is linear. As such, the effective mass of charge carriers becomes zero, and they can

be described by the Dirac Hamiltonian⁴⁸, giving rise to ballistic charge carrier transport. This effect leads to exceptionally high low-temperature charge carrier mobilities, with Du et al. reporting a landmark value of $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ⁴⁹. However, this ideal Dirac cone behaviour is often lost in practical device conditions, primarily due to Coulomb impurities in the graphene crystal itself⁵⁰, charge carrier-phonon interactions, interactions with surface adsorbates⁵¹, and strain/corrugation due to surface roughness of underlying substrates⁵². All of these effects cause charge carrier scattering⁵² and charge puddling⁵³ that reduces the mobility substantially at above-micron distances at room temperature. This is illustrated by the seminal Geim et al. graphene paper, where a graphene sheet's mobility was measured on an oxidized Si substrate, reported as $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ⁹. Only with all-around encapsulation in atomically smooth h-BN and cooling to helium temperatures is ballistic transport preserved and further enhanced at macroscopic distances, enabling mobilities exceeding $10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^{54, 55}.

The previously mentioned, the deep valence σ band makes graphene sheets mechanically robust against dislocation, making basal plane defects rare. As a result, the mean free path for charge carriers can be on the order of several microns⁴¹. Additionally, the large p-orbital overlap that contributes to the π band allows for the unbound valence electron to form extended states over multiple carbon atom sites. These aspects of its charge transport give rise to the large in-plane conductivity observed in graphene (up to $200,000 \text{ S/m}$)⁵⁶⁻⁵⁸. By contrast, the out-of-plane conductivity is at least 3 orders of magnitude lower⁵⁶. This is due to charge transport being mediated by tunnelling across the vdW gaps rather than through a highly conjugated atomic plane. Such a property is common to all vdW layered crystals.

2.1.1 GRAPHENE APPLICATIONS

Graphene's unique combination of mechanical, thermal, and electronic properties has led to a wide array of proposed applications, summarized in Figure 2.3. The linear dispersion

at the Dirac points enables exotic phenomena such as pseudo-spin chirality of charge carriers between the K and K' valleys³⁹, Berry Phases, and the anomalous quantum hall effect (AQHE)⁵⁹, which enables a range of valleytronic and spintronic applications. In particular, AQHE in graphene is now being considered for use in high precision resistance metrology standards, due to exhibiting high quality Landau peaks at relatively high temperatures and modest magnetic fields⁶⁰. Twisted bilayer graphene also allows access to even more exotic physics, creating de Moire pattern superlattices that can exhibit superconductivity⁶¹ and Mott insulator behaviour⁶² at the 'magic angle' of $\sim 1.1^\circ$.

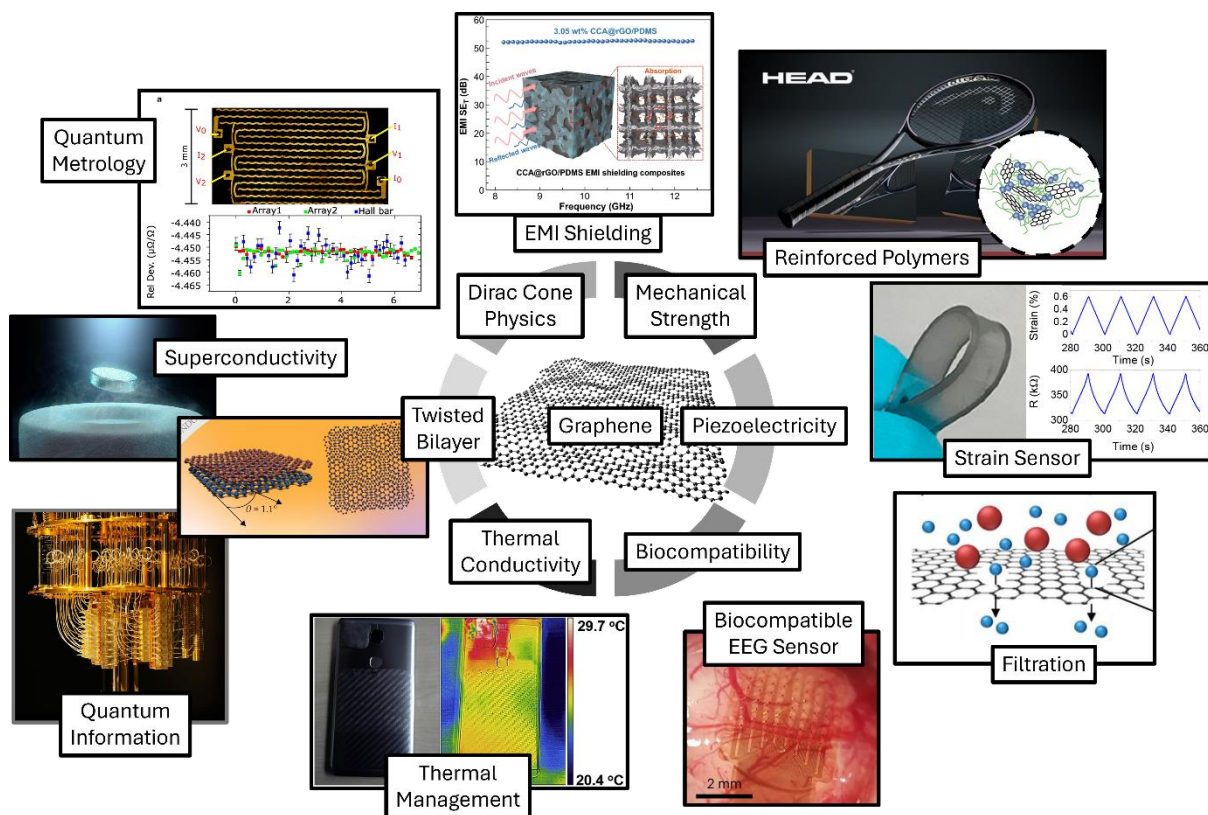


Figure 2.3: Graphene Properties & Applications. Summary of the main properties of graphene, and some examples of their emergent applications present in the literature. Adapted from refs^{60, 63-71}.

However, graphene lacks an intrinsic bandgap, severely limiting its application in semiconducting devices. Proximity coupling to heavy transition-metal dichalcogenides, such as WSe₂, can introduce spin-orbit coupling and open a gap, but experiments show this effect remains on the order of only a few meV (typically $\sim 5\text{--}13\text{ meV}$)⁷². Other strategies such

as chemical modification^{73, 74} and doping⁷⁵ can induce larger gaps, yet they often degrade graphene's exceptional carrier mobility and disrupt its pristine lattice. Therefore, 2D materials that possess an intrinsic gap in the visible range (~1–2 eV) would be preferred for switching applications.

In practice, most commercial applications of graphene have exploited other less exotic properties in multi-layer, many-sheet assemblies such as pastes, composites, and membranes. These find use in thermal management⁷⁶, energy storage⁷⁷, mechanically reinforced polymer nanocomposites⁴⁶, biocompatible flexible conductors/sensors^{64, 67, 78}, electromagnetic interference (EMI) shielding⁶⁸, and filtration^{79, 80} to name but a few examples. These applications are not as stringent in device environmental conditions as they don't rely on exotic physics of graphene's band structure, instead leveraging its conductivity, mechanical strength, and high specific surface area. The realization of such technologies depends critically on scalable production of high-quality graphene, which is discussed in Chapter 3.

2.2 TRANSITION METAL DICHALCOGENIDES

A primary limitation of graphene in semiconducting applications is its semi-metallicity. In contrast, the transition metal dichalcogenides (TMDs), with the general formula MX_2 (M = transition metals of group IV–X elements, X = chalcogens: S, Se, Te), offer a broad range of intrinsic electronic properties, from large-bandgap semiconducting⁸¹ to metallic⁸². More than 40 such layered compounds exist, with possible transition metal-chalcogen pairings illustrated by the periodic table in Figure 2.4A. Historically, the properties of few-layer TMDs have been studied since the 1960s^{83, 84} with the most famous TMD, MoS_2 , having a long-established history as a solid lubricant in aerospace and mechanical coatings⁸⁵. However it was the isolation of graphene that revived research interest in them to act as complementary semiconducting 2D material systems¹⁰.

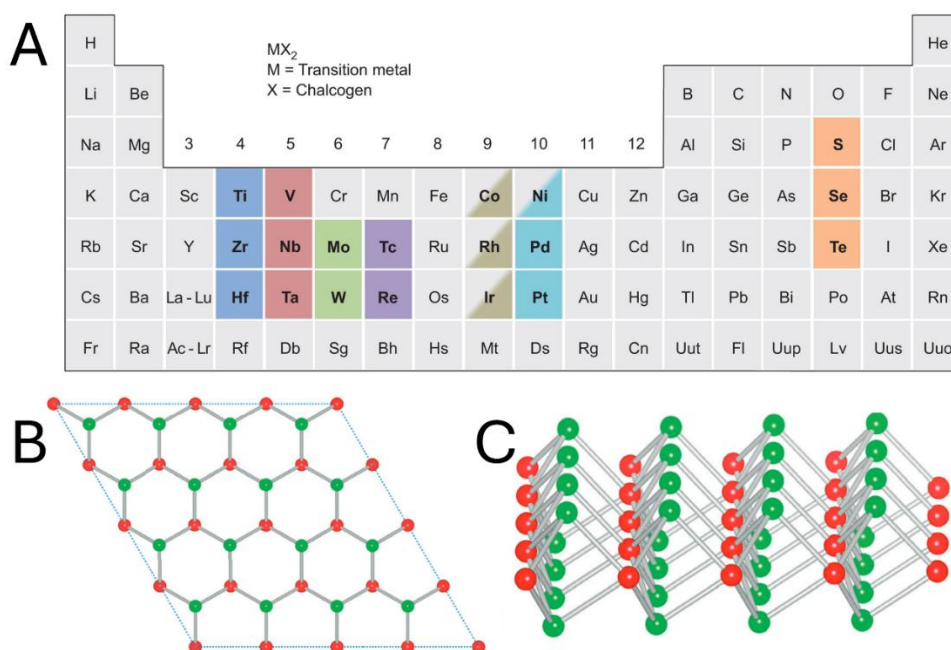


Figure 2.4: Transition Metal Dichalcogenides Composition & Structure. A - periodic table with the possible combinations of transition metal and chalcogen highlighted. Adapted from ref⁸⁶. B - top view and C - side view of the typical TMD monolayer structure, red balls representing M (group IV-X elements) and green balls representing X (chalcogens S, Se, Te). Adapted from ref⁸⁷

TMD monolayers adopt a sandwich-like X-M-X configuration, with a central hexagonal plane of transition metal atoms coordinated by two offset chalcogen planes, as is shown in Figure 2.4B and C. Hence, unlike graphene's 3.5 Å monolayer thickness of one layer of carbon atoms, TMD monolayers are typically thicker at 6-7 Å^{84, 86}. As with graphene, these monolayers stack via vdW attraction to form their complementary bulk layered crystal, and are also stabilized as monolayers via a rippling mechanism⁸⁸.

This X-M-X structure can present in a variety of stacking alignments between the chalcogen and transition metal atoms within the monolayers, leading to TMDs presenting a variety of polymorphs. This polymorphism then presents a variety of stacking arrangements of the monolayers in a layered crystal, giving rise to different polytypes. In TMDs, the most common polytypes are 1T (trigonal), 2H (octahedral), and 3R (rhombohedral)⁸⁶. In the TMD polymorph nomenclature, the number refers to the number of monolayers per unit cell, and

the letter indicates the coordination geometry. For a monolayer TMD, only 2 polymorphs are possible, 1T and 2H, both illustrated in Figure 2.5A.

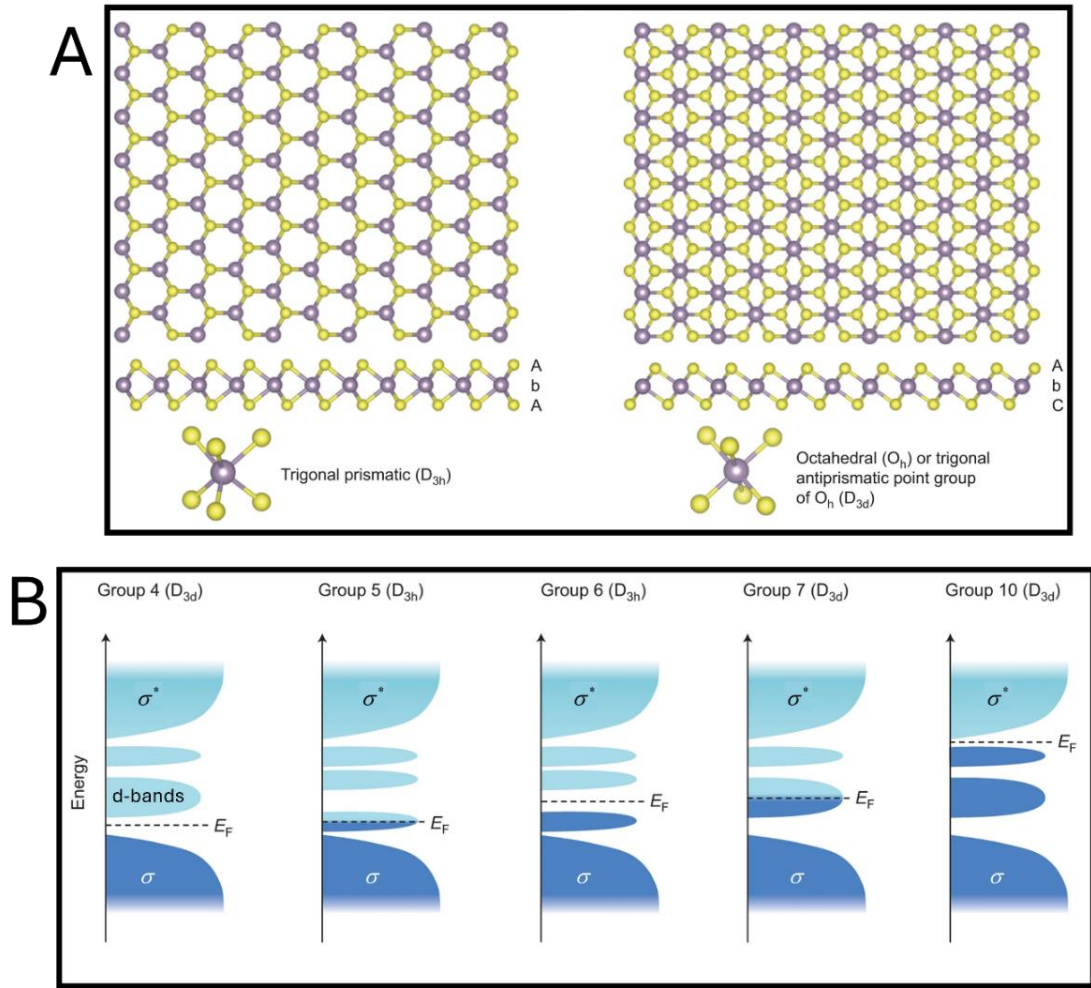


Figure 2.5: Transition Metal Dichalcogenides Polymorphism & Density of States. A – the two different polymorphs of TMD monolayers. B – Schematics of density of states in TMDs. Moving along the periodic table, the filling of the d-bands changes, which alters electronic behaviour. Both figures adapted from ref⁸⁶.

The electronic properties of TMDs are largely determined by the transition metal d-orbitals. Deep covalent bonding between s and p states in the transition metals and chalcogens results in bonding σ bands and anti-bonding σ^* bands, which make up the valence and conduction bands respectively. Like graphene, this deep covalent σ bonding contributes to the mechanical stability of the monolayer⁸⁹. Between these σ bands lie the d-bands, and depending on their filling and relative energies, the material may be semiconducting or

metallic. This is illustrated in Figure 2.5B, which shows how moving from group IV to group X corresponds to a filling of these d-states with increasing valency, yielding different relative position of the Fermi energy with respect to the valence and conduction bands. When d-bands are partially filled, the TMD exhibits metallic conductivity. The 2H phase of Group VI TMDs (e.g. MoS₂ and WSe₂) have a fully occupied d_z band, hence the Fermi energy locates between the d-bands as in Figure 2.5B, resulting in semiconducting behaviour⁹⁰.

The polymorphic structure can also influence the electronic character. As the ordering of the stacking of atoms in the monolayer affects the hybridization in the bonding, TMD polymorphs have varying band structures. For example, 2H-MoS₂ is a semiconductor with a band gap between the filled d_{z²} and empty d_{x²-y²},xy bands, while the 1T phase is metallic with Fermi level lying in the middle of degenerate d_{xy,yz,xz} single band^{91, 92}.

For electronic devices such as nanosheet network transistors, preservation of the semiconducting 2H phase is essential to enable modulation of channel conductivity by a gate voltage. The presence of metallic 1T nanosheets is therefore undesirable, as they create conduction pathways lacking gate voltage dependence⁹³, which suppresses the achievable on/off ratio and degrades transistor performance. Hence, minimising the presence of 1T phase nanosheets is a central concern of this work, as will be addressed in Chapters 3 and 6.

The electronic structure of TMDs also changes going down the transition metal groups. For example, W-based TMD systems have higher energy band structure than Mo, due to the higher energy of 5d orbitals compared to 4d⁹⁴. Going down the chalcogen group also alters the electronic structure. As chalcogen atomic number increases, the energy of the conduction band minimum (CBM) and valence band maximum (VBM) progressively shifts upwards⁹⁵, which is caused by increased covalency of the bonding⁹⁶.

A defining feature of Group VI TMDs is their layer-dependent band structure, which gives rise to a thickness-dependent bandgap, illustrated in Figure 2.6. In bulk MX_2 , the VBM is located at or near the Γ point, and the CBM is located midway between the K and Γ points. These portions of the band structure are dominated by the out-of-plane chalcogen p_z states. As the bulk crystal is thinned down to few layers and monolayers, these p_z states are relaxed, causing the VBM to decrease in energy while the CBM increases⁹⁷. This results in a widening of the bandgap, typically a $\sim 50\%$ increase between bulk and monolayer.

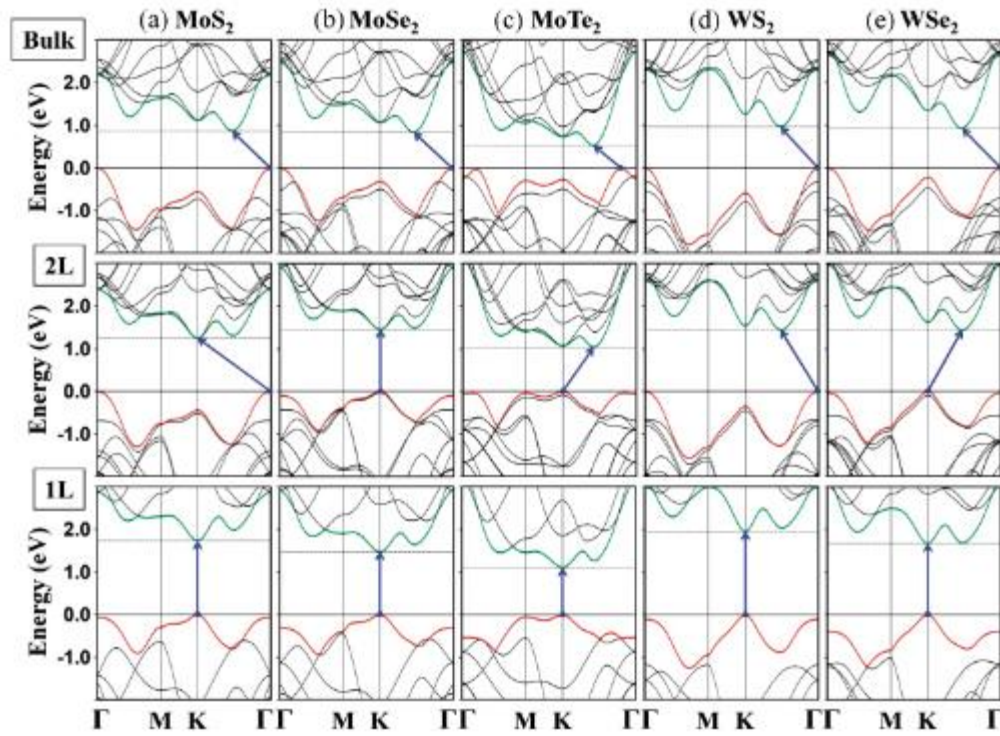


Figure 2.6: Transition Metal Dichalcogenides Band Structure. Band structures of different Group VI TMDs as the bulk crystal is thinned to bilayer and then monolayer. In all cases, thinning the crystal from bulk to monolayer is accompanied by a widening of the bandgap, with a transition from indirect gap to direct gap located at the K point. Adapted from ref⁹⁸.

As shown in Figure 2.6, in the monolayer limit, the new CBM and VBM are instead both located at the K-point, producing a direct bandgap. In this case, electron and hole recombination can occur without mediation by phonons, resulting in efficient light emission. Moreover, thinning TMDs down to monolayers increases their excitonic binding

energies from only tens of millielectronvolts to nearly half of an electronvolt owing to the reduced dielectric screening, implying the presence of tightly bound electron-hole pairs that further enhance light emission. These phenomena were experimentally supported by Mak et al.⁹⁹, who observed a 10,000-fold enhancement of photoluminescence in monolayer MoS₂ compared to bulk. The bandgaps of Group VI TMDs are typically in the visible range (1–2 eV), making them attractive for optoelectronic devices.

TMDs exhibit a good ambient stability due to the absence of dangling bonds on their basal planes⁸⁶. However, the weaker σ bonding within TMD layers compared to graphene leads to a higher defect density, commonly in the form of chalcogen vacancies. These defects introduce donor states that give rise to intrinsic n-type behaviour and, combined with larger effective masses, limit carrier mobility. While state-of-the-art MoS₂ FETs achieve mobilities up to 700 cm² V⁻¹ s⁻¹¹⁰⁰, this remains well below that of graphene. In practical TMD devices, such as FETs, defect states can also contribute to hysteresis in switching¹⁰¹.

Mechanically, TMD monolayers are robust but not as strong as graphene. Nanoindentation studies of monolayer MoS₂ report a Young's modulus of 270 ± 100 GPa, an intrinsic strength of 23 GPa, and a failure strain of $\sim 10\%$ ⁸⁸, comparable to structural steel. Other group VI TMDs have similar mechanical parameters¹⁰², supporting their suitability for flexible and mechanically resilient electronic devices.

TMDs also exhibit rich quantum phenomena, such as superconductivity, Mott insulating states¹⁰³, and spin inequivalence between the K and K' valleys arising from the lack of inversion symmetry in TMD crystals¹⁰⁴. Twisted TMD bilayers form moiré superlattices that support AQHE and topological insulator phases¹⁰⁵.

2.2.1 TMD APPLICATIONS

The spintronic, valleytronic, and hysteresis phenomena of TMDs make them promising candidates for realizing post-von Neumann, neuromorphic computing architectures^{106, 107}.

This has entered the spotlight with the recent rise of AI, as the integration of memory and logic elements into single devices may enable massive reductions in the exponentially growing compute energy demands¹⁰⁸.

The sub-nm thickness of their stable monolayers, free of dangling bonds and Fermi level pinning also promise to provide a future extension of “More than Moore” transistor fabrication and overcome the ~ 5 nm limit of silicon gate lengths¹⁰⁹. TSMC recently demonstrated a high-performance 40 nm gate length MoS₂ Gate All-Around (GAA) n-FET in 2022¹¹⁰. However, the absence of native p-type TMDs and challenges in controlled doping remain significant obstacles to CMOS integration¹⁵.

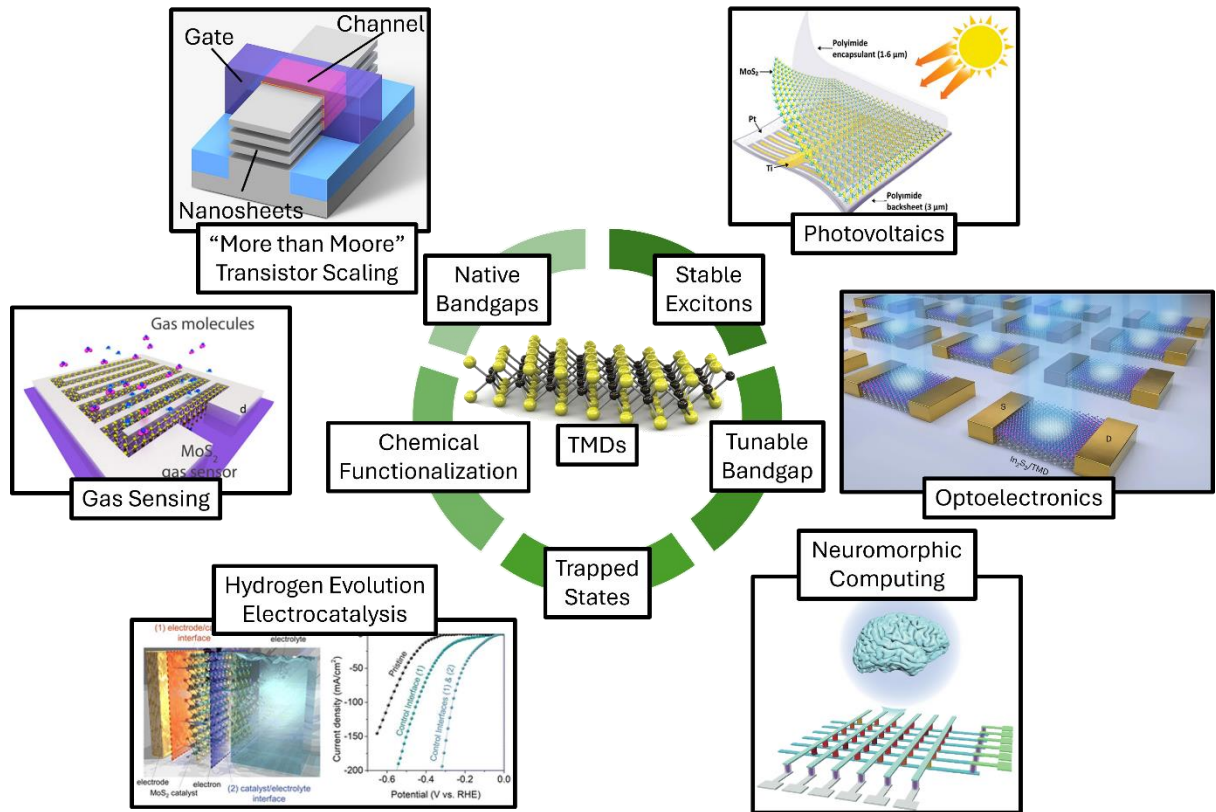


Figure 2.7: Transition Metal Dichalcogenides Applications. Summary of useful properties of TMDs and selected applications that exist in the literature. Adapted from refs¹¹¹⁻¹¹⁷.

As with graphene, the exotic phenomena in TMDs require stringent fabrication and environmental conditions, and so more mundane phenomena are typically exploited for device applications, relying on composite or network-based assemblies. Unlike graphene,

TMDs are more easily chemically functionalized, enabling applications in switchable filtration¹¹⁸, gas-sensing¹¹⁵, and energy storage applications¹¹⁹. Their electrocatalytic properties are particularly valuable for hydrogen evolution reactions (HERs) for green energy applications¹²⁰. The native bandgap in TMDs in the visible range opens them up to a wealth of photodetector and photovoltaic applications^{121, 122}. Some of these applications and technologically useful properties are summarized in Figure 2.7.

2.3 FLEXIBLE ELECTRONICS

As has been highlighted, monolayers of various 2D materials possess high Young's moduli and undergo material failure at relatively large strains (typically >10%), meaning they are simultaneously strong and elastic. Their atomic thickness also confers conformality, allowing adhesion to rough or curved substrates with minimal strain energy. This enables 2D nanosheets to bend, fold, and wrinkle without fracture, while still preserving their intrinsic properties. In addition, nanosheets have been shown to be non-toxic and biocompatible¹²³. This combination of mechanical flexibility, mechanical robustness, biocompatibility, and exceptional electrical performance outlined in the previous sections makes them uniquely suited for the next generation of flexible and wearable electronics.

Unlike conventional flexible platforms such as conductive polymers or organic semiconductors, 2D materials offer superior carrier mobility, stability, and multifunctionality. For instance, while organic field-effect transistors (OFETs) typically can show mobilities in the range of 0.1–20 cm² V⁻¹s⁻¹¹²⁴, TMDs can exceed 100 cm² V⁻¹s⁻¹ in optimized devices¹⁰⁰. Furthermore, many 2D materials exhibit superior chemical and thermal stability, and they can serve multifunctional roles such as transparent conductors¹²⁵, encapsulants¹²⁶, or dielectric barriers¹²⁷.

In wearable technologies, the unique properties of 2D materials enable a wide range of promising applications. Graphene-based strain sensors offer high gauge factors and

excellent durability under repeated mechanical deformation⁶⁴, making them ideal for motion tracking and physiological signal monitoring. Flexible, biocompatible graphene-collagen electrode arrays have also been developed for neural sensing and stimulation¹²⁸, enabling conformal, high-resolution neural interfaces. Thin films of TMDs have been integrated into flexible FETs, demonstrating their potential for computation in wearable formats^{123, 129}. TMD-based photodetectors, with their high sensitivity and tuneable spectral response, are being explored for ambient light sensing and biomedical imaging applications¹³⁰. Additionally, monolayers of MoS₂ and WS₂ have shown promise in piezoelectric and triboelectric energy harvesting devices, paving the way for self-powered wearable systems¹³¹.

These developments open the door to the next generation of biometric wearables, soft robotics, and cyber-physical systems. Such applications are where the distinctive optoelectronic and piezoresistive properties of 2D materials can be leveraged for real-time sensing, actuation, and feedback. Realizing this vision, however, hinges on overcoming key challenges in the scalable synthesis of high-quality 2D materials and the optimization of device performance for real-world deployment. This work aims to contribute to this effort as part of the wider technological endeavour outlined above.

Chapter 3

Nanosheet Synthesis

Broadly, two general approaches are used in the synthesis of nanomaterials: bottom-up and top-down methods. In the context of 2D materials, bottom-up synthesis refers to the formation of monolayers through chemical reactions of precursor compounds, the prototypical example being Chemical Vapor Deposition (CVD). In contrast, top-down approaches involve overcoming the vdW force in a layered crystal to obtain few or single layered nanosheets. The most well-known example of this is micromechanical exfoliation, first demonstrated by Novoselov in 2004⁸.

CVD (Figure 3.1A), involves the reaction of molecular precursors on a substrate in a high-temperature tube furnace. The technique has matured to yield large-area, high-quality monolayers of various 2D materials, including graphene¹³² and TMDs¹³³. While CVD can produce large area (>10 cm²) low defect density monolayer nanosheets, it faces several challenges that hinder its commercial scalability. Transferring films from the growth substrate often introduces defects and contamination and requires delicate handling¹⁵. Additionally, scaling up the area of synthesized film requires a proportionately larger

furnace volume, giving a non-linear scaling of energy and chemical precursor input costs. Recent process engineering improvements, such as multi-substrate stacking and optimization of gas and thermal flow profiles, have alleviated these issues to some extent¹³⁴. Nevertheless, similar scalability challenges are observed in other bottom-up techniques, such as Atomic Layer Deposition¹³⁵ and Pulsed Laser Deposition¹³⁶, rendering bottom-up synthesis less viable for low-cost, large-scale applications outlined in the previous chapter.

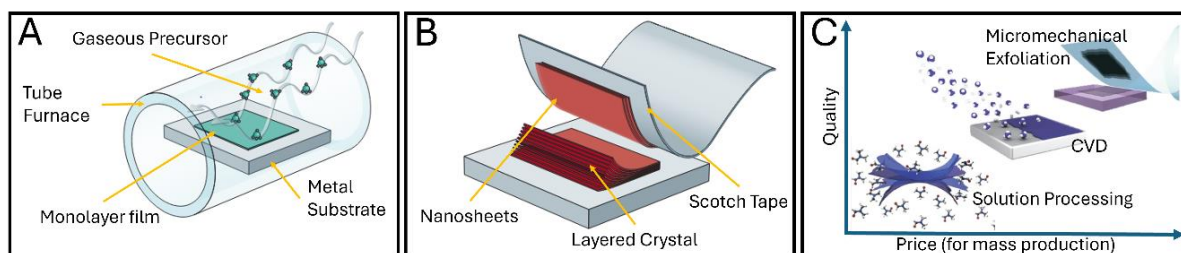


Figure 3.1: Chemical Vapour Deposition & Micromechanical Exfoliation. Schematics of A – Chemical Vapor Deposition and B – Micromechanical Exfoliation synthesis techniques. Adapted from ref¹³⁷. C – Graph comparing the material quality versus manufacturing cost for different synthesis techniques. Adapted from ref²¹.

Micromechanical exfoliation (Figure 3.1B) involves delaminating monolayers from bulk crystals using adhesive tape. This technique remains the standard for producing high quality monolayers with low defect densities used in fundamental studies of exotic 2D material physics²¹. Its simplicity and low-cost setup make it ideal for prototyping; however, the method's production rate is extremely low, rendering it even less suitable for industrial-scale manufacturing.

Given these limitations, there is a clear need for scalable, cost-effective methods to produce relatively high-quality nanosheets. One such approach is solution processing, which is discussed in detail in the following sections.

3.1 SOLUTION PROCESSING

Solution processing provides a scalable alternative to bottom-up and micromechanical methods. It encompasses a range of techniques in which layered crystals are delaminated in a liquid medium, enabling mass production of nanosheets. These approaches can be broadly classified into liquid-assisted and intercalation-assisted exfoliation. In both cases, the interlayer vdW interactions (e.g. ~ 5.9 kJ/mol for graphite¹³⁸) must be overcome.

Liquid-Phase Exfoliation (LPE) is the most widely used liquid-assisted technique, in which mechanical forces such as ultrasonication or shear overcome interlayer vdW interactions to produce scalable, low-defect nanosheet dispersions. In contrast, intercalation-assisted methods, such as chemical exfoliation, rely on the insertion of reactive species and redox processes to delaminate layered crystals. While the latter approaches can yield larger lateral-sized nanosheets ($L > 1 \mu\text{m}^{139, 140}$), they often introduce chemical modifications and structural defects. Such limitations have motivated the development of more controlled intercalation-based methods, such as electrochemical exfoliation, which is discussed in the following sections.

Following exfoliation, the resulting nanosheets are subsequently stabilised in solution through appropriate solvent selection or the use of surfactants and polymer additives. In the former case, stabilisation arises from favourable enthalpic interactions between the solvent and nanosheet surface (e.g. surface energy matching in solvents such as NMP), while in the latter, surfactants and polymers provide electrostatic or steric (entropic) barriers to reaggregation (e.g. ionic surfactant coating/polymer wrapping of the nanosheets).

3.1.1 LIQUID PHASE EXFOLIATION

Liquid-Phase Exfoliation (LPE) produces nanosheets through intense mechanical agitation of layered crystals in a stabilizing solvent. First developed just four years after graphene's isolation¹⁴¹, LPE has become the most widely adopted approach for producing 2D materials at scale due to its immense cost advantages and applicability to a broad range of 2D material systems. In this process, ultrasonic or shear forces overcome the vdW interactions within layered crystals in solution, as depicted in Figure 3.2A and B respectively. The resulting sheets are typically free of covalent modifications or undesirable phase transitions, making them ideal for electronic applications¹⁴².

Post-exfoliation, the dispersion contains a broad distribution in lateral sizes and thickness of nanosheets. As they are in solution, they may be sorted in size by centrifugation, as will be discussed in a later section. Critically, mono- and few-layer nanosheets are present in such dispersions, which are required for exploiting 2D material properties. Exfoliated dispersions also offer immense process engineering advantages, as they may be straightforwardly formulated into inks¹⁴³, pastes¹⁴⁴, or composites⁶³.

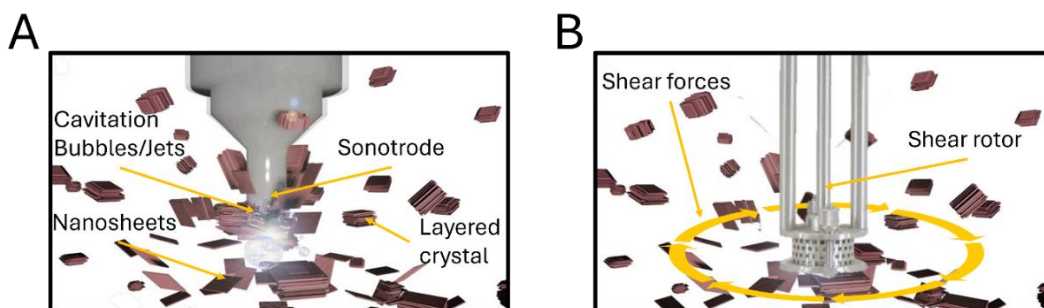


Figure 3.2: Liquid Phase Exfoliation. Schematics of A – Ultrasonication and B – Shear exfoliation of layered crystals to produce 2D material nanosheets. Adapted from ref¹²¹.

ULTRASONICATION

Ultrasonication is widely used across both academic and industrial settings. In this technique, a sonotrode introduces high-intensity acoustic waves into the liquid medium,

with energy transferred through mechanisms such as cavitation, acoustic streaming, and radiation pressure. As shown in Figure 3.2A, such waves provide the energy necessary to overcome the interlayer vdW forces in layered crystals to delaminate nanosheets. This occurs via the implosion of cavitation bubbles, which generates localized high-pressure jets that shear layers apart¹⁴⁵.

A milder variant of this is bath sonication, where the reduced intensity limits the amount of tearing that occurs along the basal planes (scission), preserving larger nanosheet lateral sizes.

Despite sonication-based LPE techniques being mechanically aggressive, low defect nanosheets have been repeatedly demonstrated for a multitude of 2D material systems^{142, 146}.

SHEAR

A key limitation of ultrasonication is its poor scalability, as acoustic energy decays rapidly with distance from the sonotrode¹⁴⁷, strongly limiting volumes that can be processed. To address this, LPE has been adapted to shear mixing¹⁴⁸, which employs rotor–stator systems to generate laminar flow with strong velocity gradients. These shear forces peel apart crystal layers into nanosheets (Figure 3.2B). Shear mixing is inherently more scalable and supports large-batch production. Repeated cycling can further increase exfoliation efficiency and yield, providing the highest yields and production rates possible in the entire field of 2D materials¹⁴⁹. However, the monolayer yield produced by this method is quite low, limiting utility of this technique for producing nanosheet dispersions with exotic optoelectronic properties.

3.1.2 CHEMICAL EXFOLIATION

Chemical exfoliation is achieved by exposing a layered crystal to reactive species that weaken or disrupt interlayer vdW interactions, as illustrated in Figure 3.3.

This method was first demonstrated by Brodie et al. in 1859, who oxidized graphite to produce graphene oxide (GO) using nitric acid and potassium chlorate¹⁵⁰. The process was later refined by Hummers, replacing the original aggressive oxidizing agents with a milder mixture of sulfuric acid, potassium permanganate, and sodium nitrate¹⁵¹, which remains the standard protocol for graphite oxidation today.

In this method, oxidation introduces hydroxyl, epoxide, and carboxyl functional groups onto the graphene basal planes. Simultaneously, gas evolution (e.g., NO₂, O₂, CO₂) from redox reactions exerts internal pressure between the layers. The combined effects of hydrophilic chemical functionalization in an aqueous environment and gas generation leads to swelling of the layered crystal, and gentle agitation can break apart the layers to yield a GO dispersion. These dispersions may then be chemically reduced to reduced graphene oxide (rGO), as demonstrated by Boehm et al. in 1961¹⁵². This synthesis remains attractive to chemists and industry for applications that benefit from GO and rGO's superior mechanical properties¹⁵³.

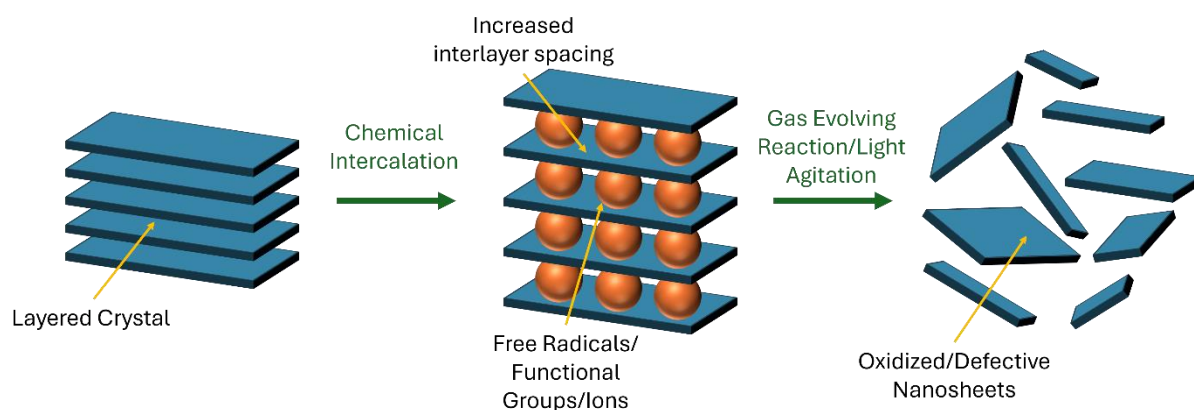


Figure 3.3: Chemical Exfoliation. Schematic illustration of chemical (intercalative) exfoliation routes.

However, the oxidative nature of this process introduces significant crystallographic defects, which degrade electronic properties. For example, rGO sheets typically exhibit sheet resistances ranging from $\sim 1 \text{ k}\Omega$ to $\sim 70 \text{ k}\Omega \text{ }\square^{-1}$ ¹⁵⁴, which are unsuitable for electronic

applications. Similar intercalation processes have been applied to TMDs, often involving alkyl-lithium compounds followed by spontaneous exfoliation in water^{139, 155}. Like GO synthesis, these methods also yield oxidized, defective nanosheets.

While this class of techniques was not used in the present work, it provides a foundation for understanding more controlled intercalation-assisted approaches. Electrochemical exfoliation represents such an approach and can be regarded as a subset of chemical exfoliation, as discussed in the following section.

3.1.3 ELECTROCHEMICAL EXFOLIATION

LPE methods are limited by long processing times and variability in nanosheet size and thickness^{156, 157}, which can complicate reproducibility and hinder applications where large, thin flakes are needed. Chemical exfoliation-based methods, by contrast, produce large-area, few-layer sheets^{139, 140}. However, these often require aggressive chemical reagents, lengthy procedures, and carefully controlled environments, all of which increase cost and reduce scalability^{138, 158}.

In addition, such harsh chemical exfoliation conditions frequently yield undesired nanosheet products, such as graphene oxide in the case of graphite exfoliation¹⁴⁰, and metallic 1T phases in the case of exfoliation of MoS₂¹³⁹. The 1T phase of MoS₂ is metastable, arising from charge injection during intercalation which drives a structural transition from the trigonal prismatic (2H) to octahedral coordination (1T). While this phase is stabilised in the presence of excess charge, it is thermodynamically unfavourable and gradually relaxes back to the semiconducting 2H phase, typically upon high temperature thermal annealing (>300 °C^{139, 159}).

While post-processing of chemically exfoliated nanosheets using strong reducing agents (e.g., hydrazine, nitric acid¹⁶⁰⁻¹⁶²) or high-temperature annealing (>500 °C^{139, 163}) can partially recover the desired material properties, these steps introduce further drawbacks. For

example, high temperatures are incompatible with polymer substrates^{164, 165} and aggressive chemicals raise safety, cost, and environmental concerns¹⁶⁶⁻¹⁶⁸. As a result, chemically exfoliated materials are generally unsuitable for mass-manufacture of versatile and inexpensive electronic devices.

Electrochemical exfoliation (EE) provides a less aggressive alternative by using an applied electric field to drive intercalation of ions and small molecules, rather than relying on reactive chemistry. The intercalated material can then be subsequently exfoliated in a stabilizing solvent environment with mild sonication to yield large lateral size, thin sheets.

Historically, initial attempts to intercalate graphite by electromotive force were characterized by employing aggressive chemical agents which still oxidized the graphite, such as the formic-sulfuric acid mixtures used by Bourelle et al. in 1998¹⁶⁹. This led to successful production of 40 nm graphene nanoparticles by Weng et al. through ammonia intercalation¹⁷⁰, although these products were still heavily oxidized. A significant improvement was introduced in 2009 by Wang et al., who used poly(sodium 4-styrenesulfonate) (PSS) as an electrolyte, yielding 1–2 μm graphene sheets with reduced defect content¹⁷¹, establishing the advantages of EE.

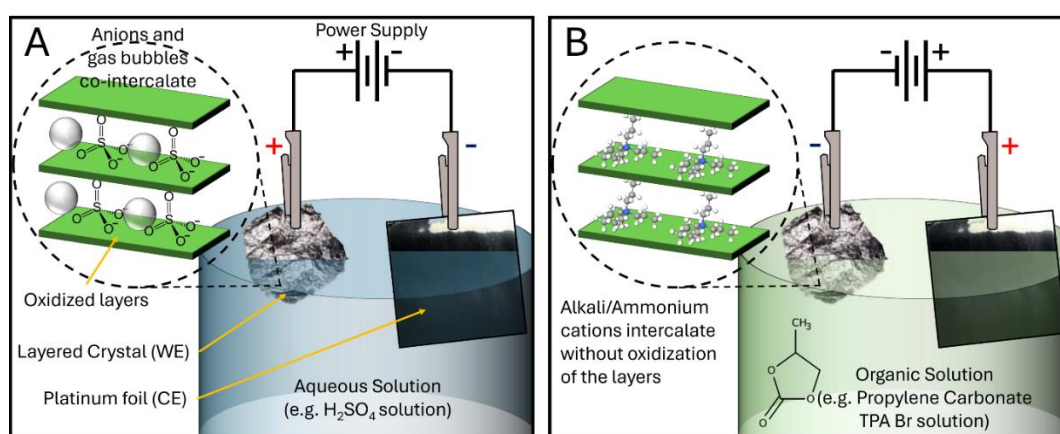


Figure 3.4: Electrochemical Exfoliation. Schematics of electrochemical exfoliation via A – anionic and B – cationic intercalation pathways. The resulting expanded crystal is subsequently exfoliated in a stabilizing environment as with LPE.

In a typical EE setup, the layered material acts as a working electrode (WE), and a counter electrode (CE) is usually made from platinum or glassy carbon. These are immersed in a solvent-electrolyte solution and connected to a power source (Figure 3.4). Application of a suitable potential drives either anion or cation intercalation in the interlayer spacings of the layered crystal, depending on the polarity of the working electrode. Based on this, EE is divided into anodic (Figure 3.4A) and cathodic (Figure 3.4B) exfoliation.

ANODIC EXFOLIATION

Anodic exfoliation uses aqueous electrolytes and a positive working electrode potential to drive the intercalation of anions and/or electrolysis-generated species into the layered crystal. One of the most effective intercalants is the sulfate ion (SO_4^{2-}), due to its ionic diameter (~ 0.46 nm) being similar to the graphite interlayer spacing (~ 0.33 nm)¹⁷².

During anodic EE, hydroxyl ($\cdot\text{OH}$) and oxide ($\cdot\text{O}$) radicals are generated by water splitting and co-intercalate with sulfate ions into the bulk crystal. These react with the formation of gaseous products (SO_2 , O_2 , H_2), the bubbles of which help delaminate the crystal through mechanical expansion^{173, 174}, similar to chemical exfoliation. This mechanism has also been demonstrated for TMDs such as MoS_2 ¹⁷⁵, as the interlayer spacing of MoS_2 (0.6 nm) is also similar to the SO_4^{2-} ionic size.

Anodic exfoliation has can produce high yields of thin (1–3 layer) graphene nanosheets with large lateral sizes (>5 μm)^{160, 173}. However, the unavoidable formation of radicals leads to significant oxidation, which is problematic for electronics. Nonetheless, this method remains useful for producing oxidized 2D materials (e.g., graphene oxide) and has been extended to other 2D materials such as black phosphorus¹⁷⁶ and MXenes¹⁷⁷. The technique is scalable, capable of producing gram-scale quantities in minutes to hours, but the oxidation inherent to aqueous anodic processes remains a key limitation for certain applications requiring pristine nanosheets.

CATHODIC EXFOLIATION

Cathodic exfoliation offers a non-oxidative alternative that better preserves the intrinsic properties of the material. It is typically carried out in non-aqueous solvents, such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethyl carbonate (DMC), or propylene carbonate (PC), with alkali metal or quaternary ammonium salts as electrolytes^{178, 179}. A negative bias is applied to the layered material working electrode, driving the intercalation of cations. The use of organic solvents has the benefit of limiting the oxidation of the nanosheets.

For graphene, cathodic EE has yielded thin (1–5 layer) sheets with low oxidation levels^{180, 181}. However, compared to anodic exfoliation, the process is slow and generally produces nanosheets of smaller lateral size, and as such cathodic exfoliation is generally regarded as unsuitable for graphene synthesis. The following sections will therefore focus on the cathodic exfoliation of TMDs, in particular MoS₂.

LITHIUM-BASED INTERCALATION

The first cathodic exfoliation of MoS₂ was demonstrated by Zeng et al.¹⁸² using Li metal and LiPF₆ in a mixed EC/DMC electrolyte. The inserted Li⁺ ions expanded the interlayer distance, and subsequent sonication in water completed the exfoliation. However, Li⁺ intercalation introduces excess electrons, destabilizing the semiconducting 2H phase and inducing a transition to the metallic 1T phase⁹¹. While this is useful for catalysis, it is a drawback for semiconductor applications.

To address this, Yang et al.¹⁸³ proposed a controlled lithiation method using a coin cell and polymer separator configuration with controlled discharges to limit material decomposition, enabling high yields of monolayer TMDs without excessive phase transition. However, this approach is complex, slow (multi-day cycles), and requires hazardous materials (e.g., Li metal), limiting its scalability.

Scalable alternatives include work by Ejigu et al., who used LiClO_4 in DMC/EC to intercalate MoS_2 ¹⁸⁴. This process predominantly produced 1T-phase flakes, approximately 4.5 nm thick and 300–500 nm in lateral size. Ejigu proposed that the Li^+ stoichiometry in the intercalated MoS_2 structure (Li_xMoS_2) determines the most favourable phase of MoS_2 , drawing on prior theoretical insights from Julien et al. on Li^+ -intercalated TMD systems¹⁸⁵. According to this model, the 2H phase remains stable when $x \leq 0.1$, while higher Li^+ content ($x > 0.1$) favours the 1T phase, with Li Y. et al. modelling full conversion to 1T at $x=0.29$ in MoS_2 ¹⁸⁶. Supporting this, Garah et al. demonstrated that 60% of the 2H phase can be retained by using LiCl in dimethyl sulfoxide (DMSO) for EE of MoS_2 ¹⁸⁷. This is attributed to the formation of a sterically hindered solvated complex, $\text{Li}^+(\text{DMSO})_x$, which limits the stoichiometric content of Li^+ in the intercalated crystal.

While cathodic Li^+ -ion intercalation offers greater control compared to chemical or anodic methods, its broader applicability remains limited by several factors: toxicity, high cost, and flammability of lithium compounds under ambient conditions posing significant safety and scalability challenges. Moreover, the inherent tendency of Li^+ intercalation to trigger a 2H-to-1T phase transition complicates the production of semiconducting nanosheets. As a result, despite its tunability, this method remains suboptimal for large-scale fabrication of high-quality TMDs for electronic applications.

AMMONIUM-BASED INTERCALATION

To overcome undesired phase transitions, quaternary ammonium cations have been proposed as alternative intercalants for cathodic intercalation. Compared to the small diameter (d) of Li^+ ions ($d \approx 2 \text{ \AA}$)¹⁸⁸ the quaternary ammonium cations (Figure 3.5), such as tetramethylammonium (TMA^+ , $d \approx 0.56 \text{ nm}$)¹⁸⁹, tetraethylammonium (TEA^+ , $d \approx 0.67 \text{ nm}$)¹⁸⁹, tetrapropylammonium (TPA^+ , $d \approx 0.74 \text{ nm}$)¹⁹⁰, tetrabutylammonium (TBA^+ , $d \approx 0.83 \text{ nm}$)¹⁸⁹, generally exhibit large diameters. Therefore, intercalating these cations naturally

limits the number of ions that can fit into the host crystal, and thus the number of electrons injected into the TMDs which induce the phase change.

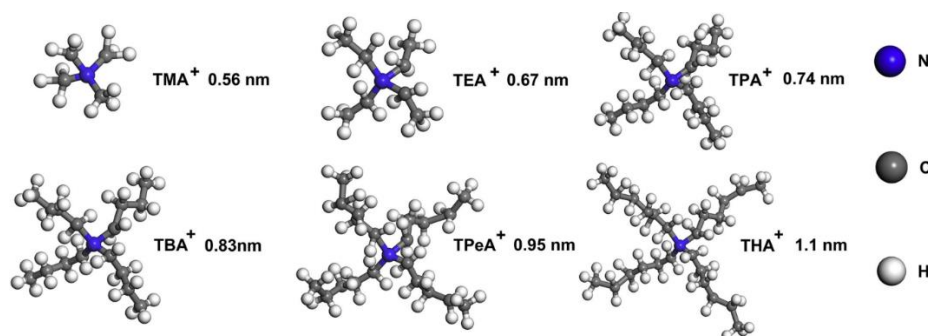


Figure 3.5: Alkylammonium Cations. The structure of various alkylammonium ions, the salts of which are used as electrolytes for cathodic exfoliation of TMDs. Adapted from ref¹⁷⁹

In 2018, Lin et al. demonstrated exfoliation of MoS₂ using THA⁺ in acetonitrile, with 2H phase purity confirmed by XPS¹⁹¹. This work represented a breakthrough, as it provided a controllable route to high-quality, phase-pure TMD nanosheets suitable for electronic applications. The stoichiometric ratio of the intercalated THA⁺ cation is relatively small, corresponding to 0.02 electrons per MoS₂ formula unit, which is well below the phase transition threshold of 0.1 electrons per MoS₂ formula unit. This yielded 10 mg mL⁻¹ of semiconducting MoS₂ with lateral sizes of 0.5–2 μ m and a thickness of $\sim$ 3.8 nm. When used as a channel material in a thin film field-effect transistor (FET), the exfoliated MoS₂ nanosheets demonstrated one of the highest mobilities in the literature ($\sim$ 10 cm² V⁻¹ s⁻¹) and an on/off ratio of 10⁶. Moreover, this method was successfully extended to WSe₂, Bi₂Se₃, NbSe₂, and other 2D systems.

Alkylammonium cathodic intercalation has now been widely adopted by other research groups to synthesize solution-processed 2D materials for fabricating FETs. For example, in 2021 Carey et al.⁷⁷ used this strategy to produce inkjet-printed MoS₂ FETs with mobilities of 0.1 cm² V⁻¹ s⁻¹¹⁹². This methodology thus represents a scalable, controllable, low-defect, and most importantly phase-pure method for producing solution-processable semiconducting 2D materials.

3.1.4 SOLVENT & SURFACTANT STABILIZATION

One of the primary challenges in solution processing is preventing the exfoliated nanosheets from reaggregating into stacked layered structures. To overcome this, the choice of solvent to exfoliate in plays a critical role. In the case of chemical exfoliation and anodic EE, the intercalated bulk material is typically hydrophilic, hence stabilization in an aqueous solvent is straightforward. For LPE and cathodic EE, the bulk material is typically hydrophobic, hence organic solvents are required.

The solvent's surface tension should closely match the surface energy of the basal plane of the 2D material to minimize energy difference between unexfoliated and exfoliated material, with the added sonic/shear energy making conversion from the former to the latter favourable. Additional stabilization can be achieved using surfactants or polymeric dispersants.

Surfactants, particularly ionic ones, adsorb non-covalently to the nanosheet surface and introduce electrostatic repulsion between sheets, allowing exfoliation in solvents that otherwise have poor surface energy matching (e.g., water for LPE and cathodic EE)^{193, 194}. Similarly, polymers non-covalently attach to the sheets, but instead stabilize dispersions via steric hindrance, creating an entropic penalty for reaggregation^{195, 196}.

Although surfactant stabilizers are typically non-covalent and removable, complete removal is difficult. Some require high-temperature annealing, which may not be compatible with substrates that have low thermal budgets (e.g., polymers). Furthermore, ionic surfactants are generally unsuitable for electronic applications due to charge trapping; therefore, polymeric stabilizers were primarily used in this work.

Solvents that are required are those with surface energies close to that of the nanomaterial. For example, it has been found that exfoliating in solvents with surface energies $\sim 70 \text{ mJ m}^{-2}$ produce higher concentration of exfoliated graphene¹⁴², as shown in Figure 3.6, which

closely matches the theoretical values for graphite's surface energy¹⁹⁷. Two typical solvents in this range are NMP and DMF. However, these high-boiling-point, toxic solvents are ill-suited for ink formulation. Fortunately, isopropanol (IPA) provides some dispersibility despite being far from the above surface energy and is usually used as a terminal solvent for redispersion following exfoliation and processing in NMP or DMF.

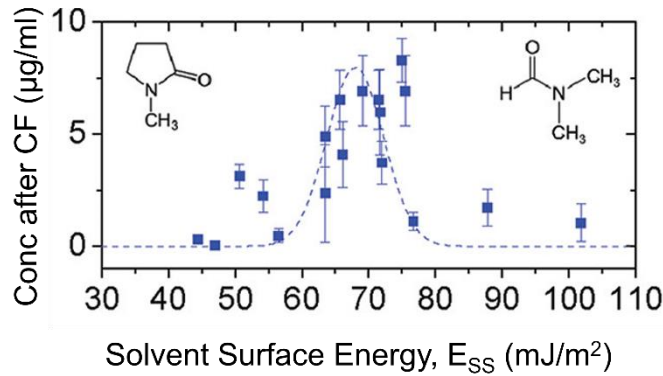


Figure 3.6: Exfoliation Solvent Stabilization. Graphene dispersion concentrations after exfoliation in different solvents plotted against solvent surface energy, showing a clear peak in graphene concentration near graphite's surface energy. Inset: structures of NMP (left) and DMF (right), the typical solvents in that surface energy range. Adapted from ref¹⁴².

Since surface energy matching alone does not fully explain dispersibility, more advanced models based on Hildebrand and Hansen solubility parameters are often applied¹⁹⁸. These models account for three contributions to intermolecular interactions: D (dispersive) P (polar) and H (hydrogen-bonding) components. The Hansen parameter for each interaction, i ($i: D, P, H$) may be expressed as:

$$\delta_i = \sqrt{\frac{E_{C,i}}{V}} \quad (\text{Eqn 3.1})$$

where $E_{C,i}$ is the molar cohesive energy density of the interaction and V is the molar volume. The total solubility parameter is then given by the Hildebrand parameter, δ_T :

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (\text{Eqn 3.2})$$

which is hence:

$$\delta_T = \sqrt{\frac{E_{C,T}}{V}} \quad (\text{Eqn 3.3})$$

describing the total cohesive energy of the solvent per unit volume. For non-polar solvents, Hildebrand theory is often sufficient, but for polar solvents, the full three-dimensional D , P , H Hansen space must be considered^{141, 199}. Interestingly, solvent polarity appears to affect exfoliation even for non-polar layered materials. This may be due to sonochemical degradation of solvents like NMP during exfoliation²⁰⁰, producing polymeric by-products which further stabilize the sheets.

3.2 SIZE SELECTION

The exfoliation of layered crystals produces nanosheets with broad distributions in lateral size and thickness, a phenomenon known as polydispersity. This arises from the intrinsic heterogeneity of the bulk crystal and from scission events during exfoliation. Incomplete delamination also contributes to variability in nanosheet thickness²⁰¹.

Polydispersity impacts the performance of 2D materials in various applications. As examples, as noted in Chapter 2 Section 2.2, electronic bandgaps of TMDs are thickness dependent. For mechanical reinforcement, large sheets are preferable⁴⁶. For catalysis and energy storage, smaller high surface area nanosheets are needed²⁰². Hence, a method of sorting for nanosheet by size is desired. The most successful technique for solution processed 2D materials is the use of sedimentation-based separation, which isolates dispersed materials by catalysing the sedimentation rate through centrifugal force.

For disk-like particles coated with a low-density surfactant layer in a liquid medium, as is typical for solution-processed nanosheets, Goldie et al. have proposed a modification of the Svedberg equation²⁰³:

$$S = \frac{(t_{NS}\Delta\rho_{NS} + 2d\Delta\rho_s)A^{1/2}}{12\eta(3/4\pi)^{1/3}} \quad (Eqn 3.4)$$

where S is sedimentation coefficient (in seconds), t_{NS} is the nanosheet thickness, $\Delta\rho_{NS}$ is the difference of nanosheet and liquid medium densities, d is the thickness of the surfactant layer, $\Delta\rho_s$ is the difference of surfactant and liquid medium densities, A is the nanosheet basal plane area, and η is the liquid viscosity. This expression incorporates the buoyant mass of both the nanosheet core and the surfactant shell, and a platelet-like drag which scales with basal plane area. It effectively states that the rate of sedimentation increases for sheets of larger size (ie. higher t_{NS} and A).

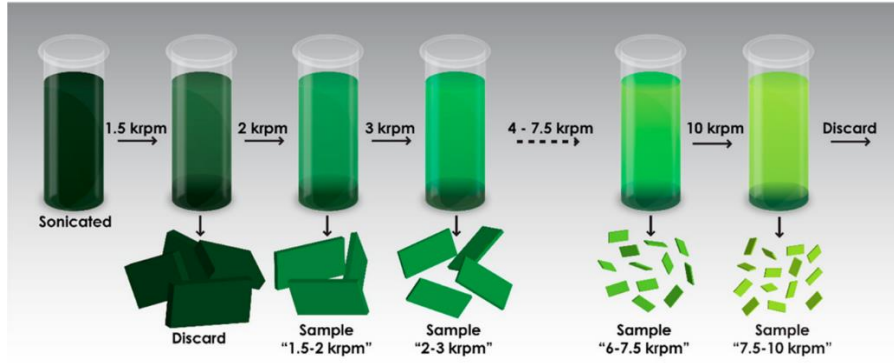


Figure 3.7: Liquid Cascade Centrifugation. Schematic of Liquid Cascade Centrifugation (LCC), showing progressive isolation of smaller nanosheets at higher spin speeds. Adapted from ref²⁰⁴.

As centrifugation causes large, thick nanosheets to sediment faster, thinner and smaller sheets are retained in the supernatant. This process has been refined by Backes et al. to yield the Liquid Cascade Centrifugation (LCC) method for sorting nanosheets from polydispersions and enriching the monolayer content²⁰⁴, illustrated in Figure 3.7. The principle of this method is to apply sequential centrifugation steps at increasing speeds, isolating the sediment each time.

For instance, an initial 1.5krpm spin removes unexfoliated bulk crystals. This leaves a supernatant with a broad range of nanosheets of varying lengths and thicknesses. This resulting supernatant is spun again at 2 krpm and sediment is collected. This sediment can

be labelled “1.5-2 krpm” and will contain large, thick nanosheets. The supernatant from this second step is then spun at 3 krpm to collect smaller sheets (“2-3 krpm”) in the sediment, and so on. Each step yields dispersions of progressively smaller and thinner nanosheets. As each step proceeds, the supernatant becomes increasingly monolayer enriched. If a specific size is desired, the desired nanosheets may be sedimented between two fixed rpm. This approach is especially important for TMDs, where thickness uniformity affects bandgap and electronic performance.

Having now examined the advantages of solution-processed 2D materials and relative merits of different methods of producing them, particularly through LPE and EE, as well as describing means of subsequent stabilization of nanosheet dispersions and centrifugal sorting of sheets by size, it follows that the next step is to consider how these nanosheets can be effectively deposited and characterized. The methods used to process nanosheet dispersions into films, as well as the techniques for evaluating their structural, optical, and electrical properties, form the core focus of the following chapter.

Chapter 4

Deposition & Characterization Techniques

Since their isolation via solution processing, research into 2D materials has followed the previously established trajectory of 0-D and 1-D materials, as well as conductive polymers, by exploring techniques for printing 2D material inks into thin films. In the case of solution processed 2D materials, this printing produces nanosheet networks, which can exploit the unique properties of 2D materials for large-area, low-cost applications.

The earliest deposition techniques employed, such as inkjet printing^{192, 205, 206}, aerosol jet printing²⁰⁷, and blade coating²⁰⁸, were adopted primarily for their established widespread use in industrial printing processes. However, these techniques impose stringent rheological requirements on the inks and surface energy constraints on the deposition substrates²⁰⁹. Such limitations hinder rapid prototyping and reduce compatibility with a broad range of 2D material formulations and device architectures.

Spray coating, a technique originally developed for photography and painting applications²¹⁰, emerged as a more suitable alternative due to its relaxed rheological

constraints. Nevertheless, films produced by spray coating often exhibit poor nanosheet alignment²⁰⁹, which adversely affects device performance for reasons to be addressed in Chapter 5. To address this, alternative methods such as spin coating²¹¹ and liquid interface assembly²¹² have been developed.

4.1 SPRAY COATING

Spray coating is a versatile and highly scalable deposition technique that has recently been applied to the fabrication of 2D material networks^{206, 213-215}. Originally developed as a technique for photographic retouching²¹⁰, it is now widely used in applications ranging from automotive manufacturing²¹⁶ to fine art²¹⁷. The technique relies on liquid atomisation, in which a compressed gas source and nozzle assembly produce a fine mist of ink droplets that are directed onto a target substrate (Figure 4.1).

Spray coating was first introduced into nanomaterials research in 2004 for the deposition of carbon nanotubes²¹⁸, establishing its potential for producing large-area nanomaterial thin films. Since then, it has been employed for depositing a range of nanomaterial systems, including silver nanowires²¹⁹, quantum dots²²⁰, and nanosheets¹²⁵.

The mechanism of spray coating is illustrated in Figure 4.1A. The process begins with the application of N₂ overpressure to the system. The ink is loaded into a reservoir and gravity-fed to the nozzle. When triggered, the needle retracts, allowing ink and N₂ back pressure to pass through the nozzle²²¹. The pressurised gas shears off small ink volumes, producing an atomised droplet plume²¹⁹. This plume is directed toward a substrate, which is typically heated to accelerate solvent evaporation and minimise droplet coalescence (Figure 4.1B). For automated large-area deposition, the spray gun can be mounted on an actuating gantry that rasters over the substrate²²².

Film thickness is controlled through ink concentration and the number of spray passes. A shadow mask can be used to define specific deposition areas, enabling features as small as

200 μm ²¹⁵. The technique is compatible with a wide range of substrates and solvents, allowing nanosheet inks to be sprayed directly from low boiling point solvents without additives or binders, thereby reducing film contamination.

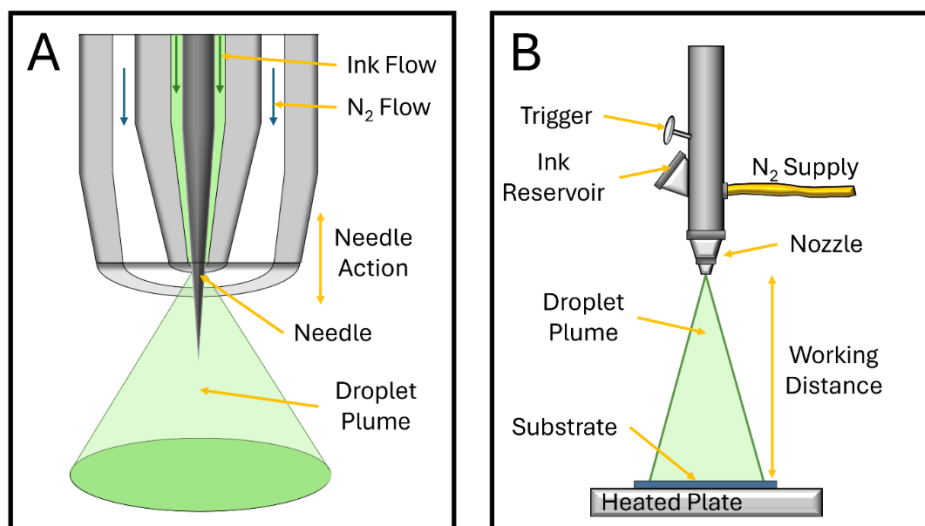


Figure 4.1 Spray Coating. A – Schematic of the spray gun nozzle, showing how N₂ overpressure and needle action aerosolizes the ink into a plume. B – Diagram of the spray coating assembly, in which the ink plume is rastered over a heated substrate to deposit a film. Adapted from ref²²¹.

Spray coating is often compared to aerosol jet printing (AJP), as both techniques rely on the atomisation of liquid inks into aerosol droplets. However, the two differ significantly in their mode of deposition. In spray coating, droplets are delivered over relatively large nozzle–substrate distances in a divergent plume, resulting in broad, unpatterned film deposition. In contrast, AJP employs a focused aerosol stream at small working distances, typically confined by a sheath gas, enabling high-resolution, direct-write patterning with feature sizes down to tens of micrometres²⁰⁷. As a result, AJP is more suited to patterned device fabrication, whereas spray coating is optimised for rapid, large-area film deposition, with higher throughput and straightforward scalability to industrial processes such as roll-to-roll manufacturing.

Although spray coating imposes minimal constraints on ink formulation, several parameters significantly affect film quality. These include spray working distance, raster

speed, substrate temperature, solvent type, nozzle diameter, ink flow rate, and N₂ back pressure^{219, 223}. The substrate must be heated sufficiently to ensure droplet evaporation without damaging nanosheets. Excess droplet deposition must be avoided to prevent coffee-ring effects, which compromise large-area uniformity.

4.2 LIQUID INTERFACE DEPOSITION

Liquid interface deposition involves the formation of 2D material films at a liquid interface via self-assembly, followed by transfer to a target substrate. Underlying this is the self-spreading behaviour of an immiscible species across a water surface, a phenomenon documented by Aristotle²²⁴ and first formally investigated by Benjamin Franklin²²⁵. Subsequent work by Rayleigh, Pockels, and Langmuir established the measurement, control, and transfer of molecular monolayers on water²²⁶⁻²²⁹, culminating in the Langmuir-Blodgett technique for deposition of monolayer films of fatty acids²³⁰. In this method, an oil film is spread on a water surface, compressed using movable barriers, and a substrate is withdrawn vertically through the interface, coating it with the film.

While Langmuir-Blodgett proved an effective technique for depositing small amphiphilic molecules, it was less suited to depositing films of large or non-amphiphilic macromolecules, which may denature or aggregate during transfer. To address this, Langmuir and Schaefer developed a horizontal transfer method for depositing protein films, known as Langmuir-Schaefer deposition²³¹, in which the substrate is brought into contact with the compressed film by lateral motion, reducing disturbance to the interface.

In nanosheet film assembly, Langmuir-based water-air interfaces have been employed²³², but suffer from material loss by mixing with the water subphase and film aggregation during assembly²³³. Additionally, the large subphase area in Langmuir troughs is impractical for small-scale prototyping, as it requires large volumes of material²³⁴. An alternative is to use a water-organic liquid-liquid interface, which enhances colloid

confinement and promotes film self-compression without the need for specialised apparatus^{235, 236}.

For spherical colloids of radius r sitting on a liquid–liquid interface, the energy required to fully detach a particle, ΔE , is given by²³⁷:

$$\Delta E = \pi r^2 \gamma_{w/o} (1 \pm \cos \theta)^2 \quad (\text{Eqn 4.1})$$

where $\gamma_{w/o}$ is the interfacial tension of the water/organic interface, and θ is the three-phase contact angle. The positive sign applies when the colloid is primarily submerged in water ($0^\circ < \theta < 90^\circ$), the negative when primarily floating in the organic phase ($90^\circ < \theta < 180^\circ$). This is depicted in Figure 4.2A.

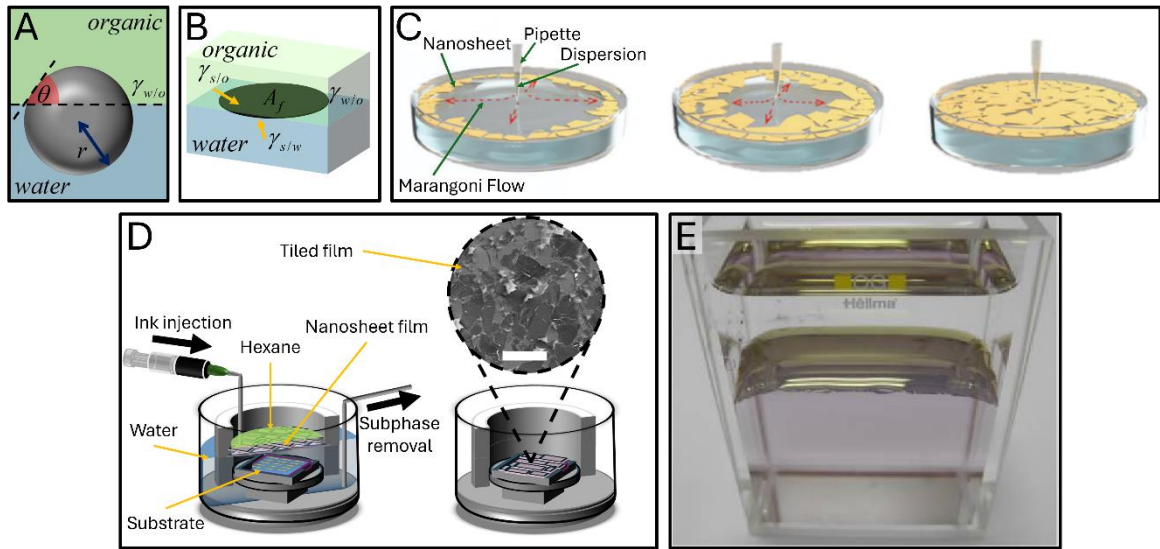


Figure 4.2: Liquid Interface Deposition. A – Model of a spherical colloid at a water-organic liquid-liquid interface. B – Model of an infinitesimally thin disk at the interface. C – Illustration of Marangoni flows driving self-spreading and compression of nanosheets. Adapted from ref²³⁸. D – Schematic of the liquid interface deposition setup used in this work, showing film assembly at a water–hexane interface and transfer by pumping water from below. Inset – SEM image of a graphene film produced by this method, showing a single flake thick, tiled nanosheet film (scalebar: 5 μm). E – Langmuir film of gold nanoparticles, showing clearly how the film lies on the interface. Adapted from ref²³⁹.

However, spherical particles are not an accurate model for 2D nanosheets. Neilson et al.²¹² proposed a modification of the above Eqn 4.1 for infinitesimally thin disks, neglecting edge contributions:

$$\Delta E = \gamma_{w/o} A_f (1 \pm \cos \theta) \quad (\text{Eqn 4.2})$$

where A_f is the area of the nanosheet basal plane. This is depicted in Figure 4.2B. Although the contact angle may seem a non-physical abstraction in the case of an infinitesimally thin disk, its physical meaning is recovered via the Young-Dupré equation:

$$\cos \theta = \frac{\gamma_{s/w} - \gamma_{s/o}}{\gamma_{w/o}} \quad (\text{Eqn 4.3})$$

where $\gamma_{s/w}$ and $\gamma_{s/o}$ are the interfacial tension of the nanosheet/water and nanosheet/organic interfaces respectively. Hence θ can be interpreted as a term measuring the nanosheet's relative affinities for the two liquids.

For a $\sim 1 \mu\text{m}^2$ MoS₂ nanosheet at a water-hexane interface ($\gamma_{w/o} = 50.5 \text{ mJ m}^{-1}$, $\theta = 99.7^\circ$), the detachment energy has been estimated as $\Delta E \approx 9.7 \times 10^6 k_B T$ ²¹², which is significantly larger than for spherical particles of equivalent surface area ($6.19 \times 10^5 k_B T$). This high detachment energy demonstrates the exceptional thermodynamic stability of nanosheet films at the interface. The large Gibbs surface energy gradient between a bare interface and one covered with nanosheets provides the driving force for self-spreading behaviour and film compression via the Marangoni effect²³⁸. In brief, this is a mass transfer process driven by a reduction in surface energy. Such self-spreading behaviour, which forms a tiled and self-compressing film of nanosheets, is illustrated in Figure 4.2C.

The self-assembly of nanosheets at a liquid-liquid interfaces, followed by transfer to a substrate, has been successfully demonstrated for a wide range of 2D materials. These include MgB₂ nanoplatelets²⁴⁰, WSe₂ nanosheets²³³, and MoS₂ nanosheets²¹². In this work, a modification of the liquid interface assembly method reported by Neilson et al.²¹² was

employed. In Neilson's work, nanosheet films were assembled at a water-hexane interface by injection of nanosheet ink as in Figure 4.2C, followed by transfer of the film onto a substrate by horizontally lifting it through the interface, analogous to Langmuir-Schaefer deposition. In this work's modified implementation, the substrate is raised through the interface by pumping water out from below, enabling a controlled and uniform transfer of the film, as will be shown in Chapter 7. A schematic of this process is shown in Figure 4.2D. This family of methods enables the fabrication of ultrathin, tiled nanosheet networks over centimetre-scale areas (Figure 4.2E). Film thickness can be tuned by sequential deposition with intermediate drying²⁴¹. The technique can produce pinhole-free nanosheet films²⁴² with minimized thickness (see Figure 4.2D inset), suitable for dielectric applications²⁰⁶.

4.3 CHARACTERIZATION

Following ink formulation, it is necessary to characterise key nanosheet properties, including chemical identity, defect presence and density, and statistical parameters such as average sheet thickness and lateral size. After film deposition, the properties of the resulting nanosheet networks, including optical activity, film thickness, nanosheet morphology, and charge transport behaviour, should be assessed to inform understanding of network physics and device performance. A variety of established material characterisation techniques are available for this purpose. The subsections below describe the methods used in this work.

4.3.1 ATOMIC FORCE MICROSCOPY

Atomic Force Microscopy (AFM) provides nanoscale topographical measurements of samples²⁴³. Since the development of solution-processed nanosheets, extensive research has examined how synthesis and processing strategies influence nanosheet size^{14, 141, 204, 244, 245}. As discussed in Chapters 2 and 5, nanosheet length and thickness strongly affect both the

individual nanosheet properties and the behaviour of nanosheet networks, and are hence important quantities to measure in a given nanosheet dispersion.

In non-contact mode AFM, an atomically sharp tip mounted on a cantilever oscillating in the z-direction is rastered over the sample in the x-y plane by sample stage actuation (Figure 4.3A). Tip-sample interactions cause deflections of the cantilever, which are detected by reflecting a laser beam onto a photodetector array. These deflections are correlated with the tip position to build a topographical image, either of isolated nanosheets (Figure 4.3B) or of continuous nanosheet films (Figure 4.3C). The images can then be analysed to extract nanosheet thickness and lateral dimensions, as shown inset in Figure 4.3B, and network thickness, as shown inset in Figure 4.3C.

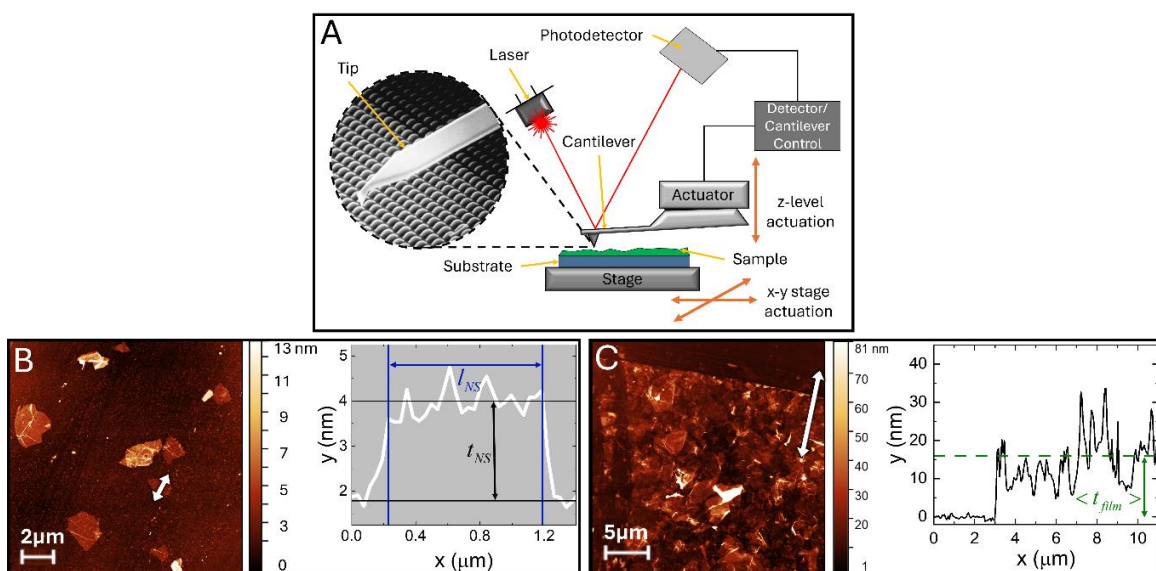


Figure 4.3: Atomic Force Microscopy. A – Schematic of an AFM, showing laser reflection from a cantilevered tip rastered over a sample. Adapted from refs^{246, 247}. B – AFM image of nanosheets with corresponding length and thickness analysis inset. C – AFM image of a nanosheet film with film thickness analysis inset.

AFM can also operate with the tip in direct contact with the sample (contact mode) or oscillating with periodic contact to the sample (tapping mode). In this work, all AFM measurements were conducted in non-contact mode.

4.3.2 ULTRAVIOLET-VISIBLE SPECTROSCOPY

Ultraviolet-visible (UV-Vis) spectroscopy probes the interaction of light with materials in the ultraviolet and visible spectral ranges²⁴⁸. It measures the attenuation of incident light by a sample, providing information on its transmission, absorption, and scattering processes. In a standard transmission geometry, a monochromatic light beam passes through a cuvette containing the nanosheet dispersion, and the transmitted intensity is recorded over a range of wavelengths (Figure 4.4A). Different experimental geometries allow selective probing of various light-matter interactions, for example, a linear setup measures transmission (extinction), while an integrating sphere setup measures absorption. UV-vis spectroscopy can also probe the light-matter interaction in transparent films.

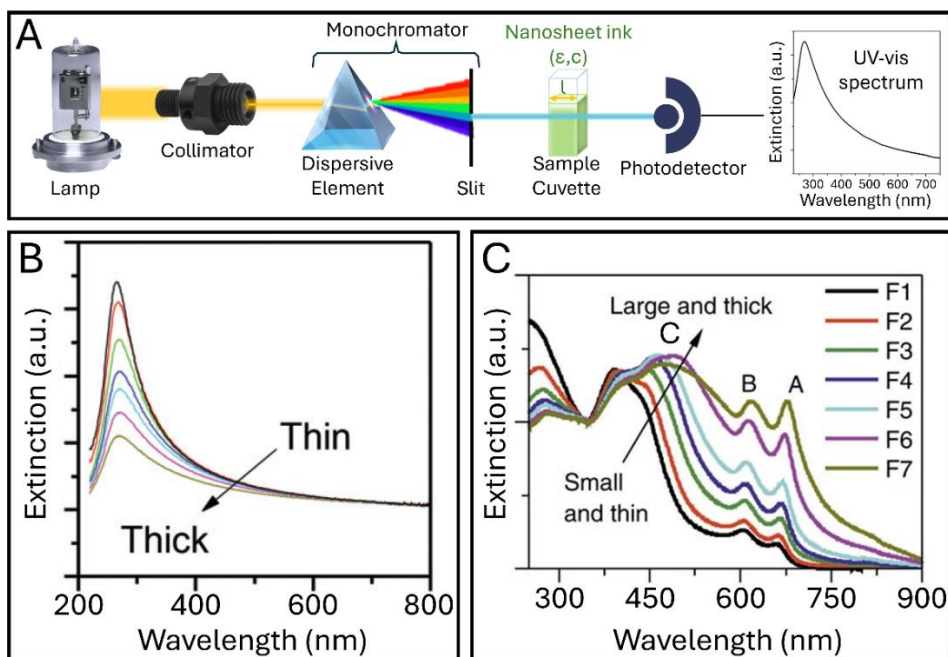


Figure 4.4: Ultraviolet-Visible Spectroscopy. A – Diagram of a UV-Vis spectrophotometer setup for nanosheet inks. Adapted from refs²⁴⁹⁻²⁵¹. B – Typical graphene extinction spectra, showing increased $\pi \rightarrow \pi^*$ peak intensity for thinner sheets. Adapted from ref²⁴⁴. C – Typical MoS₂ extinction spectrum showing increased A exciton intensity relative to the C exciton intensity for thicker sheets. Adapted from ref²⁵².

A useful measured quantity in this technique is optical extinction, ext , which quantifies the reduction in light intensity after it passes through a medium. It is defined as:

$$\text{ext} = -\log_{10} T \quad (\text{Eqn 4.4})$$

where T is the relative transmission, defined as:

$$T = \frac{I_T}{I_0} \quad (\text{Eqn 4.5})$$

where I_T and I_0 are the transmitted and incident light intensities, respectively. In chemical analysis, it is often useful to normalize optical extinction to an intrinsic material property, the extinction coefficient, ε , typically expressed in $\text{L g}^{-1} \text{m}^{-1}$. Because the optical response of materials is wavelength-dependent, the extinction coefficient is typically expressed as a function of wavelength, $\varepsilon(\lambda)$. The extinction coefficient encompasses both absorption and scattering contributions:

$$\varepsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda) \quad (\text{Eqn 4.6})$$

where $\alpha(\lambda)$ and $\sigma(\lambda)$ are the absorption and scattering coefficients, respectively.

The attenuation of light through a medium is governed by the Beer-Lambert Law, which relates extinction to analyte concentration c and path length l :

$$\text{ext} = -\log_{10} T = -\log_{10} \left(\frac{I_T}{I_0} \right) = \varepsilon c l \quad (\text{Eqn 4.7})$$

This provides a straightforward method of determining analyte concentration, provided an extinction coefficient is known for a given wavelength. Accurately determining nanosheet concentration is essential for ink formulation and achieving controlled, reproducible film deposition.

Absorption occurs when incident photons promote electrons to higher energy states, resulting in a reduction in transmitted light intensity²⁵³. In 2D materials with bandgaps in

the optical range, such as the TMDs, this results in distinct extinction peaks. These features can serve as a spectral fingerprint for qualitative identification of nanosheet species. Furthermore, as noted in Chapter 2, 2D materials display size-dependent band structures and optoelectronic properties. This makes UV-vis spectroscopy a valuable tool for inferring nanosheet size^{244, 252, 254} (see Figure 4.4B and C).

Optical scattering, $\sigma(\lambda)$, arises in media with refractive index non-uniformities, such as nanoparticle or nanosheet dispersions. In these systems, the electric field of incident light induces electric dipoles within the particles, which subsequently re-radiate light elastically in all directions. This scattering process reduces transmitted intensity and can obscure or shift absorption peaks^{255, 256}.

Depending on the relative size of the particles, D , to the wavelength of incident light, λ , different scattering regimes and behaviour exist. The wavelength dependence of scattering follows a power law $\sigma(\lambda) \propto \lambda^{-m}$, varying from the Rayleigh regime (small particles relative to wavelength, $\lambda / D > 10$, $m = 4$) to the van der Hulst (Mie) regime (large particles relative to wavelength, $\lambda / D < \pi$, $m = 2$). For solution processed nanosheets, D tends to lie between these two regimes, and the scattering exponent is some value in the range $2 < m < 4$ ²⁵⁷. Measurement of this exponent can provide an estimate of nanosheet length. Consequently, for a complete description of the optical behaviour of nanosheet dispersions, both absorption and extinction spectra should be recorded.

NANOSHEET SIZE-DEPENDENT UV-VIS

As discussed above, nanosheets exhibit size-dependent absorption and scattering behaviour in their UV-vis spectra. This variation makes it non-trivial to define a single extinction coefficient for a given nanosheet species, since the spectrum itself varies with nanosheet size¹⁵⁷. To enable accurate concentration determination, it is therefore necessary to identify spectral regions that are invariant with respect to nanosheet size.

In the early stages of research into liquid-phase exfoliated (LPE) graphene, identifying such a size-independent region was relatively straightforward. The UV region of graphene's extinction spectrum is dominated by the $\pi \rightarrow \pi^*$ transition, with minimal spectral features at longer wavelengths. Backes et al. determined that at 750 nm, where the spectrum is largely invariant to nanosheet size, the extinction coefficient for graphene dispersions is approximately $5430 \text{ L g}^{-1} \text{ m}^{-1}$ ²⁴⁴.

However, this approach is more complex for TMDs, which exhibit multiple absorption peaks arising from electronic transitions involving their d-orbitals. As such, a size-independent wavelength, typically located between absorption peaks at shorter wavelength, must be identified to determine an intrinsic extinction coefficient. Kubetschek et al. have reported extinction coefficients for several TMDs using this approach (e.g MoS₂: $\sim 6900 \text{ L g}^{-1} \text{ m}^{-1}$ at 345 nm) ²⁵⁸.

As mentioned, relative intensities of specific absorption peaks can offer insight into nanosheet dimensions. For example, graphene's $\pi \rightarrow \pi^*$ transition near 280 nm is enhanced relative to the background with decreased nanosheet thickness ²⁴⁴ (see Figure 4.4B). For MoS₂, thickness-dependent band structure effects alter the relative positions and intensities of its excitonic peaks ²⁵⁸ (see Figure 4.4C). Specifically, the intensity of the A exciton peak increases relative to the C exciton as nanosheet thickness increases, enabling estimation of sheet thickness from peak intensity ratios $I(C)/I(A)$.

4.3.3 RAMAN SPECTROSCOPY

Raman spectroscopy is based on the inelastic scattering of light by matter, a phenomenon first reported by C. V. Raman in 1928 ²⁵⁹. When light interacts with a molecule or a crystal lattice, the incident photons can induce an oscillating dipole that temporarily promotes the system to a virtual excited state. In most cases, this dipole relaxes by emission of a photon with no change in energy from the incident photon (Rayleigh scattering). In Raman

scattering, the dipole virtual state exchanges energy with vibrational modes or phonons in the material, resulting in an energy shift of the scattered photons. If the scattered photon has lower energy than the incident photon, the process is known as Stokes scattering; if the scattered photon has higher energy, it is known as anti-Stokes scattering (Figure 4.5A).

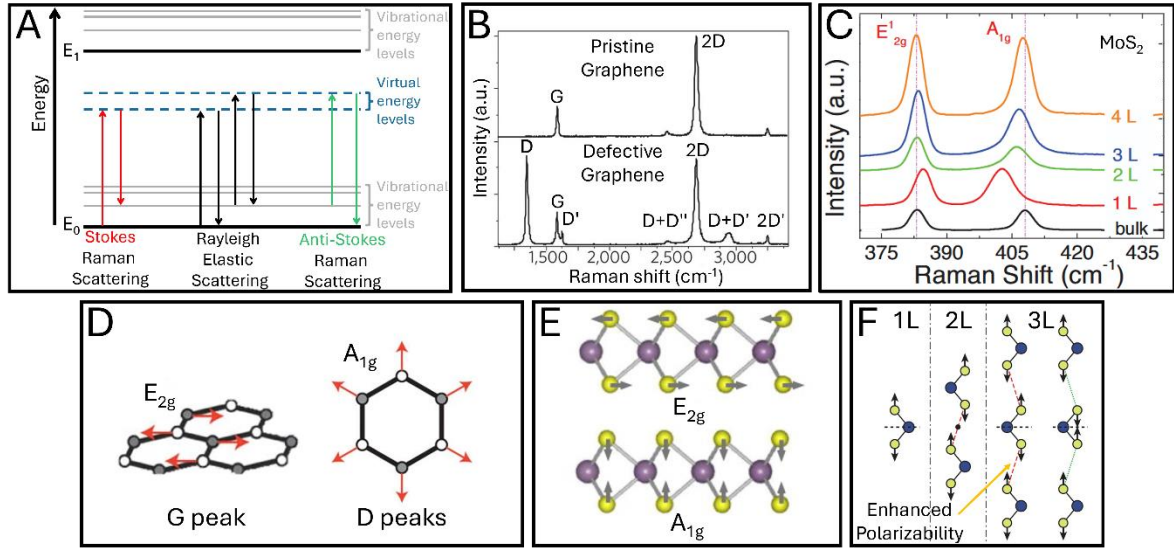


Figure 4.5: Raman Spectroscopy. A – Schematic of Stokes, Rayleigh, and anti-Stokes scattering processes. Adapted from ref²⁶⁰. B – Raman spectra of pristine and defective graphene, showing the G, 2D, and D peaks. Adapted from ref²⁶¹. C – Raman spectra of MoS₂ of different thicknesses, showing E_{2g} and A_{1g} peaks and their evolution with thickness. Adapted from ref²⁶². D – Lattice vibrations in graphene associated with the G and D peaks. Adapted from ref²⁶¹. E – Side view of lattice vibrations in TMDs associated with the E_{2g} and A_{1g} peaks. Adapted from ref²⁶³. F – Schematic illustrating the mechanism by which the A_{1g} peak couples to nanosheet thickness Adapted from ref²⁶⁴.

The Raman effect is inherently weak, with scattering events occurring for only approximately 1 in every 10⁶ to 10¹² incident photons²⁶⁵. Its application as a spectroscopic tool became practical only after the development of lasers as intense, monochromatic light sources. Raman spectra are generally expressed in terms of the Raman shift, ν , in wavenumbers (cm⁻¹), calculated from the incident (λ_i) and scattered (λ_s) wavelengths:

$$\nu = \frac{1}{\lambda_i} - \frac{1}{\lambda_s} \quad (\text{Eqn 4.8})$$

This quantity is known as the Raman shift, and peaks in the spectrum correspond to Raman-active vibrational modes of the material under study (see Figure 4.5B and C).

For a vibrational mode to be Raman active, it must induce a change in the polarizability of the molecule or crystal lattice. This allows the vibration to physically couple to the light induced dipole. In defect-free crystalline solids, the phonons must also satisfy momentum conservation with the negligible photon momenta. This typically requires that the phonons be located at the Brillouin zone centre (the zero momentum Γ -point) or that two phonons of equal and opposite momentum be involved in the scattering process. Many 2D materials possess vibrational modes that fulfil these criteria, allowing Raman spectroscopy to serve as a fingerprinting tool for species identification^{261, 264}.

In graphene, the most prominent Raman features are the G and 2D peaks (Figure 4.5B). The G peak arises from first-order scattering by in-plane inverse transverse optical (iTO) and inverse longitudinal optical (iLO) phonons at the Γ -point with E_{2g} symmetry. The 2D peak results from second-order scattering involving iTO phonons with A_{1g} symmetry at the K point²⁶¹. The lattice vibrational modes associated with these phonons are shown in Figure 4.5D. Because the 2D peak arises from a two-phonon process involving both scattering and anti-scattering, it is highly sensitive to the band structure²⁶⁶. As the number of graphene layers increases, the 2D peak broadens, splits into multiple components, and decreases in intensity relative to the G peak, enabling nanosheet thickness estimation from the spectrum.

In MoS_2 , the two dominant Raman peaks are the E_{2g} and A_{1g} peaks (Figure 4.5C). The E_{2g} peak occurs by scattering by the in-plane iLO and iTO phonons with E_{2g} symmetry, while the A_{1g} peak occurs by scattering with out-of-plane Transverse Optic (oTO) phonon with

A_{1g} symmetry, all of which are at the Γ point²⁶³. The lattice vibrations corresponding to these phonons are shown in Figure 4.5E.

As MoS₂ flakes increase in thickness, the A_{1g} mode increasingly couples to adjacent layers by a mechanism shown in Figure 4.5F, enhancing out-of-plane polarizability and increasing the scattering efficiency. This leads to a relative increase in the A_{1g} peak intensity compared to the E_{2g} peak with increasing thickness. In addition, the layers constrain the out-of-plane motion of sulphur atoms, upshifting the A_{1g} peak, while dielectrically screening the in-plane interactions that act as a restoring force against the E_{2g} motion, downshifting the E_{2g} peak²⁶². Together, these effects allow Raman spectroscopy to be used for estimating MoS₂ flake thickness. Since the polarizability is similar across many of the TMDs, this analysis can be trivially extended to other 2D TMD systems²⁶⁴.

Defects can activate otherwise Raman-inactive modes by breaking translational symmetry and providing the additional momentum required for scattering. In pristine graphene, the D peak, arising from first-order scattering from by iTO phonons at the K point, is typically forbidden as its non-zero momentum violates selection rules²⁶⁶. However, the presence of defects provides momentum that allows these phonons to participate in Raman scattering. This allows the D peak to become visible as in Figure 4.5B, with an intensity proportional to the amount of defects²⁶¹. The ratio of the D and G peaks (I_D / I_G) is widely used as a metric for defect density. In TMDs, the longitudinal acoustic (LA) mode can be similarly activated by defects, providing a similar means of quantifying defect density²⁶⁷.

Certain Raman modes are only visible in specific polymorphs. For example, the J modes, which are inactive in 2H-MoS₂, become Raman-active in the metallic 1T phase²⁶⁸. This pattern holds across various TMD systems^{269, 270}, making Raman spectroscopy an effective tool for probing phase purity and composition of 2D materials as well.

4.3.4 ELECTRON MICROSCOPY

The spatial resolution of optical microscopy is fundamentally limited by diffraction, described by the Rayleigh criterion. Under the small angle approximation, the minimum spatial resolution, δ , is given by:

$$\delta \approx 1.22 \frac{f\lambda}{D} \quad (\text{Eqn 4.9})$$

Where f is the focal length, D is the aperture diameter, and λ is the wavelength of light. For typical optical microscopes, this places a lower limit on spatial resolution of approximately 200 nm, depending on the focal length and aperture size.

Electrons exhibit wave-like behaviour, with a wavelength determined by their momentum p , according to the de Broglie relation:

$$\lambda = \frac{h}{p} \quad (\text{Eqn 4.10})$$

At high accelerating voltages, the momentum of the electrons is large, resulting in wavelengths in the nanometre to sub-angstrom range. These shorter wavelengths enable imaging with significantly higher resolution than is possible with visible light. This principle forms the basis of electron microscopy, a family of techniques essential for the characterisation of nanomaterials, particularly those with lateral dimensions below the diffraction limit of light²⁷¹.

SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM) is one of the most widely used electron microscopy techniques for nanosheet characterisation. A typical SEM system, illustrated in Figure 4.6A, employs a high-voltage potential (commonly 20–40 kV) to accelerate electrons in a vacuum from an electron source, often a field-emission tungsten tip. The electron beam is collimated, focused, and deflected using a series of electromagnetic lenses.

When the beam interacts with the sample, it generates several types of signals within a defined interaction volume, the size of which depends on both the material properties and the accelerating voltage (Figure 4.6B). These interactions produce three primary signals: (1) high-energy backscattered electrons, (2) lower-energy secondary electrons generated by ionization of the sample, and (3) X-rays emitted from electronic transitions²⁷².

Detectors collect these signals while the beam is rastered in the x-y plane, enabling construction of a high-resolution ($\delta \sim 1\text{--}3\text{ nm}$) image of the sample surface (inset Figure 4.6A).

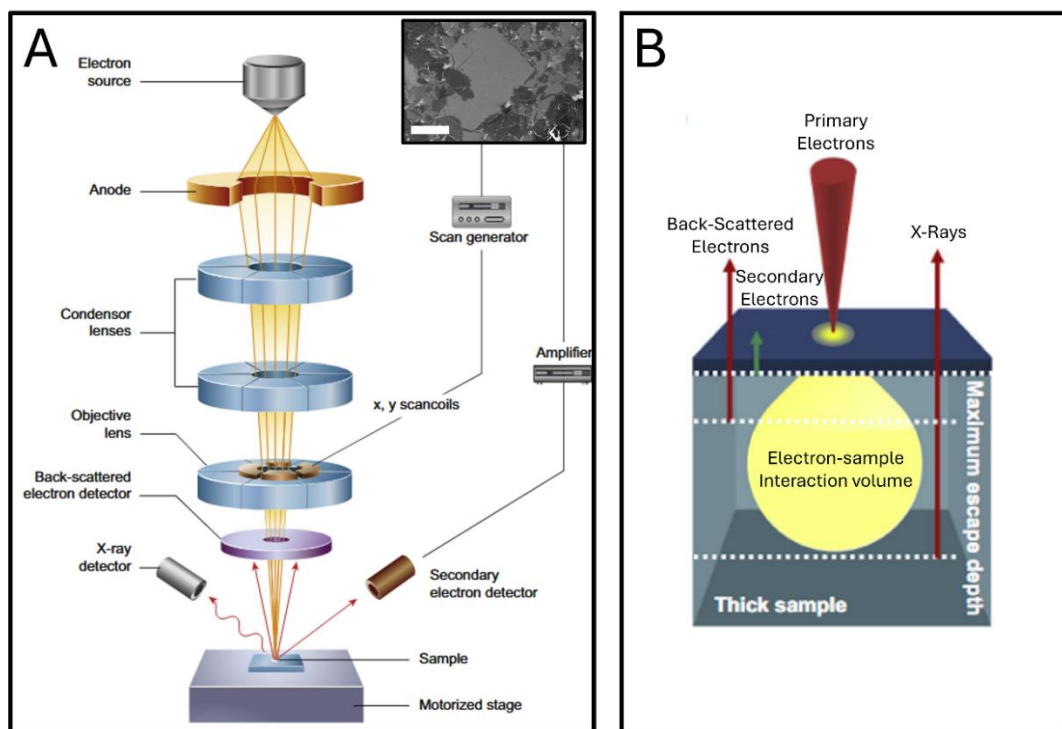


Figure 4.6: Scanning Electron Microscopy. A – Schematic of an SEM, showing beam generation, electromagnetic focusing, and detection of emitted signals. Inset: SEM image of a graphene nanosheet network (scale bar: 2 μm). B – Interaction volume and types of radiation generated during beam-sample interactions. Adapted from ref²⁷¹.

In 2D materials research, SEM is useful for measuring the lateral dimensions of nanosheets, complementing AFM. It also enables qualitative assessment of nanosheet network morphology, including substrate coverage²⁷³ and nanosheet alignment²⁰⁹.

4.4 CAMERA FILM SCANNING

Camera film scanning can be adapted as a high-throughput imaging technique for thin nanosheet films. Modern film scanners operate by illuminating the sample with a light source, typically an LED, while a scanner head charge-coupled device (CCD) array rasters across the film (Figure 4.7A). The electrical signals from the scanner head at each position are converted into pixels of a digital image. The camera film attenuates light in different amounts depending on the film exposure, and so the image on camera film is converted to a digital image. As thin nanosheet films are typically transparent and similarly attenuate light, camera film scanning presents a high-throughput technique for acquisition of detailed images of thin nanosheet film samples.

4.4.1 IMAGE PROCESSING

A digital image is represented as a matrix in which each element corresponds to a pixel, with its value denoting the pixel intensity. In grayscale images, the intensity value ranges from black (minimum intensity) to white (maximum intensity). The range of possible intensity values depends on the bit depth used for encoding. For example, an image encoded at 1 bit contains only two intensity levels (black and white), whereas a 16-bit image can represent 65,536 different grayscale levels.

For colour images, three matrices are used, corresponding to the red, green, and blue channels. The combination of these channels allows reproduction of a wide colour range²⁷⁴. Human vision is limited to perceiving approximately 200 distinct intensity levels per channel, which is why 8-bit encoding (256 levels per channel) is generally sufficient for most applications, providing over 16.7 million possible colours. However, when performing digital photographic processing, 16 bits is typically used for professional photo editing to avoid banding and preserve detail in highlights/shadows. Encoding a larger range of

values may also maintain imperceptible quantitative information that is lost at lower bit depths.

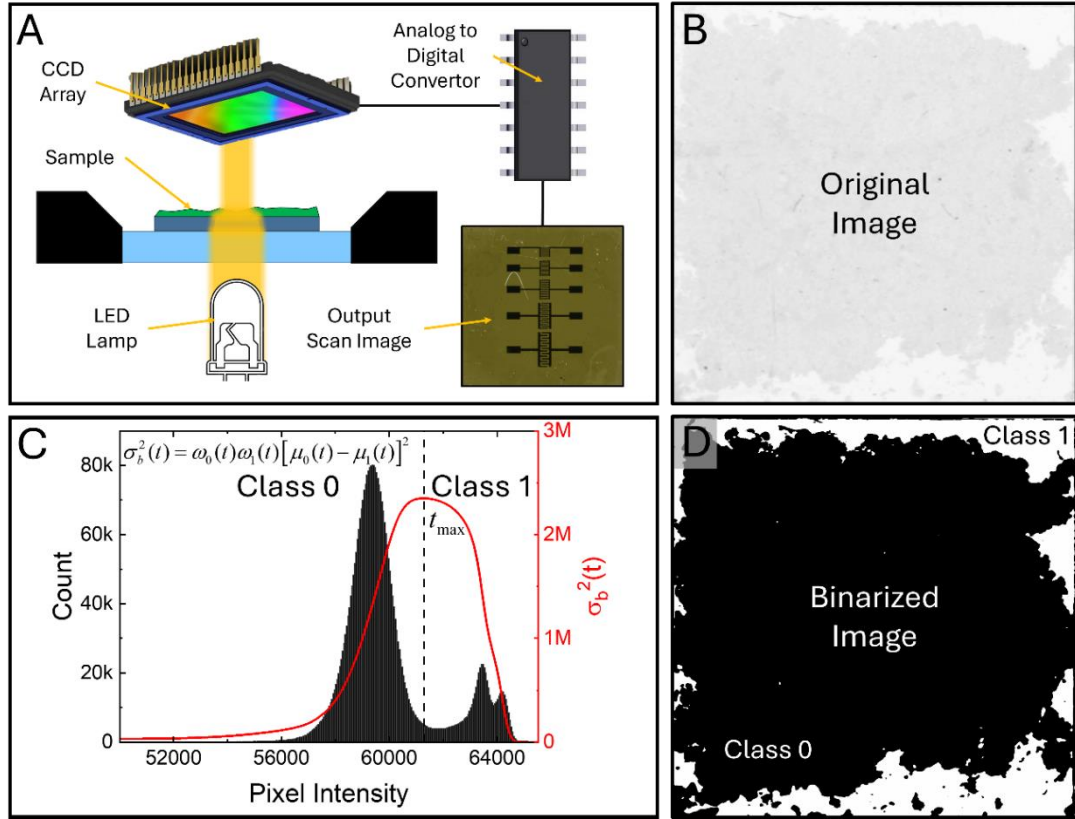


Figure 4.7: Camera Film Scanning and Processing. A – Schematic of a camera film scanner adapted for nanosheet film imaging. Adapted from ref^{275, 276}. B – An example grayscale image. C – Histogram of pixel intensities from B overlaid with the between-class variance function from Otsu's method. D – Binary image of B obtained after applying Otsu's threshold. C adapted from ref²⁷⁷.

A statistical distribution of pixel values for the sample image in Figure 4.7B is shown in Figure 4.7C. Such distributions can be used to extract quantitative descriptors of the image, including mean intensity and standard deviation, which provide measures of average contrast and intensity variation across the film, as will be demonstrated in Chapter 7.

OTSU'S THRESHOLDING

Otsu Thresholding is a common method in computer vision for binarizing between two distinct classes of pixels in an image, the foreground and background²⁷⁸. The method selects a threshold pixel intensity value, t , that maximizes the between-class variance:

$$\sigma_b^2(t) = \omega_0(t)\omega_1(t)[\mu_0(t) - \mu_1(t)]^2 \quad (\text{Eqn 4.11})$$

Here $\omega_0(t)$ is the fraction of pixels below the threshold t (class 0), $\omega_1(t)$ is the fraction of pixels above t (class 1), μ_0 is the mean pixel value of class 0, μ_1 is the mean pixel value of class 1, and $\sigma_b^2(t)$ is the inter-class variance. This function is shown plotted against the image's histogram in Figure 4.7C.

Otsu's method works by iteratively varying t , and finding the value for which $\sigma_b^2(t)$ is maximized, $t_{\max}$. Every pixel value above $t_{\max}$ is defined as the foreground (class 1), while everything below is the background (class 0). The output of this binarization process applied to the image in Figure 4.7B is shown in Figure 4.7D. This technique is powerful for binarizing images in various imaging techniques to find two distinct phases, as it reproducibly and reliably finds an optimal threshold value in grayscale images of bimodal intensity.

PARTICLE ANALYSIS

A technique that binarized images are particularly useful for is particle analysis. This is the process of identifying and measuring the connected regions of one of the classes in the binary image. Taking the example of the binary image in Figure 4.7D, this is performed by first connected-component labelling, assigning a unique label to each group of edge and diagonally connected foreground pixels. Within each labelled connected components, various geometric values can be extracted, such as the area, perimeter, or circularity. Filtering can be applied to reject connected components from being counted as particles based on chosen criteria, such as insufficient area or circularity.

The perimeter is extracted by considering the number of orthogonal n_1 and diagonal n_2 steps of pixels delineating the connected component area. The perimeter P , in pixels, can be expressed as²⁷⁹:

$$P \approx n_1 + \sqrt{2}n_2 \quad (\text{Eqn 4.12})$$

If the dots per inch (dpi) resolution of the image is known, this pixel value may be converted into a real measure of length. Such particle analysis methods are useful in a variety of areas such as material science^{280, 281}, cell biology²⁸², and environmental monitoring²⁸³. In this work, particle analysis was applied to thresholded images of nanosheet films to assess their morphology and quality. This process is described in further detail in Chapter 7.

4.5 ELECTRICAL CHARACTERIZATION

Electrical characterisation is essential for evaluating prototype nanosheet thin films for device applications. The most basic relationship governing electrical transport is Ohm's law:

$$V = IR \quad (\text{Eqn 4.13})$$

where V is the voltage across the sample, I is the current through it, and R is its resistance. A voltage sweep with simultaneous current measurement provides a simple method of determining the sample resistance. Multiple resistance measurements on samples of known geometry, combined with thickness measurements, allow extraction of the electrical conductivity. This intrinsic transport property is a key performance metric for device applications.

While direct current (DC) measurements are straightforward, they cannot fully capture the charge transport behaviour of nanosheet networks, as will be discussed in Chapter 5. For this reason, alternating current (AC) measurements are often employed, enabling extraction of the electrical impedance as a function of frequency. This is the basis of impedance spectroscopy, a particularly useful technique for systems containing both resistive and reactive components.

4.5.1 TWO-PROBE MEASUREMENTS

In a two-probe configuration, the electrical resistance is measured between two contacts placed on the sample. The channel length and width are determined by the electrode geometry (Figure 4.8A). The resistance is calculated as the ratio of the applied voltage to the measured current within the linear regime.

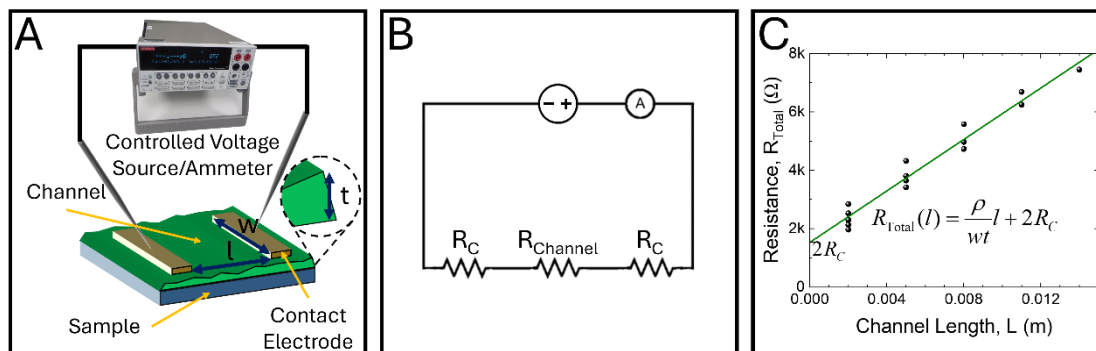


Figure 4.8: 2-Probe Measurements. A – Schematic of a two-probe measurement setup showing relevant channel dimensions. B – Circuit model of 2-probe measurement. C – Example TLM plot for extracting resistivity and contact resistance.

The measured resistance includes both the intrinsic resistance of the sample channel, $R_{Channel}$, and additional resistance from the electrical contacts. These include the resistances arising from the probe-electrode and electrode-film interfaces²⁸⁴. This combined resistance is referred to as the contact resistance R_C , illustrated in Figure 4.8B.

By contrast, in a four-probe configuration, current is sourced through an outer pair of electrodes, while the voltage drop is measured across an inner pair. As negligible current flows through the inner probes, the measured voltage is unaffected by contact resistance at the probe-electrode interfaces, allowing direct determination of the film resistance. However, accurate measurements require well-defined probe spacing and a uniform current distribution within the channel, an assumption that is often invalid for disordered nanosheet films near the percolation threshold (see Section 5.1). As an alternative, film

resistance can be determined from multiple two-probe measurements at varying electrode spacings using the Transmission Line Method (TLM).

TRANSMISSION LINE METHOD

In the circuit shown in Figure 4.8B, the total measured resistance can be expressed as:

$$R_{\text{Total}} = R_{\text{Channel}} + 2R_{\text{Contact}} \quad (\text{Eqn 4.14})$$

Assuming ohmic behaviour, the resistance of the channel R_{Channel} depends on the sample's resistivity (ρ), channel length (l), width (w), and thickness (t), given by:

$$R_{\text{Channel}} = \frac{l\rho}{wt} \quad (\text{Eqn 4.15})$$

Performing multiple two-probe measurements with varying channel lengths and plotting R_{Total} against l yields a transmission line plot, example shown in Figure 4.8C. This line can be expressed as:

$$R_{\text{Total}}(l) = \frac{\rho}{wt}l + 2R_{\text{Contact}} \quad (\text{Eqn 4.16})$$

From the slope of this line, the sample resistivity, and hence conductivity, can be determined, provided the channel width and film thickness are known. The intercept yields the contact resistance, a critical but often overlooked parameter when evaluating the performance of prototype devices.

The application of the Transmission Line Method relies on several assumptions. The contacts are assumed to be ohmic, such that the contact resistance is independent of applied voltage, and the film is assumed to be homogeneous, with uniform thickness and resistivity across all channel lengths. In addition, current spreading at the contacts is assumed to be consistent between channels, and edge effects are neglected. In practice, these assumptions may not be strictly satisfied for disordered nanosheet networks, particularly near the percolation threshold where conduction pathways are highly non-uniform (see Section 5.1),

and where film thickness may be ill-defined due to incomplete coverage. However, provided that resistance scales approximately linearly with channel length, TLM can still be used to extract effective transport parameters. Deviations from ideal behaviour typically manifest as scatter or non-linearity in the transmission line plot, and can be mitigated through averaging multiple fits or excluding outlying data points.

4.5.2 IMPEDANCE SPECTROSCOPY

As thin films of nanosheet are not monolithic, it is desirable to characterize complex charge transport phenomena within the ensemble of sheets, both to obtain greater theoretical insight into nanosheet networks and to assess key metrics of material and film performance. Electrical impedance spectroscopy (EIS) is a widely used technique for this purpose, probing frequency-dependent electrical response using alternating current (AC) sources. It is broadly applied in electrical engineering and electronic device characterization²⁸⁵⁻²⁸⁷. The measured frequency-dependent response can be interpreted in terms of charge transport parameters by fitting to equivalent circuit models, an approach commonly employed in electrochemical systems such as lithium-ion batteries, biosensors, and fuel cells²⁸⁸. In this work, the relevant model is the Randles circuit, shown in Figure 4.9C.

Circuit elements such as capacitors and inductors (Figure 4.9A), including the capacitor found in the Randles circuit, exhibit a frequency-dependent current response. The amount of current they allow to pass at a given voltage varies with voltage frequency ω . Additionally, they induce a phase shift, δ , between the input voltage and current signals, the magnitude and direction of which also depends on frequency. Both this change in magnitude and phase shift are shown graphically in Figure 4.9B. This behaviour is known as impedance, Z , which is the complex-number analogue of resistance in AC systems.

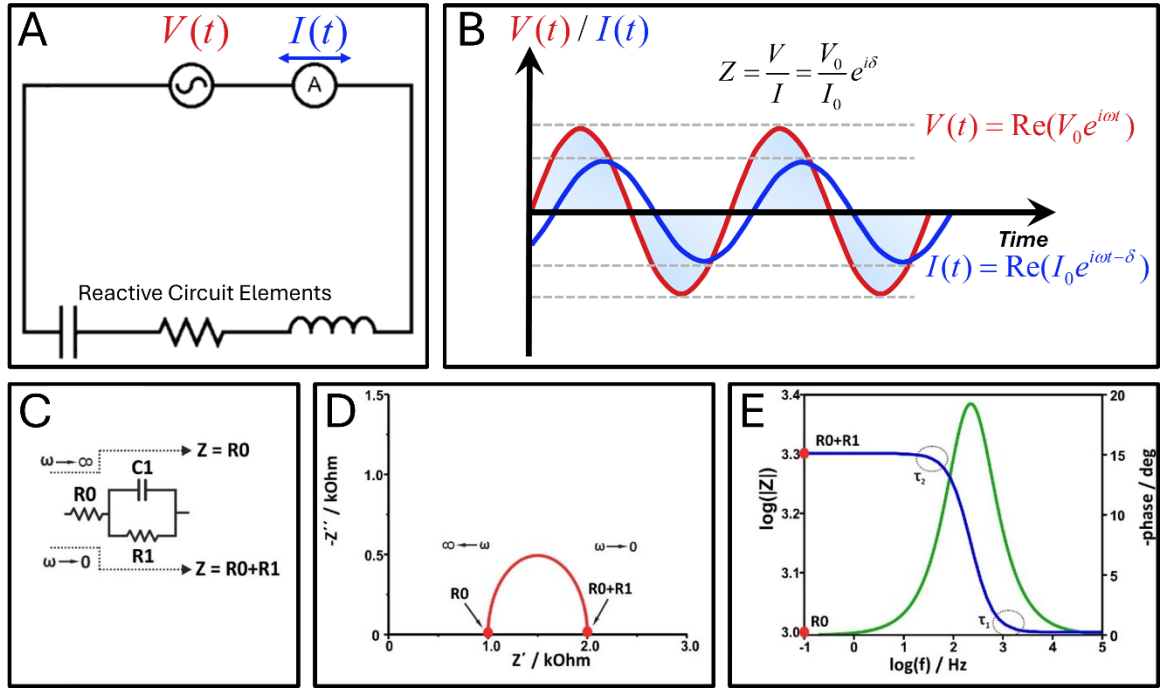


Figure 4.9: Impedance Spectroscopy. A – Impedance measurement circuit mode B – Example voltage and current waveforms showing the phase shift in a reactive system. C – The Randle's equivalent circuit. D – Nyquist or Cole-Cole plot of a Randle's circuit, the plot of imaginary vs. real impedance. E – The Bode plot of a Randle's circuit, consisting of the impedance magnitude (blue curve) and phase shift (green curve) plotted versus the input voltage frequency. Adapted from ref²⁸⁸.

From the magnitude of the current and the phase shift relative to the input voltage as in Figure 4.9B, the real and imaginary components of the impedance can be extracted. The applied AC voltage can be expressed as:

$$V(t) = \text{Re}(V_0 e^{i\omega t}) \quad (\text{Eqn 4.17})$$

where V_0 is the amplitude, ω is the angular frequency, and t is time. The corresponding current response is:

$$I(t) = \text{Re}(I_0 e^{i(\omega t - \delta)}) \quad (\text{Eqn 4.18})$$

where I_0 is the current amplitude and δ is the phase shift relative to the voltage. Using Ohm's law for AC systems, the impedance, Z , is defined as:

$$Z = \frac{V}{I} = \frac{V_0}{I_0} e^{i\delta} \quad (\text{Eqn 4.19})$$

The magnitude of the impedance is simply the ratio of voltage to current amplitudes:

$$|Z| = \frac{V_0}{I_0} \quad (\text{Eqn 4.20})$$

Hence the idea that in AC, impedance is analogous to DC resistance. To express the impedance in terms of its real and imaginary components, Euler's formula can be applied:

$$Z = \text{Re}(Z) + i\text{Im}(Z) = |Z| \cos(\delta) + i |Z| \sin(\delta) \quad (\text{Eqn 4.21})$$

These components can be visualized in several useful plots. A plot of $\text{Im}(Z)$ versus $\text{Re}(Z)$ is known as the Nyquist plot (see Figure 4.9D), which often reveals arcs or semicircles corresponding to distinct circuit elements, such as the Randles circuit shown in Figure 4.9C. A Bode plot (Figure 4.9E) represents the frequency-dependent response of a system in terms of both the magnitude of the complex impedance, $|Z|$ (blue curve), and the phase shift, δ (green curve). In the case of a Randles circuit, these plots provide complementary information to the Nyquist representation, allowing separation of resistive and capacitive contributions across different frequency regimes. Such representations allow for detailed interpretation of charge transport mechanisms in nanosheet networks when modelling using equivalent circuits, as will be explored in the following chapter.

"I think we all agree, the past is over."

George W. Bush

Chapter 5

Charge Transport in Nanosheet Networks

When dispersions of nanosheets are deposited as thin films, they form interconnected assemblies comprising billions of individual sheets, collectively referred to as nanosheet networks. Example SEM images of nanosheet networks produced by different deposition techniques are shown in Figure 5.1A and B. In these networks, each nanosheet is in physical contact with multiple neighbouring sheets. The nature of these contacts, or junctions (Figure 5.1C), governs charge transport through the film and thereby determines the macroscopic electrical properties of the network²⁰⁹.

The electrical conductivity of nanosheet networks is typically several orders of magnitude lower than that of an isolated nanosheet^{289, 290}, primarily due to the resistance of the aforementioned junctions. In device assemblies, networks span the electrodes via a series of sheets and junctions, forming multiple disordered conductive pathways. Due to this disorder, the collective contribution of such pathways to network conduction can be described by percolation theory.

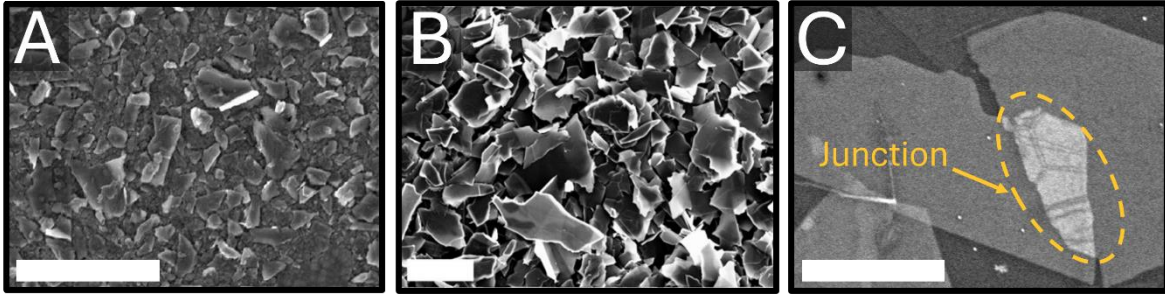


Figure 5.1: SEM Images of Nanosheet Networks & Inter-Nanosheet Junctions. A – Roll-to-roll liquid interface deposited LPE MoS₂ network. Scalebar: 0.5 μm. Adapted from ref²⁹¹. B – Spray coated LPE graphene network. Scalebar: 2 μm. Adapted from ref²⁹². C – Nanosheet junction within a network, showing inter-nanosheet contact, or a junction. Scalebar: 1 μm. Adapted from ref²⁹⁰.

5.1 PERCOLATION

Percolation theory provides a statistical framework for describing connectivity and critical phenomena in disordered systems²⁹³. It is widely used to model stochastic processes in fractal and complex structures, including the spread of forest fires²⁹⁴, oil recovery in porous rock²⁹⁵, and epidemic propagation²⁹⁶. In the modelling of such network systems (forests, porous rock, populations), a threshold concentration of active sites (flaming trees, pores, infected individuals) must be exceeded before a global connectivity transition occurs, such as a full blaze, oil flow, or an epidemic, respectively. For nanosheet networks, active sites are the conductive pathways formed by interconnected sheets, and the critical phenomenon is the emergence of conduction across the network.

Three regimes of percolation behaviour can be defined: subcritical, critical, and supercritical. These regimes are delineated by the percolation threshold ϕ_c (ie. the critical density of activated sites) and the percolation exponent n (ie. how rapidly the critical behaviour scales with activated site density). These quantities depend on the dimensionality and geometry of the system.

A simple model of percolation involves a square lattice of sufficient size to neglect boundary effects, in which the critical phenomenon is conduction between two opposite edges. Kirkpatrick proposed two versions of this model: one where site occupation provides the conductive nodes, and the other where bonds between the sites creates the nodes²⁹⁷. As the site or bond occupation probability increases, clusters of connected sites form and grow. When the system reaches the percolation threshold, a lattice-spanning cluster appears with high probability. From these models, a power-law expression for conductivity σ was derived as a function of conductive nodes ϕ :

$$\sigma = \sigma_C (\phi - \phi_C)^n \quad (\text{Eqn 5.1})$$

where σ_C is a non-physical constant of proportionality. In idealized infinite lattices, the percolation exponent depends only on the system dimensionality, with $n_{2D} = 1.3$ and $n_{3D} = 2$ ²⁹⁸. However, experimental systems, such as carbon nanotube-polymer composites, often exhibit values that diverge from this due to variability in the inter-site conductivities^{299, 300}.

In the context of nanostructured networks, percolation is typically described as a function of film thickness, though it may also be expressed in terms of the number of nanosheets per unit area^{206, 301}. A plot showing percolation scaling with thickness is plotted in Figure 5.2A, known as a percolation plot. Below the percolation thickness $t < t_C$, nanosheets are distributed as isolated islands (Figure 5.2B), the subcritical regime where no conductivity is observed. At $t = t_C$, inter-nanosheet contacts begin to form, resulting in tortuous pathways that span the network (Figure 5.2C). In this critical regime, conductivity increases superlinearly with film thickness. At a higher bulk thickness transition thickness t_x , the network becomes saturated with conductive paths (Figure 5.2D). This is the supercritical

regime, where the conductivity reaches a constant bulk value σ_B . These transitions are critical phenomena and are well-described by percolation scaling laws.

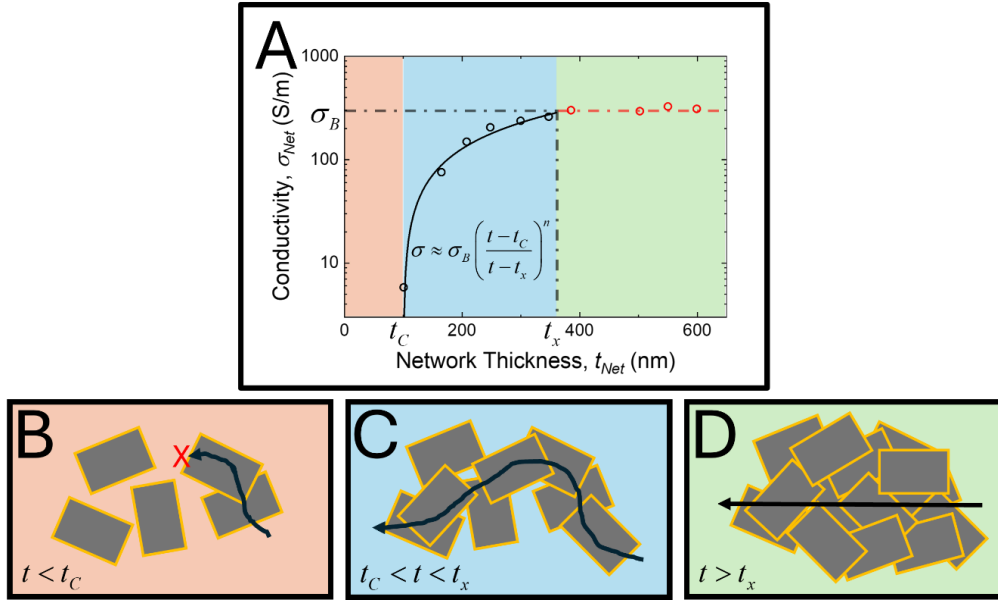


Figure 5.2: Percolation in Nanosheet Networks. A – Percolation plot for LPE graphene networks, showing how conductivity σ scales with thickness t over three percolation regimes, defined by the percolation threshold t_C , bulk conductivity thickness t_x , bulk conductivity σ_B , and the percolation exponent n . Data from ref³⁰². B – subcritical regime: disconnected nanosheet islands, no conduction. C – Critical regime: formation of tortuous conductive paths, thickness-dependent conductivity. D – Supercritical regime: saturated network with bulk conductivity independent of thickness.

A simple model that captures the behaviour in the critical regime is derived by replacing the conductive volume fraction in Eqn 5.1 with network thickness:

$$\sigma = \sigma_C (t - t_C)^n \quad (\text{Eqn 5.2})$$

This model can provide a reasonable fit in the critical region, but the prefactor σ_C lacks physical meaning. Caffrey et al. proposed an alternative expression that yields physically interpretable parameters⁶⁴:

$$\sigma \approx \sigma_B \left(\frac{t - t_C}{t - t_x} \right)^n \quad (\text{Eqn 5.3})$$

Hence the bulk conductivity σ_B is reached when $t = t_x$. However, it does not enforce conductivity saturation in the supercritical regime and introduces challenges in fitting, such as the need to manually determine t_x , which can limit reproducibility. Additionally, reliable extraction of σ_B requires extensive data in the supercritical region above t_x , which can require fabrication of an arduous number of samples with impractical amounts of material. A modelling framework that fits both critical and supercritical regions simultaneously would be preferred.

5.1.1 PERCOLATION MODELLING

A widely used approach for describing the resistivity of thin metallic films is the Fuchs-Sondheimer model, which considers the effect of surface scattering of electrons on electrical transport³⁰³. This model expresses the thin film resistivity, ρ , as the sum of the bulk resistivity, ρ_B , and an additional term inversely proportional to the film thickness t :

$$\rho = \rho_B \left[1 + \frac{3}{8} (1 - p) \frac{\lambda}{t} \right] \quad (\text{Eqn 5.4})$$

where λ is the bulk mean free path and p is the parameter representing the probability of specular electron reflection from the surface. Later models have analysed thin film resistivity in terms of surface roughness, again finding the resistivity to be equal to the bulk value plus an additive factor dependent on thickness. For example, Zhou et al.³⁰⁴ reported the following expression for rough thin films:

$$\rho = \rho_{\text{ff}} + \rho_B \sqrt{\frac{3}{2}} \frac{\lambda}{\xi} \frac{\Delta t}{t} \quad (\text{Eqn 5.5})$$

where ρ_{ff} is the resistivity of a perfectly flat film as described by Eqn 5.4, Δt is the roughness, and ξ is the correlation length associated with the surface roughness. However, this expression contains no percolative component or nonlinear scaling characteristic of nanosheet films.

Percolative behaviour can be considered intrinsic to rough films because, during deposition, there exists a minimum conductive material thickness required for the formation of continuous conductive paths. As addressed, this defines a percolation threshold t_c . An illustrative case is the one-dimensional rough film model in Figure 5.3, with mean thickness t and roughness Δt .

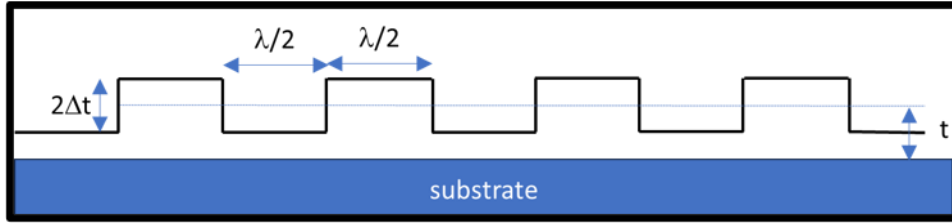


Figure 5.3: 1-D Model of a Rough Thin Film. 1D model of a thin film with mean thickness, t , and roughness, Δt .

The resistivity of the above may be approximated (see Appendix Section A.1.1) as:

$$\rho \approx \frac{\rho_{ff}}{2} \left[1 + \frac{t}{t - \Delta t} \right] \quad (\text{Eqn 5.6})$$

This equation is percolative in form, with Δt analogous to t_c , and predicts a divergence in resistivity as $t \rightarrow \Delta t$, capturing the subcritical regime.

However, Eqn 5.6 is insufficient for describing the critical regime in nanosheet films, where resistivity can change by orders of magnitude with thickness. For a model capable of capturing such behaviour, Zhou et al.³⁰⁴ combined Eqn 5.4 with a model by Namba et al.³⁰⁵ to yield:

$$\rho = \rho_{\text{ff}} + \frac{3}{8}(1-p)\rho_B \frac{\lambda(\Delta t)^2}{t^3} \quad (\text{Eqn 5.7})$$

The t^3 term in the denominator gives a rapid resistivity decrease with increasing thickness, before saturation at large t . However, this formulation still lacks an explicit percolative scaling term.

To address this, a generalized expression can be proposed, in which the resistivity is expressed as the bulk resistivity plus an additive percolative term:

$$\rho = \rho_B + \frac{\rho_0}{(t-t_c)^n} \quad (\text{Eqn 5.8})$$

this expression shares features with Eqn 5.2 and Eqn 5.6 (percolative scaling), Eqn 5.4 and Eqn 5.5 (an additive $1/t$ term) and Eqn 5.7 (an additive $1/t^n$ term).

By defining t_x such that $\sigma(t_x) = 0.8\sigma_B$, or equivalently $\rho(t_x) = 5/4 \cdot \rho_B$, Eqn 5.8 can be rewritten (see Appendix Section A.1.1) as:

$$\rho = \rho_B \left[1 + \frac{1}{4} \left(\frac{t_x - t_c}{t - t_c} \right)^n \right] \quad (\text{Eqn 5.9})$$

where the 80% σ_B criterion for t_x provides a consistent operational marker for the onset of bulk-like conduction. Alternatively, expressing Eqn 5.9 in terms of network conductivity gives:

$$\sigma = \sigma_B \left[1 + \frac{1}{4} \left(\frac{t_x - t_c}{t - t_c} \right)^n \right]^{-1} \quad (\text{Eqn 5.10})$$

This model incorporates all percolation regimes. To assess its validity, the expression was fitted to experimental conductivity-thickness data reported by Caffrey et al.⁶⁴, using parameters $\sigma_B = 260 \text{ S/m}$, $t_x = 160 \text{ nm}$, $t_c = 42 \text{ nm}$, $n = 2.8$. As shown in Figure 5.4, the model provides an excellent description of the measured behaviour across the full thickness range, accurately capturing both the critical and supercritical regimes. This demonstrates

that the model is consistent with experimental observations, and it will be further evaluated against additional data in Chapter 7.

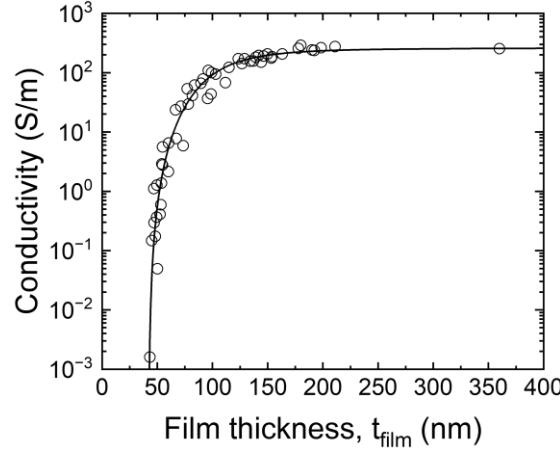


Figure 5.4: Fit of Percolation Model. Conductivity versus thickness data provided from Caffrey *et al.*⁶⁴ fitted using Eqn 5.10 with parameters $\sigma_B = 260 \text{ S/m}$, $t_x = 160 \text{ nm}$, $t_c = 42 \text{ nm}$, $n = 2.8$.

5.2 JUNCTION RESISTANCE IN NANOSHEET NETWORKS

As noted previously, charge transport in nanosheet networks is significantly hindered compared with transport through an isolated nanosheet. The conductive pathways within a network can be represented as a series of resistive elements corresponding to individual nanosheets and their interconnecting junctions, as illustrated in Figure 5.5. Charge carriers traverse the network through nanosheets, encountering a nanosheet resistance R_{NS} , and through nanosheet–nanosheet junctions, encountering a junction resistance, R_J .

R_{NS} is an intrinsic material property, determined by the electronic structure, defect density, carrier concentration, and dimensions of the nanosheets. R_J arises from the nature of the nanosheet junctions, where conduction occurs via charge hopping or tunnelling between adjacent nanosheets^{306, 307}. The degree of overlap between nanosheets and the presence of impurities within the junction space directly impact R_J , as will be discussed in Section 5.4. To relate these microscopic resistive elements to macroscopic electrical properties of a

network, and hence provide methods for measuring them, models for network charge transport in DC and AC current modes may be considered.

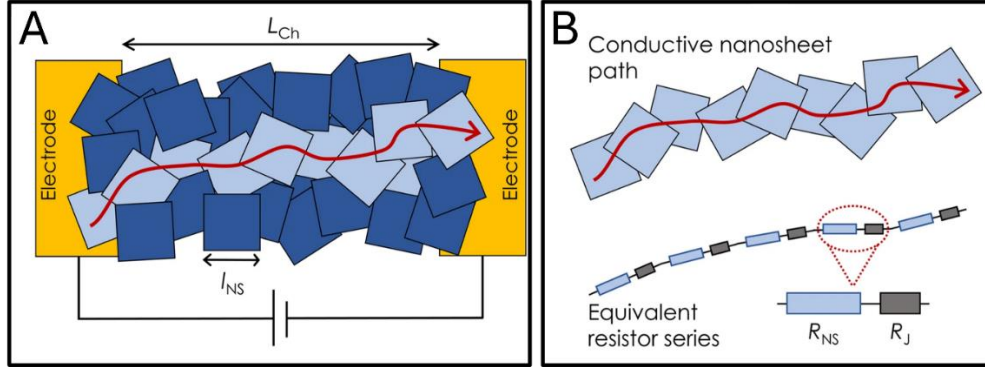


Figure 5.5: Nanosheet Network DC Resistor Model. A – Schematic of a nanosheet network, with a conductive pathway highlighted. B – An equivalent resistor series for one such conductive pathway, showing the origin of nanosheet resistance R_{NS} and junction resistance R_J . Adapted from ref²⁸⁹.

5.2.1 DC NETWORK MODEL

Gabbett et al. developed a DC resistivity model for an ensemble of resistors in series, each consisting of nanosheet-junction pairs forming the conductive pathways in a network (Figure 5.5B). Their model relates network parameters, nanosheet parameters, R_{NS} , and R_J to macroscopic network resistivity²⁸⁹:

$$\rho_{Net} \approx \frac{2t_{NS}\kappa_{Net}}{1-P_{Net}} [R_{NS} + R_J] \left[1 + \frac{2}{n_{NS}t_{NS}l_{NS}^2} \right] \quad (Eqn 5.11)$$

where ρ_{Net} is the network resistivity, t_{NS} is the average nanosheet thickness, κ_{Net} is the network tortuosity factor, P_{Net} is the network porosity, n_{NS} is the nanosheet carrier density, and l_{NS} is the average nanosheet length. The basis of the derivation is to consider the geometry and voltage drop across the nanosheet-junction pairs along a given current path, as well as the transit time τ of charge carrier within nanosheets and across junctions. This

is available in full in the Gabbett et al. paper supplementary information²⁸⁹, and is reproduced in Appendix Section A.1.2 for convenience.

From Eqn 5.11, two different conduction regimes exist, depending on the carrier density. For low carrier density nanosheets, such as semiconductors, there is much less than one carrier per sheet, and so $n_{\text{NS}} \ll (t_{\text{NS}} l_{\text{NS}}^2)^{-1}$. The leading term becomes negligible, giving:

$$\rho_{\text{Net}} \approx \frac{4(R_{\text{NS}} + R_J)\kappa_{\text{Net}}}{(1 - P_{\text{Net}})n_{\text{NS}}l_{\text{NS}}^2} \Rightarrow \sigma_{\text{Net}} \approx \frac{(1 - P_{\text{Net}})n_{\text{NS}}l_{\text{NS}}^2}{4(R_{\text{NS}} + R_J)\kappa_{\text{Net}}} \quad (\text{Eqn 5.12})$$

Conversely, for high carrier density nanosheets, such as highly doped semiconductors or metals, $n_{\text{NS}} \gg (t_{\text{NS}} l_{\text{NS}}^2)^{-1}$. In this case, the carrier density term becomes negligible:

$$\rho_{\text{Net}} \approx \frac{2t_{\text{NS}}\kappa_{\text{Net}}}{1 - P_{\text{Net}}} [R_{\text{NS}} + R_J] \Rightarrow \sigma_{\text{Net}} \approx \frac{1 - P_{\text{Net}}}{2t_{\text{NS}}(R_{\text{NS}} + R_J)\kappa_{\text{Net}}} \quad (\text{Eqn 5.13})$$

Within each regime, cases arise depending on the relative magnitude of R_J and R_{NS} :

Case 1: low n_{NS} , $1 \ll 2(n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2)^{-1}$, limited by junction resistance $R_J / R_{\text{NS}} \gg 1$:

$$\sigma_{\text{Net}} \approx \frac{(1 - P_{\text{Net}})n_{\text{NS}}l_{\text{NS}}^2}{4R_J\kappa_{\text{Net}}} \quad (\text{Eqn 5.14})$$

Case 2: low n_{NS} , $1 \ll 2(n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2)^{-1}$, with low junction resistance $R_J / R_{\text{NS}} \ll 1$:

$$\sigma_{\text{Net}} \approx \frac{(1 - P_{\text{Net}})n_{\text{NS}}l_{\text{NS}}^2}{4R_{\text{NS}}\kappa_{\text{Net}}} = \frac{\sigma_{\text{NS}}(1 - P_{\text{Net}})n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2}{2\kappa_{\text{Net}}} \quad (\text{Eqn 5.15})$$

recalling from Appendix Section A.1.2, $\rho_{\text{NS}} = R_{\text{NS}} 2t_{\text{NS}}$, therefore $R_{\text{NS}} = (\sigma_{\text{NS}} 2t_{\text{NS}})^{-1}$.

Case 3: high n_{NS} , $1 \gg 2(n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2)^{-1}$, with high junction resistance $R_J / R_{\text{NS}} \gg 1$:

$$\sigma_{\text{Net}} \approx \frac{1 - P_{\text{Net}}}{2t_{\text{NS}}R_J\kappa_{\text{Net}}} \quad (\text{Eqn 5.16})$$

Case 4: high n_{NS} , $1 \gg 2(n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2)^{-1}$, with low junction resistance $R_J / R_{\text{NS}} \ll 1$:

$$\sigma_{\text{Net}} \approx \frac{1 - P_{\text{Net}}}{2t_{\text{NS}} R_{\text{NS}} \kappa_{\text{Net}}} = \frac{\sigma_{\text{NS}} (1 - P_{\text{Net}})}{\kappa_{\text{Net}}} \quad (\text{Eqn 5.17})$$

Eqns 5.14 – 5.17 predict diverse conduction behaviours for networks of various types of nanosheet and sheet morphologies. While these DC models are useful for calculating junction parameters from conductivity data, a more direct measurement technique would be preferable. To this end, modelling of network conduction in the AC mode is needed.

5.2.2 AC NETWORK MODEL

Gabbett et al. further modelled the AC behaviour of a nanosheet network using Eqn 5.11, expressing the impedance of the network, Z_{Net} , in terms of the impedance of a single nanosheet-junction pair, $Z_{\text{NS-J}}$ ²⁸⁹:

$$Z_{\text{NS-J}} \approx \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{1 - P_{\text{Net}}}{2t_{\text{NS}} \kappa_{\text{Net}}} Z_{\text{Net}} \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2} \right]^{-1} \quad (\text{Eqn 5.18})$$

This derivation is also available in the supplementary information of the work by Gabbett et al.²⁸⁹, and is reproduced in Appendix Section A.1.3 for convenience.

Modelling junctions as simple ohmic resistors is insufficient in the AC mode. Instead, a modelling approach, taken from the analysis of grain boundaries³⁰⁸⁻³¹⁰, is to use the Randles circuit, shown in Figure 5.6A. Randles circuits have long been used to model the behaviour of interfaces in electrochemical systems, incorporating both the kinetic process of charge transfer and the double layer capacitance at the interface³¹¹.

In the AC circuit model, conductive pathways in nanosheet networks are represented as multiple Randles circuits connected in series, with each circuit element corresponding to a nanosheet-junction pair (Figure 5.6A). The number of pairs in series along an average conductive path is denoted by n . The network comprises m such conductive paths connected in parallel. Applying Kirchhoff's laws, Gabbett et al. showed that these n -chained Randles circuits connected m -fold in parallel can be reduced to a single

macroscopic Randles circuit²⁸⁹ (Figure 5.6B). As shown in the reproduced derivation in Appendix Section A.1.4, the series resistance R_s reflects the intrinsic resistance of the nanosheets R_{NS} together with the contact resistance R_C . The parallel resistance R_p accounts for the resistive contribution of junctions R_J as well as structural disorder within the network. Finally, the parallel capacitance C_p represents the capacitive response associated with the junctions C_J .

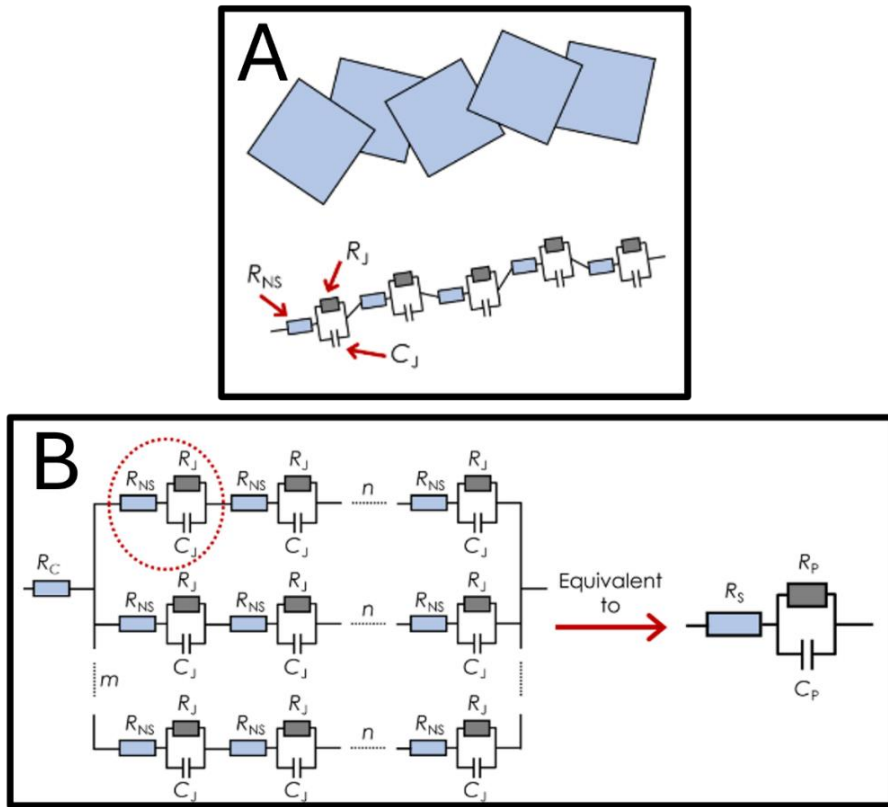


Figure 5.6: Randles Equivalent Circuits. A – Nanosheet network conductive pathway, with Randles circuit model shown giving the origins of nanosheet resistance R_{NS} , junction resistance R_J , and junction capacitance C_J . B – Schematic showing how the Randles circuit pathway ensemble is equivalent to one single Randles circuit, containing series resistance R_s (which contains R_{NS} and the contact resistance R_C), parallel resistance R_p , and parallel capacitance C_p . Adapted from ref²⁸⁹.

In the case of a nanosheet networks, this approach leads to the notion of a junction capacitance C_J in parallel with a resistive element R_J , both connected in series to R_{NS} . This better reflects the junctions' nature as being charge hopping barriers of two large conductive planes separated by a dielectric or insulating gap.

It can be shown²⁸⁸, using the impedance values for resistive ($Z = R$) and capacitive ($Z = i / \omega C$) circuit elements, and combining using Kirchoff's laws, that the impedance of the Randles equivalent circuit shown in Figure 5.6B is:

$$Z_{\text{Net}}(\omega) = R_S + \frac{R_p}{1 + (\omega R_p C_p)^2} - \frac{\omega R_p^2 C_p}{1 + (\omega R_p C_p)^2} i \quad (\text{Eqn 5.19})$$

hence the real and imaginary impedance ($\text{Re}(Z_{\text{Net}}(\omega))$ and $\text{Im}(Z_{\text{Net}}(\omega))$ respectively), in the simplest case, may be decoupled and described by:

$$\text{Re}(Z_{\text{Net}}(\omega)) = R_S + \frac{R_p}{1 + (\omega R_p C_p)^2} \quad (\text{Eqn 5.20})$$

$$-\text{Im}(Z_{\text{Net}}(\omega)) = \frac{\omega R_p^2 C_p}{1 + (\omega R_p C_p)^2} \quad (\text{Eqn 5.21})$$

Therefore R_S , R_p , and C_p can be obtained by fitting of the impedance spectra and Nyquist plots shown in Figure 5.7A and B. Each will be detailed in terms of fitting in the following section.

5.3 INTERPRETING IMPEDANCE SPECTROSCOPY

As mentioned in Chapter 4 Section 4.5.2, Bode plots represent the magnitude and phase of the complex impedance as a function of frequency. In this work, however, the real and imaginary components of the impedance are plotted directly as functions of frequency ω (Figure 5.7A), referred to here as the real and imaginary impedance spectra, respectively. These spectra provide equivalent information to conventional Bode plots for the analysis of Randles-type circuits.

For the Randles circuit, the real impedance spectrum appears as a plateau in the high frequency and low frequency domains, with logistical curve going between them. In the low frequency domain, the reactance of the capacitive element becomes infinite ($X_C = (\omega C)^{-1}$), and so all current passes through the R_p resistor. Hence the real impedance becomes $Z_{Net} = R_S + R_p$. In the high frequency domain, the reactance of the capacitive element goes to zero, with the C_p capacitor shorting the R_p resistor. Hence the real impedance becomes $Z_{Net} = R_S$. For frequencies between these regimes, a variation in impedance occurs due to the finite reactance of the capacitor, decreasing with increasing frequency. Fitting of this plot to Eqn 5.20 hence allows determination of R_S and R_p .

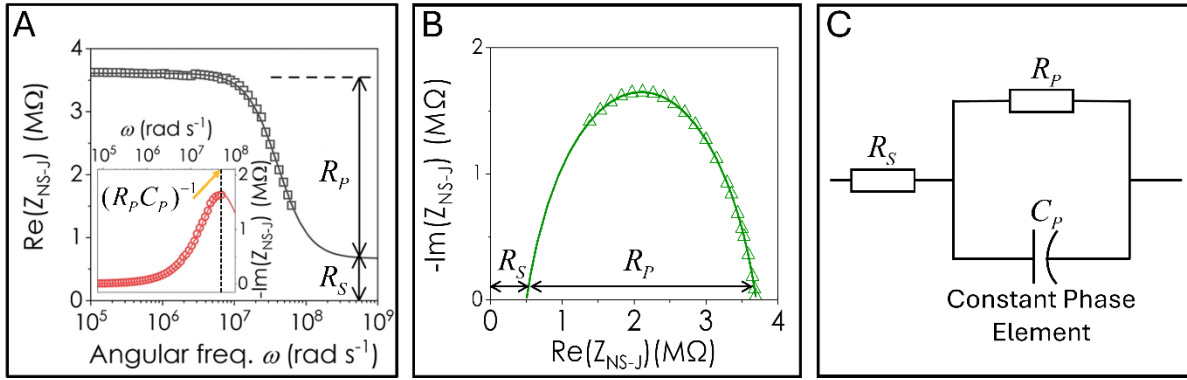


Figure 5.7: Impedance spectra and Nyquist Plots, Modified Randles Circuit. A – Impedance spectra for a nanosheet network of the real impedance and imaginary impedance (inset), both with respect to input signal frequency, showing how the parallel resistance R_p and series resistance R_S are obtained from these spectra. Adapted from ref²⁸⁹. B – Nyquist plot for a nanosheet network of imaginary versus real impedance, showing how R_p and R_S are obtained. C – Modified Randles circuit model, with constant phase element (CPE) in place of capacitor to reflect junction variability.

Another impedance spectrum is the imaginary impedance $\text{Im}(Z_{Net})$ against frequency ω (Figure 5.7A inset). In the case of the Randles circuit, this plot captures the frequency-dependent phase shift, and as such can be considered analogous to the Bode phase plot

shown in Chapter 4 Figure 4.9E. It can be shown²⁸⁸ that the frequency at the peak of this plot (ie. maximum phase shift) is the inverse of the time constant of the Randles circuit τ :

$$\omega_{\min(\text{Im}(Z_{\text{Net}}))} = \tau^{-1} = \frac{1}{R_p C_p} \quad (\text{Eqn 5.22})$$

As such, fitting of the imaginary impedance spectrum to Eqn 5.21 allows determination of C_p and validation of R_p and R_s values acquired from the real impedance spectrum.

The Nyquist plot is a plot of the imaginary versus real components of the impedance. When the Nyquist of a Randles circuit is plotted, it produces a semi-circular shape (Figure 5.7B). Again, the real impedance varies from $R_s + R_p$ in the low frequency domain to R_s in the high frequency domain, with a vanishing imaginary component of the impedance in each. As in Figure 5.7B, this respectively delineates the right and left edges of the semicircle. The middle of this, $(R_s + R_p)/2$ is hence the centre of the semicircle and the peak of $\text{Im}(Z_{\text{Net}})$ with respect to $\text{Re}(Z_{\text{Net}})$. The form of the Nyquist plot can be described as:

$$[\text{Im}(Z_{\text{Net}}(\omega))]^2 = [R_p + R_s - \text{Re}(Z_{\text{Net}}(\omega))][\text{Re}(Z_{\text{Net}}(\omega)) - R_s] \quad (\text{Eqn 5.23})$$

hence fitting of this plot can also be used to determine R_p and R_s , to validate fitting from the impedance spectra curves.

As is shown in Appendix Section A.1.4, the impedance of the network can be related to the impedance of a NS–J pair by the m/n factor, where n is the number of junctions along a conductive path and m is the number of such paths in parallel (Figure 5.6). From Eqn 5.18, this factor can be expressed as:

$$\frac{m}{n} = \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{1 - P_{\text{Net}}}{2t_{\text{NS}} \kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2} \right]^{-1} \quad (\text{Eqn 5.24})$$

Hence, expressing R_s , R_p , C_p in terms of their microscopic analogues:

$$R_{\text{NS}} = (R_S - R_C) \frac{m}{n} = (R_S - R_C) \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{1 - P_{\text{Net}}}{2t_{\text{NS}} \kappa_{\text{Net}}} Z_{\text{Net}} \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2} \right]^{-1} \quad (\text{Eqn 5.25})$$

$$R_J = R_P \frac{m}{n} = R_P \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{1 - P_{\text{Net}}}{2t_{\text{NS}} \kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2} \right]^{-1} \quad (\text{Eqn 5.26})$$

$$C_J = C_P \frac{n}{m} = C_P \frac{L_{\text{Ch}}}{A_{\text{Net}}} \frac{2t_{\text{NS}} \kappa_{\text{Net}}}{1 - P_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2} \right] \quad (\text{Eqn 5.27})$$

These quantities, combined with Eqn 5.11 and related expressions, allow extraction of nanosheet and network conductivities and mobilities from a single impedance measurement on a nanosheet network.

5.3.1 LIMITATIONS OF IDEAL NETWORK MODEL

The above expressions assume that all nanosheet–junction (NS–J) pairs are identical, with uniform R_J and C_J throughout the network. In addition, the nanosheets are treated as having uniform lateral size and thickness, such that effects arising from flake size polydispersity are neglected. Under these assumptions, the network can be represented by repeated identical Randles elements, enabling analytical reduction to a macroscopic equivalent circuit detailed above.

In practice, however, nanosheet networks are highly disordered. Variations in flake size, overlap geometry, and junction quality give rise to a distribution of resistive and capacitive elements across the network. This leads to deviations from ideal Randles behaviour, most notably in the form of depressed semicircles in Nyquist plots and non-ideal frequency response in impedance spectra.

To account for this disorder, the C_P capacitor in the Randles circuit can be modelled as a constant phase element (CPE), as shown in Figure 5.7C. The resulting deviation from ideal behaviour can be quantified by the order parameter, α , obtained by fitting the Nyquist and impedance spectra to modified versions of Eqn 5.23, Eqn 5.21 and Eqn 5.20. This extends

the Randles equivalent circuit model to non-ideal nanosheet networks and provides a measure of network homogeneity ($\alpha = 1$ corresponding to an ideal homogeneous system, with $0 < \alpha < 1$ indicating increasing inhomogeneity as α decreases). The modified expression for the real impedance spectrum is given by:

$$\text{Re}(Z_{\text{Net}}(\omega)) = R_s + R_p \frac{[1 + (\omega R_p C_p)^\alpha \cos(\alpha\pi / 2)]}{1 + 2(\omega R_p C_p)^\alpha \cos(\alpha\pi / 2) + (\omega R_p C_p)^\alpha} \quad (\text{Eqn 5.28})$$

This expression forms the basis for fitting experimental network impedance spectra, with the inclusion of the order parameter α in oscillating and power terms accounting for variability in junction properties across the network.

It must be noted that knowing the network tortuosity and porosity are key in measuring these network conduction quantities. Furthermore, while the junction resistance has been addressed at length, the specific factors that influence its magnitude have yet to be considered. As such, we will turn to a discussion of nanosheet network properties in the context of junction resistance.

5.4 NETWORK PROPERTIES

Nanosheet networks possess a number of morphological features that critically influence their charge transport behaviour. As previously outlined, the porosity of the network P_{Net} , and the tortuosity κ_{Net} of conductive pathways affect the overall conductivity according to:

$$\sigma_{\text{Net}} \propto (1 - P_{\text{Net}}) \quad (\text{Eqn 5.29})$$

$$\sigma_{\text{Net}} \propto \kappa_{\text{Net}}^{-1} \quad (\text{Eqn 5.30})$$

These two network quantities are illustrated graphically in Figure 5.8A and B.

Further to these is the magnitude of R_j . In most practical cases, junction-limited condition

$R_j \gg R_{\text{NS}}$ applies. Under such conditions, R_j directly governs the network conductivity:

$$\sigma_{\text{Net}} \propto \frac{1}{R_j} \quad (\text{Eqn 5.31})$$

The magnitude of R_j is determined by the structure of nanosheet–nanosheet junctions. Broadly, the morphological factors influencing junction resistance are: nanosheet overlap area and conformality of nanosheets, the alignment of the nanosheets, and the presence of impurities in between the nanosheets. Each of these will be addressed in turn.

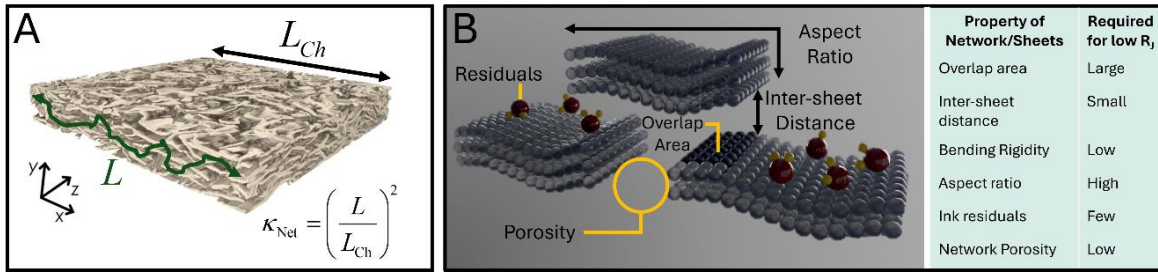


Figure 5.8: Network & Nanosheet Properties that Influence Junction Resistance. A – FIB-SEM nanotomography image of a network, illustrating the network tortuosity factor κ_{Net} . Adapted from ref²⁹². B – Schematic of the different factors that influence junction resistance. Adapted from ref²⁰⁹

5.4.1 OVERLAP AREA & CONFORMALITY

Nanosheet junctions act as a variable range charge hopping barrier^{307, 312-314}. The tunnelling conductance across a junction increases with the effective area, as a larger area provides more parallel conduction pathways. Consequently, increasing the *overlap area* reduces R_j . Additionally, decreasing the *inter-sheet distance* also reduces R_j , due to the exponential dependence of hopping probability on separation²⁸⁹. These factors are illustrated and listed in Figure 5.8B.

To maximise overlap area, it is intuitive to require nanosheet lateral size L_{NS} to be large. Large lateral size sheets have large basal plane area, hence large area overlaps, and thus reduced R_j . However, large lateral size alone is insufficient to describe overlap when also considering the inter-sheet distance. Mechanically rigid nanoparticles, such as thick

nanosheets, have been shown to form jammed systems³¹⁵. Such jamming prevents conformal contact of nanosheets and produces small, point-like junctions (Figure 5.9A) with low overlap and large intersheet distance, therefore high R_j . Large and thin nanosheets, with low *bending rigidity* D , are therefore required.

For few-layer 2D materials, bending rigidity scales as $D \propto t_{\text{NS}}^n$ ($1 < n < 3$, increasing from $n=1$ for monolayer and $n=3$ for bulk)³¹⁶. Kelly et al. modelled that two nanosheets of length L_{NS} , with inter-nanosheet adhesion energy γ , at contact angle θ will only mechanically conform to each other when the energy stabilization from adhesion exceeds the energy penalty associated with bending²⁰⁹:

$$D < \frac{\gamma L_{\text{NS}}^2}{4\theta^2} \quad (\text{Eqn 5.32})$$

Rearranging, taking $D \approx k t_{\text{NS}}^2$ ($n \approx 2$ for $6 < N < 15$, N : nanosheet layer number) where k is an arbitrary constant, this may be rewritten as:

$$\frac{L_{\text{NS}}}{t_{\text{NS}}} > \sqrt{\frac{4\theta^2 \alpha}{\gamma}} \quad (\text{Eqn 5.33})$$

As θ , α , and γ are constants of the nanosheet system, this implies there is a minimum value of the length-thickness aspect ratio $L_{\text{NS}}/t_{\text{NS}}$ above which conformality occurs. This has been shown by Kelly et al. for MoS₂ to be $L_{\text{NS}}/t_{\text{NS}} > 40$, corresponding to a bending rigidity $D \approx 3.5 \times 10^4$ eV. Hence this requirement is better stated as *high nanosheet aspect ratio* $L_{\text{NS}}/t_{\text{NS}}$ rather than simply low nanosheet thickness.

Therefore, from the above there is a need for nanosheets that are large in lateral size with high length-thickness aspect ratio. As discussed in Chapter 3, electrochemical exfoliation is a suitable method for producing such nanosheets, and as such was employed in this work.

5.4.2 NANOSHEET ALIGNMENT

Parallel alignment of nanosheets maximizes basal-plane overlap and minimizes initial contact angle, hence increasing conformality, both of which favour low R_f . Both considerations require some means of preferentially aligning the nanosheets in the network.

Non-contact methods such as inkjet printing and spray coating tend to have randomly oriented nanosheets, due to their suspension in liquid droplets prior to drying on the substrate²⁰⁹. Such random orientation can be seen in the network images in Figure 5.8A and Figure 5.9A, which have small point-like junctions with high R_f . Additionally, random sheet orientation creates pores and more tortuous conductive pathways, increasing P_{Net} and κ_{Net} .

As discussed in Chapter 4, alignment can be induced by methods such as spin coating, where centrifugal force align sheets¹⁹¹ (see Figure 5.9C), or liquid interface deposition, where interfacial tension drives alignment²⁴¹. Such methods provide a method of creating aligned nanosheet networks³¹⁷. As such, liquid interface deposition was used as the deposition method of choice in this work.

5.4.3 INTERFACIAL IMPURITIES

As has been mentioned in Chapter 3, solution-based fabrication of nanosheet inks often employs dispersants and high-boiling-point solvents to stabilise exfoliated nanosheets in solution. Although post-exfoliation washing and re-dispersion in low-boiling solvents (e.g. IPA), can reduce the concentration of these species, complete removal is uncommon. These *ink residuals* adsorb to nanosheet surfaces and become trapped at junctions after network deposition³¹⁸ (see Figure 5.8B).

These impurities increase inter-sheet separation through steric hindrance, raising R_j as the tunnelling barrier is widened. Additionally, they are typically covalent molecules with poor charge transport properties, further increasing R_j . Thermal annealing is commonly used as a post-deposition processing technique to remove these residues in the junctions, either by evaporation at low temperature or decomposition at higher temperature²⁰⁹. This process induces a collapse of the network structure³¹⁸, reducing both porosity and inter-sheet distance, thereby lowering R_j ³¹⁴.

However, most 2D materials are sensitive to oxidation at elevated temperatures, so care must be taken to perform thermal annealing in inert or vacuum conditions. Many flexible substrates, such as PET, have restrictive thermal budgets (PET's glass transition temperature: $\sim 70^\circ\text{C}$)³¹⁹. Complex post-processing also diminishes the low-cost and ease of fabrication of nanosheet devices. Therefore, care must be taken to select appropriate annealing temperatures and conditions.

Complete removal of residual stabilising species prior to deposition would be desirable, and can in principle be pursued either by stabiliser-free exfoliation³²⁰⁻³²² or by more aggressive post-exfoliation purification¹⁵⁷. However, both approaches are challenging. In solution-processing, stabiliser-free routes generally rely on carefully matched solvents and typically produce comparatively dilute or less shelf-stable dispersions, while aqueous systems without dispersants suffer more strongly from reaggregation. Likewise, enhanced washing can reduce residual surfactant, polymer, or solvent content, but repeated centrifugation and redispersion steps often lower yield, broaden batch-to-batch variability, and can alter the nanosheet size distribution through preferential loss of smaller or less well-stabilised flakes. For these reasons, residue minimisation is usually a trade-off between colloidal stability, yield, and final electronic performance rather than a simple purification step.

5.4.4 JUNCTION REGIMES

Taking together the above considerations, Kelly et al. identified 3 possible morphological regimes for MoS₂ networks based on nanosheet alignment: oblique alignment, edge-edge alignment, and basal-plane alignment²⁰⁹ (Figure 5.9A-C). The network mobility varies greatly between these 3 regimes, which indicates 3 different orders of junction resistance.

In oblique alignment (Figure 5.9A), thick LPE-produced nanosheets ($\langle t_{NS} \rangle \sim 12$ nm), deposited using spray coating form a jammed system of sheets with poor basal-plane alignment due to their high bending rigidity and lack of preferred orientation. This contributes to increased network tortuosity and porosity ($P_{Net} \sim 50\%$), as well as creating small, point-like junctions. Such junctions are poor charge transfer interfaces, due to their small area and larger intersheet distances, and therefore R_j is high and the network is low mobility ($\mu_{Net} \leq 0.2$ cm² V⁻¹ s⁻¹).

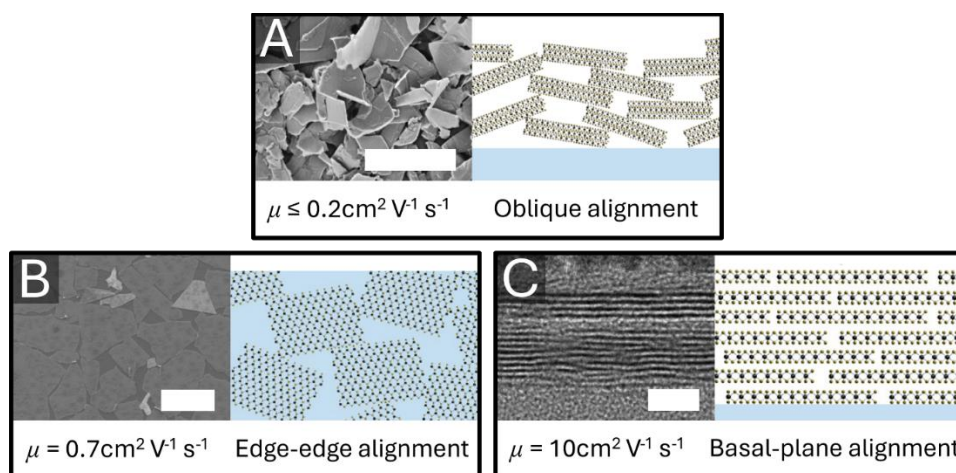


Figure 5.9: Different Junction Resistance Regimes in MoS₂ Nanosheet Networks. A – SEM image of a LPE MoS₂ spray-coated network with oblique alignment. Scalebar: 1 μm. Inset: schematic of its point-like junctions. B – SEM image of an EE MoS₂ liquid interface deposited network with edge alignment. Scalebar: 1 μm. Inset: schematic of its edge-edge junctions. C – Cross sectional TEM image of an EE MoS₂ spin-coated network with basal-plane alignment. Scalebar: 5 nm. Inset: schematic of its basal plane overlap junctions. A-C adapted from ref²⁰⁹.

In edge-to-edge alignment (Figure 5.9B), high aspect ratio bilayer EE-produced MoS₂ nanosheets ($\langle t_{\text{NS}} \rangle \sim 2 \text{ nm}$) deposited via liquid interface deposition form a monolayer network where the nanosheet basal planes are completely aligned in a densely packed structure, and junctions are formed with adjacent nanosheets by their edges. These have lower tortuosity and porosity ($P_{\text{Net}} \sim 10\%$) than with oblique alignment. The junctions are better charge transfer interfaces due to increased area, and hence R_j is reduced and consequentially the mobility is increased ($\mu_{\text{Net}} = 0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

In basal plane alignment (Figure 5.9C), EE MoS₂ sheets ($\langle t_{\text{NS}} \rangle \sim 3.8 \text{ nm}$) deposited by spin coating produces highly aligned networks with extensive basal plane overlap in the junctions. Nanosheet conformality minimizes inter-sheet distance and suppresses the tortuosity and porosity ($P_{\text{Net}} \sim 1\%$). These junctions are the ideal low R_j case for charge transfer, giving mobility comparable to CVD films ($\mu_{\text{Net}} \sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

Maximizing basal-plane alignment and overlap, while minimizing junction impurities and bending rigidity, is therefore key to achieving high-performance nanosheet network devices. Such prototype devices fabricated in this work will now be discussed.

5.5 APPLICATIONS

The modern age demands exponentially increasing numbers of sensors, memory elements, displays, and batteries, produced with ever decreasing cost and energy consumption, while relying on abundant, geopolitically stable raw materials³²³. Solution-processed nanosheet networks are attractive in this context due to their low-cost, scalable fabrication and compatibility with flexible substrates³²⁴.

Graphene networks are investigated for conductive applications, including transparent conducting films (TCFs)³²⁵, supercapacitors³²⁶, memristors³²⁷, flexible electrodes³²⁸, strain

gauges^{64, 329} and antennas.³³⁰ TMD networks, such as MoS₂, due to their semiconducting properties have been pursued for applications in thin film transistors (TFTs)^{117, 331} LEDs³³², and photodetectors³³³.

This work focuses on two representative applications, TCFs and TFTs. The performance criteria for TCFs are straightforward, requiring high optical transparency paired with high electrical conductivity. The following subsections will therefore focus on TFT principles and operation.

5.5.1 TRANSISTORS

The device at the heart of all modern information technology is the transistor. Providing a method of permitting or preventing the flow of individual signals, in its ON and OFF states respectively, combinations of this device can be used to construct circuits capable of performing logical operations on signals, or logic gates. Ensembles of these gates may be further engineered to perform computation. The performance, power efficiency, and scaling potential of transistors are fundamentally linked to the properties of the materials from which they are fabricated, making advances in material science central to continued progress in computing technology³³⁴.

Shrinking transistor dimensions to increase device density on silicon chips has been a key driver of computational performance gains, famously formalized by Gordon Moore in 1965, where he both predicted and prescribed a doubling of circuit components on chips every 2 years. The result 6 decades on is that there are now foundries routinely producing chips with transistor densities in excess of $2 \times 10^8 \text{ mm}^{-2}$ ³³⁵, with TSMC set to mass-produce chips boasting $3.18 \times 10^8 \text{ mm}^{-2}$ densities in the latter half-year of 2025³³⁶.

Associated with such strides in computational devices has been the rise of several technologies, such as wearable electronics and AI, that themselves demand further increases in performance and real-world penetration of electronic devices. Indeed, as

greater progress is made to create machine interfaces, there will be a need for a massive amount of low-grade electronics that act as peripheral sensing and processing elements, with versatility in modality and functionality. As addressed in Chapter 2 Section 2.3, 2D materials are attractive for this purpose due to their optical transparency, mechanical flexibility, and compatibility with soft substrates, among other properties, suiting them well to wearable and soft-matter electronics^{322, 324, 337}.

The most important type of transistor is the metal-oxide-semiconductor field-effect transistor (MOSFET). This is due to its low power consumption, high manufacturing yield, and its construction solely from silicon and its oxides. Figure 5.10A shows a cross-section of a MOSFET, consisting of an n-type semiconductor channel flanked by p-type source and drain regions, with a metallic gate electrode insulated from the channel by an oxide layer.

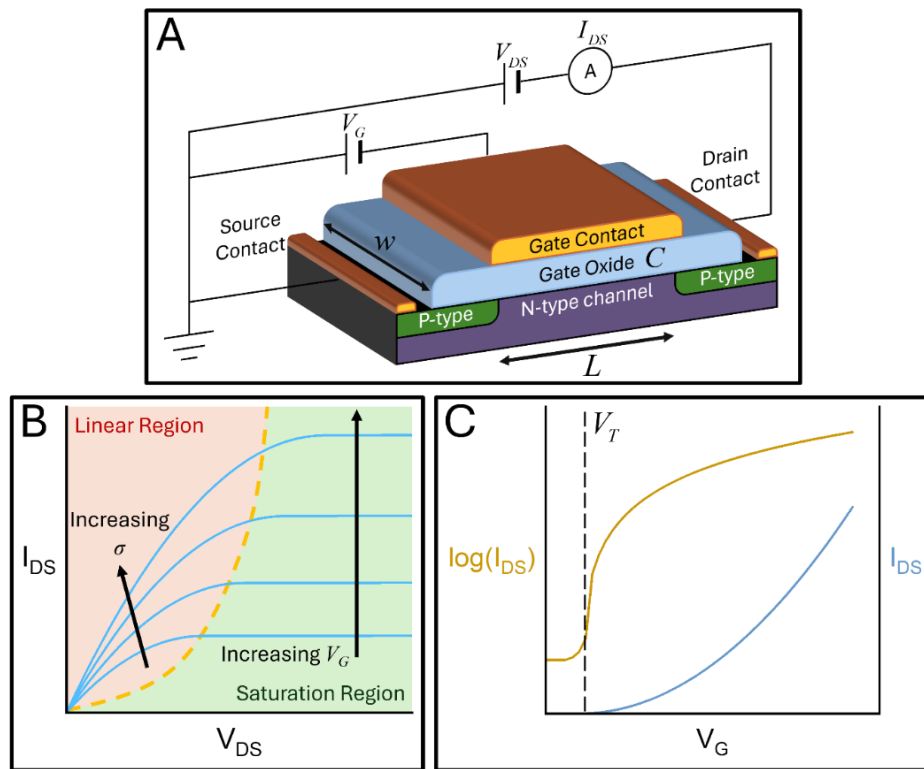


Figure 5.10: MOSFET Schematic & Transfer Curves. A – MOSFET schematic. Adapted from ref³³⁸.

B – Output curve of a MOSFET at various gate voltages. C – Transfer curve of a MOSFET.

Key device parameters include channel length L , channel width w , gate capacitance C , and substrate doping³³⁹. In operation, the source contact is the voltage reference for both the gate and the drain. With zero gate bias, the channel remains non-conductive, and minimal current flows between source and drain (OFF state). Applying a gate voltage above the threshold voltage, V_T , draws carriers from the semiconductor body to form a region at the oxide interface known as an inversion layer. The increased carrier concentration in this region substantially increases the conductivity, hence permitting a significant drain current (ON state).

Key to characterizing semiconductor operation is the relationship between the drain–source current I_{DS} and two independent variables: the drain–source voltage V_{DS} and the gate voltage V_G . Respectively, these relationships define the output characteristics (Figure 5.10B) and the transfer characteristics (Figure 5.10C) of the transistor.

In the output curves, two distinct regimes of current response arise from carrier dynamics within the inversion layer. Under application of a small V_{DS} , carriers flow between drain and source, and the channel behaves as a resistor whose conductivity is modulated by V_G .

In this linear regime, the drain current can be expressed as³⁴⁰:

$$I_{DS} = \frac{w}{L} \mu C (V_G - V_T) V_{DS} \quad (\text{Eqn 5.34})$$

where μ is the mobility, C is gate capacitance, and V_T is the threshold voltage, defined as the minimum gate potential required to induce conduction in the channel.

As V_{DS} is increased, the local potential near the drain approaches $V_G - V_T$, reducing the inversion layer thickness to zero at the drain–channel interface. This pinch-off condition marks the onset of the saturation regime, where the number of mobile carriers at the drain

is strongly reduced. In this regime, the drain current I_{DS} becomes independent of V_{DS} and is described by³⁴⁰:

$$I_{DS} = \frac{w}{2L} \mu C (V_G - V_T)^2 \quad (\text{Eqn 5.35})$$

The transfer characteristics (Figure 5.10C) plot I_{DS} as a function of V_G for a fixed V_{DS} in the saturation regime. The slope of this curve is the transconductance, g_m , which can be expressed by differentiating Eqn 5.34 with respect to V_G ³⁴⁰:

$$g_m = \left. \frac{\partial I_{DS}}{\partial V_G} \right|_{V_{DS}} = \frac{w}{L} \mu C V_{DS} \quad (\text{Eqn 5.36})$$

The transconductance quantifies the efficiency of converting small changes in gate voltage into large changes in drain current, and from Eqn 5.35 scales linearly with mobility μ . High g_m values enable faster switching, reduced power consumption, and lower heat generation, all of which are critical factors in high-performance electronics³⁴⁰. Hence, the mobility is a critical figure of merit for material performance in switching applications.

Even at zero gate bias, a small leakage current (the off-current) may be present. Minimizing this value relative to the on-current is essential, as the on:off ratio is another key figure of merit for digital switching devices.

Early demonstrations of printed, solution-processed nanosheet TFTs employed solid-state gate dielectrics. However, in thicker films, the gate field is attenuated with depth, effectively shunting the gate voltage and severely limiting performance²⁰⁵. This limitation can be mitigated by electrolytic gating, a technique first developed for organic electronics, in which a liquid electrolyte replaces the solid dielectric and forms high-capacitance electric double layers at the channel interface.

5.5.2 ELECTROLYTIC GATING

Electrolytic gating replaces the solid dielectric with an electrolyte, enabling reversible electrostatic doping of the semiconductor channel³³⁸. For permeable films, applying a gate bias forms electric double layers (EDLs) at the gate-electrolyte and electrolyte-channel interfaces. EDLs act as planar capacitors with nanoscale dielectric separation, providing large areal capacitance ($>10 \mu\text{F cm}^{-2}$), far greater than typical solid dielectrics³³⁸. The two EDLs can be modelled as capacitors in series, giving a device capacitance of $C_{\text{Total}} = (C_G^{-1} + C_{Ch}^{-1})^{-1}$ where C_G and C_{Ch} are the capacitances at the gate and channel, respectively. This relation means device capacitance is dominated by the smaller capacitance, and hence a rule of thumb is to keep the gate capacitance at least of a factor of ten higher³⁴¹. This is achieved by making gate electrode area much larger than channel area.

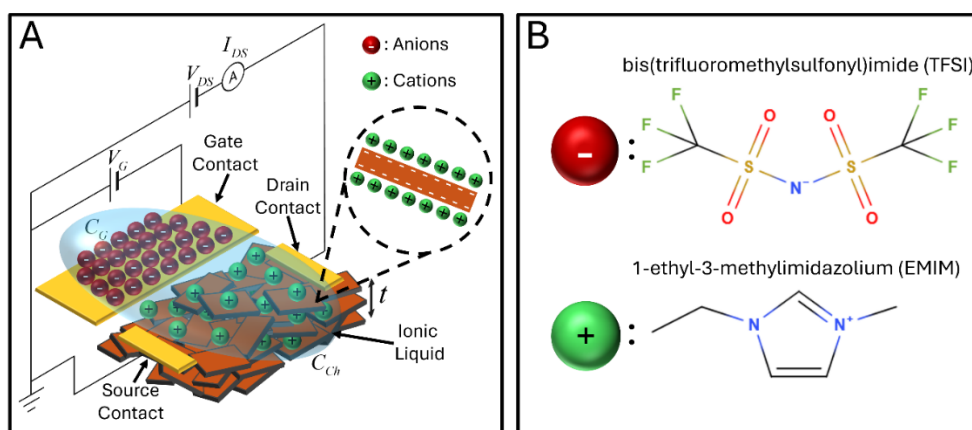


Figure 5.11: Electrolytic Gating. A – Schematic of an electrolytically gated nanosheet network transistor. Ionic liquid forms electric double layers (EDLs) at gate and inside the nanosheet channel. Inset: mechanism of mobile carrier generation. B – Structure of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI), a room-temperature ionic liquid (RTIL).

For permeable channels, such as nanosheet networks shown in Figure 5.11A, ions penetrate into the bulk, enabling volumetric gating. In this case, the capacitance term C in (Eqn 5.34) is replaced by $C_v t$, where C_v is the volumetric capacitance and t is film thickness, yielding:

$$I_{DS} = \frac{wt}{L} \mu C_V (V_G - V_T) V_{DS} \quad (\text{Eqn 5.37})$$

Unlike classical FETs, the transconductance in an electrolytically gated transistor (EGT) becomes tuneable via film thickness.

Room-temperature ionic liquids (RTILs) are ideal for electrolytic gating, offering high charge density, electrochemical stability, negligible volatility, tuneable polarity, and negligible water content³⁴²⁻³⁴⁴. The exclusion of water is key, as it widens the electrochemical window as high as 6 V³⁴⁵. Shown in Figure 5.11B is the structure of the benchmark ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI). This salt is widely used for switching applications, due to its large electrochemical window (~5.5 V) and high ionic conductivity ($\sim 10^{-3} \text{ Sm}^{-1}$)³⁴². As such, it is RTIL of choice in this work to gate nanosheet network TFTs in Chapter 6.

*"If I had asked people what they wanted, they would have said
faster horses."*

Henry Ford

Chapter 6

Electrochemical Exfoliation of Transition Metal

Dichalcogenides for 2D Thin Film Transistors

The work presented in this chapter has been adapted from the transfer report and the published work: "High-Mobility Flexible Transistors with Low-Temperature Solution-Processed Tungsten Dichalcogenides" published in ACS Nano¹²⁹. Dr. Shixin Liu performed the UV-vis spectroscopy, Dr. Kevin Synnatschke carried out the liquid interface depositions, Dr. Tian Carey performed characterisation and TFT measurements, and Dr. James Garcia performed the strain testing.

As outlined in Chapters 2 and 5, nanosheet networks present a promising avenue for thin film transistors (TFTs). The mechanical flexibility of the nanosheets allows integration with soft-matter substrates to realise flexible logic devices^{192, 346}. However, TFTs fabricated from printed films of solution-processed nanosheets have generally exhibited either low mobilities^{215, 341, 347-349}, or poor on/off ratios^{350, 351}. Both outcomes are unsuitable for practical applications for reasons outlined in

Chapter 5 Section 5.5.1³⁴⁰. The low mobilities arise primarily from the high junction resistance (R_j) inherent in printed semiconducting nanosheet networks²⁰⁹, while the low on/off ratios are associated with the use of non-semiconducting 2D materials such as graphene.

Nanosheet networks of TMDs represent an obvious choice of TFT channel material, as their intrinsic bandgaps enable high on/off ratios. Their advantage over other solution-processed flexible semiconducting materials, such as carbon nanotubes, organic polymers, and metal oxides, lies not only in their ability to maintain mobilities greater than $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature and under ambient atmosphere¹⁹¹, which is required for digital electronics^{346, 352}, but also in their compatibility with low-temperature processing. In contrast to solution-processed metal oxide semiconductors, which typically require high-temperature annealing ($>200\text{-}400^\circ\text{C}$) to achieve dense, crystalline films with high mobility, TMD nanosheet networks can be deposited and processed with minimal thermal budget, making them well-suited for flexible and polymer substrates. As addressed in Chapter 5 Section 5.4, to realise low R_j , and hence high mobility networks, large aspect ratio conformal nanosheets with a high degree of alignment are required.

Electrochemical exfoliation (EE) has emerged as a suitable method for preparing such large aspect ratio nanosheets¹³⁸. However, achieving high mobilities and on/off ratios in TMD networks requires preservation of both low defect density and the 2H polymorph. As discussed in Chapter 3 Section 3.1.2, not all EE approaches satisfy these requirements. Accordingly, in this chapter a Li-free cathodic EE method employing alkylammonium salts was selected. This approach follows the work of Lin et al.¹⁹¹, which demonstrated the production of phase-pure 2H MoS₂ nanosheets with large aspect ratios, suitable for high-mobility device fabrication.

Aligned nanosheet films, as discussed in Chapter 4 Section 4.2, can be prepared by liquid interface deposition (LID), which enables the formation of networks of densely packed and preferentially aligned nanosheet networks. In this chapter, this approach is combined with cathodic alkylammonium EE-derived nanosheets to form low- R_f networks.

The objectives of this chapter are therefore fourfold: (1) to demonstrate that cathodic alkylammonium EE produces nanosheets better suited for low- R_f networks than alternative solution processing techniques, (2) to show that this method yields high aspect ratio, low defect, phase-pure 2H nanosheets for a range of layered TMD materials, (3) to fabricate aligned nanosheet networks from these EE materials by LID, employ them as the semiconducting channel in electrolytically gated TFTs, then measure these TFT devices' performances as a figures of merit of the networks, and (4) to demonstrate such TMD TFTs may be fabricated on a flexible substrate, realizing a high mobility device capable of maintaining performance over many bending cycles.

6.1 PROCEDURE

6.1.1 EE OF TMDs

In each exfoliation, bulk crystals of MoS₂, WS₂, and WSe₂ (Figure 6.1A) were cut into pieces of approximately 0.1 × 1 × 1 mm and mounted as the working electrodes (cathode) in the electrochemical setup shown in Figure 6.1B and C. Platinum foil (Alfa Aesar) was used as the counter electrode (anode). The electrolyte consisted of ~50 mL of tetrapropylammonium bromide (TPABr, Sigma-Aldrich) dissolved in propylene carbonate (PC) at a concentration of 5 mg mL⁻¹. Both electrodes were immersed in the electrolyte and held in place using copper crocodile clips. A Gamry potentiostat supplied a constant bias of 8 V for 30 minutes. During this period, bromine was generated, causing the initially clear TPABr-PC solution to develop a yellow colour (Figure 6.1B).

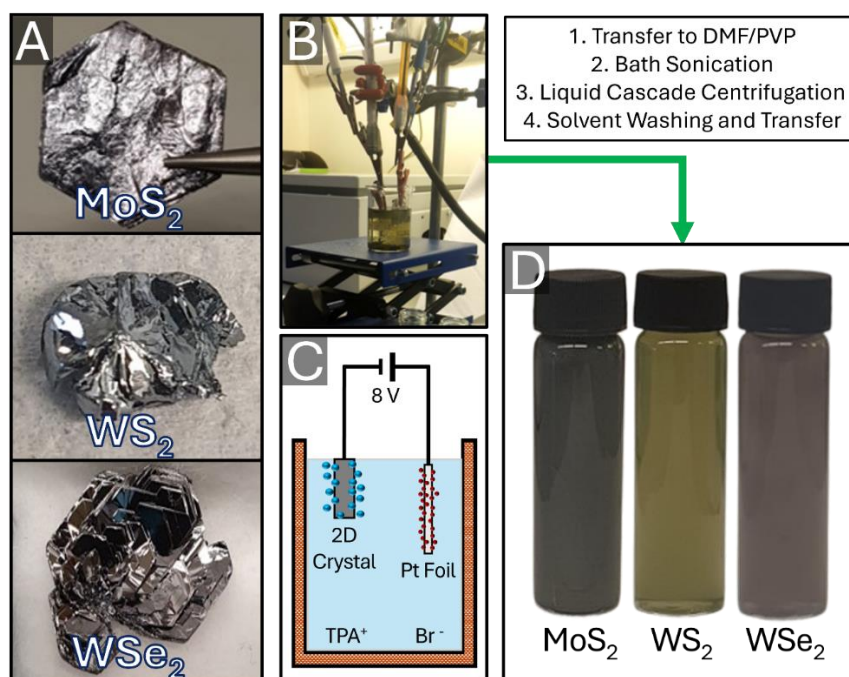


Figure 6.1 Electrochemical Exfoliation Setup. A – TMD crystals used in this study. B – Photograph of the intercalation setup. C – Schematic representation of the setup. D – Resulting EE TMD inks after exfoliating, size-selecting and solvent washing the intercalated material.

The TMD crystals expanded to approximately twice their initial volume, forming a swollen, slurry-like solid. Portions detached into the electrolyte, while others remained attached to the clips. This expanded material was collected across several intercalation cycles, washed overnight in isopropanol (IPA) to remove residual bromide, and subsequently transferred into a solution of poly(vinylpyrrolidone) (PVP, molecular weight $\sim 40,000$) in DMF at 1 mg mL^{-1} . The resulting mixture was then bath-sonicated (Fischerbrand 112xx series FB11205) at full power ($\sim 220 \text{ W}$) for 5 minutes to yield a polydisperse dispersion of exfoliated sheets.

6.1.2 SHEAR EXFOLIATION OF MoS_2

For comparison with EE, shear exfoliation of MoS_2 powder (Alfa Aesar) was performed. Bulk MoS_2 powder was suspended at 10 g L^{-1} in 500 mL of 1 g L^{-1} PVP-DMF solution by bath sonication (Fischerbrand 112xx series) at full power ($\sim 220 \text{ W}$) for 5 minutes. The suspension was then shear mixed with a four-blade rotor (Silverson Model L5M) at 8000

rpm for 8 hours, yielding a polydisperse dispersion of exfoliated sheets. The rotor-stator gap was 300 μm and the rotor diameter was 31.1 mm. To avoid overheating, the beaker containing the dispersion was cooled in an ice bath, replenished with ice approximately every 2 hours. The shear exfoliation setup used is shown in Figure 6.2.

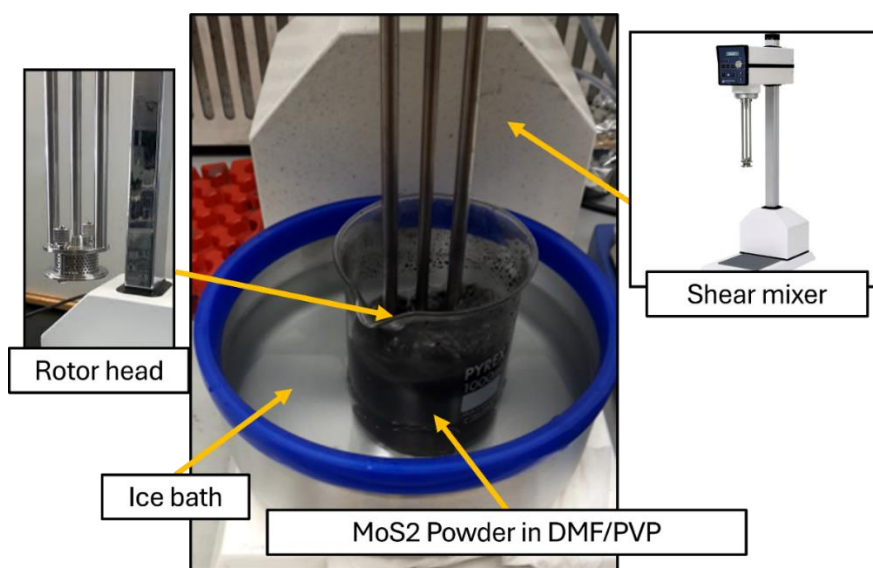


Figure 6.2 Shear Exfoliation Setup. Images showing the setup used to perform shear exfoliation of MoS₂ to provide a comparison with electrochemical exfoliation.

6.1.3 SIZE SELECTION & SOLVENT WASHING

Following exfoliation, the polydisperse EE and shear dispersions were subjected to size selection by liquid cascade centrifugation (LCC). A Hettich Mikro 220 centrifuge with rotor model 1195-A (radius 87 mm) was used. The dispersions were loaded into 1.5 mL Eppendorf tubes placed in the rotor and centrifuged sequentially.

To remove unexfoliated bulk material, an initial step at 500 rpm (24g) for 20 minutes was applied. The supernatant (90% of the tube volume) was recovered and centrifuged at 1000 rpm (97 g) for 1 hour. For each exfoliation, the sediment from this step was labelled as “97g”. To further fractionate MoS₂ dispersions for comparisons of sizes between exfoliation techniques, the 97g supernatant was centrifuged at 3000 rpm (877g) and 5000 rpm (2436g),

each for 1 hour. The sediments from each step were collected and similarly labelled according to the g-force of the upper boundary of the cascade.

PVP residues were removed by redispersing the nanosheets in 2 mL DMF and centrifuging at 10,000 rpm (9744g) for 1 hour to re-sediment the nanosheets. This step was repeated twice. To remove DMF, the sediment was diluted in 0.5 mL IPA and centrifuged again at 10,000 rpm for 1 hour. The final sediment was redispersed in ~0.5 mL IPA, producing the nanosheet inks used for characterization and film deposition (Figure 6.1D).

6.1.4 NANOSHEET CHARACTERIZATION

ATOMIC FORCE MICROSCOPY

Atomic force microscopy (AFM) was carried out on the exfoliated dispersions using a Bruker Multimode 8 system to determine apparent nanosheet thickness (t) and lateral size (L_{NS}). Each ink was diluted in IPA (1:100) and drop-cast onto Si/SiO₂ substrates. Samples were annealed at 120 °C for 15 minutes to remove residual solvent. Scans were performed on these samples in ScanAsyst mode using OLTESPA R3 cantilevers. Using Gwydion on the resulting micrographs, between 35 and 50 nanosheets were analysed per sample to obtain statistical distributions of t and L_{NS} (see Appendix Section A.2.1). As no conversion from apparent to real thickness was required for the analysis presented in this chapter, apparent thickness values were not corrected using step-height analysis and are reported directly.

RAMAN SPECTROSCOPY

Samples from each ink were prepared for measurement by drop-casting inks onto Si/SiO₂ substrates followed by annealing at 120 °C. Raman spectra these samples were recorded using a Horiba Jobin Yvon Labram HR800 system with a 532 nm excitation laser, 10x objective, and ~1 mW incident power to minimise thermal damage.

Extinction spectra were acquired for each 97g EE dispersion using a PerkinElmer Lambda 1050 spectrometer. Measurements were performed with a step size of 1 nm and a 10 mm optical length quartz cuvette. Absorption was determined using an integrating sphere configuration, and scattering was extracted as the difference between extinction and absorption spectra. The slit width was 2 nm.

6.1.5 FILM DEPOSITION

Liquid interface deposition (LID) was used to assemble aligned nanosheet networks from the EE inks. A Teflon stand (Figure 6.3A) holding a 2×2 cm Si/SiO₂ chip was submerged in deionised water (~100 mL). Approximately 20 mL of distilled hexane was added on the water surface above the substrate to create a water-hexane interface. Size-selected dispersions of EE MoS₂ (97g, 877g, 2436g), WS₂ (97 g), and WSe₂ (97 g) were deposited by drop-casting onto the interface (~140 μ L per addition) until no gaps were visible in the interfacial film. The Si/SiO₂ was then carefully extruded through the interface by vertically lifting the stand, transferring the TMD film onto the substrate (Figure 6.3B). Si/SiO₂ substrates were used to provide a smooth, chemically inert surface with well-defined dielectric properties, enabling reproducible device fabrication and electrical characterisation.

Films were dried in ambient conditions for ~ 6 hours, then annealed at 120 °C for 1 hour on a hot plate inside an N₂ glovebox (Jacomex GP campus). This mild annealing step promotes removal of residual solvent and dispersant species while improving nanosheet-substrate adhesion. The temperature was limited to 120 °C to remain compatible with flexible polymer substrates such as PET, enabling consistent processing conditions for both rigid and flexible devices.

Where necessary, the deposition process was repeated to add a second layer of nanosheets to the film. For WS₂ and WSe₂ networks, two sequential depositions were performed to improve film coverage and network connectivity, while MoS₂ networks were prepared with a single deposition due to higher initial coverage.

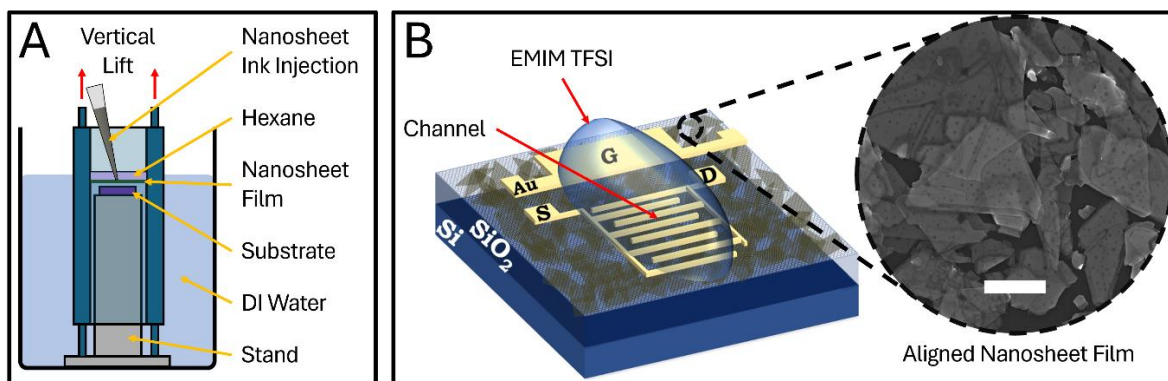


Figure 6.3 Liquid Interface Deposition Setup and Device Schematic. A – LID setup used in this work. B – Schematic of electrolytically gated TMD transistor, with S = source, D = drain, G = gate. Inset: SEM image of an MoS₂ nanosheet network. Scalebar: 1 μ m.

Gold electrodes (~ 100 nm thick) were deposited onto the resulting film by evaporation (Temescal FC-2000 Bell Jar) through a stainless-steel mask (50μ m thickness, laser cut by Laser Micromachining Ltd.). The mask defined six interdigitated electrode channels per substrate, each with width $11,000 \mu$ m and channel length 50μ m. A large gate electrode ($\sim 1.5 \times 4$ mm) was patterned 1 mm from the source-drain array. Devices were annealed again at 120°C for 1 hour in an N₂ glovebox to further reduce contact resistance and remove residual contaminants at the electrode–film interface.

The same procedure was used to fabricate the flexible WSe₂ sample, substituting Si/SiO₂ substrates with polyethylene terephthalate (PET, Novacentrix). WSe₂ was selected for this purpose due to its favourable ambient stability and device performance demonstrated in the corresponding Si/SiO₂-based devices.

6.1.6 TFT MEASUREMENTS

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI, Sigma-Aldrich) was used as the dielectric for the TFTs. Prior to use, EMIM TFSI was dried under vacuum at 100 °C for 6 hours to remove absorbed water, which can significantly reduce the electrochemical stability window of the electrolyte. A droplet of ionic liquid was applied to cover the source, drain, and gate electrodes (Figure 6.3B). Devices were kept under vacuum ($\sim 1.6 \times 10^{-4}$ mbar) in a Janis probe station overnight to remove residual moisture and trapped air, ensuring stable and reproducible gating behaviour. The chamber was then returned to ambient pressure prior to electrical measurements.

Electrical characterisation was performed using a Keithley 2612A dual-channel source-measure unit. Transfer characteristics were measured with $V_{DS} = 1$ V and a gate voltage window of -3 to 3 V at a scan rate of 50 mV s^{-1} . For each sample, all six channels were tested to obtain averaged device performance metrics (mobility, on/off ratio).

TRANSISTOR FLEXURAL TESTS

Mechanical flexibility of WSe₂ TFTs fabricated on PET substrates was evaluated using a zwickiLine (ZwickRoell) three-point flexure system. Devices were subjected to repeated bending cycles at a strain of 1%, calculated as³⁵³:

$$\varepsilon = \frac{6dD_f}{L_s^2} \quad (\text{Eqn 6.1})$$

where d is substrate thickness ($170 \text{ }\mu\text{m}$), L_s is the support span (16 mm), and D_f is the maximum deflection at the centre of the beam. Transistor performance was recorded after 0, 10, 100, and 1000 bending cycles, with 6–7 channels measured per condition.

6.1.7 MICROSCOPY

OPTICAL MICROSCOPY

Optical imaging was carried out using an Olympus DSX1000 microscope in bright-field mode at 50 $\times$ magnification. To capture full devices, multiple 70 $\times$ 70 μm images were acquired sequentially and stitched using live panorama mode with 10% overlap.

SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) was performed using a Carl Zeiss Ultra SEM operated at 4 kV with a 30 μm aperture and secondary electron detection. Samples were prepared on Si/SiO₂ (300 nm oxide) substrates without conductive coating.

6.2 RESULTS & DISCUSSION

6.2.1 SIZE-SELECTED SHEAR & EE COMPARISON AFM STATISTICS

AFM statistics of MoS₂ nanosheets produced by EE and shear exfoliation is presented in Figure 6.4. Histograms of apparent nanosheet thickness (t) and lateral size (L_{NS}) for the 97g EE and shear dispersions are shown in Figure 6.4A-D. Both sets of data exhibit lognormal distributions typical of size-selected dispersion statistics²⁰⁴. Equivalent histograms for the 877g and 2436g EE and shear dispersions are provided in Appendix Section A.2.2.

For EE MoS₂, the mean lateral size $\langle L_{\text{NS}} \rangle$ values were 1.04 ± 0.08 , 0.61 ± 0.06 , and 0.48 ± 0.03 μm for the 97 g, 877 g, and 2436 g dispersions, respectively. Corresponding mean apparent thickness $\langle t \rangle$ values were 14 ± 1 , 10 ± 1 , and 9 ± 2 nm. In contrast, shear exfoliated MoS₂ produced smaller and thicker flakes, with $\langle L_{\text{NS}} \rangle$ values of 0.44 ± 0.04 , 0.41 ± 0.01 , and 0.44 ± 0.01 μm , and $\langle t \rangle$ values of 44 ± 6 , 42 ± 3 , and 34 ± 2 nm for the same fractions. These

results demonstrate that EE yields nanosheets with significantly larger lateral sizes and reduced thickness compared with shear exfoliation.

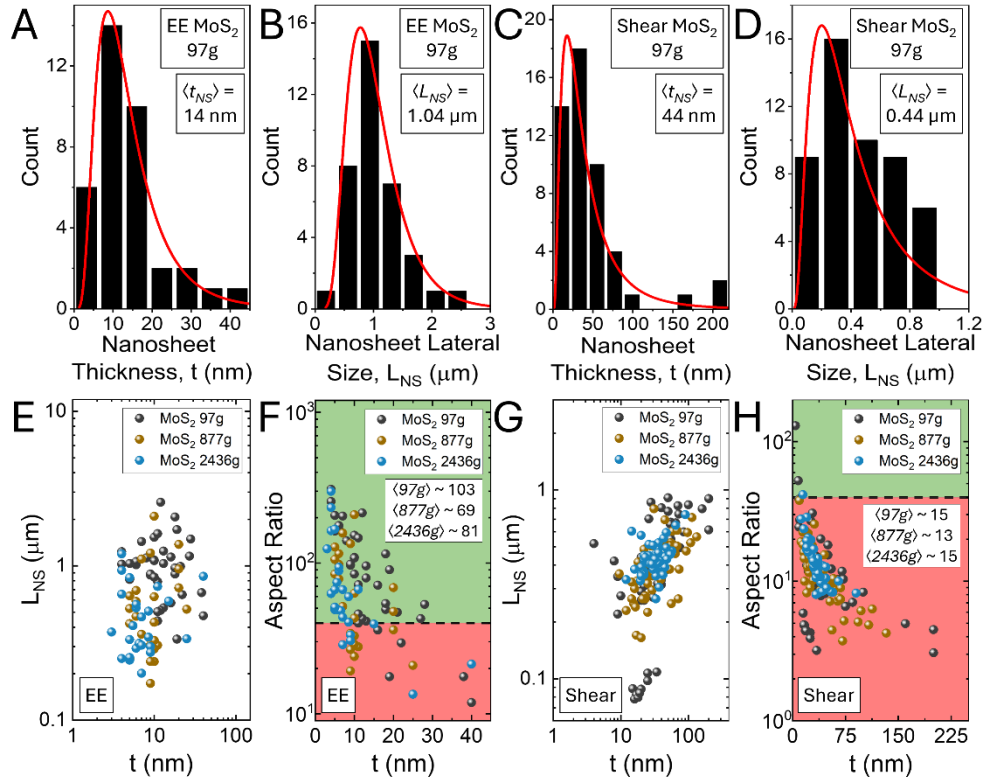


Figure 6.4 AFM Size Statistics of MoS₂ for Electrochemical & Shear Exfoliation. A – Nanosheet thickness histogram of 97g EE MoS₂. B – Nanosheet lateral size histogram of 97g EE MoS₂. C – Nanosheet thickness histogram of 97g shear MoS₂. D – Nanosheet lateral size histogram of 97g shear MoS₂. E – Lateral size versus thickness for the EE size-selected dispersions. F – Aspect ratio versus nanosheet thickness for the EE size-selected dispersions, with the majority of sheets having AR > 40. G – Lateral size versus thickness for the shear size-selected dispersions. H – Aspect ratio versus nanosheet thickness for the shear size-selected dispersions, with a majority of sheets having AR < 40.

The relationship between lateral size and thickness is shown in Figure 6.4E and G for EE and shear exfoliation, respectively. No correlation between L_{NS} and t was observed in the EE dispersions, in contrast with the positive correlation typically reported for liquid-phase exfoliated flakes²⁴⁵ and seen in Figure 6.4G for the shear exfoliated dispersions.

The aspect ratio ($AR = L_{NS} / t$) distributions are shown in Figure 6.4F and Figure 6.4H for EE and shear respectively. For EE MoS₂, the mean $\langle AR \rangle$ values were 102 ± 8 , 69 ± 5 , and 81 ± 7 for the 97g, 877g, and 2436g dispersions. By contrast, shear exfoliation produced consistently low $\langle AR \rangle$ values of 15 ± 2 , 13 ± 0.5 , and 15 ± 0.5 across the same fractions. A significant proportion of EE nanosheets satisfy the conformality condition outlined in Chapter 5 Section 5.4.1 ($AR > 40$), while the majority of shear-exfoliated nanosheets fall below this threshold, indicating their rigidity.

The approximately constant $\langle AR \rangle$ observed for shear exfoliation supports the conclusion of Backes et al.²⁴⁵ that $\langle AR \rangle$ of sheets produced by particular exfoliation protocol is determined by the fixed ratio between out-of-plane delamination energy and in-plane tearing energy. In electrochemical exfoliation, however, ion intercalation gives rise to a distribution of delamination energies, breaking this constancy and yielding dispersions with variable and generally higher $\langle AR \rangle$ values.

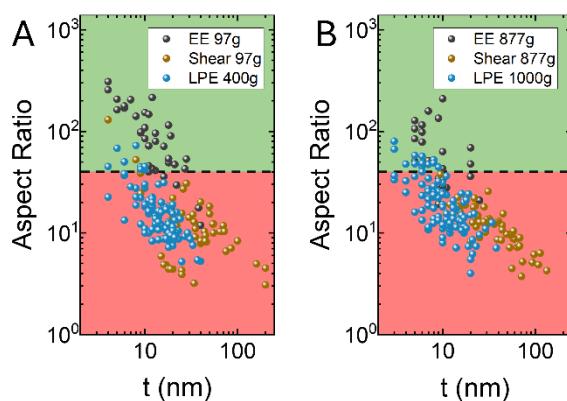


Figure 6.5 Comparison of Aspect Ratio for Different Exfoliation Techniques. A – Aspect ratio versus thickness for 97 g EE MoS₂, 97 g shear-exfoliated MoS₂, and 400 g LPE MoS₂. B – Aspect ratio versus thickness for 877 g EE MoS₂, 877 g shear-exfoliated MoS₂, and 1000 g LPE MoS₂. In both cases, EE produces the highest proportion of nanosheets with $AR > 40$, whereas shear and LPE predominantly yield nanosheets with $AR < 40$. LPE MoS₂ data adapted from ref²⁵⁴.

Figure 6.5 compares AR distributions for EE, shear exfoliation, and LPE ultrasonication²⁵⁴. EE consistently produces nanosheets with higher AR, well above the value of ~ 20 achieved

by ultrasonication, and exceeding values reported for alternative scalable techniques such as cyclic shear mixing ($AR \approx 60$)³⁵⁴ and microfluidization ($AR \approx 50$)³⁵⁵. These findings confirm EE as the most effective method among those compared for generating conformal nanosheets suitable for low junction resistance networks.

6.2.2 OTHER TMD AFM STATISTICS

AFM measurement statistics of WS_2 and WSe_2 nanosheets produced by EE are shown in Figure 6.6. Both dispersions exhibit lognormal distributions of lateral size and thickness, characteristic of size-selected nanosheets.

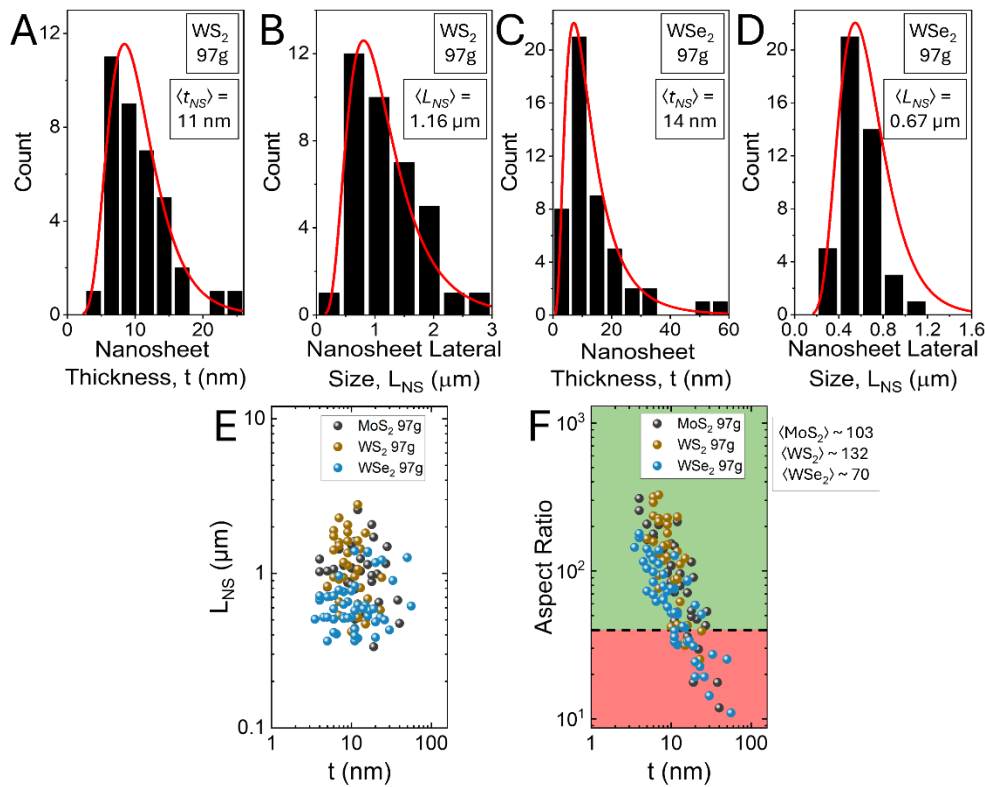


Figure 6.6 AFM Statistics of WS_2 & WSe_2 . A – Thickness histogram of 97g WS_2 . B – Lateral size histogram of 97g EE WS_2 . C – Thickness histogram of 97g EE WSe_2 . D – Lateral size histogram of 97g EE WSe_2 . E – Lateral size versus thickness for the 97g EE TMD dispersions. F – Aspect ratio versus thickness for the 97g EE TMD dispersions. In both WS_2 and WSe_2 , the majority of nanosheets have $AR > 40$, consistent with conformality.

For the 97 g WS₂ dispersion, the mean lateral size was $1.16 \pm 0.09 \mu\text{m}$ and the mean apparent thickness was $11 \pm 1 \text{ nm}$. For the 97 g WSe₂ dispersion, the mean lateral size was $0.67 \pm 0.03 \mu\text{m}$ and the mean apparent thickness was $14 \pm 2 \text{ nm}$. These values are comparable to those obtained for EE MoS₂ (Section 6.2.1).

Plots of lateral size L_{NS} versus apparent thickness t for the two materials are shown in Figure 6.6E with 97g EE MoS₂ data included for reference, and again no significant correlation between these two parameters is observed, consistent with the behaviour of EE MoS₂. The aspect ratio distributions (Figure 6.6F) indicate that most EE TMD nanosheets satisfy the conformality condition ($\text{AR} > 40$). Mean aspect ratios of 132 ± 8 for WS₂ and 70 ± 4 for WSe₂ further confirm the production of high-aspect-ratio nanosheets.

These results demonstrate that the cathodic alkylammonium EE protocol can be applied to multiple Group VI TMDs, reliably producing high-aspect-ratio nanosheets suitable for forming conformal, low-junction-resistance networks.

6.2.3 SIZE-SELECTED SHEAR & EE COMPARISON CHARACTERIZATION

Raman spectra of the MoS₂ dispersions prepared by shear and EE are shown in Figure 6.7A and B. All spectra exhibit MoS₂'s characteristic E_{2g} and A_{1g} peaks at 384 and 409 cm⁻¹, respectively, as prominent features³⁵⁶. As shown in Figure 6.7C, the intensity ratio of these peaks decreases with nanosheet thickness, in agreement with previous reports²⁶². For shear-exfoliated dispersions, the peak is downshifted to $\sim 380 \text{ cm}^{-1}$, indicative of thicker nanosheets.

The shear spectra also display broader peaks, which can be attributed to phonon confinement effects associated with increased defect density³⁵⁷. This is consistent with the lower quality of the MoS₂ powder starting material compared with the grown single crystals used for EE (Figure 6.1A). Defect-related peaks at ~ 227 and $\sim 330 \text{ cm}^{-1}$, associated with the basal-plane defect-activated longitudinal acoustic (LA) mode^{356, 357}, are visible in

the shear spectra but absent in the EE spectra (Figure 6.7A and B, insets). The ratio of the intensity of the LA peak at 330 cm^{-1} to the intensity of the E_{2g} peak, $I(LA)/I(E_{2g})$, can serve as a measure of defect density via an relation proposed by Fujisawa et al³⁵⁶:

$$\rho_{\text{defect}}(\text{nm}^{-2}) \approx 0.08 \times \frac{I(LA)}{I(E_{2g})} \quad (\text{Eqn 6.2})$$

When this is applied to the spectra in this study, it shows the EE samples to have a defect density of $<0.01 \text{ nm}^{-2}$, while the defect densities in the shear samples are $\sim 0.02 \text{ nm}^{-2}$.

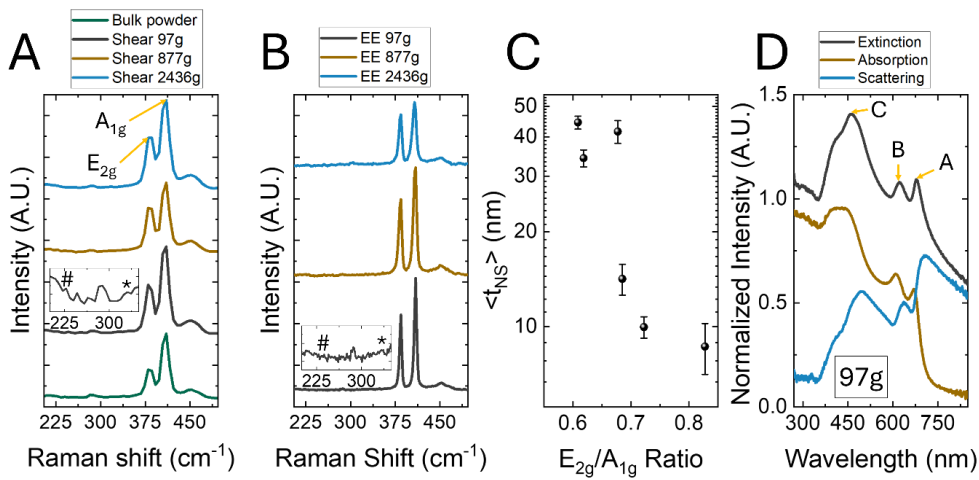


Figure 6.7: Raman & UV-vis Characterization of MoS_2 . A – Raman spectra of shear-exfoliated MoS_2 dispersions, inset: defect-activated LA peaks at ~ 227 (#) and $\sim 330 \text{ cm}^{-1}$ (*). B – Raman spectra of EE MoS_2 dispersions, inset: absence of defect LA peaks. C – Plot of average nanosheet thickness versus E_{2g}/A_{1g} peak intensity ratio, showing an inverse correlation. D – UV-vis spectrum of 97 g EE MoS_2 dispersion, displaying A, B, and C exciton peaks.

For both exfoliation methods, no J_2 (224 cm^{-1}) or J_3 (289 cm^{-1}) peaks associated with the metallic 1T phase²⁶⁸ were detected, confirming retention of the semiconducting 2H phase.

UV-vis spectra of 97g EE MoS_2 , normalized with respect to the local minima at $\sim 345 \text{ nm}$, are shown in Figure 6.7D. The distinct excitonic transitions located at 679, 623, 459 nm labelled as the A, B and C excitons respectively^{84, 204}. As discussed in Chapter 4, UV vis of nanosheet dispersions may be used to infer nanosheet lateral size and thickness. It has been shown by

Backes et al. that the relative extinction of the B exciton with respect to the minimum at 345nm relates to an estimation of L_{NS} by²⁵²:

$$L(\mu m) = \frac{3.5 Ext_B / Ext_{345} - 0.14}{11.5 - Ext_B / Ext_{345}} \quad (Eqn 6.3)$$

However, this model breaks down for larger sheets in the Mie scattering regime, where $L_{NS} > \lambda / \pi$. Given the B exciton wavelength (459nm) and the size of the sheets in Figure 6.4E, EE sheets are likely in this regime. From the extinction spectrum, Ext_B / Ext_{345} is found to be 1.08, indicating that $L_{NS} > 400nm$, which while not specific, is consistent with the AFM measurements in Section 6.2.1.

Motivated by the same consideration of using the UV-vis to determine nanosheet dimensions, Backes et al. have recently proposed a model relating an estimation of volume fraction-weighted nanosheet layer number $\langle N_{vf} \rangle$ to the relative extinction intensities of the C and A excitons (note this is currently unpublished, and shared as part of the 2-D PRINTABLE European project):

$$\langle N_{vf} \rangle = -1.06 \ln \left[\frac{Ext_C / Ext_A - 1.15}{11.46} \right] \quad (Eqn 6.4)$$

From the 97g MoS₂ extinction spectrum, Ext_C / Ext_A is calculated as 1.29, yielding $\langle N_{vf} \rangle = 4.7$. Taking the volume fraction-weighted mean apparent thickness for the 97g dispersion, $\langle t_{vf} \rangle = 17 \pm 6$ nm, and applying a conversion provided by Backes et al. from step height analysis of MoS₂ sheets (step height of 1.9nm)²⁵²:

$$\langle N_{vf} \rangle = \frac{\langle t_{vf} \rangle - 0.5}{1.9} \quad (Eqn 6.5)$$

we find $\langle N_{vf} \rangle = 9 \pm 3$. The slight discrepancy likely arises from scattering contributions in large nanosheets, which are not easily accounted for in these optical models.

These results confirm that EE produces MoS₂ nanosheets that are simultaneously high aspect ratio, low defect, and phase-pure 2H, rendering them suitable for TFT devices.

6.2.4 OTHER TMD CHARACTERIZATION

Raman and UV-vis spectra of the 97g EE WS₂ and WSe₂ dispersions are presented in Figure 6.8. As discussed in Chapters 2 and 4, the Group VI TMDs are isostructural and share analogous spectral features, and so E_{2g} and A_{1g} Raman peaks are also observed as in MoS₂. For WS₂, these peaks occur at 354 cm⁻¹ and 409 cm⁻¹, respectively³⁵⁸. For WSe₂, the corresponding modes appear at 249 and 258 cm⁻¹, overlapping into a broad feature centred near 250 cm⁻¹³⁵⁸. The downshift of these modes relative to MoS₂ arises from the heavier atomic masses and enhanced dielectric screening in WS₂ and WSe₂^{359, 360}. In WS₂, the A_{1g} mode intensity is strongly suppressed compared with MoS₂, consistent with increased spin-orbit coupling effects due to the heavier W atom in place of Mo³⁶¹.

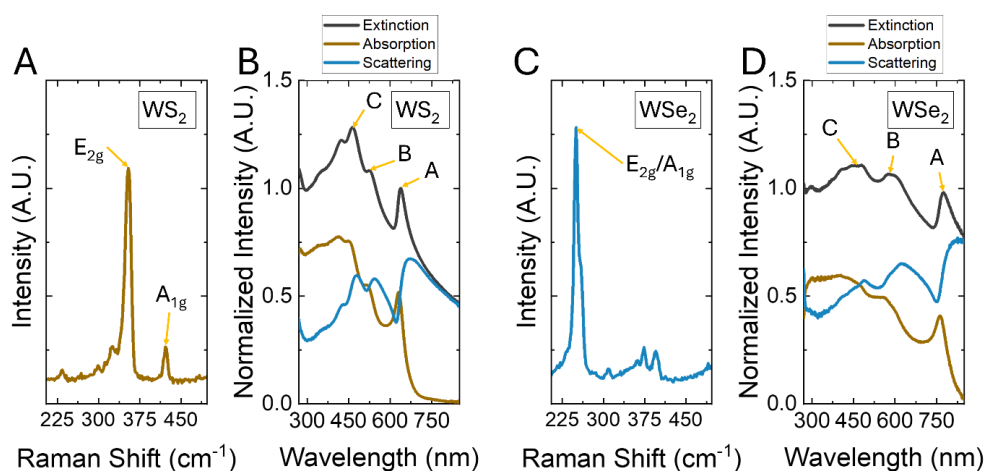


Figure 6.8 Raman & UV-vis Spectra of WS₂ & WSe₂. A – Raman spectrum of 97g EE WS₂. B – UV-vis spectra of 97g EE WS₂. C – Raman spectrum of 97g EE WSe₂. D – UV-vis spectra of 97g EE WSe₂.

No J₂ and J₃ modes, located at 218 and 236 cm⁻¹ in WS₂²⁶⁹ and at 218 and 236 cm⁻¹ for WSe₂²⁷⁰, were detected, confirming that both materials retained the semiconducting 2H phase and did not undergo conversion to the metallic 1T phase.

UV-vis spectra of WS₂ and WSe₂ dispersions (Figure 6.8B and D) show three distinct excitonic peaks, analogous to those observed in MoS₂. For WS₂, excitons A, B, and C appear at 638, 526, and 463 nm, respectively. For WSe₂, the A, B, and C excitons are located at 775, 579, and 480 nm²⁵⁴. These features confirm the semiconducting band structures of the exfoliated nanosheets and their suitability as channel materials for TFTs.

Together, these results demonstrate that the cathodic alkylammonium EE method can be applied across multiple Group VI TMDs to produce high-quality, phase-pure nanosheets with preserved semiconducting properties.

6.2.5 DIFFERENT TMD TFTs

Films of MoS₂, WS₂, and WSe₂ prepared by liquid interface deposition were incorporated as channel materials in electrolytically gated TFTs. AFM was used to measure the film thicknesses t_{film} (see Appendix Section A.2.3), while cyclic voltammetry measurements determined volumetric capacitances C_v (Appendix Section A.2.4). These values were used in mobility calculations.

Output characteristics of representative devices are shown in Figure 6.9A–C. The MoS₂ and WS₂ TFTs display n-type behaviour, conducting only under positive gate bias, while the WSe₂ device exhibits ambipolar behaviour, consistent with prior reports^{192, 341, 349}. Transfer curves for each material (Figure 6.9D–F) were obtained by sweeping V_G between +3 V and –3 V with $V_{DS} = 1$ V. Transconductance (g_m) values were extracted from the slope of I_{DS} with respect to V_G in the linear region (between $V_g \sim -1$ V to 1 V for MoS₂ and WS₂, $V_g \sim 0$ V to 1 V for WSe₂), and used to calculate the mobility according to the equation from Chapter Section 5.5.1:

$$\mu = \frac{g_m L}{w C V_{DS}} \quad (\text{Eqn 6.6})$$

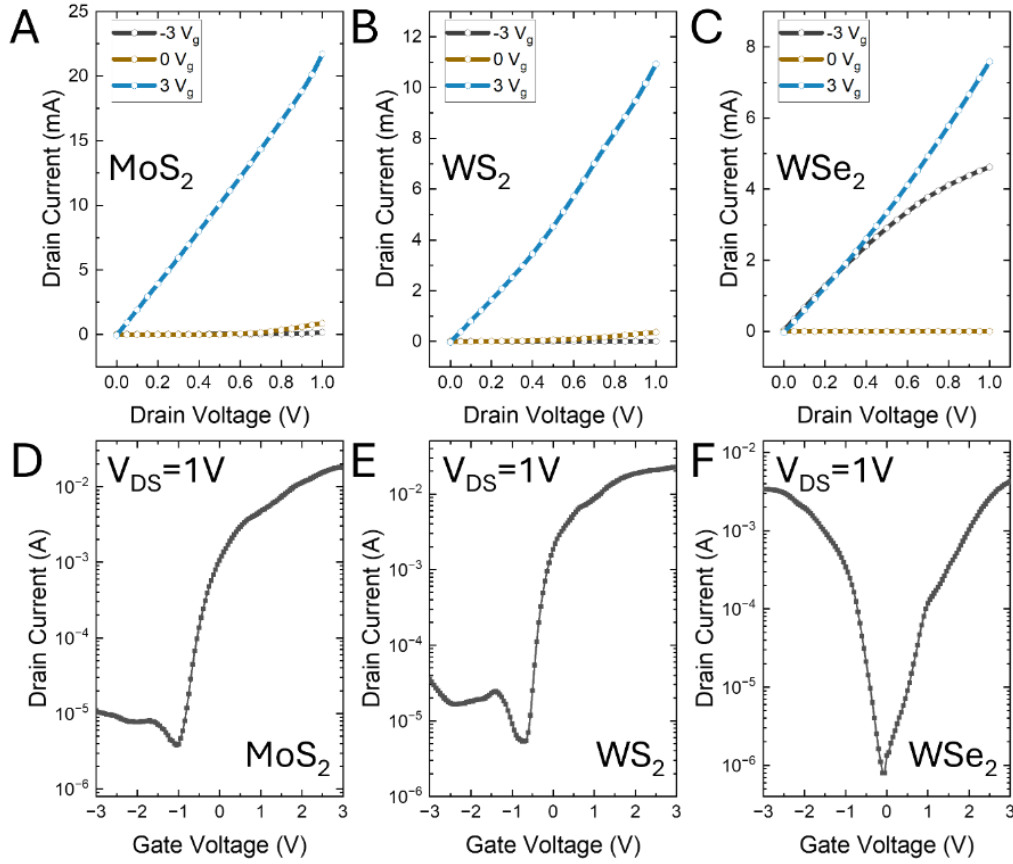


Figure 6.9 Representative Electrical Characteristics of EE TMD TFTs. A – Output curve of MoS₂ device. B – Output curve of WS₂ device. C – Output curve of WSe₂ device. D – Transfer curve of MoS₂ device. E – Transfer curve of WS₂ device. F – Transfer curve of WSe₂ device.

The average mobilities determined from 6-9 channels per sample (appendix Section A.2.5)

were $\mu_{\text{MoS}_2} \approx 10.7 \pm 0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{\text{WS}_2} \approx 9.1 \pm 2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{\text{WSe}_2} \approx 2.0 \pm 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The corresponding on/off ratios, calculated by taking the average ratio of the maximum and minimum drain currents, were $(2.6 \pm 0.4) \times 10^3$ for MoS₂, $(3.4 \pm 0.6) \times 10^3$ for WS₂, and $(4.2 \pm 1.8) \times 10^4$ for WSe₂.

Leakage currents from the ionic liquid gate were typically on the order of 10^{-5} A , and did not interfere with transistor operation. It should be noted that the mobilities extracted here are obtained using electrolytic gating, in which the formation of an electric double layer

(EDL) at the semiconductor-electrolyte interface results in very high interfacial capacitance. This can lead to an apparent enhancement of the field-effect mobility compared to conventional dielectric gating, as the large capacitance enables efficient charge accumulation even in networks with significant disorder or contact resistance. In contrast, devices gated using conventional 300 nm SiO₂ dielectrics, with capacitances on the order of $\sim 10 \text{ nF cm}^{-1}$ ¹¹⁷, typically exhibit lower extracted mobilities for comparable TMD networks due to reduced gate coupling (e.g. Xiong et al. demonstrated $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for spin-coated MoS₂ networks back-gated by 300 nm SiO₂³⁶²). As such, the mobilities reported here should be interpreted as effective mobilities under high-capacitance gating conditions.

Within this high-capacitance gating framework, the EE TMD nanosheet networks combined with liquid interface deposition enable high-performance TFTs. The mobilities and on/off ratios achieved are comparable to solution-processed semiconducting technologies such as organic polymers³⁶³⁻³⁶⁵, carbon nanotubes³⁶⁶⁻³⁶⁸, graphene³²², and metal oxides³⁶⁹⁻³⁷¹, and significantly exceed previously reported values for electrolytically gated printed TMD devices fabricated by other methods ($\mu \approx 0.01\text{--}0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{215, 341, 347-349}.

6.2.6 SIZE-SELECTED EE MoS₂ TFTs

To investigate the influence of nanosheet dimensions on device performance, TFTs were fabricated from the EE MoS₂ dispersions size-selected at 97 g, 877 g, and 2436 g. Bright-field optical microscopy images of the corresponding films are shown in Figure 6.10A. In each case, the liquid interface deposition process produced highly-aligned, tiled nanosheet networks, with basal planes visibly facing upright across the channel regions.

Transfer characteristics were recorded for devices from each fraction (Appendix Section A.2.6). Mobilities were extracted from the transconductance, averaged across 3-9 channels per sample, and plotted as a function of the mean nanosheet lateral size (Figure 6.10B). A

superlinear dependence of mobility on nanosheet length was observed, consistent with the low carrier density regime described in Chapter 5 Section 5.2.1.

Although other junction and network parameters (such as tortuosity, porosity, and junction resistance) were not independently measured, the observed scaling strongly suggests that charge transport in these films is junction-limited. This is further supported by the distribution of nanosheet thicknesses, which introduce bandgap variability and hence increased R_j ²⁰⁹. These results confirm that increasing nanosheet lateral size enhances mobility in TFT networks, validating the strategy of employing the lowest g-force fraction during size selection to maximise device performance.

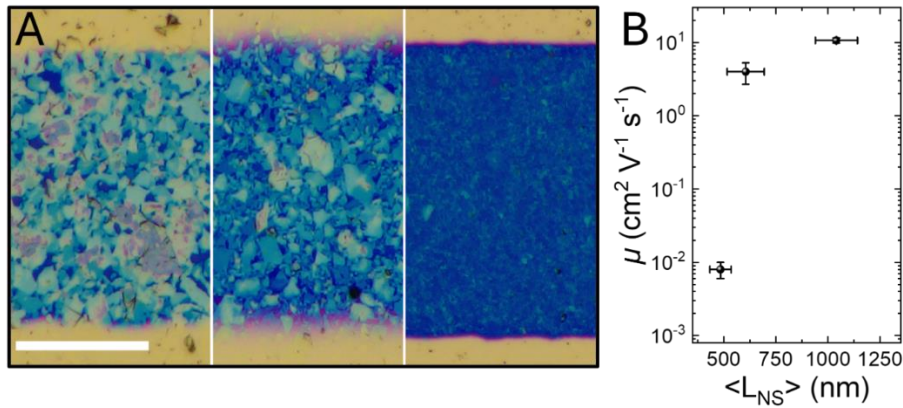


Figure 6.10: Device Mobility Scaling with Lateral Size in EE MoS₂. A – Optical microscopy images of channel regions fabricated from 97 g (left), 877 g (middle), and 2436 g (right) dispersions (scalebar: 25 μm). B – Mobility as a function of mean nanosheet lateral size, showing superlinear scaling.

6.2.7 FLEXIBLE TFT

To demonstrate the applicability of EE TMDs for flexible electronics, WSe₂ nanosheet films were deposited onto PET substrates using liquid interface deposition. Optical images of the resulting device are shown in Figure 6.11A. The channel regions again display a well-tiled, aligned nanosheet network. The device was mounted in a three-point bending apparatus for mechanical testing.

Transfer curves measured before and after bending cycles are shown in Figure 6.11B. This again exhibits the ambipolar behaviour characteristic of WSe₂. Prior to bending, the average mobility was found to be $\mu \approx 1.9 \pm 0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with $I_{on}/I_{off} \approx (2.9 \pm 0.9) \times 10^3$, values consistent with those of the rigid WSe₂ TFTs. This shows the successful transfer of the device properties from a silicon to a flexible substrate despite its increased roughness. As is shown plotted in Figure 6.11C, this high mobility is retained for 10, 100, and 1000 bending cycles at 1% strain, finding $\mu \approx 1.9 \pm 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ following 1000 bending cycles.

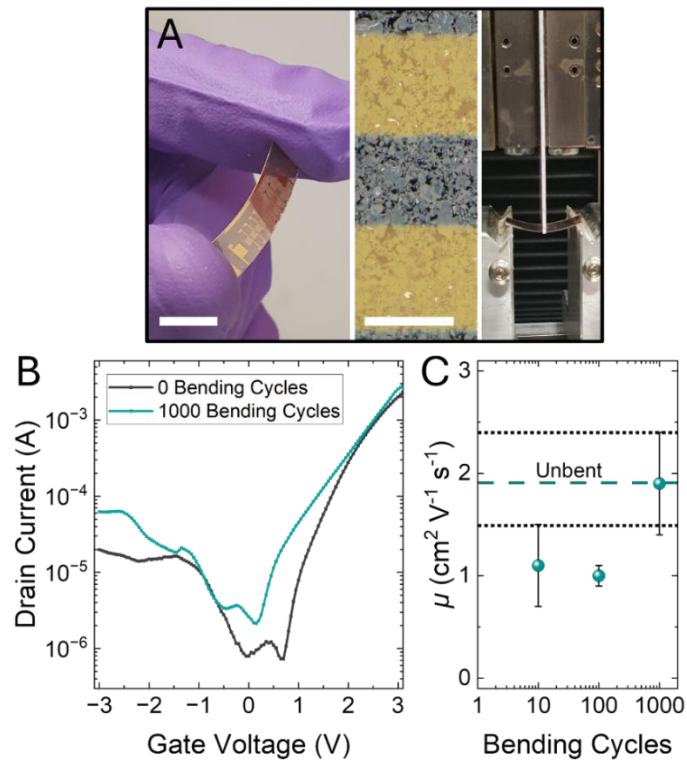


Figure 6.11: Flexible WSe₂ TFT. A – Optical images of the flexible device during bending (left, scalebar: 1 cm), channel region under optical microscopy (middle, scalebar: 50 μm), and device mounted in a three-point bending stage (right). B – Transfer curves of the device before bending and after 1000 bending cycles ($V_{DS} = 1 \text{ V}$). C – Mobility as a function of bending cycles, showing stable performance under strain.

A shift in the transfer curve along the gate voltage axis is observed after the bending cycles, corresponding to a change in threshold voltage. As fresh ionic liquid was applied prior to

each measurement set, variations in electrolyte gating conditions are expected. These may include differences in coverage and electric double layer formation, and are likely to contribute to the observed shift rather than it arising solely from strain-induced changes in the network. Despite this, the consistent slopes of the transfer curves, and hence the extracted mobility, indicate that the intrinsic transport properties of the device remain largely unaffected.

These results confirm that EE-derived nanosheet films can be processed at low temperature and without harsh chemical treatments to produce flexible TFTs. The mechanical robustness and retention of high mobility under strain highlight the suitability of this approach for the flexible logic applications outlined in Chapters 2 and 5.

6.3 CONCLUSIONS

This chapter has demonstrated that cathodic electrochemical exfoliation using alkylammonium intercalants is an effective method for preparing high-quality TMD nanosheets. AFM, Raman, and UV-vis characterization confirmed that the method yields nanosheets with large aspect ratios, low defect densities, and preserved 2H semiconducting phase. These characteristics distinguish EE from shear exfoliation and other solution-processing techniques, which typically produce smaller, thicker, or defect-rich nanosheets.

The protocol was shown to be applicable to MoS₂, WS₂, and WSe₂, each yielding nanosheets suitable for the fabrication of low junction resistance semiconducting nanosheet networks. Liquid interface deposition enabled the assembly of these dispersions into aligned thin films, which were then employed as the channel material in electrolytically gated TFTs. The resulting devices achieved mobilities of $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with on/off ratios of 10^3 – 10^4 , values comparable to the best-performing solution-processed semiconductors in the literature.

Network mobility was found to scale superlinearly with nanosheet lateral size, supporting the interpretation that transport is limited by nanosheet–nanosheet junction resistance. This result provides partial validation of the network transport models presented in Chapter 5.

Finally, the fabrication of a flexible WSe₂ TFT demonstrated that high device performance can be retained over repeated bending cycles, confirming the suitability of this approach for flexible logic applications.

Overall, the combination of cathodic EE and liquid interface deposition provides a scalable, low-temperature route to producing high-performance TMD TFTs. This establishes a pathway towards the realisation of flexible, solution-processed electronic devices based on nanosheet networks.

"To achieve great things, two things are needed: a plan, and
not quite enough time."

Leonard Bernstein

Chapter 7

Development of Liquid Interface Deposition for Low Junction Resistance Nanosheet Networks

The work presented in this chapter has been adapted from the published work: "Layer-by-layer assembly yields thin graphene films with near theoretical conductivity" published in npj 2D Materials and Applications³⁷². The graphene used in this chapter was exfoliated and characterized by Dr. Jose Munuera, film depositions and thickness measurements were performed by Dr. Kevin Synnatschke, SEM measurements were carried out by Dr. Luke Doolan.

As discussed in Chapter 2, films fabricated from solution-processed graphene nanosheets enable a wide range of device applications, such as transparent conducting films (TCFs)³²⁵, flexible electrodes³²⁸, gas sensors³⁷³, strain gauges^{64, 329} and antennas³³⁰. A critical performance parameter for many of these devices is the film conductivity. Reported values typically do not exceed approximately 10^5 S/m, with the highest conductivities usually achieved only for thick graphene films with thickness

greater than $0.5\ \mu\text{m}$ ^{214, 328, 329, 374-379}. Thinner films exhibit reduced conductivity due to non-uniformity, disorder, and percolation effects^{64, 143, 160, 301, 380, 381}.

However, many printed device applications require maximising conductivity while maintaining minimal thickness³⁸², to avoid the need to deposit excessively thick films to achieve a target sheet resistance. While bulk graphite conductivity values approaching $10^6\ \text{S/m}$ may be achieved in thin films fabricated by chemical vapour deposition (CVD)^{132, 383}, as discussed in Chapter 3, such techniques lack the scalability of solution-based methods³⁵⁰.

In solution-processed graphene films, conductivities typically remain below $10^5\ \text{S/m}$, somewhat lower than the in-plane conductivity of graphite ($\sim 10^5\text{--}10^6\ \text{S/m}$)³⁸⁴. As discussed in Chapter 5, this arises because such films consist of networks of nanosheets, where charge transport is limited by inter-nanosheet junction resistance (R_J)^{209, 289}. This effect is even more pronounced for thin films (i.e., those with thickness $< 50\ \text{nm}$), as no conductivity larger than $1.6 \times 10^4\ \text{S/m}$ has been observed in such films without the use of complex post-processing strategies¹⁶⁰. Reported strategies to overcome this include graphitisation through annealing above $1000\ ^\circ\text{C}$ ^{161, 163, 385, 386}, or chemical reduction of graphene oxide with strong reducing agents such as hydrazine or nitric acid^{160-162, 386-388}. Although these methods can yield conductivities beyond $10^5\ \text{S/m}$ ^{160, 385}, many processed films display values no higher than $2.5 \times 10^4\ \text{S/m}$ ^{161-163, 386-388}.

For flexible devices, high-temperature processing is unsuitable because polymer substrates have low thermal stability^{164, 165}. Strong chemical treatments are also undesirable due to safety, cost, and environmental concerns¹⁶⁶⁻¹⁶⁸. Thus, the aforementioned post-processing approaches are not viable for scalable manufacture of inexpensive devices, where production costs must fall below $\sim \text{€ } 1$ per cm^2 of device area to remain cost competitive. This threshold is set by the current cost of CVD graphene, which is now below $\text{€ } 2$ per cm^2

at production scale^{389, 390}. It would therefore be desirable to find a route to high conductivity graphene networks without such post-processing.

As emphasised in Chapter 5, maximising the conductivity of nanosheet networks requires minimising R_j ^{209, 391}. At low film thicknesses, conductivity also depends on suppressing percolation effects³⁰¹ and minimising disorder, in particular nanosheet misalignment that is common in printed films²⁹². These factors are closely linked, since well-aligned networks yield larger inter-nanosheet contact areas and lower junction resistance.

Horizontally oriented networks can be most effectively fabricated by Langmuir-type deposition methods, which spread nanosheets flat at a high surface tension liquid interfaces²¹². Repeated deposition can build up films with excellent alignment and controlled thickness³⁹². As discussed in Chapter 5, high aspect ratio (AR) nanosheets are required to form conformal inter-sheet contacts with each other and thereby reduce R_j ²⁰⁹. As highlighted in Chapter 3, such high AR sheets are best obtained by intercalation-based exfoliation techniques, including electrochemical and chemical exfoliation^{393, 394}.

Despite the success of using LID to deposit networks of MoS₂ in Chapter 6, the initial implementation exhibited variability in film quality between depositions, with outcomes sensitive to factors such as pipette addition rate, ink volume and concentration, and manual film transfer by substrate extrusion by the user. While this variability was not systematically quantified, it was consistently observed during early stages of process development. This motivated the development of a systematic method for optimising deposition parameters, as described in this chapter, alongside a refined setup for controlled, reproducible stacking multiple layers to produce thicker films.

The objectives of this chapter are therefore fourfold: (1) to systematically investigate the effect of the deposition parameters, ink concentration and nanosheet areal mass load, on film quality for LID of electrochemically exfoliated graphene (EEG), (2) to identify optimal

deposition parameters for single-layer films and to employ these in a refined layer-by-layer deposition method to fabricate thicker EEG films as rigid TCF devices. (3) to model the percolative behaviour of these networks and attempt to quantify R_j to assess whether EEG combined with LID yields reduced junction resistance, (4) to demonstrate a flexible TCF by depositing EEG onto a polymer substrate using this layer-by-layer method.

7.1 PROCEDURE

7.1.1 GRAPHENE INK PREPARATION

Graphene nanosheets were prepared by bipolar electrochemical exfoliation¹³⁸. Two graphite foil electrodes (Alfa Aesar, dimensions $50 \times 30 \times 0.25 \text{ mm}^3$) were immersed in 100 mL of 0.1 M $(\text{NH}_4)_2\text{SO}_4$ with a separation of 2 cm, and a 10 V bias was applied for 30 minutes. The current increased from approximately 1 A to 1.8 A during intercalation and expansion. The expanded material was filtered, repeatedly washed with deionised water ($\sim 1 \text{ L}$), and then transferred to and sonicated in 100 mL DMF for 10 minutes to complete the exfoliation. The resulting polydispersion was centrifuged at 3000 rpm (940 g) for 20 minutes to remove incompletely exfoliated particles. Graphene sheets were then sedimented at 6000 rpm (3780 g) for 90 minutes and redispersed in IPA. This final step was repeated once more to remove residual DMF. The resulting $\sim 1 \text{ g L}^{-1}$ 3780 g graphene ink in IPA was used for the study.

7.1.2 NANOSHEET INK CHARACTERIZATION

UV-VIS SPECTROSCOPY

Extinction spectra were measured on a Cary 50 spectrophotometer. For each spectrum, the IPA solvent backgrounds was subtracted. For general characterization, the sampling interval was 0.5 nm with 4 mm optical path length. For ink concentration measurements,

the interval was 1 nm with a 1 mm path length. An extinction coefficient of $2640 \text{ g L}^{-1} \text{ m}^{-1}$ at 660 nm was used to extract concentration from the spectra.

AFM

AFM (Bruker Multimode 8, ScanAsyst, non-contact, OLTESPA-R3 cantilevers) was used to determine apparent nanosheet thickness and lateral size, and to measure films depicted in the Appendix. For nanosheets, apparent thicknesses were corrected by subtracting 1 nm (trapped solvent) and dividing by 0.95 nm (apparent monolayer height) to estimate layer number N , then multiplying by 0.34 nm (crystallographic thickness of a graphene layer) to obtain actual thickness¹⁴⁸, as detailed in Appendix Section A.3.1.

7.1.3 OPTIMIZATION STUDY FILM DEPOSITION

To obtain optimal film deposition parameters, multiple films by LID using the setup in Figure 7.1. The setup was assembled from custom mill-cut PTFE parts depicted in Appendix Section A.3.2. Two main deposition parameters were varied: the ink concentration and areal mass loading of nanosheets injected into the interface. To this end, 36 films were deposited, using 6 different concentrations ($0.54\text{--}0.02 \text{ g L}^{-1}$) and 6 different nanosheet aerial mass loads ($3\text{--}21 \text{ mg m}^{-2}$) for each ink concentration.

To deposit 6 samples per ink concentration, target KOH-treated glass substrates (Appendix Section A.3.3) were immersed in particle filtered, $18 \text{ M}\Omega \text{ cm}^{-1}$ deionized water. $\sim 5 \text{ mL}$ of distilled hexane was pipetted onto the water interfaces, and then specific volumes of the graphene ink concentration was pipetted onto the water-hexane interface to form interfacial films. The films were then transferred onto the substrates by vacuuming out the water from below the waterline as indicated in Figure 7.1A. Following deposition, samples were dried in ambient for 4 hours, then annealed in inert conditions at 120°C for approximately 1 hour.

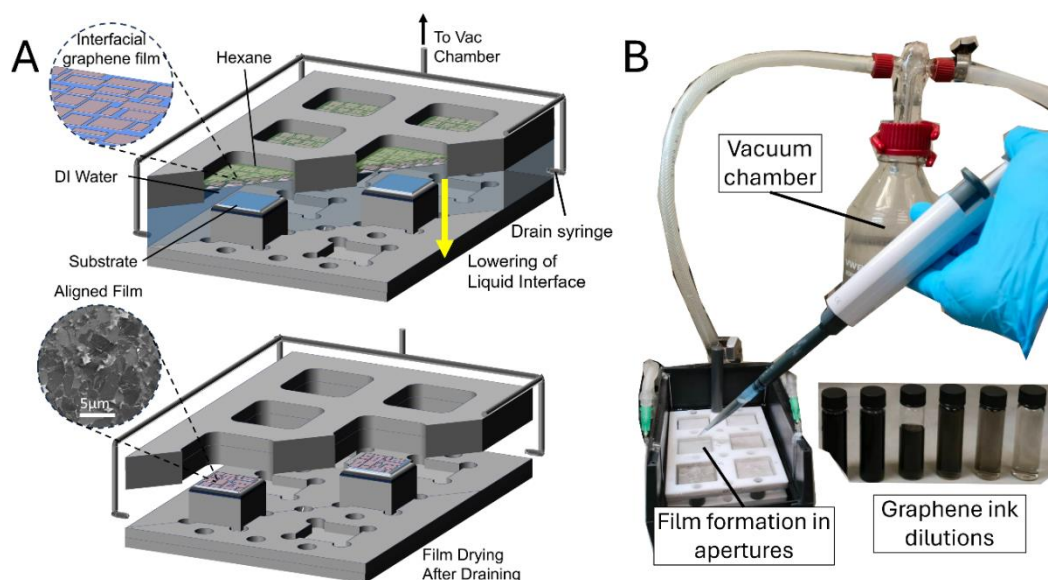


Figure 7.1: Optimization Deposition Setup. A – Schematic of the liquid interface deposition method used in this study, shown in cross section. A high surface tension interface is formed between DI water and distilled hexane. Graphene ink is injected into the interface to assemble a film of aligned nanosheets. The water is then evacuated by vacuum to transfer the nanosheet film onto substrates positioned below the interface. Inset below: SEM image of a representative film showing aligned nanosheets. Scalebar: 5 μm . B – Photograph of the experimental setup showing the cavities for substrate placement, film formation, and transfer via water evacuation into a vacuum chamber.

7.1.4 OPTIMIZATION FILM CHARACTERIZATION

TRANSMISSION SCANNING

The graphene films were imaged with an EPSON Perfection V850 Pro flatbed scanner. Using results of calibration with neutral density filters (Appendix Section A.3.4), the resultant scan image pixel intensities were converted to transmittance, then to extinction using $\text{Ext} = -\log(T)$. Distributions of these extinction values and the scan images were used to quantify the metrics of film quality described below.

An example scan image is shown in Figure 7.2A, which presents a transmission scan of a poor-quality film. A random sample of extinction data from this image is shown in

Figure 7.2B. The histogram indicates the presence of multiple local thicknesses across the film (as $\text{Ext} = \epsilon t_{\text{Film}}$, where ϵ is the film extinction coefficient and t_{Film} is the local film thickness). Coloured boxes in Figure 7.2A correspond to the coloured regions in the histogram in Figure 7.2B. These regions represent uncovered substrate (green), thick aggregated nanosheet material (blue), and homogeneous nanosheet film regions (orange).

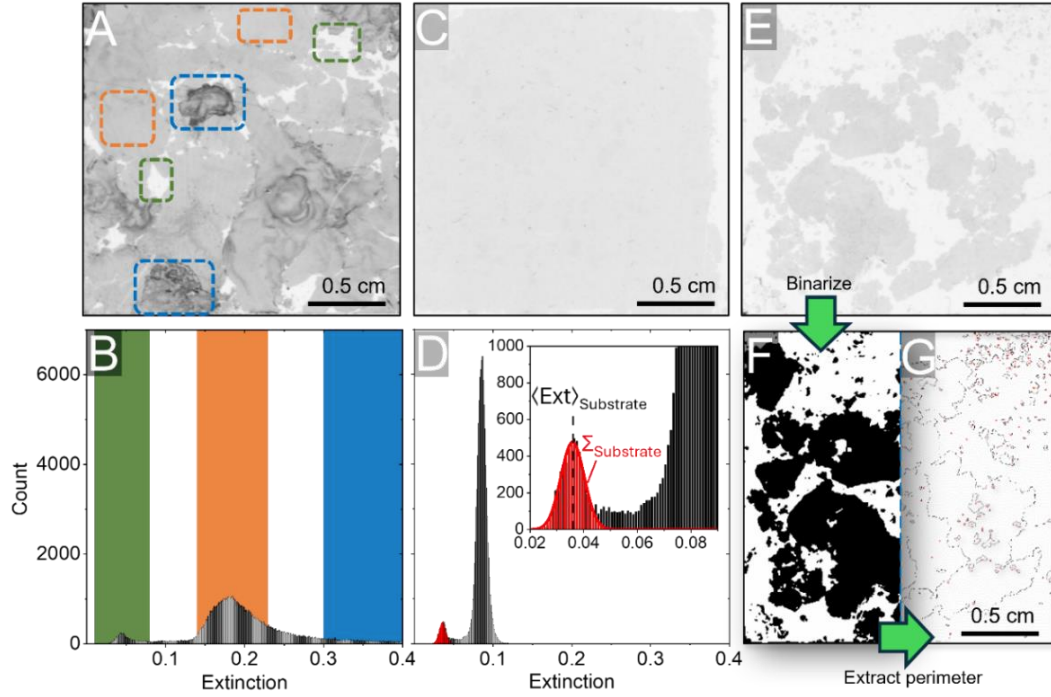


Figure 7.2: Transmission Scan Characterization. A – Optical scan of a deposited film. Regions of bare substrate (green), homogeneous film coverage (orange), and aggregated material (blue) are highlighted. B – Histogram of extinction values calculated from 100,000 randomly sampled pixels in image (A). C – Transmission scan of another film with more homogeneous quality but incomplete coverage. D – Extinction histogram for image in C. Inset: determination of substrate extinction, $\langle \text{Ext} \rangle_{\text{Substrate}}$, the substrate pixel sum $\Sigma_{\text{Substrate}}$. E – Determination of film perimeter length by binarization of the image between film and substrate domains as shown in F and then applying particle analysis to find the sum of the perimeter of the boundary between the two regions, the result of which can be seen in G.

For higher quality films, such as the example in Figure 7.2C, the extinction histogram (Figure 7.2D) is well described by a bimodal Gaussian distribution. In this case, uncovered substrate pixels at the edges of the film can be distinguished from covered film regions. These correspond to the red and black peaks in Figure 7.2D, respectively. The number of pixels associated with uncovered substrate is denoted $\Sigma_{\text{substrate}}$, and the number associated with film coverage is Σ_{film} . The mean substrate extinction, $\langle \text{Ext} \rangle_{\text{substrate}}$, is also determined from the substrate peak position, allowing correction of the measured extinction values for the effect of the substrate to yield Ext_{film} .

From the transmission scans three metrics of film quality are obtained: relative coverage, thickness homogeneity, and perimeter length. The following will outline how each is extracted and their physical meaning.

The coverage metric is defined by the ratio $(1 - \Sigma_{\text{substrate}} / \Sigma_{\text{film}})$. A value of 1 corresponds to complete coverage of the substrate by graphene.

As described in further detail in Appendix Section A.3.5, the extinction distributions yield the mean film extinction, $\langle \text{Ext} \rangle_{\text{film}}$, and its standard deviation, $\Delta \text{Ext}_{\text{film}}$. Thickness homogeneity is defined as the ratio $\langle \text{Ext} \rangle_{\text{film}} / \Delta \text{Ext}_{\text{film}}$, which is equivalent to the ratio of mean film thickness to its standard deviation ($\langle t \rangle_{\text{film}} / \Delta t_{\text{film}}$). This metric gives a relative value of variation in optically measured thickness across the film, and a higher value indicates greater uniformity in thickness.

The relative perimeter length is determined by binarization of the transmission image into substrate and film regions, followed by particle analysis (Figure 7.2E-G). Further detail of this procedure is given in Appendix Section A.3.5. The perimeter lengths (in m) are normalised by the total film area (in m²), yielding a relative film perimeter metric in m m⁻².

This quantifies the granularity of the film; a smaller value indicates a more continuous film without holes.

ELECTRICAL MEASUREMENT

The distribution of conductivity of each of the films were measured. A mask pattern (Appendix Section A.3.3) was used to define a set of 18 gold contacts that were evaporated onto the films using a Temescal FC-2000 bell-jar deposition system. The resulting electrode geometry allowed measurements of resistances between multiple electrode pairs across each film.

Two-point probe measurements were carried out using a Keithley source meter connected to a Karl SUSS PM probe station (Appendix Section A.3.6). Resistance values were collected for combinations of electrodes along each row to sample multiple conduction pathways. This enabled determination of the conductivity by the transmission line method, whereby the contact resistance was extracted and de-embedded from the measured two-probe resistance to obtain the intrinsic film resistance, and hence the film conductivity. This approach also allowed evaluation of spatial variations in conductivity across the film surface.

From these measurements, a fourth metric of film quality was obtained in addition to those extracted from transmission scans. The conductivity homogeneity is calculated from the ratio $\langle \sigma \rangle_{\text{film}} / \Delta \sigma_{\text{film}}$, where $\langle \sigma \rangle_{\text{film}}$ is the mean film conductivity and $\Delta \sigma_{\text{film}}$ is the average uncertainty in film conductivity. A larger ratio indicates a more homogeneous conductivity distribution across the film.

SEM

SEM was performed using a Carl Zeiss Ultra SEM operating at 2 kV with a 30 μm aperture at a working distance of 5 mm. Images are acquired using the secondary electron inlens detector for highly resolved imaging of nanosheets at the low accelerating voltage.

RAMAN SPECTROSCOPY

The Raman spectrum of the optimized film was measured using a WITec Raman spectrometer with a 532 nm wavelength laser, 100 $\times$ objective, and incident power of ~ 1 mW. The spectra were averaged over 3 accumulations.

7.1.5 LAYER-BY-LAYER FILM DEPOSITION

Following identification of the optimal single-layer deposition parameters, the LID method was refined to enable sequential layer-by-layer assembly of thicker films. The setup used for this purpose is shown in Figure 7.3. Compared with the square cavities employed in the optimisation study (Figure 7.1), the refined design utilised a circular cavity and a rotating stage, which facilitated more uniform addition of ink during injection. This change also altered the absolute injection volume required to achieve a given areal mass load, which was adjusted accordingly.

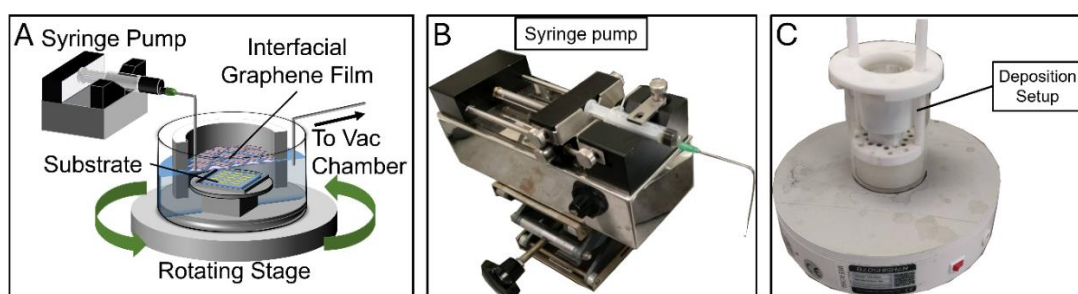


Figure 7.3: Multilayer Deposition Setup. A – Schematic of the setup used for the layer-by-layer deposition study and fabrication of the flexible conductor. A water–air interface is employed. B – Syringe pump providing steady ink injection across the interface at controlled flow rate. C – Rotating

stage used to maintain orbital motion of the interface, improving uniformity and reproducibility of film formation.

A syringe pump (Figure 7.3B) was incorporated to steadily inject ink across the interface at a constant rate of $100 \mu\text{L min}^{-1}$. This ensured reproducibility by minimising fluctuations in ink delivery that were found to affect film uniformity in earlier implementations. The rotating stage Figure 7.3C maintained gentle orbital motion of the water–air interface relative to the syringe needle, further improving homogeneity of ink addition. Full detail of this adjusted setup is provided in Appendix Section A.3.7.

Before deposition, the stock 1 g L^{-1} EEG dispersion was first stabilised to mitigate colloidal degradation observed over extended storage times (~ 2 months). This was achieved by centrifuging at 200 g for 30 minutes, repeated in five sequential steps, each time discarding the sediment and retaining the supernatant. This yielded an ink enriched in monolayer nanosheets. The concentration of the remaining supernatant was determined by UV–vis as in Section 7.1.2 and diluted to 0.02 g L^{-1} with IPA to match the optimal concentration identified in the optimisation study.

The resulting ink was injected into the water–air interface using the syringe pump and transferred by vacuum pumping out the water subphase onto KOH-treated glass substrates pre-patterned with Au electrode arrays. After deposition, the films were placed on a hotplate at 80°C , covered, and left to dry for 1 hour. They were subsequently annealed in ambient conditions at 120°C for 1 hour, followed by a brief dip in acetone to prepare the surface for deposition of the next layer. This procedure was repeated to build films with sequential deposition numbers from 1 to 16 layers. This procedure is further detailed in Appendix Section A.3.7.

After fabrication, the multilayer films were annealed at 500°C under vacuum for 1 hour to remove residual organic contaminants. Transmission scanning and electrical

measurements, as described in Section 7.1.4, were carried out on all samples, with modifications for handling multilayer scans as detailed in Appendix Section A.3.7.

Using EEG films of varying thickness, achieved by repeated LID of the material onto masked glass substrates, the extinction coefficient was determined by a calibration of scanner-acquired extinction against AFM thickness profiles (see Appendix Section A.3.9). From this analysis, the extinction coefficient of EEG films was found to be $(1.65 \pm 0.03) \times 10^7 \text{ m}^{-1}$. This value was used to determine film thickness of the above multilayer films from their values of $\langle \text{Ext} \rangle_{\text{film}}$.

7.1.6 FLEXIBLE DEVICE DEPOSITION & CHARACTERIZATION

The refined layer-by-layer protocol was also applied to deposit films on a flexible polymer substrate. Kapton was selected as the target substrate due to its thermal stability and mechanical robustness. Using the setup shown in Figure 7.3A, a graphene film was deposited by sequentially repeating 13 deposition cycles.

The resulting film thickness was estimated from extinction measurements acquired by transmission scanning as before in Sections 7.1.4 and 7.1.5. A UV-vis extinction spectrum was also obtained by mounting the sample inside a Cary-50 spectrometer, the 800-200 nm range in 1 nm steps with a 1mm slit width.

For electromechanical testing, the film was tested using a Zwick Z0.5 ProLine Tensile Tester (100 N Load Cell). The sample was contacted using silver wires attached using silver paint directly on the graphene film. Film resistance was measured using a Keithley KE2601 source meter controlled by a 2-probe LabView program. Electromechanical measurements were made using a maximum strain amplitude of 0.5%, strain rate of $0.2\% \text{ s}^{-1}$.

7.2 RESULTS AND DISCUSSION

7.2.1 GRAPHENE CHARACTERIZATION

Figure 7.4A shows the extinction spectrum of the EEG dispersion, normalised at 750 nm. The spectrum exhibits a peak near 270 nm that corresponds to the $\pi - \pi^*$ transition, as well as a broad, flat region at longer wavelengths. This spectral profile is characteristic of graphene nanosheets dispersed in liquid media and is associated with relatively thin nanosheets²⁴⁴. Previous work has shown this peak wavelength value to be associated with relatively thin nanosheets with $\langle N \rangle \sim 4$ ²⁴⁴.

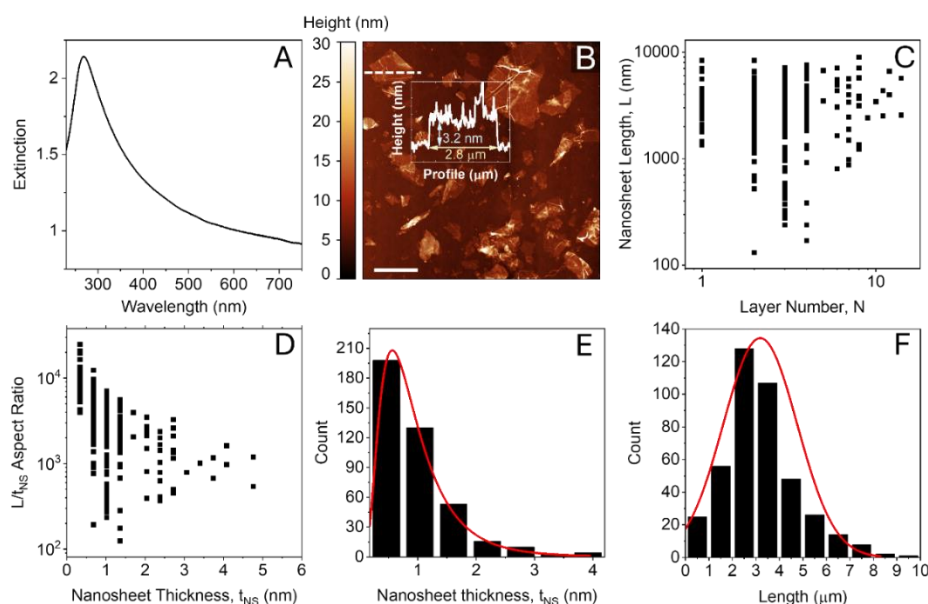


Figure 7.4: Electrochemically Exfoliated Graphene Characterization. A – Extinction spectrum of an EEG dispersion in isopropanol, normalised at 750 nm. The profile displays the characteristic graphene peak at ~ 270 nm. B – AFM image of nanosheets deposited on a Si substrate. Inset: a line profile across an individual nanosheet to determine length and thickness. Scalebar: 3 μ m. C – Plot of nanosheet length versus nanosheet layer number. D – length/thickness aspect ratio versus nanosheet thickness for a sample of graphene nanosheets measured by AFM. E – Histograms of thickness and F – lengths of the EEG nanosheets.

Figure 7.4B depicts a representative AFM image with multiple EEG nanosheets. Examples of nanosheet height profiles are given in the inset and Appendix Section A.3.1. Such profiles are used to extract a distribution in nanosheet length L and apparent thickness t . t values were converted into layer numbers (N) using the AFM step-height correction procedure outlined in Appendix Section A.3.1 and in prior reports³⁹⁵⁻³⁹⁸:

$$N = \frac{(t-1)}{0.95} \quad (\text{Eqn 7.1})$$

The resultant nanosheet L is plotted versus N in Figure 7.4C. Evidently, the nanosheets have N -values between 1 and 15, and maximum L -values approaching 10 μm . N values were converted to nanosheet thickness t_{NS} using the crystallographic interlayer spacing of graphene (0.34 nm per layer)¹⁴⁸, yielding the data in Figure 7.4D where L/t_{NS} aspect ratio (AR) is plotted against t_{NS} . The average AR was 4540 ± 180 , with a range from 125 to 24,660. while ~90% of nanosheets displayed $\text{AR} > 1000$.

The histogram of t_{NS} is shown in Figure 7.4E, shows a distribution from 0.35 nm to 4.9 nm, with a mean value $\langle t \rangle_{\text{NS}}$ of 0.97 ± 0.03 nm. The histogram of L in Figure 7.4F indicates a mean lateral size $\langle L \rangle$ of 3.18 ± 0.08 μm . This appears to be typical of electrochemically exfoliated graphene, as previous studies report measured nanosheet thicknesses ranging from 0.8 – 7 nm, and lengths ranging from 1 to 40 μm ^{138, 399, 400}. These results confirm that the electrochemical exfoliation procedure produced large, thin, and high-AR nanosheets that are suitable for assembling conformal networks with low R_f .

7.2.2 DEPOSITION OPTIMIZATION

The optimisation study produced a clear dependence of film quality on both ink concentration and nanosheet areal mass load. Figure 7.5A shows the optical scans each film

formed under different deposition conditions. At low areal mass loads the films were incomplete, with uncovered regions of substrate visible. At higher mass loads the films showed continuous coverage, although at the highest concentrations evidence of aggregation and inhomogeneity was observed.

Heatmaps of the metrics described in Section 7.1.4 are shown in Figure 7.5B-D. A full coverage of the substrate tends to be achieved at injection masses of $\sim 17\text{--}21\text{ mg m}^{-2}$ over all concentrations (Figure 7.5B), while the film thickness homogeneity (Figure 7.5C) and length of nanosheet film perimeter (Figure 7.5D) are best for the injection of 17 mg m^{-2} at the lowest concentration (0.02 g L^{-1}). The heatmap corresponding to the conductivity homogeneity metric described in Section 7.1.3 is shown in Figure 7.5E. This clearly shows the lowest concentration and highest mass per unit area (0.02 g L^{-1} , 21 mg m^{-2}) yields the most optimal film.

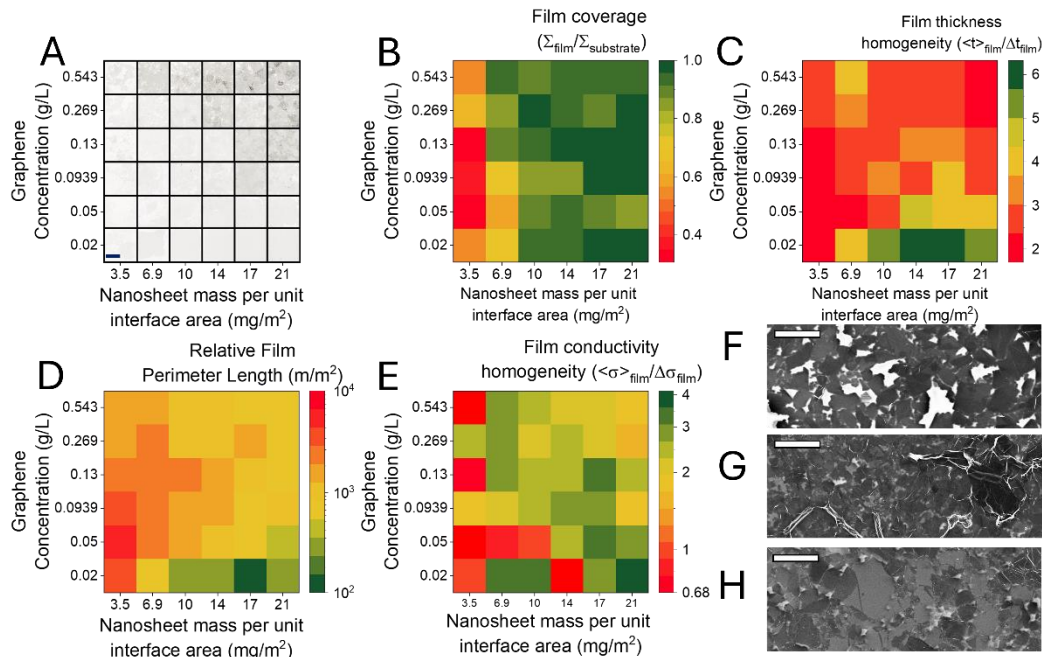


Figure 7.5: Deposition Optimization Results. A – Optical scans of films from the optimisation study, with ink concentration (g L^{-1}) and nanosheet areal mass load (mg m^{-2}) indicated. Scalebar: 1 cm.

B – Heatmap of film coverage. C – Heatmap of film thickness homogeneity ($\langle \text{Ext} \rangle_{\text{film}} / \Delta \text{Ext}_{\text{film}}$).

D – Heatmap of relative film perimeter. E – Heatmap of film conductivity homogeneity

$(\langle \sigma \rangle_{\text{film}} / \Delta \sigma_{\text{film}})$. F – SEM image of the 0.0939 g L⁻¹, 6.9 mg m⁻² film. G – SEM image of the 0.543 g L⁻¹, 21 mg m⁻² film. H – SEM image of the 0.02 g L⁻¹, 21 mg m⁻² film. Scalebars: 5 μ m.

Based on the metrics, the region of high areal mass load and low ink concentration consistently yielded films with the most desirable values for each metric. Conversely, films produced by low areal mass load appear to have low coverage, non-contiguous film domains, poor homogeneity in thickness, and are least conductive. A SEM image in Figure 7.5F shows the microstructure of such a film, produced using a graphene ink concentration of ~ 0.1 g L⁻¹, injected to an aerial mass load of 6.9 mg m⁻², showing numerous holes and gaps apparent between the individual nanosheets. Films produced by high concentration, while having relatively high coverage and contiguous film domains, appear to have even poorer thickness homogeneity and subpar conductivity homogeneity. An SEM image in Figure 7.5G shows the microstructure of a film, produced using a graphene ink concentration of ~ 0.5 g L⁻¹, injected to an aerial mass load of 21 mg m⁻², show the appearance of aggregated structures, made of folds and creases in the nanosheets.

As discussed previously, the best film quality was obtained at low dispersion concentration and high mass loading. This is illustrated by the SEM image of the 0.02 g L⁻¹, 21 mg m⁻² film (Figure 7.5H), which shows densely packed, well-aligned sheets without gaps or aggregated structures.

Lower concentrations are not suitable for the deposition process, as mixing of the graphene with the water sub-phase is observed for higher ink injection volumes required for complete substrate coverage at concentrations below 0.02 g L⁻¹. This is discussed in further detail in Appendix Section A.3.7.

Notably, these results represent a general technique for optimizing film deposition for a particular nanosheet ink. Further work is needed to determine the bearing of these results on the physics of interfacial films of nanosheets.

7.2.3 LAYER BY LAYER FILMS

Figure 7.6A shows the Raman spectrum of a single layer EEG film. The spectrum displays peaks at 1350 cm^{-1} and 1580 cm^{-1} , which respectively correspond to the D and G bands characteristic of graphene²⁶⁶. The D/G band intensity ratio (1.15) observed is consistent with a considerable number of basal plane defects, and is comparable to the value observed for reduced GO (~ 1.1 -1.5)⁴⁰¹, which is reported in the literature for similar preparation protocols of EEG by anodic and bipolar electrochemical exfoliation^{399, 400}, indicating that defects are introduced during the exfoliation process. This was expected to reduce the conductivity of the nanosheets.

Transmission scans for films of deposition numbers from 1-16 (images shown in Appendix Section A.3.7) were converted into extinction histograms, a selection of which are shown in Figure 7.6B. The curves show a systematic shift towards higher extinction and larger full width half maximum (FWHM) with increasing deposition number.

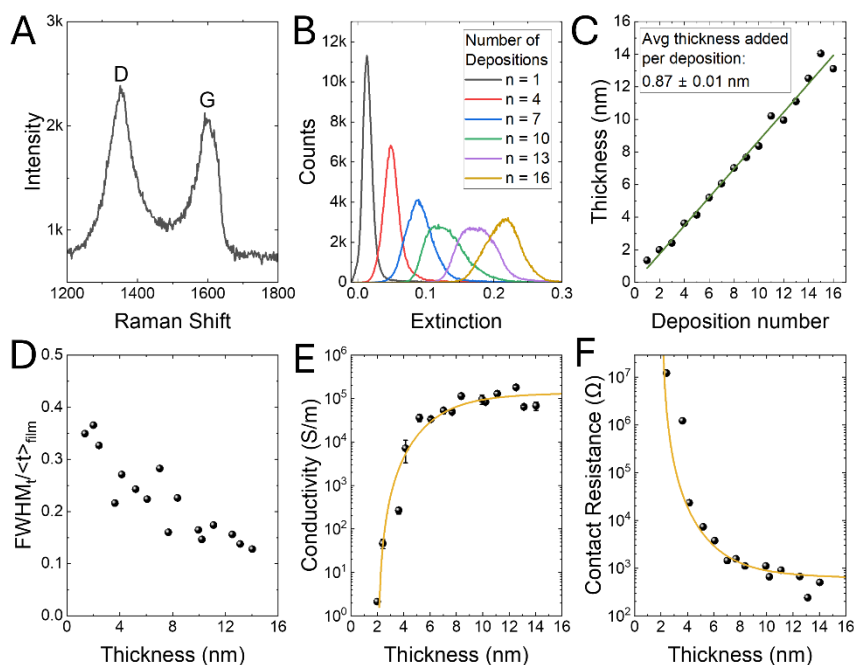


Figure 7.6: Multilayer Deposition Results. A – Raman spectrum of an EE-gra film, D and G peaks labelled. B – Transmission scan extinction histograms of a selection of multilayer films. C – Average

film thickness $\langle t \rangle_{\text{film}}$ versus deposition number. D – Ratio of film thickness full width half maxima (FWHM) to $\langle t \rangle_{\text{film}}$ for each sample. E – Graph of film conductivity versus $\langle t \rangle_{\text{film}}$, indicating a bulk conductivity of 1.3×10^5 S/m. F – Graph of average film contact resistance versus $\langle t \rangle_{\text{film}}$.

The mean film extinction values, $\langle \text{Ext} \rangle_{\text{film}}$ as well as their standard deviation, $\Delta \text{Ext}_{\text{film}}$ were extracted from these distributions as detailed in Appendix Section A.3.5. The FWHM in extinction for each film was found by fitting a gaussian function to each extinction histogram. $\langle \text{Ext} \rangle_{\text{film}}$ was converted to the average film thickness, $\langle t \rangle_{\text{film}}$, using the extinction coefficient mentioned in Section 7.1.5. As plotted in Figure 7.6C, $\langle t \rangle_{\text{film}}$ shows a linear increase with deposition number, indicating that each deposition sequentially adds layers of approximately equal thickness. From the slope, we can extract that approximately 0.87 nm is added with each deposited layer, consistent with each layer consisting of graphene nanosheets each with an average N of ~ 3 .

The FWHM of each extinction distribution was converted to the thickness FWHM, and used to calculate the ratio of this to the mean film thickness, $\text{FWHM}_t / \langle t \rangle_{\text{film}}$, as shown in Figure 7.6D. This parameter is a measure of the relative roughness of the films and falls steadily with increasing deposition number. This means the films become relatively more uniform as more material is added.

The results of the transmission line method was used to extract the conductivity and contact resistances, σ and R_c respectively, of each deposited film, with the contact resistance de-embedded to obtain the intrinsic film conductivity. These are plotted against $\langle t \rangle_{\text{film}}$ in Figure 7.6E and F.

The first two layers had near-negligible conductivity, contrary to the conductivity for single layers in the initial optimization study. This may be due to a variety of reasons. One aspect

is that a concentration change of the ink was observed after prolonged storage times. It was assumed that partial aggregation of higher layer numbers occurs over time, and therefore a slight change of the concentration and the monolayer content in the dispersion. Hence, a smaller effective mass load was used for the same injection volume. Additionally, a mass load below a complete film is in fact desirable for depositing multiple layers, as the lack of close packing avoids the nanosheet folds observed in Figure 7.5H. Such folds contribute to the formation of pores in a multilayer network and hence reduce its conductivity. As such, individual layers deposited with the aged material were homogenous according to the transmission scans, but below the percolation threshold (see Appendix Section A.3.7).

The film conductivity increases rapidly with increasing thickness, before saturating at $1.3 \times 10^5 \text{ S m}^{-1}$ for thicknesses above 8 nm (layer numbers above 10). As discussed in Chapter 5 Section 5.1, such thickness-dependent behaviour is as expected for thin nanostructured films due to percolation effects.

Shown in Chapter 5 Section 5.1.1 is a derivation for a novel semi-empirical model for a system that is percolative at low thickness. Restating Eqn 5.10, the derived expression for film conductivity, σ , as a function of mean film thickness t :

$$\sigma = \sigma_B \left[1 + \frac{1}{4} \left(\frac{t_x - t_C}{t - t_C} \right)^n \right]^{-1} \quad (\text{Eqn 7.2})$$

As before, σ_B is the thickness of a thick (bulklike) film, t_C is the percolation threshold (the thickness below which no conduction occurs), t_x is defined as the thickness where the film conductivity reaches 80% of the bulklike value ($\sigma(t_x) = 0.8\sigma_B$) while n is the percolation exponent. It was found this equation fits the data in Figure 7.6D with fit parameters of $t_x = 12 \text{ nm}$, $t_C = 2 \text{ nm}$, $\sigma_B = 1.4 \times 10^5 \text{ S m}^{-1}$ and $n = 3$. This fit implies the transition to bulk-like conductivity to occur at a film thickness of 12 nm. This is a relatively low value of t_x

for graphene networks compared to others in the literature, as the lowest reported value is that obtained by fitting to data from Neilson et al. (Appendix Section A.3.8), giving $t_x = 6$ nm.

Data for R_c as a function of film thickness is shown in Figure 7.6E. Here, a sharp decrease in contact resistance with increasing film thickness is seen, before saturating at thicknesses above 8 nm. This is the inverse of the behaviour displayed by the conductivity. In fact, as displayed by the solid line in Figure 7.6E, R_c is directly proportional to the inverse of the function used to fit the conductivity data in Eqn 7.2 ($R_c = 8.4 \times 10^7 / \sigma$). This implies that the contact resistance is directly linked to the film resistivity, likely via the resistance associated with the current spreading from the contacts to flow through the entire thickness of the film.

COMPARISON TO LITERATURE

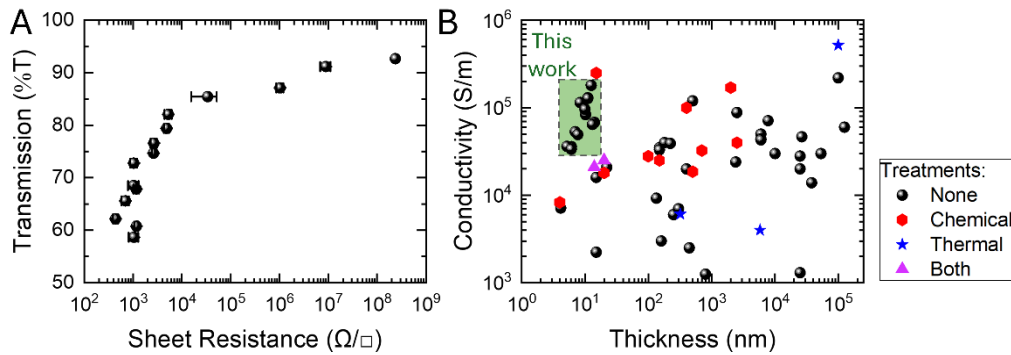


Figure 7.7: Comparison of the Rigid TCFs Produced with Existing Literature. A – Thin-film transmission plotted against sheet resistance. B – Thin-film conductivity as a function of film thickness for various literature graphene films subjected to different post-deposition treatments, compared to the films produced in this work (see Appendix Section A.3.11 for a table of this data).

The significance of this work is that it yields solution-processed graphene films with combinations of reasonably high conductivity and relatively low thickness that surpass any previous reports. It should be noted that measured conductivities for solution-processed

graphene films comparable to the conductivities reported here, $(1.3 \pm 0.2) \times 10^5 \text{ S m}^{-1}$ at $11.1 \pm 0.2 \text{ nm}$, have only previously been achieved for significantly thicker films (e.g., $1.2 \times 10^5 \text{ S m}^{-1}$ at a thickness of 500 nm)²¹⁴ or for thin ($< 50 \text{ nm}$) films using aggressive post-processing techniques ($2.5 \times 10^5 \text{ S m}^{-1}$ at 15 nm after $65\% \text{ HNO}_3$ treatment)¹⁶⁰. For published thin films similar to those here (i.e., $t < 50 \text{ nm}$ without high temperature or chemical post-processing), the record conductivity is an order of magnitude lower ($1.6 \times 10^4 \text{ S m}^{-1}$ at a thickness of 15 nm)¹⁶⁰. As such, this method demonstrates its utility for fabricating films with state-of-the-art conductivities at extremely low thicknesses. A thinner film ($6.1 \pm 0.2 \text{ nm}$) fabricated in this study exhibited a transmission of 82% and conductivity of $(3.6 \pm 0.6) \times 10^4 \text{ S m}^{-1}$, which corresponds to a sheet resistance R_s of $4.5 \text{ k}\Omega \square^{-1}$. This is competitive with the lowest sheet resistance of a lightly-processed graphene TCF device found in the literature (measured transmission of 85% , R_s of $4.1 \text{ k}\Omega \square^{-1}$)¹⁶⁰. For further comparison to existing graphene films reported in the literature, see Figure 7.7 and Appendix Section A.3.11.

JUNCTION RESISTANCE CALCULATION

As outlined in Chapter 5 Section 5.2.1, Gabbett et al.²⁸⁹ have shown that the conductivity of a network, σ_{Net} , can be expressed as:

$$\sigma_{\text{Net}} \approx \frac{1 - P_{\text{Net}}}{2t_{\text{NS}}(R_{\text{NS}} + R_J)\kappa_{\text{Net}}} \quad (\text{Eqn 7.3})$$

For a film above percolation ($\kappa_{\text{Net}} \approx 1$), this expression may be rewritten for the bulk conductivity σ_B :

$$\sigma_B \approx \frac{1 - P_{\text{Net}}}{\sigma_{\text{NS}}^{-1} + 2t_{\text{NS}}R_J} \quad (\text{Eqn 7.4})$$

Recalling from Appendix Section A.1.2 that $\sigma_{\text{NS}} = (2t_{\text{NS}}R_{\text{NS}})^{-1}$. t_{NS} is approximately 1 nm here, and it can be assumed $P_{\text{Net}} \sim 0$ for a tightly packed network of conformal nanosheets, allowing Eqn 7.4 to be rewritten as:

$$R_J = \frac{(\sigma_B^{-1} - \sigma_{\text{NS}}^{-1})}{2t_{\text{NS}}} \quad (\text{Eqn 7.5})$$

σ_{NS} can be assumed to be the in-plane conductivity of graphite, which has been reported in the range 10^5 - 10^6 S m^{-1} ³⁸⁴. Although the exact conductivity of the graphite used here is not known, the maximum possible junction resistance can be calculated by taking the upper limit of graphite conductivity as the value for σ_{NS} . Then, taking $\sigma_B = 1.4 \times 10^5 \text{ S m}^{-1}$ and $t_{\text{NS}} = 1 \text{ nm}$, $R_J < 3 \text{ k}\Omega$. However, because the graphene used here is quite defective (see Raman discussion above), its conductivity is likely below this maximum. Taking a more realistic value of $\sigma_{\text{NS}} = 2 \times 10^5 \text{ S m}^{-1}$ yields $R_J \approx 1 \text{ k}\Omega$ and a nanosheet resistance of $R_{\text{NS}} \sim 2.5 \text{ k}\Omega$. This corresponds to a ratio $R_J / R_{\text{NS}} \approx 0.4$ placing these networks in the material-limited regime. By comparison, a graphene network produced by spray coating has been previously measured to have $R_J \approx 3.3 \text{ k}\Omega$ ²⁸⁹, hence $R_J / R_{\text{NS}} \approx 1.32$, the junction-limited regime. These results suggest that the LID technique yields networks with more conductive junctions when compared to other printing techniques.

7.2.4 FLEXIBLE TCF

Pictured in Figure 7.8A is the flexible TCF produced by 13 sequential depositions of the EEG dispersion onto Kapton, with an SEM image of the network inset. As can be seen in Figure 7.8B, this film had substantially lower transparency than the samples in Figure 7.7A.

Figure 7.8C shows a cyclic resistance curve, showing the device maintains conductivity over many 0.5% strain cycles, compatible with flexible device applications. However,

unstrained conductivity ($R = 33.8 \text{ k}\Omega$, $t = 18.2 \text{ nm}$, $w = 0.48 \text{ cm}$ $L_C = 1.0 \text{ cm}$) is only $\sim 3500 \text{ S/m}$, a substantially higher sheet resistance ($R_s = 15.7 \text{ k}\Omega/\square$) than the films in Section 7.2.3.

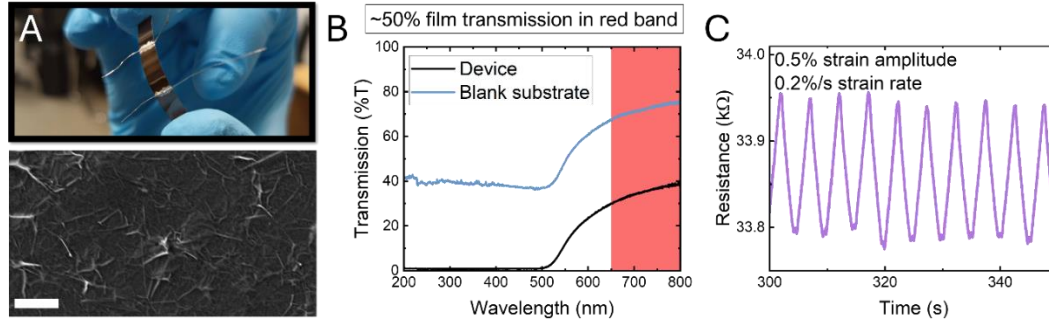


Figure 7.8: Flexible EE-Graphene Transparent Conducting Film. A – Optical image of the flexible TCF fabricated in this work, with SEM image of the 13 layer network inset. Scalebar: $2 \mu\text{m}$. B – UV-vis transmission spectra of the blank Kapton substrate (blue line) and the TCF device (black line). C – Cyclic resistance response of the $18 \pm 1 \text{ nm}$ thick device.

There are few possible reasons why the superior electrical and optical transparency properties of LID EEG networks were not successfully transferred to a Kapton substrate. The increased substrate roughness of the Kapton relative to KOH treated glass may have adversely affected network morphology. In addition, ink aging (~ 12 months) may have caused the dispersion to undergo further colloidal degradation described in Section 7.1.5.

Furthermore, the reduced thermal budget of the Kapton precludes the 500°C vacuum anneal post-processing step. For the samples on glass, this likely induces a collapse in network structure and lowers R_j substantially^{209, 318}. Further work is thus needed to process such films at lower temperatures to transfer their electrical properties to flexible substrates.

7.3 CONCLUSIONS

In this chapter, a general methodology for optimizing a LID method was demonstrated, and the deposition parameters required to deposit a homogeneous film of EEG was found ($c_{\text{ink}} = 0.02 \text{ g L}^{-1}$, mass/area = 21 mg m^{-2}).

It was then shown that stacking of multiple layers of LID EEG makes it possible to produce films with high conductivities ($1.3 \times 10^5 \text{ S m}^{-1}$) at low thicknesses (11 nm). Such conductivities are comparable to the state of the art for graphene films in general²¹⁴ and an order of magnitude increase compared to thin printed graphene films without the use of complex post-processing strategies¹⁶⁰.

The percolative behaviour of such thin conductive networks was also modelled. A novel model which incorporates both bulk-like and thickness scaling terms similar to both previous modelling approaches for thin metal films^{303, 304} and for thin nanoparticle networks^{64, 301}, was derived in Chapter 5 and successfully tested on the data in this chapter.

A model from Gabbett et al.²⁸⁹ was applied to the conductivity data of the multilayer films, demonstrating them to have low junction resistance of $\sim 1 \text{ k}\Omega$, markedly lower than the $3 \text{ k}\Omega$ achieved by Gabbett et al. for spray coated graphene networks²⁸⁹. This reduction is attributed primarily to the preferential alignment of nanosheets during LID, which promotes conformal stacking, increases effective overlap area, and reduces inter-sheet separation. These results evidence the suitability of LID for deposition of low R_j networks.

Finally, it was shown that the protocol for layer-by-layer LID may be used to fabricate a TCF on a flexible substrate. While the device maintained conductivity over multiple strain cycles, its transparency and conductivity was greatly reduced compared to equivalent films deposited on glass. Further work is needed to transfer this method to flexible substrates.

"Every great advance in science has issues from a new audacity of imagination."

John Dewey

Chapter 8

Thickness Dependence of Junction Resistance

This chapter is unpublished work, building on the EE technique shown in Chapter 6 and the multilayer LID method shown in Chapter 7. Emmet Coleman performed the spray deposition and impedance measurements. Eoin Caffrey and Jack Doran performed the profilometry. Anthony Dawson, Oran Brennan, and Sean Byrne assisted with the AFM measurements.

The concept of junction resistance has been examined in detail in Chapter 5. While earlier studies have related this parameter, along with broader network properties, to the electrical characteristics of nanosheet networks²⁸⁹, a more direct quantification of junction resistance in terms of nanosheet parameters would be desired. Such an approach has previously proven effective in advancing the understanding of nanostructured network physics^{209, 292, 402}, which is essential for the development of high-performance nanosheet-based devices.

A hypothesised simplified model of a nanosheet–nanosheet junction is shown in Figure 8.1. Prior to entering and after leaving the junction, the current density can be approximated as

a uniform sheet current centred within the nanosheet bulk, consistent with conventional treatments of current flow in thin films⁴⁰³. To enter the junction, current must traverse out-of-plane across half the nanosheet thickness ($t/2$) encountering an out-of-plane resistivity, ρ_{OOP} , over a junction area A_J . This results in a resistance contribution of $\rho_{\text{OOP}}t/2A_J$. The charge carriers then tunnel across the intrinsic junction barrier, characterised by an intrinsic junction resistance R_{J0} . Upon entering the adjacent nanosheet, current again traverses in-plane towards the sheet centre, encountering a further resistance $\rho_{\text{OOP}}t/2A_J$. The total junction resistance may therefore be expressed as:

$$R_J = \frac{\rho_{\text{OOP}}t}{A_J} + R_{J0} \quad (\text{Eqn 8.1})$$

This expression indicates that junction resistance scales with nanosheet thickness, t_{NS} , divided by the junction area, which is proportional to the square of the nanosheet lateral dimension, L_{NS}^2 . Consequently, plotting R_J as a function of $t_{\text{NS}}/L_{\text{NS}}^2$ provides a means of extracting values proportional to ρ_{OOP} and R_{J0} from the slope and intercept, respectively.

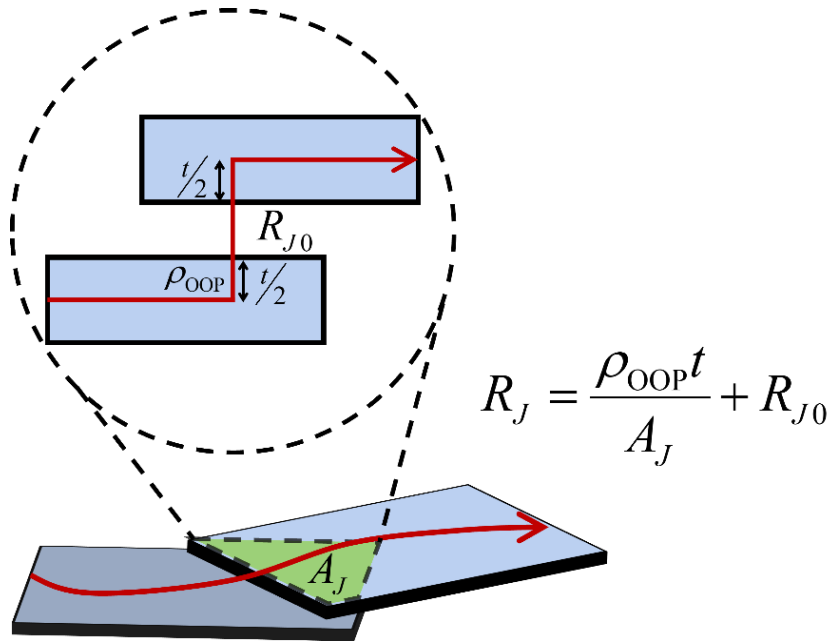


Figure 8.1: Schematic of Junction Conduction Model. Schematic of the junction conduction model proposed for investigation in this work.

(Eqn 8.1 assumes that nanosheet thickness and junction area are independent parameters. In practice, however, these quantities are often correlated, as thicker nanosheets may also exhibit larger lateral dimensions. Furthermore, variations in overlap area, junction morphology, and network disorder can obscure any direct dependence of R_j on t_{NS} . As such, the correlation between junction resistance and nanosheet thickness may not be clearly resolved in experimental data.

As discussed in Chapter 5, R_j can be experimentally determined by impedance spectroscopy. However, in this work producing samples with impedance spectra that could be consistently fitted to the AC network models²⁸⁹ proved difficult. This limitation arose from the analyser's maximum input frequency of 30 MHz, which was lower than the characteristic frequencies of most nanosheet networks fabricated, given by $\tau^{-1} = (R_j C_j)^{-1}$. For most samples, τ^{-1} exceeded 30 MHz, making the frequency at which R_j is shorted inaccessible within the measurable frequency range. To address this, thicker nanosheets were required, which as above yield larger R_j and hence lower τ^{-1} . Lower-temperature annealing was also necessary to maintain higher R_j values.

The objectives of this chapter are therefore twofold: (1) to develop a method of size selection capable of isolating sufficiently thick EE MoS₂ nanosheets for this study, (2) to fabricate networks from these dispersions by LID and spray coating, measure R_j of these networks using impedance spectroscopy, and compare the extracted junction resistance values as a function of nanosheet dimensions t_{NS}/L_{NS}^2 . This was also intended to provide a direct

comparison between the two deposition techniques in terms of the R_f values of the resulting networks.

8.1 PROCEDURE

8.1.1 THICKNESS SELECTION

Single-crystal MoS₂ was intercalated and exfoliated following the protocol described in Chapter 6. After the 5-minute bath sonication step, portions of the expanded material remained unsuspended at the bottom of the DMF-PVP solution. These were subjected to a second bath sonication under identical conditions in 1 mg mL⁻¹ DMF-PVP. The resulting polydispersions were designated as the first and second exfoliations, respectively.

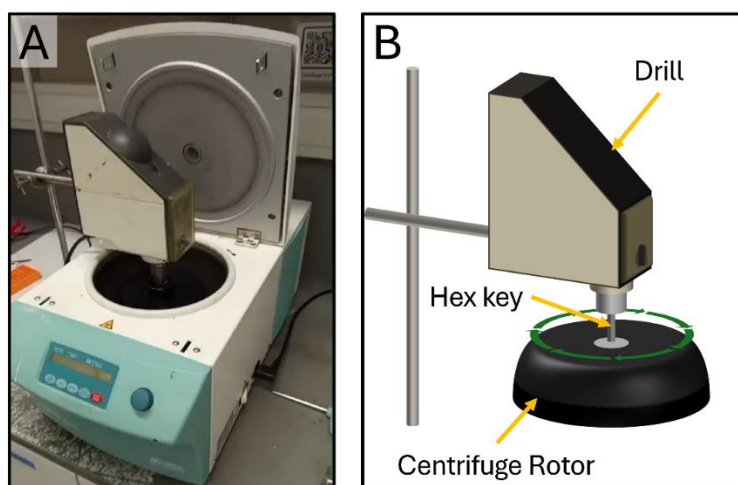


Figure 8.2: Drill Centrifugation Setup. A – Photograph of the drill-driven centrifuge assembly used to achieve low-speed centrifugation. B – Schematic of the adapted centrifugation configuration.

To enrich thicker nanosheets, reduced centrifugation speeds were employed. To achieve such low rotation speeds, a modified centrifuge setup was used. In this configuration, the rotor was driven by an electric drill operating at 40–400 rpm, housed within a repurposed centrifuge casing (Figure 8.2). For the first exfoliation, an initial centrifugation at 100 rpm (1 g) for 20 minutes removed unexfoliated bulk. Subsequent sedimentation steps of the

supernatant were performed at 150 rpm (2.2g), 200 rpm (3.9g), 250 rpm (6.1g), 300 rpm (8.8g), 400 rpm (15.6g), 500 rpm (24.3g), and 1000 rpm (97g), each for 20 minutes (the latter two using a functioning centrifuge). Dispersions were labelled according to the g force at which they sedimented.

For the second exfoliation, the same 1 g bulk-removal step was applied, followed by centrifugations at 150 rpm (2.2g), 171 rpm (2.8g), 172 rpm (2.9g), 175 rpm (3.0g), 180 rpm (3.2g), 190 rpm (3.5g), 210 rpm (4.3g), 230 rpm (5.1g), 380 rpm (14.0g), and 500 rpm (24.3g). Aside from the 150 rpm fraction, each individual dispersion was too dilute for deposition. To address this, groups of adjacent fractions (150rpm, 171-180rpm, 190-230rpm and 380-500rpm) were mixed and relabelled as 2.2g (2), 3.2g (2), 5.1g (2), and 24.3g (2) respectively.

Each dispersion was washed of PVP and DMF and transferred to IPA by the protocol in Chapter 6.

8.1.2 UV-VIS SPECTROSCOPY

Extinction spectra were acquired using a PerkinElmer Lambda 1050 spectrometer in a 20 mm optical path quartz cuvette. A slit width of 2 nm and step size of 1 nm were used. Concentrations were determined using an extinction coefficient of $6900 \text{ L g}^{-1} \text{ cm}^{-1}$ at 345nm^{258} .

8.1.3 AFM

AFM (Bruker Multimode 8, ScanAsyst, OLTESPA-R3 cantilevers) was employed to determine nanosheet thickness and lateral size for the 2.2g, 8.8g, 11.9g, 15.6g, and 97g dispersions. These results were used to infer average nanosheet dimensions for the remaining dispersions. Apparent thicknesses were corrected by subtracting 0.5 nm to account for trapped solvent, dividing by 1.9 nm (apparent monolayer step height²⁵⁴), and

multiplying by the MoS₂ crystallographic monolayer thickness of 0.65 nm⁸⁴. This procedure yielded estimates of nanosheet layer number N and real thickness, as described in Appendix Section A.4.1.

8.1.4 SUBSTRATE PREPARATION

Gold electrodes (~50 nm) were deposited by evaporation (Temescal FC-2000 Bell Jar) through a stainless-steel mask (50 μ m thick, laser-cut by Laser Micromachining Ltd.). The mask defined 12 interdigitated electrode channels with a width of 19.55 mm and lengths of 35–150 μ m in 10 μ m increments. KOH-treated fused silica substrates were used for LID samples (Appendix Section A.3.3), while ultrasonically cleaned glass slides were used for spray-coated samples.

8.1.5 LIQUID INTERFACE DEPOSITION

Dispersions were diluted to ~0.25 mg mL⁻¹ and injected onto a hexane–water interface using the multilayer LID setup described in Chapter 7 Section 7.1.5, at an areal loading of ~72 g m⁻². Films were transferred onto fused silica substrates, air dried for 2 hours, and annealed at 60 °C in an N₂ glovebox for 30 minutes. Between sequential depositions, samples were washed with acetone. Two sequential layers were deposited for all samples to suppress percolative effects. Dispersions with sufficient yield to fabricate samples by this technique were 3.9g, 6.1g, 8.8g, 15.6g, 24.3g, 97g, 2.2g (2), 5.1g (2), and 24.3g (2). Each sample was labelled by dispersion and method (e.g., “3.9 g LID”).

8.1.6 SPRAY COATING

Inks were diluted to ~0.01 mg mL⁻¹ and spray-deposited using a Harder and Steenbeck Infinity airbrush mounted on a computer-controlled Janome JR2300N gantry. Deposition employed an N₂ back pressure of 45 psi, nozzle diameter of 400 μ m, and stand-off distance of 100 mm²¹⁹. Substrates were heated to 80 °C during deposition, followed by annealing in

an N₂ glovebox at 60 °C for 30 minutes. Dispersions with sufficient material to fabricate samples by this method were 2.2g, 3.9g, 6.1g, 8.8g, 11.9g, 97g, and 3.2g (2). Samples were labelled accordingly (e.g., “2.2g spray”).

8.1.7 FILM THICKNESS MEASUREMENT

PHASE SHIFT INTERFEROMETRY

Film thickness was determined using a Profilm3D Optical Profiler (Filmetrics, KLA Corp.) in phase-shift interferometry mode with a 50× objective. Scratches made with fine tweezers exposed the substrate as reference. Histograms of pixel height values yielded bimodal distributions, from which film thickness, $\langle t_{\text{film}} \rangle$, was obtained as the separation between substrate and film peaks. Representative images of this are shown in Appendix Section A.4.2.

AFM

For films too rough for PSI (Appendix Section A.4.2), AFM was used to measure the film surfaces as before in Section 8.1.3. Thickness values were determined from Gwyddion edge height functions applied to multiple line profiles and averaged for each film to obtain $\langle t_{\text{film}} \rangle$ (Appendix Section A.4.3).

8.1.8 IMPEDANCE SPECTROSCOPY

Impedance spectra were collected using a Keysight E4990A analyser (30 MHz maximum). A 16047E test fixture minimised wire length to ~50 mm, reducing parasitic effects at high frequency. Contact pads were probed with spring-loaded Sensepeek SP10 connectors. To subtract contact resistance, spectra were collected across all twelve electrode channel lengths. Measurements used a 500 mV AC amplitude and precision speed setting of 3. Prior to measurement, DC sweeps in the range of AC amplitude confirmed linear response.

8.1.9 OPTICAL MICROSCOPY

Optical imaging was performed using an Olympus DSX1000 microscope in bright-field mode at 40× magnification. Representative images are included in Appendix Section A.4.5.

8.2 RESULTS & DISCUSSION

8.2.1 UV-VIS SPECTROSCOPY

The extinction spectra of the size-selected dispersions are shown in Figure 8.3A and B, normalised at 345 nm. The relative intensities of the A, B, and C excitons vary systematically across the dispersions, consistent with prior observations of the optical behaviour of size-selected MoS₂ dispersions²⁵². As discussed in Chapter 4, relative exciton peak intensities in TMD UV-vis spectra may be used to infer nanosheet dimensions. Again, restating the model shared by Backes et al. via 2D-PRINTABLE previously used in Chapter 6, which relates the ratio of extinctions of the C and A exciton peaks to the dispersion's volume fraction weighted-mean nanosheet layer number:

$$\langle N_{\text{vf}} \rangle = -1.06 \ln \left[\frac{\text{Ext}_C / \text{Ext}_A - 1.15}{11.46} \right] \quad (\text{Eqn 8.2})$$

Application of this model to the measured spectra yields the plots shown in Figure 8.3C and D. The C/A extinction ratio increases superlinearly with centrifugation product (CF = time × rotational velocity, units: rad² s⁻¹), while the inferred values of $\langle N_{\text{vf}} \rangle$ decrease superlinearly with CF. This behaviour indicates that higher centrifugation speeds preferentially isolate thinner nanosheets. These results confirm that the adapted centrifugation protocol provides a degree of separation by nanosheet thickness, at sufficiently low sedimentation rates to enable preparation of dispersions enriched with thicker nanosheets. Further confirmation of nanosheet dimensions was obtained by AFM.

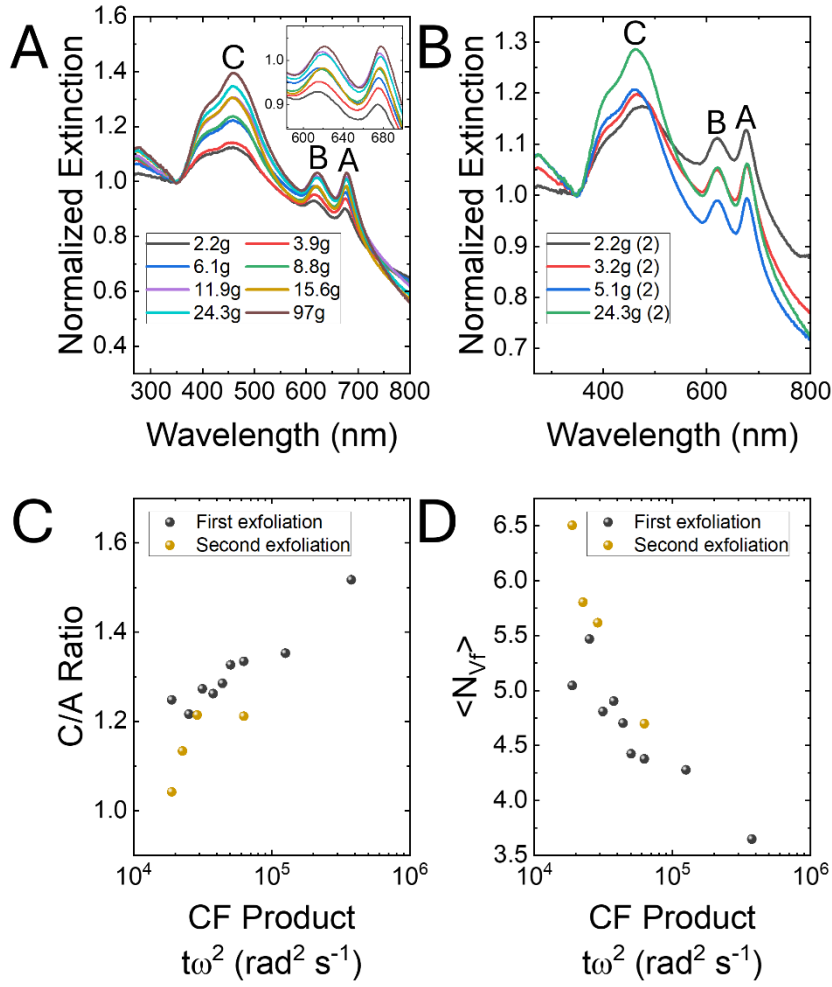


Figure 8.3: Thickness Selection UV-vis Spectra. A – Extinction spectra of the first exfoliation dispersions. B – Extinction spectra of the second exfoliation dispersions. All spectra are normalized to the value at 345nm. C – Plot of ratio of C and A peak extinctions with respect to the centrifugation product. D – Plot of $\langle N_{vf} \rangle$ versus centrifugation product, calculated by Backes' empirical model.

8.2.2 AFM STATISTICS

Shown in Figure 8.4 are the lateral size and layer number histograms extracted for each of the 5 dispersions measured by AFM. These exhibit $\langle L_{NS} \rangle$ values of 14.0 ± 0.7 , 8.1 ± 0.4 , 6.8 ± 0.3 , 5.1 ± 0.2 , 2.0 ± 0.1 μm for the 2.2g, 8.8g, 11.9g, 15.6g, 97g dispersions respectively. Corresponding $\langle t_{NS} \rangle$ values were 11.0 ± 0.7 , 6.1 ± 0.3 , 5.1 ± 0.4 , 4.3 ± 0.3 , 3.4 ± 0.2 nm. These values are consistent with the large lateral size and thin morphology characteristic of electrochemically exfoliated nanosheets.

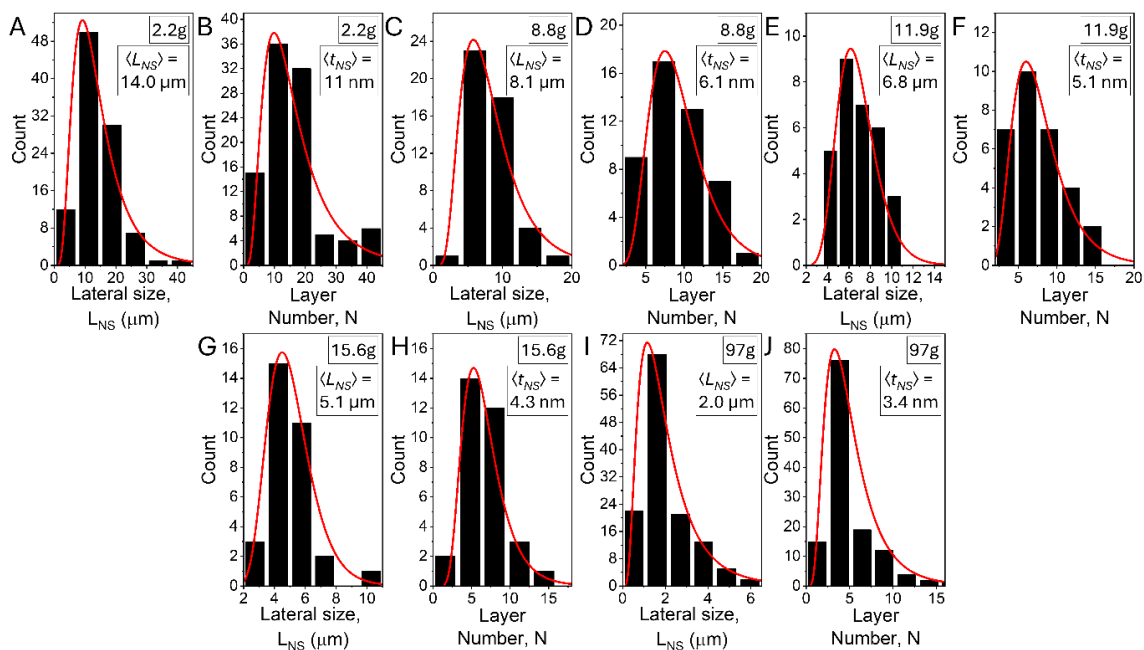


Figure 8.4: AFM Statistics for Thickness Selected Dispersions. (A, C, E, G, I) Lateral size histograms of the 2.2 g, 8.8 g, 11.9 g, 15.6 g, and 97 g dispersions, respectively. (B, D, F, H, J) Corresponding layer number histograms of the same dispersions.

To reduce the experimental effort, nanosheet dimensions for other dispersions were inferred using centrifugation theory²⁰³. In brief, nanosheet dimensions of size-selected dispersions are found to be directly related to the rotational velocities they sediment at.

Firstly, the lateral size-thickness product ($\langle L_{NS} \rangle \langle t_{NS} \rangle$) is linearly fitted against the square inverse of the dispersions' revolutions per minute ($1/\text{rpm}^2$) (Figure 8.5A). Centrifugation theory predicts that this relationship should yield an intercept close to zero, corresponding to negligible sheet dimension at infinite centrifugation speed²⁰³. Consistent with this prediction, the fit gives an intercept of $(3.3 \pm 1) \times 10^{-15} \text{ m}^{-1}$, supporting the use of centrifugation theory to infer sheet sizes. The slope of $\langle L_{NS} \rangle$ versus $1/\text{rpm}$ was $2.17 \times 10^{-13} \text{ m}$ (Figure 8.5B), while slope of $\langle t_{NS} \rangle$ versus $1/\text{rpm}$ was $1.8 \times 10^{-6} \text{ m}$ (Figure 8.5C). These slopes were then used to infer $\langle L_{NS} \rangle$ and $\langle t_{NS} \rangle$ values for each

dispersion, which were in turn used for determining R_j values and plotting these against

$$\langle t_{NS} \rangle / \langle L_{NS} \rangle^2.$$

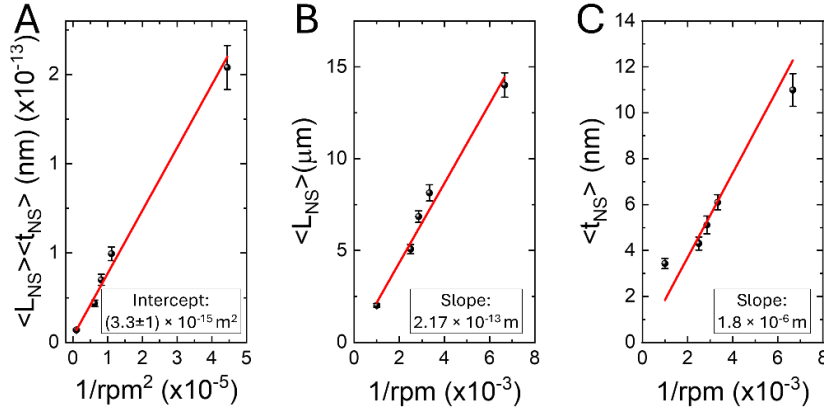


Figure 8.5: Centrifugation Theory Plots for Inferring Dispersion Statistics. A – Plot of $\langle L_{NS} \rangle \langle t_{NS} \rangle$ versus $1/\text{rpm}^2$, showing a near-zero intercept. B – Plot of $\langle L_{NS} \rangle$ versus $1/\text{rpm}$. C – Plot of $\langle t_{NS} \rangle$ versus $1/\text{rpm}$.

8.2.3 IMPEDANCE SPECTROSCOPY

Representative real impedance spectra are shown in Figure 8.6 for the 3.2g spray-coated sample. The spectra were fitted using a modified Randles expression incorporating a constant phase element (CPE) to account for network inhomogeneity²⁸⁹:

$$Z'(\omega) = R_s + R_p \frac{[1 + (\omega R_p C_p)^\alpha \cos(\alpha\pi/2)]}{1 + 2(\omega R_p C_p)^\alpha \cos(\alpha\pi/2) + (\omega R_p C_p)^\alpha} \quad (\text{Eqn 8.3})$$

The values of R_p obtained from fitting of Eqn 8.3 were converted to junction resistances,

R_j , using the relation outlined in Chapter 5 Section 5.2.2:

$$R_j = R_p \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{1 - P_{\text{Net}}}{2t_{\text{NS}} \kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2} \right]^{-1} \quad (\text{Eqn 8.4})$$

Here, network porosity P_{Net} was assumed to be $\sim 2\%$, network tortuosity $\kappa_{\text{Net}} \approx 1$, and nanosheet carrier density $n_{\text{NS}} = 2 \times 10^{18} \text{ cm}^{-3}$ (typical of reported carrier concentration values for MoS_2 ⁴⁰⁴). Channel cross-sectional area A_{Net} was determined as the product of film thickness and channel width, $w \times \langle t_{\text{film}} \rangle$. t_{NS} and L_{NS} are taken as $\langle t_{\text{NS}} \rangle$ and $\langle L_{\text{NS}} \rangle$ respectively, both determined by the results in Section 8.2.2.

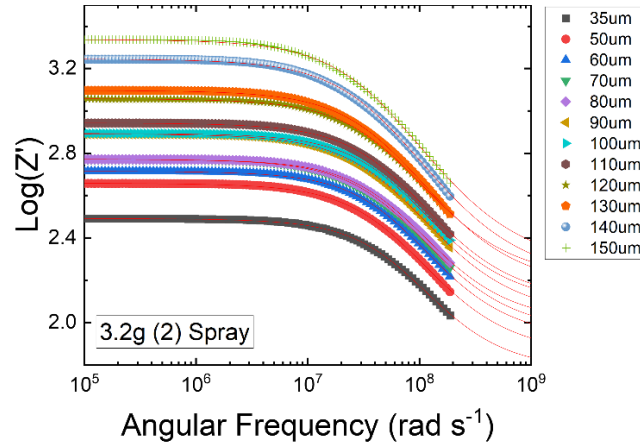


Figure 8.6: Impedance Spectra. Representative impedance spectra for the 12 channels on the 3.2g spray-coated sample. The complete set of spectra for each sample are plotted in Appendix Section A.4.4.

Averaged values of R_j were determined for each sample from the 12 spectra, with uncertainties obtained from standard deviation of the mean.

8.3 R_j VERSUS NANOSHEET DIMENSIONS

Figure 8.7 presents plots of average R_j against $\langle t_{\text{NS}} \rangle / \langle L_{\text{NS}} \rangle^2$ for networks produced by LID and spray coating. Three outliers (97g LID, 97g spray, and 24.3g LID) were excluded due to abnormally high values of R_j . For both deposition techniques, the data show at most a weak positive trend, but with substantial scatter. As such, the linear dependence predicted by (Eqn 8.1 is not clearly resolved experimentally. Nevertheless, spray-coated samples

systematically exhibit higher R_J values than LID samples at comparable values of $\langle t_{NS} \rangle / \langle L_{NS} \rangle^2$, consistent with spray deposition producing networks with intrinsically lower junction quality. This is attributed to poorer nanosheet alignment and reduced conformality in spray-coated films, in agreement with the discussion in Chapter 5.

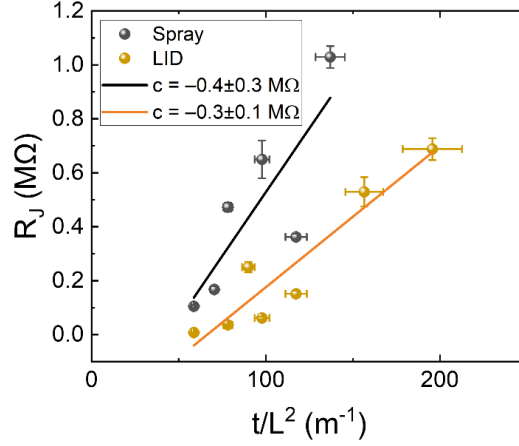


Figure 8.7: Plots of Junction Resistance versus Sheet Dimensions. Plots of R_J versus t_{NS} / L_{NS}^2 for the LID and spray-coated sample. Both show only a weak positive trend, contradicting the model. Linear fits to both datasets yield negative intercepts, further indicating inconsistency with the model.

Linear fits to the two datasets yield negative intercepts (Spray: -0.4 ± 0.3 MΩ, LID: -0.3 ± 0.1 MΩ), inconsistent with Eqn 8.1, which predicts a positive intercept corresponding to R_{J0} . This indicates that the simple junction model does not adequately capture the experimental variability in these films. A likely reason is that the data points do not represent networks differing only in dimensions of their constituent nanosheets by $\langle t_{NS} \rangle / \langle L_{NS} \rangle^2$, but rather networks that also vary in morphology, packing, overlap geometry, and junction quality. In such a case, any dependence of R_J on $\langle t_{NS} \rangle / \langle L_{NS} \rangle^2$ is obscured by broader structural variability. Another possible reason is that the networks may have had too poor-quality morphology to reliably resolve R_J , as junction quality throughout the networks varied considerably. This is supported by low values of the order

parameter, α , obtained from the fitting of each set of impedance spectra ($\alpha \sim 0.7$ for the spray sample, ~ 0.9 for the LID samples).

Additional scatter may have arisen because the values of $\langle t_{\text{NS}} \rangle / \langle L_{\text{NS}} \rangle^2$ were inferred from centrifugation theory rather than measured directly by AFM for each sample. Moreover, as the centrifugation procedure was performed at relatively low speeds and was not systematically optimised, each dispersion likely retained substantial internal polydispersity. The resulting spread in nanosheet dimensions, combined with network-to-network differences in morphology, likely dominates the variability in Figure 8.7. In addition, residual ionic species from the exfoliation and deposition processes may remain trapped at nanosheet junctions, particularly given the relatively low annealing temperatures employed, increasing inter-sheet separation and contributing to variability in R_j .

For all these reasons outlined above, these results should be interpreted as providing qualitative support for the expected trend, rather than a quantitative validation of (Eqn 8.1.

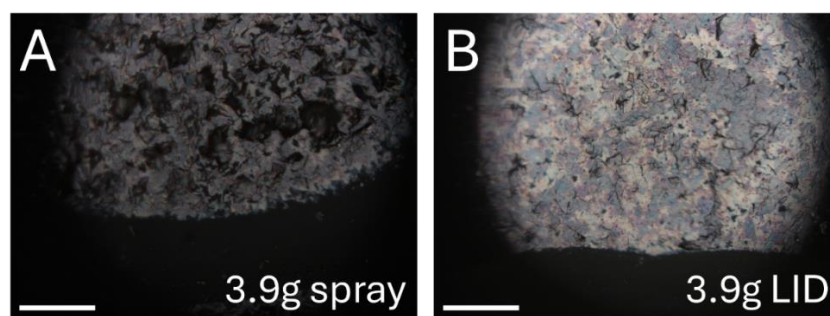


Figure 8.8 Optical Microscopy Images Comparing Deposition Techniques. A – Spray coated film produced with the 3.9g dispersion. B – LID film produced from the 3.9g dispersion. Scalebars: 50 μm . Full set of sample images are shown in Appendix Section A.4.5.

Optical microscopy images comparing spray-coated and LID films prepared from the same dispersion are shown in Figure 8.8A and B respectively. The spray-coated film exhibits

misaligned nanosheets and porosity, while the LID film displays close-packing with clear conformal overlaps. Based on the arguments laid out in Section 5.4, it is likely the latter has better quality morphology for low junction resistance. These observations support the impedance results, confirming LID produces higher-quality networks with lower junction resistance. Additional representative images are provided in Appendix Section A.4.5.

8.4 CONCLUSIONS

This preliminary study investigated the dependence of junction resistance on nanosheet thickness and lateral size in EE MoS₂ networks. Size selection by low-speed centrifugation enabled isolation of dispersions of thick nanosheets, confirmed by UV-vis and AFM. These dispersions were deposited by both spray coating and liquid interface deposition (LID), yielding films measured by impedance spectroscopy to extract junction resistance.

Plots of R_j against $\langle t_{NS} \rangle / \langle L_{NS} \rangle^2$ exhibited at most a weak positive trend, with substantial scatter, indicating that the linear dependence predicted by Eqn 8.1 is not clearly resolved experimentally. This variability likely arises from dispersion polydispersity, morphological variability within networks, junction inhomogeneity, and residual species present at nanosheet interfaces. Notably, LID consistently produced lower junction resistances compared to spray coating, consistent with enhanced nanosheet alignment and conformality observed in microscopy images.

Although the extracted linear fits yielded negative intercepts, inconsistent with the expected intrinsic junction resistance term, the results nevertheless indicate that both nanosheet dimensions and deposition method influence junction resistance. These findings support liquid interface deposition as a preferred method for fabricating nanosheet networks with reduced junction resistance, while highlighting the limitations of the simplified geometric model when applied to disordered, solution-processed system.

Finally, this work provides an experimental framework for the further refinement of impedance-based junction resistance measurements in nanosheet networks.

"Life is like being at the dentist. You always think that the worst is still to come, and yet it is over already."

Otto von Bismarck

Chapter 9

Conclusions & Future Work

This thesis has addressed nanosheet networks of solution-processed 2D material nanosheets, focusing on improving their performance for device applications by reducing the network junction resistance. The results presented here demonstrate that both the nanosheet preparation technique and the deposition method are key considerations in developing effective strategies for this goal.

While networks of TMD nanosheets are promising candidates for flexible TFT channel materials, previously demonstrated devices rarely exceeded mobilities of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This limitation stemmed from the low nanosheet aspect ratios produced by existing solution-processing methods and from the sub-optimal network morphologies associated with conventional printing techniques. Lin et al.¹⁹¹ had previously shown that cathodic electrochemical exfoliation using alkylammonium salts could yield semiconducting MoS_2 nanosheets with high aspect ratio, and that spin coating of such dispersions could achieve mobilities of $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Motivated by these findings, electrochemical exfoliation was

selected in this work to prepare inks of three TMD systems: MoS₂, WS₂ and WSe₂. Comparison of EE MoS₂ with shear-exfoliated MoS₂ confirmed that EE produces substantially higher aspect ratio nanosheets than LPE. The three EE TMD materials were deposited using LID onto rigid substrates, followed by electrolytic gating with EMIM-TFSI. The resulting films exhibited average mobilities of $10.7 \pm 0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (MoS₂), $9.1 \pm 2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (WS₂), and $2.0 \pm 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (WSe₂) with corresponding on/off ratios of $(2.6 \pm 0.4) \times 10^3$, $(3.4 \pm 0.6) \times 10^3$, and $(4.2 \pm 1.8) \times 10^4$. These values are consistent with previous reports for EE TMDs. TFTs fabricated from different size-selected fractions of EE MoS₂ further demonstrated a lateral-size dependence of mobility, in agreement with models of network conductivity for low-carrier-density nanosheets. Finally, a WSe₂ network deposited by LID onto PET yielded a flexible TFT with mobilities of $1.9 \pm 0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratios of $(2.9 \pm 0.9) \times 10^3$, which retained this performance over 1000 bending cycles. These results demonstrate that EE combined with LID enables the fabrication of high-mobility, flexible, solution-processed electronic devices, with the observed improvements attributable to reduced junction resistance.

In Chapter 6, LID was observed to have substantial batch-to-batch variability, motivating a focus on improving reproducibility. To address this, an optimisation procedure was developed for a given ink, with film-quality metrics defined from optical and electrical measurements. For thin, high-aspect-ratio graphene produced by bipolar electrochemical exfoliation, homogeneous films were obtained at an ink concentration of 0.02 g L^{-1} , and interface areal mass load of 21 mg m^{-2} . Applying these parameters, together with refinements to the LID apparatus, enabled sequential stacking of LID EE graphene layers on glass, yielding high conductivities ($1.3 \times 10^5 \text{ S m}^{-1}$) at low thicknesses (11 nm). Conductivity-thickness data were fitted with a novel percolative scaling model, giving a low bulk transition thickness ($t_x = 12 \text{ nm}$), comparable to the state of the art for graphene networks. In the supercritical regime, the extracted junction resistance was approximately

1 k Ω , indicating material-limited transport and evidencing the suitability of LID for producing low junction resistance networks. Finally, the layer-by-layer LID protocol was then applied to deposit EE graphene on Kapton to produce a flexible transparent conducting film. Although the device maintained conductivity ($\sim 3.5 \times 10^3 \text{ S m}^{-1}$) under repeated strain cycles, its transparency ($\sim 50\%$) and sheet resistance ($15.7 \text{ k}\Omega \square^{-1}$) were inferior to glass-based films, likely due to the restricted annealing temperature imposed by the polymer substrate's thermal budget.

As others had identified junction resistance as the key transport bottleneck²⁰⁹, a preliminary effort was made to measure this quantity directly and relate it to nanosheet dimensions. To this end, a thickness-selection protocol was implemented to isolate EE MoS₂ nanosheets of different thicknesses, followed by film deposition of the resulting dispersions by both LID and spray coating. Impedance spectroscopy was then used to extract junction resistance. Plots of junction resistance against nanosheet thickness, normalised to sheet area, showed at most a weak positive trend, failing to verify the proposed model owing to substantial scatter. The poor correlation was attributed to junction inhomogeneity and to limitations in the size-selection process, with the resulting negative intercept contradicting the model predictions. Nonetheless, LID consistently produced lower junction resistance samples than spray coating, reinforcing its suitability for producing low-resistance networks. Overall, however, the study was inconclusive, and further refinement of the thickness-selection method and experimental design will be required.

The methods and results presented here represent progress towards the development of low junction resistance nanosheet networks and their implementation in functional devices. The following sections outline immediate next steps to extend this work, as well as broader directions for future research.

NEXT STEPS AND EXPERIMENTAL DIRECTIONS

Several immediate experimental directions can be identified to further improve nanosheet network performance and better resolve the relationship between structure and transport.

Further optimisation of electrochemical exfoliation (EE) of TMDs is required to improve nanosheet quality and control nanosheet dimensions. In particular, the use of alternative intercalants to tetrapropylammonium, with varying molecular size and charge, should be explored to better regulate interlayer expansion and potentially enable control over nanosheet lateral size and thickness. Systematic variation of intercalation potential and duration may also provide additional control over exfoliation efficiency and nanosheet dimensions. Furthermore, the development of dispersant-free exfoliation protocols in non-toxic, low-boiling-point solvents would be desirable to improve process safety, reduce residual contamination at nanosheet junctions, and minimise the need for post-deposition thermal annealing, while also maintaining colloidal stability. Such advances would enable the production of TMD nanosheets more suitable for low junction resistance networks and device applications.

A second direction is the extension of the systematic optimisation of liquid interface deposition (LID) to other 2D material systems, alongside investigation of the physics of film formation at the liquid–liquid interface (e.g. through measurement of interfacial tension during nanosheet addition, and in-situ microscopy or spectroscopy). In particular, the roles of solvent selection, interfacial tension, and deposition environment should be explored, including the use of alternative solvent pairs (e.g. ethylene glycol–hexane in place of water–hexane) and inert atmospheres to improve film quality and reproducibility.

Finally, improved control over nanosheet size selection is required to enable meaningful validation of junction resistance models. The thickness-selection protocol employed in Chapter 8 introduced significant polydispersity, obscuring correlations between R_j and

nanosheet dimensions. Implementation of higher-resolution centrifugation protocols or complementary size-selection techniques, combined with direct AFM characterisation of each fraction, would allow more accurate determination of $\langle t_{\text{NS}} \rangle / \langle L_{\text{NS}} \rangle^2$, and enable rigorous testing of the proposed scaling relationships.

Having outlined these direct experimental next steps, broader considerations for the future direction of solution-processed nanosheet networks are now discussed.

CATHODIC EXFOLIATION SCALE-UP

A persistent limitation of the electrochemically exfoliated TMD materials used in Chapters 6 and 8 was the slow production rate of high-quality nanosheet inks. Days of processing yielded only milligram-scale quantities, with the intercalation step as the primary bottleneck. This not only restricts fundamental studies but also poses a major barrier to commercialisation. Process rationalisation, such as scaling the working electrode to include larger mechanically cleaved single crystals, may improve throughput, but a more scalable method is desirable. Literature reports have demonstrated intercalation of pressed powder pellets in scalable setups, producing gram-scale yields^{405–407}. However, the defective nature of powder starting material has limited electronic quality, with mobilities of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported by Wells et al.⁴⁰⁵ Further work is therefore needed to match the electronic quality of single-crystal-derived EE nanosheets while achieving scalable production, to render TMD nanosheet network devices commercially viable.

JUNCTION ENGINEERING

The use of EE and LID in this work was aimed at tailoring junctions to enhance network electrical properties by approaching the intrinsic performance of individual nanosheets. This aligns with the emerging concept of junction engineering, recently formalised by Kelly et al.²⁹⁰ Beyond material preparation and deposition, new strategies are being developed that directly target junction resistance. Orbital-overlap engineering, through either material

selection (e.g. Te-containing TMDs in place of S-based analogues)^{408, 409} or applied pressure^{410, 411}, can enhance interlayer orbital coupling and reduce the hopping barrier, though at the risk of inducing metallisation in semiconductors. Chemical approaches, such as embedding metallic nanoparticles to bridge junctions⁴¹² or using molecular linkers (e.g. dithiols) to form covalent inter-sheet bonds³⁴⁸, have shown substantial improvements in network mobility and on/off ratio. Orientation engineering, involving control of twist angles at junctions, offers another possibility, potentially mitigating steric separation and enabling moiré-induced localisation^{413, 414}, though systematic control in disordered networks remains challenging. Integrating such orbital, chemical, and orientation strategies into the EE-LID framework established here could enable junction resistances comparable to, or even lower than, intrinsic nanosheet resistance.

MODELLING OF JUNCTION CONDUCTION

Building on the preliminary modelling of Chapter 8, future work should develop more explicit models of junction conduction that directly incorporate nanosheet size and thickness. Such models would be of immense use for junction engineering. Recent work by Caffrey et al. has shown that nanosheet aspect ratio dictates whether junctions behave as point contacts or conformal overlaps⁴¹⁵, verifying the discussion in Chapter 5. Extending this experimental insight to networks of thickness-selected nanosheets, which as before will require an optimized technique for thickness selection, will allow proper verification of the model proposed here. Such modelling would allow nanosheet size distributions to be directly linked to network-level electrical properties. Incorporating such approaches into device-scale simulations could allow future studies to predict the optimal size distributions for a given application. Applying this framework to semiconducting nanosheet systems, where transport is strongly junction-limited, would be particularly valuable for advancing high-mobility, solution-processed devices.

FINAL WORDS

Overall, recent years have seen significant progress toward the commercial application of 2D material nanosheet networks, driven by improvements in performance and a clearer theoretical understanding of charge transport. In particular, junction resistance has been identified, quantified, and actively reduced as the dominant bottleneck. In line with the central aim of this thesis, the strategies developed here provide pathways to further lower junction resistance and advance nanosheet networks toward device applications.

Appendix A

A.1 THEORY CHAPTER 5

A.1.1 PERCOLATION DERIVATION

1-D MODEL

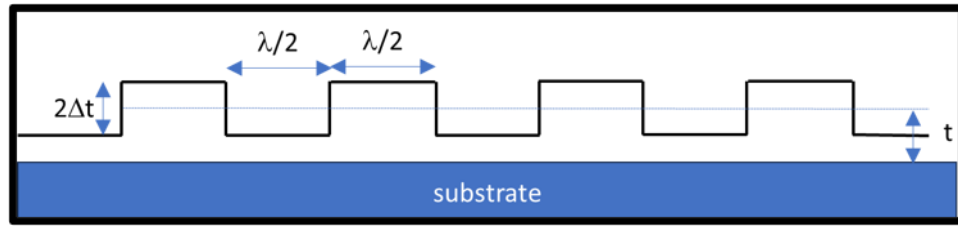


Figure A.1: Simple 1D model of a thin film with mean thickness, t , and roughness, Δt .

Neglecting surface scattering, the resistivity of this film can be calculated by working out the resistance of one thin and one thick section:

$$R = \frac{\rho_{\text{ff}} \lambda / 2}{w(t - \Delta t)} + \frac{\rho_{\text{ff}} \lambda / 2}{w(t + \Delta t)} \quad (\text{Eqn A.1})$$

Where W is channel width. Converting into an average resistivity ($\rho = Rwt / \lambda$) yields:

$$\rho = \frac{\rho_{\text{ff}}}{2} \left[\frac{t}{t - \Delta t} + \frac{t}{t + \Delta t} \right] \quad (\text{Eqn A.2})$$

Because $t > \Delta t$ in all cases, the second term is slowly varying and is always between 0.5 and 1, usually closer to 1. This allows the approximation:

$$\rho \approx \frac{\rho_{\text{ff}}}{2} \left[1 + \frac{t}{t - \Delta t} \right] \quad (\text{Eqn A.3})$$

DEFINING ρ_0

$$\rho = \rho_B + \frac{\rho_0}{(t - t_c)^n} \quad (\text{Eqn A.4})$$

The ρ_0 parameter can be redefined as one with physical meaning by defining t_x as the thickness where the conductivity reaches 80% of the bulk value *i.e.*, $\sigma(t_x) = 0.8\sigma_B$ or equivalently $\rho(t_x) = 5/4 \cdot \rho_B$. Then:

$$\rho(t_x) = \frac{5}{4}\rho_B = \rho_B + \rho_0(t_x - t_c)^{-n} \quad (\text{Eqn A.5})$$

Rearranging:

$$\rho_0 = \frac{(t_x - t_c)^n \rho_B}{4} \quad (\text{Eqn A.6})$$

and so:

$$\rho = \rho_B \left[1 + \frac{1}{4} \left(\frac{t_x - t_c}{t - t_c} \right)^n \right] \quad (\text{Eqn A.7})$$

A.1.2 DC NETWORK DERIVATION

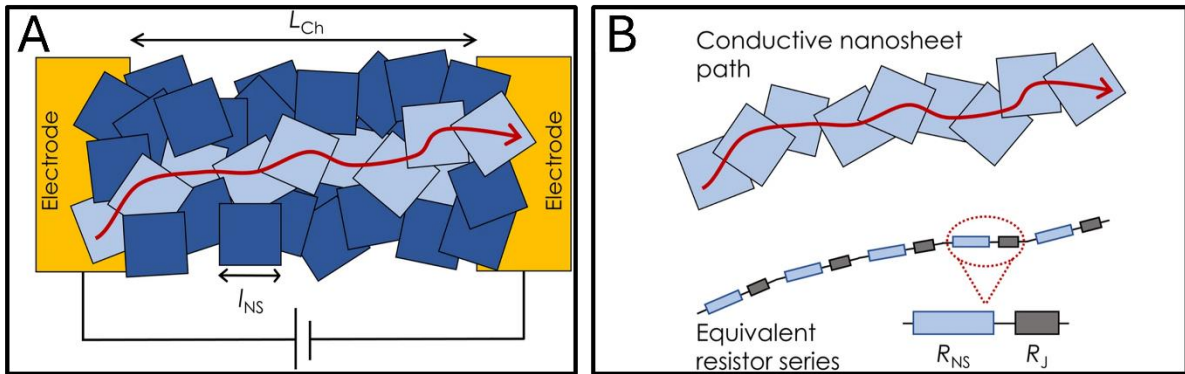


Figure A.2: Nanosheet network resistor model. A – Schematic of a nanosheet network, with a conductive pathway highlighted. B – An equivalent resistor series for one such conductive nanosheet path, showing the origin of R_{NS} and R_J . Adapted from ref²⁸⁹.

In a network, every time an electron is transferred through a nanosheet, must also pass through a junction to get to the next nanosheet, as shown in Figure A.2A. Each current path is made up of many nanosheet-junction pairs, shown in Figure A.2B.

On the application of a voltage, V , to the network, the voltage is dropped across the entire current path of nanosheet-junction pairs. The number of such pairs in a path is simply

$$N = \frac{L}{d_{NS} + d_J} \quad (\text{Eqn A.8})$$

Where L is the channel length, d_{NS} is the average distance an electron travels through a single nanosheet, and d_J is the forward distance travelled on charge hopping to the next nanosheet via a junction (in the case of a nanosheet networks it's expected $d_J \ll d_{NS}$). The average voltage drop across one nanosheet junction pair, V_p , is hence:

$$V_p = \frac{V}{N} = V \frac{d_{NS} + d_J}{L} \quad (\text{Eqn A.9})$$

This can be separated into voltage drops across the nanoparticle and junction, $V_p = V_J + V_{NS}$. Rewriting in terms of resistances: $V_p = IR_J + IR_{NS}$, factorizing out a term for V_J :

$$V_p = IR_J \left(\frac{R_J + R_{NS}}{R_J} \right) = V_J \left(\frac{R_J + R_{NS}}{R_J} \right) \quad (\text{Eqn A.10})$$

The above equation can hence give the voltage drop across a junction:

$$V_J = \frac{R_J}{R_J + R_{NS}} V \frac{d_{NS} + d_J}{L} \quad (\text{Eqn A.11})$$

By a similar reasoning, Eqn A.9 can also be rewritten to give the voltage drop across a nanosheet:

$$V_{\text{NS}} = \frac{R_{\text{NS}}}{R_J + R_{\text{NS}}} V \frac{d_{\text{NS}} + d_J}{L} \quad (\text{Eqn A.12})$$

The average transit time, τ , of a charge carrier in a channel can be written as:

$$\tau = \frac{L}{\mu E} \quad (\text{Eqn A.13})$$

Where L is the channel length, μ is the charge carrier mobility, and E is the applied electric field ($E = V/L$). Rewriting in terms of nanosheet networks and the voltage applied:

$$\tau_{\text{Net}} = \frac{L_{\text{Ch}}}{\mu_{\text{Net}} E} = \frac{L_{\text{Ch}}^2}{\mu_{\text{Net}} V} \quad (\text{Eqn A.14})$$

As there are N nanoparticle junction pairs, each with their own charge carrier transit time τ_{NP} and τ_J :

$$\tau_{\text{Net}} \approx N(\tau_{\text{NS}} + \tau_J) = \frac{L}{d_{\text{NS}} + d_J} (\tau_{\text{NS}} + \tau_J) \quad (\text{Eqn A.15})$$

The above Eqn A.14 for the nanosheet network transit time may be rewritten for an individual nanosheet, using Eqn A.12:

$$\tau_{\text{NS}} = \frac{d_{\text{NS}}^2}{\mu_{\text{NS}} V_{\text{NS}}} = \frac{d_{\text{NS}}^2}{\mu_{\text{NS}}} \frac{R_J + R_{\text{NS}}}{R_{\text{NS}}} \frac{L}{(d_{\text{NS}} + d_J)V} \quad (\text{Eqn A.16})$$

The time to cross the junction may similarly related to the current flowing across the junction, using Eqn A.14 and Eqn A.11:

$$\tau_J = \frac{e}{I_J} = \frac{eR_J}{V_J} = e(R_J + R_{\text{NS}}) \frac{L}{(d_{\text{NS}} + d_J)V} \quad (\text{Eqn A.17})$$

Therefore, rewriting Eqn A.15 and giving it in terms of an expression including μ_{Net} :

$$\tau_{\text{Net}} = \frac{L_{\text{Ch}}^2}{\mu_{\text{Net}} V} \approx \frac{L}{d_{\text{NS}} + d_J} \left[\frac{d_{\text{NS}}^2}{\mu_{\text{NS}}} \frac{R_J + R_{\text{NS}}}{R_{\text{NS}}} \frac{L}{(d_{\text{NS}} + d_J)V} + e(R_J + R_{\text{NS}}) \frac{L}{(d_{\text{NS}} + d_J)V} \right] \quad (\text{Eqn A.18})$$

Tidying this expression up, and including the network tortuosity factor $\kappa_{\text{Net}} = \left(\frac{L}{L_{\text{Ch}}} \right)^2$:

$$\frac{1}{\mu_{\text{Net}}} \approx \kappa_{\text{Net}} \frac{R_J + R_{\text{NS}}}{(d_{\text{NS}} + d_J)^2} \left[\frac{d_{\text{NS}}^2}{\mu_{\text{NS}} R_{\text{NS}}} + e \right] \quad (\text{Eqn A.19})$$

Factorizing:

$$\frac{1}{\mu_{\text{Net}}} \approx \frac{1 + \frac{R_J}{R_{\text{NS}}}}{(d_{\text{NP}} + d_J)^2 / d_{\text{NS}}^2} \left[\frac{\kappa_{\text{Net}}}{\mu_{\text{NS}}} \left(1 + \frac{\mu_{\text{NS}} e R_{\text{NS}}}{d_{\text{NS}}^2} \right) \right] \quad (\text{Eqn A.20})$$

Followed by inverting:

$$\mu_{\text{Net}} \approx \frac{(d_{\text{NS}} + d_J)^2 / d_{\text{NS}}^2}{\left(1 + \frac{R_J}{R_{\text{NS}}} \right)} \frac{\mu_{\text{NS}} / \kappa_{\text{Net}}}{\left[1 + \frac{\mu_{\text{NS}} e R_{\text{NS}}}{d_{\text{NS}}^2} \right]} \quad (\text{Eqn A.21})$$

As $d_J \ll d_{\text{NS}}$, and $\sigma = ne\mu$:

$$\mu_{\text{Net}} \approx \frac{\mu_{\text{NS}} / \kappa_{\text{Net}}}{\left(1 + \frac{R_J}{R_{\text{NS}}} \right) \left[1 + \frac{\mu_{\text{NS}} e R_{\text{NS}}}{d_{\text{NS}}^2} \right]} = \frac{\mu_{\text{NS}} / \kappa_{\text{Net}}}{\left(1 + \frac{R_J}{R_{\text{NS}}} \right) \left[1 + \frac{\sigma_{\text{NS}} R_{\text{NS}}}{n_{\text{NS}} d_{\text{NS}}^2} \right]} = \frac{\mu_{\text{NS}} / \kappa_{\text{Net}}}{\left(1 + \frac{R_J}{R_{\text{NS}}} \right) \left[1 + \frac{1}{n_{\text{NS}} A_{\text{NS}} d_{\text{NS}}} \right]} \quad (\text{Eqn A.22})$$

Where A_{NS} is the nanosheet cross section, with $R_{\text{NS}} = d_{\text{NS}} (\sigma_{\text{NS}} A_{\text{NS}})^{-1}$ - assumption that sheets are square.

Underlying this derivation is the assumption that the mobility of the network is the same as the mobility along an average current path.

More useful than this is to model these network conduction parameters in terms of network conductivity. Assuming charge carriers only exist in the network within the nanosheets, which is valid for a network of one type of material above percolation, the network charge carrier density n_{net} :

$$n_{\text{Net}} = n_{\text{NS}} (1 - P_{\text{Net}}) \quad (\text{Eqn A.23})$$

Where P_{net} is the network porosity, the proportion of the network made up by void. This implies that the network conductivity σ_{Net} is:

$$\sigma_{Net} = n_{NS} e \mu_{Net} (1 - P_{Net}) \quad (Eqn A.24)$$

therefore, from the above Eqn A.22 for network mobility:

$$\sigma_{Net} \approx \frac{\sigma_{NS} (1 - P_{Net}) / \kappa_{Net}}{\left(1 + \frac{R_J}{R_{NS}}\right) \left[1 + \frac{1}{n_{NS} A_{NS} d_{NS}}\right]} \quad (Eqn A.25)$$

In a nanosheet network, the average cross section can be taken as the product of the average nanosheet thickness t_{NS} and nanosheet length l_{NS} :

$$A_{NS} = t_{NS} l_{NS} \quad (Eqn A.26)$$

The transit length in a nanosheet can vary randomly from approximately zero (ie. entering and then exiting the sheet immediately) to the full length of the nanosheet l_{NS} . Hence by averaging:

$$d_{NS} = \frac{l_{NS}}{2} \quad (Eqn A.27)$$

Substituting Eqn A.26 and Eqn A.27 into Eqn A.25 yields:

$$\sigma_{Net} \approx \frac{\sigma_{NS} (1 - P_{Net}) / \kappa_{Net}}{\left(1 + \frac{R_J}{R_{NS}}\right) \left[1 + \frac{2}{n_{NS} t_{NS} l_{NS}^2}\right]} \quad (Eqn A.28)$$

Alternatively, in terms of network resistivity:

$$\rho_{Net} \approx \frac{\rho_{NS} \kappa_{Net}}{1 - P_{Net}} \left[1 + \frac{R_J}{R_{NS}}\right] \left[1 + \frac{2}{n_{NS} t_{NS} l_{NS}^2}\right] \quad (Eqn A.29)$$

Recalling $R_{NS} = d_{NS} (\sigma_{NS} A_{NS})^{-1}$, $d_{NS} = l_{NS} / 2$, hence $R_{NS} = (\sigma_{NS} 2 t_{NS})^{-1} = \rho_{NS} / 2 t_{NS}$,

therefore $\rho_{NS} = R_{NS} 2 t_{NS}$, Eqn A.29 may be rewritten:

$$\rho_{\text{Net}} \approx \frac{2t_{\text{NS}}\kappa_{\text{Net}}}{1-P_{\text{Net}}} [R_{\text{NS}} + R_J] \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right] \quad (\text{Eqn A.30})$$

ie. the expression used in the main text.

A.1.3 AC NETWORK DERIVATION

Restating the general formula for network resistivity:

$$\rho_{\text{Net}} \approx \frac{2t_{\text{NS}}\kappa_{\text{Net}}}{1-P_{\text{Net}}} [R_{\text{NS}} + R_J] \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right] \quad (\text{Eqn A.31})$$

$R_{\text{NS}} + R_J$ can be more generally stated as the impedance of a nanosheet junction pair $Z_{\text{NS-J}}$. The network impedance relates to the network resistivity via $Z_{\text{Net}} = \rho_{\text{Net}} L_{\text{Ch}} / A_{\text{Net}}$, where L_{Ch} is the channel length and A_{Net} is the network cross-sectional area. Hence:

$$Z_{\text{Net}} \approx \frac{L_{\text{Ch}}}{A_{\text{Net}}} \frac{2t_{\text{NS}}\kappa_{\text{Net}}}{1-P_{\text{Net}}} Z_{\text{NS-J}} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right] \quad (\text{Eqn A.32})$$

This can be used to convert real and imaginary impedance spectra of the network to spectra of the real and imaginary components of $Z_{\text{NS-J}}$ such that:

$$Z_{\text{NS-J}} \approx \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{1-P_{\text{Net}}}{2t_{\text{NS}}\kappa_{\text{Net}}} Z_{\text{Net}} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right]^{-1} \quad (\text{Eqn A.33})$$

the equation used in the main text.

A.1.4 RANGLES EQUIVALENT CIRCUIT MODELLING

Impedance measurements of a network Z_{Net} probe many nanosheet junction $\text{NS} - J$ pairs, arranged into a number of linear current paths. Each $\text{NS} - J$ pair can be represented by the circuit elements circled above in Figure 5.6B, with impedance $Z_{\text{NS-J}}$. In the above model, there can be considered to be m parallel conductive paths, each made of an average n number of the $\text{NS} - J$ pairs in series.

In this case, with all $NS - J$ pairs the same, using Kirchoff's rules:

$$Z_{eq} = \sum Z_n \quad (Eqn A.34)$$

for elements in series.

$$\frac{1}{Z_{eq}} = \sum \frac{1}{Z_n} \quad (Eqn A.35)$$

for parallel elements. The network impedance is hence

$$Z_{Net} = \frac{n}{m} Z_{NS-J} \quad (Eqn A.36)$$

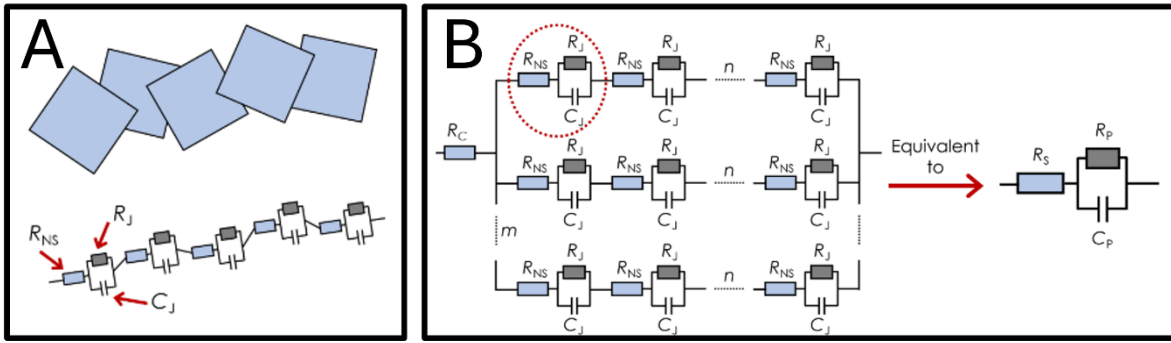


Figure A.3: Randles equivalent circuits. A – Nanosheet network conductive pathway, with its equivalent Randles circuit model shown giving the origins of R_{NS} , R_J , and C_J . B – Schematic showing how the Randles circuit pathway ensemble is equivalent to one single Randles circuit, contain R_S , R_P , and C_P . Adapted from ref²⁸⁹.

This shows that there is a simple factor relating the two quantities, which is given in Eqn A.33. This multiplicative relationship means that the network may be represented by an equivalent Randles circuit of the same form as the $NS - J$ model. Here, it is expected:

$$R_P = R_J \frac{n}{m} \quad (Eqn A.37)$$

Meanwhile R_S has contributions from both nanosheets and contact resistance:

$$R_S = R_C + R_{NS} \frac{n}{m} \quad (\text{Eqn A.38})$$

If contact resistance is minimized:

$$R_S \approx R_{NS} \frac{n}{m} \quad (\text{Eqn A.39})$$

Similarly, C_p arises due to the capacitive nature of the junctions:

$$C_p = C_J \frac{m}{n} \quad (\text{Eqn A.40})$$

due to the laws of summing capacitors in series and in parallel:

$$\frac{1}{C_{eq}} = \sum \frac{1}{C_n} \quad (\text{Eqn A.41})$$

for capacitors in series,

$$C_{eq} = \sum C_n \quad (\text{Eqn A.42})$$

for capacitors in parallel.

A.2 EXPERIMENTAL 1

A.2.1 AFM FLAKE COUNTING

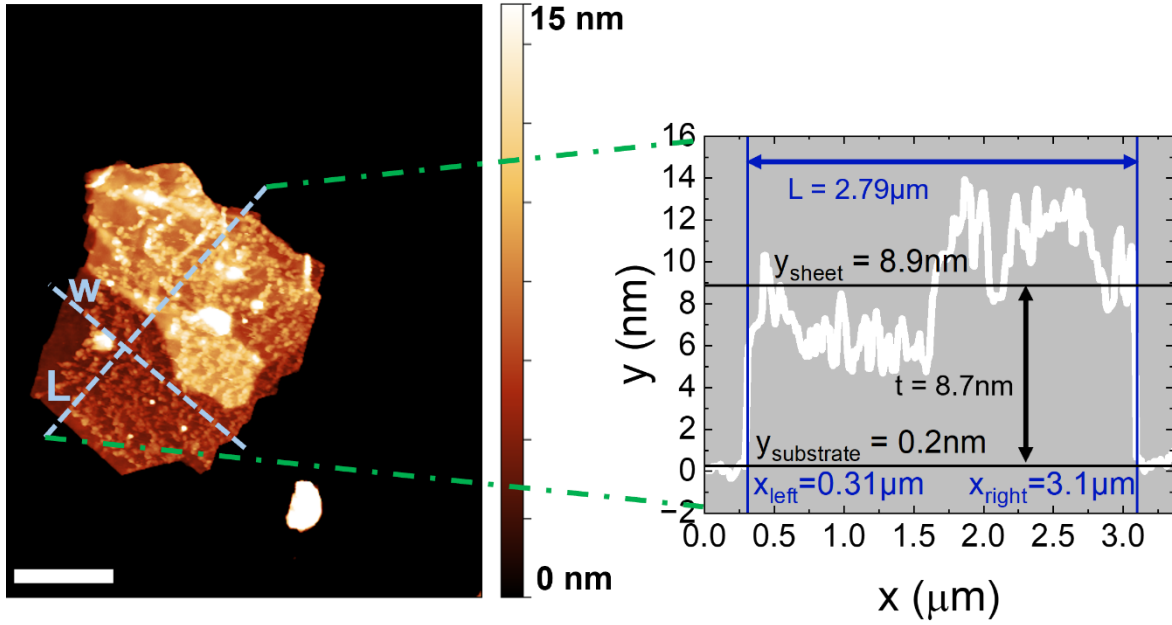


Figure A.4: AFM flake counting. AFM image of a 97 g EE MoS₂ nanosheet with line profile inset showing determination of nanosheet dimensions.

A representative AFM image of a 97 g EE MoS₂ nanosheet is shown in Figure A.4. Two perpendicular line profiles were taken across the flake, with the length L and width w extracted from the lateral distance between the flake edges in each profile. The apparent thickness t was determined by subtracting the average substrate height from the average flake height, as shown in the inset. Lateral size L_{NS} was taken as the square root of the product of the extracted length and width, $\sqrt{Lw}$.

A.2.2 SIZE-SELECTION HISTOGRAMS

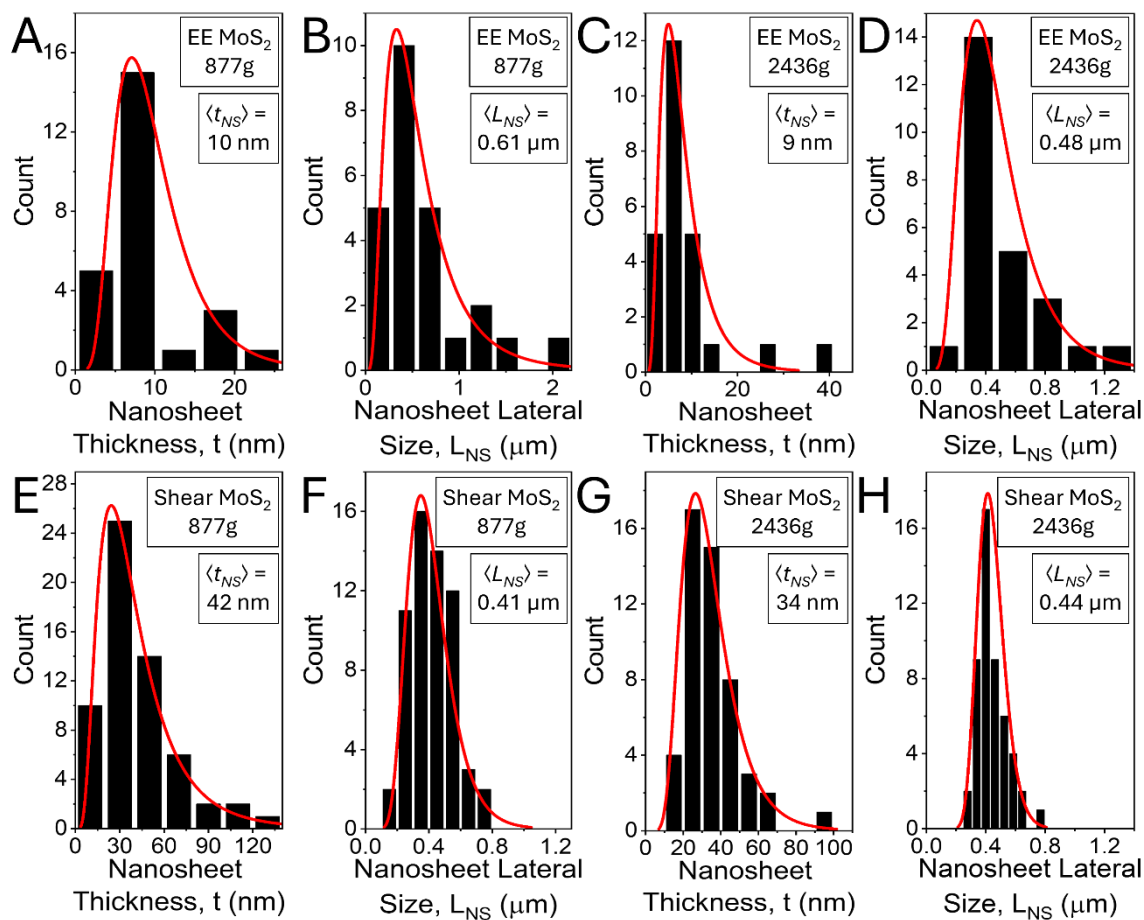


Figure A.5: Histograms of the addition size selected dispersions. A – Apparent thickness histogram of the 877g EE MoS₂ dispersion. B – Lateral size histogram of the 877g EE MoS₂ dispersion. C – Apparent thickness histogram of the 2436g EE MoS₂ dispersion. D – Lateral size histogram of the 2436g EE MoS₂ dispersion. E – Apparent thickness histogram of the 877g shear MoS₂ dispersion. F – Lateral size histogram of the 877g shear MoS₂ dispersion. G – Apparent thickness histogram of the 2436g shear MoS₂ dispersion. H – Lateral size histogram of the 2436g shear MoS₂ dispersion.

Histograms for the higher-g-force fractions of EE and shear-exfoliated MoS₂ dispersions are shown in Figure A.5. All distributions follow lognormal behaviour, consistent with size-selected nanosheet populations.

A.2.3 FILM THICKNESS AFM MEASUREMENTS

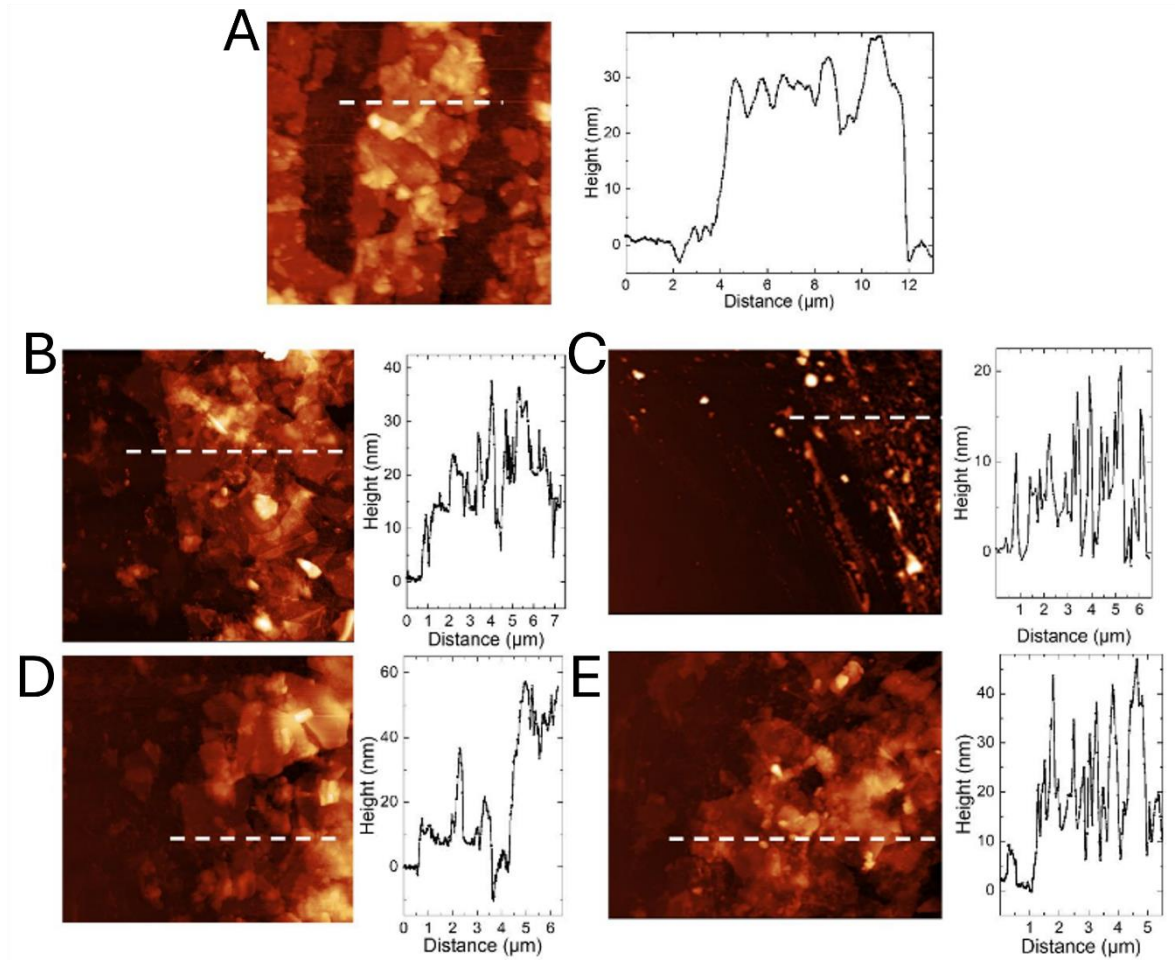


Figure A.6: AFM measurement of film thickness t . A – WS_2 network from 97 g EE dispersion. B – WSe_2 network from 97 g EE dispersion. C – MoS_2 network from 2436 g EE dispersion. D – WSe_2 network from 97 g EE dispersion. E – MoS_2 network from 877 g EE dispersion. Each image includes a height profile used to determine film thickness.

A Bruker Multimode 8 microscope was used to carry out AFM and analyse the film thickness t_{film} of the TFT films, using an OLTESPA R3 cantilever in ScanAsyst mode. Shown in Figure A.6A-E is each of the resulting micrographs, with the line profiles used to extract t_{film} inset.

Analysis of the line profiles provided thicknesses of ~25 nm for 97 g WS₂, ~40 nm for 97 g WSe₂, ~25 nm for 97 g MoS₂, ~25 nm for 877 g MoS₂, and ~10 nm for 2436 g MoS₂. These values were used to calculate device mobilities for the main text.

A.2.4 CYCLIC VOLTAMMETRY

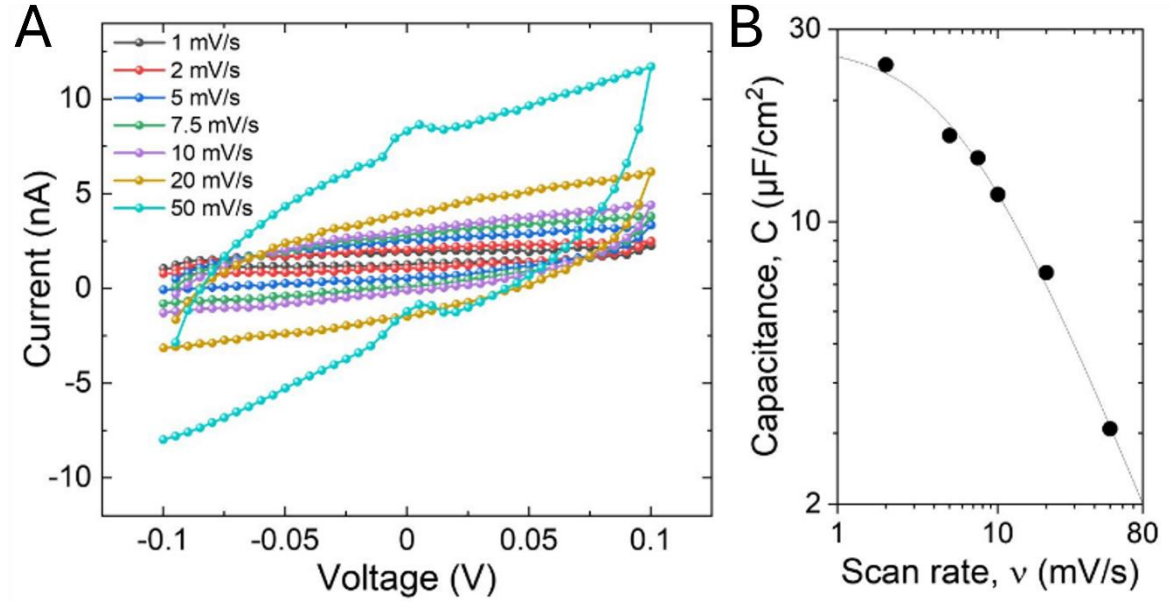


Figure A.7: Electrochemical characterisation of EE networks. A – Cyclic voltammogram of MoS₂ in EMIM TFSI. B – Areal capacitance as a function of scan rate with fitted model.

Cyclic voltammetry was performed using a Gamry Reference 600 potentiostat with EMIM TFSI as the electrolyte. The ionic liquid was pre-dried under vacuum at 120 °C. Gate currents were measured over a ± 0.2 V window, ΔV , at multiple scan rates, ν . Capacitance was extracted from the enclosed area of the CV curves by:

$$C_{Meas} = \frac{1}{2\Delta V\nu} \int IdV \quad (\text{Eqn A.43})$$

and then corrected for double layer background capacitance, $C_{BG} = \epsilon_r \epsilon_0 A_{electrodes} / \lambda$, Where λ (taken as 1 nm) is the double layer thickness, ϵ_r is taken to be 10, and $A_{electrodes} = 0.75$ mm² in this study. Fitting the areal capacitance versus scan rate to⁴¹⁶:

$$C = C_{Low-rate} \left[1 - \frac{v\tau}{\Delta V} (1 - e^{-\Delta V/v\tau}) \right] \quad (Eqn A.44)$$

(where τ is charge-discharge characteristic time) yielded a low-frequency capacitance

$C_{Low-rate}$ of $\sim 28 \mu\text{F cm}^{-2}$, consistent with volumetric charging.

For the case of electrolytically gated TFTs, $C_{Low-rate}$ is equal to the product of the volumetric capacitance of the device C_V and the film thickness t_{film} . It was assumed that $C_{Low-rate}$ of each TMD network in EMIM TFSI would be the same as the MoS_2 network. The above value of $C_{Low-rate}$, combined with AFM-measured film thickness, was used to determine the effective device areal capacitances for each: $\sim 3.1 \mu\text{F cm}^{-2}$ for 97 g MoS_2 , $\sim 3.1 \mu\text{F cm}^{-2}$ for 877 g MoS_2 , $\sim 3.1 \mu\text{F cm}^{-2}$ for 2436 g MoS_2 , $\sim 3.1 \mu\text{F cm}^{-2}$ for 97 g WS_2 , and $\sim 4.9 \mu\text{F cm}^{-2}$ for 97 g WSe_2 .

A.2.5 FULL TFT MEASUREMENTS

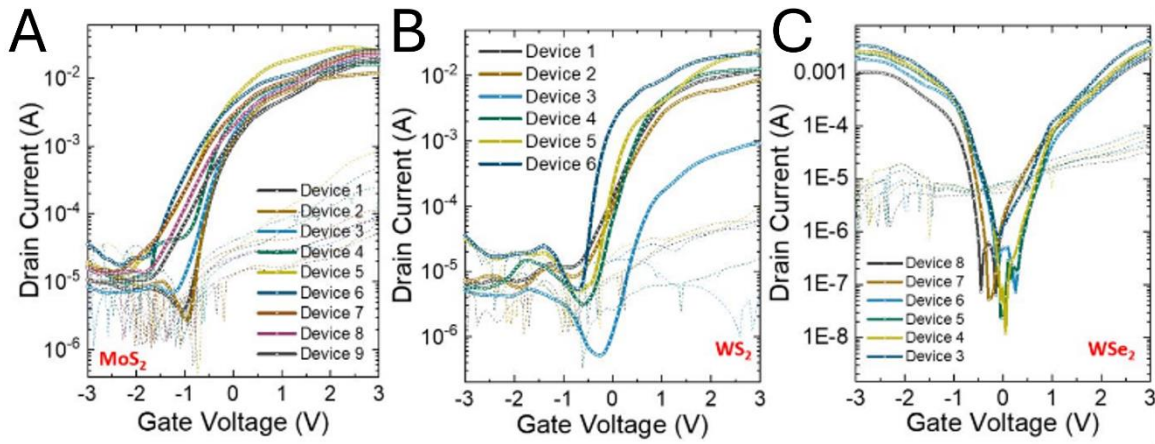


Figure A.8: Full transfer curves of EE TMD TFTs. A – MoS_2 . B – WS_2 . C – WSe_2 . $V_{DS} = 1 \text{ V}$.

The dashed line indicates gate leakage current.

Complete transfer characteristics of EE MoS_2 , WS_2 , and WSe_2 devices are shown in Figure A.8. Multiple channels were measured per sample using EMIM TFSI gating by the protocol

in the main text. The leakage current remained negligible relative to the drain current, confirming stable transistor operation.

A.2.6 SIZE-SELECTED TFT MEASUREMENT

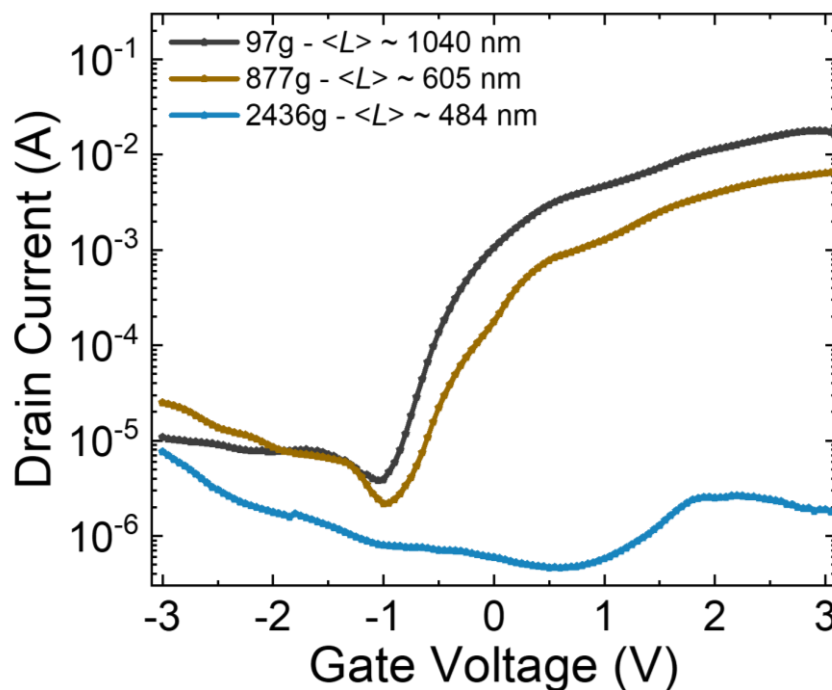


Figure A.9: Transfer curves of size-selected EE MoS₂ TFTs measured at $V_{DS} = 1$ V.

Transfer characteristics of TFTs fabricated from 97 g, 877 g, and 2436 g MoS₂ dispersions are shown in Figure A.9. The 97 g and 877 g devices display n-type behaviour, while the 2436 g device exhibits ambipolar characteristics, possibly due to residual polymer, solvent, or oxygen functionalisation⁴¹⁷. Mobilities were extracted from the transconductance and averaged over three channels per sample (the 6 additional channels for the other 97 g MoS₂ sample were included in statistics for this study and vice versa).

A.3 EXPERIMENTAL 2

A.3.1 AFM MEASUREMENTS

To accurately determine the nanosheet dimensions after centrifugation, statistical AFM analysis was performed on drop-cast nanosheet samples. The evaluation includes manual measurement of the sheet length L and apparent thickness t of >400 individual nanosheets from the stock-like dispersion by use of height profiles. An example of a measured height profile may be seen in Figure A.10A and B. L could be determined from the range of x values in the nanosheet plateau, as indicated in Figure A.10B. t was determined by finding the difference between the average substrate y value and plateau y value, as also indicated in Figure A.10A.

For better comparability to other exfoliated graphite samples, the measured thickness was converted into the nanosheet layer number (N). As reported in previous work, to convert the apparent thickness of a graphene nanosheet to nanosheet layer number, a 0.5 nm correction must first be subtracted off the apparent thickness to account for trapped solvent between the nanosheets and the substrate, followed by dividing the thickness by 0.95 nm, the apparent thickness of a graphene monolayer, obtained previously by step height analysis¹⁴⁸. The real nanosheet thickness (t_{NS}) can then be obtained by multiplying the layer number by the crystallographic thickness of graphene (0.34 nm). This leads to the following 2 relations used to obtain N and t_{NS} from t (in nm):

$$N = \frac{(t-1)}{0.95} \quad (Eqn A.45)$$

$$t_{NS} = N \cdot 0.34 \text{ nm} \quad (Eqn A.46)$$

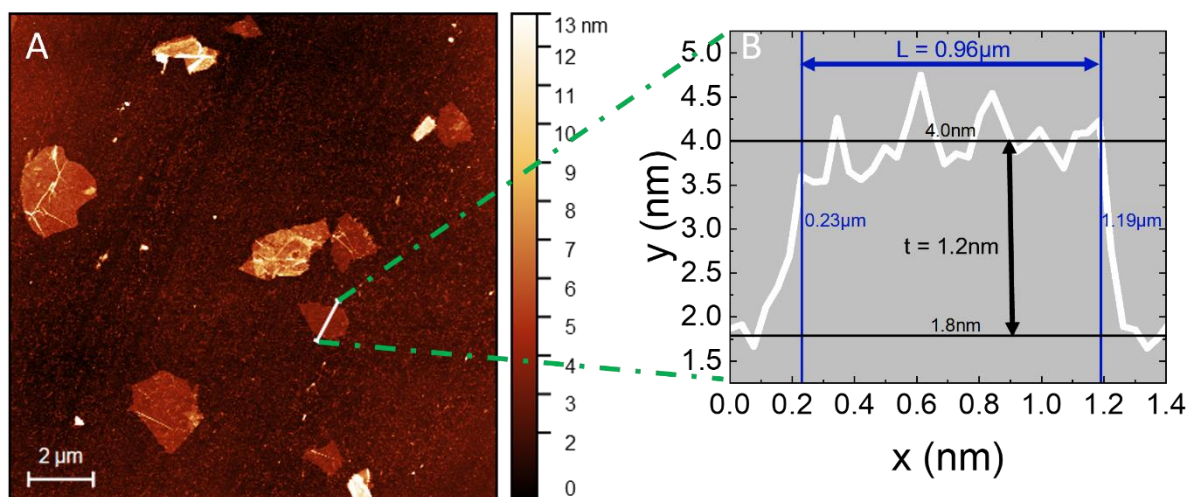


Figure A.10: AFM measurement of nanosheets: A – AFM image of a sample of nanosheets on an SiO_2 substrate. A sample height profile was extracted from the white line, giving the profile in (B), which shows how lateral size L and apparent thickness t were extracted.

A.3.2 OPTIMIZATION STUDY DEPOSITION SETUP

To find optimal ink parameters for film quality, a number of films (36 in total) was fabricated. Hence, a setup capable of depositing 6 films at a time was designed. This consisted of a mill cut PTFE block with 6 square holes cut into it, each to serve as troughs in which hexane-water interfaces were created and material was injected to form an interfacial film. Additionally, 6 smaller blocks and a large block with slots to hold each of these blocks in were also milled. These smaller blocks were for holding the substrates, so they would sit directly below the interfaces inside each of the troughs. CAD designs for these can be seen in Figure A.11A. To vacuum out water from below the hexane-water interfaces, a box with pipe system, designed from syringes and an aquarium tubing set was created, and can be seen in Figure A.11B. This pipe system was attached to a vacuum chamber to extract the water after each of the films were formed.

After the water was vacuumed out of the apparatus, the wet films were left to dry in the apparatus for 4 hours under ambient conditions in the fume hood, with a foil cover placed

above them to avoid contamination by dust particles. Subsequent to drying, the films were transferred to a glovebox with an argon atmosphere, in which they were annealed at 120°C.

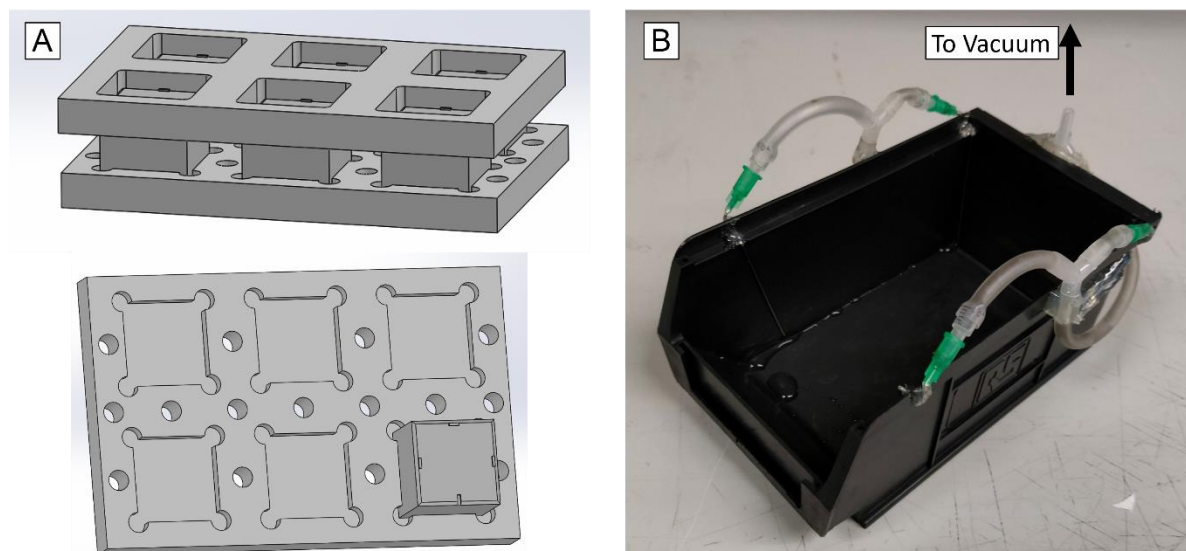


Figure A.11: Deposition setup for the optimization study: A – CAD designs for the mill cut PTFE parts that were used to form graphene interfacial films to transfer onto glass substrates, 6 at a time. B – the box which the PTFE parts sat in, which was filled with water. This was attached to a vacuum chamber to extract the water from below, lowering the interfaces onto the substrates.

A.3.3 KOH GLASS TREATMENT & MASK

Throughout both deposition studies, standard 2 cm × 2 cm glass cover glass slides were used as substrates. To make the glass suitably smooth for thin film deposition, a treatment protocol was adapted from Chada et al.⁴¹⁸ Using the setup shown in Figure A.12A, the substrates were immersed in an ethanol-potassium oxide solution and placed in an ultrasonic bath for 3 minutes. The setup was removed safely by the rod attachment, and the substrates were immersed in deionized water and ultrasonicated for 3 minutes. This process was repeated with 3-minute sonications each time using acetone, IPA, and then finally DI water again to achieve a smooth and clean glass surface. After treatment, substrates were kept immersed in deionized water in the setup in Figure A.12A for storage purposes, only to be removed for deposition or electrode patterning (upon the latter, the

substrates were dried with compressed nitrogen). Following this protocol, solvent residues can be avoided on the substrate surface.

After the films had been deposited in the film optimization study, and before they were deposited in the multilayer film study, samples were patterned with an electrode mask containing 3 rows of 6 rectangular electrodes each, for 18 electrodes in total. A schematic of this mask is shown in Figure A.12B. Such masks were attached to the underside of samples using Kapton tape, and the masked samples were placed in a Temescal FC-2000 Bell Jar Deposition System to transfer 1 nm of titanium (an adhesion layer) followed by 100nm of gold, patterning the samples with rows of electrodes

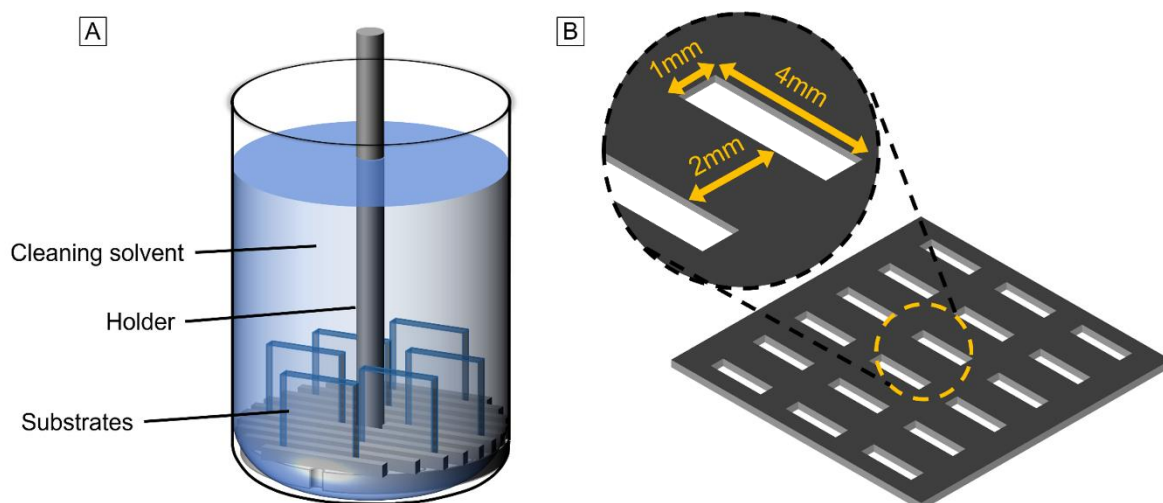


Figure A.12: Substrate Treatment Setup and Mask: A – Setup used to safely clean substrates in ethoxide solution with easy transfer to subsequent cleaning solvents. B – Mask used to deposit electrodes onto samples for electrical measurements, inset: the relevant mask dimensions

A.3.4 SCANNER CALIBRATION

To characterize the films' extinction and homogeneity, an Epson Perfection V850 Pro bed scanner was used. Images produced by this scanner had a resolution of 2400 dpi ($\sim 10.6 \mu\text{m}$ per pixel), and were saved in Multi-TIFF format with red, green, and blue colour channels. To convert the pixel intensity output by the scanner to transmission, an initial calibration

using neutral density filters was carried out. Images of each filter was taken using the scanner, examples of which can be seen in Figure A.13A. Corresponding transmission spectra were measured using a Varian UV-vis spectrometer in the range 800-200nm with a sampling interval of 1 nm, examples of which can be seen in Figure A.13B.

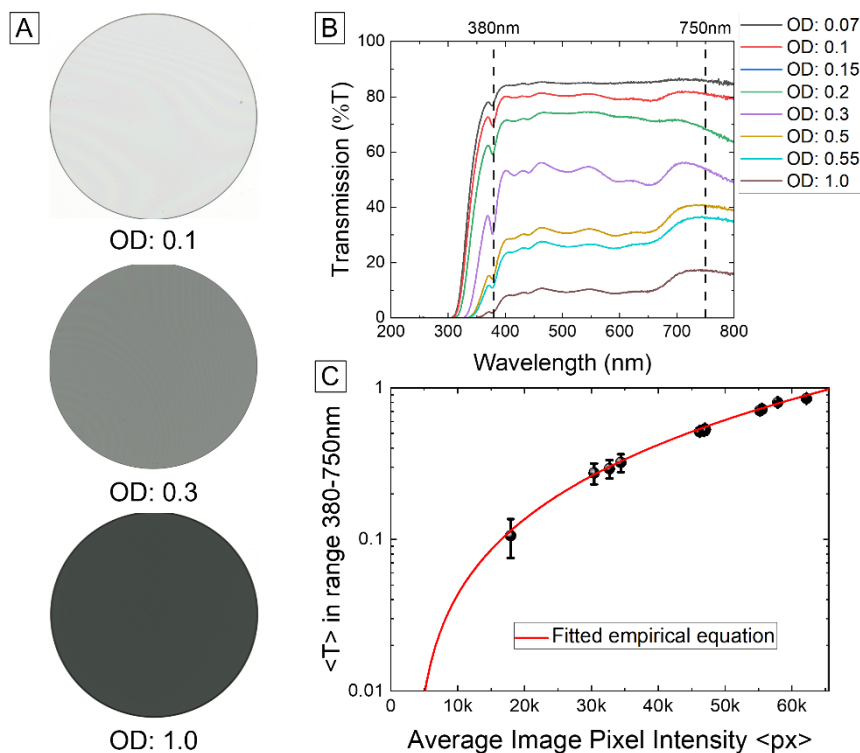


Figure A.13: Calibration of EPSON scanner to provide transmission data A – Example scans of the neutral density filters (NDFs) used for the calibration which had their (B) UV-vis spectra taken from 200-800 nm in a Varian UV-vis spectrometer. The average transmission between 380-750 nm was taken as $\langle T \rangle$, while the average pixel intensity extracted from the NDFs' respective scans is taken as $\langle px \rangle$, the plot of which is shown with fitted calibration curve in (C). Note this empirical relation is unsuitable for sample of $T < 10\%$.

To process the images, the blue channel of each was extracted, as this channel presented minimal interference fringes produced from contact between the scanner bed glass and the filters. From each image's blue channel, the mean pixel intensity value, $\langle px \rangle$, was extracted. From each spectrum, the mean transmission value in the visible range, $\langle T \rangle$, was extracted.

Both values for all filters were plotted against each other to yield a calibration plot that can be seen in Figure A.13C. To this plot the following empirical equation was fitted:

$$\langle T \rangle = -0.01622 + (4.1922 \cdot 10^{-6}) \langle px \rangle + (1.6598 \cdot 10^{-10}) \langle px \rangle^2 \quad (Eqn A.47)$$

This empirical relation was used to extract optical transmission for each pixel of an image, which was converted to optical extinction per pixel using $Ext = -\log(T)$.

A.3.5 SCAN ANALYSIS

PROCESSING FOR $\langle Ext \rangle_{film}$, ΔExt_{film} , & Σ_{film}

Having obtained a method for reliably extracting optical extinction statistics for large sample areas, scans of each film were captured prior to electrical measurements. Using the code in Appendix Section B.1, large numbers of images could be processed by the following protocol (brackets denoting the script from the appendix used):

- Extraction of blue channel and saving as a .tiff file (fiji_run.py)
- Conversion of blue channel image pixel values to extinction (scans_run.py)
- Extraction of the mean extinction ($\langle Ext \rangle$) and extinction standard deviation (ΔExt) of all pixels in the image and writing to a .csv file (scans_run.py)
- Extracting a .csv file containing a random sample of 100,000 extinction values from the image (scans_run.py)
- Loading extinction sample .csv file data into origin for plotting as histograms (origin_run.py)

Examples of the.csv files can also be seen in Appendix Section B.1. Examples of histograms produced by this can be seen in the main text. The histograms were then analysed to obtain the average extinction due to exposed substrate in the image, $\langle Ext \rangle_{\text{substrate}}$, and the sum of exposed pixels in the sample $\Sigma_{\text{substrate}}$. In brief, all bins in the histogram above ~ 0.05 are

masked, and a Gaussian plot is fitted to the remaining unmasked bins. $\langle \text{Ext} \rangle_{\text{substrate}}$ was taken as the centre of this distribution, and $\Sigma_{\text{substrate}}$ was taken as its integral. In the cases of samples which did not have exposed substrates in their image (ie. of complete coverage) an average of $\langle \text{Ext} \rangle_{\text{substrate}}$ obtained for all other samples was used, and $\Sigma_{\text{substrate}}$ was taken as 0 (ie. no pixels of exposed substrate in the sample). A histogram of a sample where this was the case can be seen in in the main text (the optimal film, 0.02 g L^{-1} , 21 mg m^{-2}).

The masking was then flipped, and a Gaussian plot was fitted to the remaining unmasked data, the integral of which yielded Σ_{film} , the sum of film pixels in the sample. The ratio of this and $\Sigma_{\text{substrate}}$ was used to form the film coverage metric.

From this, $\langle \text{Ext} \rangle_{\text{film}}$ could be extracted by subtracting $\langle \text{Ext} \rangle_{\text{substrate}}$, the average extinction of the substrate, from $\langle \text{Ext} \rangle$, the average extinction extracted from the image:

$$\langle \text{Ext} \rangle_{\text{film}} = \langle \text{Ext} \rangle - \langle \text{Ext} \rangle_{\text{substrate}} \quad (\text{Eqn A.48})$$

$\Delta \text{Ext}_{\text{film}}$, the film extinction standard deviation, was considered as equivalent to ΔExt , the image extinction standard deviation.

All these quantities were used to form the metrics displayed in the heatmaps in the main text.

PROCESSING FOR RELATIVE FILM PERIMETER LENGTH

To quantify the granularity of each film, a film perimeter length parameter was devised. How this was acquired was by binarization of each film scan, using the ‘‘Otsu Threshold’’ functionality in ImageJ (settings shown in Appendix Section B.2). After thresholding, ImageJ’s ‘‘Smooth’’ function was applied, followed by a Gaussian Blur filter with a sigma value of 2. The resulting image was binarized again after this using ‘‘Make Binary’’. This step was taken to remove any artefacts, such as dust particles, that may have been present

in the substrate domain in the image. Example results of this binarization protocol is shown in Figure A.14C.

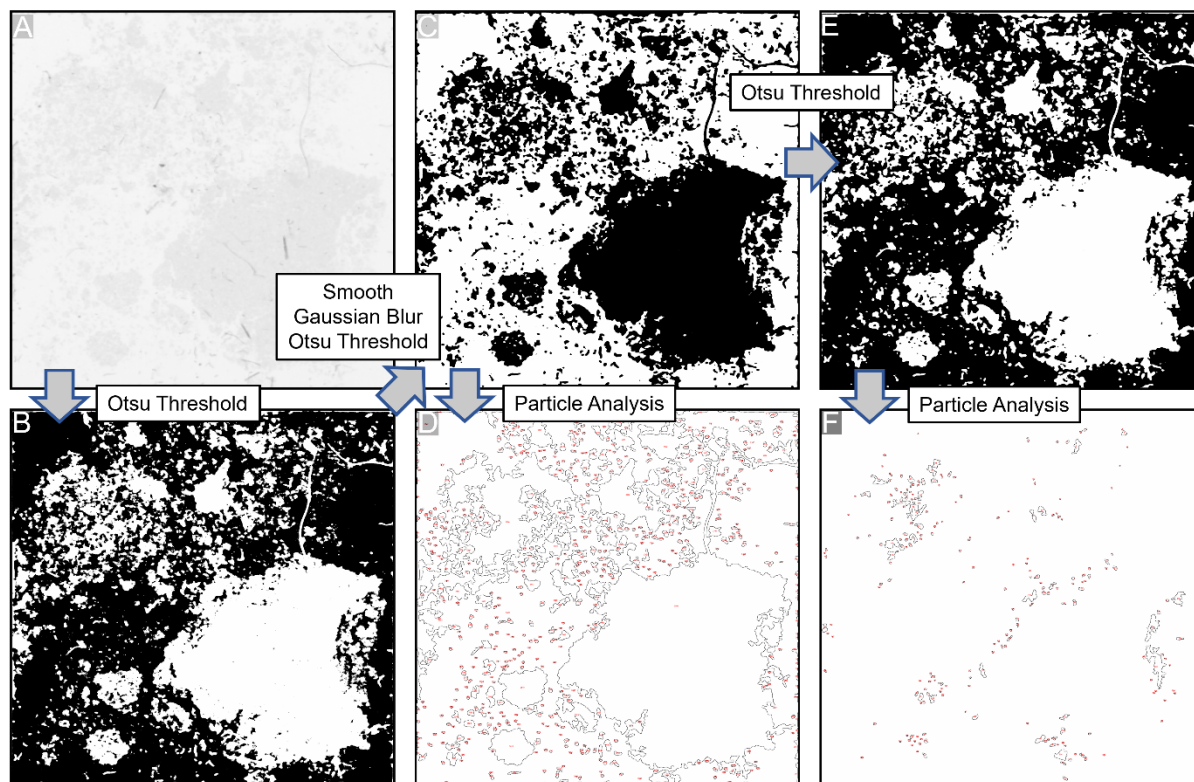


Figure A.14: Protocol for extracting film perimeter: A – Example of an optical scan image that was firstly binarized using Otsu thresholding, the result shown in (B). The binarized image is denoised by applying ImageJ’s “smooth” functionality and a Gaussian blur filter of $\sigma=2$, followed by Otsu thresholding to re-binarize the denoised image. This results in the image shown in (C). Particle analysis is subsequently applied to the new image, including perimeter on the edges and of holes, resulting in an image of determined perimeter outlines shown in (D). The image shown in (C) is inverted by re-applying Otsu thresholding, resulting in the image shown in (E). (E) then has particle analysis applied, excluding perimeter on edges and of holes, resulting in the measuring of perimeter outlines seen in (F). The configuration for each processing step, as well as code for subsequent post-processing, are shown in Appendix Section B.2.

Following this, ImageJ’s “Analyze Particles” functionality was used. This was set to include only particles of size 10 pixels² or larger, as shown in Appendix Section B.2. For this first particle analysis the “Exclude on edges” was deactivated and the “Include holes” function

was activated. The resulting data, shown in Appendix Section B.2, was saved, and the image was thresholded again to flip the binarization, the result of which is shown in Figure A.14E. Subsequently the “Analyze Particles” function was run on the binarized image. However, this time the “Exclude on edges” function was active and “Include holes” was deactivated. This data was also saved. Examples of the image outputs of the perimeter outlines measured by both particle analysis steps can be seen Figure A.14D and F.

From the saved particle analysis data, the sum of all particle perimeters was taken. This could then be converted to metres using the 2400 dpi value of each image (i.e. dividing the number of pixels by 94488.2). The length of the edge of each image was then determined, using the code shown in Appendix Section B.2. This was subtracted from each of the particle perimeter lengths to yield the film perimeter length. This was further processed into a relative metric by determining the image area. The film perimeter was divided by image area to yield the relative film perimeter length, a measure of how granular a film is, with smaller lengths indicating a continuous film without macroscopic holes. This metric was used for the heatmap shown in the main text.

A.3.6 ELECTRICAL MEASUREMENTS

To measure conductivity, 2-point probe measurements using a Keithley multimeter system (shown in Figure A.15A) were taken at multiple channel lengths for each row of electrodes. To extract conductivity, the transmission line method was used, taking plots of channel resistance versus channel length to extract the conductivity from the slope (equivalent to the reciprocal of the product of σ and channel cross-section area A_{channel} , $(\sigma A_{\text{channel}})^{-1}$) and the contact resistance R_C from the intercept (equivalent to $2R_C$). A schematic of how these measurements were extracted from the fit of R versus channel length L can be seen in Figure A.15C.

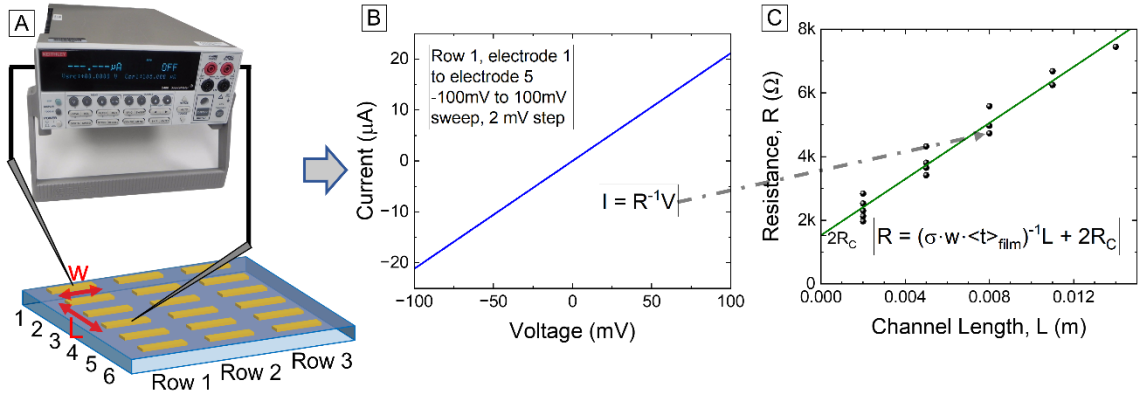


Figure A.15: Transmission line method for measuring conductivity and contact resistance: A – Schematic experimental setup for 2-point probe measurement of each channel in each electrode row for all the samples measured, showing the convention for identifying electrode combinations by row and number, as well as the channel dimensions w_{channel} and L_{channel} . B – Measured I/V curves yield ohmic transport behaviour for the films under study. C – The inverse slope of each I/V measurement, R , plotted against the L_{channel} for each electrode row to extract transmission lines. The conductivity of the row, σ , was extracted from slope of the transmission line. Further, the contact resistance R_C was extracted from the intercept. For each sample, these quantities were averaged over all 3 rows to yield film conductivity, $\langle \sigma \rangle_{\text{film}}$, and contact resistance, R_C . The uncertainty of the extracted conductivity for each row was averaged to yield $\Delta \sigma_{\text{film}}$, which taken with $\langle \sigma \rangle_{\text{film}}$ formed the conductivity homogeneity metric $\langle \sigma \rangle_{\text{film}} / \Delta \sigma_{\text{film}}$.

To extract all the resistances measured for each channel, the code shown in Appendix Section B.4 was used to extract the resistances from raw I/V data (shown in Figure A.15B) and to load into origin files to plot as resistance versus channel length scatter plots for each of the 3 rows of electrodes, an example of which is seen in Figure A.15C. The transmission slope, m_T , and intercept, $2R_C$, for each row of electrodes was then extracted from the origin plots manually by linear regression. The slopes were then converted into conductivity by

use of the product of film thickness $\langle t \rangle_{\text{film}}$ and electrode width w_{channel} (A_{channel}), giving the following formula:

$$\sigma = (m_T \cdot A_{\text{channel}})^{-1} = (m_T \cdot \langle t \rangle_{\text{film}} \cdot w_{\text{channel}})^{-1} \quad (\text{Eqn A.49})$$

The average value of conductivity for each of the 3 rows was taken as $\langle \sigma \rangle_{\text{film}}$, and the averaged uncertainty used as $\Delta \sigma_{\text{film}}$. For the optimization study, the ratio of these values, $\langle \sigma \rangle_{\text{film}} / \Delta \sigma_{\text{film}}$, the conductivity homogeneity, was used as a film quality metric and is seen plotted in a heatmap for each of the samples in the main text. For the multilayer study, $\langle \sigma \rangle_{\text{film}}$ and R_c were both plotted against $\langle t \rangle_{\text{film}}$ to extract the network's percolative behaviour.

A.3.7 LAYER-BY-LAYER DEPOSITION

SETUP AND IMAGE PROCESSING

The deposition setup was iterated on for multilayer depositions. To spread material on the interface surface in a homogeneous, steady fashion, with greater reproducibility, a setup consisting of a syringe pump, beaker, rotating stage, and a new set of PTFE milled parts was devised. The syringe pump acquired from Darwin Microfluidics, picture in Figure A.16A, could provide a steady flow of 100 μ L/min onto the interface. A ComXim rotating stage (Figure A.16B) was used to rotate the entire setup at a rate of ~ 2 rpm, allowing the interface to orbit around the edge of the PTFE trough during the injection. The PTFE parts now consisted of a single trough, as shown in Figure A.16B and in CAD drawings in Figure A.16C. A modification was made to the substrate holder, where now there were ~ 2 mm high PTFE walls around the edges of the substrate to hold liquid in while leaving it to dry on top of the substrate (Figure A.16D). Furthermore, this adjustment also counteracts changes to the meniscus in case substrates with a different surface energy are used (*e.g.*, fused silica or PET).

The procedure for depositing each layer was as follows: transfer of film onto substrate using the setup in the main text, drying in air at 80°C for 1 hour, annealing in ambient conditions at 120°C for 1 hour, a brief (<2 min) dip in acetone followed by transfer back to the deposition setup to repeat again. This was repeated n times for each n layers shown in Figure A.16E.

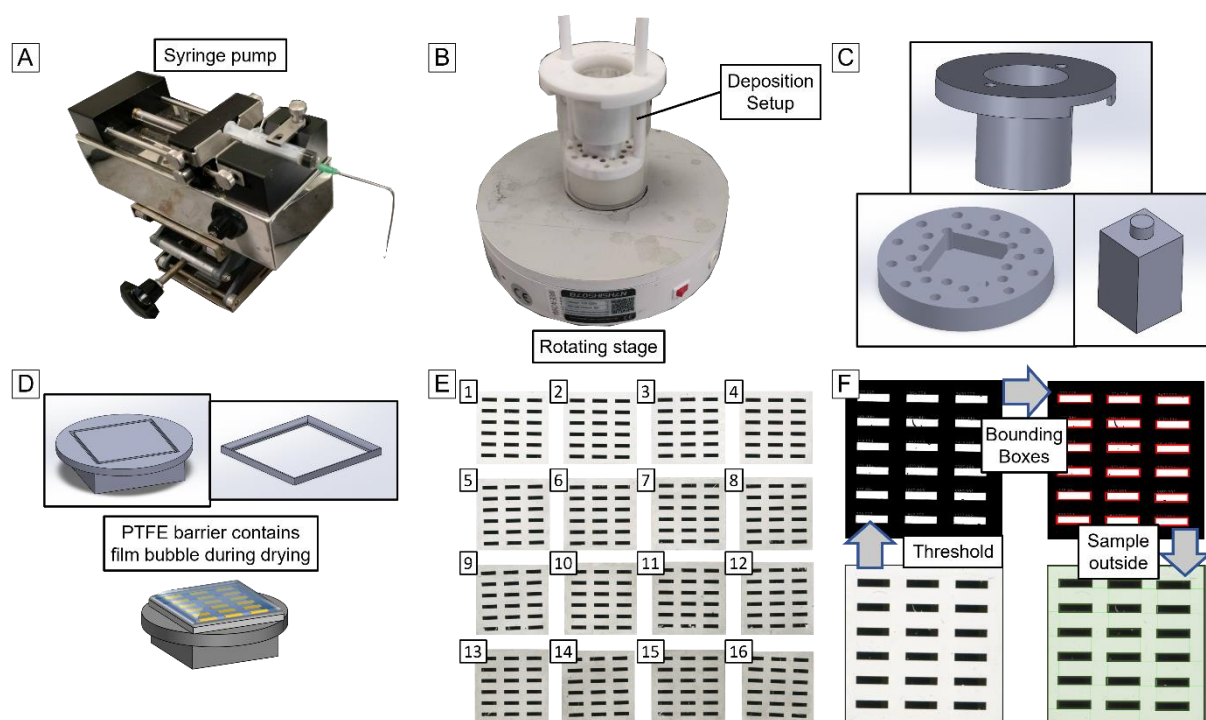


Figure A.16: Setup for the multilayer depositions: A – The syringe pump, used to inject defined volumes of ink at a controlled rate (500 μL at 100 $\mu\text{L}/\text{min}$). B – The rotating stage the deposition setup was placed on top of, which allowed the syringe pump's needle to orbit around the walls of the setup during the injection to homogeneously spread material across the entire interface. C – CAD drawings of the parts for the setup depicted in figure 6A. D – The PTFE wall setup used to avoid material from sliding off the substrate during transfer and drying. E – Transmission scans of the 16 samples fabricated. F – Schematic of how the code in Appendix 5 operates. The transmission scan is thresholded in a way that the image is binarized between regions of film and electrode. Opencv's "find contours" method is used to provide bounding boxes around each electrode. All areas of the image outside the bounding boxes are sampled to yield $\langle \text{Ext} \rangle$ for the image.

As also mentioned in the main text, a water-air interface was used instead of water-hexane. It was found this produces more homogeneous films for the deposition of graphene. This may imply that the optimal surface tension of the binary solvent system may depend on the chemical characteristics of the material used, however this is outside of the scope of this study. An alternative interpretation of this behaviour is that the surface energy of the nanomaterial and the substrate must be tailored to achieve a homogenous film after drying. Further work is needed in this area to better understand the dynamics of Langmuir film formation.

Films were also deposited onto bottom contacted electrodes, as opposed to top contacting after the deposition as in the optimization study. This created some complexity in extracting $\langle \text{Ext} \rangle$ for each scan of each film, as the image contained shadows of the electrodes as depicted in Figure A.16E. However, this was worked around by use of a computer vision algorithm appended to the usual running of scans_run.py that was previously used. With this, the electrodes in the image were automatically detected, and only the parts of the images outside of these areas were used to determine $\langle \text{Ext} \rangle$ and ΔExt . This can be seen schematically in Figure A.16F. The code is shown in Appendix Section B.5.

For this part of the study, $\langle \text{Ext} \rangle_{\text{substrate}}$ was determined from averaging the $\langle \text{Ext} \rangle$ obtained from 8 scans of blank glass slides taken at different locations in the scanner bed. This was subtracted off the $\langle \text{Ext} \rangle$ yielded for each scan to yield $\langle \text{Ext} \rangle_{\text{film}}$, and to produce the substrate-corrected extinction histograms seen in the main text.

LOW CONDUCTIVITY OF FIRST TWO LAYERS

After suitable protocols for multilayer deposition were employed, the 1g/L ink was centrifuged (200 g, 5x30 min) to remove aggregates that formed after extended shelf storage (i.e., ~2 months). The change of the ink concentration after centrifugation was accounted for by using UV-Vis spectroscopy and fixed the injection volume accordingly.

While the coverage based on transmission scans is identical to results achieved before, the conductivity of the network was very low for the first two depositions. The exact reason for this distinction is unclear. It cannot be excluded that some of the material is being washed off during the acetone treatment. Further, it is possible that the average layer number or area of the nanomaterial in the ink has changed slightly after removing aggregates. Further, it is also possible that slight oxidation occurs over time. While the colloidal stability of the graphene ink was not in focus of this work, problems with ink stability should be studied and addressed in further detail in future work.

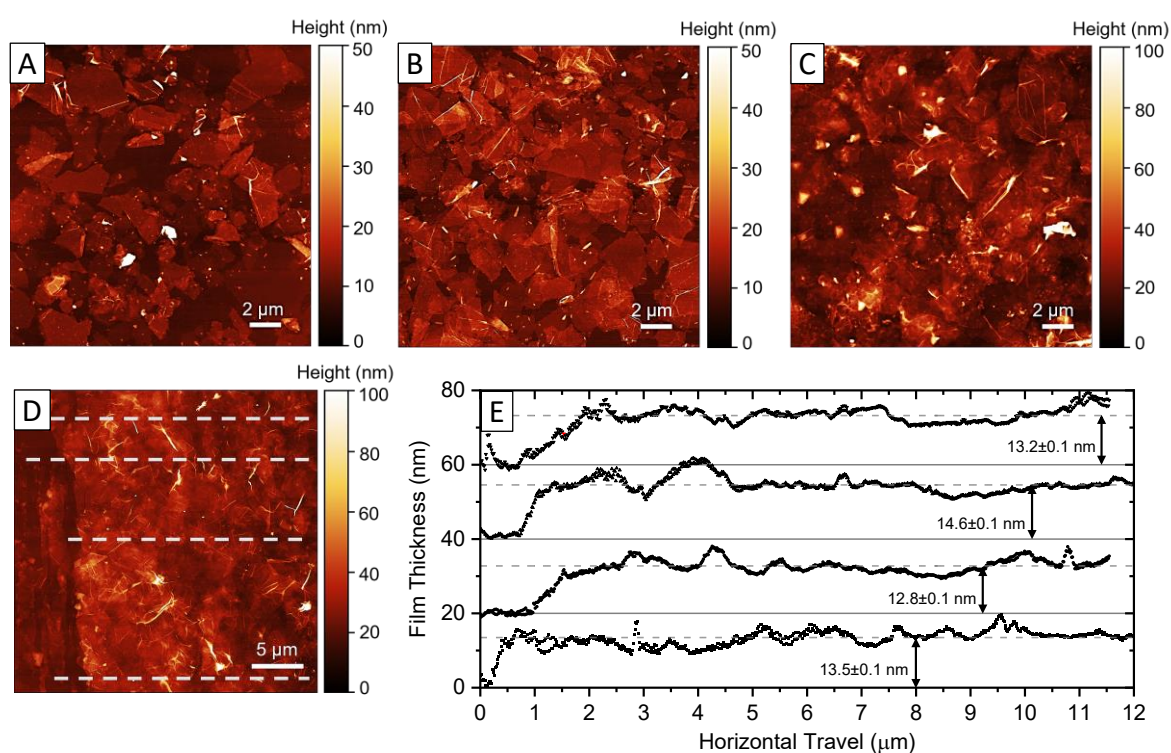


Figure A.17: AFM measurements on nanosheet networks after distinct deposition iterations: A-C – Representative AFM overview image of samples after a single (A), two (B) and three (C) iterations of the LLID. All three measurements show homogenous coverage of the nanomaterial to a tiled network of nanosheets. Small areas of exposed substrate can be found for the first two depositions (A-B). D – AFM overview image on a graphene network after 16 subsequent depositions. The sample surface was scratched to extract the thickness of the network. E – Exemplary AFM height profiles corresponding to dashed lines shown in (D). The average thickness of the network after 16 depositions

based on AFM measurements is 13.5 ± 0.4 nm, which is in perfect agreement with the thickness determined from transmission scans over the entire substrate area (13.1 nm).

However, to identify if material is being washed off, or if the morphology of the network is affected after the acetone treatment, we performed AFM measurements on samples after a single, two, three and 16 depositions, respectively. Examples are shown in Figure A.17.

As measuring AFM over a large area is time consuming and tedious, SEM imaging was also performed on the sample after the first deposition to check for spot-to-spot variations. Exemplary images of the network are shown at different magnification in Figure A.18.

The measurements indicate a homogenous coverage of the substrate with graphene nanosheets, consistent to observations made with AFM and further corroborated by the transmission scans discussed in the main text.

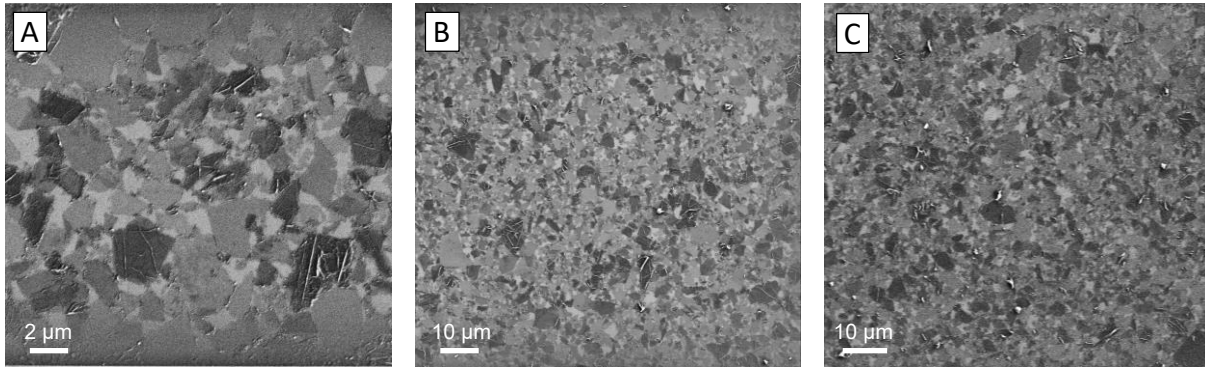


Figure A.18: SEM measurements on a tiled graphene networks after a single LLID. A – Individual nanosheets in close proximity in edge-to-edge alignment. B-C – Overview images of the network measured at two different spots of the network. Overall, a homogenous coverage of the substrate is observed in SEM, which is also supported by transmission scans. Bright spots are exposed substrate.

A.3.8 FITTING OF NEILSON ET AL. DATA

Figure A.19 shows data from Neilson et al.²⁴¹ fitted using the percolation model in Eqn 5.10 from Section 5.1.1, using parameters $\sigma_B = 64000$ S/m $t_x = 6$ nm, $t_C = 1$ nm, $n = 3$.

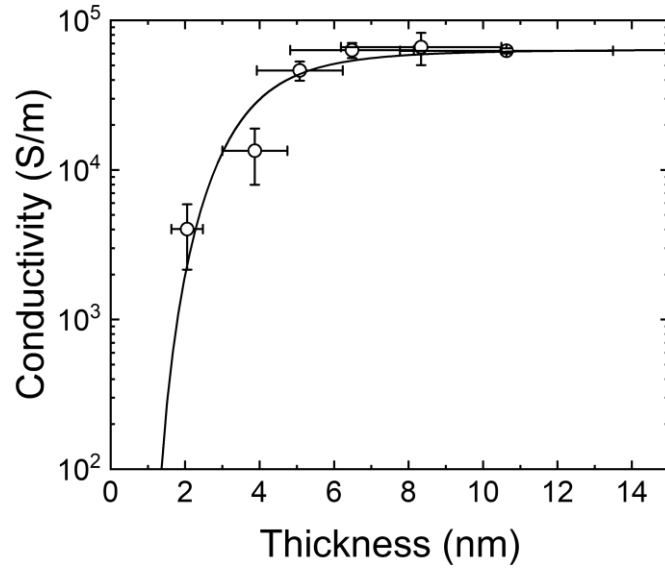


Figure A.19: Graphene network conductivity versus thickness data provided from Neilson *et al.*²⁴¹, fitted using Eqn 5.10 from Section 5.1.1 with parameters $\sigma_B = 64000 \text{ S/m}$, $t_x = 6 \text{ nm}$, $t_c = 1 \text{ nm}$, $n = 3$.

A.3.9 EEG EXTINCTION MEASUREMENT

For the measurement of the average film thickness, $\langle t \rangle_{\text{film}}$, a method of measuring the extinction coefficient of electrochemically exfoliated graphene films deposited using the LID technique was devised. This involved depositing multiple layers of EEG, using the setup detailed in Appendix Section A.3.2, onto substrates with masked regions using a square piece of a silicon wafer. This was done to produce 4 samples of 4 different layer numbers, depicted in Figure A.20A. On each sample, multiple positions were marked with pen, at substrate-film boundaries or on manually added scratches. The transmission scans of each of the samples were taken. AFM measurements were taken at each of the marked spots. Examples are shown as inset in Figure A.20A.

Each marked section was cropped for analysis using the same $\langle \text{Ext} \rangle$ extraction technique shown in Appendix Section A.3.5. $\langle \text{Ext} \rangle_{\text{substrate}}$ was extracted as the average extinction from

a blank glass substrate, which was subtracted from $\langle \text{Ext} \rangle$ to yield $\langle \text{Ext} \rangle_{\text{film}}$. A schematic of this sampling for $\langle \text{Ext} \rangle_{\text{film}}$ for given spots of AFM measurement is shown in Figure A.20B.

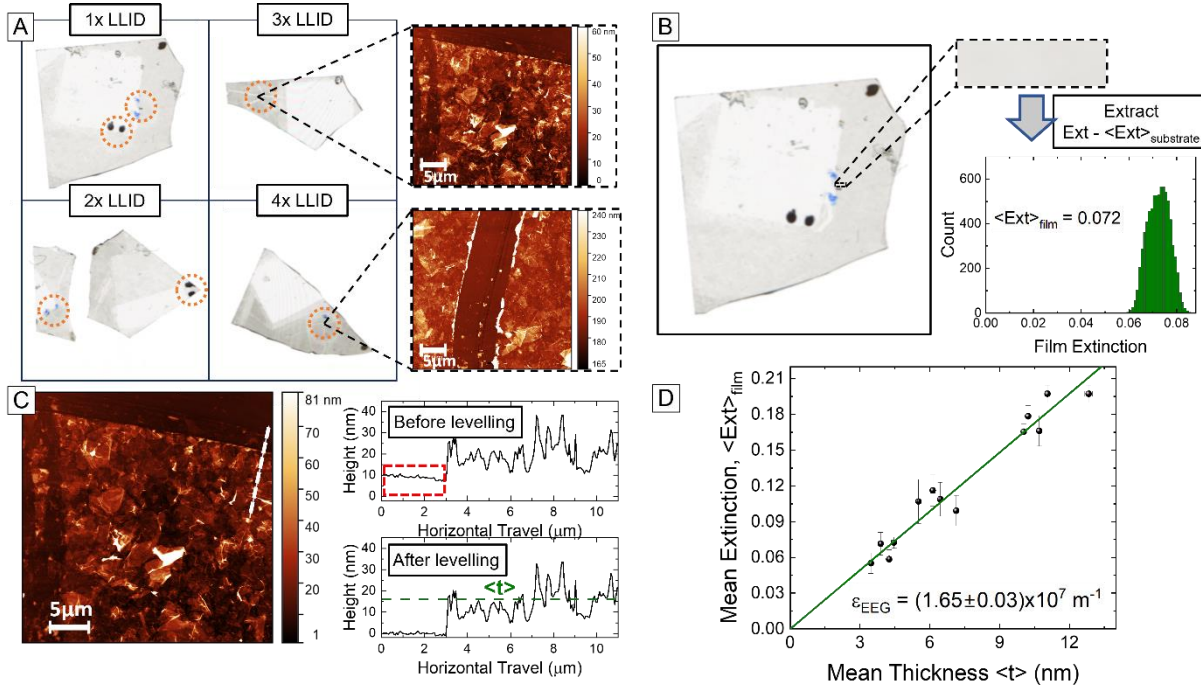


Figure A.20: Measurement of extinction coefficient of electrochemically exfoliated graphene: A – The 4 multilayered samples fabricated for the measurement by repeat deposition of graphene onto masked glass substrates. Orange circles highlight the marked areas where AFM measurements were taken and values of $\langle \text{Ext} \rangle_{\text{film}}$ were extracted inset: example AFM images taken at points on each film. B – Schematic of how $\langle \text{Ext} \rangle_{\text{film}}$ was extracted for a particular spot for AFM measurement. C – Example of how line profiles were extracted from each image and then levelled using the code in appendix 3, with the average height after levelling taken as $\langle t \rangle_{\text{film}}$. D – Plot of $\langle \text{Ext} \rangle_{\text{film}}$ versus $\langle t \rangle_{\text{film}}$, yielding the extinction coefficient of $(1.65 \pm 0.03) \times 10^7 \text{ m}^{-1}$.

Line profiles on each of the AFM images were taken, ensuring a region of uncovered substrate was included in each. An example of this is shown in Figure A.20C. These were then levelled, using the average slope of the substrate region, using the code in Appendix Section B.3. Further to this, the portion of the now levelled line profile corresponding to

substrate was masked, and an average height of the film profile was taken to yield film thickness $\langle t \rangle_{\text{film}}$.

$\langle t \rangle_{\text{film}}$ and $\langle \text{Ext} \rangle_{\text{film}}$ of each of the marked spots were then plotted against each other, shown in Figure A.20D. This yielded the extinction coefficient, $(1.65 \pm 0.03) \times 10^7 \text{ m}^{-1}$. This was used to determine absolute film thickness from $\langle \text{Ext} \rangle_{\text{film}}$ for conductivity measurements in both the optimization and multilayer studies.

A.3.10 CONCENTRATION LIMITS FOR INTERFACIAL FILM FORMATION

While the lowest ink concentration appeared to yield the best sample homogeneity, it is conceivable that even lower concentrations could further enhance film characteristics. However, preliminary experiments were designed to identify the optimal concentration range for the LID method.

Unlike the comprehensive experiments discussed in the main text, which involved a variety of different measurements to get a representative image on nature and homogeneity of the produced networks, including optical microscopy, transmission scans, AFM and SEM measurements and conductivity measurements over large areas of the substrate, the preliminary tests primarily relied on transmission scans and SEM imaging.

For this purpose, the concentration of the graphene ink was adjusted to a concentration between 0.008 g/L and 1 g/L. At high concentration, aggregation and island formation of the injected material was clearly observed even before a complete film had formed. However, for using concentrations below 0.02 g/L, the liquid/liquid interface dissipated into a single phase upon injection of the necessary volume to achieve comparable mass loads per surface area as with higher concentrations. For this reason, we fixed 6 distinct concentrations of our ink between 0.5 g/L and 0.02 g/L for thorough characterisation and systematic optimization. The targeted concentration was adjusted using dilution of the ink

in the required volumes of distilled isopropanol and pipetting errors were corrected by measuring the sample absorbance after dilution and calculating the actual concentration using the Beer-Lambert law.

A.3.11 TCF LITERATURE COMPARISON

For the present work, an extensive review of the literature was undertaken. It should be noted that most graphene films in the literature are substantially thicker ($t > 500\text{nm}$). A useful source of thin graphene films ($t < 50\text{nm}$), comparable to those fabricated in this study, were papers concerning solution-processed graphene transparent conducting films (TCFs). Although transparent graphene networks exhibit unsuitably high sheet resistances, and are therefore not appropriate for technologically viable TCF applications, the conductivity data available from such studies is useful for illustrating the superior conductivity demonstrated in films fabricated in this study. The sheet resistances measured for each film in this study are also found to be competitive with previous attempts at graphene TCFs.

Notably the publication record for solution-processed graphene TCFs seems to end around 2013, with more recent work utilizing metal-graphene hybrids⁴¹⁹, polymer-graphene hybrids⁴²⁰, or CVD techniques³⁸⁹ to produce graphene TCFs. As such, this work stands out in attempting to further the use of purely graphene as a material, and solution-processing as a technique.

It should also be noted a substantial portion of the literature on thin graphene films shows high processing temperatures ($T > 1000^\circ\text{C}$) and the use of aggressive chemical agents such as hydrazine and nitric acid. It is therefore notable that the processing temperature of 500°C , while incompatible with flexible substrates such as PDMS and PET, is still competitive with the established literature. A table detailing a selection of papers, with details of the material, process, achieved film thickness (t), conductivity (σ), sheet resistance R_s and film optical transmission %T is detailed below in table S1.

Table 1: Review of graphene films, for thick (>500nm) and thin (<50nm) suitable for TCF applications. The asterisk (*) indicates an entry refers to another film from the same work. These are plotted in the main text.

Author	Year	Exfoliation Method/ Material	Process	Post-process	t (nm)	σ (S/m)	$R_s(k\Omega/\square)$ / %T
Clifford et al. ²¹⁴	2024	Shear exfoliation	Spray coating		500	1.2×10^5	0.02 n/a
He P. et al. ³⁷⁶	2024	Acid exfoliation	Vacuum filtration	Chemical reduction of GO	2000	1.7×10^5	0.003 n/a
Gang Z. et al. ³⁷⁷	2022	Acid exfoliation	Vacuum filtration	2800°C annealing + calendaring	10^5	5.2×10^5	2×10^{-5} n/a
Barwich et al. ²⁷³	2021	Shear exfoliation	Vacuum filtration	Calendaring	10^5	2.2×10^5	5×10^{-5} n/a
Wöbke nberg et al. ³⁸⁸	2011	Acid exfoliation	Langmuir Blodgett	500°C anneal in forming gas	4	8.3×10^3	30 95%
Parvez et al. ¹⁶⁰	2013	Electrochemic al exfoliation	Vacuum Filtration	200°C annealing	15	1.6×10^4	4.1 85%
Parvez et al. ¹⁶⁰	*	*	*	Additional HNO ₃ treatment	15	2.5×10^5	0.27 85%
Kymaki s et al. ¹⁶³	2011	Acid exfoliation	Spin coating	1000°C anneal in hydrazine	20	2.5×10^4	2 75%

Wang et al. ³⁸⁶	2010	Acid exfoliation	Vacuum filtration	400°C anneal in hydrazine + 1100°C anneal	14	2.1x10 ⁴	280%
This Work	2024	Electrochemical exfoliation	Liquid-liquid interface deposition	500°C anneal in vacuum	6.1	3.6x10 ⁴	4.282%
This Work	*	*	*	*	11.1	1.3x10 ⁵	0.766%

A.4 EXPERIMENTAL 3

A.4.1 AFM OF MoS₂ NANOSHEETS

Statistical AFM analysis was performed on drop-cast nanosheet samples to determine lateral size and thickness. For each of five dispersions, approximately 50 nanosheets were measured using height profiles by the same method in Appendix Sections A.2.1 and A.3.1.

Lateral size, L_{NS} was determined as before for Chapter 6:

$$L_{NS} = \sqrt{Lw} \quad (Eqn A.50)$$

In order to obtain a physical thickness for determining R_j and plotting as a function of nanosheet dimensions, real nanosheet thickness (t_{NS}) is required. To convert AFM apparent thickness, t into real nanosheet thickness, a correction from step-height analysis was applied²⁵⁴. A 0.5 nm offset was subtracted to account for trapped solvent, then divided by 1.9 nm (the apparent monolayer step height), and multiplied by the crystallographic thickness of MoS₂ (0.65 nm)⁸⁴.

$$N = \frac{(t - 0.5)}{1.9} \quad (\text{Eqn A.51})$$

$$t_{\text{NS}} = N \cdot 0.65 \text{ nm} \quad (\text{Eqn A.52})$$

Where N is nanosheet layer number.

A.4.2 PHASE SHIFT INTERFEROMETRY

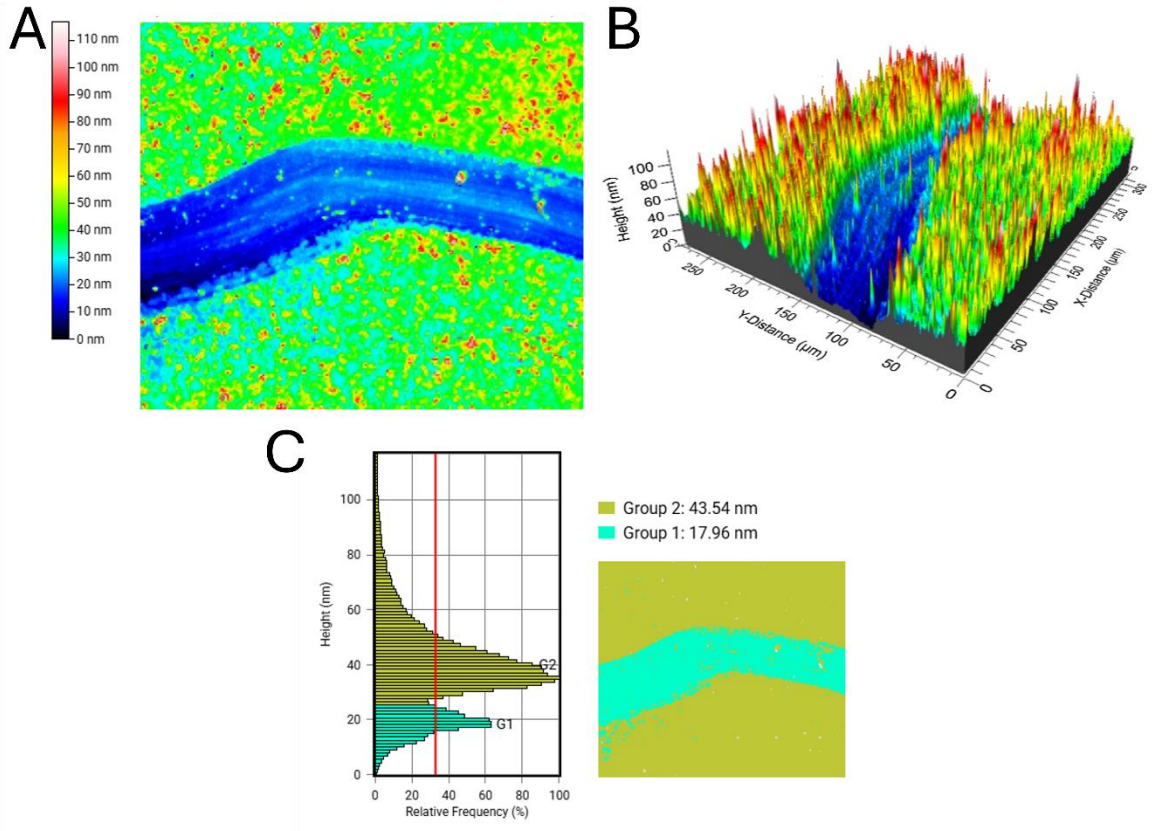


Figure A.21: Phase-shift interferometry of a representative film. A – Profilometry image with a scratch exposing the substrate, the corresponding height map of which is shown in (B). C – Histogram of pixel heights, separated into substrate and film distributions, used to determine thickness.

Shown in Figure A.22 is a PSI image for a representative sample. As can be seen in Figure A.22A and B, prior to imaging a scratch was produced in the film to expose the substrate. With a heightmap, the two heights in the image can be grouped: Group 1 (substrate), and

Group 2 (film). This is done using the histogram of measured height values shown in Figure A.21C. The difference between the averages of the two groups yields $\langle t_{\text{film}} \rangle$.

FAILED PSI

For some films, PSI failed to resolve two distinct distributions due to roughness and porosity as depicted in Figure A.22, particularly in spray-coated films of thicker nanosheets (2.2 g, 3.9 g, 6.1 g, 8.8 g, 11.9 g). In these cases, film thickness could not be extracted by PSI and was instead measured using AFM.

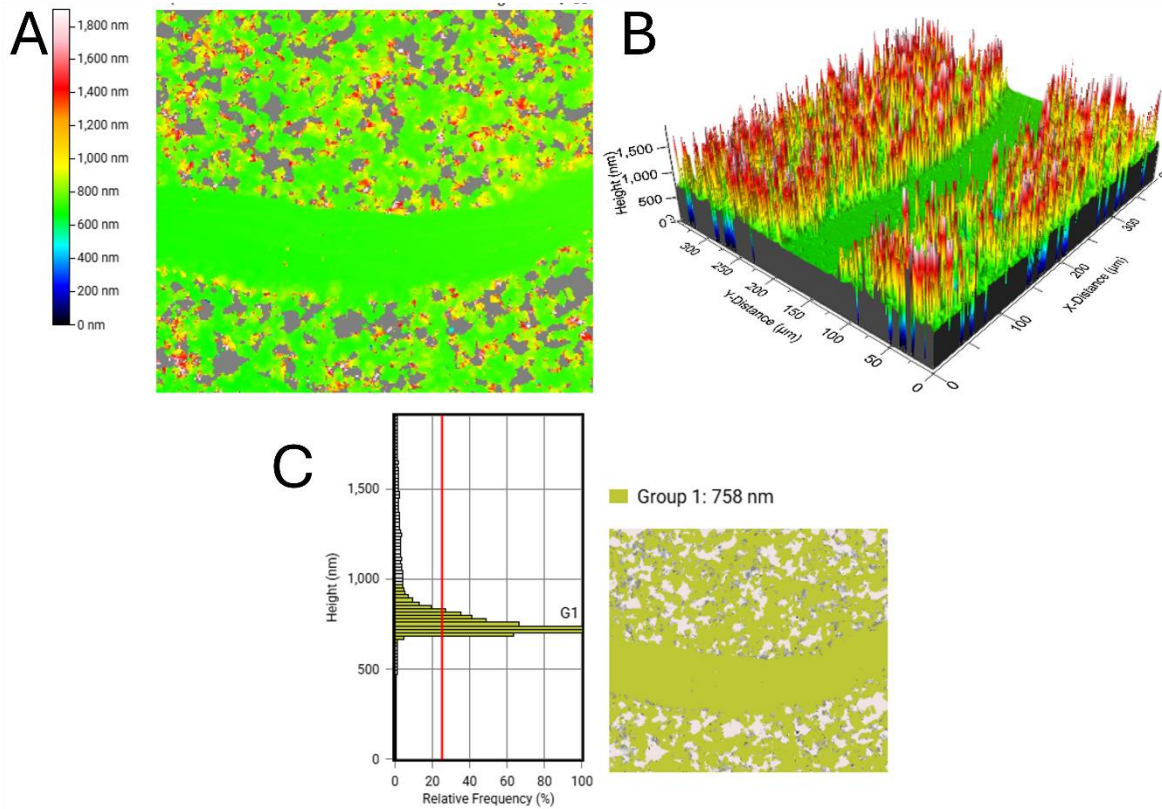


Figure A.22: Failed PSI measurement. A – Optical image of a rough spray-coated film, heightmap of which is shown in (B) showing large inhomogeneity. C – Histogram of pixel heights lacking two distinct distributions, preventing extraction of film thickness.

A.4.3 AFM MEASUREMENTS

For films where PSI was unsuccessful, AFM edge-height analysis was used. Representative images with inset line profiles are shown in Figure A.23. Such line profiles were analysed using Gwydion's Edge Height feature to extract a film height. For each film, at least 10 such line profiles were analysed from a number of images and averaged to produce values for $\langle t_{\text{film}} \rangle$.

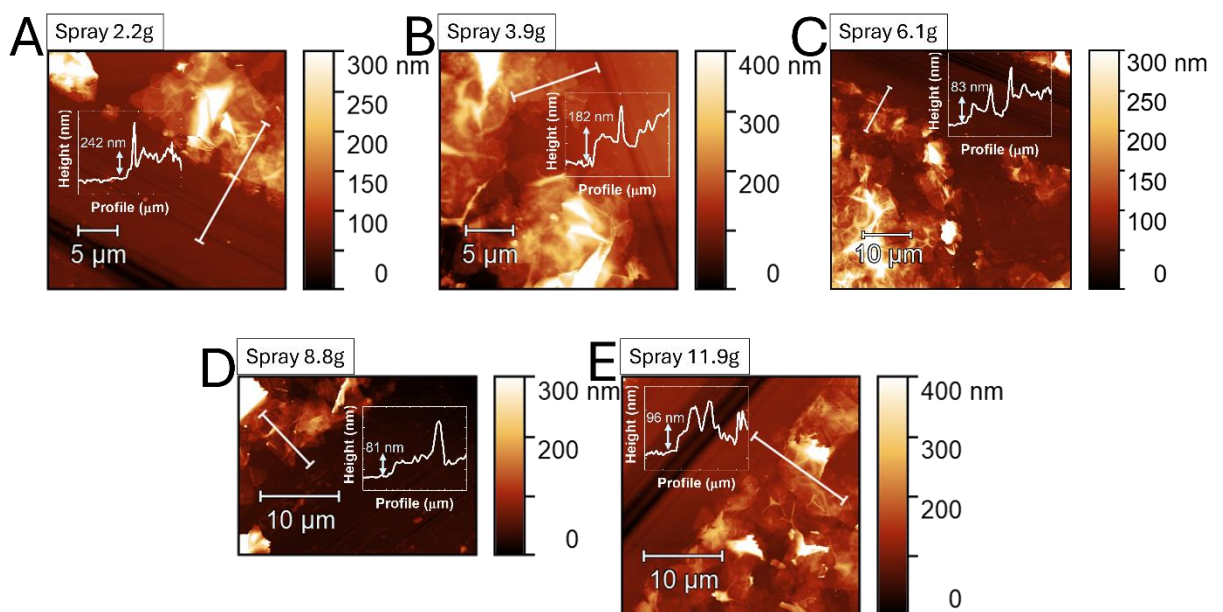


Figure A.23: AFM thickness measurements for films unsuitable for PSI. A-E – Representative AFM images of spray-coated films, with inset line profiles. Thickness was obtained from the average output of an edge-height function applied to 10 such line profiles.

A.4.4 IMPEDANCE MEASUREMENTS

Representative impedance spectra for spray- and LID-deposited samples are shown in Figure A.24, Figure A.25 and Figure A.26. All spectra were fitted to the circuit model described in the main text. Three outliers (97g Spray, 97g LID, 24.3 g LID) exhibited anomalously high junction resistance and was excluded from the dataset presented in Chapter 8.

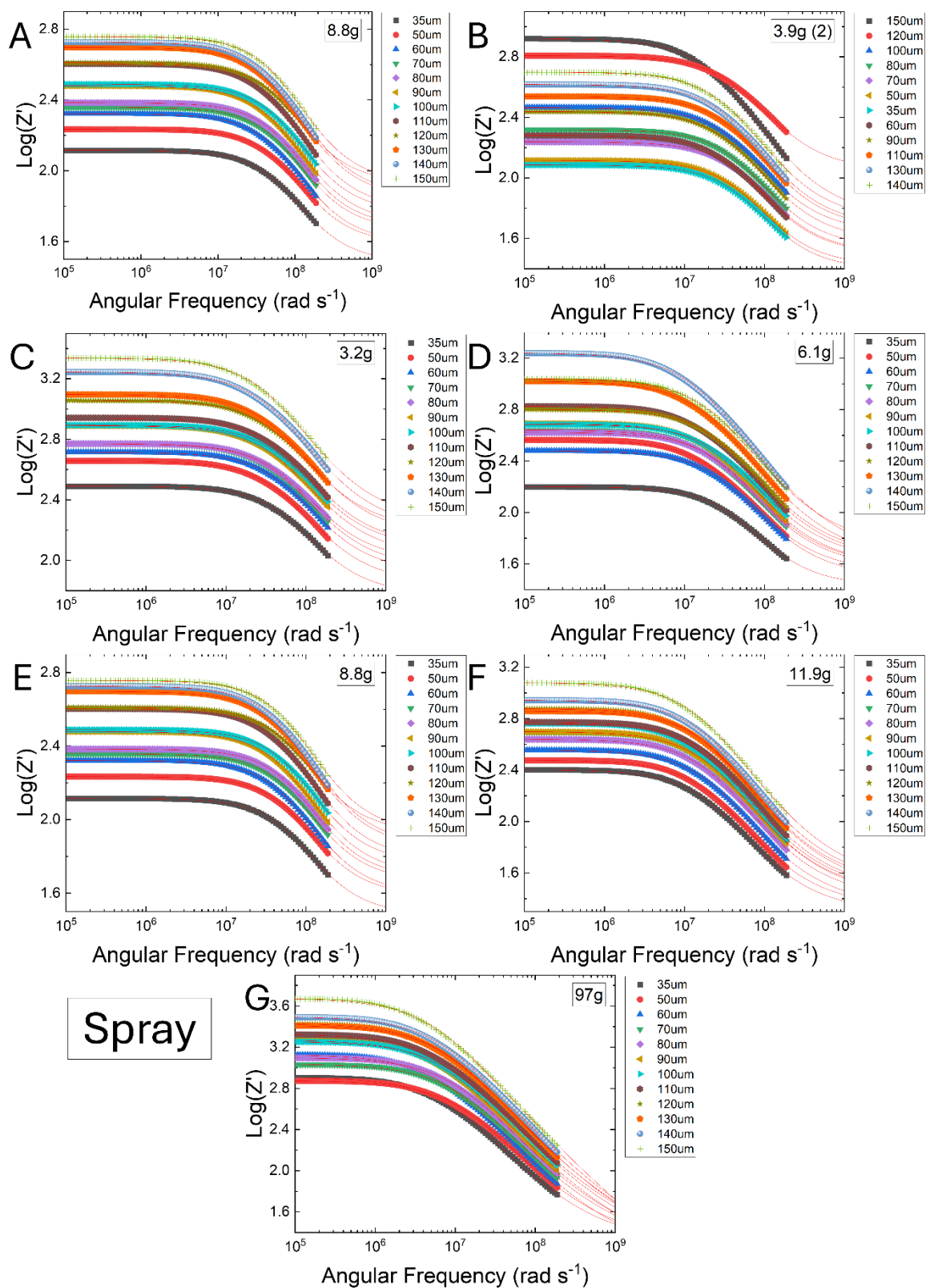


Figure A.24: Impedance spectra for spray-coated samples. A-G – Spectra for sprayed films deposited from different dispersions, with channel lengths and the dispersions used indicated.

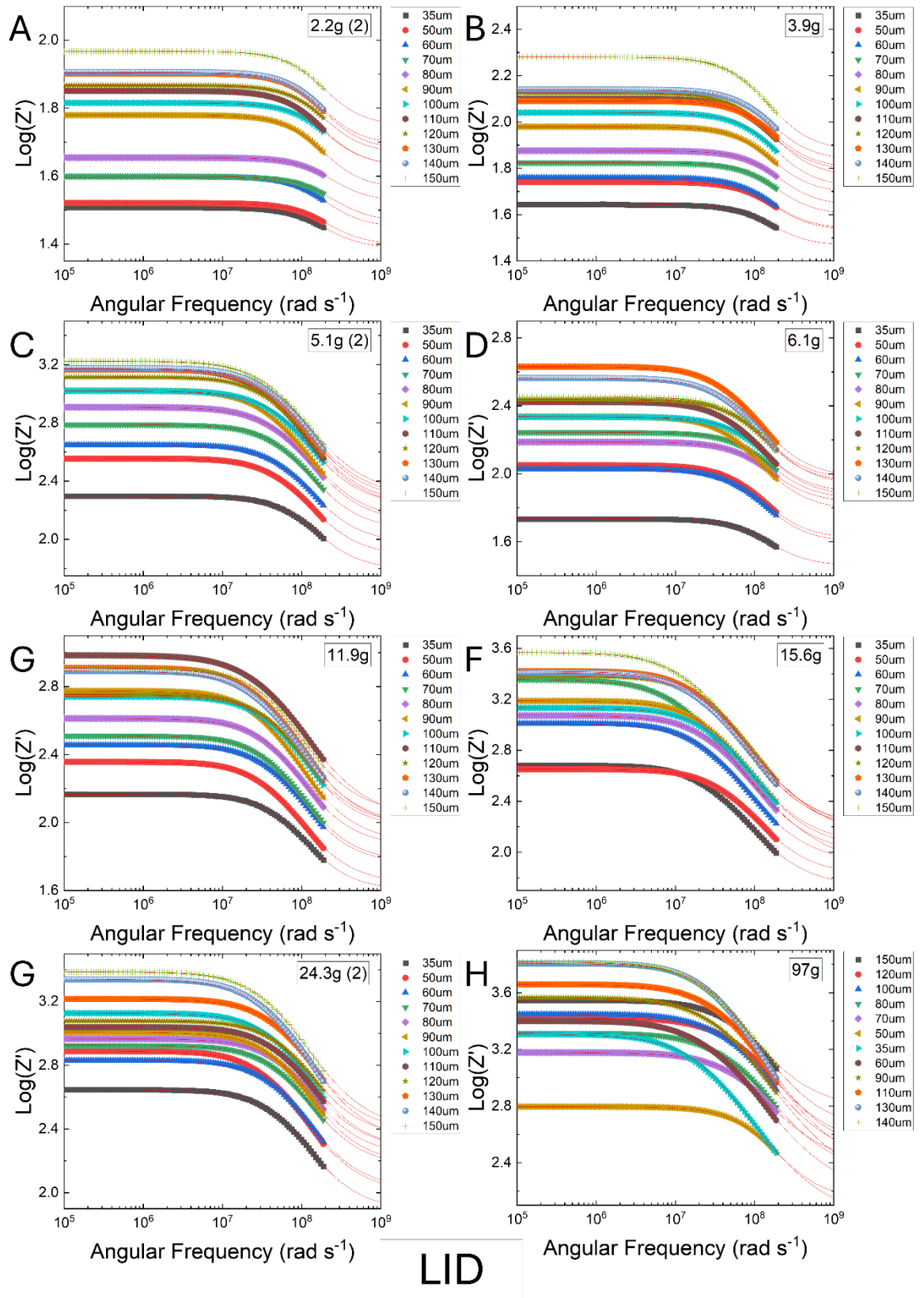


Figure A.25: Impedance spectra for LID samples. A-H – Spectra for LID films deposited from different dispersions, with channel lengths and the dispersions used indicated.

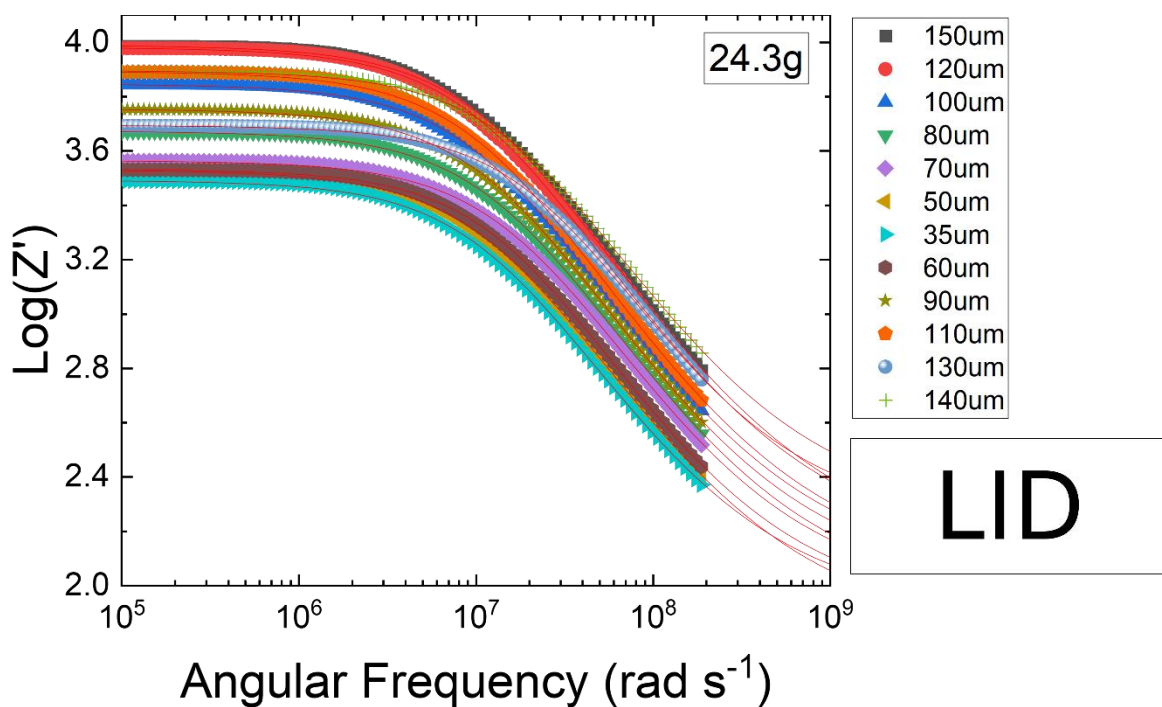


Figure A.26 Impedance spectra of the 24.3 g LID sample. This sample exhibited anomalously high junction resistance and was excluded from the analysis presented in the main text.

A.4.5 OPTICAL MICROSCOPY

Optical images comparing spray and LID films are shown in Figure A.27 and Figure A.28. For images in Figure A.27A-J, the adjacent images provide a visual comparison of samples fabricated from the same or similar inks using the two different techniques. The spray samples show substantial misalignment and porosity, whereas the LID samples appear to be close-packed, with the basal planes visibly aligned upright. Hence, LID appears to produce higher quality nanosheet networks with optimal morphology for low junction resistance.

In addition, it is likely that the porosity and tortuosity are increased in the sprayed samples, and may be much higher than the assumed $P \sim 2\%$ and $\kappa \sim 1$ used in the main text. Hence, R_j may in fact be lower for the spray samples than calculated and reported in the main text.

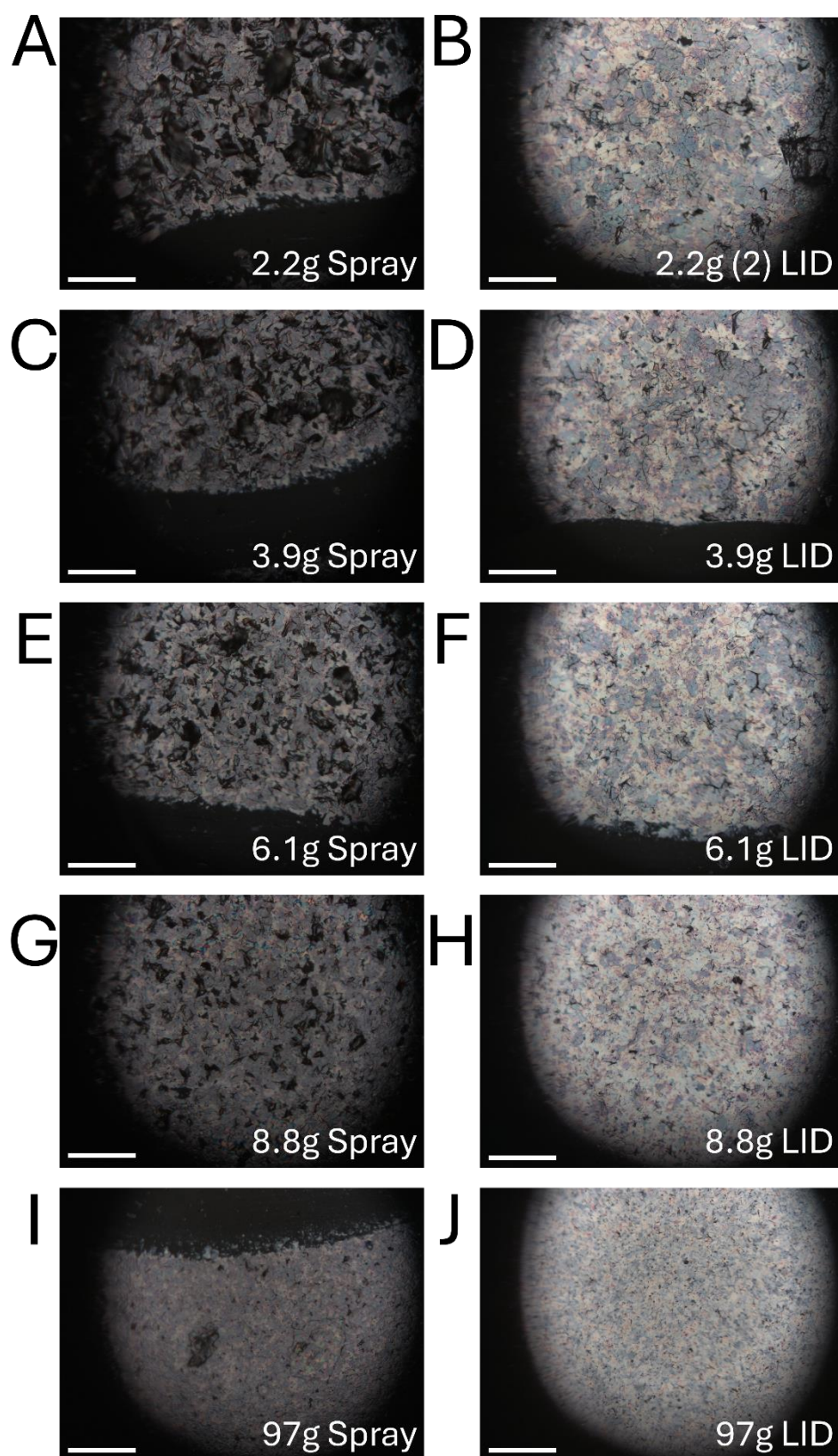


Figure A.27: Optical microscopy comparison of spray- and LID-deposited films from the same dispersions. Scalebars: 50 μm .

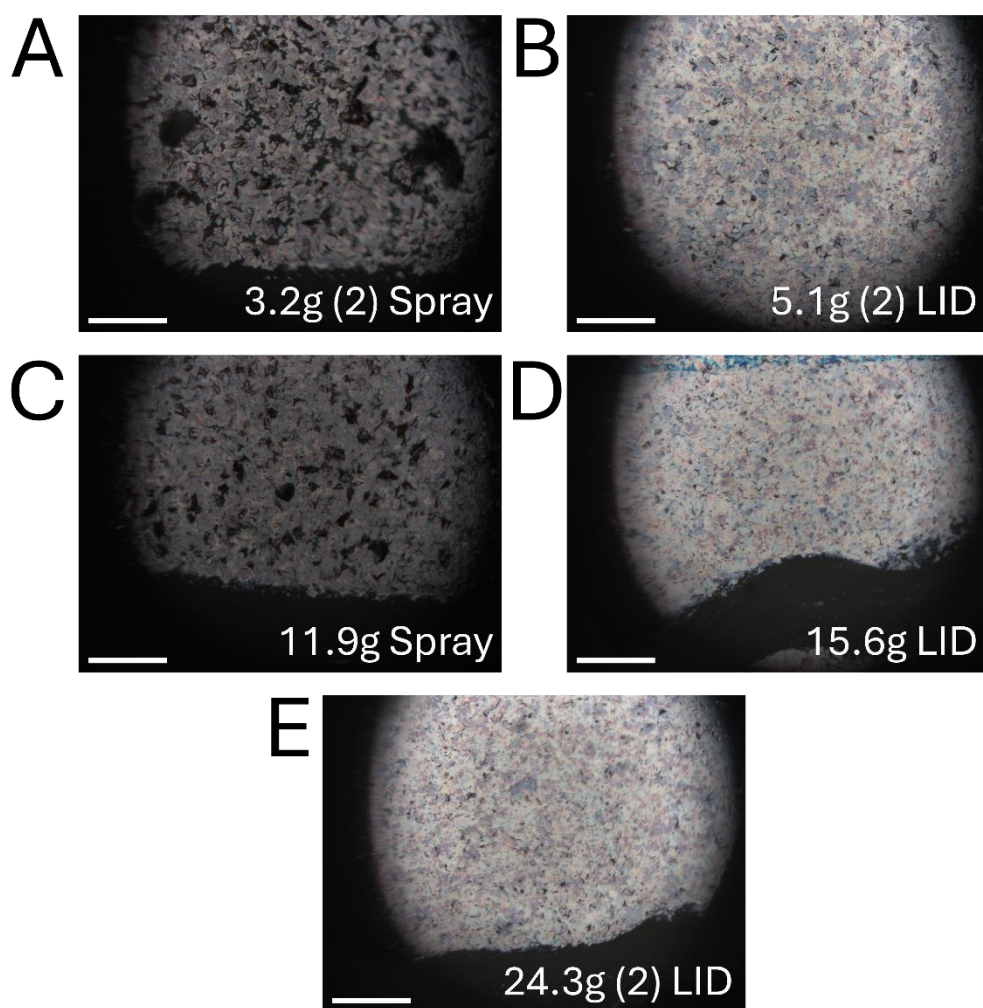


Figure A.28: Additional optical microscopy images of films prepared by a single deposition method. Scalebars: 50 μm .

Appendix B

To run any of the code, install python <https://www.python.org/downloads/>. Before running any script, ensure the listed required packages are installed, by running in the command line:

```
py -m pip install **required packages here**
```

B.1 PROCESSING FOR $\langle \text{EXT} \rangle_{\text{FILM}}$, $\Delta \text{EXT}_{\text{FILM}}$, & Σ_{FILM}

fiji_run.py

- Install Fiji (installation: <https://fiji.sc/>).
- Open Fiji, then do Plugins>New>Macro.
- In the macro editor, do Language>Python (Jython).
- Paste in the following code, ensuring to paste in the directory the scans into the src_path string.
- In the macro editor, do Run>Run.

```
import os
from ij import IJ
from ij.plugin import ChannelSplitter
from ij.io import FileSaver

# PASTE IN DIRECTORY IN THIS STRING
src_path = r""
blu_path = src_path + "/scans_blue"

if not os.path.isdir(blu_path):
    os.makedirs(blu_path)

# iterates over all .tif files in directory, saves blue channel version
for im in [i for i in os.listdir(src_path) if '.tif' in i]:
    if os.path.isfile(blu_path+'/'+im):
        continue
    else:
        imp = IJ.openImage(src_path+"/"+im)
```

```

imp_blue = ChannelSplitter().split(imp)[2]
fs = FileSaver(imp_blue)
fs.saveAsTiff(blu_path+"/"+im)

```

scans_run.py

Required packages: numpy pillow

```

from PIL import Image
import numpy as np
import os

# PASTE IN DIRECTORY OF SCANS HERE
src_path = r""

if src_path[-11:] != r"\scans_blue":
    src_path += "/scans_blue"

ext_path = src_path.replace("scans_blue", "extinction_data")

if not os.path.isdir(ext_path):
    os.makedirs(ext_path)

BASE = -0.01622
FAC = 4.2922E-6
FAC2 = 1.6598E-10

def convert_to_ext(img_path):
    img = np.array(Image.open(f'{img_path}^{404, 421}')).flatten()
    img = img.astype(float)
    img = BASE + (FAC*img) + (FAC2*img**2)
    ext_array = -np.log10(img)
    ext_array = ext_array[~np.isnan(ext_array)]
    mean, std = np.mean(ext_array), np.std(ext_array)
    ext_array = np.random.choice(ext_array, 100000, False)
    return(ext_array, mean, std)

f = open(f"{ext_path}/results.csv", 'w')
f.write("Name,<Ext>,Std Ext\n")

for im in [i for i in os.listdir(src_path) if '.tif' in i]:
    img_path = rf"{src_path}\{im}"
    img_name = im.replace('.tif', '').replace(',', ' ').replace('"', '.')
    ext_array, mean, std = convert_to_ext(img_path)
    ext_array.tofile(f'{ext_path}/{im}.csv', sep='\n', format='%10.5f')
    f.write(f"{img_name},^{67},{std}\n")

f.close()

```

Save this script as a .py file (ensuring to paste in the scans directory in the `src_path` string) and then run in the command line with:

py **directory for script file here**

origin_run.py

- Install and open Origin (<https://www.originlab.com/>).
- Save the origin project as "histos.opju" in the scan folder.
- Do Connectivity>Python Packages...
- Click "Install...".
- Type in "numpy" into the box.
- In the origin taskbar, click the gear  icon to open the Code Builder.
- In the Code Builder, do File>New
- Select "Python File", and save.
- Paste in the code below into the editor, changing `src_path` as directed.
- Click the play  icon in the Code Builder toolbar to run

```
import originpro as op
import os
import numpy as np

# PASTE IN YOUR SCANS DIRECTORY HERE
src_path = r""

op.open(src_path + "/histos.opju")

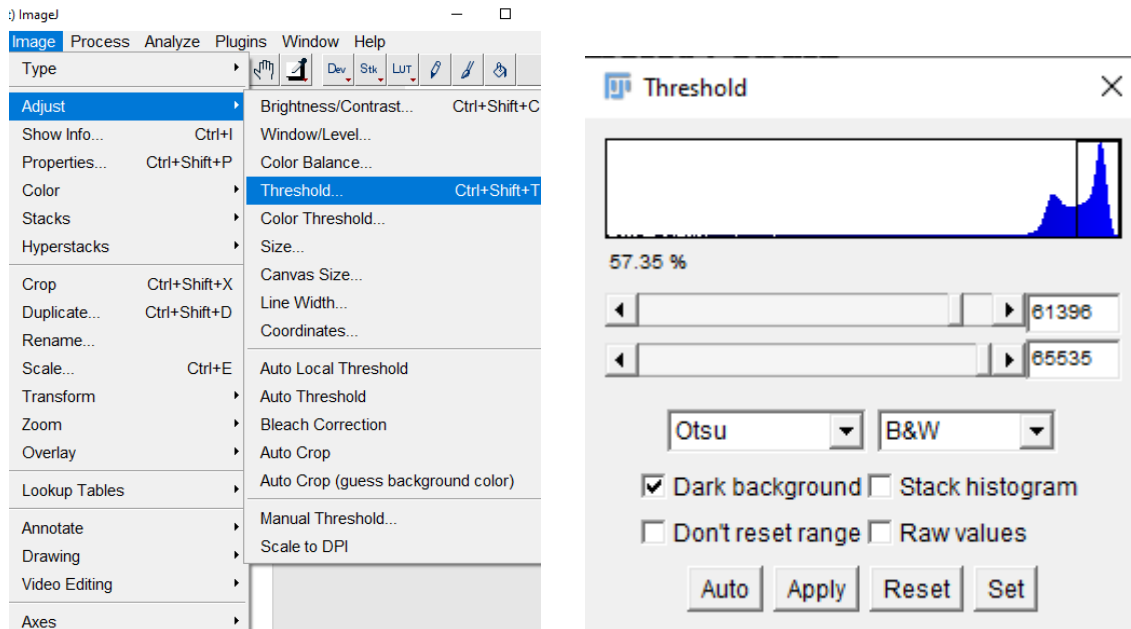
src_path += r"\extinction_data"
os.chdir(src_path)
wb = op.new_book('w', 'data')

for file in [i for i in os.listdir(src_path) if '.csv' in i and i !=
'results.csv']:
    arr = list(np.genfromtxt(file, delimiter="\n"))
    wks = wb.add_sheet(file.replace('.csv', ''))
    wks.from_list(0, arr)
    wks.obj[0].SetLongName("Original Extinction")
    wks.obj[1].SetLongName('Extinction')
```

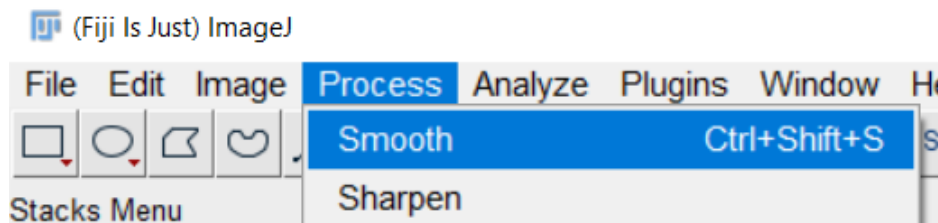
B.2 RELATIVE FILM PERIMETER LENGTH

PROTOCOL IN IMAGEJ

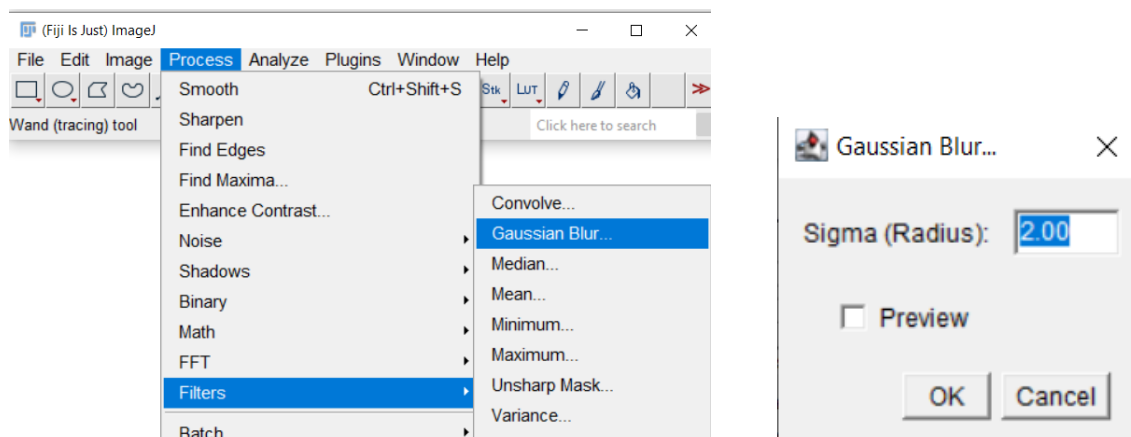
To process each image, firstly use Otsu thresholding on default range:



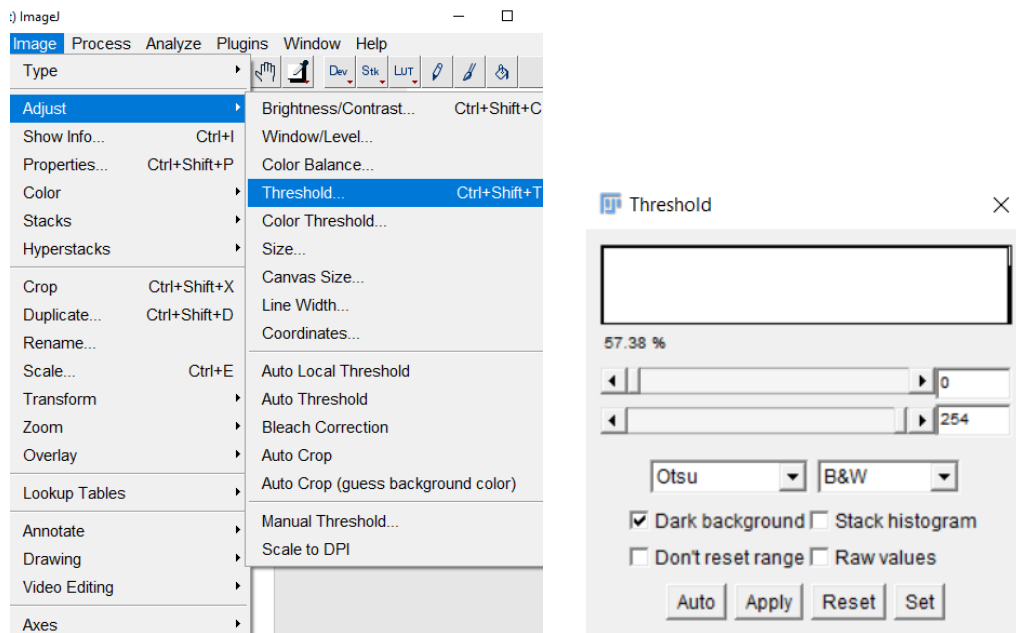
Then smooth:



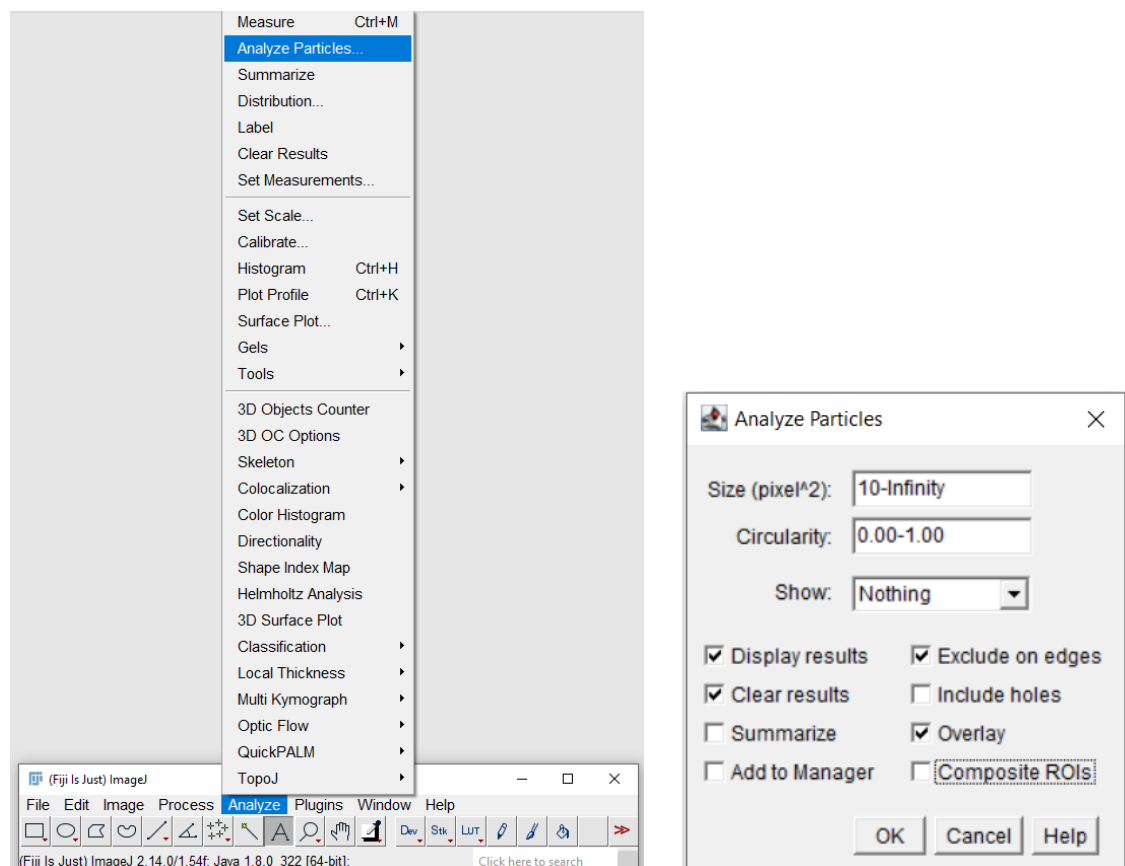
Then Gaussian blur, setting sigma to 2:



Then otsu threshold again:



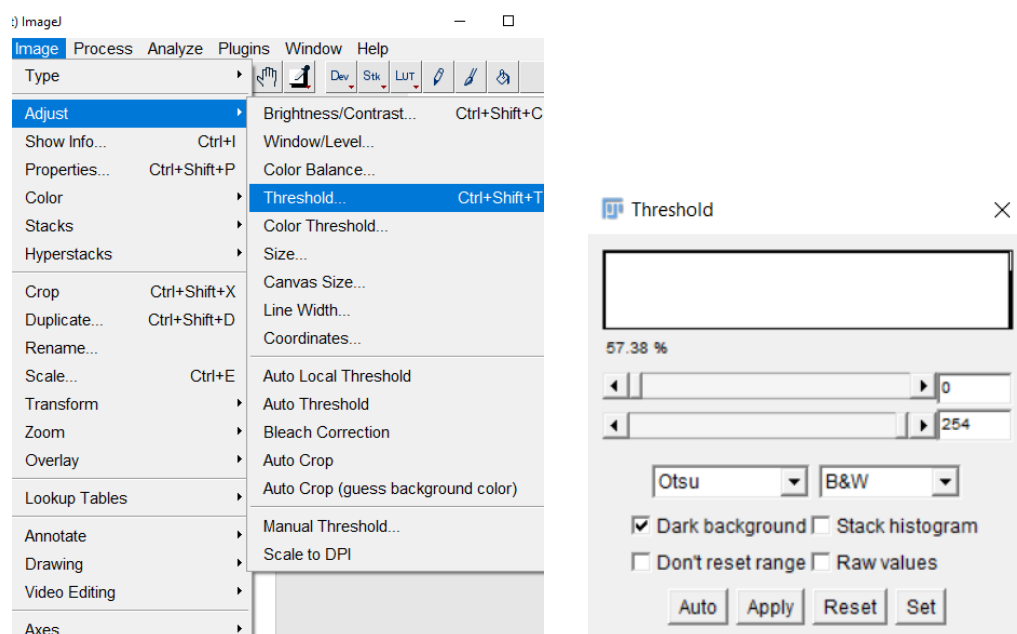
Then analyze particles, with “Size (pixel²)” set as “10-Infinity”, and “Exclude on edges” unchecked, “Include holes” checked:



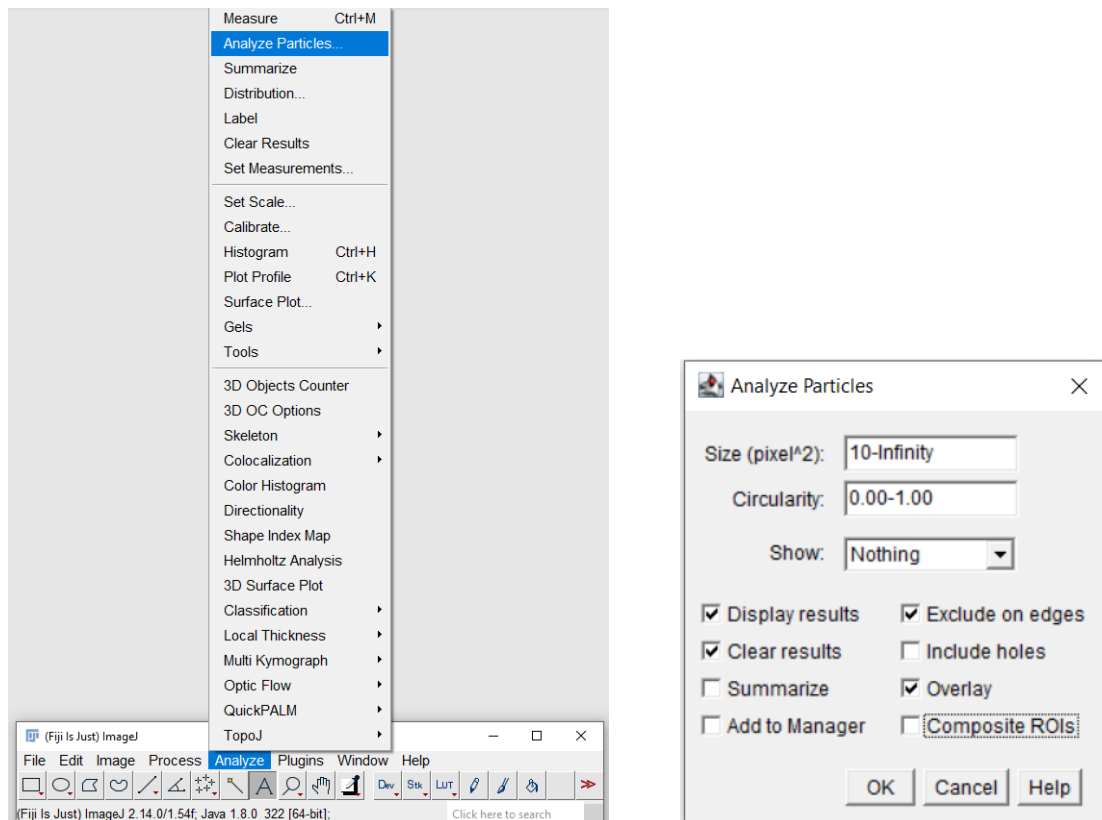
This produces a table of results. Save this:

Results					
File	Edit	Font	Results		
	Area	Mean	Min	Max	Perim.
540	129	255	255	255	40.870
541	53	255	255	255	25.556
542	129	255	255	255	41.456
543	168	255	255	255	50.042
544	74	255	255	255	31.213

Otsu threshold again:



Then analyze particles, this time with “Exclude on edges” checked and “Include holes” unchecked:



Again, another table of results is produced. Save this and amalgamate with the other table and take a total for the “Perim.” column. This is the total film perimeter, including the edge of the image, in pixels.

image_perim-area.py

Required packages: pillow

```
import os
from PIL import Image

src_path = r"C:\Users\Administrator.ADMINTR-CCF0RUE\Documents\MyDocuments\research_data\LS-ee-gra_optimise\scans_noelectrode"
dst_path = src_path + "/film-perimeter_data"

if not os.path.isdir(dst_path):
    os.makedirs(dst_path)

f = open(f"{dst_path}/perim-area.csv", 'w')
f.write('Name,Perimeter,Area\n')

for im in [i for i in os.listdir(src_path) if '.tif' in i]:
    img_name = im.replace('.tif', '').replace(',', ' ').replace('"', '.')
    img = Image.open(f"{src_path}/{im}")
```

```

perim = (2*(img.height+img.width))/94488.2
area = (img.height*img.width)/94488.2**2
f.write(f"{img_name},{perim},{area}\n")

f.close()

```

B.3 MEASUREMENT OF EEG EXTINCTION COEFFICIENT

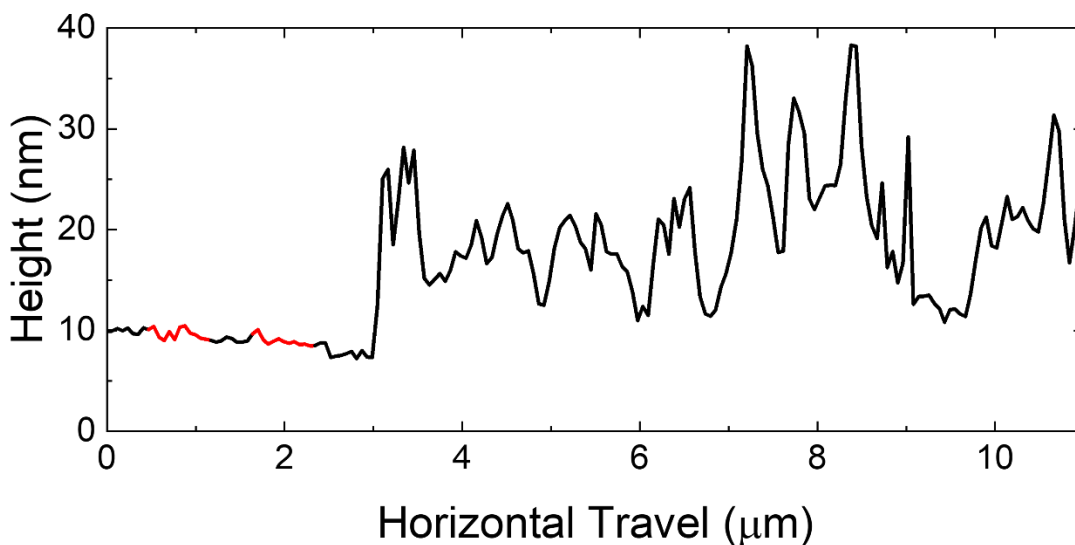
profile_level.py

- Install and open Origin (<https://www.originlab.com/>).
- Ensure numpy is installed, as was for Appendix B.1 origin_run.py
- In Book1, paste the .txt file containing the line profile data.
- Plot this profile to find the ranges for the line of best fit for the substrate – the ranges to be averaged into p1 and p2 for the following formulae for m and c, the parameters for the equation of the line:

$$m = \frac{y_2 - y_1}{x_2 - x_1} \quad (\text{Eqn B.1})$$

$$c = y_1 - mx_1 \quad (\text{Eqn B.2})$$

For example, in this profile, datapoints 10-20 were picked for the p1 range, and datapoints 30-40 were picked for the p2 range.



The ranges should be at least ~5 points wide to account for noise. Different ranges may need to be selected if levelling does not occur satisfactorily.

- Save the project.
- Open the Code Builder by clicking the gear  icon in the toolbar.
- Paste in the code below into the Code Builder after opening a new python file, same as in Appendix B.1 `origin_run.py`
- Paste in the project directory, the name of the sheet containing the profile data, and the index ranges for p1 and p2 as directed.
- Click the play  icon in the Code Builder toolbar to run.

```
import originpro as op
import numpy as np

# PASTE PATH TO PROJECT HERE
src_path = r"C:\Users\Administrator.ADMINTR-CCF0RUE\Documents\MyDocuments\research_data\LS-ee-gra_extinction\AFM\Oran - 3x LS\for fig.opju"
# PASTE IN NAME OF SHEET IN PROJECT HERE
sheet_name = "for fig"
# TYPE IN RANGE OF DATAPOINTS INDEX TO SAMPLE FOR P1 OF SUBSTRATE LINE
p1_lower, p1_upper = 10,20
# TYPE IN RANGE OF DATAPOINTS INDEX TO SAMPLE FOR P2 OF SUBSTRATE LINE
p2_lower, p2_upper = 30,40

op.open(src_path)

wks = op.find_sheet('w', f"[Book1]{sheet_name}")
x = wks.to_list(0)
y = wks.to_list(1)

x1 = np.mean(x[p1_lower:p1_upper])
y1 = np.mean(y[p1_lower:p1_upper])
x2 = np.mean(x[p2_lower:p2_upper])
y2 = np.mean(y[p2_lower:p2_upper])

m = (y2-y1)/(x2-x1)
c = y1 - x1*m

for i in range(len(y)):
    y[i] -= m*x[i] + c

wks.from_list(2, y)
```

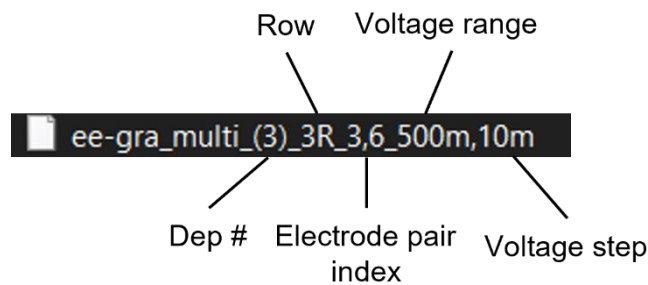
This will produce a 3rd column, containing the height values for the levelled profile, which may be replotted.

B.4 CONDUCTIVITY MEASUREMENT

iv_data.py

Required packages: pandas numpy scikit-learn

Note, the following code was designed for the indexing system used for the title of each I/V curve file:



It will not work without using this convention.

```
import os
import pandas as pd
import numpy as np
from sklearn.linear_model import LinearRegression

# PASTE IN DIRECTORY OF THE I/V DATA FILES HERE
src_path = r""

os.chdir(src_path)

names = []
pairs = []

for file in [i for i in os.listdir(os.getcwd()) if 'ee-gra' in i]:
    names.append('_'.join(file.split('_')[:4]))
    pairs.append(file.split('_')[4])

value_list = []
names = list(set(names))
pairs = list(set(pairs))
```

```

pairs.sort()
names.sort(key=lambda x: (int(x.split('_')[2][1:-1]), int(x[-2])))

for pair in pairs:
    values = list(np.full(len(names), np.nan))
    for i, name in enumerate(names):
        for file in os.listdir(os.getcwd()):

            if pair in file and name in file:
                with open(file) as f:
                    V = []
                    I = []

                    for row in f.read().split('\n'):
                        cols = row.split("\t")
                        if len(cols) == 3:
                            I.append([float(cols[1])])
                            V.append(float(cols[0]))

                    model = LinearRegression().fit(I, V)
                    resistance = model.coef_[0]
                    values[i] = resistance

    value_list.append(values)

df = pd.DataFrame(value_list, index=pairs, columns=names)
df.to_csv('results.csv')

```

Save this script as a .py file, paste in the directory into the `src_path` string as directed, and then run from the command line with:

```
py **directory for script file here**
```

`origin_iv_run.py`

(Note, for origin to not crash, the data for each deposition number sample must be loaded into separate projects. This is why the script below is designed to run on 16 individual projects)

- Open Origin
- Ensure pandas and numpy are installed on origin using the same process as in Appendix 1 `origin_run.py`

- Save your project with a name indicating which deposition number it is for.
- Open the Code Builder by clicking the gear  icon in the toolbar.
- Paste in the code below into the Code Builder after opening a new python file, same as in Appendix B.1 `origin_run.py`
- Paste in the I/V data path, the filename of the project you've saved, and the deposition number to be analysed in the project where it is indicated.
- Click the play  icon in the Code Builder toolbar to run.

```
import originpro as op
import pandas as pd
import numpy as np

# PASTE DIRECTORY CONTAINING THE I/V DATA HERE
src_path = r""
# PASTE THE FILENAME OF YOUR ORIGIN PROJECT HERE
project_file = ""
# PASTE WHICH DEPOSITION NUMBER YOU WANT TO ANALYSE
dep_num =

op.open(f"{src_path}/{project_file}")

if src_path[-12:] != r"\results.csv":
    src_path += "/results.csv"

dep_num = f"({dep_num})"

color_list = ['#000', '#f00', '#0f0', '#00f', '#ff0']

array = np.array([])
for i in np.arange(0.016, 0.001, -0.003):
    array = np.concatenate((array, np.array(np.arange(0.002, i, 0.003))))

rc = pd.read_csv(src_path, index_col=0)

wb = op.new_book('w', 'transmission lines')

for column in rc.columns:
    if dep_num not in column:
        continue
    resistances = list(rc[column])
    wks = wb.add_sheet(column)
    wks.from_list(0, np.arange(0.002, 0.017, 0.003), lname='Channel Length',
units='m')
    wks.set_label(0, 'Channel Length')
    index = 0
```

```

    for i in range(5):
        wks.from_list(i+1, resistances[index:index+i], lname='Resistance',
units='Ω', comments=f"Electrode {i+1}")
        index += i

wks.from_list(6, array, lname='Channel Length', units='m')
wks.from_list(7, resistances, lname='Resistance', units='Ω')

gp = op.new_graph(f"{column}_multi")[0]
for i in range(5):
    plt = gp.add_plot(wks, i+1, 0, type = 's')
    plt.symbol_kind = i+1
    plt.color = color_list[i]

gp.rescale()

gp = op.new_graph(column)[0]
plt = gp.add_plot(wks, 7, 6, type = 's')
gp.rescale()

```

This produces a project populated by transmission line graphs, which can be fitted as appropriate. These fits were used to obtain the conductivity and contact resistances for the row of each sample.

B.5 MULTILAYER DEPOSITION CODE

Run `fiji_run` as before.

`scans_electrodes_run.py`

Required packages: `opencv-python` `numpy` `pillow`

```

import os
import cv2 as cv
from cv2 import boundingRect
import numpy as np
from PIL import Image

# PASTE IN DIRECTORY FOR THE SCANS HERE
src_path = r""
# CHANGE THIS IF THE THRESHOLDING ISN'T WORKING
thresh_lower = 75

if src_path[-11:] != r"\scans_blue":
    src_path += "/scans_blue"

```

```

ext_path = src_path.replace("scans_blue", "extinction_data")
cv_path = src_path.replace("scans_blue", "cv_output")

if not os.path.isdir(ext_path):
    os.makedirs(ext_path)

if not os.path.isdir(cv_path):
    os.makedirs(cv_path)

BASE = -0.01622
FAC = 4.2922E-6
FAC2 = 1.6598E-10

def create_eltrd_cnts(filename, img_name):
    img = cv.imread(filename)
    gray = cv.cvtColor(img, cv.COLOR_BGR2GRAY)
    thresh = cv.threshold(gray, thresh_lower, 255, cv.THRESH_BINARY_INV)[1]

    kernel = np.ones((5, 5), np.uint8)
    img_dilated = cv.dilate(thresh, kernel, iterations = 1)
    cnts = cv.findContours(img_dilated.copy(), cv.RETR_EXTERNAL,
cv.CHAIN_APPROX_SIMPLE)[0]
    for cnt in cnts:
        x, y, w, h = cv.boundingRect(cnt)
        cv.rectangle(thresh, (x, y), (x + w, y + h), (255,0,0), 2)
        if w > 100:
            cv.putText(thresh, f"{x},{w}", (x, y), cv.FONT_HERSHEY_SIMPLEX,
4, (255, 0, 0), 2, cv.LINE_AA)
        cv.imwrite(f"{cv_path}/{img_name}_thresh.png", thresh)

    return cnts

def cluster(cnts):
    rects = []
    rects_used = []

    for cnt in cnts:
        rects.append(boundingRect(cnt))
        rects_used.append(False)

    def getXFromRect(item):
        return item[0]
    rects.sort(key = getXFromRect)

    eltrd_rects = []

    xThr = 150
    yThr = 150

    for supIdx, supVal in enumerate(rects):

```

```

        if (rects_used[supIdx] == False):
            # Initialize current rect
            currxMin = supVal[0]
            currxMax = supVal[0] + supVal[2]
            curryMin = supVal[1]
            curryMax = supVal[1] + supVal[3]

            # This bounding rect is used
            rects_used[supIdx] = True

            # Iterate all initial bounding rects starting from the next
            for subIdx, subVal in enumerate(rects[(supIdx+1):], start =
(supIdx+1)):
                # Initialize merge candidate
                candxMin = subVal[0]
                candxMax = subVal[0] + subVal[2]
                candyMin = subVal[1]
                candyMax = subVal[1] + subVal[3]
                # Check if distances between current rect and merge
candidate is small enough
                if (candxMin <= currxMax + xThr and candxMax >= currxMin -
xThr):
                    if (candyMin <= curryMax + yThr and candyMin >= curryMin
- yThr):
                        # Reset coordinates of current rect
                        currxMin = min(currxMin, candxMin)
                        currxMax = max(currxMax, candxMax)
                        curryMin = min(curryMin, candyMin)
                        curryMax = max(curryMax, candyMax)

                        # Merge candidate rect is used
                        rects_used[subIdx] = True
                    else:
                        continue

                # No more merge candidates possible, accept current rect
                eltrd_rects.append([currxMin, curryMin, currxMax - currxMin,
curryMax - curryMin])

            eltrd_rects = [rect for rect in eltrd_rects if rect[2] > 800]

        return eltrd_rects

def group_row(eltrd_rects):
    electrode_dict = {}
    grouped_rects = []
    for rect in eltrd_rects:
        grouped_rects.append(False)
    def get_y_from_rect(item):
        return item[1]
    row_num = 4

```

```

for supIdx, supVal in enumerate(eltrd_rects):
    # Checks if electrode has been grouped
    if (grouped_rects[supIdx] == False):
        # Iterates row number (image is reversed)
        row_num -= 1
        # Puts initial electrode into row
        row = [supVal]
        # Initializes electrode x data
        xMin = supVal[0]
        xMax = supVal[0] + supVal[2]

        # Sets electrode as grouped
        grouped_rects[supIdx] = True

        # Starts from next electrode in list
        for subIdx, subVal in enumerate(eltrd_rects[(supIdx+1):], start
= (supIdx+1)):
            # Initializes candidate electrode
            candxMin = subVal[0]
            candxMax = subVal[0] + subVal[2]

            # Checks if candidate electrode can be added
            if (candxMin >= xMin and candxMin <= xMax) or (candxMax >=
xMin and candxMax <= xMax):
                # Sets candidate electrode as grouped, adds to row
                grouped_rects[subIdx] = True
                row.append(subVal)
            else:
                continue
            row.sort(key = get_y_from_rect)
            electrode_dict[f"{row_num}R"] = row

    return electrode_dict

def get_image_dims(filename):
    image = cv.imread(filename)
    height, width = image.shape[:2]
    height -= 1
    width -= 1
    return height, width

def get_areas(electrode_dict, height, width):
    areas = []
    channels = {}

    first_row = True
    for j, (key, row) in enumerate(electrode_dict.items()):
        init_y = 0
        if first_row:
            init_x = np.zeros(len(row))
            first_row = False

```

```

last_row = True if j == len(electrode_dict.keys())-1 else False

for i, eltrd in enumerate(row):
    x,y,w,h = eltrd[0], eltrd[1], eltrd[2], eltrd[3]
    last_eltrd = True if i == len(row)-1 else False

    top = [x, init_y, w, y-init_y]
    left = [init_x[i], init_y, x-init_x[i], (y-init_y)+h]

    areas.append(list(map(int, top)))
    areas.append(list(map(int, left)))
    if init_y != 0:
        channels[f"244_{i},{i+1}"] = top

    if last_eltrd and not last_row:
        bottom = [init_x[i], y+h, (x-init_x[i])+w, height-(y+h)]
        areas.append(list(map(int, bottom)))

    if last_row:
        right = [x+w, init_y, width-(x+w), (y-init_y)+h]
        areas.append(list(map(int, right)))
        if last_eltrd:
            bottom = [init_x[i], y+h, width-init_x[i], height-(y+h)]
            areas.append(list(map(int, bottom)))

    init_y = y+h+1
    init_x[i] = x+w+1

return areas, channels

def generic_output(rects, filename, img_name):
    image_copy = cv.imread(filename)
    for rect in rects:
        cv.rectangle(image_copy, (rect[0], rect[1]), (rect[0] + rect[2],
rect[1] + rect[3]), (0, 255, 0), 2)
        # cv.putText(image_copy, f"{rect[2]}", (rect[0], rect[1]),
cv.FONT_HERSHEY_SIMPLEX, 4, (0, 0, 255), 2, cv.LINE_AA)
    cv.imwrite(f"{cv_path}/{img_name}_areas.png", image_copy)

def sample_area_data(sample_area_rects, filename):
    def get_area(area):
        w,h = area[2], area[3]
        return w*h

    image_data = np.array(Image.open(filename))

    total_area = 0
    whole_img_sample = []
    for area in sample_area_rects:
        total_area += get_area(area)

```

```

    for i, area in enumerate(sample_area_rects):
        x,y,w,h = area[0], area[1], area[2], area[3]
        sample = int((get_area(area)/total_area)*200000)
        area_array = image_data[y:y+h,x:x+w]
        area_array = area_array.flatten()
        area_sample = np.random.choice(area_array, sample, False)
        area_sample = [px for px in area_sample if px != 0]
        whole_img_sample.extend(area_sample)

    return whole_img_sample

def convert_to_ext(whole_img_sample):
    whole_img_sample = whole_img_sample.astype(float)
    whole_img_sample = BASE + (FAC*whole_img_sample) +
(FAC2*whole_img_sample**2)
    ext_array = -np.log10(whole_img_sample)
    mean, std = np.mean(ext_array), np.std(ext_array)
    return(ext_array, mean, std)

f = open(f"{ext_path}/results.csv", 'w')
f.write("Name,<Ext>,Std Ext\n")

for im in [i for i in os.listdir(src_path) if '.tif' in i]:
    filename = f"{src_path}/{im}"
    img_name = im.replace('.tif', '').replace(',', ' ')
    print(img_name)

    cnts = create_eltrd_cnts(filename, img_name)
    eltrd_rects = cluster(cnts)
    electrode_dict = group_row(eltrd_rects)
    height, width = get_image_dims(filename)
    areas, channels = get_areas(electrode_dict, height, width)
    generic_output(areas, filename, img_name)
    whole_img_sample = np.array(sample_area_data(areas, filename))

    ext_array, mean, std = convert_to_ext(whole_img_sample)
    ext_array.tofile(f"{ext_path}/{img_name}.csv", sep='\n',format='%10.5f')
    f.write(f"{img_name},{std}\n")

f.close()

```

Save this script as a .py file (ensuring to paste in the scans directory in the src_path string as directed) and then run in the command line with:

```
py **directory for script file here**
```

In the new `extinction_data` folder, `results.csv` has the values for $\langle \text{Ext} \rangle$ and ΔExt for each sample (statistics taken from random sample of 200,000 datapoints). The extinction histograms can then be produced in origin using the code in Appendix 1, `origin_run.py`

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