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PERCOLATION EFFECTS IN
NANOSTRUCTURED THIN FILMS

PAUL J KING

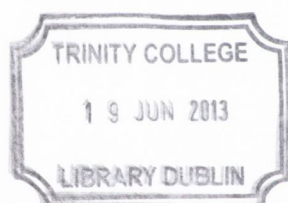


A thesis submitted for the degree of
Doctor of Philosophy

Supervised by Prof. Jonathan N Coleman
Chemical Physics of Low Dimensional Nanostructures Group

School of Physics
Trinity College Dublin

2013



Thesis 10141

DECLARATION

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Paul J King

ABSTRACT

Typically, materials with high electrical conductivity such as metals are opaque, and materials with high optical transparency such as glass are insulating. Finding materials that are both transparent to visible light and electrically conductive has proven to be a significant challenge. There is an ever increasing need for such materials as many of today's popular electronic devices require one or more layers to be both transparent while simultaneously applying a voltage or conducting a current. Indium tin oxide (ITO) is by far the most common material as it satisfies industry requirements for most devices. However, it has several critical drawbacks (for example, brittleness, high cost and being typically deposited via sputtering under vacuum). In recent years solution processed nanomaterials have emerged as a potential alternative. These materials can be deposited over large areas at low temperatures, greatly increasing yield and throughput and reducing cost, while the nanomaterial topology enables flexible devices.

We prepare graphene rich dispersions by exfoliating graphite in water stabilised by surfactant. Thin disordered films of randomly stacked oxide-free, graphene have been deposited by vacuum filtration. The as prepared films are transparent with a direct current conductivity of $1.5 \times 10^3 \text{ S/m}$, this can be further increased by an order of magnitude by annealing the films. The conductivity is stable under flexing for at least 2000 cycles. The electrical properties are limited by disorder and the resistance at the junctions between flakes.

We demonstrate a simple water-based method to prepare graphene/carbon nanotube hybrids. We observe an optimum composition of $\sim 3 \text{ wt\%}$ graphene, which results in a peak in the DC conductivity. We calculate a figure of merit, the DC to optical conductivity ratio, $\sigma_{\text{DC}}/\sigma_{\text{Op}}$, which also shows a peak at this composition. Acid treatment increases both σ_{DC} and $\sigma_{\text{DC}}/\sigma_{\text{Op}}$ by a factor of ~ 2.5 . Interestingly, acid treatment is more effective for films close to the optimum composition. This has

the effect of sharpening the peaks in both σ_{DC} and σ_{DC}/σ_{Op} . For acid-treated films, addition of 3 wt % graphene results in a 40% increase in σ_{DC}/σ_{Op} compared to the nanotube-only film, from 12.5 to 18.

With such intense research into finding ITO replacement materials it is important to have a metric to rate the performance of new materials and benchmark them against known standards. This is generally achieved using figures of merit (FoMs) such as the DC to optical conductivity ratio. Transparent electrodes typically require high visible transmittances, $T > 90\%$. For most nanostructured films thin enough to display $T > 90\%$, the conduction can be described by percolation theory. This means DC conductivities are lower than in bulk, giving correspondingly higher sheet resistances, R_s . *De. et al.* define a percolative figure of merit, Π , for which high values result in high T and low R_s . High values of Π are achieved for high DC conductivity and low optical conductivity. In addition, the film thickness, t_{min} , where the DC conductivity first deviates from its bulk value and the percolation exponent, n , must both be as low as possible. Using this model we demonstrate the deficiencies of standard bulk theory and the importance of understanding percolation by measuring R_s and T for networks of silver flakes. We measure the bulk ratio of DC to optical conductivity to be 35, suggesting $R_s = 100\Omega/sq$ and $T = 90\%$ are attainable. However, the large flake thickness results in high t_{min} and so low Π , resulting in actual values of $T = 26\%$ for $R_s = 100\Omega/sq$. This makes this material completely unsuitable for transparent conductor applications.

Finally, we examine the thickness dependence of the properties of supercapacitors with carbon nanotubes as the electrodes. We find the equivalent series resistance, R_{ESR} , and volumetric capacitance, C_V , to be thickness independent for relatively thick electrodes. However, similar to transparent electrodes once the electrode thickness falls below a threshold thickness t_{min} ($\sim 100nm$ for R_{ESR} and $\sim 20nm$ for C_V), the properties of the electrode become thickness dependent. We show the thickness dependence of both R_{ESR} and C_V to be consistent with percolation theory. The percolation scaling of the capacitance is unexpected and occurs because, for sparse networks, the capacitance is proportional to the fraction of nanotubes connected to the main network. This fraction, in turn, follows a percolation scaling law. This allows us to understand and

quantify the limitations on the achievable capacitance of transparent supercapacitors. We find that supercapacitors with thickness independent R_{ESR} and C_V occupy a well-defined region of the Ragone plot. However, supercapacitors whose electrodes are limited by percolation display significantly lower performance with greatly reduced values of energy and power density.

PUBLICATIONS

1. De, S.; Lyons, P. E.; Sorrel, S.; Doherty, E. M.; King, P. J.; Blau, W. J.; Nirmalraj, P. N.; Boland, J. J.; Scardaci, V.; Joimel, J. Transparent, Flexible, and Highly Conductive Thin Films Based on Polymer–Nanotube Composites *ACS Nano* 2009, 3, 714
2. Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z.; McGovern, I. T.; Duesberg, G. S.; Coleman, J. N. Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions *J. Am. Chem. Soc.* 2009, 131, 3611–3620
3. De, S.; King, P. J.; Lotya, M.; O'Neill, A.; Doherty, E. M.; Hernandez, Y.; Duesberg, G. S.; Coleman, J. N. Flexible, Transparent, Conducting Films of Randomly Stacked Graphene from Surfactant-Stabilized, Oxide-Free Graphene Dispersions *Small* 2010, 6, 458–464
4. Lotya, M.; King, P. J.; Khan, U.; De, S.; Coleman, J. N. High-Concentration, Surfactant-Stabilized Graphene Dispersions *ACS Nano* 2010, 4, 3155–3162
5. King, P. J.; Khan, U.; Lotya, M.; De, S.; Coleman, J. N. Improvement of Transparent Conducting Nanotube Films by Addition of Small Quantities of Graphene *ACS Nano* 2010, 4, 4238
6. De, S.; King, P. J.; Lyons, P. E.; Khan, U.; Coleman, J. N. Size Effects and the Problem with Percolation in Nanostructured Transparent Conductors *ACS Nano* 2010, 4, 7064
7. Coleman, J. N.; Lotya, M.; O'Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; Shvets, I. V.; Arora, S. K.; Stanton, G.; Kim, H. Y.; Lee, K.; Kim, G. T.; Duesberg, G. S.; Hallam, T.; Boland, J. J.; Wang, J. J.; Donegan, J. F.; Grunlan, J. C.; Moriarty, G.; Shmeliov, A.; Nicholls, R. J.; Perkins, J.

- M.; Grieveson, E. M.; Theuwissen, K.; McComb, D. W.; Nellist, P. D.; Nicolosi, V. Two-dimensional nanosheets produced by liquid exfoliation of layered materials *Science* 2011, 331, 568– 571
8. Smith, R. J.; King, P. J.; Lotya, M.; Wirtz, C.; Khan, U.; De, S.; O'Neill, A.; Duesberg, G. S.; Grunlan, J. C.; Moriarty, G.; Chen, J.; Wang, J. Z.; Minett, A. I.; Nicolosi, V.; Coleman, J. N. Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions *Adv. Mater.* 2011, 23, 3944– 3948
 9. De, S., Boland, C. S., King, P. J., Sorel, S., Lotya, M., Patel, U., Xiao, Z. L., and Coleman, J. N. Transparent conducting films from NbSe₃ nanowires. *Nanotechnology* (2011) 22, 285202
 10. Smith, R. J., King, P. J., Wirtz, C., Duesberg, G. S., and Coleman, J. N. Lateral size selection of surfactant-stabilised graphene flakes using size exclusion chromatography. *Chemical Physics Letters* (2012) 531, 169 – 172
 11. Paul J. King, Thomas M. Higgins, Sukanta De, Norbert Nicoloso, and Jonathan N. Coleman *ACS Nano* (2012) 6 (2), 1732–1741
 12. Gregory P. Moriarty, Sukanta De, Paul J. King, Umar Khan, Michael Via, Julia A. King, Jonathan N. Coleman, and Jaime C. Grunlan *Journal of Polymer Science Part B: Polymer Physics* published online

*"Never inhibit or limit yourself by the seemingly impossible. Place no limits upon yourself
and you will have none. Think that you're strong...and you are."*

Joseph Greenstein, The Mighty Atom

"Stronger people are harder to kill than weak people, and more useful in general"

-Mark Rippetoe

"Fortitudine Vincimus"

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INTRODUCTION

1.1 MOTIVATION

Transparent conductors (TCs) are extremely common in our modern world. Over the past decade the market for TCs has seen exponential growth due to the proliferation of iPhones, Kindles, big screen LCDs and thin-film solar cells. Each of these various devices contains a material that is transparent to visible light and yet electrically conductive as an indispensable element in the device stack. Although these devices are typically found on rigid surfaces, there is a continued trend towards flexible light-weight devices.

Doped metal oxides, especially tin-doped indium oxide (ITO), dominate modern TC technology. These materials have been well researched and refined for over fifty years. ITO remains the material of choice due to its superior combination of high optical transparency and low resistance, the two most important features of a transparent conductor; emerging nanomaterials struggle to compete with ITO in these respects. ITO has been developed to near perfection but still suffers from several drawbacks relating both to various material properties and to cost. Since ITO is a ceramic, it can crack and fracture under low strains. This effect is further exacerbated over cyclic testing meant to replicate device use. These micro cracks can propagate, eventually leading to a sharp decrease in the film's electrical conductivity. Failure at low strains may not be a significant factor for rigid devices but places a severe limitation on the durability of flexible devices. The supply of indium is constrained by both mining and geo-political issues. ITO consists of a ratio of indium (*III*) oxide (In_2O_3) and tin (*IV*) oxide (SnO_2), with optimal electro-optic properties occurring at a 90/10 ratio. Therefore, Indium composes nearly 75% of the mass of a typical ITO film, and ITO consumes 75% of the global indium consumption. Increased demand coupled with

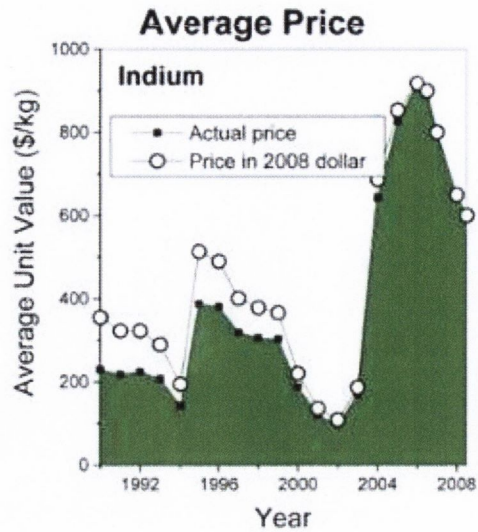


Figure 1.1: Average price of Indium over the last several decades. Source: Alex Freundlich of the University of Houston, citing data from the U.S. Geological Survey

limited supply of Indium has led to widely varying pricing for ITO from \$100-\$900/kg. (See Figure 1.1). Other problems with metal oxides include their high refractive index and the high cost of producing large area coatings.

Thus, is it obvious that new transparent conducting materials are required. These must have a number of specific properties: they must retain their electrical conductivity after repeated flexing; it must be possible to deposit them over large areas using low-temperature processing; they must have deposition and material costs comparable to ITO; and, most importantly, they must match ITO in terms of opto-electronic properties. For example, it must be possible to form these materials into films with transmittance $T > 90\%$. This is not challenging, as any material can be made extremely transparent just by making it sufficiently thin. The most difficult goal is finding a material that has high enough electrical conductivity such that, even when formed in a very thin film, it displays sheet resistance low enough to be useful.

Networks of conducting nanomaterials have been the focus of many researchers seeking to fulfill these criteria. Probably the most studied material are carbon nanotubes (CNTs) but in the last few years many publications have appeared on another form of carbon, graphene and disordered arrays of exfoliated graphene flakes. Another

contender is nanostructured metals such as metal nanowires of copper, silver and gold [2–4]. Due to the relatively small size of nanoscale forms of highly conducting “wires” or “sheets”, these materials can be solubilised by fairly straightforward and inexpensive techniques. This allows for low temperature deposition from solution using industry friendly techniques such as spraying and roll-to-roll coating. These materials have an intrinsically large DC conductivity which enables ultrathin, optically transparent films of the order 1-100nm thick to have appropriate conductance. If one considers for example the web-like topology of carbon nanotube networks, because adjacent tubes interact only weakly, intertube junctions can move locally under strain. As intertube charge transport is independent of junction position, the electrical properties tend to be independent of strain, resulting in great electrical stability under flexing. These material properties, combined with inexpensive materials costs and deposition make these emerging nanomaterials very attractive for use as printed transparent electrodes as ITO replacement materials. However, one major problem remains. The industry standards for a transparent electrode as set by our collaborators Hewlett Packard (HP) are a transmittance $T \geq 90\%$ and sheet resistance $R_s \leq 100\Omega/sq$; very few previous studies have demonstrated nanostructured networks that are thin enough to achieve these requirements.

This work will focus on the opto-electronic properties of networks of liquid-exfoliated graphene flakes and hybrids with carbon nanotubes. For both network types it will be shown that a deviation from bulk-like behaviour occurs at thicknesses below the industrially relevant regime ($T \geq 90\%$). This means DC conductivities are lower than in bulk, giving correspondingly higher sheet resistances, R_s . To improve our understanding of the consequences of this, we develop a model which relates T to R_s in the percolation regime. We have also explored the effects of percolation on the properties of supercapacitors with thin nanotube networks as electrodes. We observe that the key properties of a supercapacitor, namely the equivalent series resistance R_{ESR} and volumetric capacitance C_V , become thickness dependent below a threshold thickness. Again we show the thickness dependence of these quantities to be consistent with percolation theory.

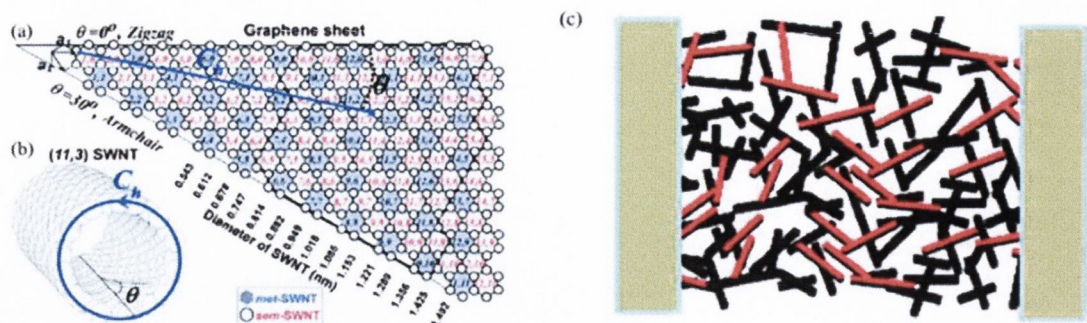


Figure 1.2: (a) Chirality (θ) and diameter (d_t) (n,m) map of SWNTs according to direction of rolling chiral vector, $C_h = na_1 + ma_2$ into a circle. Here, a_1 and a_2 are the unit vectors of the graphene sheets. (b) Formation of a SWNT by rolling graphene sheet along a chiral vector C_h , such as the (11,3) vector shown here. (c) Schematic drawings of SWNT networks composed of 1/3 metallic (black rods) and 2/3 semiconducting (red rods) [10].

1.2 CARBON NANOTUBES (CNTS)

1.2.1 Properties

First experimental observations of CNTs were made by Iijima in the early 1990s [5], and fundamental transport properties were investigated during the subsequent decade [6–8]. Nanotubes can be thought of, as sheets of sp^2 –hybridised carbon atoms known as graphene, rolled into a cylindrical shape and exist both as a single-walled nanotube (SWCNT) and as a multiwalled nanotube (MWCNT). Depending on the chirality along the graphene sheet either semiconducting or metallic electronic states are created [9] as can be seen in Figure 1.2. Both experiments and theory have shown that SWCNTs possess high mobility (on the order of $100000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) [11], high conductivity (up to $400000\text{S}\text{cm}^{-1}$), and, for semiconducting nanotubes, tube diameter-dependent band gap ($E_{\text{gap}} \approx 1/R_{\text{tube}}$) [12, 13]. However, despite their outstanding electrical, optical and mechanical properties, CNTs have been slow to find a commercial use. One of the major roadblocks towards widespread usage of CNTs is the inability to obtain bulk quantities of material with suitable purity. CNTs have been produced by three major methods; arc discharge, laser ablation and chemical vapor deposition (CVD). CNTs, as

produced, typically contain a mixture of various materials including catalyst particles, catalyst support, amorphous carbon and a mixture of nanotubes of various lengths, diameters, tube number and chiralities. For use in applications with macroscopic dimensions, random networks (also called thin films Figure 1.2C) of CNTs were reported throughout the mid-2000s as a new transparent electronic material [14, 15].

1.2.2 Dispersion

Most reports on CNT transparent film deposition have followed the solution route, except in a few cases where transparent CNT films were prepared by directly drawing from super-aligned CNT arrays [16–18]. In general, the solution approach uses a two-step strategy, first reported in 1997 [19], of disassembling CNTs in a liquid medium, and then assembling them into a network structure with random orientation. To disperse and stabilize CNTs in a liquid involves overcoming and shielding the van der Waals interaction between CNTs by careful design and manipulation of a CNT-solution interface. Therefore, one of the primary areas of research for making transparent conductive films is in processing the purified CNT material into printable inks. There are three major approaches to dispersing CNTs: a) dispersing CNTs in neat organic solvents [20–22] or superacids [23], b) dispersing CNTs in aqueous media with the use of dispersing agents such as surfactants, dispersants, or other solubilisation agents [24], c) adding functional groups which will help draw the CNTs in solution [25]. Each of these methods has advantages and disadvantages in terms of making processable CNT-based inks.

From a manufacturing perspective, direct solubilisation of CNTs in a suitable solvent is perhaps the simplest method and most favorable. No solubilisation agents would be involved which could create processing issues during manufacturing, and also lead to decreased conductivity in the deposited film. The major issue with using organic solvents has been the inability to disperse CNTs at a concentration high enough to be useful for industrial applications ($> 0.1\text{mg/ml}$). Studies have shown that a solvent's effectiveness in dispersing CNTs is related to the Hildenbrand solubility parameter,

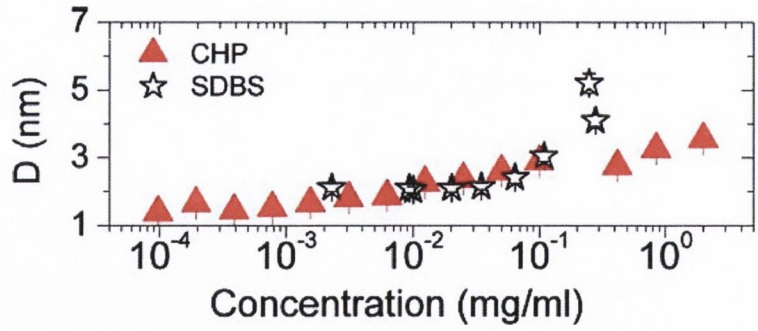


Figure 1.3: Rms bundle diameter versus ink concentration for CNTs in various solvents as measured by AFM [27]

particularly a dispersive component between $17\text{--}18\text{MPa}^{1/2}$ [26]. Some of the most effective solvents at dispersing un-functionalized CNTs are dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), chloroform, and dichlorobenzene. However, none of these solvents can disperse CNTs at levels greater than 0.1mg/ml . Recently, work by Prof. Coleman’s group has shown that the solvent cyclohexylpyrrolidone (CHP) can disperse CNTs up to 2mg/ml with high levels of individual tubes or small bundles, as shown in Figure 1.3 [27]. However, the high boiling point (154°C) of this solvent may be an issue in high speed roll-to-roll manufacturing on plastic. Continuing to search for optimal solvents which can disperse CNTs at high concentrations and have a reasonably low boiling point (below 150°C) could lead to a successful manufacturing process for high performance transparent conductive films.

Solubilisation of CNTs in water-based inks is most often assisted by various solubilisation agents, the most common being surface active agents known as surfactants. The amphilic properties of the surfactant assist in the suspension of the hydrophobic CNT particle in water [28]. Figure 1.4 shows a schematic representation of how surfactants may adsorb onto the nanotube surface. There are three classes of surfactants: anionic (negative charge in water), cationic (positive charge in water), and nonionic (neutrally charged in water). The hydrophobic end of a surfactant will attach to CNTs, while the hydrophilic end helps pull the CNTs into solvents such as water. It has been found that the π -like stacking of benzene rings benefits the binding of surfactant and CNTs. The headgroup, chain length, and surfactant weight are found to affect the dispersion

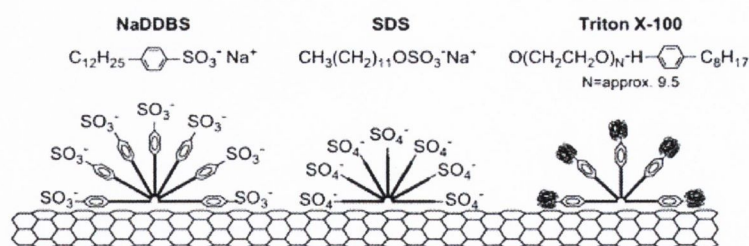


Figure 1.4: Schematic representation of how surfactants may adsorb onto the nanotube surface.[29]

ability of the surfactant. Among surfactants, Triton X-100, sodiumdodecyl sulfate (SDS), and sodium dodecylbenzene sulfonate (NaDDBS) are the most widely studied.

CNT stabilization depends on the surfactant molecules that lie on the tube surface parallel to the cylindrical axis. These surfactants lead to a high fraction of individualized CNTs after dispersion, resulting in higher CNT film conductivity. Resasco et al. and Yodh et al. have extensively studied the interaction between surfactants and CNTs [29, 30]. The phenomenon depends on the chemical characteristics of CNTs, the surfactant, and the solvent nature. The major forces are the Coulombic attraction between the charged surfactant heads, the hydrophobic bonding between the surfactant tails and the CNT surface and the CNT- aromatic ring interactions. Therefore, understanding the surface charge of CNTs is important for studying their interactions with surfactants. There are three states for surfactants in dispersions: free surfactant, micelles, and adsorbed onto CNTs. The adsorption of surfactant onto a CNT surface depends on the surfactant, CNT concentration, and the system charge nature (pH value). Sonication is required for surfactant-assisted CNT dispersion. Dispersion occurs by the formation of gaps or spaces at the bundle ends in the high shear environment of the ultrasonicated solution. The adsorbed surfactant diffuses into this space along the bundle length, thereby separating the CNTs. The stability of the dispersion is largely determined by the electrostatic repulsion due to the surface charge. The Zeta-potential, an abbreviation for electrokinetic potential in a colloidal system, is the potential difference between the dispersion medium and the stationary layer of fluid. Because it is a good measure of colloidal stability, different ionic surfactants can be evaluated for their ability to stabilize CNTs in solution in terms of the Zeta potential of the dispersion. One of the

major issues with surfactant assisted solubilisation schemes is that the presence of large amounts of surfactant in the as deposited films can lead to significantly lower conductivity levels .

1.2.3 *Film Fabrication*

Once a stable CNT dispersion is made, deposition onto an appropriate substrate proves a significant challenge. Solution based processing is preferred to direct CVD for obvious reasons. The low temperature process allows deposition onto arbitrary substrates, can be easily scaled to large areas, and no vacuum is needed, which significantly reduces cost. The basic concept of a solution-based deposition process is to uniformly dry the solution without causing agglomeration. Therefore, solution/substrate interactions need to be considered. A brief description of thin film deposition will now be outlined with an emphasis on vacuum filtration, the technique used to deposit all films in this work.

Vacuum filtration has several advantages

- Homogeneity of the films is guaranteed by the process itself. As the nanotubes accumulate, they generate a filter cake that acts to impede the permeation rate. If a region becomes thicker, the local permeation rate and associated deposition rate slow down, allowing thinner regions to catch up.
- Because of their extreme rigidity (for objects of such small diameters), the nanotubes have long persistence lengths. They consequently tend to lie straight, gaining maximal overlap and interpenetration within the film as they accumulate. This yields maximal electrical conductivity and mechanical integrity through-out the films.
- The film thickness is readily controlled, with nanoscale precision, by the nanotube concentration and volume of the suspension filtered.

- Composite films can be prepared with excellent control over the mass fraction [31, 32]. Film size is ultimately limited only by the dimensions of the filtration membranes, which are available in rolls as large as 30 cm by 10 m (Millipore).

The “Langmuir Blodgett” (LB) method, is based on the hydrophobic behaviour of CNTs. Good surface spreading of CNTs on water is key. The deposition can be achieved in a layer-by-layer fashion through either a horizontal lifting or a vertical dipping method. Thin films on a surface can quickly and cheaply be formed by self-assembly (SA). SA depends on the interactions between the surface and the CNTs. Silane or polymer treatment of substrates helps the interactions between CNTs and the substrate [33]. When a substrate is placed in a dispersion, CNTs will randomly strike the surface and may or may not adhere depending on the chemical groups, which causes this process to be slow. This interaction can be guided by chemical preparation of CNTs or the surface, by charging the surface locally, or by microfluidic guidance .

Dip coating is a simple process and provides great potential to scale up for large-scale coating. The pick-up of the solution depends on the solution viscosity, the interaction between substrate and the dispersion, and the coating speed. Afterward, the drying process is critical to achieve high-quality films. The substrate can be treated with aminopropyltriethoxysilane (APTES) as an adhesion promoter. The thickness can be controlled by the concentration of the solution and the time of dip coating. One disadvantage of dip coating is that both sides of the substrate are coated, which may not be preferred for certain applications. Other coating methods include spin coating and drop casting where a high shear rate is involved. A small amount of solution is dropped onto a substrate followed by high-speed spinning of the substrate (spin coating), or simply air drying (drop casting). Spin coating is useful for generating submonolayer CNT films due to the low viscosity of CNT solutions.

Electrophoretic deposition (EPD) has also been used to deposit CNT thin films on conductive substrates. The CNTs are locally charged, and so become polarized under a DC electric field. The CNTs wrapped with surfactants and the CNTs functionalized with COOH groups acquire a negative charge in water and are attracted to the positive side of the electrode under a DC electric field. Another similar method is called

dielectrophoresis (DEP), which uses an AC electric field. DEP can allow the deposition and separation of CNTs at the same time. DEP relies on the motion of polarizable objects due to an external inhomogeneous electric field.

Spray coating is a simple and quick method to deposit CNT film. CNT ink is sprayed onto a heated substrate. The substrate is heated to facilitate the drying of the liquid. The set temperature for the substrate is adjusted by the choice of solvent. By using diluted solution and multiple spray coating steps, homogeneous films can be obtained.

The most widespread deposition method in industry involves depositing solution on a substrate by one of several methods (including Mayer Rod, Slot Die, and Gravure), followed by controlled drying. Inkjet printing is an old and popular technology due to its ability to print fine and easily controllable patterns, noncontact injection, solution saving, high repeatability, and scalability. It is very prevalent in printed electronics. In a typical ink jet printing process, the droplet size is around ~ 10 pL and, on the substrate, has a diameter of around 20- 50 μm . Printing on paper is much easier than printing on a plastic or glass substrate, due to the high liquid absorption of the paper, which avoids the dewetting of the liquid on substrates. The liquid droplet and substrate interaction is crucial for uniform drying of the liquid.

Each of the above methods has its own advantages. The requirements for dispersion, substrate, volume, and ink - substrate interaction are different. For example, Mayer rod coating and dip coating have more stringent requirements for the dispersion rheology, while spray coating and filtration do not. Spin coating is valid for making submonolayer networks on rough surfaces, while filtration, Mayer rod coating, and inkjet printing can generate films with arbitrary thickness. The application of the liquid on substrates is different for different methods, and the drying rate of the liquid on substrate is crucial. The ability to scale up for manufacturing should also be considered for industrial applications. Mayer rod coating, dip coating, and inkjet printing can reasonably lead to scaled CNT coatings, while spin coating is not compatible with existing scale-up processes, especially for large-scale plastic electronics. The most useful forms of deposition involve roll to roll coating of a CNT ink into large rolls of plastic. This leverages various existing techniques such as forward/reverse gravure,

forward/reverse roll, slot die and fountain/curtain coating. These techniques can coat film up to 2m wide at speeds up to 500m/min.

1.2.4 *Properties of Nanotube Thin Films*

The electronic, transport, optical and mechanical properties of individual CNTs have been extensively studied and well documented. The exact properties of CNTs are extremely sensitive to degree of graphitization, diameter and chirality. In a nanotube network (NTN) ensemble averaging over a large number of tubes suppresses effects due to individual variations. These networks will have the collective behaviour of the individual tubes with additional properties arising from tube-tube interactions. The single most important factor in the eventual utilisation of CNT films for various applications is the continued improvement in the film's DC conductivity (σ_{DC}). A high σ_{DC} enables CNT films to simultaneously have suitably high sheet conductance (low sheet resistance) and high transmission. Transparent CNT films useful for most applications are typically in a thickness range from sub-nanometer to 50nm thick, and follow several scaling laws with respect to film density, thickness, tube length, tube wall number and bundle diameter. Other factors that influence the transport are film purity (presence of non CNT material), tube doping level, CNT-surface interactions, and metallic/semiconducting ratio [34].

The σ_{DC} of a single CNT can be up to $200,000 S cm^{-1}$, while a randomly oriented CNT film has managed a highest conductivity of only $6600 S cm^{-1}$ [14]. Using conductive AFM Nirmalraj et. al demonstrated that transport in single-walled carbon nanotubes (SWCNTs) networks is dominated by resistance at network junctions which scales with the size of the interconnecting bundles [35]. The magnitude of this inter-tube resistance depends on several factors, but is typically of the order $200 k\Omega - 20 M\Omega$ [36], while the resistance along a single CNT one micrometer or longer is $\sim 6 k\Omega / \mu m$ [37]. It is therefore clear that for CNTs in the typical length range of $2 - 4 \mu m$ the resistance of a film is largely dominated by the intertube (junction) resistance [35]. Hence, it might be anticipated that longer CNTs will lead to more highly conductive

films, as this will limit the number of CNT junctions per unit area of film. *Hecht et al.* have shown that σ_{DC} of CNT films does indeed vary with tube length as a power law ($\sigma_{DC} \sim L^{1.46}$) [38]. The diameter of CNT bundles in a film will also impact the film conductivity. Experiments have shown that smaller bundles will lead to more highly conductive films [39]; this is likely due to the presence of non-current carrying tubes in the middle of CNT bundles. Similarly, films made from multi-walled CNTs show dramatically lower conductivity than films made from single- or double-walled CNTs [40–42], as the inner walls again act as non-current carrying voids in the film. Therefore, a film consisting of highly de-bundled single or double walled CNTs is desirable. However, although small bundles are advantageous, larger diameters CNTs are preferred for high film conductivity [43]. Larger diameter semi-conducting CNTs will have a smaller bandgap, and a correspondingly higher number of charge carriers at room temperature.

Film density is another critical scaling parameter, as demonstrated by *Hu et al.* [44]. Percolation is the onset of conductivity across a previously insulating region once conducting links have been added at a density exceeding some critical value, the percolation threshold. As more links are added, new conducting paths are formed and the conductivity increases. Very low density films follow a percolation scaling law in two dimensions, where the critical threshold for percolation depends on the aspect ratio (length/diameter) of the average CNT bundle. Due to the highly one dimensional nature of CNTs and CNT bundles, the percolation threshold is very low, typically less than 1% surface coverage (and is inversely proportional to the tube length squared). Above the percolation threshold, the sheet conductance increases rapidly with network density (tubes/area) as a power law with exponent ranging from 1–1.5 (1.33 for the ideal 2D case). The film conductivity continues to increase with increasing film thickness until the film is ~ 100 times the density where percolation first begins (or ~ 50 nm thick), in which case the conductivity approaches that of the bulk material, as shown in Figure 1.5. This phenomenon is important since many applications exist for films in the thickness range of 5–10 nm (visible transmission about 95–90%); unfortunately, the film conductivity in this thickness range can be as little as 50% of its maximum thick film conductivity. Furthermore, because in this

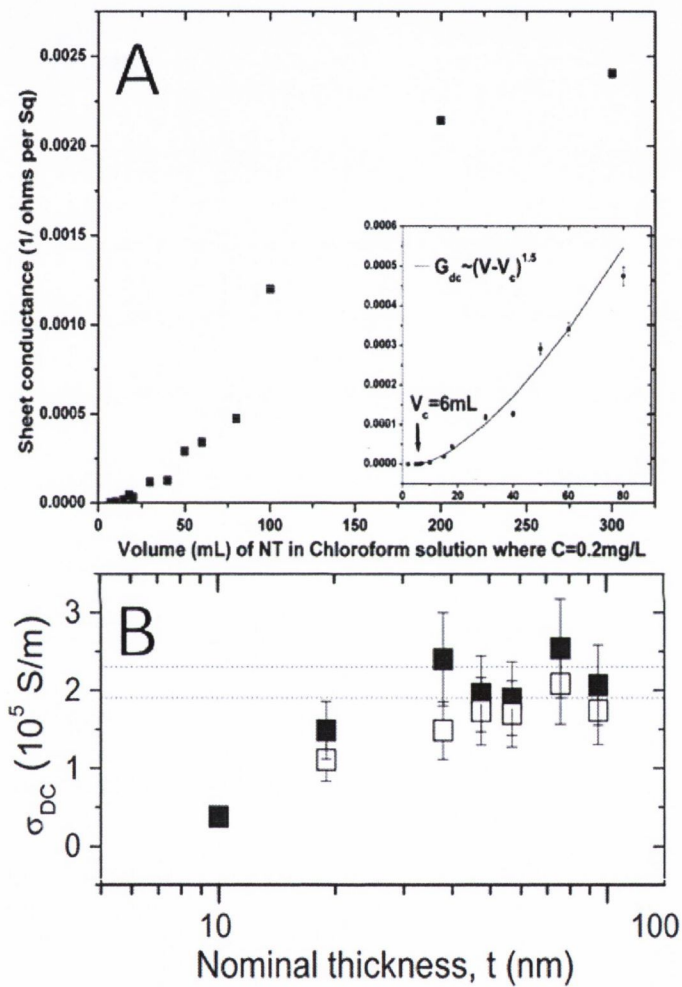


Figure 1.5: A) Sheet conductance of CNT films as a function of the film density (film density is proportional to the volume of ink filtered) [44]. B) DC conductivity of CNT film as a function of film thickness [45].

very thin film limit the conductivity increases quite rapidly with film density, small variations in film density lead to relatively large variations in sheet resistance [46]. This is evidenced by the fact that for very thin films, the sheet resistance becomes more non-uniform [45].

The conductivity of CNT thin films is determined by many parameters; continued research is needed into how to optimize these parameters to obtain films with increasingly high σ_{DC} . Typically, factors that increase the CNT purity, lattice perfection, or aspect ratio will increase the film conductivity. Therefore, one could expect that long, pure, debundled, single or double walled tubes would be optimal. Additional improvements of σ_{DC} could be made in several ways. Since the limiting resistance of the film comes from the contact resistance between tubes, lowering that resistance seems to be the most effective method to dramatically improve film conductivity. Alternatively, increasing the metallic to semiconducting tube ratio, or finding a stable dopant, would also dramatically increase film conductivity.

1.3 GRAPHENE

1.3.1 *Properties*

Once thought to be thermodynamically unstable [47, 48], and nothing more than an academic construct, graphene has become the latest material to fascinate the scientific community. Graphene is the name given to a two-dimensional sheet of sp^2 -hybridised carbon. The carbon atoms are arranged in a honeycomb network which provides the foundation for all graphitic carbon forms i.e. a graphene sheet can be wrapped up to produce 0-D fullerenes, rolled into a 1-D nanotube or stacked in layers to form 3-D graphite. Graphene is a zero-gap semiconductor, an electronic state of matter that is precisely between a semiconductor and a metal. Semiconductors are characterised by an appreciable energy gap between the valence and conduction band, whereas in metals the two bands largely overlap. In graphene the interaction between the electrons and the periodic potential of the honeycomb lattice results in a band structure in which

the valence and conduction bands touch at just two points, rather than overlapping. This leads to the formation of “valleys” in the electronic structure. At these so-called Dirac points, the electrons behave as relativistic quasiparticles called Dirac fermions. These fermions always move with a speed that is independent of their energy and direction. This is a property they share with photons which always move at the speed of light c , irrespective of their energy, although the Dirac fermions in graphene are much slower, moving at about $c/300$ [49]. The important point to note here is that it is impossible to slow them down, which means that their charge mobility is very high.

The first free-standing mono- and few-layer-graphene (FLG) flakes were isolated by Geim and co-workers at Manchester University in 2004 via mechanical exfoliation [50]. Theoretical studies on the behaviour of graphene had predicted properties such as extremely high carrier mobility, which motivated the first measurements on mechanically exfoliated flakes by e-beam lithography. These samples revealed a host of novel electronic properties such as ambipolar field effect [51], room temperature quantum Hall Effect [52] and the breakdown of the Born-Oppenheimer approximation [53]. These extraordinary electronic properties in graphene are due to the high quality of its 2 – D crystal lattice. Charge transport is usually inhibited by defects which serve as scattering centres; the high quality of the graphene lattice implies an unusually low density of defects. This is reflected by carrier mobilities in excess of $200,000\text{cm}^2/\text{Vs}$ for a single layer flake [54]. This is two orders of magnitude higher than that of modern silicon transistors. At such high carrier mobility, charge transport is essentially ballistic on the micrometer-scale at room temperature. This could have major implications for the semiconductor industry because, in principle, it enables the fabrication of all-ballistic devices. These electronic properties give graphene its exceptional in-plane conductivity, enabling it to have a low sheet resistance despite being a single atomic layer (0.34nm) in thickness.

The optical properties of Graphene have also been investigated. *Nair et al.* have demonstrated that the fine structure constant, $\alpha = e^2/\hbar c \approx 1/137$ (where c is the speed of light) defines the opacity of suspended graphene [55]. Graphene absorbs a significant fraction of incident white light ($\pi\alpha = 2.3\%$), despite being merely one atom thick. This is a consequence of graphenes’ unique electronic structure. The experimental

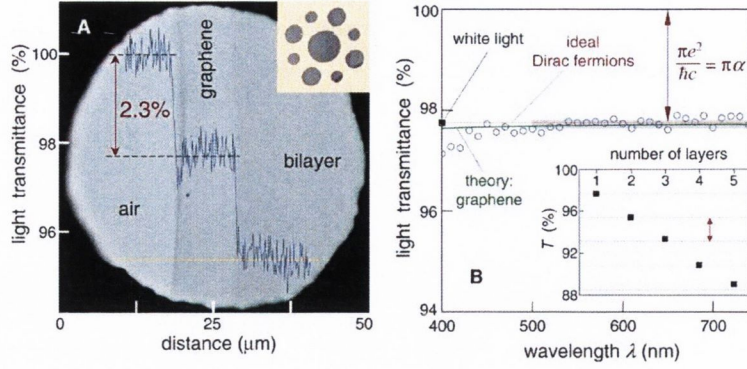


Figure 1.6: (A) Photograph of a 50- μm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. (B) Transmittance spectrum of single-layer graphene (open circles). The red line is the transmittance $T = (1 + 0.5\pi\alpha)^{-2}$ expected for two-dimensional Dirac fermions, whereas the green curve takes into account a non linearity and triangular warping of graphene's electronic spectrum. (Inset) Transmittance of white light as a function of the number of graphene layers (squares). The dashed lines correspond to an intensity reduction by $\pi\alpha$ with each added layer [55]

measurements match the behavior expected for ideal Dirac fermions, and the opacity is found to increase with membrane thickness so that each graphene layer adds another 2.3% (Figure 1.6).

Coupled with its unique electronic and optical properties graphene is the strongest material ever measured. Using atomic force microscopy (AFM) nano-indentation *Lee et al.* have shown that it has a breaking strength 200 times greater than steel [56]. *Firsov et al.* found that a graphene film exhibits a strong ambipolar electric field effect showing electron/hole concentrations up to $N_i \sim 10^{13}/\text{cm}^2$ and room temperature mobilities of $\mu 10^4 \text{cm}^2/\text{Vs}$ [50]. Based on these values *Peumans et al.* predicts the sheet resistance of graphene is

$$R_s = \frac{1}{e\mu N_i N} = \frac{62.4\Omega/\text{sq}}{N} \quad (1.1)$$

where N is the number of monolayers [57]. It is the combination of these properties that has led many researchers to believe that graphene could be useful as a transparent conductor and an alternative to ITO.

1.3.2 Fabrication Methods

Mechanical Exfoliation

Various methods to make thin films of graphene have been developed such as the mechanical exfoliation (scotch tape method), epitaxial growth, chemical vapour deposition (CVD) and liquid phase exfoliation. Although it is not a high throughput method, mechanical exfoliation produces the highest quality samples, providing an excellent platform for studying the fundamental transport and optical properties of individual sheets [50]. In its most simple form the “scotch tape” peeling method involved utilising cellophane tape to successively remove layers from a graphite flake. The flakes were deposited on silicon capped with a 300nm thick SiO₂ layer. This enhanced the optical contrast under white light illumination [58]. To determine flake thickness a combination of optical, electron-beam and atomic force microscopy were used. This approach has yielded the highest quality samples to date with crystallites larger than 1mm currently available. However, there are a number of issues with this process, the throughput is very low, the cost per flake is up to \$100,000,000/cm² and it is hard to see how it could be scaled up for industry-level production. Thus, alternative methods of production must be sought for large scale synthesis.

Epitaxial graphene and Chemical Vapour Deposition (CVD)

In addition to mechanical exfoliation, chemical synthesis routes can grow relatively large graphene flakes over large areas. Various methods have been reported on different but specific substrates, which are typically expensive. *De Heer* and co-workers at Georgia Tech. have pioneered an epitaxial method in which graphene results from the reduction of silicon carbide [59, 60]. The process is relatively straightforward, as silicon desorbs around 1000°C in ultrahigh vacuum. This leaves behind small islands of graphitized carbon, which were first located by Scanning Tunnelling Microscopy (STM) and electron diffraction experiments. The transport properties show that electrons in

the interfacial graphene layer dominate the transport and that they are Dirac fermions, as recently observed in mechanically exfoliated graphene layers.

The second substrate deposition method is CVD of graphene on transition metal films. Groups at MIT and in Korea pioneered the process, which relies on the carbon-saturation of a transition metal upon exposure to a hydrocarbon gas at high temperature [61, 62]. Most often, nickel films were used with methane gas. Upon cooling the substrate, the solubility of carbon in the transition metal decreases and a thin film of carbon is thought to precipitate from the surface. However, graphene grown on Ni seems to be limited by its small grain size, presence of multilayers at the grain boundaries, and the high solubility of carbon. *Li et al.* grew large-area graphene films of the order of centimeters on copper substrates by chemical vapor deposition using methane [63]. The films are predominantly single-layer graphene, with a small percentage (less than 5%) of the area having few layers, and are continuous across copper surface steps and grain boundaries. They suggested that the low solubility of carbon in copper appears to help make the growth process self-limiting [63].

Liquid Phase Exfoliation

The previously described methods for producing graphene have been very successful to date. However, it is likely that many future industrial applications of graphene will be in sectors such as large-area coatings or composite fillers, which will require very large quantities to be produced [64, 65]. To this end, it is likely that liquid phase production methods will be required. Two categories should be clearly distinguished with regard to methods for industrial scale processing a) those that start with graphite or comparable starting material not containing any oxygen functionalities and b) those which involve the exfoliation of graphite oxide (GO) followed by reduction. A solution-based process for producing single-layer graphene was first demonstrated in 2006 [66]. This involved harsh oxidation of graphite in the presence of strong acids and oxidants, usually by the Hummers method [67], to produce graphite oxide (GO). GO still possesses a layered structure, but is much lighter in colour than graphite due to

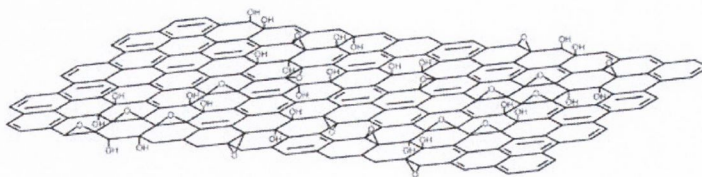


Figure 1.7: Chemical structure of graphite oxide [69]. For clarity, minor functional groups, carboxylic groups and carbonyl groups have been omitted at the edges.

the loss of electronic conjugation brought about during the oxidation. The basal planes of the graphene sheets in GO are decorated mostly with epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups, which are located at the edges as can be seen in Figure 1.7 [68]. The van der Waals interaction between the layers of GO are altered by the oxygen functionalities which render them hydrophilic, thus enabling their hydration and exfoliation in aqueous media. GO can be completely exfoliated to produce colloidal suspensions of graphene oxide sheets by simple sonication in both aqueous and various organic solvents [66, 70]. Concentrations of up to and above 1mg/ml are achievable in a wide range of solvents.

It is clear that this approach is scalable, affording the possibility of high-volume production at low cost. However, there is considerable disruption of the electronic structure of the graphene. As a result of the chemical functionalisation, structural defects are formed, rendering the GO semiconducting. These defects are virtually impossible to remove completely, as evidenced by X-ray photoelectron spectroscopy [71]. The graphitic network can never be completely restored but substantial reduction of graphene oxide by chemical methods (using reducing agents such as hydrazine [72, 73]), thermal methods [74] and ultraviolet-assisted methods [75] has produced electrically conducting chemically modified graphene (CMG). Dispersions of CMG have been deposited in a number of ways to form both transparent conductors [76] and free-standing paper [77].

It was clear that a less destructive method of graphene production, which removed the need for oxidation or reduction, was required. Recently, a significant breakthrough was made when two groups independently demonstrated that sonication of graphite in certain solvents produced dispersions of defect-free mono- and few layer- graphene at

reasonable concentrations, up to 0.01mg/ml in N-methyl pyrrolidone (NMP) [78, 79]. This method relies on selecting particular solvents whose surface energy is so well matched to that of graphene that exfoliation occurs freely [78]. The low concentrations previously reported make many applications completely impractical. This issue has since been resolved by members of our group. *Khan et al.* [80] utilized mild bath sonication of high graphite concentrations for long periods (up to 460 hours) in NMP yielding graphene dispersions with concentration up to 1.2mg/ml . These high concentration dispersions could then be vacuum filtered into free-standing films with reasonable electrical and mechanical properties. Although this process circumvents the need to oxidise and reduce graphite, there remain a number of drawbacks.

The solvents used such as NMP are harmful and thus require special care when handling. In addition, they tend to have high boiling points, making it difficult to deposit individual monolayers on surfaces. Unfortunately, the most useful solvent of all, water, has a surface energy that is much too high to work on its own as an exfoliant for graphene. An alternative, liquid phase process that results in the exfoliation of graphite to give graphene at reasonably high yield is required. The method should be non-oxidative and should not require high temperature processes or chemical post treatments. In addition, it should be compatible with safe, user-friendly, low boiling-point solvents, preferably water.

In a manner similar to surfactant-aided nanotube dispersion [28, 81, 82] *Lotya et al.* demonstrated a method to exfoliate graphite in surfactant-water solutions [83]. Atomic resolution transmission electron microscopy (TEM) shows the flakes to be well-graphitized and largely defect free. Raman, IR, and X-ray photoelectron spectroscopies also show the graphene to be relatively defect-free and only very slightly oxidized. However, as with the initial solvent work, the concentration of surfactant-stabilised dispersions achieved was very low ($< 0.003\text{mg/ml}$). In order to exploit dispersions of pristine graphene using surfactants, it is of critical importance to increase the maximum concentration that can be obtained while maintaining the quality of the graphene flakes. Similar to *Khan et al.* [80] we applied mild sonication, for long periods (up to 460 hours). We demonstrated graphene can be effectively dispersed in water-sodium cholate solutions at concentrations of up to $\approx 0.4\text{mg/ml}$. Potential utilisation

of these dispersions has also been sought in the form of transparent conductors and as free-standing electrodes [31, 32, 84].

1.3.3 *Transparent conducting graphene networks*

There has been substantial effort in developing graphene networks or composites for large scale optoelectronic device applications [85–88]. In particular, solution processed graphene thin film fabrication has attracted much academic and industrial attention since it can be scaled up using roll-to-roll processing for practical incorporation into devices. In practice, graphene networks consisting of graphene sheets fabricated via solution-based processing contain multiple boundaries and incorporate defects that dramatically decrease the conductivity when compared to a film made of a large, single sheet without defects. There has been steady progress demonstrating a decrease in the sheet resistance R_s of transparent graphene networks, from $\sim 1\text{M}\Omega/\text{sq}$ down to typically $300\Omega/\text{sq}$ [62, 85, 89] for films in industrially-relevant transparency ranges. Graphene and CNTs share very similar sp^2 carbon chemistry [90], and therefore, the developed methods and understanding for CNTs over the past 15 years can be directly transferred to graphene research. However, the fundamental geometrical difference between CNTs and graphene leads to different processing techniques and performance as a transparent electrode. Using eqn. 1.1 one can predict some startling theoretical properties for a doped graphene film of four sheets such as sheet resistance $15.6\Omega/\text{sq}$ and 90.8% transmittance in the visible region (550nm). If realisable, these values are more than suitable for most commercial applications. However, to date, experimental results have not equalled this theoretically limiting performance with solution-processed graphene typically the poorest performer.

One must ask, what is limiting the optoelectronic performance of graphene films from what is theoretically possible? An analogy with CNTs may be useful here. For CNTs, the largest source of resistance in a macroscopic film comes at the intersections between CNT bundles [35]. Therefore, longer CNTs tend to lead to films with higher conductivities [38]. Similarly, for graphene films consisting of a random network of

overlapping graphene flakes, larger flakes are desirable to optimize performance. Also, for CNT films, it is thought that smaller CNT bundles lead to higher conductivity; this is because inner tubes within a bundle may be partially shielded from electrical contact with the overall network, and so will not fully participate in the current carrying capacity of the network [38]. Similarly, graphene films consisting of fewer layers of graphene should be advantageous (with a true monolayer of graphene being optimal). Of course, maintaining the perfection of the graphene lattice is critical, as defects will introduce scattering sites that will increase resistance. Furthermore, surfactants or other dispersants used in the liquid phase will lower the overall film conductivity if not completely removed after film deposition. Doping will also play a critical role in enhancing the performance of graphene films. The sheet resistance of undoped graphene is on the order of $6k\Omega/sq$ [91], but this can be reduced via chemical doping by materials such as polyvinyl alcohol (n-type doping) [79] or nitric acid (p-type doping) [92]. For real-world applications, it is important to test the stability of dopants under such accelerated ageing conditions as high heat, humidity, and UV light.

1.4 TRANSPARENT CONDUCTORS

As stated previously, modern TC technology is dominated by ITO. It fulfils a wide range of roles all of which require high transparency. It is widely utilised in applications from lighting, touch panels, displays, and photovoltaics to smart windows, and electromagnetic interference EMI shielding. This application space spans a range of product requirements and manufacturing methods (Table 1.1). Researchers have been evaluating emerging transparent conductors such as graphene and carbon nanotube networks as replacements for traditional sputtered materials with a view for cost reduction and manufacturing simplification. These emerging conductors are not just replacement technologies but also technical and product enablers, especially in the current development of flexible/printed electronic devices and the use of low-cost manufacturing methods. It is paramount in the development of new conductors to keep in mind the key features and electrode requirements for a particular application. Each

DeviceType	Electrode Type	%T Range	R_s Range (Ω/sq)
Resistive touch panel	Touch side	86-90	300-500
	Device side	88-90	200-500
Projected Capacitive touch panel	Top or Bottom	88-92	100-300
Surface Capacitive touch panel	Primary	88-90	900-1500
LCD	Pixel	87-90	100-300
	Common	87-90	30-80

Table 1.1: Various device electrode requirements (%T indicates total visible transmission through both the conductive film and the substrate) [93].

role has a particular resistance requirement, with the entire set spanning a wide range. For example, conducting films for static dissipation can function with a sheet resistance of $> 1k\Omega/sq$, touch screens generally require a few hundred Ω/sq , electrodes require a few tens of Ω/sq while, to minimize resistive losses, solar cell electrodes require sheet resistances of $< 10\Omega/sq$. We make the assumption that it will not be difficult to find materials that fulfil the less stringent, high sheet resistance applications. For example, a range of nanostructured materials have achieved transmittance above 90% coupled with sheet resistance above $1k\Omega/sq$. However, achieving transmittance above 90% coupled with sheet resistance below $200\Omega/sq$ has proven much more difficult.

Various nanostructured materials have been investigated for transparent electrodes over the past decade. Due to the wide variety of materials used it is useful to use figures of merit (FoM) to express the performance of a given film type to facilitate comparison with other data sets and industrial requirements. The most useful FoMs are those based on the physics of the system under study. For TCs FoMs should link the film transmittance, T , to its sheet resistance, R_s . This can be accomplished by combining physical expressions for transmittance and sheet resistance of thin films, both as a function of thickness, t . For thin conducting films, the transmittance scales with thickness as

$$T = \left(1 + \frac{Z_0}{2} \sigma_{op} t\right)^{-2} \quad (1.2)$$

where Z_0 is the impedance of free space (377Ω), and σ_{op} is the optical conductivity (related to the absorption coefficient α as $\sigma_{op} \approx \alpha/Z_0$) [94].

The sheet resistance of a bulk like film is defined as

$$R_s = (\sigma_{DC,B} t)^{-1} \quad (1.3)$$

By combining this expression with eqn. 1.2 and eliminating t we obtain an expression relating T and R_s .

$$T = \left[1 + \frac{Z_0}{2R_s} \frac{\sigma_{op}}{\sigma_{DC,B}}\right]^{-2} \quad (1.4)$$

Note that this expression is appropriate for a bulk-like material (i.e. one whose DC conductivity is invariant with sample thickness). This equation is valid assuming 1) the film is much thinner than the wavelength of light being measured and 2) the reflection is much less than the absorption. The conductivity ratio $\sigma_{DC,B}/\sigma_{op}$ is often used as a FoM for transparent conductors as high values of $\sigma_{DC,B}/\sigma_{op}$ lead to films with high T and low R_s . In fact, a material with a given value of $\sigma_{DC,B}/\sigma_{op}$ can be formed into films with a range of T and R_s values depending on thickness. In this work we have prepared films of various nanoconductors with a range of thicknesses, measured T and R_s for each thickness, and then fit the (T, R_s) data to eqn. 1.4 to extract $\sigma_{DC,B}/\sigma_{op}$ as can be seen in Figure 1.8. Here, transmittance is plotted as a function of sheet resistance for thin films of graphene (this work)[31], SWNTs [45], silver flakes (this work), and Ag nanowires [3]. In each case, the bottom left portion of the data (corresponding to thicker films) is fit to Equation 1.4 (solid lines), giving values of $\sigma_{DC,B}/\sigma_{op}$ of 0.7, 11.2, 35, and 415, respectively. Usually these numbers are assumed to encode all the relevant information about the optoelectrical properties of these films. In order to achieve the target of $T \geq 90\%$ and $R_s \leq 100\Omega/sq$, Equation 1.4 can be used to show that $\sigma_{DC,B}/\sigma_{op} \geq 35$ is required.

However, upon closer inspection of the fits in Figure 1.8, it is clear that the data tend to deviate severely from the fits for lower thickness (more transparent) films. This

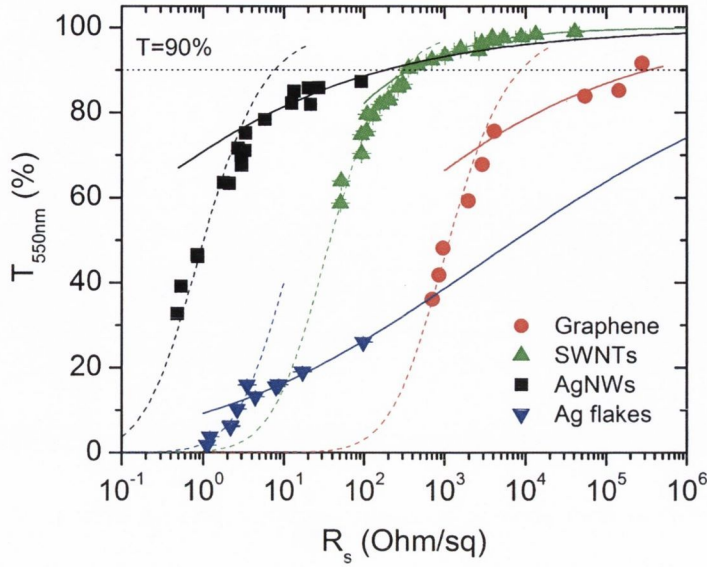


Figure 1.8: Transmittance (550 nm) plotted as a function of sheet resistance for thin films prepared from four nanostructured materials-graphene, singlewalled carbon nanotubes, silver nanowires and silver flakes [3, 31, 45, 95]. The dashed lines represent fits to the bulk regime using equation 5.6, while the solid lines represent fits to the percolative regime using equation 5.17

deviation has been observed before [3, 4, 31, 45, 96] and tends to occur for films with T between 50% and 92%. This is important because applications requiring TCs usually require $T \geq 90\%$. Thus, $\sigma_{DC,B}/\sigma_{op}$ fails to describe the relationship between T and R_s in the technologically relevant regime. This means that in many cases, $\sigma_{DC,B}/\sigma_{op}$, or indeed any FoMs based on bulk properties, are not entirely appropriate, particularly when high transparency is required. In this work we show that the deviation from bulk-like behavior as described in Equation 1.4, can be explained by percolation effects. Such effects become important for very sparse networks of nano-conductors. When the number of nanoconductors per unit area is very low, a continuous conducting path from one side of the sample to the other will generally not exist. As more nanoconductors are added, at some point (the percolation threshold) the first conducting path will be formed. As more material is added, more conductive paths are formed, and the conductivity of the network increases rapidly. Eventually it reaches a “bulk-like” value above which it remains constant. Percolation theory describes how the DC conductivity

Ref.	σ_{DC}/σ_{Op}	T (%)	$R_s(\Omega/sq)$	Material
De et al [3]	171	85	13	AgNws
Wu et al. [98]	70	90	50	Cu Nanofibers
Rathmell et al. [2]	52	65	15	CuNws
Rathmell et al. [99]	35	84	60	Cupronickel Nws
Hecht et al. [100]	64	91	60	SWNT from superacid
Geng et al. [101]	23	80	70	Acid treated SWNTs
Wang et al.[76]	0.42	64	1800	Reduced Graphene Oxide
Green et al. [102]	0.6			Sorted pristine graphene

Table 1.2: Values of σ_{DC}/σ_{Op} , T and R_s for a selection of materials from the literature

of sparse networks depends on network thickness and predicts a non-linear, power law dependence [97]:

$$\sigma_{DC} \propto (t - t_c)^n$$

where t is the estimated thickness of the network, t_c is the thickness associated with the percolation threshold, and n is the percolation exponent. This leads to a new relationship between T and R_s , which applies to thin, transparent networks this will be derived in Chapter 6.

A selection of data from the literature for a range of materials is given in Table 1.2. On comparison of the data in Table 1.2 with the device requirements (Table 1.1) it is clear that many materials fall short of the requirements in particular displaying low R_s at high T ($T > 90\%$).

1.4.1 *Transparent energy storage*

The next stage in the development of flexible electronics may require all components of the device to be transparent for use in applications such as transparent displays [103]. If switched off, a transparent display may appear as an ordinary window which allows a clear view of everything behind it. On demand, this see-through device may be used to directly display arbitrary information without using elaborate projection techniques. For many such applications, transparent energy storage devices will be required [104]. To this end, a number of groups have demonstrated transparent supercapacitors or batteries [104–108]. Research has focused on using nanomaterials to produce thin but high surface area electrodes which can be transparent if made thin enough [105, 109, 110]. In the simplest case, these electrodes can then be combined with a suitable electrolyte and separator to produce a supercapacitor. Electrochemical double-layer capacitors (EDLC), also known as supercapacitors (SC), are devices that store charge and so energy at the interface between a conducting electrode and an electrolyte [111]. To maximize the charge storage capacity (the capacitance), the electrode must have high surface area. It should also be highly conductive to avoid the need for a current collector. Finally, it should be stable in the presence of the electrolyte.

1.5 ELECTROCHEMICAL DOUBLE LAYER CAPACITORS

Electrochemical capacitors fill the gap between batteries and conventional capacitors such as electrolytic capacitors (Figure 1.9). In terms of specific energy as well as in terms of specific power this gap spans several orders of magnitude. Batteries and low temperature fuel cells are typical low power devices whereas conventional capacitors may have a power density of $> 10^6$ watts per dm^3 at very low energy density. Thus, electrochemical capacitors may improve battery performance in terms of power density or may improve capacitor performance in terms of energy density when combined with the respective device. In addition, electrochemical capacitors are expected to have

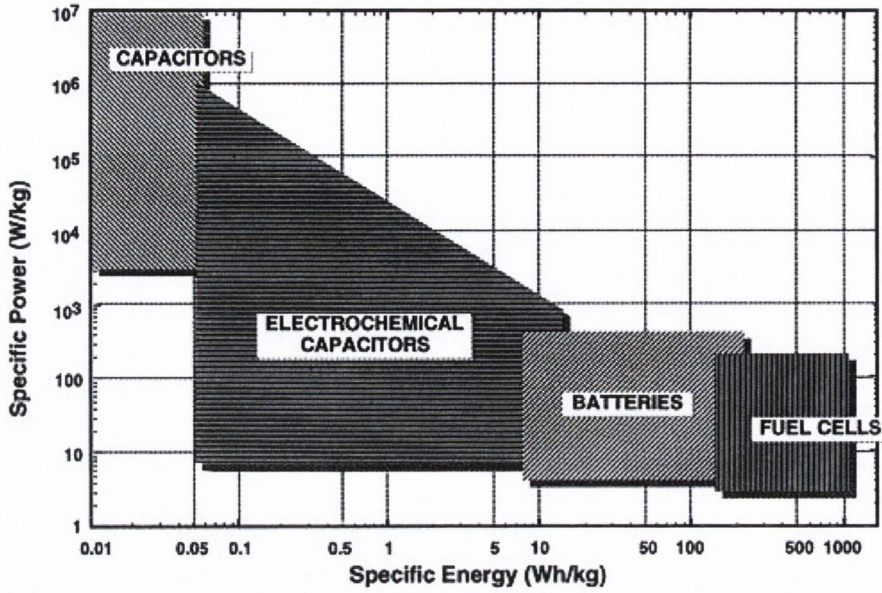


Figure 1.9: Sketch of Ragone plot for various energy storage and conversion devices. The indicated areas are rough guide lines [112].

a much longer cycle life than batteries because, no or negligibly small chemical charge transfer reactions are involved.

Electrochemical capacitors store the electric energy in an electrochemical double layer (Helmholtz Layer) formed at a solid:electrolyte interface. Positive and negative ionic charges within the electrolyte accumulate at the surface of the solid electrode and compensate for the electronic charge at the electrode surface. The thickness of the double layer depends on the concentration of the electrolyte and on the size of the ions and is of order $5 - 10 \text{ \AA}$, for concentrated electrolytes. The double layer capacitance is about $10\text{--}20 \mu\text{F}/\text{cm}^2$ for a smooth electrode in concentrated electrolyte solution and can be estimated according to equation eqn. 1.5

$$C/A = \epsilon_0 \epsilon_r / d \tag{1.5}$$

assuming a relative dielectric constant ϵ_r of 10 for water in the double layer, d being the thickness of the double-layer with surface area A .

In order to achieve a higher capacitance the electrode surface area is also increased by using porous electrodes with an extremely large internal effective surface. Combination of two such electrodes gives an electrochemical capacitor of rather high capacitance.

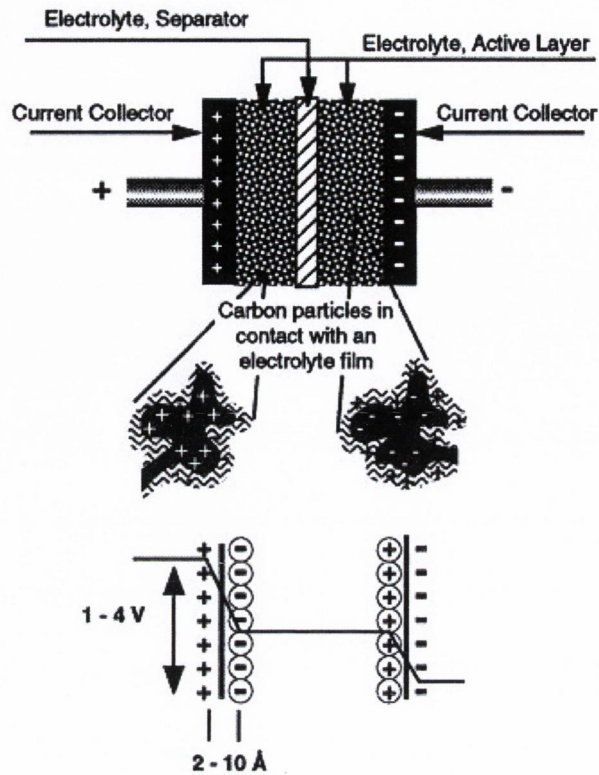


Figure 1.10: Principle of a single-cell double-layer capacitor and illustration of the potential drop at the electrode/electrolyte interface [112].

Figure 1.10 shows a schematic diagram of an electrochemical double-layer capacitor consisting of a single cell with a high surface area electrode material, which is loaded with electrolyte. The electrodes are separated by a porous separator, containing the same electrolyte as the active material. The potential drop across the cell is also shown in Figure 1.10.

The capacitance of a single electrode can be estimated by assuming a high surface area carbon with $1000\text{m}^2/\text{g}$ and a double layer capacitance of $10\mu\text{F}/\text{cm}^2$. This leads to a specific capacitance of $100\text{F}/\text{g}$ for one electrode. For a capacitor two electrodes are needed with doubled weight and half the total capacitance ($1/C = 1/C_1 + 1/C_2$) resulting in $25\text{F}/\text{g}$ of active capacitor mass for this example. The difference between single electrode values and specifications given for the complete capacitor is of significant importance. Whenever specifications of an electrochemical capacitor are given, one should indicate whether the values correspond to single electrode measurement

or are calculated for a complete capacitor. The difference between these two situations is a factor of four and is therefore of significant [113].

The maximum energy stored in such a capacitor is given by

$$E = 1/2CV_0^2 \quad (1.6)$$

With a cell voltage V_0 of 1 V (aqueous electrolyte) one obtains a specific energy of about 3.5Wh/kg of active mass. Using an organic electrolyte with a typical cell voltage of 2.3 V one obtains about 18Wh/kg of active mass. These values are considerably lower than those obtained for available batteries but much higher than for conventional capacitors. It should be mentioned that the above values depend on the double layer capacitance, the specific surface area of the respective electrode material, the wetting behaviour of the pores, and on the nominal cell voltage.

Summary

A general overview of the topics relevant to this work has been discussed. The primary focus is on thin films of graphene and carbon nanotubes as potential ITO replacement materials. The relevant theory and experimental methods will be covered in the next chapter

THEORY AND EXPERIMENTAL METHODS

2.1 INTRODUCTION

In this chapter the methods used in this study to characterise samples will be outlined. The focus is on determining the opto-electronic properties of a number of materials. We also assess the state of the material after processing and the quality of films made. The liquid phase dispersion of carbon nanomaterials was achieved by sonicating the material in a surfactant-water solution. This was followed by centrifugation to remove undispersed material and larger aggregates. Thin films were prepared by vacuum filtering the supernatant of these dispersions onto porous filter membranes. To control the thickness of a film being deposited, the concentration of the dispersion must first be determined. UV-Vis spectroscopy was used to measure this. Once the dispersion had been filtered and transferred onto a transparent substrate (glass or PET), the transmittance was determined via UV-Vis. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to look at the morphology and measure the thickness of the films. Raman spectroscopy was used to determine the composition of films. The electrical properties were measured using the four-probe technique [114]. Electrochemical measurements were performed with a three-electrode cell connected to a potentiostat. The techniques and relevant theory used will now be discussed in greater detail with appropriate reference to the literature.

2.2 OPTICAL COEFFICIENTS

Figure 2.1 shows a beam of light incident on an optical medium. The beam can interact with the medium in a number of different ways. Some of the light is reflected from the

front surface, while the rest enters the medium and propagates through it. If any of this light reaches the back surface, it can be reflected again, or it can be transmitted through to the other side. The amount of light transmitted is therefore related to the reflectivity at the front and back surfaces and also to the way the light propagates through the medium. The main process that we are concerned with is absorption of light within the material. Absorption occurs during light propagation if the frequency of the light is resonant with the transition frequencies of the molecules in the medium. In this case, the beam will be attenuated as it progresses. The transmission in the medium is clearly related to the absorption, because only unabsorbed light will be transmitted. Selective absorption is responsible for the colouration of many optical materials.

The reflection at the surfaces is described by the coefficient of reflection or reflectivity. This is defined as the ratio of the reflected power to the incident power on the surface and is given the symbol R . The coefficient of transmission T is defined as the ratio of transmitted power to incident power. By conservation of energy we must have for a non-absorbing material

$$R + T = 1 \quad (2.1)$$

The refractive index n is used to describe the propagation of the beam through a transparent medium. The ratio of the speed of light in free space to the velocity of light in the medium defines n

$$n = \frac{c}{v} \quad (2.2)$$

The absorption coefficient α is used to quantify the absorption of light by an optical medium. This is defined as the fraction of the power absorbed in a unit length of the medium. If the beam is propagating in the x direction, and the intensity at position x is $I(x)$, then the decrease of the intensity in an incremental slice of thickness dx is given by:

$$dI = -\alpha I(x)dx \quad (2.3)$$

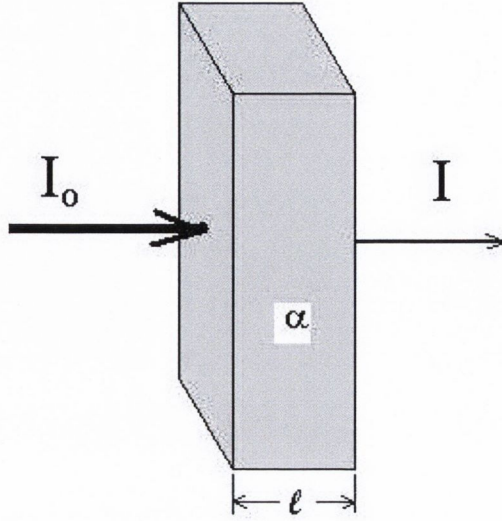


Figure 2.1: Representation of Beer's law

This can be integrated to obtain Beer's law:

$$I(x) = I_0 e^{(-\alpha x)} \quad (2.4)$$

where I_0 is the optical intensity at $x = 0$. The absorption and refraction of a medium can be described by a single quantity, the complex refractive index $\hat{n}$ given by

$$\hat{n} = n + i\kappa \quad (2.5)$$

The real part of $\hat{n}$, n , is the normal refractive index as defined in eqn. 2.2. The imaginary part κ , is directly related to the absorption coefficient α of the medium.

Consider a plane electromagnetic wave propagating through a medium with a complex refractive index. If the wave is propagating in the x direction, the spatial and time dependence of the electric field is given by

$$E(x, t) = E_0 e^{i(kx - \omega t)} \quad (2.6)$$

where k the wave is vector of the light and ω is the angular frequency. $|E_0|$ is the amplitude at $x = 0$. In a non-absorbing medium of refractive index n , the wavelength of the light is reduced by a factor n compared to the free space wavelength λ . k and ω are therefore related to each other through:

$$k = \frac{2\pi}{(\lambda/n)} = \frac{n\omega}{c}. \quad (2.7)$$

This can be generalised to the case of an absorbing medium by allowing the refractive index to be complex:

$$k = \frac{\hat{n}\omega}{c} = (n + i\kappa)\frac{\omega}{c}. \quad (2.8)$$

On substituting into eqn. 2.6

$$\begin{aligned} E(x, t) &= E_0 e^{i(\hat{n}\omega x/c - \omega t)} \\ &= E_0 e^{(-\kappa\omega x)} e^{i(n\omega x/c - \omega t)} \end{aligned} \quad (2.9)$$

This shows that a non-zero extinction coefficient leads to an exponential decay of the wave in the medium.

The optical intensity of a light wave is proportional to the square of the electric field, $I \propto EE^*$. From eqn. 2.9 we can deduce that the intensity falls off exponentially in the medium with a decay constant equal to $2 \times (\kappa\omega/c)$. If we compare this to Beer's law eqn. 2.4 we see that

$$\alpha = \frac{2\kappa\omega}{c} = \frac{4\pi\kappa}{\lambda}, \quad (2.10)$$

where λ is the free space wavelength of the light. This shows that κ is directly proportional to the absorption coefficient.

We can relate the refractive index of a medium to its relative dielectric constant ϵ_r by using the standard result derived from Maxwell's equations

$$n = \sqrt{(\epsilon_r)} \quad (2.11)$$

This shows that if n is complex, then ϵ_r must also be complex. One can therefore define the complex relative dielectric constant $\hat{\epsilon}_r$ according to:

$$\hat{\epsilon}_r = \epsilon_1 + i\epsilon_2 \quad (2.12)$$

One can see that $\hat{n}$ and $\hat{\epsilon}_r$ are related to each other through:

$$\hat{n}^2 = \hat{\epsilon}_r \quad (2.13)$$

By combining eqns. 2.5, 2.12 and 2.13 we can work out explicit relationships between the real and imaginary parts of $\hat{n}_r$ and $\hat{\epsilon}_r$. These are

$$\epsilon_1 = n^2 - \kappa^2 \quad (2.14)$$

$$\epsilon_2 = 2n\kappa \quad (2.15)$$

and

$$n = \frac{1}{\sqrt{2}} \left(\epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} \right)^{\frac{1}{2}} \quad (2.16)$$

$$\kappa = \frac{1}{\sqrt{2}} \left(-\epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} \right)^{\frac{1}{2}} \quad (2.17)$$

2.3 ABSORPTION SPECTROSCOPY

Absorption spectroscopy is a technique that measures the absorption of radiation as a function of frequency or wavelength, due to its interaction with a sample. The ratio of the transmitted intensity, I , to the incident intensity I_0 , at a given frequency is called the transmittance, T , of a sample at that frequency:

$$T = \frac{I}{I_0} \quad (2.18)$$

It is found empirically that the transmitted intensity varies with the length, l , of the sample and concentration, C , of the absorbing species according to the Beer Lambert law:

$$I = I_0 \ln(-\epsilon Cl) \quad (2.19)$$

ϵ is called the extinction coefficient which depends on the frequency of the incident radiation and is greatest where the absorption is most intense. One can define absorbance as

$$A = -\log \frac{I}{I_0} = -\log T \quad (2.20)$$

Combining this with eqn. 2.19 we see that for a solid

$$A = \alpha l \quad (2.21)$$

In a solution or liquid dispersion

$$A = \epsilon Cl = \sigma Nl \quad (2.22)$$

Where α = absorption coefficient [m^{-1}], l = sample thickness [m], ϵ = extinction coefficient [$Lg^{-1}m^{-1}$], C = concentration, [$mgml^{-1}$], σ = optical cross section [m^2], N = number of molecules per volume. In general A and hence α , ϵ or σ are all measured as a function of the wavelength, λ , or equivalently photon energy, E , of the light being absorbed

$$E = \frac{hc}{\lambda} \quad (2.23)$$

The result is an absorption spectrum. Absorption and transmittance spectra were measured using a Varian Cary 6000i spectrophotometer. A schematic of the machine is shown in Figure 2.2. Baseline spectra were taken before all sample scans.

2.4 WHITE LIGHT TRANSMISSION SPECTROSCOPY

Multiple transmission spectra were obtained for each thin film studied during this work. This allowed the average transmittance to be measured for each sample. However, performing multiple scans does not give information about the spatial optical uniformity. Transmission scans were made using an Epson Perfection V700 Photo flat-bed, white light, transmission scanner with a bit depth of 48 bits per pixel and a

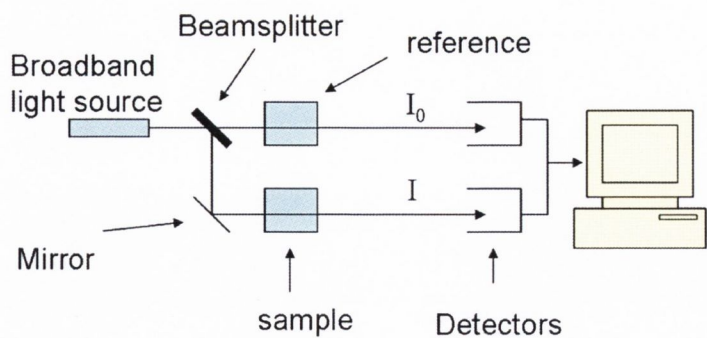


Figure 2.2: UV-Vis spectrophotometer

spatial resolution of 6400 dpi. The numerical output of the scanner was calibrated by scanning a range of neutral density filters. The resultant calibration curve was used to transform the output to represent transmittance. This resulted in a transmittance map with a transmittance value for every pixel. In some cases the transmittance was transformed to absorbance on a pixel by pixel basis using $A = -\ln T$. The mean and standard deviation of the transmittance/absorbance were calculated for the entire data set i.e. from the entire set of transmittance/absorbance per pixel values. We define the non-uniformity of the film as the ratio of the standard deviation of the absorbance to the mean absorbance [45].

$$Non - uniformity = \Delta A / \langle A \rangle \tag{2.24}$$

2.5 INFRARED SPECTROSCOPY

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the

frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. For a molecule to show infrared absorptions it must possess a specific feature, i.e. an electric dipole moment of the molecule must change during the vibration. This is the selection rule for infrared spectroscopy. A chain of carbon atoms or a graphitic network does not possess IR-active vibrational modes. However, functional groups such as C=O or C=OH are IR-active. Hence, Fourier transform infrared (FTIR) spectroscopy can be used to ascertain the large-scale presences of residual oxides. It can aid in assessing the quality of graphene. Attenuated total reflectance (ATR-FTIR) spectra in this thesis were taken on thin film samples. Spectra were collected with a Perkin Elmer Spectrum 100 equipped with a diamond ATR crystal. An IR background was taken prior to sample scan acquisition.

2.6 RAMAN SPECTROSCOPY

When a beam of monochromatic light is incident on a sample, some of the light is scattered. Most of this scattered light has the same wavelength as the incident light. However, a small fraction of the incident light is shifted in wavelength by the molecular vibrations and rotations of the molecules in the sample. The spectrum is called a Raman spectrum and was first reported by Sir C.V. Raman in 1928 [115]. This technique is widely used for investigating the physical properties and quality of carbon materials such as graphene and carbon nanotubes [1, 116, 117]. IR absorption arises from a direct resonance between the frequency of the IR radiation and the vibrational frequency of a particular normal mode of vibration. IR absorption is a one-photon event. The IR photon encounters the molecule, the photon disappears, and the molecule is elevated in vibrational energy by the energy of the photon at the frequency of vibrational resonance.

In contrast, Raman scattering is a two-photon event. In this case, the property involved is the change in the polarisability of the molecule with respect to its vibrational motion. The interaction of the polarisability with the incoming radiation creates an induced dipole moment in the molecule, and the radiation emitted by this induced

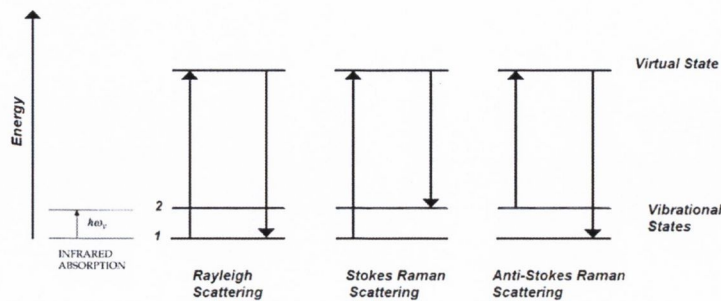


Figure 2.3: Energy level diagram for infrared absorption and stokes Raman scattering

dipole moment contains the observed Raman scattering. The light scattered by the induced dipole of the molecule consists of both Rayleigh scattering and Raman scattering. Rayleigh scattering corresponds to the light scattered at the frequency of the incident radiation, whereas the Raman radiation is shifted in frequency, and hence energy, from the frequency of the incident radiation by the vibrational energy that is gained or lost in the molecule.

An energy-level diagram is given in Fig. 2.3, which illustrates IR absorption and Raman scattering. In both cases the initial state is the zeroth vibrational level of the ground electronic state (1) and the final state is the first vibrational level of the ground electronic state (2). IR absorption achieves this state change in one step, whereas Raman scattering requires two steps involving photon energies that are well above that of the IR photon or energy of the vibrational transition. An incident photon with a frequency ω_1 creates an electron-hole pair. This scatters inelastically with the emission of a phonon ω_{ph} and then recombines with the emission of a scattered photon ω_2 . Energy and momentum are conserved .

$$\hbar\omega_1 = \hbar\omega_2 \pm \hbar\omega_{ph} \tag{2.25}$$

$$q_1 = q_2 \pm q_{ph} \quad (2.26)$$

This process can be simply envisaged looking at energy level diagrams such as that shown in Figure 2.3 whereby interaction with the incident photon promotes a molecule to a virtual state. If the molecule returns to a higher energy level then the photon will have lost energy on interaction with the molecule. The emitted photon will have less energy and a longer wavelength. This is known as Stokes Raman scattering. If the molecule returns to a lower energy level than the one it started in, the photon will have gained energy on interaction with the molecule and the emitted photon will be of higher energy and shorter wavelength than the incident photon. This is known as anti-Stokes Raman scattering.

When incident photons interact with a molecule's electron cloud, the strength of the interaction depends on the polarisability of the molecule. For a sample to be Raman active its polarisability must change on interaction with an external field. Molecules with distributed electron clouds such as π -bonds which are easily polarised are very strong Raman scatterers and so Raman spectroscopy is a particularly useful characterisation technique for a wide array of nanocarbon materials.

2.6.1 Raman Spectroscopy of Graphene and Graphene Layers

Figure 2.4 compares the Raman spectra of graphene and bulk graphite measured at 514.5nm excitation [1]. The spectra have three principal features, these are denoted the *D*, *G* and 2*D* bands and are observed at $\sim 1340\text{cm}^{-1}$, $\sim 1580\text{cm}^{-1}$ and 2700cm^{-1} respectively.

The *D* band is related to defects and disorder in sp^2 -hybridised carbon materials. This transition is forbidden in perfect graphitic systems and requires a defect for its activation. These defects can be atomic vacancies, functional groups bound to sp^3 -hybridised sites or the edges of the sp^2 -network. The stretching of the C – C bond in graphitic materials gives rise to the so-called *G*-band Raman feature which is common to all sp^2 -carbon systems. A third band, characteristic of graphene/graphite

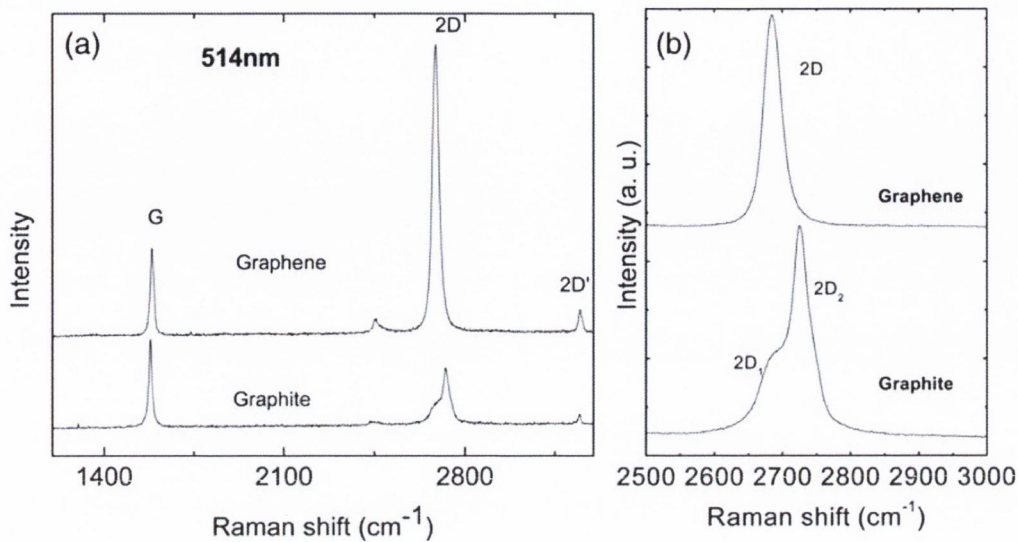


Figure 2.4: Raman spectra of graphite and graphene [1]

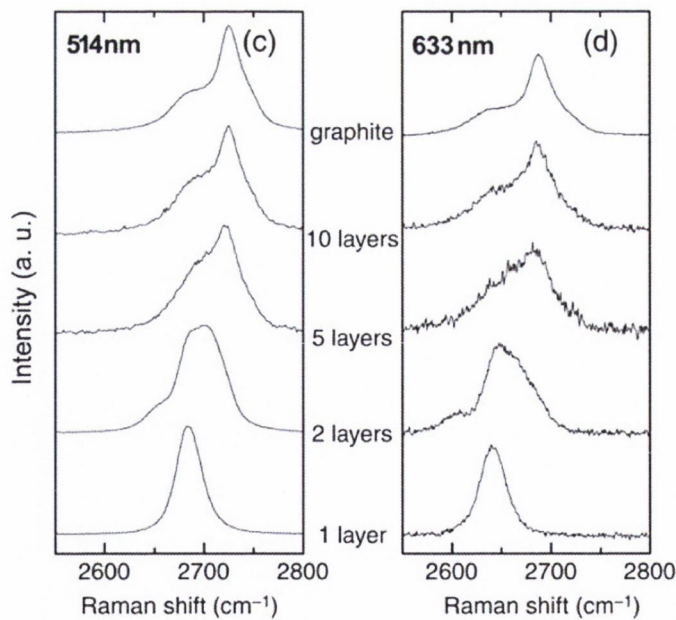


Figure 2.5: Evolution of the 2D peak as a function of number of layers for 514 and 633 nm excitations [1].

is centred around 2700cm^{-1} and is referred to as the $2D$ -band. Figure 2.4 shows a significant change in the shape and intensity of the $2D$ peak of graphene compared to bulk graphite. The $2D$ peak in bulk graphite consists of two components $2D_1$ and $2D_2$, roughly $1/4$ and $1/2$ the height of the G peak, respectively. Graphene has a single, sharp $2D$ peak, roughly four times more intense than the G peak. The evolution of the $2D$ band from graphene to graphite was first shown by *Ferrari et al.* Figure 2.5 [1].

The number of layers (up to the screening length i.e. transition from few layer graphene to bulk graphite) can be inferred through observations of gradual changes in the Raman spectrum in a “finger print” fashion. The Raman features of graphene and graphite directly reflect changes in the electronic structure from stacking of successive layers. Hence, Raman spectroscopy is a reliable method to confirm graphene thickness and quality in a high-throughput fashion.

2.7 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) was used in this work to look at the surface morphology of films and to measure their thickness. A Zeiss Ultra Plus Field Emission SEM was used. A coherent, monochromatic stream of electrons is formed by an electron source (thermionic emission or field emission) and accelerated toward the specimen. This stream is confined and focused using metal apertures and magnetic lenses into a thin beam that is directed at the sample as can be seen in Figure 2.6.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The angle and energy at which the electrons are scattered (by elastic and inelastic collisions) allows them

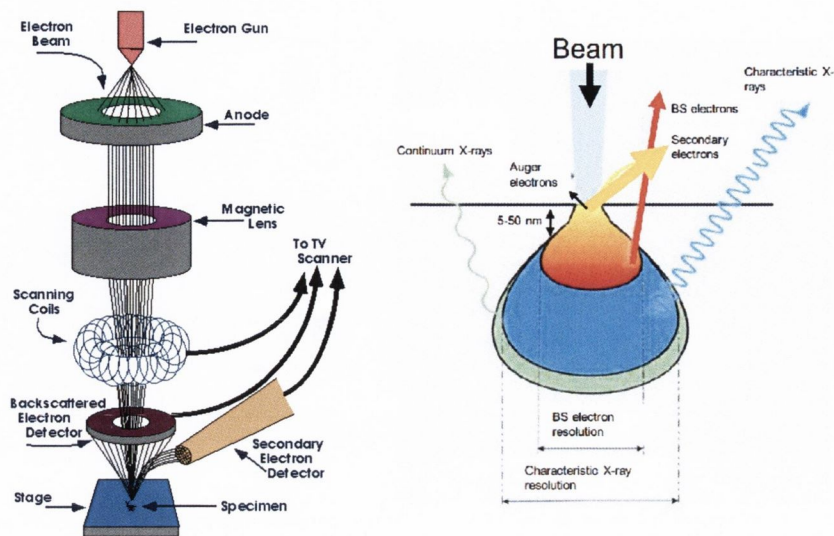


Figure 2.6: Schematic of Scanning Electron Microscope

to be classified as backscattered, secondary or auger electrons/characteristic X-rays. Images were taken of the surface of samples at various magnifications to ascertain morphological information. Samples were also mounted parallel to the incident beam to look at the cross section for thickness measurements.

2.8 ATOMIC FORCE MICROSCOPY

Atomic force microscopy (AFM) is a scanning probe technique that maps surface topography. A basic schematic of an AFM is shown in Figure 2.7. It consists of a cantilever with a tip at its end that is used to scan the surface of the sample. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law:

$$F = -kx \tag{2.27}$$

where x is the displacement [m], F is the restoring force [N], k is the spring constant [Nm⁻¹].

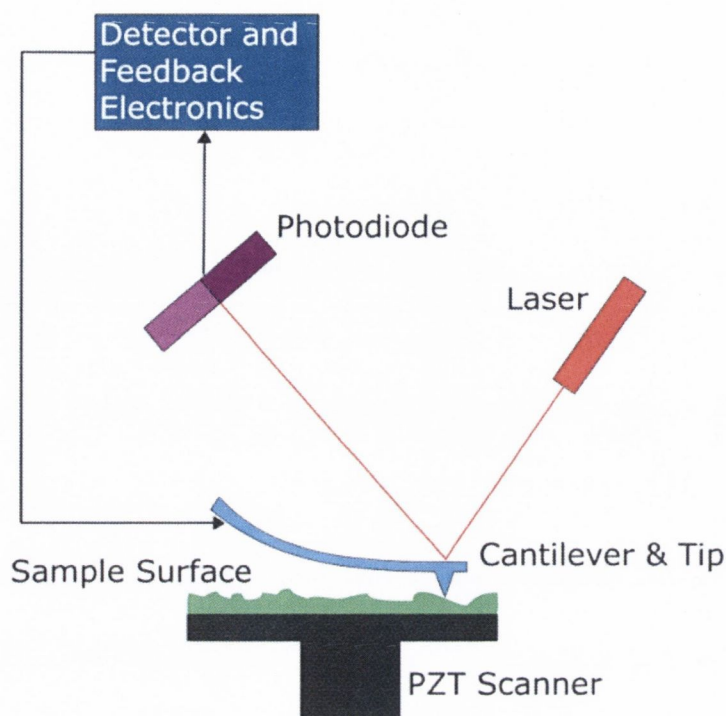


Figure 2.7: Basic schematic diagram of AFM apparatus

There are a number of different modes of operation of an AFM: contact mode, non-contact mode and tapping mode. For contact mode the tip is dragged across a surface. Atoms in the tip and surface interact, generating a force. Feedback loops adjust the tip height such that the tip sample force is constant. The position of the tip is measured with great sensitivity by reflecting a laser off the cantilever. The vertical position is then plotted as a relief map over the required area of the surface. This gives height resolution of $\sim 0.1\text{nm}$ and lateral resolution of $\sim 10 - 50\text{nm}$. In non contact mode the tip oscillates at its resonant frequency but does not come in contact with the surface. The resonance is modified by tip-surface interactions (e.g. van der Waals forces). Changes in oscillation phase and amplitude are detected as the tip is scanned. An image is built up by scanning the surface.

The most common mode of operation is tapping mode. In tapping mode, the cantilever is driven to oscillate up and down near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder similar to non-contact mode. The interaction of forces acting on the cantilever when the tip comes close to the

surface i.e. Van der Waals force, dipole-dipole interaction and electrostatic forces cause the amplitude of this oscillation to decrease as the tip gets closer to the sample. An electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample. The servo adjusts the height to maintain a set cantilever oscillation amplitude as the cantilever is scanned over the sample. A tapping AFM image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface.

AFM was performed in this work to measure film thickness and surface roughness. A Digital Instruments Nanoscope IIIA from Veeco systems was used. All measurements are carried out under ambient atmosphere in tapping mode using monolithic silicon tips having resonance frequency 300kHz , force constant 40Nm^{-1} and tip radius $8 - 10\text{nm}$

2.9 ELECTRICAL PROPERTIES OF THIN FILMS

According to Ohm's law, the current flowing in a wire is proportional to the potential drop V along the wire:

$$V = IR \quad (2.28)$$

where R , the resistance of the wire, depends on its dimensions but is independent of the size of the current or potential drop. The dependence of R on the shape of the wire can be eliminated by introducing a quantity characteristic of the metal of which the wire is composed. The resistivity ρ is defined to be the proportionality constant between the electric field $\mathbf{E}$ at a point in the metal and the current density $\mathbf{j}$ that it induces

$$\mathbf{E} = \rho \mathbf{j} \quad (2.29)$$

The current density $\mathbf{j}$ is a vector, parallel to the flow of charge, whose magnitude is the amount of charge per unit time crossing a unit area perpendicular to the flow. Thus if a uniform current I flows through a wire of length L and cross-sectional area

A , the current density will be $j = I/A$. Since the potential drop along the wire will be $V = EL$, eqn. 2.29 gives $V = I\rho L/A$, and hence

$$R = \rho L/A = \frac{1}{\sigma} L/A \quad (2.30)$$

When investigating the electrical properties of thin uniform films the resistance is often given by a 2-Dimensional quantity known as the sheet resistance R_s . From Equation 2.30 we have

$$R = \frac{1}{\sigma} \frac{L}{wd} \quad (2.31)$$

where w and t are the width and thickness which make up the cross sectional area A of the sample. The resistivity is simply the reciprocal of the conductivity. Grouping the resistivity and thickness together results in

$$R = \frac{\rho}{t} \frac{L}{W} = R_s \frac{l}{w} \quad (2.32)$$

This gives the expression for sheet resistance

$$R_s = R \frac{w}{l} \quad (2.33)$$

And finally, linking the conductivity to the sheet resistance gives

$$R_s = \frac{1}{\sigma_{DC} t} \quad (2.34)$$

The four-probe method was used to measure R_s of the films (Figure 2.8) [114]. This method is more accurate than the two-probe method. The contact resistance made between the material surface and the probe touching the surface and the spreading resistance caused by current flowing into the sample surface are removed due to the use of two additional probes. These probes do not carry any current, thus eliminating both the contact and spreading resistances inherent in the two-probe method. The experimental setup can be seen in Figure 2.8. Using silver conducting paint four collinear, equidistant, strips were painted onto the film. Then silver wires were connected to each contact and this arrangement was connected to a Keithley 2400 source meter.

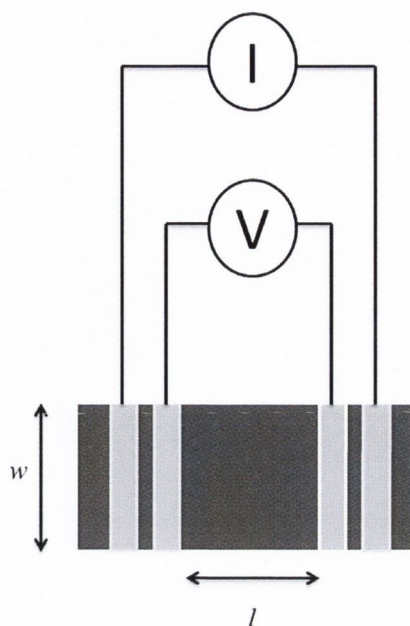


Figure 2.8: Four point probe setup

The distance between the middle two contacts (l) was measured using digital vernier callipers. The length of the strips (w) was also determined.

A current I was passed through the sample via the outer probes, also known as the force probes. The current flowing through the sample sets up an electrical potential gradient, and the resulting difference in potential (V) between the two inner probes, referred to as the sense probes, was measured with a high-impedance voltmeter. The applied current I flows only through the force probes, not the sense probes. The current through the sense probes was kept extremely small, and so the error in V due to ohmic potential drops in the sense lead wires and sense probe contact resistances is negligible. This ensures that the measured difference in potential is equal to the difference in potential across the sample. An I/V curve was generated, the inverse slope of which gave the resistance R by ohms law $R = V/I$.

2.10 ELECTROCHEMICAL DOUBLE LAYER CAPACITORS

In electrochemical systems, we are concerned with the processes and factors that affect the transport of charge across the interface between chemical phases, for example,

between an electronic conductor (an electrode) and an ionic conductor (an electrolyte). The events that occur at the electrode/electrolyte interface when a potential is applied and current passes are of main interest. We use an electrochemical cell to study this interface. It usually consists of two electrodes separated by an electrolyte phase. A difference in electric potential can be measured between the electrodes in an electrochemical cell. This cell potential, measured in volts (V), is a measure of the energy available to drive charge externally between the electrodes. The transition in electric potential in crossing from one conducting phase to another usually occurs almost entirely at the interface. The sharpness of the transition implies that a very high electric field exists at the interface, and one can expect it to affect the behaviour of charge carriers (electrons or ions) in the interfacial region. Also, the magnitude of the potential difference at an interface affects the relative energies of the carriers in the two phases; hence it controls the direction and the rate of charge transfer. Thus, the measurement and control of cell potential is one of the most important aspects of experimental electrochemistry.

The overall chemical reaction taking place in a cell is made up of two independent half-reactions, which describe the real chemical changes at the two electrodes. Each half-reaction responds to the interfacial potential difference at the corresponding electrode. We are interested in one of these half reactions and the electrode at which this occurs is called the working electrode. In order to focus on it the other half cell is standardised by using a reference electrode. The reference electrode is made up of phases having essentially constant composition, because of this constant make up its potential is fixed. Therefore, any changes in the cell are ascribable to the working electrode. We say that we observe or control the potential of the working electrode with respect to the reference, and that is equivalent to observing or controlling the energy of the electrons within the working electrode. By driving the electrode to more negative potentials, the energy of the electrons is raised. They can reach a level high enough to transfer into vacant electronic states in species in the electrolyte. In that case, a flow of electrons from electrode to solution (a reduction current) occurs (Figure 2.9A). Similarly, the energy of the electrons can be lowered by imposing a more positive potential, and at some point electrons on solutes in the electrolyte will find a more

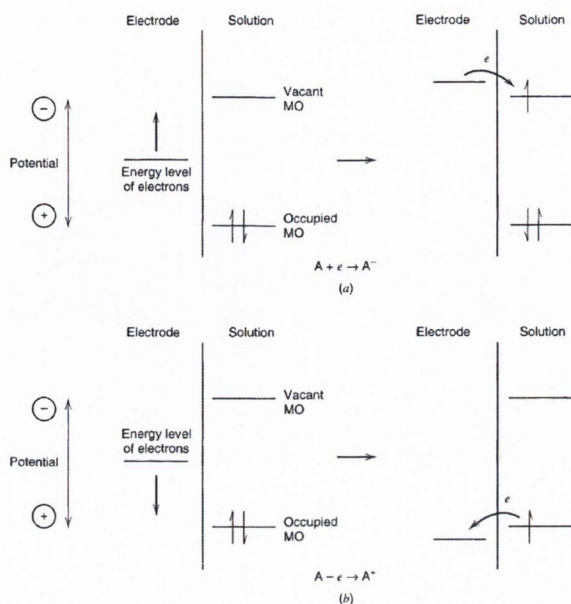


Figure 2.9: Representation of (a) reduction and (b) oxidation process of a species, A, in solution.

The molecular orbitals (MO) of species A shown are the highest occupied MO and the lowest vacant MO. These correspond in an approximate way to the E° s of the A/A^- and A^+/A couples, respectively [118].

favourable energy on the electrode and will transfer there. Their flow, from solution to electrode, is an oxidation current (Figure 2.9B). The critical potentials at which these processes occur are related to the standard potentials, E° , for the specific chemical substances in the system.

In this work we are concerned with energy storage at the interface between the electrode and electrolyte. Two types of processes occur at electrodes that can lead to charge storage. One kind comprises reactions like those just discussed, in which charges (e.g., electrons) are transferred across the metal-solution interface. Electron transfer causes oxidation or reduction to occur. Since such reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called faradaic processes. The second process is non faradaic in which charge accumulation is achieved electrostatically by positive and negative charges residing on two interfaces separated by a molecular dielectric.

An electrode at which no charge transfer can occur across the metal-solution interface, regardless of the potential imposed by an outside source of voltage, is called an ideal polarised electrode (IPE). Since charge cannot cross the IPE interface when the potential across it is changed, the behaviour of the electrode-solution interface is analogous to that of a capacitor. If we consider a cell consisting of an IPE and an ideal reversible electrode. This can be approximated by an electrical circuit with a resistor, R_s , representing solution resistance and a capacitor, C_d , representing the double layer. A capacitor is an electrical circuit element composed of two metal sheets separated by a dielectric material. The behaviour of a capacitor is governed by the following equation

$$\frac{q}{V} = C \quad (2.35)$$

where q is the charge stored on the capacitor (in Coulombs, C), V is the potential across the capacitor (in volts), and C is the capacitance (in Farads, F). When a potential is applied across a capacitor charge will accumulate on its metal plates until q satisfies eqn. 2.35. During this charging process, a current (called the charging current) will flow. The charge on the capacitor consists of an excess of electrons on one plate and a deficiency on the other.

The energy E stored in a capacitor can be calculated in joules by equation 2.36

$$E = 1/2CV^2 \quad (2.36)$$

An ideal capacitor with no current flow will store energy and charge for ever.

Power drawn from a capacitor during charge or discharge is proportional to the capacitor's voltage and the electrical current, given by Equation 2.37

$$P = VI \quad (2.37)$$

P is the power in watts (w) and I is the electrical current in amperes (A). An ideal capacitor loses no power or energy during charge or discharge.

However, the ideal capacitor does not exist and always have limitations. Capacitors can only operate within a "voltage window" with both an upper and lower voltage limit. The range of the voltage window strongly depends on the electrolyte which can

be aqueous or non-aqueous. Voltages outside of this window can cause electrolyte decomposition damaging the device. Non-aqueous electrolytes can have a much wider voltage window.

Real capacitors suffer from power loss during charge and discharge. This loss is caused by resistances in electrical contacts, electrodes, and electrolyte. The sum of these resistances is called Equivalent Series Resistance (*ESR*).

Information about an electrochemical system is often gained by applying an electrical perturbation to the system and observing the resulting changes in the characteristics of the system. We now consider the response of the IPE system, represented by the circuit elements R_s and C_d in series, to several common electrical perturbations.

(a) Potential step

The result of a potential step to the IPE is the familiar RC circuit problem. The charge, q , on a capacitor as a function of the voltage across it, V_c :

$$q = C_d V_c \quad (2.38)$$

At any time the sum of the voltages, V_r and V_c , across the resistor and the capacitor, respectively must equal the applied voltage; hence

$$V = V_R + V_C = iR_s + \frac{q}{C_d} \quad (2.39)$$

Noting that $i = dq/dt$ and rearranging yields

$$\frac{dq}{dt} = \frac{-q}{R_s C_d} + \frac{V}{R_s} \quad (2.40)$$

If we assume that the capacitor is initially uncharged ($q = 0$ at $t = 0$), then the solution of is

$$q = VC_d \left[1 - e^{-t/R_s C_d} \right] \quad (2.41)$$

differentiating with respect to time gives

$$i = \frac{V}{R_s} e^{-t/R_s C_d} \quad (2.42)$$

The behaviour of the current, i , with time t , when applying a potential step of magnitude E . Hence for a potential step input, there is an exponentially decaying current having a time constant, $\tau = R_s C_d$. The current for charging the double-layer capacitance drops to 37% of its initial value at $t = \tau$, and to 5% at $t = 3\tau$.

(b) Current Step

When the $R_s C_d$ circuit is charged by a constant current, then equation 2.39 again applies. Since

$$q = \int i dt$$

and i is a constant

$$V = iR_s + \frac{i}{C_d} \int_0^t dt$$

or

$$V = i (R_s + t/C_d)$$

Hence, the potential increases linearly with time for a current step.

(c) Voltage Ramp (Potential Sweep)

A voltage ramp or linear potential sweep is a potential that increases linearly with time starting at some initial value (here assumed to be zero) at a sweep rate ν (in V/s).

If such a ramp is applied to the $R_s C_d$ circuit, equation 2.39 still applies; hence

$$V = \nu t = R_s (dq/dt) + q/C_d$$

If $q = 0$ at $t = 0$ see appendix section 8.1

$$i = \nu C_d [1 - \exp(-t/R_s C_d)]$$

The current rises from zero as the scan starts and attains a steady-state value, νC_d . This steady state current can be used to estimate C_d . If the time constant, $R_s C_d$, is small compared to ν , the instantaneous current can be used to measure C_d as a function of E .

If one instead applies a triangular wave (i.e., a ramp whose sweep rate switches from ν to $-\nu$ at some potential, E_λ), then the steady-state current changes from νC_d

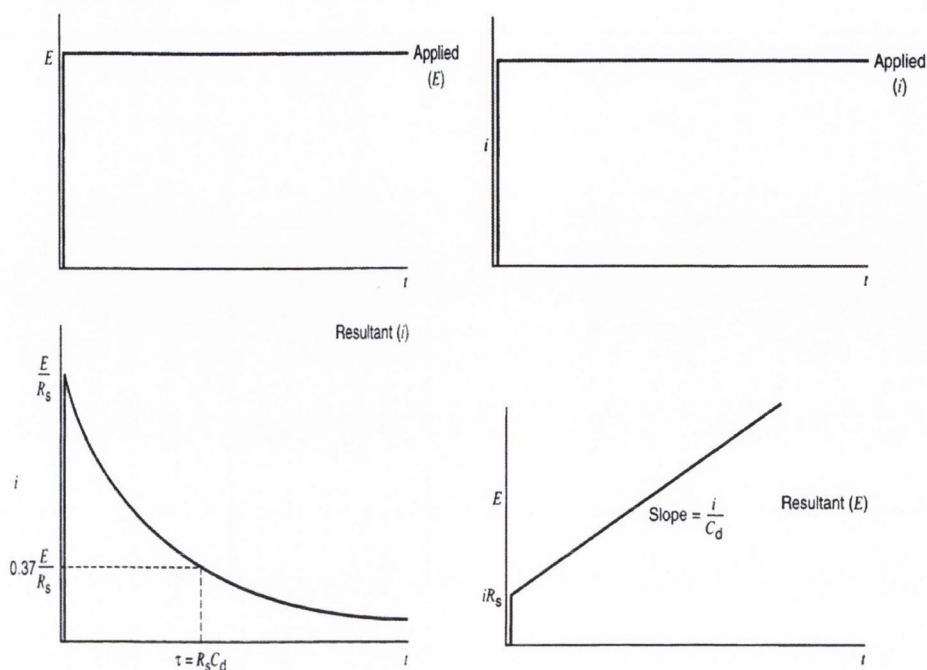


Figure 2.10: Current transient (i vs. t) resulting from a potential step experiment. V- t behaviour resulting from a current step experiment [118].

during the forward (increasing V) scan to $-vC_d$ during the reverse (decreasing V) scan. The result for a system with constant C_d is shown in Figure 2.11

2.10.1 Electrochemical Impedance Spectroscopy (EIS)

Electrical resistance is the ability of a circuit element to resist the flow of electrical current. Ohm's law (Eqn. 2.28) defines resistance in terms of the ratio between voltage and current. However, in terms of circuits this relationship is limited to only one circuit element - the ideal resistor. An ideal resistor has several simplifying properties:

- It follows Ohm's Law at all current and voltage levels.
- Its resistance value is independent of frequency.
- AC current and voltage signals through a resistor are in phase with each other.

However, most circuit elements exhibit much more complex behaviour. To describe these elements we use a more general circuit parameter than resistance, impedance.

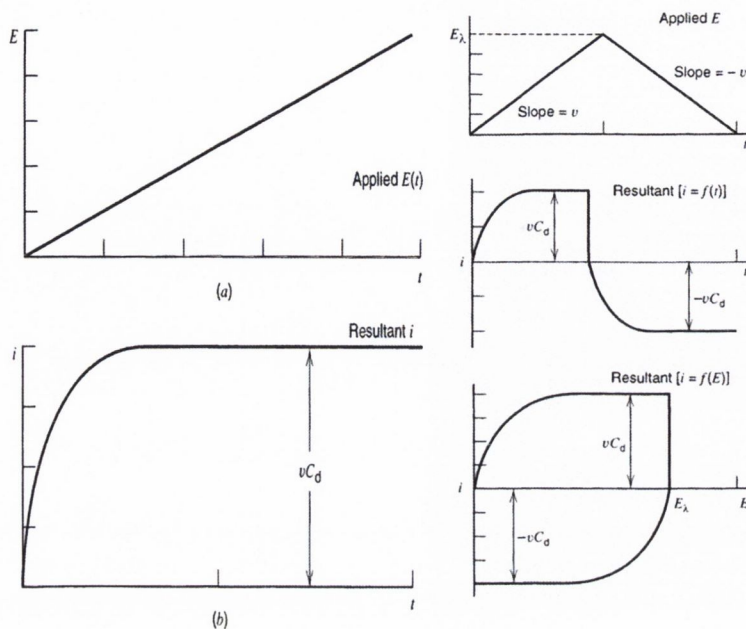


Figure 2.11: Current-time and current-potential plots resulting from a cyclic linear potential sweep(or triangular wave) applied to a RC circuit [118].

Impedance is a measure of the ability of a circuit to resist the flow of electrical current, but unlike resistance, it is not limited by the simplifying properties listed above.

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. If we assume that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal. This current signal can be analysed as a sum of sinusoidal functions (a Fourier series). Electrochemical impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

The excitation signal, expressed as a function of time has the form

$$E_t = E_0 \sin(\omega t) \quad (2.43)$$

where E_t is the potential at time t , E_0 is the amplitude of the signal, and ω is the angular frequency.

In a linear system, the response signal, I_t , is shifted in phase (ϕ) and has a different amplitude, I_0

$$I_t = I_0 \sin(\omega t + \phi) \quad (2.44)$$

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

$$Z = \frac{E_t}{I_t} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (2.45)$$

With Eulers relationship,

$$\exp(j\phi) = \cos \phi + j \sin \phi \quad (2.46)$$

it is possible to express the impedance as a complex function. The potential is described as

$$E_t = E_0 \exp(j\omega t) \quad (2.47)$$

and the current response as

$$I_t = I_0 \exp(j\omega t - \phi) \quad (2.48)$$

The impedance is then represented as a complex number,

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0 (\cos \phi + j \sin \phi) \quad (2.49)$$

The expression for $Z(\omega)$ (equation 2.49) is composed of a real and an imaginary part. If the real part is plotted on the X-axis and the negative of the imaginary part is plotted on the Y-axis of a chart, we get a "Nyquist Plot" (Figure 2.12)

On the Nyquist Plot the impedance can be represented as a vector (arrow) of length $|Z|$. The angle between this vector and the X-axis, commonly called the "phase angle", is $\phi (= \arg Z)$.

In the previous section the response of an IPE and an ideal reversible electrode to various perturbations was described. The equivalent circuit for such a system was a

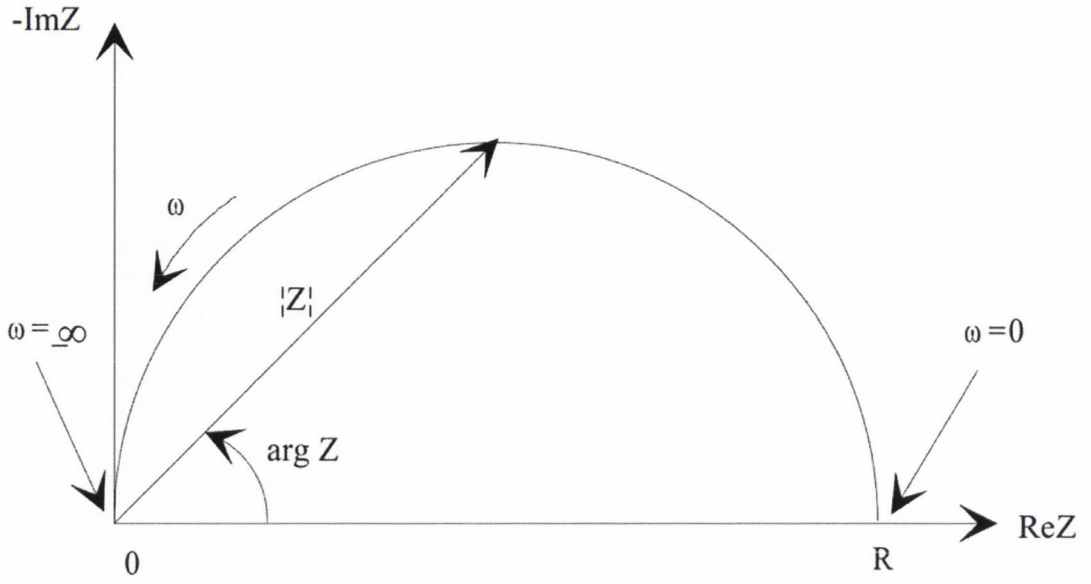


Figure 2.12: Nyquist Plot with Impedance Vector

resistor R_s in series with a capacitor C_d . The impedance of these circuit elements are given by the following equations

$$Z_{R_s} = R_s \tag{2.50}$$

$$Z_{C_d} = \frac{1}{j\omega C_d} \tag{2.51}$$

For impedances in series

$$Z = Z_{R_s} + Z_{C_d} = R_s + 1/j\omega C_d \tag{2.52}$$

In chapter 7 we use this to calculate the ESR of carbon nanotube electrodes. At high frequency the Z_{C_d} component goes to zero and $Z = R_s = R_{ESR}$.

Summary

The experimental techniques and relevant theory used throughout this work have been described. The exact procedure for sample preparation will be detailed in each subsequent chapter.

FLEXIBLE, TRANSPARENT, CONDUCTING FILMS OF RANDOMLY STACKED GRAPHENE FROM SURFACTANT-STABILISED, OXIDE-FREE GRAPHENE DISPERSIONS

3.1 INTRODUCTION

Over the last decade a number of new materials to replace ITO have been proposed. Numerous publications have emerged describing carbon-nanotube films as transparent conductors. To date, carbon nanotube films have been prepared with direct current (DC) conductivities close to $6.5 \times 10^5 Sm^{-1}$ [14, 43]. This value is important because it represents the threshold, above which films can be prepared with $T > 90\%$ for $R_s < 100\Omega/sq$. These are the minimum requirements as set by companies such as Hewlett-Packard for a material to be industrially useful as a transparent conductor. Additionally, nanotube films and polymer-nanotube composite films have been shown to be electromechanically stable under flexing for a large number of cycles with no deterioration in the electrical properties [45, 96]. However, while nanotubes may seem very attractive they remain very expensive. Arc-discharge single walled nanotubes (SWNTs), which are known to form the most conductive films, cost approximately $\$1500g^{-1}$ (Iljin Nanotech)[45]. By contrast, the graphite powder used for this work costs $\approx \$5kg^{-1}$.

An alternative solution would be the identification of a cheaper, alternative form of graphitic nanoscale carbon that can be formed into highly conductive, thin, transparent films. It was believed that thin films of layered (but not Bernal, i.e. AB, stacked) may have been a suitable alternative. In this work we have used surfactant-stabilized dispersions of graphene in water to prepare a range of thin films with varying thickness [31, 83]. We compare the results obtained to the data from the literature and have

examined the suitability of networks of graphene flakes as potential ITO replacement materials.

3.2 RESULTS AND DISCUSSION

3.2.1 Characterisation

The ability to exfoliate graphite in the liquid phase to give graphene without any oxidation or significant defect formation is key to this work. We employ the simple approach of sonicating graphite powder in a water surfactant solution to give dark-coloured dispersions. Sodium cholate (SC) is well-known as an efficient surfactant for carbon nanotubes [82, 119]. After centrifugation we get grey dispersions with a concentration of up to 0.04 mg/ml but typically $\approx 0.005\text{ mg/ml}$ (Figure 3.1A). The procedure used is similar to the one previously outlined for graphite exfoliation using the surfactant sodium dodecyl benzene sulfonate (SDBS) [83]. However, at the time we believed that sodium cholate to be superior in terms of the concentration and degree of exfoliation achievable. This assumption has subsequently been shown to be true by work done in our group by *Smith et al.* [120]. After centrifugation transmission electron microscopy analysis of the dispersions shows large quantities of mono- and few-layer graphene (Figure 3.1B). The high degree of exfoliation achievable in these dispersions suggests that they may be ideal for applications such as the preparation of thin conducting films.

We have prepared thin graphitic films by vacuum filtration of these graphene-rich, surfactant stabilised dispersions [83]. A photograph of an as-prepared film is shown in Figure 3.1C. These films look uniform to the naked eye but we can quantify the optical uniformity using a transmission scanner. The spatial non-uniformity of the transmittance was $\Delta T/T < 4\%$ (standard deviation of local transmittance measured over $500 \times 500\text{ }\mu\text{m}$ sized pixels $\div$ mean transmission). Using SEM we investigated the film surface ($t = 72\text{ nm}$) more closely as shown in Figure 3.1D. It is clear from this image that these films consist of a disordered array of graphitic flakes lying approximately

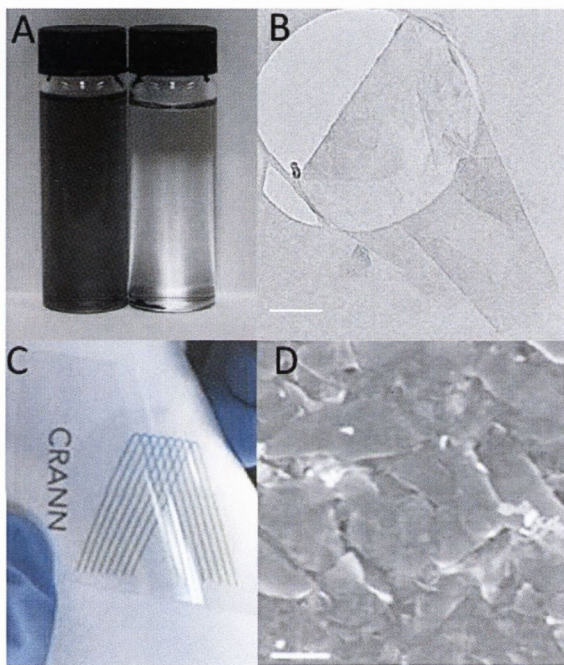


Figure 3.1: Photograph of a water/sodium cholate graphene dispersion before (left) and after (right) centrifugation. B) TEM image of a graphene flake deposited from sodium cholate stabilized aqueous graphene dispersion. (scale bar 100nm) C) Photograph of a graphitic film on PET D) SEM image of a 72-nm-thick graphitic film (scale bar 200nm)

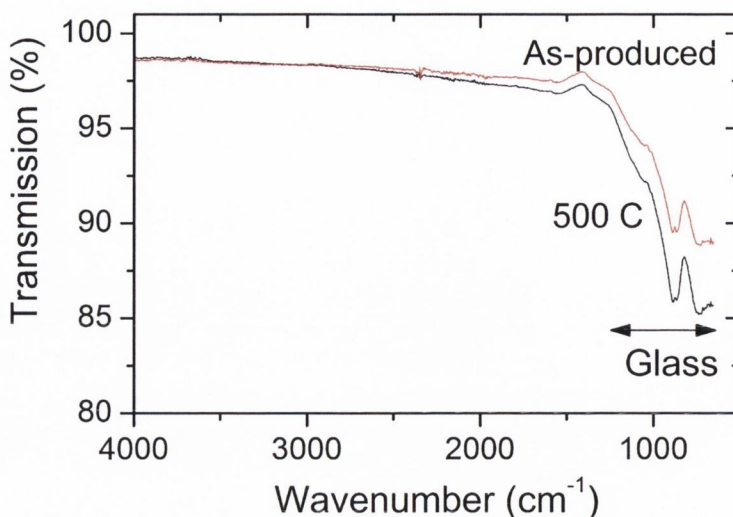


Figure 3.2: ATR-FTIR spectra for both as-produced and annealed graphitic films. Neither spectrum shows any evidence of oxidation.

in the plane of the film. These flakes have lateral dimensions ranging from hundreds of nanometres to a few microns. While it is impossible to gauge their thickness from these images, a number of the flakes appear significantly thicker than monolayers suggesting that some aggregation of the graphene flakes has occurred during film formation. However, some flakes appear partially transparent to the electron beam, suggesting them to be relatively thin.

It is important to note that we prepare these films from dispersions of graphene not graphene oxide [83]; measurements have shown that the dispersion process does not introduce significant quantities of defects or oxides to the flakes. Nevertheless, it is important to confirm the absence of defects or oxides in these filtered films. We test for oxides using FTIR as shown in Figure 3.2. Oxides such as $C=O$ or $C-O$ groups have characteristic features at 1000cm^{-1} and 1600cm^{-1} respectively. These features tend to be relatively intense in FTIR spectra of graphene oxide films [121]. No such features are observed here. We note that the features appearing in Figure 3.2 in the range $600 - 1300\text{cm}^{-1}$ are associated with the quartz substrate.

We can also test for the presence of structural defects using Raman spectroscopy. It is noteworthy that the Raman spot size is approximately ($5\mu\text{m}$) and that this is much larger than flakes meaning one generally will see edges. Examples of typical spectra for

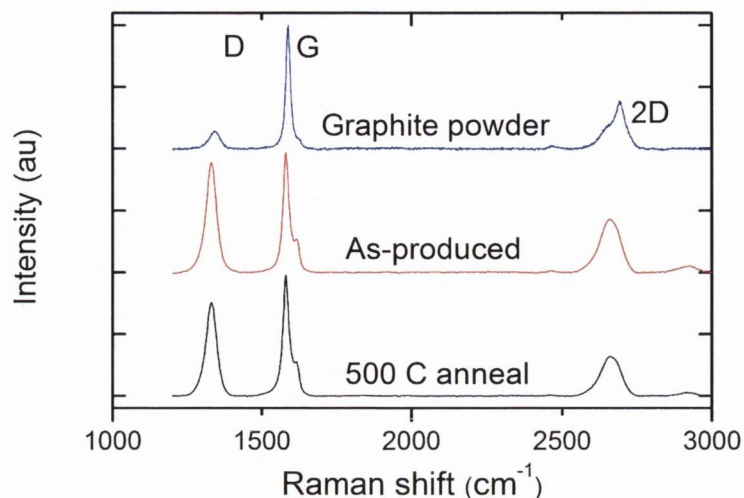


Figure 3.3: Raman spectra (633 nm) for graphite powder, an as-produced film and an annealed film.

a thin film deposited on glass are shown in Figure 3.3. A significant difference between the spectra of the starting graphite powder and the thin films is apparent. Three bands are immediately clear; the *D* band around 1300cm^{-1} , the *G* band around 1600cm^{-1} and the *2D* band around 2650cm^{-1} . The *D* and *2D* bands are of most interest. The *D* band is indicative of the presence of defects, which in graphene are generally divided into basal plane defects and edge defects. Previous studies of graphene exfoliated from graphite using surfactants or amide solvents have shown very small *D* bands which have been attributed to flake edges. In the thin film shown here, this band is relatively intense compared to the smaller band observed in the graphite powder. (In addition the growth of the shoulder at $\approx 1615\text{cm}^{-1}$, known as the *D'* band and is indicative of some defect creation.) [122] At first sight this suggests the presence of basal plane defects, possibly induced during sonication. However, the sonication time employed during this study was a maximum of 5hrs. *Lotya et al.* through a combination of Raman spectroscopy and TEM analysis have demonstrated that the scaling of the Raman *D*-band to *G*-band ratio, I_D/I_G , shows that prolonged sonication up to 460hrs did not measurably damage the flakes or reduce their lateral dimensions through sonication induced scission. Additionally, increasing the centrifugation rate resulted in a reduction of flake dimensions. The I_D/I_G scaling with centrifugation rate is largely consistent with new edges being observed due to overall flake size reductions. The

I_D/I_G ratio observed in this work for dispersion centrifuged at 5000 rpm is consistent with that observed by Lotya *et al.* for the same centrifugation rate [84]. The flake size and Raman data correlate well with surfactant dispersed graphene flakes physically separated by size using column chromatography [123]. The formation of edge defects is inevitable as the sonication process breaks up the starting graphite crystals to form smaller graphene flakes. These flakes have more edges per unit flake area, resulting in a higher edge defect population and hence a higher $D : G$ ratio. Although we have shown that our graphitic films have low defect contents compared to CMGs, it may be advantageous to use a post treatment similar to how graphene oxide is reduced such as an annealing step. There are two reasons for this: micromechanically cleaved graphene is generally annealed to improve electrical performance [91] and by analogy with nanotube films a post-treatment may remove residual surfactant [124].

3.2.2 Thickness dependence

We have measured the thickness dependence of optical and electrical properties of these as-produced and annealed graphitic films. Films were deposited on cellulose membranes by vacuum filtration. These were cut in half and transferred onto glass substrates. This means that the edge of the film corresponding to the cut is reasonably well defined. The edges were imaged by AFM as shown in Figure 3.4 for a film of thickness approximately 30nm. By measuring the step height at the edge, we can measure the film thickness. The film thickness was initially estimated from the concentration of the dispersion. This was calculated as the film volume (M_{film}/ρ_{film}) over the film area (A_{film}), from the absorbance of the dispersions used to prepare the films using:

$$t_{est} = \frac{M_{film}}{\rho_{film}A_{film}} = \frac{A_{disp}V_{disp}}{\alpha_{disp}l} \frac{1}{\rho_{film}\pi R_{film}^2} \quad (3.1)$$

Where A_{disp} and V_{disp} are the dispersion absorbance and volume, α_{disp} is the dispersion absorption coefficient ($1390\text{mlmg}^{-1}\text{m}^{-1}$ [83]), ρ_{film} is the film density (taken as 2200kg/m^3) and R_{film} is the film radius (18mm). The measured film thickness is

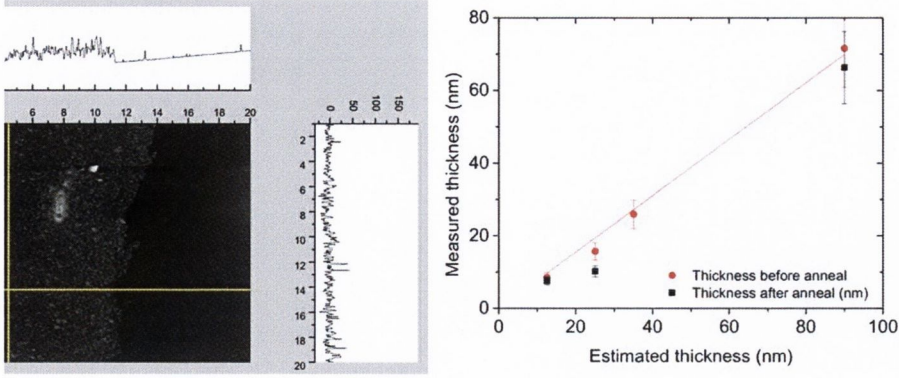


Figure 3.4: AFM image of a film edge. The graphs show film topology along the horizontal and vertical lines shown. Measured film thickness plotted versus estimated film thickness.

plotted versus estimated thickness in Figure 3.4. The slope of this curve can then be used to calculate the true film thickness for all films.

Shown in Figure 3.5 are optical transmission spectra for a range of films. These spectra are broad and featureless as expected for a material composed of 2-dimensional entities. Typically the transmittance varies from 90% to 35% as the thickness increases from 6nm to 88nm (Figure 3.5).

For thin conducting films, the transmittance scales with thickness as

$$T = \left(1 + \frac{Z_0}{2} \sigma_{Op} t\right)^{-2} \quad (3.2)$$

This expression fits well to both data sets with a value of $\sigma_{Op} \approx 4.2 \times 10^4 S/m$ (Figure 3.6A). When one analyses data presented in the literature for reduced GO films, one finds values of σ_{Op} in the range $5 - 10 \times 10^4 S/m$, in reasonable agreement with our value [71, 76, 86]. Shown in Figure 3.6B is data for R_s for each film type. While both data sets decrease with increasing film thickness, the annealed data is significantly lower than the as-produced. In addition while both data sets scale inversely with thickness at high thicknesses, both sets display anomalously high sheet resistances at lower film thickness. This has been observed for films of both carbon nanotubes [45] and silver nanowires [3] and will be expanded upon in chapter 5.

To see this more clearly we calculate the DC conductivity from $\sigma_{DC} = 1/R_s t$, as shown in Figure 3.6C. Note that the conductivity ratio, σ_{DC}/σ_{Op} , is shown on the

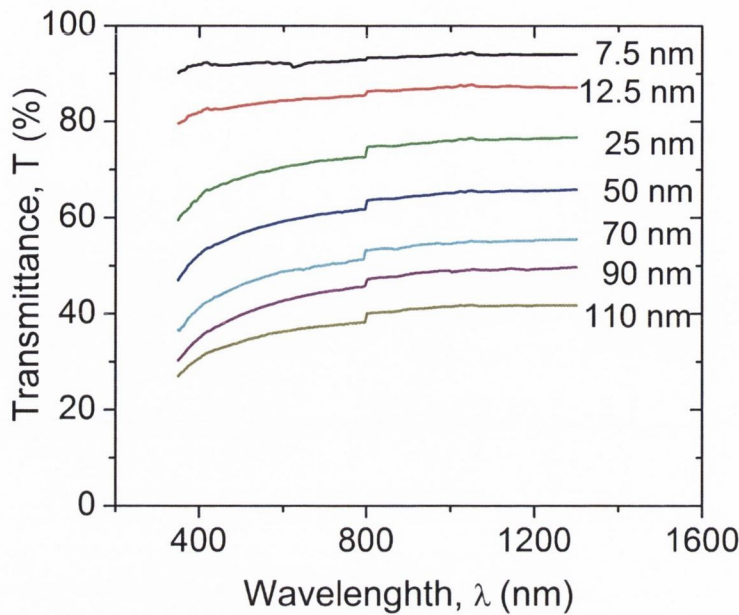


Figure 3.5: Transmittance spectra for thin as-produced graphitic films of various thicknesses. (NB the spectra were not altered by annealing.)

right axis. For both film types the DC conductivity is constant for thicknesses above 20 nm. For the annealed film, $\sigma_{DC} = 1.5 \times 10^4 S/m$ above 20nm. This is equivalent to $\sigma_{DC}/\sigma_{Op} \sim 0.35$. Such a DC conductivity value is close to the best data for chemically modified graphene films [125]. However for thinner films the conductivity falls off significantly. Such behaviour is observed for other nano-structured thin films[3, 45, 96, 101] and has previously been attributed to thickness non-uniformity at low thickness [3, 45]. To study this we measure the film thickness non-uniformity by measuring the spatially resolved absorbance using a transmittance scanner . We define the non-uniformity as the standard deviation of absorbance divided by the mean absorbance. We plot this parameter for both film types in Figure 3.6D. In both cases, the non-uniformity is constant for thicknesses above 20 nm. However below $t = 20nm$ the non-uniformity increases substantially. This behaviour was not well understood at the time of doing this work. A more complete explanation will be given in Chapter 5. For nanotube and nanowire films, it has been suggested that the increase in non-uniformity tends to occur for thicknesses close to twice the nanotube bundle / nanowire diameter [3, 45]. If a similar rule applied here, it would suggest that the graphitic flakes making

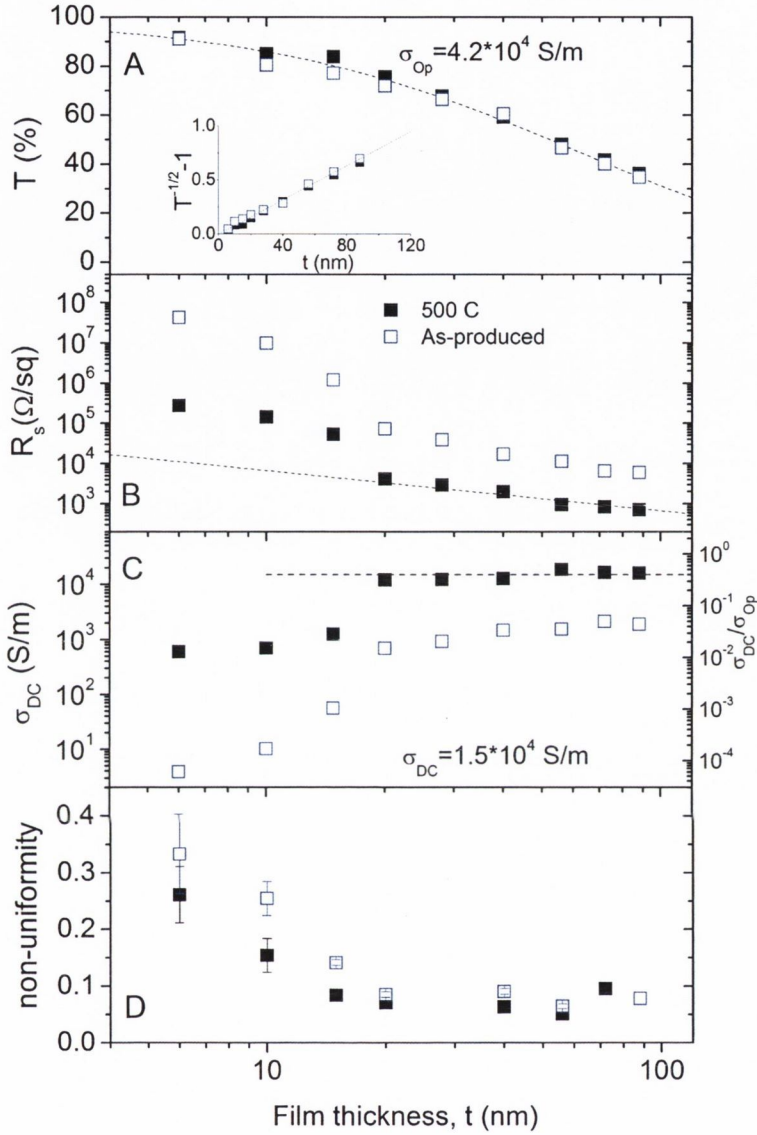


Figure 3.6: Optical, electrical and uniformity data for as-produced and annealed (500⁰C) films. A) Transmittance (550 nm) plotted as a function of film thickness. The dashed line is a fit to equation 2 and is defined by $\sigma_{Op} = 4.2 \times 10^4 S/m$. Inset: The same data is plotted to illustrate the applicability of equation 2. B) Sheet resistance as a function of thickness. The dashed line illustrates bulk behaviour. C) DC conductivity plotted versus film thickness. Note that the DC conductivity falls off below $t = 20nm$. The right axis denotes σ_{DC}/σ_{Op} . D) Film non-uniformity plotted versus film thickness. The non-uniformity is defined as the standard deviation of a set of spatially resolved absorbance measurements divided by the mean absorbance.

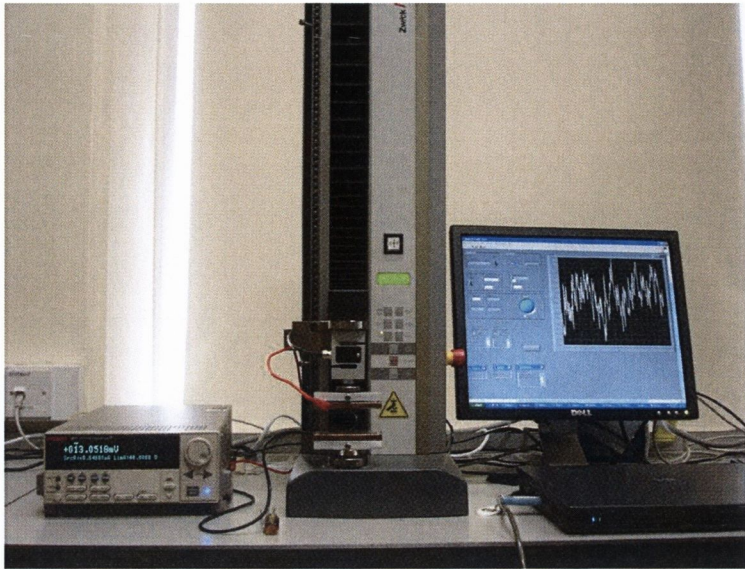


Figure 3.7: Electromechanical test set-up

up the films are 10nm in thickness. This suggests significant aggregation has occurred during film formation. We note that the uniformity is better in the annealed samples. To test this further we performed atomic force microscopy on a number of our films. Such images showed graphitic flakes of sizes similar to those in the SEM images. These flakes displayed a range of heights from a few nm to 10s of nm. We measured the root mean square roughness for films before and after annealing finding values of 13nm and 11nm respectively. The films after annealing were consistently about 20% less rough suggesting that some re-organisation occurs during annealing (Figure 3.4).

3.2.3 Mechanical Properties

Nano-structured, thin, transparent films are most likely to be used in e-paper type applications. Thus they must retain their conductivity under flexing. We monitored the film conductivity under both tensile and compressive bending for two graphitic films on PET of thickness 40 nm and 88 nm as shown in Figure 3.8(The experimental test set-up is shown in Figure 3.7). The films were bent from an initial radius of curvature of 7.5 mm to a final radius of 2.5 mm before being relaxed. This was repeated over many bend cycles. During the first bend cycle (insets) the resistance increased slightly for

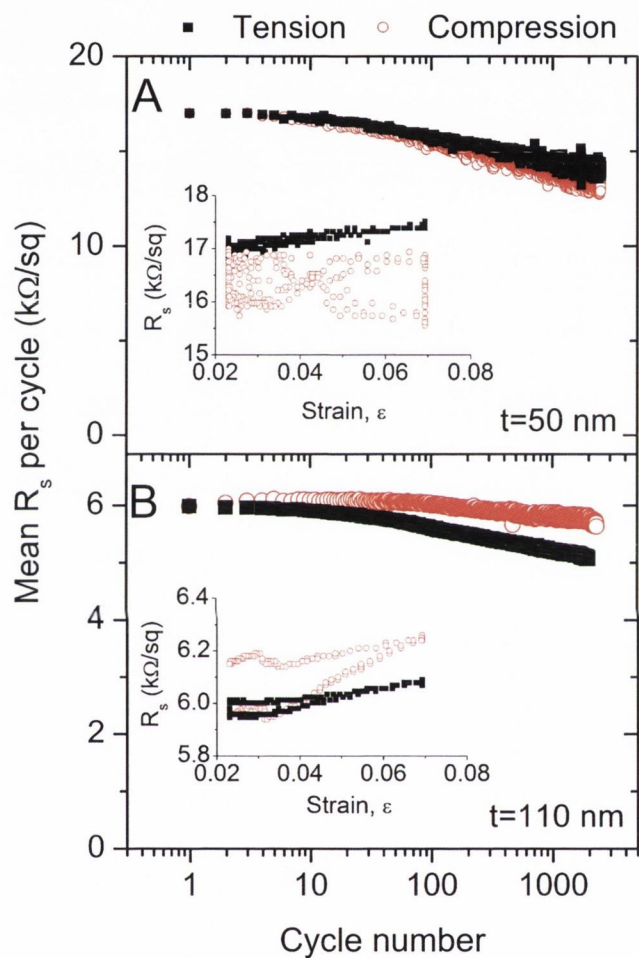


Figure 3.8: Sheet resistance during bending for as-produced films deposited on PET. Measurements were made for films both in tension and compression. Data for A) a 40 nm thick film and B) a 88 nm thick film. Inset: Resistance versus strain for the first cycle. Main graph: Mean resistance per cycle versus cycle number

the films in tension. The compressively bent films displayed more complex behaviour but varied by no more than 6% from the initial resistance. We also plot the mean sheet resistance per cycle for both films. In each case the resistance falls slightly over 2000 cycles. We note that none of the films failed. Rather the measurement was limited by time constraints. The decrease in resistance for films cycled in both tension and compression may be due to some reordering of the network. The repeated cycling could result in a greater connectivity in the network resulting in a lower sheet resistance [126]. Similar behaviour has been observed for films of carbon nanotubes [45].

3.2.4 Comparison with the literature

In general for thin metallic films the transmittance is related to the sheet resistance by [44, 127]

$$T = \left(1 + \frac{Z_0}{2R_s} \frac{\sigma_{Op}}{\sigma_{DC}}\right)^{-2} \quad (3.3)$$

where Z_0 is the impedance of free space and σ_{DC} and σ_{Op} are the DC and optical conductivity, respectively. To that end the transmittance is plotted as a function of sheet resistance in Figure 3.9. Here, both transmittance and sheet resistance fall off as thickness increases. Eqn. 3.3 can be fitted to the data in Figure 3.9 with a good fit obtained for films with $t > 20nm$. This fit gives a value of $\sigma_{DC}/\sigma_{Op} \approx 0.04$ for the as prepared films and $\sigma_{DC}/\sigma_{Op} \approx 0.4$ for the annealed films.

One can use equation 3.3 to estimate σ_{DC}/σ_{Op} from the data presented in the literature for transparent films based on reduced graphene oxide. In all cases these films were reduced thermally with σ_{DC}/σ_{Op} increasing with anneal temperature. For example, *Eda et al.* produced films from hydrazine reduced GO which had been annealed at 200°C [86]. These films had $R_s \sim 10^5 \Omega/sq$ @ $T \sim 85\%$ giving $\sigma_{DC}/\sigma_{Op} = 0.02$. *Li et al.* exfoliated graphite with the aid of acid allowing them to prepare films by the LB technique [121]. These were annealed at 800°C to remove oxides, resulting in films with $\sigma_{DC}/\sigma_{Op} \sim 0.2$ ($R_s \sim 10^4 \Omega/sq$ @ $T \sim 80\%$). *Wu et al.* spun cast GO to produce films which were subsequently annealed at 1100°C to give σ_{DC}/σ_{Op} 0.5

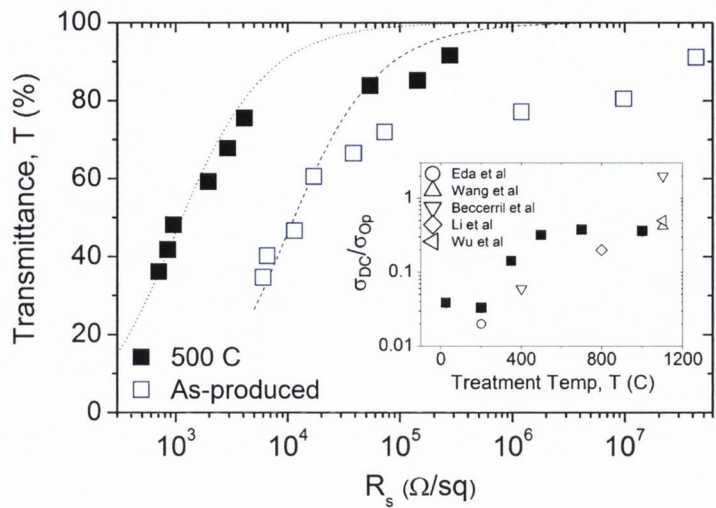


Figure 3.9: Transmittance (550 nm) plotted as a function of sheet resistance for both as-produced and annealed (500C) films. The dashed lines are fits to equation 3.3 and are defined by $\sigma_{DC}/\sigma_{Op} \approx 0.04$ and $\sigma_{DC}/\sigma_{Op} \approx 0.4$ for as-produced and annealed films respectively.

($R_s \sim 3,500\Omega/sq$ @ $T \sim 82\%$) [88]. Wang *et al.* prepared films of GO by dip-coating followed by annealing at 1100°C with $\sigma_{DC}/\sigma_{Op} \sim 0.42$ (R_s $1,800\Omega/sq$ @ $T \sim 64\%$ at 550 nm (quoted data: 70% at 1000 nm)) [76]. Similarly Becerril *et al.* produced GO films by spin coating. By using a combination of hydrazine reduction and annealing at 400°C they achieved $R_s \sim 10^4 k\Omega/sq$ @ $T \sim 60\%$, resulting in $\sigma_{DC}/\sigma_{Op} \sim 0.06$ [71]. By annealing at 1100°C they produced films with $R_s \sim 330\Omega/sq$ @ $T \sim 60\%$, resulting in $\sigma_{DC}/\sigma_{Op} \sim 2$. For comparison purposes, this data is summarised in Figure 3.9 (inset). We note from this data that our graphitic films out-perform the reduced CMG films at all anneal temperatures below 1100°C . We note that while $\sigma_{DC}/\sigma_{Op} \approx 0.4$ is close to the state-of-the-art for thin films from CMG, it is a long way from industrial requirements. The minimum industry standards as set by HP for a transparent electrode are $T > 90\%$ for $R_s < 100\Omega/sq$. This equates to a minimum acceptable value of $\sigma_{DC}/\sigma_{Op} = 35$ for the conductivity ratio. The reasons for this shortfall will be explained in the following section.

3.2.5 Limitations

We use the ratio of DC to optical conductivity, σ_{DC}/σ_{Op} as a figure of merit FoM to compare results for different graphitic film types. The DC conductivity describes charge transport due to constant applied fields, while σ_{Op} controls the motion of electrons in response to optical fields. Both the 2-dimensional DC (static) and optical (dynamic) conductivities of graphene are known and take on quantised values of : $\sigma_{2D,DC} = 4e^2/h$ and $\sigma_{2D,Op} = e^2/4\hbar$, respectively. Hence, a theoretical limit for σ_{DC}/σ_{Op} in monolayer graphene may be considered. Although graphene is a 2-dimensional object and we have been considering 3-dimensional quantities (σ_{DC} and σ_{Op}) it might be suggested that the conductivity ratio in 3-D is equal to its 2-D counter part i.e.

$$\frac{\sigma_{DC}}{\sigma_{Op}} = \frac{\sigma_{2D,DC}}{\sigma_{2D,Op}} = \frac{4e^2/h}{e^2/4\hbar} = \frac{8}{\pi} = 2.55 \quad (3.4)$$

This represents an upper value for σ_{DC}/σ_{Op} for a pristine graphene monolayer or indeed for a stack of weakly interacting monolayers (i.e., randomly stacked monolayers). We may also consider some experimental data. When analysed using Equation 3.2, Nair's transmittance data for micromechanically cleaved graphene suggests $\sigma_{Op} \approx 1.8 \times 10^5 \text{ Sm}^{-1}$ [55]. The sheet resistance of undoped graphene is of the order of $6k\Omega/sq$ (one conductivity quantum per species of charge carriers) [91]. Combining these values yields $\sigma_{DC}/\sigma_{Op} = 2.57$ in close agreement with the theoretical limit. Much like the graphitic films this falls short of meeting minimum industrial requirements. *De et. al* have shown that conductivity ratio values for networks of solution processed graphene flakes cluster around $\sigma_{DC}/\sigma_{Op} = 0.7$ and that this represents fundamental limiting values [128]. They show that similar to carbon nanotube films the DC conductivity controls the variation in σ_{DC}/σ_{Op} . A large variation in σ_{DC} means that the factors pertaining to current flow vary strongly from film to film. It is noteworthy that films made from CMG and pristine graphene have similar conductivity ratios. The fact that these two classes of material are not well differentiated shows that defects common to CMG flakes do not limit the conductivity. This confirms that the conductivity is limited by interflake junctions in both material types rather than the flakes themselves.

3.3 CONCLUSIONS

We have demonstrated the preparation of thin transparent graphitic films from graphene rich surfactant stabilised dispersions. The electrical stability coupled with the high levels of transparency observed and the low cost of graphite make these films attractive as transparent conductors. However, like CMG-based films, these films have a DC conductivity that is much too low for use in transparent electrodes. The DC conductivity is limited by the interflake junction resistance. In addition, the need to anneal although not intrinsic is a big disadvantage.

3.4 EXPERIMENTAL PROCEDURE

Graphite flakes were purchased from Branwell Graphite Ltd (Branwell natural graphite, grade 2369, typical cost $\$5\text{kg}^{-1}$) while sodium cholate surfactant was purchased from Aldrich. Both products were used as supplied. A stock solution of sodium cholate (SC) (5mg/ml) was prepared by stirring overnight in Millipore water. This was subsequently diluted for further use. Graphite (initial concentration 0.75mg/ml) was dispersed in 25ml SC solution (concentration 0.5mg/ml) by sonication for 140min in a low power ultrasonic bath (Branson 1510E-MT bath sonicator). The resulting dispersion was left to stand for 24hr to allow any unstable aggregates to form. The top 80% of the dispersion was decanted and discarded. SC was then added to maintain the starting volume of dispersion at 25ml . This was then sonicated for a further 140mins . Again the dispersion was left to stand overnight and then centrifuged at 5000rpm for 90min (Hettich Mikro 22R). After centrifugation the top 80% of supernatant was decanted and retained for use. The post centrifuge graphene concentration was determined from absorbance measurements (Varian Cary 6000i) using the measured extinction coefficient of graphene in surfactant water solutions ($1390\text{mlmg}^{-1}\text{m}^{-1}$) [83]. The resulting dispersions were vacuum filtered using porous cellulose filter membranes (MF-Millipore membrane, mixed cellulose esters, hydrophilic, $0.025\mu\text{m}$ 47mm) to give thin graphitic films. The thickness of these films was controlled by the volume of

dispersion filtered, and hence the deposited graphene mass. The deposited films were then transferred onto glass slides using iso-propanol to remove trapped air between the film and substrate thus improving adhesion. The cellulose filter membrane was then removed by treatment with acetone vapour and subsequent acetone liquid baths followed by a methanol bath[14]. The final film diameter was 36mm. The film thickness, t , was measured by atomic force microscopy (AFM) . Films were annealed at various temperatures under H_2/Ar flow for 2hr. Optical transmission spectra were recorded before and after annealing using a Varian Cary 6000i. In all cases, a glass slide was used as the reference. Sheet resistance measurements were made before and after annealing using the four-probe technique with silver electrodes of dimensions and spacings typically of ~mm size and a Keithley 2400 source meter. Transmission scans were made using an Epson Perfection V700 photo flat-bed transmission scanner with a bit depth of 48 bits per pixel and a spatial resolution of 6400dpi [45]. The numerical output of the scanner was calibrated by scanning a range of neutral density filters. The resultant calibration curve was used to transform the output to represent transmittance which could be transformed in to absorbance using the Lambert-Beer law. This results in a transmittance/absorbance map with a datum for every pixel. Scanning electron microscopy measurements were made using a Zeiss Ultra plus SEM. Raman spectra were taken on a Horiba Jobin Yvon LabRAM-HR using a 100 $\times$ objective lens with a 633nm laser excitation. Attenuated total reflectance FTIR spectra of these films were taken on a Perkin-Elmer Spectrum 100. AFM measurements for surface roughness and thickness were taken with a Digital Instruments Nanoscope IIIA from Veeco Systems in tapping mode using silicon tips with a resonance frequency of 320kHz. Electromechanical measurements were made using a Zwick Zo.5 Proline tensile tester. In this case, the nanotube film was deposited on PET and was bent into a semicircle which was constrained by the grips of the tensile tester. The film was connected via two electrodes (attached to the grips) to a Keithley KE 2601. The bend radius was then defined by the distance between the grips. The inter-grip distance was then oscillated between typically 15mm and 5mm over many cycles. LabVIEW software recorded film resistance, inter-grip distance and cycle number [45, 96].

IMPROVEMENT OF TRANSPARENT CONDUCTING NANOTUBE FILMS BY ADDITION OF SMALL QUANTITIES OF GRAPHENE

4.1 INTRODUCTION

In terms of ITO replacement materials carbon nanotubes are probably the most intensely studied material, displaying performance close to that required for industry with reports of σ_{DC}/σ_{Op} between 25 and 35 [10, 14, 35, 101]. However, while many papers have been published, only marginal improvements have been reported for nanotube films over the past few years. The state of the art for nanotube films has remained virtually unchanged over the last 3 years and stands at $R_s = 100\Omega/sq$ for $T \sim 85\%$ (this works out to be equivalent to $\sigma_{DC}/\sigma_{Op} = 25$; while $\sigma_{DC}/\sigma_{Op} = 35$ has been reported, this was for films with lower transmittance, $T = 70\%$) [35, 101]. Effectively, the conductivity of nanotube networks has not improved over this period, remaining close to $5 \times 10^5 S/m$ (after post-treatment such as acid treatment) [35, 101]. Further improvements are required to challenge indium tin oxide as a viable alternative material for transparent conductors. We believe that this will require a significant shift away from the current strategies of improving film formation and post-treatment techniques.

Recently, it was reported that hydrazine-reduced, SWNT/graphene oxide hybrid films displayed improved sheet resistance and transmittance relative to either nanotube-only or graphene-oxide-only films [129]. This result is important as it shows that nanotube films can be improved upon. However, in an industrial setting, the requirement for hydrazine reduction will be a barrier to the uptake of this technology if a cheaper, easier alternative is available. In fact, reduction, either thermally or by chemical treatment, is unnecessary if pristine graphene is used rather than graphene oxide.

In the previous chapter we examined the suitability of networks of graphene flakes as an alternative to ITO as a transparent conductor due to graphite costing much less than carbon nanotubes. Although unsuited as a transparent electrode the advancements made in terms of liquid phase processing of graphene enable the production of graphene/SWNT hybrids without the need for oxidation or reduction.

In this work, we demonstrate such a method to prepare graphene/nanotube hybrid films. We build on our previous work which demonstrated that graphene can be exfoliated non-destructively using certain solvents or surfactants [31, 78, 83, 130]. We show that individual surfactant-stabilized nanotube and graphene suspensions can be blended to prepare hybrid suspensions which can be cast into hybrid films. These hybrid films display an optimum composition compared to the nanotube-only film resulting in a peak in the DC conductivity [32].

4.2 RESULTS AND DISCUSSION

4.2.1 *Film Morphology*

We prepare a series of hybrid films with a constant thickness of 60nm but with varying graphene content from 0% (SWNT only) to 100%. Shown in Figure 4.1 is a set of representative SEM images of the surfaces of hybrids of various compositions. Figure 4.1A is typical of a thin nanotube film, showing a random array of bundles and significant porosity. Figure 4.1B shows a 3wt% graphene hybrid. Here a small number of isolated submicrometer graphene flakes appear dispersed within the nanotube matrix. As the graphene content is increased from Figure 4.1C to Figure 4.1E, the graphene flakes first appear to fill the pores between nanotubes before starting to dominate the films. Figure 4.1F is an image of graphene-only film which clearly shows the flake size to range from $< 100nm$ to a few hundred nanometres.

The SEM images discussed above give no real information about the aggregation state of the graphene. However, we can get some information on the flake thickness from Raman spectroscopy [1]. We measured the Raman spectra of the films described

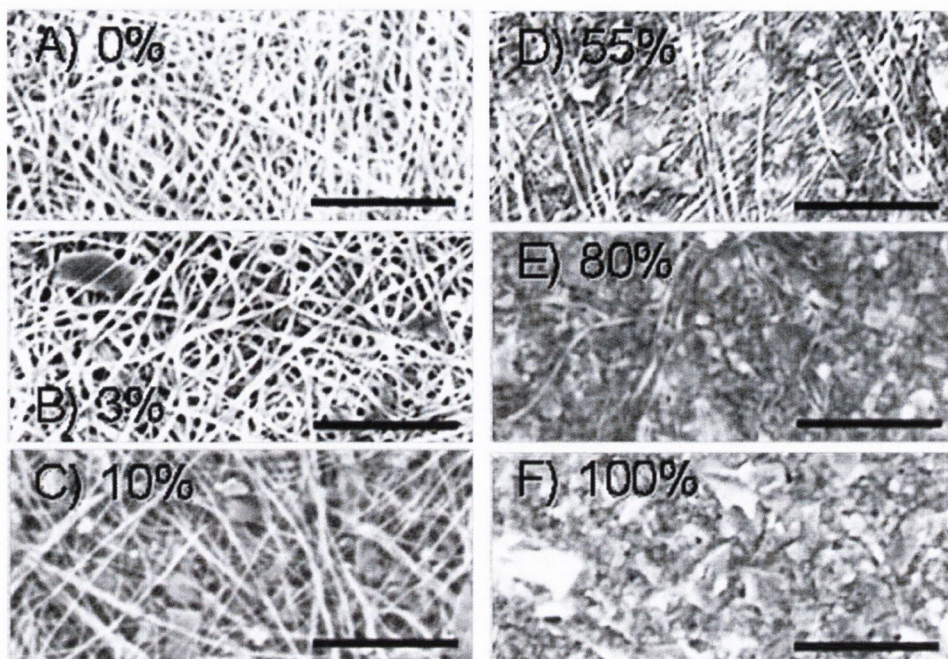


Figure 4.1: SEM images of some of the films studied in this work. A) A 0% graphene (nanotube-only) film, B), C), D), E) Hybrid films with 3wt%, 10wt%, 55wt% and 80wt% graphene respectively. F) 100% graphene film. In all cases the scale bar is 500nm

above. For each film, we measured five spectra, normalized, and averaged them to give a representative spectrum for each composition. A subset of these averaged spectra are shown in Figure 4.2 along with the spectrum of graphite powder for comparison. In general, as all hybrid spectra are dominated by the nanotube component, we focus on hybrids with low nanotube content. For example, the G band ($\sim 1600\text{cm}^{-1}$) becomes dominated by the nanotube component even for the 90 wt % graphene film. However, of most interest is the 2D band close to 2600cm^{-1} . The 2D band for the graphene-only film is clearly different than that of the graphite powder. For the graphene film, the more symmetric line shape is representative of graphene flakes with 2 – 5 layers and shows that the flakes remain exfoliated, even during film formation [1, 122]. The 2D band of the 90wt% graphene hybrid is dominated by the nanotube component. However, the shoulder due to the graphene component can be seen between 2650cm^{-1} and 2700cm^{-1} . This shoulder is at the same position as the graphene 2D band but is clearly too low in wavenumber to be associated with the graphite 2D band. This

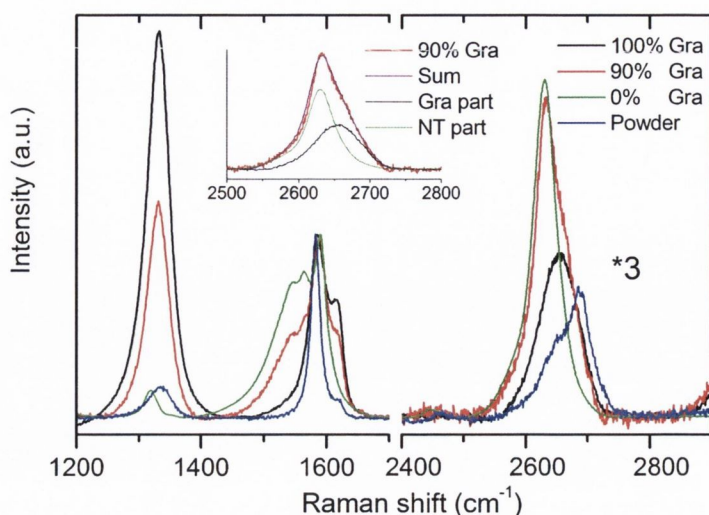


Figure 4.2: Raman spectra for some of the films studied in this work, 100% graphene, 90% graphene and 0% graphene (nanotube-only). Shown for comparison is a Raman spectrum of the starting graphite powder. N.B. The portion of the graph above 2400cm^{-1} has been multiplied by a factor of 3 for clarity. Inset: Spectra for graphene-only (black) and nanotube-only (green) films. A weighted average of these (purple) gives a spectrum almost identical to the 90% graphene spectrum (red).

suggests that the graphene in the 90% film remains exfoliated even after film formation. If this is the case, the 2D band for the 90% graphene hybrid should be identical to a weighted summation of the 2D peaks for the nanotube-only and graphene-only films. This is illustrated in the inset where the peak marked “sum” is the weighted sum of the graphene and nanotube parts (also shown, these components were produced by weighting the curves in the main figure by factors of 0.75 and 0.65, respectively). The sum peak is almost identical to the measured peak for the 90% hybrid. This shows that, during film formation, graphene does not re-stack to form graphite but remains in the form of flakes with 2 – 5 layers. Given that this is the case for films with 90 and 100% graphene, it is very likely to hold for hybrids with lower graphene content.

4.2.2 Dependence of Optical and Electrical Properties on Film Composition

Transmission spectra were measured for all films using a Carian Cary 6000i spectrophotometer. All spectra were reasonably flat in the visible regime (Figure 4.3). The

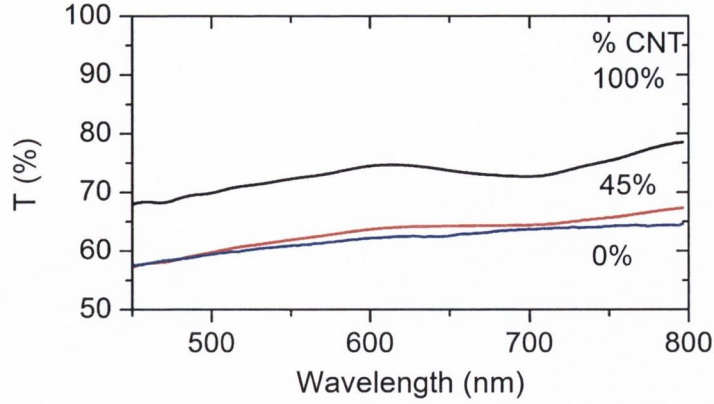


Figure 4.3: Transmittance spectra for a number of 60 nm thick films.

transmittance (550nm) is plotted as a function of mass fraction in Figure 4.4A (black squares). The transmittance decreases with increasing graphene content, falling from 73 – 70% for $< 10wt\%$ graphene samples to 60% for the $100wt\%$ film. This is due to the fact that graphene is a highly absorbing material (each graphene sheet absorbs 2.3% of incident light) [55]. While the optical conductivity for nanotube networks is close to $\sigma_{Op} \sim 1.7 \times 10^4 S/m$ [45], that for networks of graphene flakes is significantly higher, taking values up to $\sigma_{Op} \sim 2 \times 10^5 S/m$ [31, 128], due to the higher optical conductivity of graphene itself [55]. The optical conductivity of the graphene films used in this work was measured in the previous chapter as $\sigma_{Op} \approx 4.2 \times 10^4 S/m$.

Sheet resistance (R_s) measurements were made using the four-probe technique with silver electrodes of dimensions and spacings typically of approximately millimeter size and a Keithley 2400 source meter. Shown in Figure 4.4B is the sheet resistance measured for 60nm thick hybrid films of varying graphene content. The sheet resistance of the 100% nanotube sample was $165\Omega/sq$. Interestingly, the resistance decreases slightly to a minimum of $140\Omega/sq$ for the 3 wt % graphene sample, before increasing steadily with increasing graphene content, reaching $8.4k\Omega/sq$ for the graphene-only film. We can calculate the nominal direct current (DC) conductivity, DC, from the sheet resistance using $\sigma_{DC} = (Rst)^{-1}$, where t is the film thickness (Figure 4.4C). The DC conductivity increases from $10^5 S/m$ for the nanotube-only sample to a maximum of $1.2 \times 10^5 S/m$ for the 3wt% graphene sample before falling off to $2,000 S/m$ for the graphene-only sample. The presence of a peak in DC conductivity is interesting as it

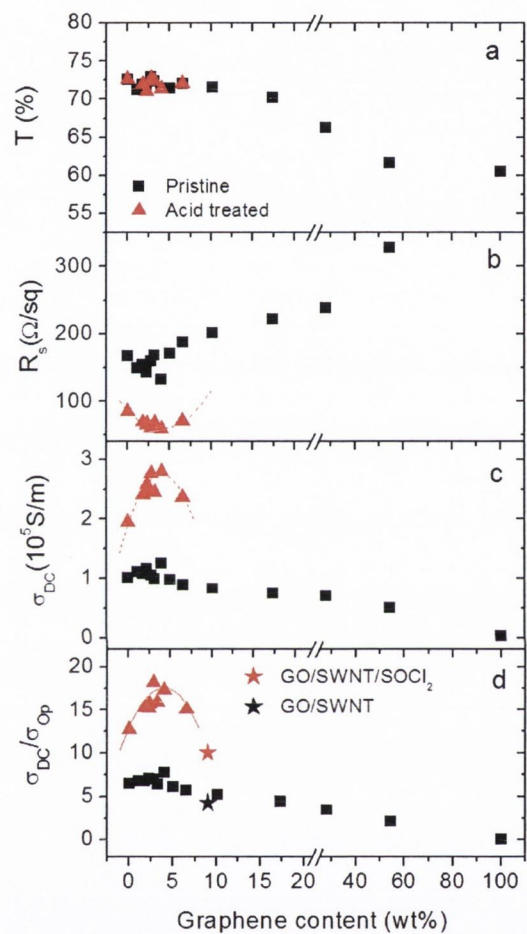


Figure 4.4: Optical and electrical properties of graphene/nanotube hybrid films as a function of graphene content for both pristine and acid treated films. A) Transmittance (550 nm), A) sheet resistance, C) DC conductivity and D) DC to optical conductivity ratio. In B), C) and D), the dashed line is a guide to the eye. Also marked in D) are the results of *Tung et al.* for hydrazine reduced graphene-oxide / SWNT films both before and after doping with SOCl_2 .

suggests that addition of graphene can actually improve the electrical properties of nanotube-based films. This is in spite of the fact that graphene networks tend to have DC conductivity significantly below $10^5 S/m$ (and lower than the best nanotube films [14, 45, 101]) . However, it must be noted that it is very difficult to accurately measure the film thickness for nanostructured networks. This means that, while sheet resistance measurements are reliable, DC conductivity measurements can have significant error. Thus, the peak referred to above may not actually exist. This means that such an observation must be confirmed by a measurement which does not rely on accurate knowledge of film thickness.

In order to avoid the effects of inaccurate thickness measurements and to facilitate comparison with other systems, we can characterize the films in terms of the DC to optical conductivity ratio, σ_{DC}/σ_{Op} .

$$T = \left(1 + \frac{Z_0}{2R_s} \frac{\sigma_{DC}}{\sigma_{Op}}\right)^{-2} \quad (4.1)$$

Shown in Figure 4.4D are the calculated values of σ_{DC}/σ_{Op} as a function of graphene content. The conductivity ratio does indeed show a peak, increasing from 6.5 for the nanotube-only film to 7.6 for the 3wt% graphene film before falling off to 0.08 for the graphene-only film. This peak is important as it illustrates the presence of an optimum composition. Higher values of σ_{DC}/σ_{Op} result in better transparent conductors. Thus, addition of very small amounts of graphene can noticeably improve the properties of the material. This is vital for materials such as nanotubes where only marginal improvements in performance have been observed in recent years.

We note that the values of σ_{DC} and σ_{DC}/σ_{Op} for the nanotube-only films are slightly lower than expected for these tubes [45, 101]. These results were obtained from a recently purchased batch of arc discharge SWNTs (ILIIN Nanotech.), which gave films of slightly lower conductivity than previous batches (possibly due to shorter tube length distribution [38]). However, we note that similar improvements at low graphene content were also observed for preliminary measurements made with a previous, more conductive batch of nanotubes [45]. With that batch, we obtained NT films and hybrids with conductivity ratios of 10.5 and 13.5, respectively (no acid treatment). We note that $\sigma_{DC}/\sigma_{Op} = 10$ is close to the best reported performance of nanotube

films without post-treatment [35, 45, 96, 101]. (Acid treatment generally results in the increase in performance to $\sigma_{DC}/\sigma_{Op} = 25 - 35$) [35, 101]. This shows that the observed improvements apply to state of the art films rather than just films with lower performance.

We can compare the data in Figure 4.4D with the results of *Tung et al.* on hydrazine-reduced graphene oxide/nanotube films [129]. Their best results were for a graphene oxide content of 8wt%, where we calculate that they achieved $\sigma_{DC}/\sigma_{Op} \approx 4$. Interestingly, this datum falls close to our data (Figure 4.4D)

4.2.3 Film Thickness dependence

We have identified an optimum composition of 3wt% graphene from our data and prepared films with a range of nominal thicknesses from $t = 15nm$ to $200nm$. As t increases, T falls off monotonically, as shown in Figure 4.5A. We can model this behaviour using the expression

$$T = (1 + Z_0\sigma_{Op}t/2)^{-2} \quad (4.2)$$

The fits is excellent giving $\sigma_{Op} = 1.64 \times 10^4 S/m$ similar to the values of $1.5 - 2.0 \times 10^4 S/m$ reported for carbon nanotube films [45, 124].

In addition, R_s decreases with increasing thickness, reaching $40\Omega/sq$ for $t = 200nm$. We note that anomalously high R_s was observed at lower film thicknesses. This can be seen in the slight deviation between the measured data in Figure 4.5B and the dashed line that illustrates bulk-like behaviour (defined by $\sigma_{DC} = 1.3 \times 10^5 S/m$). This can be seen more clearly by plotting σ_{DC} or σ_{DC}/σ_{Op} (Figure 4.5C,D) versus thickness. Both quantities are reasonably constant for $t > 40nm$, displaying values of $\sigma_{DC} = 1.5 \times 10^5 S/m$ and $\sigma_{DC}/\sigma_{Op} = 8$. However, for thinner films, both fall off significantly. This is commonly observed in thin films of nanostructured materials and occurs when the film thickness approaches the dimensions of the nanostructure making up the film (i.e., the nanotube bundle diameter or the graphene flake thickness) [3, 31, 45, 101]. This phenomenon has been attributed to a combination of percolative effects and thickness

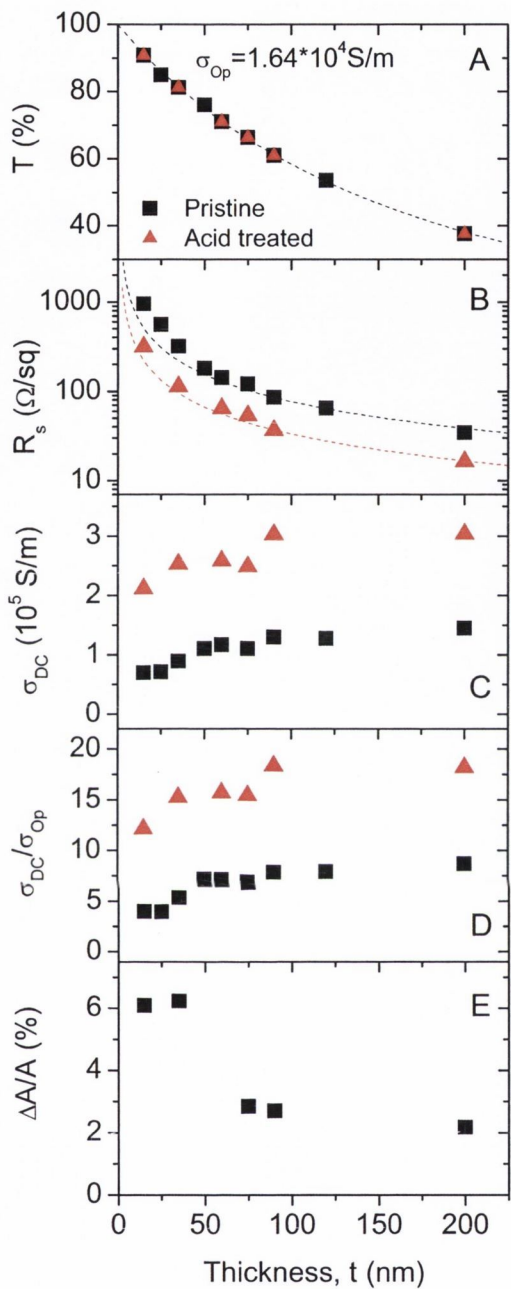


Figure 4.5: Optical and electrical properties of graphene/nanotube hybrid films with optimized graphene content (3wt%), as a function of film thickness both before and after acid treatment. (A) Transmittance (550nm), (B) sheet resistance, (C) DC conductivity, (D) DC to optical conductivity ratio, and (E) optical non-uniformity of films. In (A), the dashed line is fit to eqn. 4.2. In (B), the dashed lines represent bulk behaviour as described by $R_s = (\sigma_{DC}t)^{-1}$ with $\sigma_{DC} = 1.3 \times 10^5$ and $3 \times 10^5 \text{ S/m}$ for the pristine and acid-treated films, respectively. Note the deviation from bulk behaviour for $t < 50 \text{ nm}$. This is also seen in (D) and (E).

non-uniformity at low thickness. Similar trends have been observed for films of carbon nanotubes, graphene, and silver nanowires [3, 31, 45, 101]. We can gauge the thickness non-uniformity by measuring the spatially resolved transmittance (pixel size $5\mu\text{m}$) using a transmission scanner, defining the non-uniformity as the standard deviation of local absorbance divided by the mean absorbance, $\Delta A/A$ [45]. This parameter is plotted in Figure 4.5E. $\Delta A/A$ is constant for thicknesses above 40 nm. Below this, the non-uniformity increases substantially. We plot transmittance versus sheet resistance for varying thickness (3 wt % graphene) in Figure 4.6. Equation 4.1 can be fitted to these data with a good fit obtained for films with $t > 40\text{nm}$. This fit gives a value of $\sigma_{DC}/\sigma_{Op} = 8$ for the as-prepared films.

4.2.4 Acid Treatment

It is well-known that acid treatment significantly reduces R_s for nanotube networks due to reduction of junction resistance [35, 101]. *Geng et al.* have shown that acid treatment of sodium dodecyl sulphate (SDS) dispersed CNT networks resulted in the removal of a considerable amount of SDS such that the conductivity of the film was significantly improved [101]. No significant doping effects were observed. *Nirmalraj et al.* found that the junction resistance of nitric acid treated CNT networks was reduced over that of pristine tubes [35]. The largest reduction was observed for junctions comprised of single tubes, where a 3-fold drop is observed. They also found that acid treatment only results in a small increase ($\sim 30\%$) in tube conductivity. Therefore, increases in film conductivity attributed to acid treatment have much more to do with a 3-fold reduction in junction resistance rather than a small increase in the conductivity of the interconnecting tubes. Hence, we have treated a number of films of varying mass fraction around the optimum (3wt%) by soaking them in concentrated nitric acid and rinsing with water [101]. We measured the transmittance and sheet resistance of such films. In addition, we calculated σ_{DC} and σ_{DC}/σ_{Op} . While it does not affect the film transmittance (Figure 4.5A), acid treatment reduces R_s by a factor of 2.5 – 3, as shown in Figure 4.5B. We observed a well-defined peak in the R_s versus composition curve

with a minimum sheet resistance of $R_s = 60\Omega/sq$ at a graphene content of 3wt%. In addition, commensurate increases were observed for both σ_{DC} and σ_{DC}/σ_{Op} (Figure 4.4C,D). Notably, the peaks in σ_{DC} and σ_{DC}/σ_{Op} become much more well-defined, confirming the presence of an optimum composition. The best results occur for the acid-treated 2.8wt % graphene film which displays $\sigma_{DC} = 2.8 \times 10^5 S/m$ and $\sigma_{DC}/\sigma_{Op} = 18$. Thus, after acid treatment, addition of graphene to a nanotube film results in an increase in σ_{DC}/σ_{Op} from 12.5 to 18, an increase of 40%. Tung *et al.* chemically treated their graphene oxide/nanotube films with $SOCl_2$, achieving $\sigma_{DC}/\sigma_{Op} \approx 10$ [129]. We note that our best results are significantly higher. This, coupled with the simplicity of our technique, makes this a promising process.

We have also measured the thickness dependence of the optical and electrical properties of the acid-treated films, as shown in Figure 4.5A. As with the pristine films, both σ_{DC} and σ_{DC}/σ_{Op} are constant at thickness $< 40nm$ but tend to fall off at lower thickness. Shown in Figure 4.6 is the transmittance for the acid-treated films plotted as a function of sheet resistance. This shows that we can achieve films with transmittance of 80% coupled with a sheet resistance of $100\Omega/sq$. We note that these acid-treated films are very stable. We have measured the transmittance and sheet resistance of the films shown in Figure 4.6 three months after preparation. No discernible changes in the properties were found. Similar stability was found by Dan *et al.* for acid-treated nanotube films [94].

4.2.5 Mechanism

It is important to understand the nature of the peak in DC conductivity, and hence σ_{DC}/σ_{Op} , for compositions close to 3wt%. It is known that the conductivity of carbon nanotube networks is limited by the intertube junction resistance [35, 46]. We propose that the junction resistance between a nanotube and a graphene flake may be significantly smaller than that between two nanotubes (or two bundles). Thus, the presence of a graphene sheet in contact with two nearby nanotubes could act to circumvent the nanotube-nanotube junction and promote internanotube charge transport.

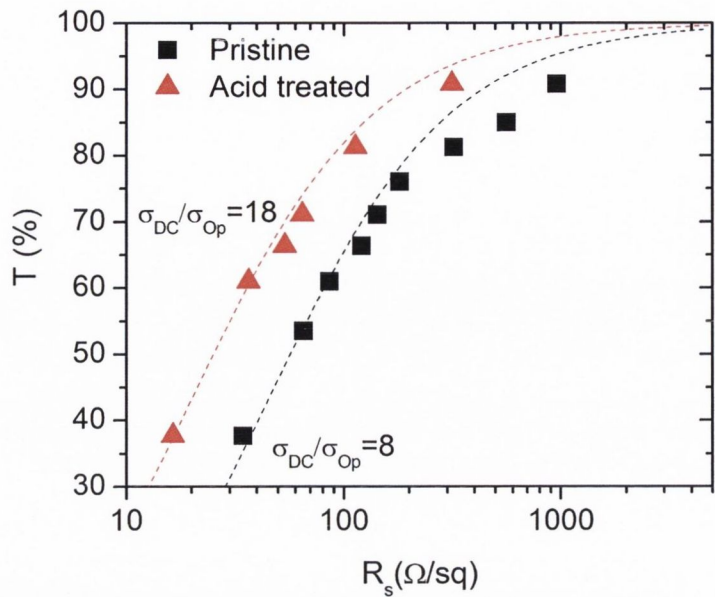


Figure 4.6: Opto-electrical properties of hybrid films with optimised graphene content (3wt%). Transmittance (550 nm) is plotted as a function of sheet resistance for both as produced films and acid treated films. The dashed lines are fits to equation 4.1.

This would be manifested by an increase in the conductivity of the film. Within this hypothesis, addition of small amounts of graphene should result in a conductivity increase which scales with graphene content. However, as the graphene content is increased further, the graphene may act to swell the nanotube network, thus increasing the resistance of the nanotube-nanotube junctions still carrying appreciable current. This would be manifested by a turnover and subsequent drop in film conductivity. It is likely that smaller flakes can fit into the space between SWNTs without deforming the network. As the graphene content is increased further, the electrical properties of the film become dominated by the graphene with the DC conductivity approaching that for a graphene-only film. This model is also consistent with the observation that the electrical properties improve markedly on acid treatment. Exposure to acid tends to remove residual surfactant, resulting in a decrease in junction resistance [35, 124]. Surfactant removal may be more effective for nanotube-graphene junctions resulting in an amplification of the peak after acid treatment.

4.3 CONCLUSIONS

A simple water-based technique to prepare nanotube-graphene hybrids has been demonstrated. An optimum composition of 3wt% graphene was found. Acid treatment of the films results in an increase in figure of merit by 40%. The strength of this process is that it can be used to improve already good quality films.

4.4 EXPERIMENTAL PROCEDURE

We prepared graphene dispersions by adding graphite (Branwell natural graphite, grade 2369) to a solution of sodium cholate (NaC) surfactant in water (0.1mg/mL NaC) such that the graphite concentration was 5mg/mL. This dispersion was then sonicated in a sonic bath for 48h. The resulting dispersion was left to stand for 24 h to allow any unstable aggregates to form. This was then centrifuged at 15000 rpm for 90 min (Hettich Mikro 22R). After centrifugation, the top 80% of supernatant was decanted and retained for use. We prepared single walled nanotube (Iljin nanotech) dispersions in a similar manner by adding nanotubes to a solution of NaC surfactant in water (5mg/mL NaC) such that the nanotube concentration was 1 mg/mL. This dispersion was subjected to 5 min of high-power tip sonication (VibraCell CVX; 750W, 20% 60kHz), then placed in a sonic bath for 1 h, and then subjected to another 5 min of high-power sonication. The dispersions were then allowed to rest overnight before being centrifuged at 5500 rpm for 90 min. The supernatant was carefully decanted and saved. We measured the concentration after centrifugation by measuring the absorbance spectrum of each dispersion and recording the absorbance per unit cell length, A/l , at 660 nm. From the Lambert Beer law, this gives the concentration once the extinction coefficient, is known ($A = \alpha Cl$). The extinction coefficient for surfactant-dispersed nanotubes has been measured to be $\alpha_{SWNT} = 3389 \text{ mLmg}^{-1} \text{m}^{-1}$ [28]. We determined the extinction co-efficient for the NaC-dispersed graphene by measuring A/l at 660nm for a large known volume of dispersion, sonication time 24hr, centrifugation rate 5000 rpm. This dispersion (in excess of 400 mL volume) was filtered

through a preweighed porous membrane. The membrane was dried and reweighed to give the deposited mass. The proportion of graphitic mass on the filter membrane was determined using TGA analysis. This gave a value of $\alpha_G = 6600 \text{ mL mg}^{-1} \text{ m}^{-1}$ [84]. Once the concentrations were determined, these dispersions were blended in the ratio required to give the desired graphene/nanotube mass fraction. Mass fractions between 0 and 100% graphene were prepared. The mixtures were then sonicated for 15 min in a sonic bath to homogenize. The resulting dispersions were vacuum-filtered using porous cellulose filter membranes (MF-Millipore membrane, mixed cellulose esters, hydrophilic, 0.025 μm , 47 mm) to give thin films. The thickness of these films was controlled by the volume of dispersion filtered and hence the deposited mass. The deposited films were washed with 200 mL of Millipore water followed by a wet transfer to a polyethylene terephthalate (PET) substrate using heat and pressure [14]. The cellulose filter membrane was then removed by treatment with acetone vapour and subsequent acetone liquid baths followed by a methanol bath. The final film diameter was 36 mm. For acid treatment, films were immersed in 65% nitric acid for 2 hr followed by rinsing with Millipore water. Optical transmission spectra were recorded in the visible range (400 – 800 nm) using a Varian Cary 6000i. In all cases, PET was used as the reference. R_S measurements were made using the four-probe technique with silver electrodes of dimensions and spacings typically of approximately millimeter size and a Keithley 2400 source meter. Transmission scans were made using an Epson Perfection V700 photo flat-bed transmission scanner with a bit depth of 48 bits per pixel and a spatial resolution of 6400 dpi. SEM measurements were made using a Zeiss Ultra plus SEM. Raman spectra were obtained using (Horiba Jobin Yvon LAbRAM-HR, 633 nm) on films transferred to glass substrates.

SIZE EFFECTS AND THE PROBLEM WITH PERCOLATION IN NANOSTRUCTURED TRANSPARENT CONDUCTORS

5.1 BACKGROUND

It is crucial to rate and benchmark the performance of new materials against known standards in transparent conductor research. To facilitate this a figure of merit (FoM) may be introduced. In the past, FoMs based on the Lambert Beer law have been used. According to this law, the transmission of light (T) through a film of homogeneous material can be modelled as

$$T = I/I_0 \quad (5.1)$$

$$T = e^{-\alpha t} \quad (5.2)$$

where I_0 and I are the intensity of incident and transmitted light, α is the absorption coefficient and t is the film thickness. The sheet resistance is defined as

$$R_s = \rho/t = 1/(\sigma t) \quad (5.3)$$

where ρ is the material resistivity. Combining the equations for T and R_s yields

$$R_s = -\frac{\alpha \rho}{\ln T} \quad (5.4)$$

or

$$T = \exp\left(-\frac{\alpha \rho}{R_s}\right) \quad (5.5)$$

One can define $(\alpha \rho)$ as a FoM₁. For a uniform and homogeneous material, $(\alpha \rho)$ is a constant parameter; therefore, sheet resistance depends linearly on $(-1/\ln T)$

with FOM_1 as the slope (Intuitively, FOM_1 is also the sheet resistance of a film with a transparency of $e^{-1} = 36.8\%$) [94].

In the specific area of transparent conductors from nanostructured materials, a slightly different but analogous system is often used. As shown in section 1.4 the transmittance is related to the sheet resistance by the following equation

$$T = \left(1 + \frac{Z_0}{2R_s} \frac{\sigma_{Op}}{\sigma_{DC,B}}\right)^{-2} \quad (5.6)$$

Here the FoM is the ratio of the DC to optical conductivity, $\sigma_{DC,B}/\sigma_{Op}$. The authors favour this expression because of the aesthetic advantages of a dimensionless FoM. However, we note that eqns. 5.5 and 5.6 are essentially equivalent (i.e., by expanding to first order) [94]. In addition, in both eqns. 5.5 and 5.6, we use the bulk value of the DC conductivity (σ_{DC}) as is implicitly assumed in all transparent conductor papers. However, as we will see below, this is not always appropriate. Using eqn. 5.6, the requirement that $R_s < 100\Omega/sq$ coupled with transmittance $T > 90\%$ can be stated very simply as $\sigma_{DC,B}/\sigma_{Op} > 35$. This has been surpassed for networks of silver nanowires with values of $\sigma_{DC,B}/\sigma_{Op} > 400$ reported [3]. This extremely high conductivity ratio for silver nanowire networks would suggest that the problem of ITO replacement has been solved. However, if one looks more closely at the data this conductivity ratio was achieved for a transmittance approaching 32% for $R_s \sim 0.5\Omega/sq$. On inspection of the full data set for T versus R_s one finds that the data fits to eqn. 5.6 only for low R_s corresponding to thick films (Figure 5.1, black dashed line). For $R_s > 3\Omega/sq$, the data deviates significantly from the theoretical line. The same behaviour is observed for other nanostructured materials such as graphene as illustrated within this work and carbon-nanotubes [45]. Figure 5.1 shows data for single walled nanotubes, silver nanowire and graphene published by our group [3, 31, 45]. The same behaviour can be observed in published data for a large number of nanostructured materials. In the majority of cases, the deviation from expected behaviour begins to occur for films with $T < 90\%$. This is significant as it means the expected bulk-like behaviour does not occur in the technologically relevant regime ($T > 90\%$).

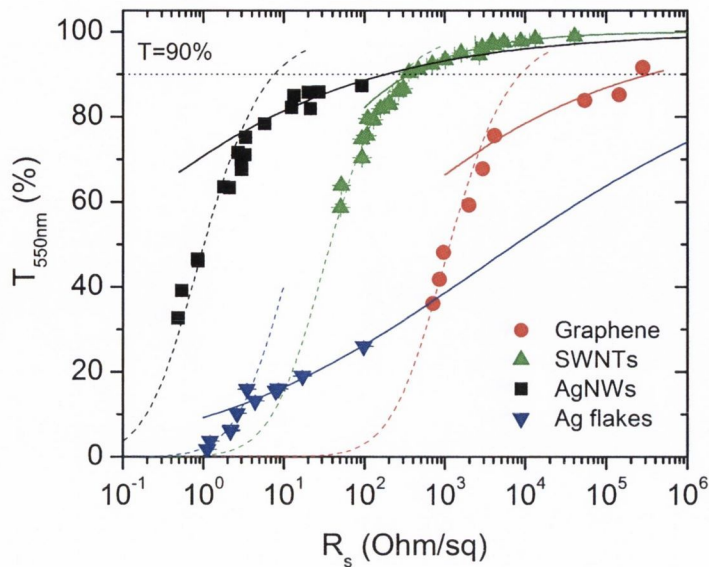


Figure 5.1: Transmittance (550 nm) plotted as a function of sheet resistance for thin films prepared from four nanostructured materials-graphene, singlewalled carbon nanotubes, silver nanowires and silver flakes [3, 31, 45, 95]. The dashed lines represent fits to the bulk regime using equation 5.6, while the solid lines represent fits to the percolative regime using equation 5.17

This would suggest that FoMs such as the conductivity ratio which are based on bulk quantities do not adequately describe the properties of networks in the relevant regime. This point is more clearly illustrated if we consider films made from silver flakes (Ag Flakes).

5.2 RESULTS AND DISCUSSION

5.2.1 Silver Flake films

We have prepared films from silver flakes of varying thickness and measured the opto-electronic properties as can be seen in Figure 5.2. For thin conducting films, the transmittance scales with thickness as

$$T = \left(1 + \frac{Z_0}{2} \sigma_{Op} t\right)^{-2} \tag{5.7}$$

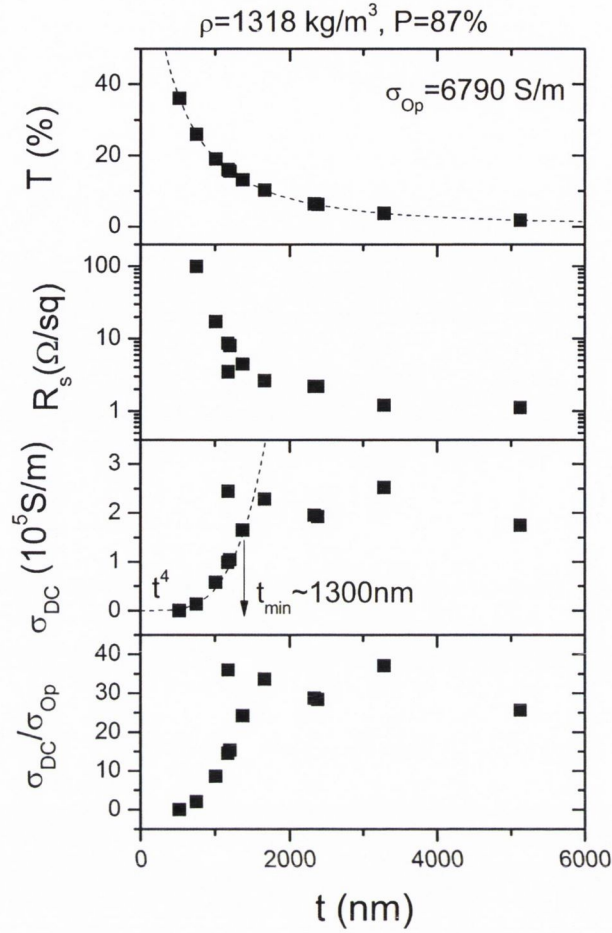


Figure 5.2: Physical properties of films of silver flakes as a function of film thickness

This expression can be fitted well to the data with an optical conductivity of $\sigma_{Op} \approx 6790 \text{ Sm}^{-1}$ (Figure 5.2A).This value is quite low compared to graphene and carbon nanotubes as discussed in previous chapters. The reason for this is the high porosity of these film which is around 87%. The porosity (P) was calculated according to the following equation

$$P = 1 - \frac{\rho_{film}}{\rho_{bulk}} \tag{5.8}$$

where ρ_{film} is the density of the film ($\rho_{film} = 1318\text{kgm}^{-3}$) and ρ_{bulk} is the density of the bulk material, in this case silver ($\rho_{bulk} = 10490\text{kgm}^{-3}$). The thickness of a number of films was measured using SEM. The denstiy was calculated from the thickness and mass per unit area of silver deposited.

$$\rho = \frac{M}{V} = \frac{M}{A} \frac{1}{t} \quad (5.9)$$

where M is the mass deposited, A is the area of the filtered film (diameter 36mm) and t is the film thickness.

Shown in Figure 5.2B is the sheet resistance data. While the data scales inversely with thickness at high thicknesses, anomalously high R_s is observed at lower film thickness as has been observed for films of carbon nanotubes, graphene and silver nanowires [3, 31, 45].

To illustrate this more clearly we have calculated the DC conductivity from $\sigma_{DC} = 1/R_s t$ as shown in Figure 5.2C. $\sigma_{DC} \approx 2.4 \times 10^5 \text{ Sm}^{-1}$ for thicknesses above 1300nm. However, for thinner films the conductivity falls off significantly. The same behaviour is reflected in the conductivity ratio which shows promisingly high conductivity ratio of $\sigma_{DC}/\sigma_{Op} \sim 35$. However, films demonstrating such a high ratio are above 1300nm in thickness have a transmittance $T < 20\%$ making them unsuited for any applications as a transparent conductor. This would suggest that it is not only the material properties such as the DC and optical conductivities that will determine the suitability of a material as a transparent conductor and that bulk FoMs such as $\sigma_{DC,B}/\sigma_{Op}$ or $\sigma_{DC,B}/\alpha$ cannot predict performance for many nanostructured materials.

5.2.2 Deviation from Bulk-like Behaviour for Thin Films

For networks of graphene, carbon nanotubes, nanowires and now silver flakes below some critical thickness, t_{min} , the DC conductivity begins to decrease with decreasing thickness. A deviation from the bulk occurs, and we have thickness independent quantities (such as DC conductivity) displaying thickness dependence, this behaviour is reminiscent of electrical percolation.

Percolation is the onset of conductivity across a previously insulating region once conducting links have been added at a density exceeding some critical value, the percolation threshold. As more links are added, new conducting paths are formed

and the conductivity increases. For example, when conducting rods are randomly deposited in-plane, the conductivity follows the percolation scaling law,

$$\sigma_{DC} \propto (N_A - N_{A,c})^\alpha \quad (5.10)$$

where N_A is the number of rods per unit area, $N_{A,c}$ is the percolation threshold, and α is the critical exponent. We note that this expression is only valid close to the percolation threshold [97].

As more rods are added, the network becomes extensive enough that all rods are interconnected in a continuous network. In principle, such a situation should be far enough from the percolation threshold such that the percolation scaling law no longer applies. However, this does not mean that the conductivity stops increasing as new rods are added. Studies on nanotube networks show that the conductivity continues to increase long after a dense continuous network is formed [45]. In fact, while the percolation threshold has been shown to occur for nanotube networks of average thickness of $1nm$ [131], the conductivity keeps increasing with thickness until the networks are $40nm$ thick when the behaviour becomes bulk-like [45, 131]. (N.B. The thicknesses quoted above are effective thicknesses and represent the thickness of a film with a given N_A and uniform density, N :

$$t = N_A \langle V_{cond} \rangle \rho_{cond} / \rho_N \quad (5.11)$$

where $\langle V_{cond} \rangle$ is the average volume of the conducting links and ρ_{cond} their density. For thin films, ρ_N is taken to be the same as that of a very thick network. We note that this definition of t allows the existence of films with thickness below that of the conducting entities making up the film.)

The behaviour at thicknesses greater than a few nanometers is distinct from true percolation and probably occurs as non-uniformities associated with thin networks getting smoothed out as the thickness increases (see below) [3, 31, 45]. We can think of this as an intermediate regime between true percolative behaviour and bulk behaviour. However, we note that percolation-like conductivity scaling has been observed for a number of systems far from the percolation threshold [132]. In fact, for the work described in ref [131], the conductivity data were consistent with a single power law

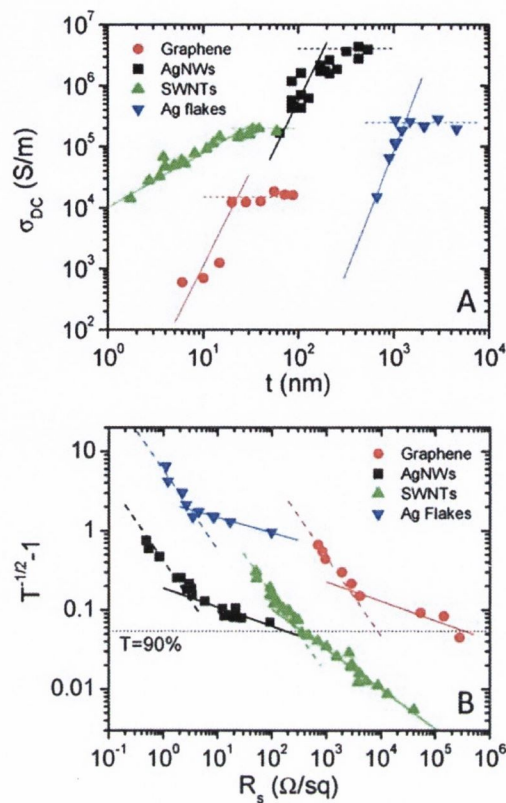


Figure 5.3: A) DC conductivity plotted as a function of estimated film thickness for the materials shown in Figure 5.1. The dashed lines represent the bulk conductivity, while the solid lines represent fits to the percolative regime using equation . B) The same data as plotted in Figure 5.1 is represented as $T^{-1/2} - 1$ vs R_s on a log-log plot. Note $T^{-1/2} - 1$ is proportional to film thickness. The dashed lines represent fits to the bulk regime using equation 5.6, while the solid lines represent fits to the percolative regime using equation 5.17.

extending from $t = 1$ nm all the way to $t = 40$ nm, where the transition to bulk behaviour occurred. This suggests that the conductivity of nanostructured transparent conducting networks in the intermediate regime can be described by a percolation-type power law with an exponent similar to that in the true percolation regime. We illustrate this by plotting the measured conductivity, DC, for the materials plotted in Figure 5.3A as a function of estimated film thickness (as reported in the relevant publications, Figure 5.1). In each case, below some well-defined thickness, the conductivity becomes thickness-dependent, displaying approximate power law behaviour, suggestive of percolation. However, in all cases, these films are so thick that this is likely to reflect

the intermediate regime rather than the true percolative regime. As such, for the rest of this thesis, we will assume that a percolation-like scaling law can be extended into the intermediate regime. For simplicity, we will refer to thickness-dependent conductivity as percolation, although (as discussed above) this is not true in the strictest sense.

5.2.3 Relationship between T and R_s in the percolation regime

To enhance our understanding we believe it crucial to investigate the relationship between T and R_s in the percolation regime. To do this *De et al.* have derived an expression, analogous to eqn. 5.6 but relevant in the percolation regime. The percolation scaling law expressed in eqn. 5.10 can be written in terms of films thickness rather than conductor number density [44]:

$$\sigma_{DC} \propto (t - t_c)^n \quad (5.12)$$

t_c is the threshold thickness and n is the percolation exponent. As discussed above, they assume that this expression holds in the thickness regime under study. However, they use the exponent n rather than α to illustrate that the exponent in the thicker intermediate regime is not necessarily identical to the true percolation exponent [133]. Scaling as described by eqn. 5.12 has been observed for thin films of carbon nanotubes by a number of researchers [44, 134, 135]. For a network with conductivity high enough to be industrially relevant, $t \gg t_c$, allowing us to write:

$$\sigma_{DC} = \sigma_{DC,B} (t/t_{min})^n \quad (5.13)$$

Here, as described above, the conductivity reaches its bulk value, $\sigma_{DC,B}$ at thickness t_{min} . The measured sheet resistance, R_s , is related to the actual DC conductivity by $R_s = (\sigma_{DC} t)^{-1}$. Note that this expression differs from eqn. 5.3 because they now realize that DC can differ from its bulk value ($\sigma_{DC,B}$) for thin films. Substituting eqn. 5.13 into the expression for R_s given above, they get the sheet resistance of a percolation network:

$$R_s = (\sigma_{DC,B}(t/t_{min})^n t)^{-1} = (\sigma_{DC,B} t^{n+1}/t_{min}^n)^{-1} = \frac{t_{min}^{n+1}}{t_{min} \sigma_{DC,B} t^{n+1}} \quad (5.14)$$

Solving for t and substituting into eqn. 5.7, they obtain

$$T = \left(1 + \frac{Z_0}{2} \sigma_{Op} t_{min} (t_{min} \sigma_{DC,B} R_s)^{-1/n+1} \right)^{-2} \quad (5.15)$$

This can be written as

$$T = \left[1 + \frac{1}{2} \left(\frac{Z_0}{R_s} \right)^{1/(n+1)} \left(\frac{(Z_0 t_{min} \sigma_{Op})^n}{\sigma_{DC,B} / \sigma_{Op}} \right)^{1/(n+1)} \right]^{-2} \quad (5.16)$$

Note that this expression reverts to eqn. 5.6 when $n = 0$ as expected. One can express eqn. 5.16 more compactly as

$$T = \left[1 + \frac{1}{\Pi} \left(\frac{Z_0}{R_s} \right)^{1/(n+1)} \right]^{-2} \quad (5.17)$$

where they denote Π as the percolative FoM:

$$\Pi = 2 \left[\frac{\sigma_{DC,B} / \sigma_{Op}}{(Z_0 t_{min} \sigma_{Op})^n} \right]^{1/(n+1)} \quad (5.18)$$

Π is a dimensionless number where large values of Π give low R_s coupled with high T . Equation 5.17 suggests that the percolative regime can be identified as a straight line on a log-log plot $T^{-1/2} - 1$ versus R_s (equivalent to a graph of t vs R_s). Fitting these data then gives both n and Π . The data for the materials examined in this work i.e. graphene networks and silver flake networks along with other work from our group (carbon nanotubes [45] and silver nanowires[3]) are shown in Figure 5.1 in this form in Figure 5.3. It is clear that for each data set two regimes are present; a range with slope of -1 , consistent with eqn. 5.6 (the bulk regime) and a region with less negative slope, described by eqn. 5.17 (the percolation regime). By fitting both regimes, we obtain $\sigma_{DC,B}/\sigma_{Op}$, Π and n for each material which we report in Table 5.1. We have also reproduced the fit, plotted as $T(R_s)$, to describe the percolative region in Figure 5.1. In all cases very good agreement is found. We note that the exponents n vary from 1 to 4. This range is within the bounds expected for true percolation exponents, suggesting that n and α may be similar. We note that percolation exponents are generally found

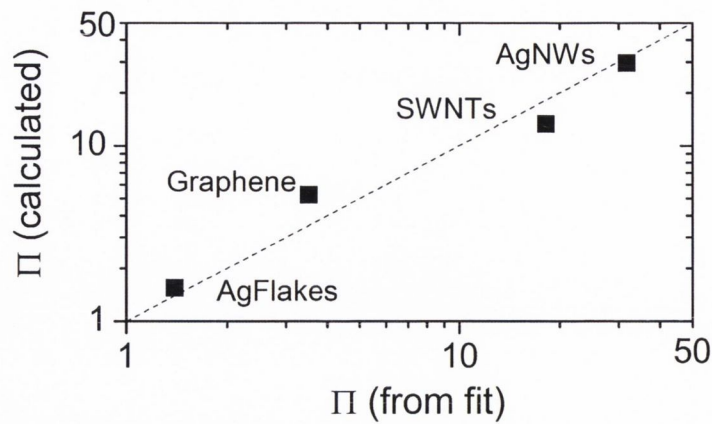


Figure 5.4: Percolative figure of merit, Π , calculated using equation 5.18 plotted as a function of the value of Π found by fitting the data in Figure 5.3B with equation 5.17.

by plotting σ_{DC} versus t as in Figure 5.3. However, because of the inherent difficulty of measuring the thickness of thin films, especially for thicknesses comparable to the dimensions of the entities making up the film, the data are generally scattered. Our treatment enables n to be determined by fitting R_s and T data using eqn. 5.17 and is probably superior. It is also noteworthy that the bulk and percolative FOMs follow a similar order (AgNWs > AgFlakes > SWNTs > graphene, for bulk FoM). The difference is that, when ranked by Π , the silver flakes come last in keeping with their poorer thin film performance.

All of the parameters in eqn. 5.18 are now known, $\sigma_{DC,B}/\sigma_{Op}$, Π , and n from the fits described above while σ_{Op} can be found from the thickness dependence of the film transmittance using eqn. 5.7; values reported in Table 5.1. This allows us to calculate Π from eqn. 5.18 and so test the consistency of the calculated value of Π with that found from fitting the data in Figure 5.3B. We plot the calculated values as a function of the fitted values in Figure 5.3A. We find almost perfect agreement. We note that the different parameters in equation are found from different portions of the data; Π and n from the percolative regime, $\sigma_{DC,B}/\sigma_{Op}$, from the bulk regime and t_{min} from the point of their intersection. The agreement shown in figure 5.4 confirms that these regimes are correlated as predicted by equation 5.18.

Material	ref	$\sigma_{DC,B}/\sigma_{Op}$	Π	n	$\sigma_{Op}(S/m)$	$t_{min}(nm)$	$D(nm)$
AgNws	[3]	415	31.7	1.9	6472	160	85
SWNTs	[45]	11.2	18.2	1	1.6×10^4	40	20
Graphene	Chapter 3	0.7	3.5	3.1	3.3×10^4	20	10
Ag Flakes	this Chapter	35	1.4	4	6790	1300	360

Table 5.1: Values of $\sigma_{DC,B}/\sigma_{Op}$, σ_{Op} , Π , n and t_{min} were found by analysis of the thickness dependence of the T and R_s data as described in this work for graphene and silver flakes and for AgNws and SWNTs in the relevant papers [3, 45]

Requirements of a good transparent conductor

We can now consider what makes a good nanostructured transparent conductor. Ideally, bulk-like behaviour would hold down to film thicknesses low enough to give $T > 90\%$. In this case, equation 5.6 applies and we want $\sigma_{DC,B}/\sigma_{Op}$ as high as possible. However, as shown in figure 5.1, this does not generally occur. In reality, films thin enough to display $T > 90\%$ tend to fall in the percolative regime. Here equation 5.17 holds and we require Π to be as large as possible (equation 5.18). As in the bulk case, this means we need large values of $\sigma_{DC,B}/\sigma_{Op}$. Also, intuitively, a low value of σ_{Op} is required. However, we can also identify two further requirements: t_{min} and n (as we will see below) must be as small as possible.

Can we control t_{min} ?

It is worth considering what controls t_{min} . In previous papers we suggested that t_{min} scales with the smallest dimension, D , of the nanostructure forming the network [3, 31, 45]. This smallest dimension would be the diameter in the case of wires or nanotubes, or the flake thickness in the case of graphene or silver flakes. The rationale behind this was that once the film was a few times thicker than D , non-uniformities in the network would have averaged out and it could be considered bulk-like. We can

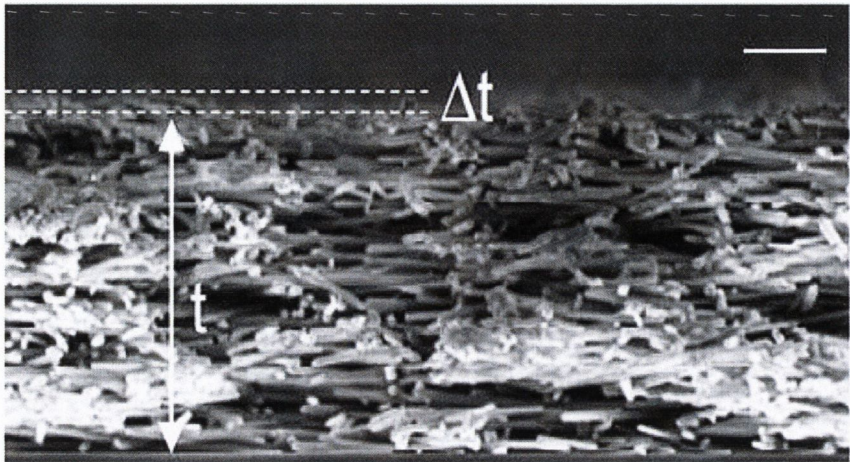


Figure 5.5: SEM image of the cross-section of a thick network of AgNWs (scalebar $1\mu m$). The dashed lines illustrate the non-uniformity in film thickness, Δt .

illustrate this using Figure 5.5. This is an image of the cross section of a relatively thick network of AgNWs. Such images are often used to measure film thickness as shown. However, it is clear from this image that the film thickness is slightly non-uniform as illustrated by the dashed lines. The degree of non-uniformity, Δt , is or the order of the wire diameter, D . For thick films such as that shown, this non-uniformity has no effect on the film conductivity. However for films with thickness approaching D and below, this non-uniformity will translate into non-uniformity of the network as a whole. Effectively, N_A will vary from place to place within the network, resulting in a significant reduction in DC conductivity as the thickness is decreased. Such thickness dependent non-uniformities have been observed for a number of nano-structured films [3, 31, 45, 136]. Thus, we expect t_{min} to scale with D . We can illustrate this behaviour with a combination of published data and data for the silver flakes measured as part of this study.

We take measurements of D from our previous work for SWNT bundles and AgNWs and graphene films [3, 31, 45, 131]. (We note that for graphene, $D = 10nm$. This is because during film formation, the graphene sheets aggregated into rather thick graphitic flakes.) In addition, we measured the thickness of the Ag flakes to be $D = 360 \pm 100nm$ as shown in Figure 5.6. We take t_{min} from the relevant papers and plot $t_{min} \propto D$ in Figure 5.7, finding very good linearity as described by $t_{min} = 2.33D$.

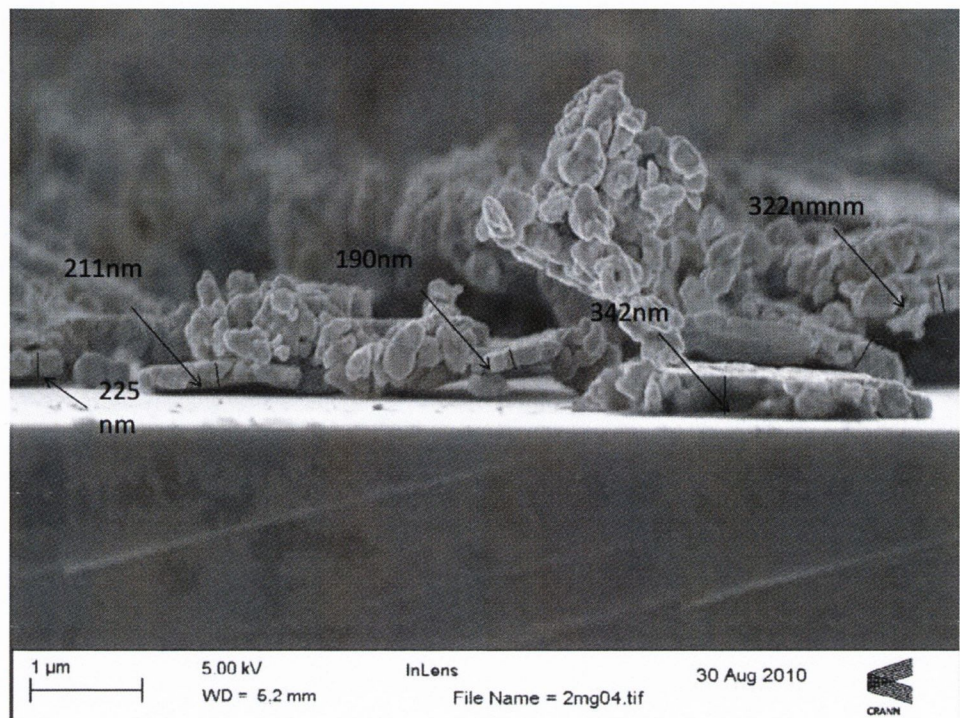


Figure 5.6: SEM images of the edge of a thin film of silver flakes.

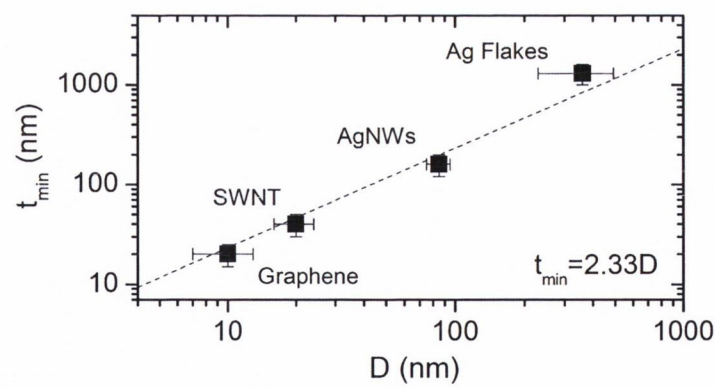


Figure 5.7: The film thickness where percolation begins, t_{min} , plotted as a function of the smallest dimension of the nanostructured material making up the film, D . For example, for nanotubes or nanowires, D is the diameter, while for platelets, D is the thickness

This makes it absolutely clear, to reduce t_{min} and so enhance performance, it is necessary to use nanotubes/nanowires with low diameter or nano-platelets with low thickness. For example, extremely good results have been achieved with AgNWs with diameter of $85nm$ [3]. If AgNWs with significantly lower diameter could be obtained, even better results might be expected. We note that nominally SWNTs have $D \sim 1nm$. However, during film formation SWNT always aggregate into bundles with $D \gg 1nm$. Frustrating this bundling process would greatly reduce D and so t_{min} , leading to better films. In any case, it is important to emphasise that this is a general result. Reduction of the shortest dimension (D) of a conducting nanostructure will result in higher percolative figure of merit, Π , and so improved T and R_s . Thus, low diameter nanowires or nanotube bundles are required. Alternatively, thin metal platelets could result in good quality films. However, due to their high absorbance, it is unlikely that networks of graphene monolayers will reach industry standards of T 90% for $R_s < 100\Omega/sq$ [128].

As described above, reduction of D should result in significantly improved films. However, it is important to realise that, if D could be decreased dramatically, it would be possible to produce film such that $T = 90\%$ was achieved in the bulk rather than the percolative regime. This would result in significantly reduced R_s . By substituting $t_{min} = 2.33D$, into equation 5.7, we can show that this occurs when $D > 0.05/Z_0\sigma_{Op}$. For AgNWs, this gives $D < 18nm$, much lower than what is commercially available. (We note that this estimation assumes that σ_{Op} is invariant with D . While this is unlikely, we know of no studies giving the actual dependence of σ_{Op} on D ; see below for more discussion.)

Effect of n on Film Properties

Before discussing the effect of n on film properties, we note that, as described above, n may be very close to the true percolative exponent, α (i.e., $n \approx \alpha$). In that case, it is worth considering what controls α in a percolative system. The percolation exponent was originally expected to take on the universal value of $\alpha_{un} = 2$ for a three-dimensional

system or $\alpha_{un} = 1.3$ for a two-dimensional system [97]. By the late 1980s, it was realized that higher values were possible [137–139]. Such non-universal exponents have been linked to the presence of a distribution of junction resistances at conductor–conductor junctions [133, 138, 140, 141]. For example, in three-dimensional films, it has been shown that for a distribution of junction resistances, $\alpha > \alpha_{un}$ with $\alpha - \alpha_{un}$ controlled by the shape of the distribution [138, 139, 141]. For nanotube films, it is known that the junction resistances can be large and their distributions quite broad [35]. Post treatment can be used to reduce the junction resistance thus improving $\sigma_{DC,B}/\sigma_{Op}$. If one applies our model to data from *Chandra et al.* the doping of their SWNT films results in an increase in $\sigma_{DC,B}/\sigma_{Op}$ from 8.5 to 19.5 [142] an increase in Π from 12.3 to 23.8 and a change in n . We propose that post-treatments might be developed which can both improve $\sigma_{DC,B}/\sigma_{Op}$ and controllably tune n , resulting in significant increase in Π . The data described above show that lower values of D give better values of n and Π , with respect to opto-electronic applications. However, having two parameters describing the performance is not ideal. A single FoM which could directly be linked to performance would be much more desirable. For industrial applications the transmittance generally needs to be above 90% while the sheet resistance must be as low as possible. With this in mind, a useful parameter is the sheet resistance of a film with $T = 90\%$, $R_s^{T=90\%}$. As discussed above networks with $T = 90\%$ generally reside in the percolative regime, this can be found by rearranging equation 5.17:

$$R_s^{T=90\%} = Z_0(0.054\Pi)^{-(n+1)} \quad (5.19)$$

(here the factor of 0.054 comes from setting $T = 90\%$ in the factor $(T^{-1/2} - 1)$. Alternatively, we can write $R_s^{T=90\%}$ in terms of more fundamental quantities by combining equations (5.17) and (5.18) and reorganizing the resultant expression to give

$$R_s^{T=90\%} \approx \frac{Z_0}{0.11\sigma_{DC,B}/\sigma_{Op}} \left(\frac{Z_0 t_{min} \sigma_{Op}}{0.11} \right)^n \quad (5.20)$$

(here the factor of 0.11 comes from setting $T = 90\%$ in the factor $2(T^{-1/2} - 1)$. This expression displays an exponential relationship between $R_s^{T=90\%}$ and n , underlining the importance of n and so network uniformity. This reinforces the importance of

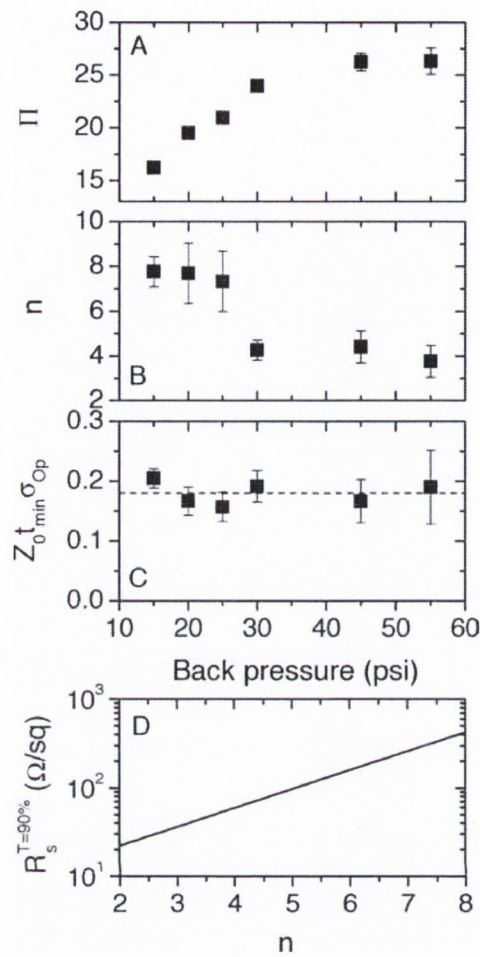


Figure 5.8: A) Percolative figure of merit, Π , and B) percolative exponent, n , plotted as a function of back pressure. C) Product of $Z_0 t_{min} \sigma_{Op}$. D) Expected value of $R_s^{T=90\%}$ as a function of n [143].

decreasing D in these systems. In any case, if a method could be found to control n for a given system, reducing n should result in increases in T and reductions in R_s , leading to improved thin films.

Such a method has been demonstrated by *Scardaci et al.* by elucidating the relationship between the morphology and opto-electronic properties of spray deposited AgNw networks [143]. They control the droplet size by tuning the back pressure of the spray system, which controls the network uniformity. Non-uniform networks would tend to have a broad distribution of inter-nanowire junction resistances leading to large percolation exponents. By contrast uniform networks have narrow junction

resistance distributions and so lower percolation exponents leading to improved film performances. By varying the back pressure n could be decreased resulting in higher values of Π (Figure 5.8). Lower values of n enabled networks to be prepared with lower R_s in the technologically relevant regime i.e. $T = 90\%$. A sheet resistance $R_s \approx 50\Omega/sq$ was achieved at a transparency of $T = 90\%$ compared to $R_s \approx 200\Omega/sq$ for vacuum filtered films prepared at the same transmittance [3].

5.3 CONCLUSIONS

De et al. have shown that in the industrially relevant (high transmittance) regime, the electrical properties of nanostructured networks tend to be controlled by percolation. This means that the DC conductivity is lower than in the bulk regime resulting in higher than expected sheet resistances, R_s . FoMs based on bulk quantities such as DC conductivity fail to rank materials appropriately as illustrated in this work by networks of silver flakes. They have developed a simple model which relates T to R_s in the percolative regime. This is controlled by a percolative figure of merit Π . High values of Π , leading to high T and low R_s , are found when $\sigma_{DC,B}$ is high but σ_{Op} is low. In addition, the percolative exponent n must be low, as must the film thickness at which the conductivity becomes thickness-dependent (t_{min}). This model fits well to data for networks of graphene and silver flakes as examined in this work and also carbon nanotubes and metallic nanowires. We show that t_{min} scales linearly with the smallest dimension of the nanostructure making the film. This shows that low diameter nanowires/nanotubes or thin platelets are best for transparent conducting applications.

5.4 PREPARATION OF SILVER FLAKE FILMS

Silver flakes were purchased from Ferro (silver flake SF77A), while isopropyl alcohol (IPA) was purchased from Aldrich. The silver flakes were heated to 160°C for 0.5hr in an oven prior to suspension in IPA. The silver flakes were then added to IPA such

that the silver concentration was 0.5mg/ml . This dispersion was then sonicated for 2hr in a sonic bath (Branson 1510MT). The resulting dispersions were vacuum-filtered using porous cellulose filter membranes (MF-Millipore membrane mixed cellulose esters, hydrophilic, $0.025\mu\text{m}$, 47mm) to give thin films. The thickness of these films was controlled by the volume of dispersion filtered and hence the mass deposited. The films were then transferred to polyethylene terephthalate (PET) using IPA to adhere the film to the substrate. The cellulose filter membrane was removed using acetone vapour followed by immersion in acetone baths. Optical transmission spectra were recorded in the visible range ($400 - 800\text{nm}$) using a Varian Cary 6000*i*. In all cases, PET was used as the reference. Sheet resistance measurements were made using the four-probe technique with silver electrodes of dimensions and spacings typically of approximately millimetre size and a Keithley 2400 sourcemeter. Flake and film thicknesses were gauged by measuring the height profile of a fractured cross section for a number of films of various thickness (Figure 5.6). This was achieved by mounting the sample parallel to electron beam in a Zeiss Ultra plus SEM.

PERCOLATION EFFECTS IN SUPERCAPACITORS WITH THIN, TRANSPARENT CARBON NANOTUBE ELECTRODES

6.1 BACKGROUND

In the last number of years there has been increasing interest in flexible electronics. Many believe that the next stage in the development of flexible electronics will require all of the device components to be transparent for use in applications such as transparent displays or heads up displays [103]. For many such applications, transparent energy storage devices will be required [104]. To this end, a number of groups have demonstrated transparent supercapacitors or batteries [104–108, 144]. In general, the research has focused on using nanomaterials to produce thin but high surface area electrodes which can be transparent if made thin enough [109, 110, 145]. In the simplest case, these electrodes can then be combined with a suitable electrolyte and separator to produce a supercapacitor [146].

6.2 RESULTS AND DISCUSSION

6.2.1 Bulk to percolation transition

The supercapacitor electrodes studied during this work were prepared by vacuum filtration of aqueous carbon nanotube dispersions to give thin nanotube films with a range of thickness from 5 to 500nm (see below). Shown in Figure 6.1 are SEM images of very thin films (5 and 12nm average thickness). To facilitate imaging, these were transferred from the filter membrane to AuPd-coated glass. Figure 6.1A represents a portion of a 5nm thick film and shows the nanotubes to be arrayed in bundles

(estimated mean diameter and length of 23nm and $1.3\mu\text{m}$, respectively) which are randomly arranged on the surface. Figure 6.1 B shows a lower magnification image of the same film which demonstrates considerable spatial nonuniformity. While some regions of the film contain clusters of nanotubes, other regions are relatively sparsely populated. Such nonuniformity has been observed before by both Raman mapping and spatially resolved transmittance measurements [45, 131]. In addition, the inset illustrates a small cluster of tubes that are only weakly connected (if at all) to the rest of the network. Figure 6.1 C shows a portion of a 12nm thick film showing a considerably larger nanotube density.

For detailed characterization, the nanotube networks were transferred from the filter membrane to transparent plastic substrates (PET). We performed initial characterization by measuring the optical transmittance spectra and four probe sheet resistances for each film. The transmittance (550nm) varied from 97 to 13%, while the sheet resistance varied from $10^5 - 10^2\Omega/\text{sq}$ over the same thickness range. The measured transmittance (550nm) is plotted as a function of sheet resistance in Figure 6.2A. For thin conducting films, where the DC conductivity is thickness independent, the transmittance is related to the sheet resistance by

$$T = \left(1 + \frac{Z_0}{2} \frac{\sigma_{Op}}{\sigma_{DC,B}}\right)^{-2} \quad (6.1)$$

where $Z_0 = 377\Omega$ is the impedance of free space and σ_{Op} and $\sigma_{DC,B}$ are the optical conductivity and the (bulk-like) DC conductivity, respectively. For relatively thick films, $\sigma_{DC,B}/\sigma_{Op}$ is thickness independent and can be used as a figure of merit (FoM), representing a simple way of comparing different samples [95]. This expression can be fitted to the data in Figure 6.2A, as indicated by the dashed line. A good fit was obtained for films with transmittance $T < 45\%$. This fit gives a value of $\sigma_{DC,B}/\sigma_{Op} \approx 1.9$ for these films, which is typical of the values found for carbon nanotube networks. Given that the optical conductivity of carbon nanotube networks is known to be $\sigma_{Op} = 1.7 \times 10^4\text{S}/m$ [45, 124, 147], this allows us to estimate the bulk DC conductivity of the thick networks to be $\sigma_{DC} \approx 3 \times 10^4\text{S}/m$.

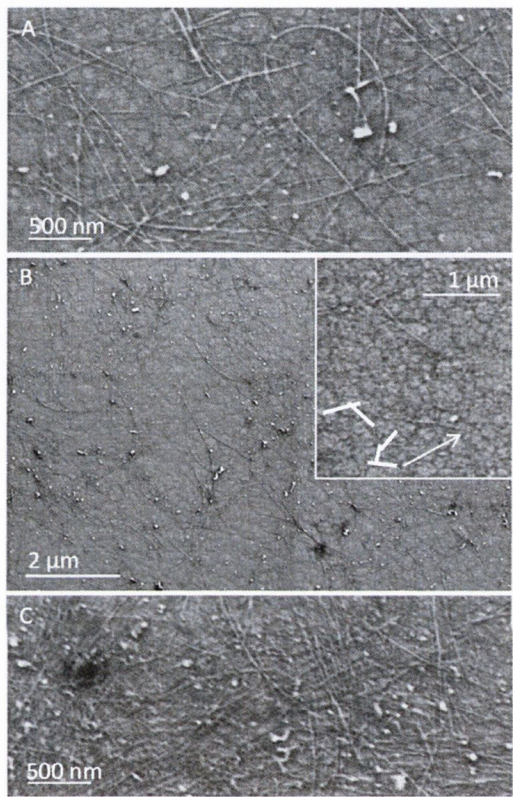


Figure 6.1: SEM images of nanotube networks. (A) SEM image of a 5 nm thick SWNT film. (B) Wide field image of the same film. Inset: Thin networks such as this contain nanotubes which are isolated or only weakly connected to the network. This is shown in the SEM, although the poor contrast achieved for these sparse networks makes it difficult to see isolated nanotubes. The motif in white is a schematic demonstrating the shape of the array of nanotubes in this image. The arrow links part of the schematic to the equivalent position in the image. (C) SEM image of a 12 nm thick SWNT film.

However, we observe significant deviation from this bulk-like behaviour for thin films with $T > 45\%$. As the transmittance is increased above 45%, the thickness falls below t_{min} , and percolative effects begin to control the DC conductivity. Such a transition has been observed for thin films of nanotubes, nanowires, and graphene sheets as described in chapters 3 and 5. We have recently shown that, in the percolation regime, the transmittance is related to the sheet resistance by

$$T = \left[1 + \frac{1}{\Pi} \left(\frac{Z_0}{R_s} \right)^{1/(n_{DC}+1)} \right]^{-2} \quad (6.2)$$

where Π is known as the percolative FoM and n_{DC} is the percolation exponent. Equation 6.2 can be fitted to the high T data in Figure 6.2A. The data fits extremely well for films with $T > 45\%$ yielding $\Pi = 3.1$ and $n_{DC} = 0.6$. Again, these values are typical of nanotube films [95]. These data clearly show that percolation effects are present in these thin nanotube films so long as the transmittance is above 45%. Such percolation effects have been observed in many nanostructured networks as described in the previous chapter, with the transition from bulk-like to percolative behaviour occurring for networks with transmittances from 45 to 92% [95]. To be incorporated into transparent electronics, components are likely to require $T > 90\%$. Thus, it is clear that technologically relevant network devices will operate in the percolation regime.

6.2.2 Supercapacitor electrode thickness dependence

It is clear that if transparent films are to be used as electrodes in a supercapacitor percolation will play a limiting role. Hence, it is important to understand the impact these percolation effects may have on the parameters governing electrode performance namely the capacitance (C) and equivalent series resistance (R_{ESR}). To examine this we performed standard electrochemical tests on our nanotube networks in a three electrode cell. We note that because of this three-electrode configuration our measurements of C and R_{ESR} apply to a single electrode and not to a supercapacitor device. No additional current collectors were used. To quantitatively evaluate the performance of the electrodes, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry

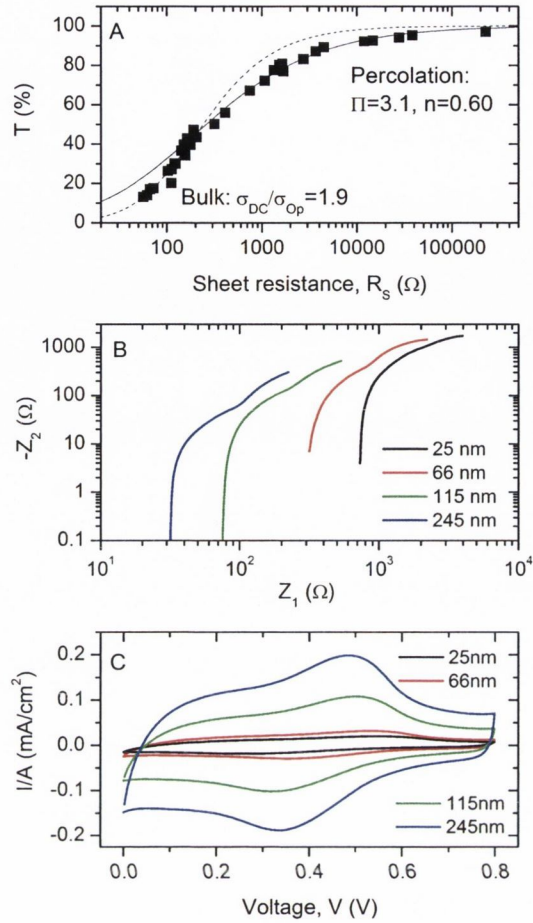


Figure 6.2: A) Optical transmittance (550nm) plotted as a function of sheet resistance for the electrodes (deposited on PET) used in this work. The dashed and solid lines are fits to equations 2 (bulk) and 3 (percolation) respectively. B) Nyquist plots and C) Cyclic voltammograms for selected electrode thicknesses.

(CV) were performed (electrolyte $1.0M H_2SO_4$). Examples of Nyquist plots for various electrode thicknesses (see below) are shown in Figure 6.2B. These are typical of nanotube electrodes and consist of a semicircle at high frequency which intercepts with the Z_1 (real) axis to give R_{ESR} . In the low-frequency regime, Z_2 increases almost linearly with Z_1 . It is unclear whether this is indicative of the presence of another semicircle or of the presence of a Warburg impedance. Some examples of the CV curves (recorded after 20 cycles) can be seen in Figure 6.2C (scan rate 50mV/s). The CV curves are typical of those of carbon nanotubes functionalised with carboxylic acid groups with broad reduction and oxidation features [148].

In order to ascertain the effects of percolation, it is necessary to analyse the electrochemical data as a function of film thickness. To do this, the network thickness must be estimated with reasonable accuracy. For thin conducting films, the transmittance scales with thickness as [127]

$$T = \left(1 + \frac{Z_0}{2} \sigma_{op} t\right)^{-2} \quad (6.3)$$

It is well-known that the optical conductivity of carbon nanotube networks is close to $\sigma_{Op} = 1.7 \times 10^4 S/m$ [45, 124, 147]. Using this value and eqn. 6.3, we can calculate film thickness from the transmittance data. To illustrate this, we plot the measured film transmittance as a function of calculated thickness in Figure 6.3A. It is important to note that real capacitors have two electrodes. This means that, if for example, an overall transmittance of $T > 80\%$ is required, then each electrode must have $T > 89\%$. This corresponds to a thickness of $t < 17nm$ and falls well inside the percolation regime. In addition, we plot the sheet resistance data as a function of film thickness in Figure 6.3B. As expected for bulk-like materials, for the thicker films, R_s scales inversely with thickness as illustrated by the dashed line. However, below a critical thickness, $t_{min,DC} \approx 100nm$, the data deviate from this line as percolation effects become important. In the previous chapter we showed that the thickness where the bulk to percolation transition occurs is related to the bundle diameter, D , by $t_{min,DC} \approx 2.33D$ [95]. That the measured mean bundle diameter is 23 nm predicts that $t_{min,DC} = 54nm$. The reason for the disagreement is unclear.

We measured the equivalent series resistance from the impedance data for all electrode thicknesses. The thickness dependence of the R_{ESR} is plotted in Figure 6.3C. It is noteworthy that R_{ESR} displays a thickness dependence almost identical to that of R_s , displaying bulk-like behaviour above a thickness of $t_{min,ESR} = 100nm$ but percolative behaviour below this transition thickness. We plot R_{ESR} versus R_s in the inset of Figure 6.3C, finding almost perfect linearity. This would be expected for an electrode where the active material also plays the role of the current collector and the electrolyte resistance is negligible. The capacitance was determined from the cyclic voltammetry curves. We calculated the electrode capacitance after 20 cycles using

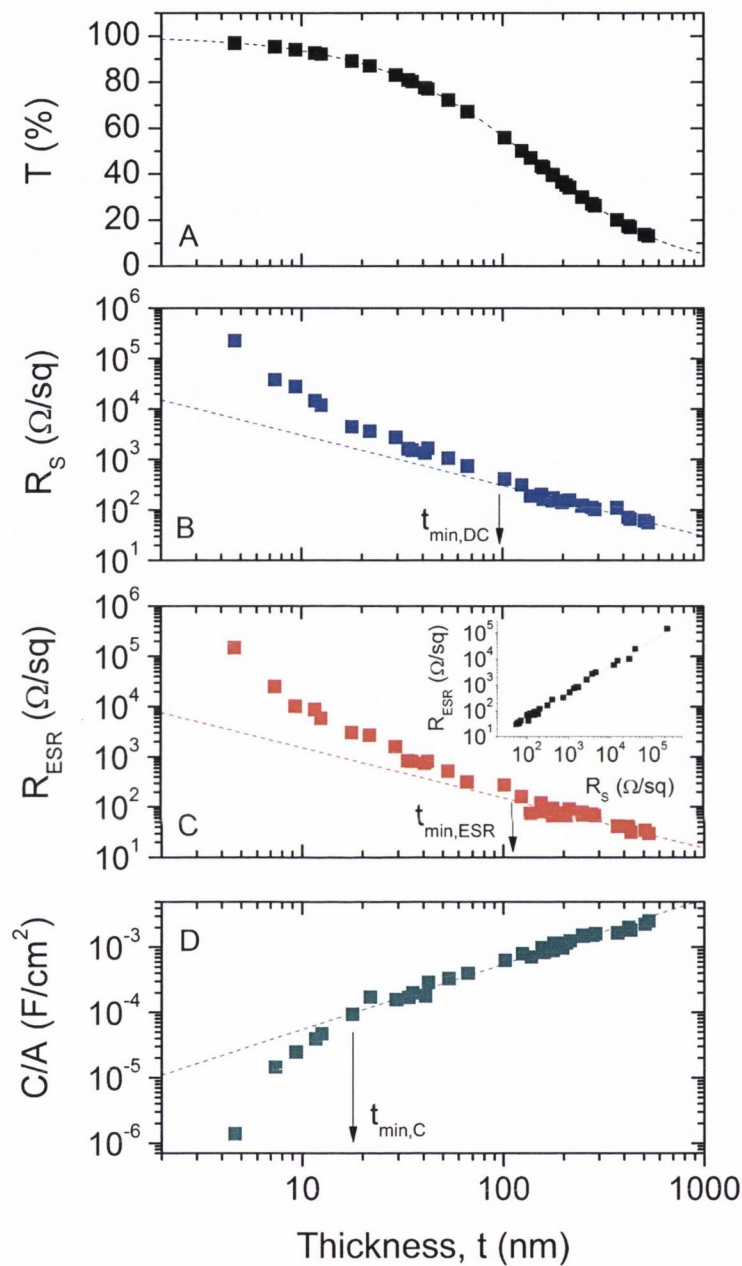


Figure 6.3: Electrode properties plotted as a function of network thickness, as calculated from the transmittance. A) Network transmittance, B) sheet resistance, C) equivalent series resistance and D) capacitance per unit area. Shown in the inset of C) is a plot of equivalent series resistance versus sheet resistance. In B), C) and D), the dashed lines represent the behaviour expected for bulk-like electrode. The arrows indicate the point of deviation from bulk-like behaviour.

$I = CdV/dt$ [113]. The current was normalized to the electrode area (constant for all films at 2.83cm^2) and averaged over the entire potential range to give the capacitance per unit area (C/A) which is plotted against thickness in Figure 6.3D. For thicknesses above a minimum value ($t_{\min,C} \approx 20\text{nm}$), the capacitance scales linearly with thickness as expected for a bulk-like material. It is worth noting that this linear behaviour occurs when the electrolyte effectively wets the electrode. This is the case here because the electrolyte is aqueous and the nanotubes making up the electrode are functionalized with carboxylic groups rendering the electrode surface hydrophilic. However, below this threshold, the capacitance falls off more rapidly than expected. This is a significant effect with the thinnest film displaying capacitance an order of magnitude lower than expected. Comparison with the behaviour of R_s and R_{ESR} strongly suggests this behaviour to be percolative in nature. To the best of our knowledge, this effect has not been reported previously.

Similar to the analysis presented in the previous chapter the data above suggests the presence of percolation effects, such phenomena can be demonstrated more clearly by plotting as a function of thickness a parameter such as DC conductivity, which is normally thickness invariant. To do this, we calculate the DC conductivity of the electrode from the sheet resistance using $\sigma_{\text{DC}} = 1/(R_s t)$. We can also calculate an effective conductivity associated with the ESR which we define as $\sigma_{\text{ESR}} = 1/(R_{\text{ESR}} t)$. These conductivities are plotted against thickness in Figure 6.4A. For thicknesses above $\sim 100\text{nm}$, we observe both conductivities to be constant within error as would be expected for a bulk-like electrode. However, for thicknesses below $\sim 100\text{nm}$, both conductivities tend to fall nonlinearly with decreasing thickness. Similar behaviour has been previously observed for thin conducting films of nano-structured materials such as carbon nanotubes, graphene, and metallic nanowires [3, 31, 45, 95, 101]. We emphasize that the same behaviour is observed for the ESR as the DC conductivity because the ESR is dominated by the resistance of the electrode.

We can confirm that this behaviour is due to percolation by showing that the conductivity scales with thickness as described by the percolation scaling law as expressed in the previous chapter (eqn. 6.4). This is clearly demonstrated in the inset of Figure 6.4A for both the DC and effective conductivities at thickness below $t_{\min,\text{DC}}$ and

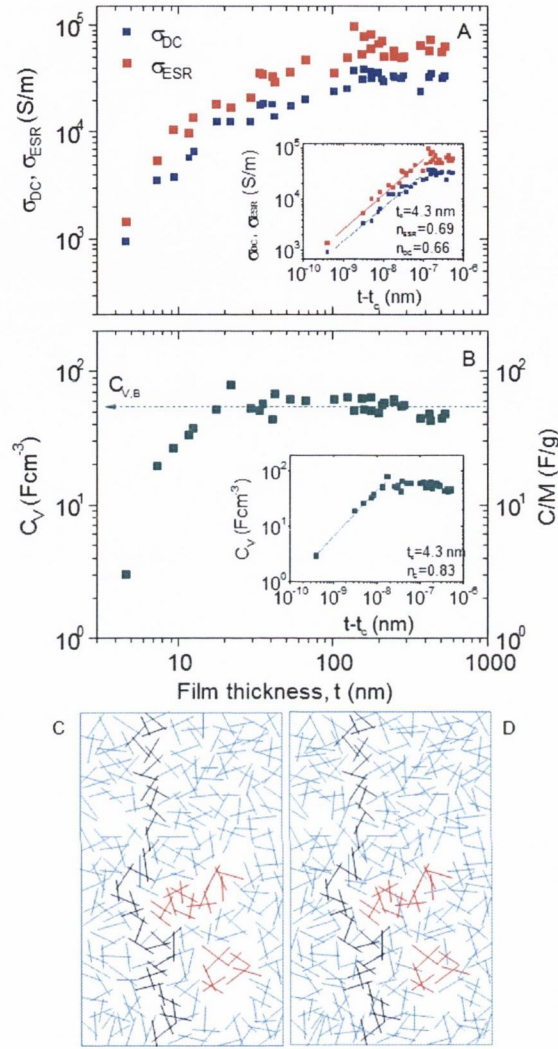


Figure 6.4: Percolation effects in these electrodes. A) Electrode DC conductivity (calculated from the sheet resistance) and the equivalent ESR conductivity, defined as $\sigma_{ESR} = 1/(R_{ESR}t)$ plotted as a function of film thickness. Inset: the same data plotted as a percolation curve. The fit gives a percolation threshold of $t_c = 4.3$ nm and percolation exponents of $n_{ESR} = 0.69$ and $n_{DC} = 0.66$. B) Capacitance per film volume plotted as a function of film thickness. The right axis shows the capacitance in F/g (taking $\rho = 1000$ kg/m³). Inset: the same data plotted as a percolation curve. The fit gives a percolation threshold of $t_c = 4.3$ nm and a percolation exponents of $n_C = 0.83$. (C,D) Schematics of random two-dimensional networks of sticks. The stick densities in (C) and (D) are $4.3L^{-2}$ and $4.9L^{-2}$, where L is the mean stick length. In each case, the dark blue sticks illustrate a percolating path, while the red sticks in (C) represent two isolated clusters. In (D), these clusters are now connected to the rest of the network.

$t_{min,ESR}$, respectively. From the fits, we find the percolation threshold to be $t_c = 4.3nm$ in each case. The percolation exponents were $n_{ESR} = 0.69$ and $n_{DC} = 0.66$. These values are much smaller than the universal value of 1.3, expected for two-dimensional systems [97]. However, we note that such low values are commonly found for carbon nanotube networks. The reason for this discrepancy is unknown.

We can perform a similar analysis to above to explore the possibility of percolation of capacitance by plotting the capacitance per electrode volume $C_V = C/At$, as a function of film thickness as shown in Figure 6.4B. Assuming that the nanotube network has a well-defined surface area per unit volume, then this volumetric capacitance should be independent of film thickness for a bulk-like film (assuming good electrolyte wetting). As was the case for the conductivity data, we observe constant volumetric capacitance for thicknesses above $20nm$. We denote this constant volumetric capacitance for thick bulk-like films, $C_{V,B}$, which has a mean value of $55Fcm^{-3}$. However, a significant fall off in volumetric capacitance is observed at lower thicknesses. If this fall off is a percolation effect, then we expect the volumetric capacitance to scale with thickness in the thin film regime as

$$C_V \propto (t - t_c)^{n_c} \quad (6.4)$$

We believe the capacitance will follow this form because a wide range of phenomena described by percolation theory can be modelled using this type of function [97]. However a more rigorous justification will be given below. The inset of Figure 6.4B shows this model to fit the data extremely well giving values $t_c = 4.3nm$ and $n_C = 0.83$. These values are similar to those obtained for the sheet resistance and ESR. We can use the thick film data to estimate the specific capacitance, taking an estimated network density of $1000kg/m^3$ (as measured for a thick free-standing film). This is displayed on the right axis of Figure 6.4 and shows the capacitance per unit mass to saturate at $\sim 55F/g$ in the bulk-like region. This is in line with a number of papers on nanotube-based transparent supercapacitor electrodes [105, 106, 108, 145].

It is interesting that while the percolation threshold is the same for DC conductivity, equivalent circuit resistance, and capacitance data ($t_c = 4.3nm$) the transition from

percolative to bulk-like behaviour occurs at a lower thickness ($t_{min,C} \approx 20nm$) for the capacitance than it does for the sheet resistance or ESR ($t_{min,DC} \approx t_{min,ESR} \approx 100nm$). It is unsurprising that the percolation threshold should be the same in all cases. The measurements of R_{ESR} , σ_{DC} , and C/A all require current flow in the network, so should all give the same value of t_c . However, the thickness where percolative behaviour transitions to bulk-like behaviour, t_{min} , is more subtle. It has been shown previously for nanostructured networks that this transition occurs at the same thickness as a transformation from spatially nonuniform to greater network uniformity [3, 31, 45]. This transition tends to occur at a network thickness that is ~ 2.3 times the diameter of the nanowires or nanotubes making up the network[95]. However, the volumetric capacitance is unlikely to be sensitive to the network nonuniformity. More probably, the capacitance is sensitive to the connectivity of the network. For very sparse networks, not all nanotubes will be connected to the main network. We might expect the capacitance to depend on the number of nanotubes that are directly connected to the main network and to become thickness independent when the last isolated nanotube cluster becomes connected to the rest of the network. This is likely to occur significantly before the nonuniformity to uniformity transition in line with what is experimentally observed.

We illustrate this behaviour in Figure 6.4C,D. Figure 6.4C shows a schematic of a sparse network of randomly arranged sticks. This network is above the percolation threshold as illustrated by the conductive path marked by dark blue sticks. However, it is sparse enough to be quite nonuniform; the bottom right portion has considerably lower stick density than the top right for example. As shown previously, such nonuniformity is associated with thickness dependent DC conductivity and so behaviour characteristic of electrical percolation [3, 31, 45]. In addition, it has a number of clusters (illustrated by red sticks) which are not connected to the rest of the network. These clusters can contribute to neither current flow nor capacitance. Thus we expect this network to have an effective thickness which is below both $t_{min,DC}$ and $t_{min,C}$. Shown in Figure 6.4D is the same network, but where 50 more sticks have been added randomly. It is clear that this network is still spatially nonuniform. Thus thickness-dependent conductivity is still expected ($t < t_{min,DC}$). However, all sticks are now connected to the network and so can contribute to the capacitance. This suggests that $t > t_{min,C}$. This

supports the possibility of a scenario where a network can have thickness such that $t_{min,C} < t < t_{min,DC}$, as suggested by our experiments. This concept also allows us to justify our use of eqn. 6.4 to describe the capacitance. As the capacitance scales with the surface area of the electrode, we would expect it to be proportional to the fraction of nanotubes connected to the network (i.e., those not isolated like the red rods in Figure 6.4C). However, percolation theory shows that the probability that a nanotube is connected to the network (i.e., the fraction of nanotubes which are connected) scales as $P \propto (N_A - N_{A,C})^\beta$, where β is a scaling exponent [97]. Because we expect $C/A \propto P$, this shows that the capacitance should indeed follow the scaling law described by eqn. 6.4.

6.2.3 Electrode performance

As electrode thicknesses are reduced to increase transmittance, the absolute capacitance falls not only because of percolation but also because the electrode mass scales with thickness. This is important because the energy storage capability of the capacitor is proportional to the capacitance. We explore this trade-off between transmittance and capacitance by plotting the measured transmittance versus the areal capacitance in Figure 6.5A. The absolute capacitance expected for a two-electrode device with these electrodes is shown on the top axis (taking an electrode area of 2.83cm^2 and dividing by 2 to correct for 2 electrodes per device). We see that thicker films have high C/A and low T , while thin films display the opposite. For a bulk-like electrode, the areal capacitance is related to the thickness by $C/A = C_{V,B}t$, where $C_{V,B}$ is the bulk-like volumetric capacitance. Combining this with eqn. 6.3 to eliminate t gives an equation which relates the transmittance to the areal capacitance for bulk-like electrodes:

$$T = \left[1 + \frac{Z_0 \sigma_{Op}}{2C_{V,B}} \frac{C}{A} \right]^{-2} \quad (6.5)$$

The dashed line in Figure 6.5A is a fit to this equation 6.6. Very good agreement is observed for $Z_0 \sigma_{Op} / 2C_{V,B} = 566\text{cm}^2/F$.

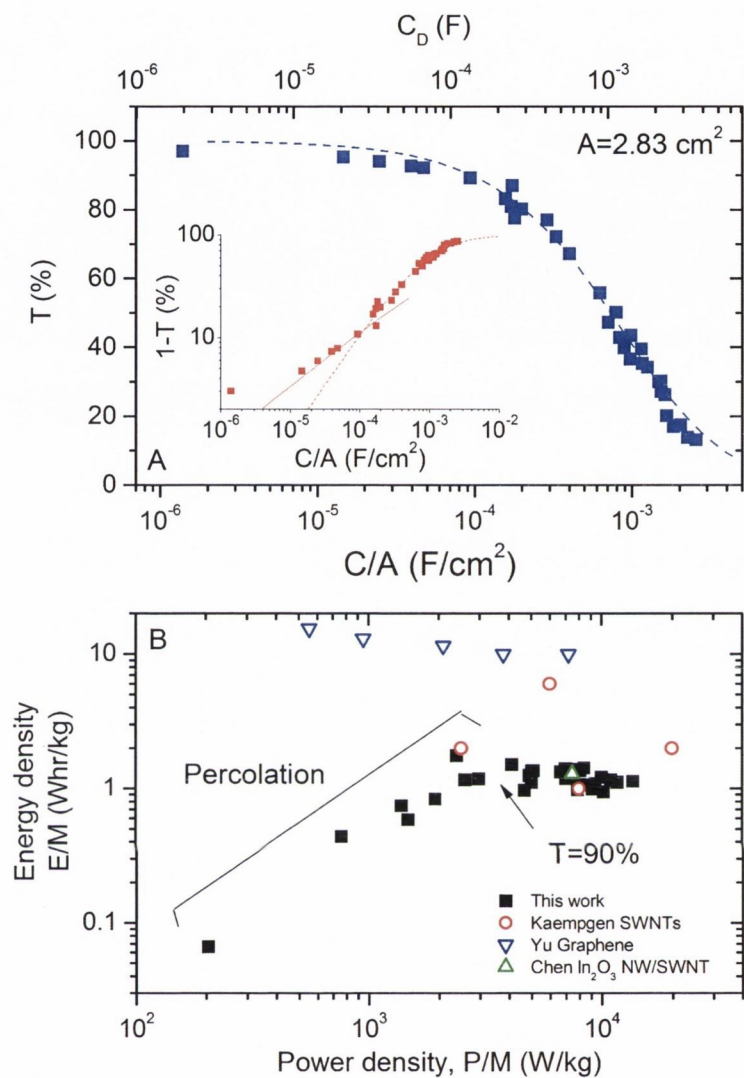


Figure 6.5: A) Measured transmittance (550nm) plotted as a function of areal capacitance (the absolute capacitance for a two electrode device of equal area is shown on the top axis). The dashed line is a fit to equation 6.5 and represents bulk-like behaviour. Inset: The same data plotted as $1 - T$ to more clearly show the deviation from bulk-like behaviour due to percolation. The solid line is a plot of equation 6.6 using the constants described in the text and represents percolation. Note that the solid line deviates from the point with lowest C/A due approximation in the derivation. B) Ragone plot comparing the data described in this paper to other transparent supercapacitors described in the literature. The bracket indicates the region of the data dominated by percolation. The arrow indicates the boundary between film with $T > 90\%$ and $T < 90\%$.

We note that the data appear to deviate from the fit line for $C/A < 10^4 \text{ F/cm}^2$ due to percolation. This can be seen more clearly in the inset which plots $1 - T$ versus C/A . We can use percolation theory to derive an expression for C/A for films with $t < t_{\min,C}$, following the procedure described in the previous chapter (Appendix 8.3). We can rewrite eqn. 6.4, making the approximation $t - t_C \approx t$ and note that, at the percolation to bulk transition, $t = t_{\min,C}$ and $C_V = C_{V,B}$, allowing us to write $C_V = C_{V,B}(t/t_{\min,C})^{n_C}$, where $C_{V,B}$ is the volumetric capacitance for a bulk-like film. Inserting this expression into $C/A = C_V t$ (true for all thicknesses) gives an equation which can be substituted into eqn. 6.3 (eliminating t) to give

$$T = \left[1 + \frac{Z_0 \sigma_{Op} t_{\min,C}}{2} \left(\frac{C/A}{C_{V,B} t_{\min,C}} \right)^{1/(n_C+1)} \right]^{-2} \quad (6.6)$$

All of the parameters in this expression have been described in this paper, $\sigma_{Op} = 1.7 \times 10^4 \text{ S/m}$, $t_{\min,C} \approx 20 \text{ nm}$ (Figure 6.4D), $C_{V,B} \approx 55 \text{ Fcm}^{-3}$ (Figure 6.4B), and $n_C = 0.83$. Using these known values, we can plot eqn. 6.6 on the Figure 6.5A inset. The result is the solid line and matches the data extremely well. We note that the disagreement between the theoretical line and the data point with smallest C/A is due to the approximation $t - t_C \approx t$.

It is useful to consider what capacitance can be achieved for a film with $T = 90\%$. This can be derived by rearranging eqn. 6.6 while setting $T = 90\%$ to give

$$\begin{aligned} \left(\frac{C}{A} \right)_{T=90\%} &= \frac{C_{V,B}}{t_{\min,C}^{n_C}} \left(\frac{0.11}{Z_0 \sigma_{Op}} \right)^{n_C+1} \\ &= C_{V,B} t_{\min,C} \left(\frac{0.11}{Z_0 \sigma_{Op} t_{\min,C}} \right)^{n_C+1} \end{aligned}$$

This means that to have high T coupled with high C/A one needs low σ_{Op} and $t_{\min,C}$ coupled with high $C_{V,B}$. We note that while σ_{Op} is generally a materials property, both $t_{\min,C}$ (ref [95]) and $C_{V,B}$ depend on nanotube bundle diameter such that low diameters should give better results. In addition, we note high values of n_C are favourable for high C/A . For electrical percolation, it is known that n_{DC} is controlled by the distribution of junction resistances in the network and so scales with network nonuniformity [133, 138, 143]. However, it is not yet clear what parameters control

n_C . However, if we assume that n_C also scales with network nonuniformity, the requirement for high n_C would suggest that non-uniform networks are preferred for thin, transparent supercapacitors. However, we note that the sheet resistance (and so the ESR) for percolating networks also scales with n_{DC} (or n_{ESR}) [95, 131]. This means that networks with high n_C (and so presumably n_{DC}) will have higher C/A but also higher R_{ESR} . This trade-off will need to be considered for particular applications.

The energy density and power density of a symmetric supercapacitor can be calculated using

$$E/M = C_D \Delta V^2 / 2M$$

and

$$P/M = \Delta V^2 / 4R_{ESR,D}M$$

where ΔV is the operating voltage (taken as 0.8V in this case) and M is twice the mass of SWNTs per electrode. We note that the device capacitance, C_D , is half the measured electrode capacitance, while the device ESR, $R_{ESR,D}$ is twice the measured electrode ESR (due to the fact that we work with a three-electrode cell) . In Figure 6.5B we have plotted E/M versus P/M . We have also included data reported in the literature for other transparent supercapacitors [105, 106, 144]. The SCs with bulk-like electrodes prepared here tend to cluster in the top right portion of the graph, while the thinner percolative networks extend down toward the bottom left. We note that all data points to the right of the arrow represent electrodes with $T < 90\%$. It is clear from this graph that our transparent electrodes with thicknesses in the bulk regime behave similarly to transparent electrochemical capacitor electrodes published in the literature. However, importantly, we show that increasing the transparency is accompanied by a rapidly diminishing power and energy densities due to percolative effects. The data in Figure 6.3A shows that for the tubes used here a transmittance of 90% per electrode (i.e., 81% per capacitor assuming a perfectly transparent electrolyte) limits the attainable areal capacitance to $\sim 10^4 F/cm^2$ per electrode or $\sim 1.5 \times 10^4 F$ for a two-electrode device with the area used here. This would be equivalent to

a stored energy of $\sim 10^4 J$. We note that due to percolation effects the achievable capacitance/energy is much reduced if $T > 90\%$ is required. Without knowing the exact role that transparent capacitors will play, it is difficult to assess whether these energies are large enough for applications. However, we emphasize that much work is currently ongoing into autonomous sensing/communication platforms [149]. These miniature devices will incorporate sensors which can communicate a detection event to the outside world via a radio frequency antenna. The communication event is likely to be powered by a supercapacitor which can later be recharged perhaps using photovoltaic technology. Transparency may be an advantage for such integrated devices for reasons of camouflage or to make them unobtrusive for aesthetic reasons. It has been estimated that the energy requirements for communication would be tens of microjoules per event [150]. These power requirements appear to be compatible with the transparent nanostructured supercapacitors described here.

6.3 CONCLUSIONS

We have examined the thickness dependence of the properties of supercapacitor electrodes prepared from carbon nanotube films. Measurements of the electrode transmittance and sheet resistance show a distinct transition from percolative to bulk-like behaviour as the electrode thickness is increased. The equivalent series resistance also underwent a percolation to bulk transition at the same electrode thickness of $100nm$. Interestingly, similar results were observed for the areal capacitance albeit with a lower transition thickness of $20nm$. The DC conductivity, effective ESR conductivity, and volumetric capacitance of thin films were all well described by percolation theory. All data could be described by percolation thresholds of $4.3nm$ and critical exponents of $n_{DC} = 0.66$, $n_{ESR} = 0.69$, and $n_C = 0.83$. We found the areal capacitance to be controlled by percolation for electrodes with $T > 90\%$. At $T = 90\%$, the capacitance was $10^4 F/cm^2$, enough to power burst communication for an integrated sensing device. We found that for bulk-like electrodes the energy and power densities clustered in a well-defined area of the Ragone plot. However, the percolative data formed a

long tail toward the bottom left corner of the graph. This work illustrates that, if high transparency is required, a severe cost in both power and energy must be paid. However, that cost can be readily estimated using percolation theory.

6.4 EXPERIMENTAL PROCEDURE

We prepared dispersions by adding *P3* single-walled carbon nanotubes (Carbon-Solutions Inc.) to Millipore water such that the nanotube concentration was 1mg/mL . The dispersion was then subjected to 0.5hr of high power tip sonication (VibraCell CVX; 750W , 20% 60kHz) and then left to settle overnight before being centrifuged at 5500 rpm for 90min . The supernatant was carefully decanted and saved for further use. We measure the concentration after centrifugation by measuring the absorbance spectrum and recording the absorbance per unit cell length, A/l , at 660nm . The Lambert Beer law ($A = \alpha Cl$) gives the concentration using the extinction coefficient, $\alpha = 3389\text{mLmg}^{-1}\text{m}^{-1}$ [28]. The resulting dispersions were vacuum-filtered using porous cellulose filter membranes (MF-Millipore membrane, mixed cellulose esters, hydrophilic, $0.025\mu\text{m}$, 47mm) to give thin films. The thickness of these films was controlled by the volume of dispersion filtered and hence the deposited mass. The deposited films were transferred to polyethylene terephthalate (PET) (or AuPd-coated glass) substrates using heat and pressure as described previously [14]. The cellulose filter membrane was then removed by treatment with acetone vapour and subsequent acetone liquid baths followed by a methanol bath. The final film diameter was 36mm . SEM was performed using a Zeiss Ultra plus SEM. Optical transmission spectra were recorded in the visible range ($400 - 800\text{nm}$) using a Varian Cary 6000i. In all cases, PET was used as the reference. Sheet resistance measurements were made using the four-probe technique with silver electrodes of dimensions and spacings typically of approximately millimeter size and a Keithley 2400 source meter. For electrochemical measurements, all nanotube electrodes had the same shape and lateral dimensions (length and width). This is critical to avoid scatter in the ESR measurements. Electrochemical characterization consisted of cyclic voltammetry and electrochemical impedance spectroscopy

using a three-electrode electrochemical cell and Gamry Reference600 potentiostat. Transparent electrodes were used as the working electrode with a carbon counter electrode and $Ag/AgCl$ ($3MNaCl$) reference electrode. The supporting electrolyte used for all characterisation was $1.0MH_2SO_4$ (Sigma-Aldrich). We determined the capacitive performance of transparent electrodes by cyclic voltammetry within the potential window 0 to 0.8V vs $Ag/AgCl$ at a scan rate of $50mVs^{-1}$. We determined the equivalent series resistance of the interface by electrochemical impedance spectroscopy (100kHz to 100mHz). An AC perturbation of 10mV was applied to the interface within the frequency range 0.1MHz to 10mHz.

CONCLUSIONS

Graphene films deposited from surfactant stabilised dispersions have been examined as a potential ITO replacement material. Although these films meet some of the requirements such as low temperature solution processing, high transparency and stability under flexing, the DC conductivity of $1.5 \times 10^4 \text{ S/m}$ is too low. A conductivity ratio $\sigma_{\text{DC}}/\sigma_{\text{Op}} \approx 0.4$ was achieved, close to the limiting value proposed by *De et al.* of $\sigma_{\text{DC}}/\sigma_{\text{Op}} = 0.7$ [128]. This would suggest little room for improvement. These films are still promising candidates for transparent conducting applications where extremely low R_s is not required due to the ease of processing, electromechanical stability, low cost. In addition, high temperature annealing of these films is not an intrinsic processing step.

The ability to exfoliate graphene in surfactant-water solutions in a manner similar to carbon nanotubes led to the formation of graphene/carbon nanotube hybrids. An optimum composition of 3wt% graphene was found. This hybrid displayed greater DC conductivity and conductivity ratio than the graphene or nanotube only films. After treatment with acid, to decrease the junction resistance, the conductivity ratio of the 3wt% increased by 40% compared to the nanotube only film of similar thickness from 12 to 18.5. Strategies to improve the conductivity of nanotube films involving improvements to the dispersion quality and film formation have yielded marginal improvements. Addition of small quantities of graphene show significant improvement to already good quality films.

Figures of Merit (FoMs) used to rate transparent conductors against known standards are typically based on bulk quantities. However, we have shown that for many potential materials in the technologically relevant regime, i.e. $T > 90\%$, the DC conductivity displays values lower than expected. The electrical properties tend to be controlled by percolation in that we observe thickness independent quantities such as

DC conductivity displaying thickness dependant behaviour. To improve our understanding of the consequences of this, a model has been developed by *De et al.* which relates T to R_s in the percolation regime. A percolative figure of merit, Π was defined, for which high values result in high T and low R_s . High values of Π are achieved for high DC conductivity and low optical conductivity. In addition, the film thickness, t_{min} , where the DC conductivity first deviates from its bulk value and the percolation exponent, n , must both be as low as possible. We demonstrate that t_{min} depends on the smallest dimension (D) of the entity making up the film by $t_{min} \approx 2.33D$ (i.e. diameter for wires or thickness for flakes).

The importance of understanding percolation and deficiencies of standard bulk theory are clearly highlighted by measuring the opto-electronic properties of networks of silver flakes. The bulk ratio of DC to optical conductivity was measured to be ~ 35 , suggesting the minimum industry requirements as set by Hewlett Packard (HP) of $R_s = 100\Omega/sq$ and $T = 90\%$ are achievable. However, due to the large flake thickness t_{min} is high and so Π is low, resulting in actual values of $T = 26\%$ for $R_s = 100\Omega/sq$. This makes this material completely unsuitable for transparent conductor applications a fact that would be overlooked when considering bulk FoMs only.

The relationship between R_s and T is defined by two parameters; the percolative FoM which is controlled by the properties of the material and the percolation exponent which is determined by the properties of the network. This suggests two distinct approaches to improve network performance. One can either improve the material making up the network or improve the network as a whole.

The effect of percolation on the properties of supercapacitor electrodes has been examined. Measurements of the electrode sheet resistance and transmittance as a function of thickness show similar behaviour to networks of graphene and silver nanowires. We find a distinct transition from percolative to bulk-like behaviour for our carbon nanotube electrodes as the thickness is increased above $100nm$. As expected the equivalent series resistance also underwent a percolation to bulk transition at this thickness. Similar results were observed for the areal capacitance, although a lower transition thickness of $20nm$ was observed. We found the areal capacitance to be controlled by percolation for electrodes with $T > 90\%$. We also show that the

thickness dependence of both R_{ESR} and volumetric capacitance C_v are consistent with percolation theory. While this result may be expected for R_{ESR} , it is unexpected that the capacitance follows a percolation scaling law. The reason for this is that, for sparse networks, the capacitance is proportional to the fraction of nanotubes connected to the main network. This fraction, in turn, follows a percolation scaling law. In terms of the energy and power density we find that in the bulk regime our data is clustered in a well defined region of the Ragone plot with values similar to that of other transparent supercapacitors. However, in the percolation regime a significant fall off towards lower energy and power density is observed as the film transmittance is increased. Hence if high transparency is required, a severe cost in both power and energy must be paid. However, that cost can be readily estimated using percolation theory.

Solution processed graphene films will not replace ITO as a transparent electrode. Addition of small quantities of graphene to carbon nanotube networks results in significant improvement. Percolation effects must be considered for nanostructured electrodes in the technologically relevant regime as a considerable performance price must be paid for very high transparency.

7.1 FUTURE WORK

In terms of future high performance transparent conductors, low diameter metallic nanowires display superlative performance to solution processed carbon nanoconductors due to the much lower junction resistance. The most significant recent advancement in this field is work done by Rathmell *et al.* [99]. They synthesised copper nanowires with nickel shell and measured the temperature dependence of the sheet resistance. Their results show that for copper and silver nanowire films sheet resistance R_s will double after 3 and 36 months at room temperature respectively. The sheet resistance of cupronickel nanowires containing 20mol% nickel will double in about 400 years. These properties, and the fact that copper and nickel are 1000 times more abundant than indium or silver, make cupronickel nanowires a very promising alternative for the sustainable, efficient production of transparent conductors.

There is significant room for improvement in the power and energy densities for transparent supercapacitors in the technologically relevant regime. There are two areas that I feel warrant further investigation.

To maximize power and energy density for high T electrodes, it would be necessary to shift the transition from bulk-like to percolative behaviour to lower thickness, that is, $t_{min,ESR}$ and $t_{min,C}$ must be reduced. It is known that $t_{min,DC}$ scales linearly with the diameter of the rods making up the network, in this case the nanotube bundle diameter, and it is reasonable to assume the same for $t_{min,ESR}$ and $t_{min,C}$. Thus, it is possible that percolation effects can be minimized or avoided altogether by using better exfoliated nanotubes. According to Figure 6.3A, $T = 90\%$ can be achieved for $t = 16nm$. We recently showed that $t_{min,DC} \approx 2.33D$, where D is the bundle diameter [95]. Thus, the onset of electrical percolation could be suppressed to below $t_{min,DC} = 16nm$ so long as $D < 7nm$.

To increase the energy density, the nanotube network could be coated with a pseudo-capacitive material such as MnO_x [151]. It has been demonstrated that such Faradaic or hybrid double-layer supercapacitors can yield much higher specific capacitance and energy density than pure electrochemical double-layer capacitors [111]. This will increase the volumetric capacitance, although the percolation effects discussed here will still be present.

A straightforward method to coat carbon surfaces with MnO_x is the reduction of permanganate [152]. In this general method, the carbon substrate serves as a sacrificial reductant and converts aqueous permanganate (MnO_4^-) to insoluble MnO_2 . It would be important to control the thickness of the coating applied to see the effect of coating thickness on the optical, electrical and electrochemical performance of the films.

Recently our group in collaboration with Prof. Nicolosi's group (Oxford) have demonstrated a method to efficiently disperse a host of layered compounds in common solvents, and in water with the aid of surfactant stabilisation [153, 154]. Applications of films of exfoliated layered compounds in many areas will be limited by their relatively low electrical conductivity. *Cunningham et al.* have shown that for MoS_2 -SWNT composites conductivities as high as $\sim 40S/m$ can be achieved at SWNT volume fractions as low as $\sim 4\%$ [155]. Work is currently underway in our group to exfoliate

layered pseudocapacitive materials such as MnO_2 and MoO_3 . Dispersions of these materials would be blended with dispersions of carbon nanoconductors similar to the work done in Chapter 4. The SWNTs will greatly increase the conductivity of the composite and due to the web like morphology of SWNT network should increase the porosity and hence electrolyte accessibility. In the case of MnO_2 it is imperative to fabricate an open porous network because only a very thin layer is involved in the charge storage process [156].

APPENDIX

8.1 VOLTAGE RAMP (POTENTIAL SWEEP)

$$vt = iR_s + \frac{q}{C_d}$$

$$\frac{dq}{dt} + \frac{q}{RC} = \frac{vt}{R}$$

Let

$$P(t) = \frac{1}{RC}$$

$$Q(t) = \frac{vt}{R}$$

substituting into equation

$$\frac{dq}{dt} + P(t)q = Q(t)$$

use integrating factor

$$\mu = e^{\int P(t)} = e^{\int \frac{1}{RC}} = e^{\frac{t}{RC}}$$

now

$$q = \frac{1}{\mu} \int \mu Q(t) dt$$

$$q = e^{-\frac{t}{RC}} \int e^{-\frac{t}{RC}} \frac{vt}{R} dt$$

$$q = \frac{v}{R} e^{-\frac{t}{RC}} \int e^{\frac{t}{RC}} t dt$$

Use integration by parts on $\int e^{\frac{t}{RC}} t dt$

$$\int u dv = uv - \int v du$$

let $u = t$, $du = 1$, $dv = e^{-\frac{t}{RC}}$, $v = RCe^{-\frac{t}{RC}}$

$$q = \frac{\nu}{R} e^{-\frac{t}{RC}} \int u dv = \frac{\nu}{R} e^{-\frac{t}{RC}} \left[uv - \int v du \right]$$

$$q = \frac{\nu}{R} e^{-\frac{t}{RC}} \left[RCe^{-\frac{t}{RC}} - \int RCe^{-\frac{t}{RC}} \right]$$

$$q = \frac{\nu}{R} e^{-\frac{t}{RC}} \left[RCe^{-\frac{t}{RC}} - R^2 C^2 e^{-\frac{t}{RC}} + \beta \right] = \nu C t - \nu R C^2 + \beta \frac{\nu}{R} e^{-\frac{t}{RC}}$$

Initially, $q = 0$ when $t = 0$

$$\nu R C^2 = \beta \frac{\nu}{R}$$

$$\beta = R^2 C^2$$

$$q = \nu C t - \nu R C^2 + \nu R C^2 e^{-\frac{t}{RC}}$$

Thus

$$\frac{dq}{dt} = \nu C - \nu C e^{-\frac{t}{RC}}$$

$$i = \nu C \left[1 - e^{-\frac{t}{RC}} \right]$$

8.2 R_s AT $T=90\%$

$$T = \left[1 + \frac{1}{\Pi} \left(\frac{Z_0}{R_s} \right)^{1/(n+1)} \right]^{-2}$$

$$\Pi = 2 \left[\frac{\sigma_{DC,B}/\sigma_{Op}}{(Z_0 t_{min} \sigma_{Op})^n} \right]^{1/(n+1)}$$

substituting for Π

$$T = \left[1 + \frac{1}{2 \left[\frac{\sigma_{DC,B}/\sigma_{Op}}{(Z_0 t_{min} \sigma_{Op})^n} \right]^{1/(n+1)}} \left(\frac{Z_0}{R_s} \right)^{1/(n+1)} \right]^{-2}$$

$$2(T^{-1/2} - 1) = \left(\frac{(Z_0 t_{min} \sigma_{Op})^n}{\sigma_{DC,B}/\sigma_{Op}} \right)^{\frac{1}{(n+1)}} \left(\frac{Z_0}{R_s} \right)^{\frac{1}{(n+1)}}$$

$$T = 90\%$$

$$0.11 \approx \left[\frac{(Z_0 t_{min} \sigma_{Op})^n}{\sigma_{DC,B}/\sigma_{Op}} \left(\frac{Z_0}{R_s^{T=90\%}} \right) \right]^{\frac{1}{(n+1)}}$$

$$0.11^{(n+1)} \approx \left[\frac{(Z_0 t_{min} \sigma_{Op})^n}{\sigma_{DC,B}/\sigma_{Op}} \left(\frac{Z_0}{R_s^{T=90\%}} \right) \right]$$

$$0.11(0.11)^n \approx \frac{(Z_0 t_{min} \sigma_{Op})^n}{\sigma_{DC,B}/\sigma_{Op}} \left(\frac{Z_0}{R_s^{T=90\%}} \right)$$

$$R_s^{T=90\%} \approx \frac{Z_0}{0.11 \sigma_{DC,B}/\sigma_{Op}} \left(\frac{Z_0 t_{min} \sigma_{Op}}{0.11} \right)$$

8.3 PERCOLATION EFFECTS IN SUPERCAPACITORS

We expect the volumetric capacitance to scale with thickness in the thin film regime as

$$C_V \propto (t - t_c)^{n_c}$$

For a bulk-like electrode, the areal capacitance is related to the thickness by

$$C/A = C_{V,B} t$$

substituting into

$$T = \left(1 + \frac{Z_0}{2} \sigma_{Op} t \right)^{-2}$$

to eliminate t gives

$$T = \left[1 + \frac{Z_0 \sigma_{Op}}{2 C_{V,B}} \frac{C}{A} \right]^{-2}$$

We can use percolation theory to derive an expression for C/A for films with $t < t_{min,C}$

make approximation

$$t - t_c \approx t$$

note that at the percolation to bulk transition

$$t = t_{min,C}$$

$$C_V \propto t^{n_C}$$

and

$$C_V = C_{V,B}$$

We have

$$C_V = kt^{n_C}$$

$$C_{V,B} = kt_{min}^{n_C}$$

$$C_V = C_{V,B} (t/t_{min})^{n_C}$$

$$C_V = C/At$$

$$\frac{C}{A} = C_{V,B} \left(\frac{t}{t_{min}} \right)^{n_C} t$$

$$\frac{C/A}{C_{V,B}} = \frac{t^{n_C+1}}{t_{min}^{n_C}}$$

$$\frac{C/A}{C_{V,B}} t_{min}^{n_C} = t^{n_C+1}$$

$$t = \left(\frac{C/A}{C_{V,B}} \right)^{\frac{1}{n_C+1}} (t_{min,C})^{\frac{n_C}{n_C+1}}$$

$$t = \left(\frac{C/A}{C_{V,B}} \right)^{\frac{1}{n_C+1}} (t_{min,C})^{\frac{n_C+1-1}{n_C+1}}$$

$$t = \left(\frac{C/A}{C_{V,B}} \right)^{\frac{1}{n_C+1}} (t_{min,C})^{\frac{n_C+1}{n_C+1}} (t_{min,C})^{-\frac{1}{n_C+1}}$$

$$t = \left(\frac{C/A}{C_{V,B}} \right)^{\frac{1}{n_C+1}} t_{min,C} \left(\frac{1}{t_{min,C}} \right)^{\frac{1}{n_C+1}}$$

$$t = \left(\frac{C/A}{C_{V,B} t_{min,C}} \right)^{\frac{1}{n_C+1}} t_{min,C}$$

substituting into

$$T = \left(1 + \frac{Z_0}{2} \sigma_{Op} t \right)^{-2}$$

$$T = \left(1 + \frac{Z_0 \sigma_{Op} t_{min,C}}{2} \left(\frac{C/A}{C_{V,B} t_{min,C}} \right)^{\frac{1}{n_C+1}} \right)^{-2}$$

BIBLIOGRAPHY

- [1] Ferrari, A. C., Meyer, J. C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K. S., Roth, S., and Geim, A. K. (2006) Raman Spectrum of Graphene and Graphene Layers. *Physical Review Letters* 97.
- [2] Rathmell, A. R., Bergin, S. M., Hua, Y., Li, Z., and Wiley, B. J. (2010) The Growth Mechanism of Copper Nanowires and Their Properties in Flexible, Transparent Conducting Films. *Advanced Materials* 22, 3558–3563.
- [3] De, S., Higgins, T. M., Lyons, P. E., Doherty, E. M., Nirmalraj, P. N., Blau, W. J., Boland, J. J., and Coleman, J. N. (2009) Silver Nanowire Networks as Flexible, Transparent, Conducting Films: Extremely High DC to Optical Conductivity Ratios. *ACS Nano* 3, 1767–1774.
- [4] Lyons, P. E., De, S., Elias, J., Schamel, M., Philippe, L., Bellew, A. T., Boland, J. J., and Coleman, J. N. (2011) High-Performance Transparent Conductors from Networks of Gold Nanowires. *The Journal of Physical Chemistry Letters* 2, 3058–3062.
- [5] Iijima, S. (1991) Helical microtubules of graphitic carbon. *Nature* 354, 56–58.
- [6] Ebbesen, T. W., Lezec, H. J., Hiura, H., Bennett, J. W., Ghaemi, H. F., and Thio, T. (1996) Electrical conductivity of individual carbon nanotubes. *Nature* 382, 54–56.
- [7] Odom, T. W., Huang, J.-L., Kim, P., and Lieber, C. M. (1998) Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature* 391, 62–64.
- [8] Wilder, J. W. G., Venema, L. C., Rinzler, A. G., Smalley, R. E., and Dekker, C. (1998) Electronic structure of atomically resolved carbon nanotubes. *Nature* 391, 59–62.

- [9] Dresselhaus, M. S., Dresselhaus, G., and Saito, R. (1992) Carbon fibers based on C 60 and their symmetry. *Phys. Rev. B* 45, 6234–6242.
- [10] Hu, L., Hecht, D. S., and Gruner, G. Carbon Nanotube Thin Films: Fabrication, Properties, and Applications. *Chemical Reviews* 0.
- [11] Durkop, T., Getty, S. A., Cobas, E., and Fuhrer, M. S. (2004) Extraordinary Mobility in Semiconducting Carbon Nanotubes. *Nano Letters* 4, 35–39.
- [12] Mintmire, J. W., and White, C. T. (1998) Universal Density of States for Carbon Nanotubes. *Phys. Rev. Lett.* 81, 2506–2509.
- [13] Kane, C. L., and Mele, E. J. (1997) Size, Shape, and Low Energy Electronic Structure of Carbon Nanotubes. *Phys. Rev. Lett.* 78, 1932–1935.
- [14] others,, et al. (2004) Transparent, conductive carbon nanotube films. *Science* 305, 1273.
- [15] Gruner, G. (2006) Carbon nanotube films for transparent and plastic electronics. *Journal of Materials Chemistry* 16, 3533–3539.
- [16] Feng, C., Liu, K., Wu, J.-S., Liu, L., Cheng, J.-S., Zhang, Y., Sun, Y., Li, Q., Fan, S., and Jiang, K. (2010) Flexible, Stretchable, Transparent Conducting Films Made from Superaligned Carbon Nanotubes. *Advanced Functional Materials* 20, 885–891.
- [17] Zhang, M., Fang, S., Zakhidov, A. A., Lee, S. B., Aliev, A. E., Williams, C. D., Atkinson, K. R., and Baughman, R. H. (2005) Strong, Transparent, Multifunctional, Carbon Nanotube Sheets. *Science* 309, 1215–1219.
- [18] Jiang, K., Li, Q., and Fan, S. (2002) Nanotechnology: Spinning continuous carbon nanotube yarns. *Nature* 419, 801–801.
- [19] Niu, C., Sichel, E. K., Hoch, R., Moy, D., and Tennent, H. (1997) High power electrochemical capacitors based on carbon nanotube electrodes. *Applied Physics Letters* 70, 1480–1482.

- [20] Jeffrey L. Bahr, M. J. B. R. E. S., Edward T. Mickelson, and Tour, J. M. (2001) Dissolution of small diameter single-wall carbon nanotubes in organic solvents? *Chemical Communications* 193–194.
- [21] Giordani, S., Bergin, S., Nicolosi, V., Lebedkin, S., Blau, W. J., and Coleman, J. N. (2006) Fabrication of stable dispersions containing up to 70% individual carbon nanotubes in a common organic solvent. *physica status solidi (b)* 243, 3058–3062.
- [22] Bergin, S. D., Nicolosi, V., Streich, P. V., Giordani, S., Sun, Z., Windle, A. H., Ryan, P., Niraj, N. P. P., Wang, Z.-T. T., Carpenter, L., Blau, W. J., Boland, J. J., Hamilton, J. P., and Coleman, J. N. (2008) Towards Solutions of Single-Walled Carbon Nanotubes in Common Solvents. *Advanced Materials* 20, 1876–1881.
- [23] Ramesh, S., Ericson, L. M., Davis, V. A., Saini, R. K., Kittrell, C., Pasquali, M., Billups, W. E., Adams, W. W., Hauge, R. H., and Smalley, R. E. (2004) Dissolution of Pristine Single Walled Carbon Nanotubes in Superacids by Direct Protonation. *The Journal of Physical Chemistry B* 108, 8794–8798.
- [24] Moore, V. C., Strano, M. S., Haroz, E. H., Hauge, R. H., Smalley, R. E., Schmidt, J., and Talmon, Y. (2003) Individually Suspended Single-Walled Carbon Nanotubes in Various Surfactants. *Nano Letters* 3, 1379–1382.
- [25] Chen, J., Rao, A. M., Lyuksyutov, S., Itkis, M. E., Hamon, M. A., Hu, H., Cohn, R. W., Eklund, P. C., Colbert, D. T., Smalley, R. E., and Haddon, R. C. (2001) Dissolution of Full-Length Single-Walled Carbon Nanotubes. *J. Phys. Chem. B* 105, 2525–2528.
- [26] Ham, H. T., Choi, Y. S., and Chung, I. J. (2005) An explanation of dispersion states of single-walled carbon nanotubes in solvents and aqueous surfactant solutions using solubility parameters. *Journal of Colloid and Interface Science* 286, 216 – 223.
- [27] Bergin, S. D., Sun, Z., Streich, P., Hamilton, J., and Coleman, J. N. (2010) New Solvents for Nanotubes: Approaching the Dispersibility of Surfactants. *The Journal of Physical Chemistry C* 114, 231–237.

- [28] Bergin, S., Nicolosi, V., Cathcart, H., Lotya, M., Rickard, D., Sun, Z., Blau, W., and Coleman, J. (2008) Large Populations of Individual Nanotubes in Surfactant-Based Dispersions without the Need for Ultracentrifugation. *Journal of Physical Chemistry C* 112, 972–977.
- [29] Islam, M. F., Rojas, E., Bergey, D. M., Johnson, A. T., and Yodh, A. G. (2003) High Weight Fraction Surfactant Solubilization of Single-Wall Carbon Nanotubes in Water. *Nano Lett.* 3, 269–273.
- [30] Matarredona, O., Rhoads, H., Li, Z., Harwell, J. H., Balzano, L., and Resasco, D. E. (2003) Dispersion of Single-Walled Carbon Nanotubes in Aqueous Solutions of the Anionic Surfactant NaDDBS. *The Journal of Physical Chemistry B* 107, 13357–13367.
- [31] De, S., King, P. J., Lotya, M., O'Neill, A., Doherty, E. M., Hernandez, Y., Duesberg, G. S., and Coleman, J. N. (2009) Flexible, Transparent, Conducting Films of Randomly Stacked Graphene from Surfactant-Stabilized, Oxide-Free Graphene Dispersions. *Small* 9999, NA.
- [32] King, P. J., Khan, U., Lotya, M., De, S., and Coleman, J. N. (2010) Improvement of Transparent Conducting Nanotube Films by Addition of Small Quantities of Graphene. *ACS Nano* 4, 4238–4246.
- [33] Liu, K., Roth, S., Duesberg, G., Wagenhals, M., Journet, C., and Dernier, P. (1999) Transport properties of single-walled carbon nanotubes. *Synthetic Metals* 103, 2513 – 2514.
- [34] Li, Z., Kandel, H. R., Dervishi, E., Saini, V., Xu, Y., Biris, A. R., Lupu, D., Salamo, G. J., and Biris, A. S. (2008) Comparative Study on Different Carbon Nanotube Materials in Terms of Transparent Conductive Coatings. *Langmuir* 24, 2655–2662, f.
- [35] Nirmalraj, P. N., Lyons, P. E., De, S., Coleman, J. N., and Boland, J. J. (2009) Electrical Connectivity in Single-Walled Carbon Nanotube Networks. *Nano Letters* 9, 3890–3895.

- [36] Fuhrer, M. S., Nygard, J., Shih, L., Forero, M., Yoon, Y.-G., Mazzone, M. S. C., Choi, H. J., Ihm, J., Louie, S. G., Zettl, A., and McEuen, P. L. (2000) Crossed Nanotube Junctions. *Science* 288, 494–497.
- [37] Li, S., Yu, Z., Rutherglen, C., and Burke, P. J. (2004) Electrical Properties of 0.4 cm Long Single-Walled Carbon Nanotubes. *Nano Letters* 4, 2003–2007.
- [38] Hecht, D., Hu, L., and Gruner, G. (2006) Conductivity scaling with bundle length and diameter in single walled carbon nanotube networks. *Applied Physics Letters* 89, 133112–133112-3.
- [39] Shin, D. H., Shim, H. C., Song, J.-W., Kim, S., and Han, C.-S. (2009) Conductivity of films made from single-walled carbon nanotubes in terms of bundle diameter. *Scripta Materialia* 60, 607 – 610.
- [40] Li, Z., Kandel, H. R., Dervishi, E., Saini, V., Biris, A. S., Biris, A. R., and Lupu, D. (2007) Does the wall number of carbon nanotubes matter as conductive transparent material? *Applied Physics Letters* 91, 053115.
- [41] Hong-Zhang Geng, K. K. K. S. J. K. J. J. B., Dae Sik Lee, and Lee, Y. H. (2008) Effect of Carbon Nanotube Types in Fabricating Flexible Transparent Conducting Films. *J. Korean Phys.Soc.* 53, 979–985.
- [42] Kaempgen, M., Duesberg, G., and Roth, S. (2005) Transparent carbon nanotube coatings. *Applied Surface Science* 252, 425–429.
- [43] Geng, K. K. K. L. K. K. G. Y. C. H. K. L. D. S. A. K. H. L. Y. H. C. Y. L. Y. S. K. B., Hong-Zhang, and LEE, Y. J. (2007) Dependence of material quality on performance of flexible transparent conducting films with single -walled carbon nanotubes. *Nano* 02, 157–167.
- [44] Hu, L., Hecht, D., and Gruner, G. (2004) Percolation in transparent and conducting carbon nanotube networks. *Nano Letters* 4, 2513–2517.
- [45] Doherty, E. M., De, S., Lyons, P. E., Shmeliov, A., Nirmalraj, P. N., Scardaci, V., Joimel, J., Blau, W. J., Boland, J. J., and Coleman, J. N. (2009) The spatial unifor-

mity and electromechanical stability of transparent, conductive films of single walled nanotubes. *Carbon* 47, 2466–2473.

- [46] Topinka, M. A., Rowell, M. W., Goldhaber-Gordon, D., McGehee, M. D., Hecht, D. S., and Gruner, G. (2009) Charge Transport in Interpenetrating Networks of Semiconducting and Metallic Carbon Nanotubes. *Nano Letters* 9, 1866–1871.
- [47] Landau, L. (1937) Zur Theorie der phasenumwandlungen II. *Phys. Z. Sowjetunion* 11, 26–35.
- [48] Peierls, R. E. Quelques proprietes typiques des corps solide. *Ann. I. H. Poincare* 5, 177–222.
- [49] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Katsnelson, M. I., Grigorieva, I. V., Dubonos, S. V., and Firsov, A. A. (2005) Two-dimensional gas of massless Dirac fermions in graphene. *Nature* 438, 197–200.
- [50] Novoselov, K. S. (2004) Electric Field Effect in Atomically Thin Carbon Films. *Science* 306, 666–669.
- [51] Katsnelson, M. I., Novoselov, K. S., and Geim, A. K. (2006) Chiral tunnelling and the Klein paradox in a graphene. *Nature Physics* 2, 620–625.
- [52] Zhang, Y., Tan, Y., Stormer, H. L., and Kim, P. (2005) Experimental observation of the quantum Hall effect and Berry’s phase in graphene. *Nature* 438, 201–204.
- [53] Pisana, S., Lazzeri, M., Casiraghi, C., Novoselov, K. S., Geim, A. K., Ferrari, A. C., and Mauri, F. (2007) Breakdown of the adiabatic Born-Oppenheimer approximation in graphene. *Nat Mater* 6, 198–201.
- [54] Du, X., Skachko, I., Barker, A., and Andrei, E. Y. (2008) Approaching ballistic transport in suspended graphene. *Nat Nano* 3, 491–495.
- [55] Nair, R. R., Blake, P., Grigorenko, A. N., Novoselov, K. S., Booth, T. J., Stauber, T., Peres, N. M. R., and Geim, A. K. (2008) Fine Structure Constant Defines Visual Transparency of Graphene. *Science* 320, 1308–1308.

- [56] Lee, C., Wei, X., Kysar, J. W., and Hone, J. (2008) Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* 321, 385–388.
- [57] Wu, J., Agrawal, M., Becerril, H. A., Bao, Z., Liu, Z., Chen, Y., and Peumans, P. (2009) Organic Light-Emitting Diodes on Solution-Processed Graphene Transparent Electrodes. *ACS Nano* 4, 43–48.
- [58] Blake, P., Hill, E. W., Castro Neto, A. H., Novoselov, K. S., Jiang, D., Yang, R., Booth, T. J., and Geim, A. K. (2007) Making graphene visible. *Applied Physics Letters* 91, 063124.
- [59] de Heer, W. A., Berger, C., Wu, X., First, P. N., Conrad, E. H., Li, X., Li, T., Sprinkle, M., Hass, J., Sadowski, M. L., Potemski, M., and Martinez, G. (2007) Epitaxial graphene. *Solid State Communications* 143, 92–100.
- [60] Berger, C., Song, Z., Li, X., Wu, X., Brown, N., Naud, C., Mayou, D., Li, T., Hass, J., Marchenkov, A. N., Conrad, E. H., First, P. N., and de Heer, W. A. (2006) Electronic Confinement and Coherence in Patterned Epitaxial Graphene. *Science* 312, 1191–1196.
- [61] Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., Bulovic, V., Dresselhaus, M. S., and Kong, J. (2009) Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Letters* 9, 30–35.
- [62] Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., Kim, J. M., Kim, K. S., Ahn, J. H., Kim, P., Choi, J. Y., and Hong, B. H. (2009) Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* 457, 706–710.
- [63] Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., Tutuc, E., Banerjee, S. K., Colombo, L., and Ruoff, R. S. (2009) Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* 324, 1312–1314.
- [64] Segal, M. (2009) Selling graphene by the ton. *Nature Nanotechnology* 4, 612–614.
- [65] Ruoff, R. (2008) Calling all chemists. *Nature Nanotechnology* 3, 10–11.

- [66] Stankovich, S., Piner, R. D., Chen, X., Wu, N., Nguyen, S. T., and Ruoff, R. S. (2006) Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). *Journal of Materials Chemistry* 16, 155–158.
- [67] Hummers, W. S., and Offeman, R. E. (1958) Preparation of Graphitic Oxide. *Journal of the American Chemical Society* 80, 1339.
- [68] He, H., Riedl, T., Lerf, A., and Klinowski, J. (1996) Solid-State NMR Studies of the Structure of Graphite Oxide. *The Journal of Physical Chemistry* 100, 19954–19958.
- [69] He, H., Klinowski, J., Forster, M., and Lerf, A. (1998) A new structural model for graphite oxide. *Chemical Physics Letters* 287, 53 – 56.
- [70] Paredes, J. I., Villar-Rodil, S., Martı́nez-Alonso, A., and Tascołn, J. M. D. (2008) Graphene Oxide Dispersions in Organic Solvents. *Langmuir* 24, 10560–10564.
- [71] Becerril, H. A., Mao, J., Liu, Z., Stoltenberg, R. M., Bao, Z., and Chen, Y. (2008) Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors. *ACS Nano* 2, 463–470.
- [72] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., and Ruoff, R. S. (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45, 1558–1565.
- [73] Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W., and Tour, J. M. (2008) Diazonium Functionalization of Surfactant-Wrapped Chemically Converted Graphene Sheets. *Journal of the American Chemical Society* 130, 16201–16206.
- [74] Schniepp, H. C., Li, J., McAllister, M. J., Sai, H., Herrera-Alonso, M., Adamson, D. H., Prud'homme, R. K., Car, R., Saville, D. A., and Aksay, I. A. (2006) Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide. *The Journal of Physical Chemistry B* 110, 8535–8539.

- [75] Williams, G., Seger, B., and Kamat, P. V. (2008) TiO₂-Graphene Nanocomposites UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* 2, 1487–1491.
- [76] Wang, X., Zhi, L., and Mullen, K. (2008) Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells. *Nano Letters* 8, 323–327.
- [77] Dikin, D. A., Stankovich, S., Zimney, E. J., Piner, R. D., Dommett, G. H. B., Evmenenko, G., Nguyen, S. T., and Ruoff, R. S. (2007) Preparation and characterization of graphene oxide paper. *Nature* 448, 457–460.
- [78] Hernandez, Y. et al. (2008) High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology* 3, 563–568.
- [79] Blake, P., Brimicombe, P. D., Nair, R. R., Booth, T. J., Jiang, D., Schedin, F., Ponomarenko, L. A., Morozov, S. V., Gleeson, H. F., Hill, E. W., Geim, A. K., and Novoselov, K. S. (2008) Graphene-Based Liquid Crystal Device. *Nano Letters* 8, 1704–1708.
- [80] Khan, U., O'Neill, A., Lotya, M., De, S., and Coleman, J. N. (2010) High-Concentration Solvent Exfoliation of Graphene. *Small* 6, 864–871.
- [81] Kovtyukhova, N. I., Mallouk, T. E., Pan, L., and Dickey, E. C. (2003) Individual Single-Walled Nanotubes and Hydrogels Made by Oxidative Exfoliation of Carbon Nanotube Ropes. *Journal of the American Chemical Society* 125, 9761–9769.
- [82] Sun, Z., Nicolosi, V., Rickard, D., Bergin, S. D., Aherne, D., and Coleman, J. N. (2008) Quantitative Evaluation of Surfactant-stabilized Single-walled Carbon Nanotubes: Dispersion Quality and Its Correlation with Zeta Potential. *Journal of Physical Chemistry C* 112, 10692–10699.
- [83] Lotya, M., Hernandez, Y., King, P. J., Smith, R. J., Nicolosi, V., Karlsson, L. S., Blighe, F. M., De, S., Wang, Z., McGovern, I. T., Duesberg, G. S., and Coleman, J. N. (2009) Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. *Journal of the American Chemical Society* 131, 3611–3620.

- [84] Lotya, M., King, P. J., Khan, U., De, S., and Coleman, J. N. (2010) High-Concentration, Surfactant-Stabilized Graphene Dispersions. *ACS Nano* 4(6), 3155–3162.
- [85] Eda, G., Fanchini, G., and Chhowalla, M. (2008) Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotechnology* 3, 270–274.
- [86] Eda, G., Lin, Y., Miller, S., Chen, C., Su, W., and Chhowalla, M. (2008) Transparent and conducting electrodes for organic electronics from reduced graphene oxide. *Applied Physics Letters* 92, 233305.
- [87] Cai, W., Zhu, Y., Li, X., Piner, R. D., and Ruoff, R. S. (2009) Large area few-layer graphene/graphite films as transparent thin conducting electrodes. *Applied Physics Letters* 95, 123115–3.
- [88] Wu, J., Becerril, H. A., Bao, Z., Liu, Z., Chen, Y., and Peumans, P. (2008) Organic solar cells with solution-processed graphene transparent electrodes. *Applied Physics Letters* 92, 263302.
- [89] Tung, V. C., Allen, M. J., Yang, Y., and Kaner, R. B. (2008) High-throughput solution processing of large-scale graphene. *Nature Nanotechnology* 4, 25–29.
- [90] Avouris, P., Chen, Z., and Perebeinos, V. (2007) Carbon-based electronics. *Nature nanotechnology* 2, 605–615.
- [91] Geim, A. K., and Novoselov, K. S. (2007) The rise of graphene. *Nat Mater* 6, 183–191.
- [92] Bae, S. et al. (2010) Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat Nano advance online publication*.
- [93] Hecht, D. S., Hu, L., and Irvin, G. (2011) Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures. *Advanced Materials* 23, 1482–1513.

- [94] Dan, B., Irvin, G. C., and Pasquali, M. (2009) Continuous and Scalable Fabrication of Transparent Conducting Carbon Nanotube Films. *ACS Nano* 3, 835–843.
- [95] De, S., King, P. J., Lyons, P. E., Khan, U., and Coleman, J. N. (2010) Size Effects and the Problem with Percolation in Nanostructured Transparent Conductors. *ACS Nano* 4, 7064–7072.
- [96] De, S., Lyons, P. E., Sorel, S., Doherty, E. M., King, P. J., Blau, W. J., Nirmalraj, P. N., Boland, J. J., Scardaci, V., Joimel, J., and Coleman, J. N. (2009) Transparent, Flexible, and Highly Conductive Thin Films Based on Polymer Nanotube Composites. *ACS Nano* 3, 714–720.
- [97] Stauffer, A. A., D *Introduction to Percolation Theory*; Taylor and Francis, 1994.
- [98] Wu, H., Hu, L., Rowell, M. W., Kong, D., Cha, J. J., McDonough, J. R., Zhu, J., Yang, Y., McGehee, M. D., and Cui, Y. (2010) Electrospun Metal Nanofiber Webs as High-Performance Transparent Electrode. *Nano Letters* 10, 4242–4248.
- [99] Rathmell, A. R., Nguyen, M., Chi, M., and Wiley, B. J. (2012) Synthesis of Oxidation-Resistant Cupronickel Nanowires for Transparent Conducting Nanowire Networks. *Nano Letters* 12, 3193–3199.
- [100] Hecht, D. S., Heintz, A. M., Lee, R., Hu, L., Moore, B., Cucksey, C., and Risser, S. (2011) High conductivity transparent carbon nanotube films deposited from superacid. *Nanotechnology* 22, 075201.
- [101] Geng, H.-Z., Kim, K. K., So, K. P., Lee, Y. S., Chang, Y., and Lee, Y. H. (2007) Effect of Acid Treatment on Carbon Nanotube-Based Flexible Transparent Conducting Films. *Journal of the American Chemical Society* 129, 7758–7759.
- [102] Green, A. A., and Hersam, M. C. Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation. *Nano Letters* 0.
- [103] Riedl, T., Gornn, P., and Kowalsky, W. (2009) Transparent Electronics for See-Through AMOLED Displays. *Journal of Display Technology* 5, 501–508.

- [104] Yang Y FAU Jeong, S., Jeong S FAU Hu, L., Hu L FAU Wu, H., Wu H FAU Lee, S. W., Lee SW FAU Cui, Y., and Y, C. (2011) Transparent lithium-ion batteries. *Proceedings of the National Academy of Sciences* 109, 13013–13018.
- [105] Chen, P., Shen, G., Sukcharoenchoke, S., and Zhou, C. (2009) Flexible and transparent supercapacitor based on ITO nanowire/carbon nanotube heterogeneous films. *Applied Physics Letters* 94, 043113.
- [106] Kaempgen, M., Chan, C. K., Ma, J., Cui, Y., and Gruner, G. (2009) Printable Thin Film Supercapacitors Using Single-Walled Carbon Nanotubes. *Nano Letters* 9, 1872–1876.
- [107] Hu, Y., Zhu, H., Wang, J., and Chen, Z. (2011) Synthesis of layered birnessite-type manganese oxide thin films on plastic substrates by chemical bath deposition for flexible transparent supercapacitors. *Journal of Alloys and Compounds* 509, 10234–10240.
- [108] Jun Ge, G. C., and Chen, L. (2011) Transparent and flexible electrodes and supercapacitors using polyaniline-single-walled carbon nanotube composite thin films. *Nanoscale* 3, 3084–3088.
- [109] Feng, J., Sun, X., Wu, C., Peng, L., Lin, C., Hu, S., Yang, J., and Xie, Y. (2011) Metallic Few-Layered VS₂ Ultrathin Nanosheets: High Two-Dimensional Conductivity for In-Plane Supercapacitors. *Journal of the American Chemical Society* 133, 17832–17838.
- [110] Yoo, J. J., Balakrishnan, K., Huang, J., Meunier, V., Sumpter, B. G., Srivastava, A., Conway, M., Mohana Reddy, A. L., Yu, J., Vajtai, R., and Ajayan, P. M. (2011) Ultrathin Planar Graphene Supercapacitors. *Nano Letters* 11, 1423–1427.
- [111] Conway, B. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*; Springer, 1999.
- [112] Kotz, R., and Carlen, M. (2000) Principles and applications of electrochemical capacitors. *Electrochimica Acta* 45, 2483–2498.

- [113] Stoller, M. D., and Ruoff, R. S. (2010) Best practice methods for determining an electrode material's performance for ultracapacitors. *Energy & Environmental Science* 3, 1294.
- [114] Roth, S., and Carroll, D. *One-Dimensional Metals*; Wiley-VCH Verlag GmbH & Co. KGaA, 2005; pp 113–151.
- [115] Raman, C. V. (1928) A new radiation. *Indian Journal of physics* 2, 387–398.
- [116] Malard, L. M., Pimenta, M. A., Dresselhaus, G., and Dresselhaus, M. S. (2009) Raman spectroscopy in graphene. *Physics Reports*
- [117] Ferrari, A. C., and Robertson, J. (2000) Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B* 61, 14095, Copyright (C) 2009 The American Physical Society; Please report any problems to prola@aps.org.
- [118] Allen J. Bard, L. R. F. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons Inc., 2001.
- [119] Hertel, T., Hagen, A., Talalaev, V., Arnold, K., Hennrich, F., Kappes, M., Rosenthal, S., McBride, J., Ulbricht, H., and Flahaut, E. (2005) Spectroscopy of Single- and Double-Wall Carbon Nanotubes in Different Environments. *Nano Letters* 5, 511–514.
- [120] Smith, R., Lotya, M., and Coleman, J. (2010) The importance of repulsive potential barriers for the dispersion of graphene using surfactants. *New Journal of Physics* 12, 125008.
- [121] Li, X., Zhang, G., Bai, X., Sun, X., Wang, X., Wang, E., and Dai, H. (2008) Highly conducting graphene sheets and Langmuir Blodgett films. *Nature Nanotechnology* 3, 538–542.
- [122] Malard, L., Pimenta, M., Dresselhaus, G., and Dresselhaus, M. (2009) Raman spectroscopy in graphene. *Physics Reports* 473, 51–87.

- [123] Smith, R. J., King, P. J., Wirtz, C., Duesberg, G. S., and Coleman, J. N. (2012) Lateral size selection of surfactant-stabilised graphene flakes using size exclusion chromatography. *Chemical Physics Letters* 531, 169 – 172.
- [124] Geng, H., Lee, D. S., Kim, K. K., Han, G. H., Park, H. K., and Lee, Y. H. (2008) Absorption spectroscopy of surfactant-dispersed carbon nanotube film: Modulation of electronic structures. *Chemical Physics Letters* 455, 275–278.
- [125] Park, S., and Ruoff, R. S. (2009) Chemical methods for the production of graphenes. *Nature Nanotechnology* 4, 217–224.
- [126] Lyons, P. E., De, S., Blighe, F., Nicolosi, V., Pereira, L. F. C., Ferreira, M. S., and Coleman, J. N. (2008) The relationship between network morphology and conductivity in nanotube films. *Journal of Applied Physics* 104, 044302–8.
- [127] Dressel, M., and Gruner, G. *Electrodynamics of Solids - Cambridge University Press*; Cambridge Press, 2002.
- [128] De, S., and Coleman, J. N. Are There Fundamental Limitations on the Sheet Resistance and Transmittance of Thin Graphene Films? *ACS Nano* 0.
- [129] Tung, V. C., Chen, L., Allen, M. J., Wassei, J. K., Nelson, K., Kaner, R. B., and Yang, Y. (2009) Low-Temperature Solution Processing of Graphene-Carbon Nanotube Hybrid Materials for High-Performance Transparent Conductors. *Nano Letters* 9, 1949–1955.
- [130] Hernandez, Y., Lotya, M., Rickard, D., Bergin, S. D., and Coleman, J. N. (2010) Measurement of Multicomponent Solubility Parameters for Graphene Facilitates Solvent Discovery. *Langmuir* 26, 3208–3213.
- [131] Scardaci, V., Coull, R., and Coleman, J. N. (2010) Very thin transparent, conductive carbon nanotube films on flexible substrates. *Applied Physics Letters* 97, 023114.
- [132] Blighe, F. M., Hernandez, Y. R., Blau, W. J., and Coleman, J. N. (2007) Observation of Percolation-like Scaling Far from the Percolation Threshold in High Volume Fraction, High Conductivity Polymer-Nanotube Composite Films. *Advanced Materials* 19, 4443–4447.

- [133] Johner, N., Grimaldi, C., Balberg, I., and Ryser, P. (2008) Transport exponent in a three-dimensional continuum tunneling-percolation model. *Phys. Rev. B* 77, 174204.
- [134] Unalan, H. E., Fanchini, G., Kanwal, A., Du Pasquier, A., and Chhowalla, M. (2006) Design Criteria for Transparent Single-Wall Carbon Nanotube Thin-Film Transistors. *Nano Letters* 6, 677–682.
- [135] Zhang, Q., Vichchulada, P., Cauble, M., and Lay, M. (2009) Percolation in networks of aligned SWNTs formed with laminar flow deposition. *Journal of Materials Science* 44, 1206–1211.
- [136] De, S., Boland, C. S., King, P. J., Sorel, S., Lotya, M., Patel, U., Xiao, Z. L., and Coleman, J. N. (2011) Transparent conducting films from NbSe₃ nanowires. *Nanotechnology* 22, 285202.
- [137] Bauhofer, W., and Kovacs, J. Z. (2009) A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology* 69, 1486 – 1498, CNT-NET 07 Special Issue with regular papers.
- [138] Balberg, I. (1987) Tunneling and nonuniversal conductivity in composite materials. *Phys. Rev. Lett.* 59, 1305–1308.
- [139] Kogut, P. M., and Straley, J. P. (1979) Distribution-induced non-universality of the percolation conductivity exponents. *Journal of Physics C: Solid State Physics* 12, 2151.
- [140] Grimaldi, C., and Balberg, I. (2006) Tunneling and Nonuniversality in Continuum Percolation Systems. *Phys. Rev. Lett.* 96, 066602.
- [141] Balberg, I. (1998) Limits on the continuum-percolation transport exponents. *Phys. Rev. B* 57, 13351–13354.
- [142] Chandra, B., Afzali, A., Khare, N., El-Ashry, M. M., and Tulevski, G. S. (2010) Stable Charge-Transfer Doping of Transparent Single-Walled Carbon Nanotube Films. *Chemistry of Materials* 22, 5179–5183.

- [143] Scardaci, V., Coull, R., Lyons, P. E., Rickard, D., and Coleman, J. N. (2011) Spray Deposition of Highly Transparent, Low-Resistance Networks of Silver Nanowires over Large Areas. *Small* 7, 2621–2628.
- [144] Yu, A., Roes, I., Davies, A., and Chen, Z. (2010) Ultrathin, transparent, and flexible graphene films for supercapacitor application. *Applied Physics Letters* 96, 253105.
- [145] Chen, P., Chen, H., Qiu, J., and Zhou, C. (2010) Inkjet printing of single-walled carbon nanotube/RuO₂ nanowire supercapacitors on cloth fabrics and flexible substrates. *Nano Research* 3, 594–603.
- [146] Zhang, L. L., and Zhao, X. S. (2009) Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews* 38, 2520–2531.
- [147] Ugawa, A., Hwang, J., Gommans, H., Tashiro, H., Rinzler, A., and Tanner, D. (2001) Far-infrared to visible optical conductivity of single-wall carbon nanotubes. *Current Applied Physics* 1, 45–49, International Workshop on Quantum Transport in Synthetic Metals.
- [148] Luo, H., Shi, Z., Li, N., Gu, Z., and Zhuang, Q. (2001) Investigation of the Electrochemical and Electrocatalytic Behavior of Single-Wall Carbon Nanotube Film on a Glassy Carbon Electrode. *Anal. Chem.* 73, 915–920.
- [149] Sample, A., Yeager, D., Powledge, P., Mamishev, A., and Smith, J. (2008) Design of an RFID-Based Battery-Free Programmable Sensing Platform. *Instrumentation and Measurement, IEEE Transactions on* 57, 2608–2615.
- [150] Roy, S., Jandhyala, V., Smith, J., Wetherall, D., Otis, B., Chakraborty, R., Buettner, M., Yeager, D., Ko, Y.-C., and Sample, A. (2010) RFID: From Supply Chains to Sensor Nets. *Proceedings of the IEEE* 98, 1583–1592.
- [151] Kim, J., Lee, K. H., Overzet, L. J., and Lee, G. S. (2011) Synthesis and Electrochemical Properties of Spin-Capable Carbon Nanotube Sheet/MnO_x Composites for High-Performance Energy Storage Devices. *Nano Lett.* 11, 2611–2617.

- [152] Fischer, A. E., Pettigrew, K. A., Rolison, D. R., Stroud, R. M., and Long, J. W. (2007) Incorporation of Homogeneous, Nanoscale MnO₂ within Ultraporous Carbon Structures via Self-Limiting Electroless Deposition: Implications for Electrochemical Capacitors. *Nano Lett.* 7, 281–286.
- [153] Coleman, J. N. et al. (2011) Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* 331, 568–571.
- [154] Smith, R. J., King, P. J., Lotya, M., Wirtz, C., Khan, U., De, S., O'Neill, A., Duesberg, G. S., Grunlan, J. C., Moriarty, G., Chen, J., Wang, J., Minett, A. I., Nicolosi, V., and Coleman, J. N. (2011) Large Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions. *Advanced Materials* 23, 3944–3948.
- [155] Graeme Cunningham, N. M. G. S. D. P. v. d. S., Mustafa Lotya, and Coleman, J. N. (2012) Percolation scaling in composites of exfoliated MoS₂ filled with nanotubes and graphene. *Nanoscale*
- [156] Toupin, M., Brousse, T., and Belanger, D. (2004) Charge Storage Mechanism of MnO₂ Electrode Used in Aqueous Electrochemical Capacitor. *Chemistry of Materials* 16, 3184–3190.