

# Development of a Spray-On Version of GraphExeter



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## Abstract

Future wearable electronics, displays and photovoltaic devices rely on highly conductive, transparent and flexible materials that can be scaled for industrial production. A new material that meets these requirements called graphexeter was developed in Exeter. The goal of this project is to develop graphexeter in a sprayable liquid so that it can be deposited on any substrate. To do this graphene is fabricated by exfoliation of graphite in a liquid dispersion, using liquid phase exfoliation (LPE) [2]. To enhance the conductivity of these graphene layers, we have developed a liquid phase intercalation (LPI) method. The LPI method, which has never been explored before, is based on sonication and heating the graphene dispersions with added ferric chloride.

Highest quality few layer graphene (FLG) dispersions are made using graphite from Madagascar by sonicating for 40 hours. The best intercalated dispersions result from 7-10 hours of LPI after 40 hours LPE. A broadening of the G peak in the Raman spectrum was seen after LPI which suggests partial intercalation.

## Introduction

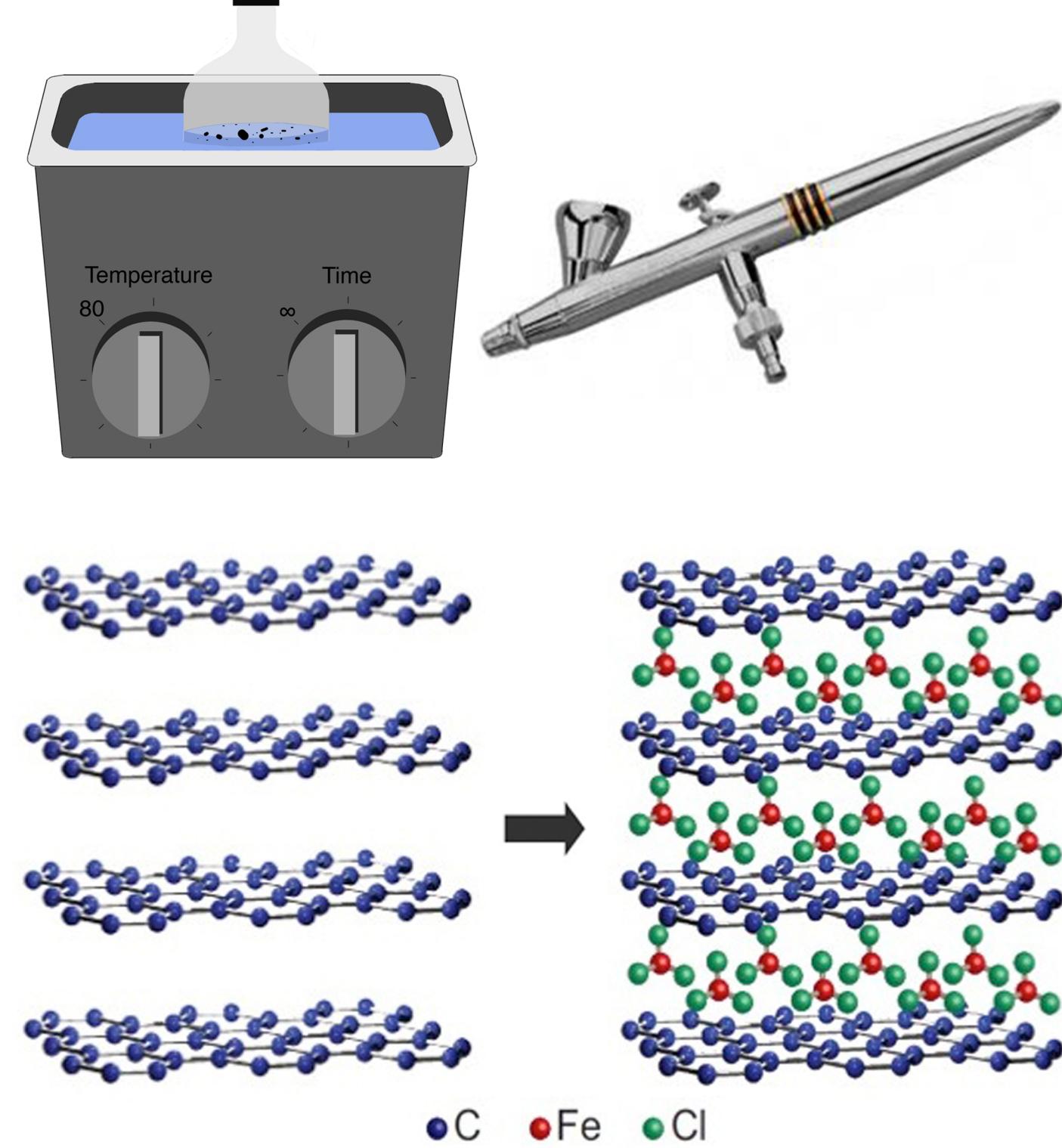
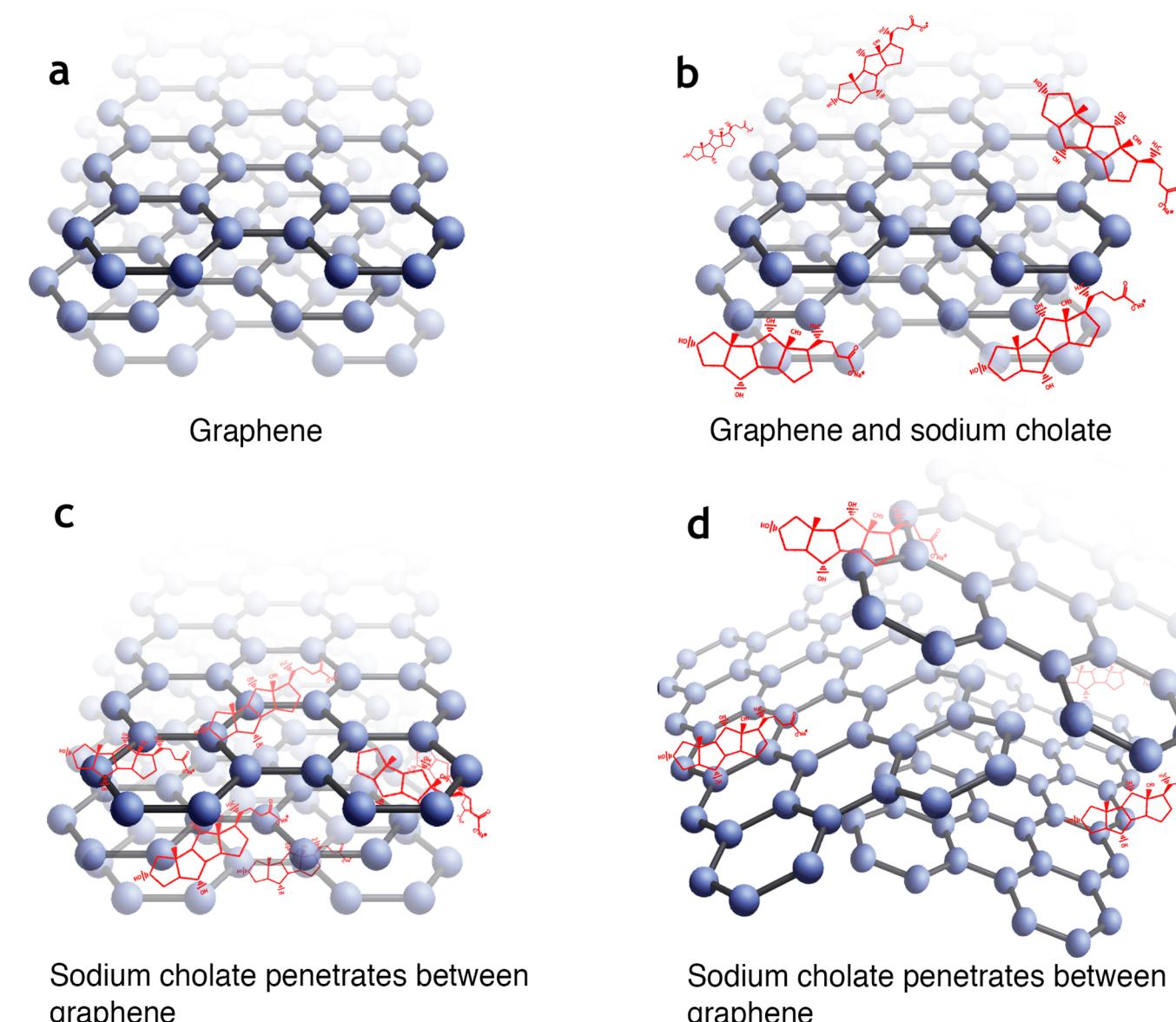
Graphene was first fabricated in 2004 using mechanical exfoliation of graphite [1]. It is a thin, transparent, flexible conductor with a high electrical and thermal conductivity. However in optoelectronic applications, pristine graphene's sheet resistance ( $30\Omega/\text{sq}$ ) does not rival the most widespread conductor in the field; that of Indium Tin Oxide (ITO) ( $10\Omega/\text{sq}$ ). A new graphene intercalated compound graphexeter [3] has a lower sheet resistance than ITO of  $8.8\Omega/\text{sq}$ , whilst still retaining a high level of optical transmittance (84%), flexibility and stability.

Recent studies use LPE with high boiling point solvents with similar surface energies to graphene, in order to provide sufficient solvent-graphene interaction energy to balance the energy cost of exfoliation. The aim of this project is to produce graphexeter at low temperatures with only sodium cholate and water.

A method of LPI will then be developed to produce graphexeter. This solution can then be sprayed onto a silicon substrate using an airbrush to be characterised using raman spectroscopy. A spray on version of graphexeter can provide industry with an easily scalable and non destructive deposition procedure of a transparent flexible conductor for anything from fabrics to flexible plastic.

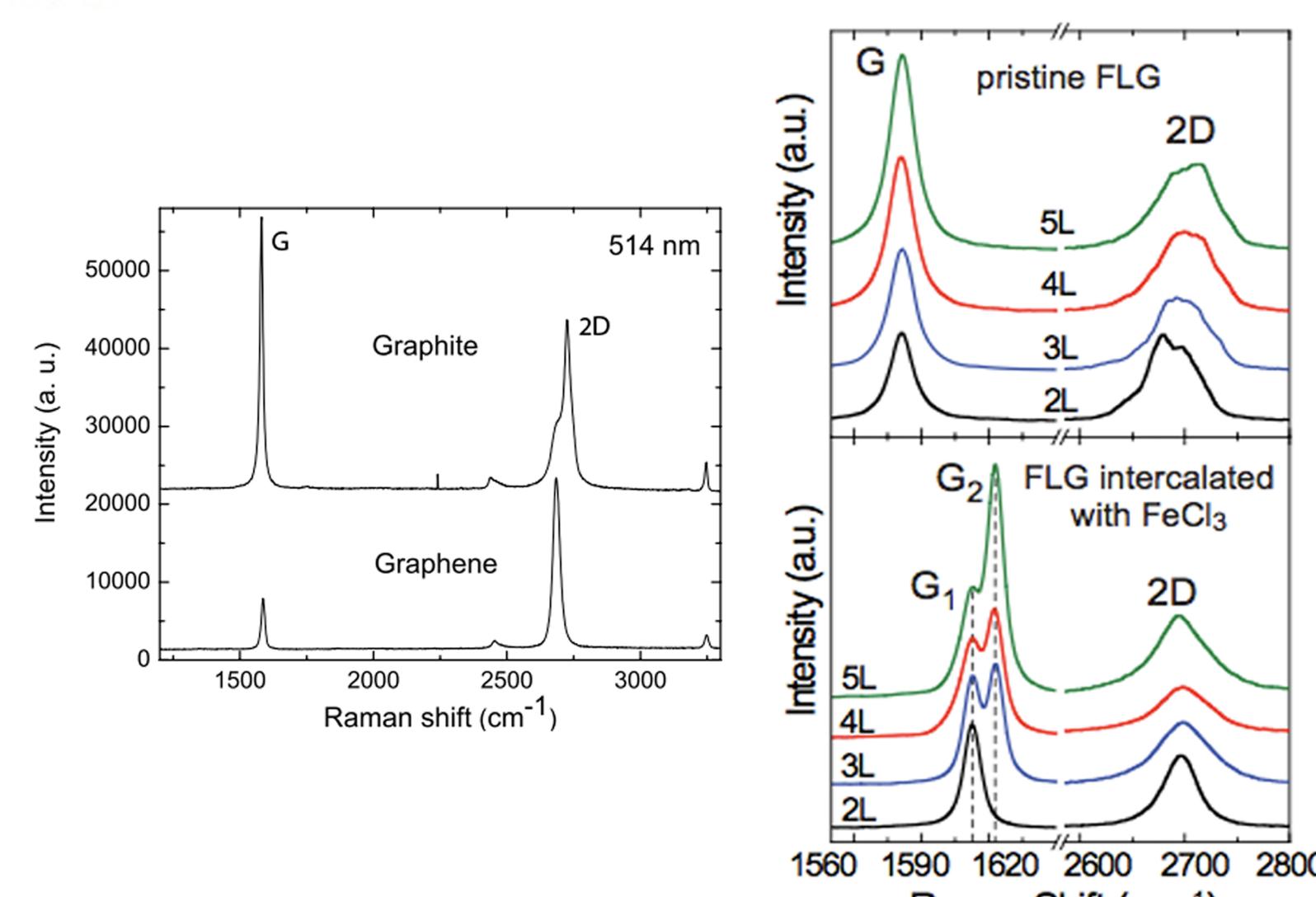
## Theory

In the LPE process sodium cholate is used as a surfactant, which has a surface energy similar to that of the graphite and helps to overcome the van der Waals forces between the layers [2]. A solution of DI water, sodium cholate and powdered graphite is sonicated at 15kHz. Sonication adds energy to the system to help graphene layers break off of bulk graphite. After sonication, the solution is centrifuged to force the heaviest flakes to the bottom of the vial to be discarded, leaving a slightly grey, transparent dispersion of FLG.



GraphExeter is made up of FLG interlaced with layers of ferric chloride. The ferric chloride molecules are acceptors of electrons and therefore increase the number of holes in the graphene to carry charge. Graphexeter is the most conductive graphene intercalated compound to date with a charge carrier density of  $8.9 \times 10^{14} \text{ cm}^{-2}$  and a microscopic mean free path at room temperature. It is also stable in air for over a year [3].

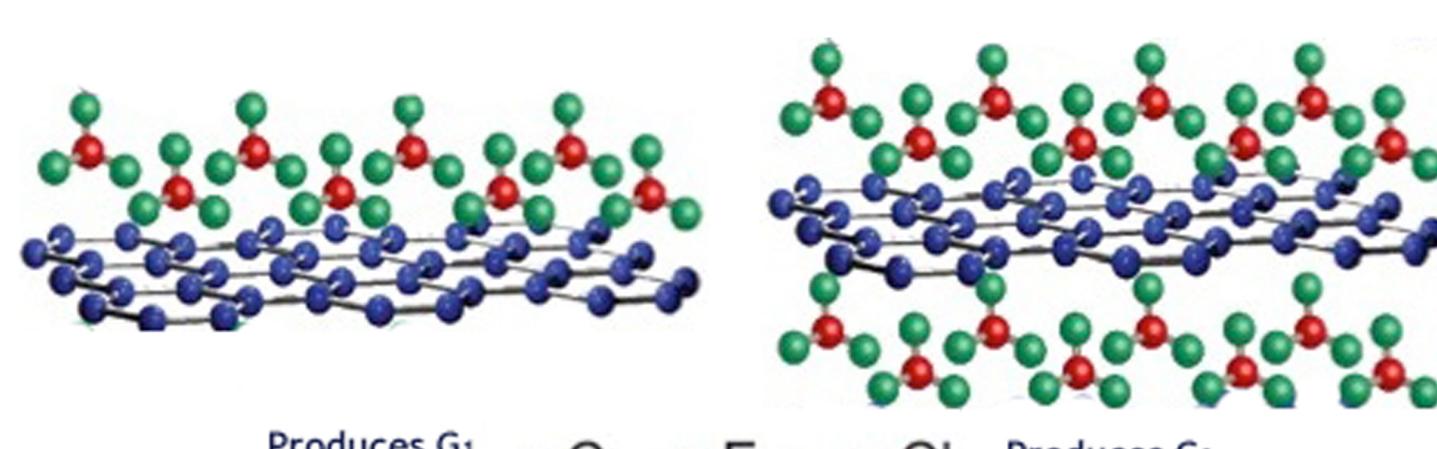
A LPI method in this project is investigated by adding ferric chloride powder to a graphene dispersion after LPE, and further sonicating at 80°C. LPI is also attempted during LPE at 80°C.



Raman spectroscopy is used to characterise the graphitic flakes. The main peaks in the raman spectrum of graphite are D ( $1350\text{cm}^{-1}$ ), G ( $1580\text{cm}^{-1}$ ) and 2D ( $1700\text{cm}^{-1}$ ).

The shape of the 2D peak is an indicator of the number of graphene layers up to 3, becoming less symmetrical with an increasing number of layers. The G peak position is sensitive to doping.

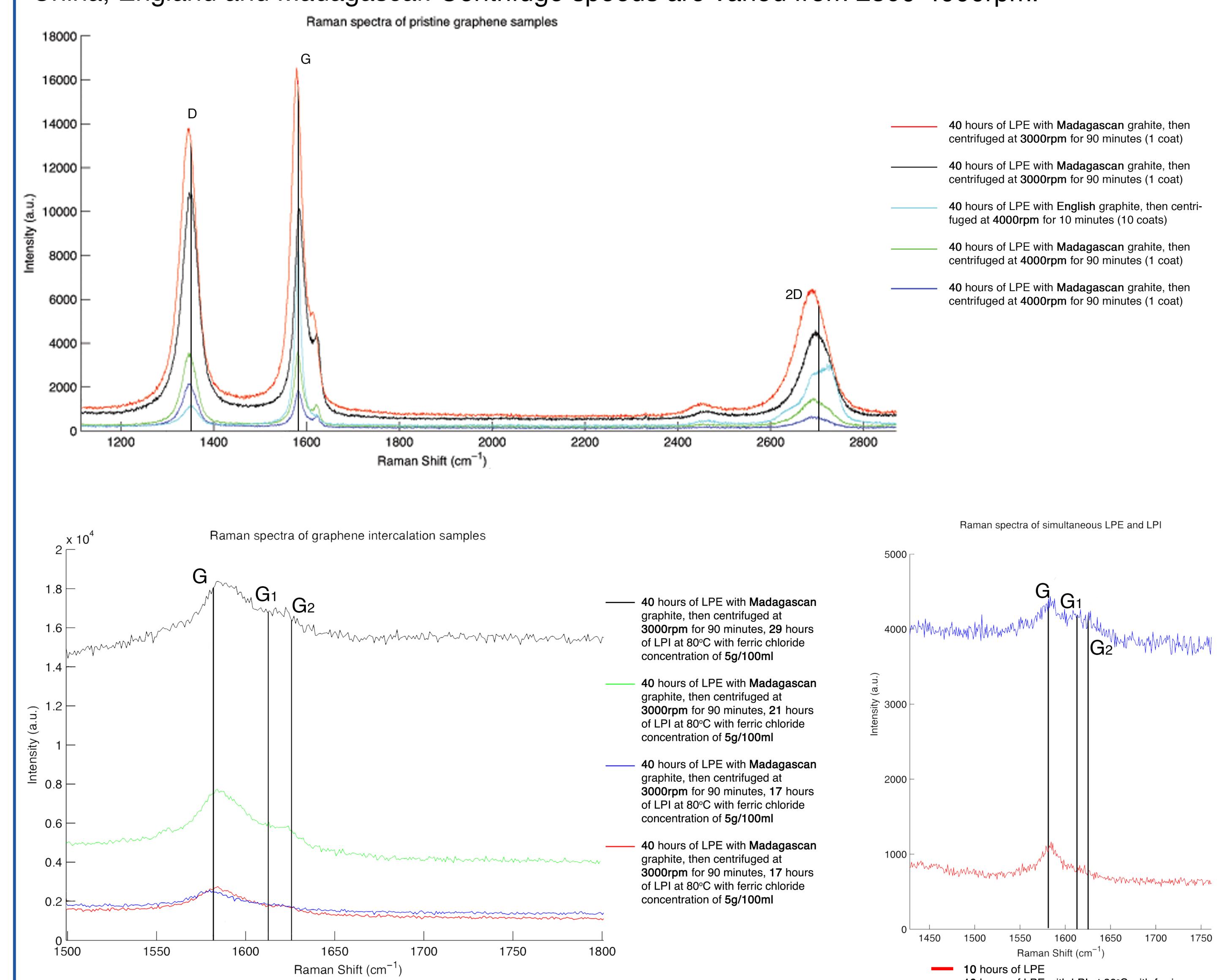
The D peak is an indication of defects. On a silicon substrate, the Si peak will be seen through the graphene layers; the higher the Si peak the thinner the graphene flake. The ratio of intensities of the G and Si peak ( $I_G/I_{Si}$ ) can give the number of layers up to 5.



When few layer graphene has been intercalated the G peak splits into two peaks G1 ( $1612\text{cm}^{-1}$ ) and G2 ( $1625\text{cm}^{-1}$ ), with G1 signifying a layer of ferric chloride adjacent to a flake and G2 signifying two adjacent layers.

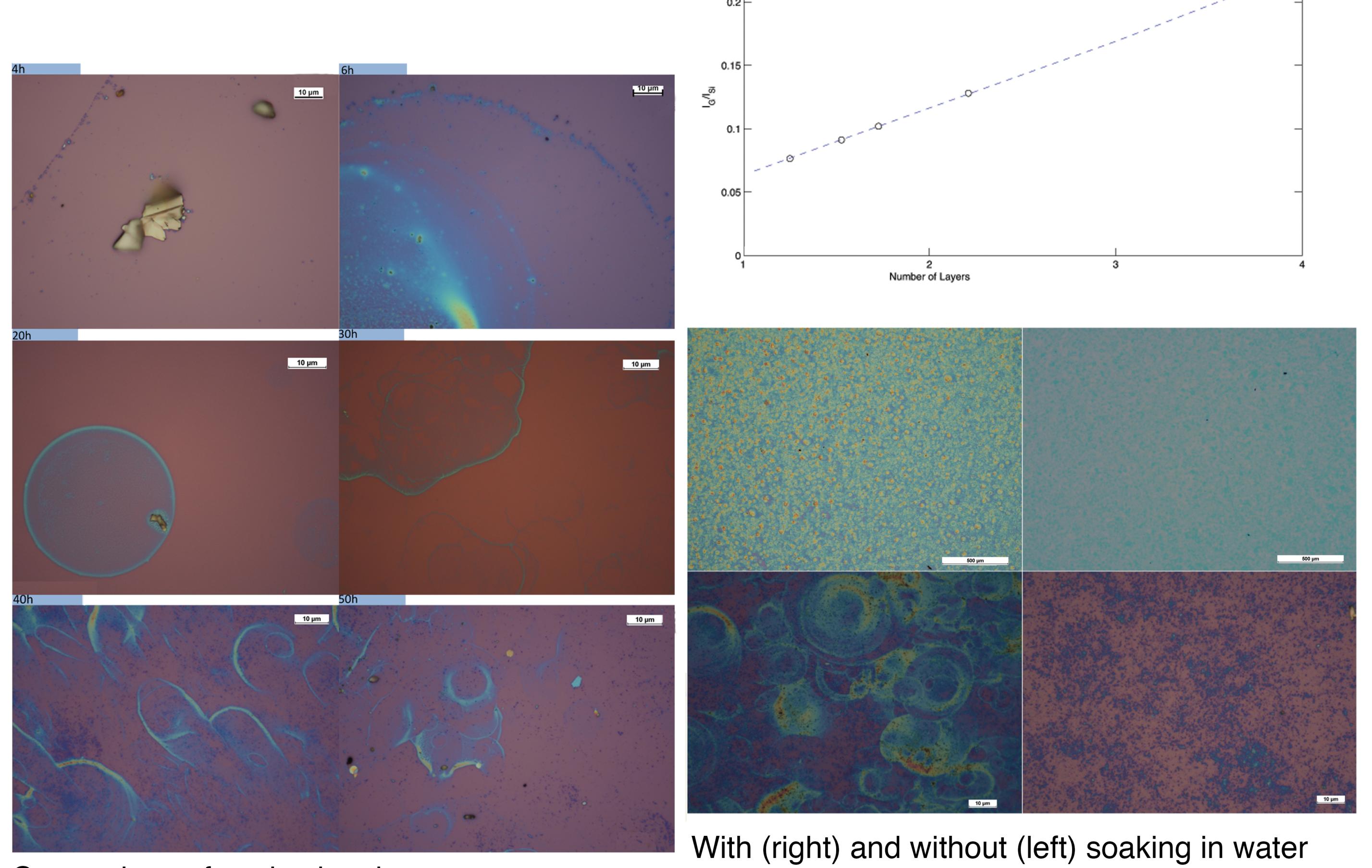
## Results

Parameters investigated for LPE: Sonication times varied from 2-50 hours. Graphite is sourced from China, England and Madagascar. Centrifuge speeds are varied from 2500-4000rpm.



Parameters investigated to improve coverage of pristine graphene: The number of spray coats is increased up to 10 to increase the density of flakes after deposition. Spray coating is performed with and without soaking in water between coats. Soaking the sample removes sodium cholate residue and helps to make sure contact is taking place between flakes for electrical conduction and also helps to identify flakes under the microscope during raman spectroscopy.

Determination of thickness of flakes: Past results of  $I_G/I_{Si}$  [4] from mechanical exfoliation are used to fit our values of  $I_G/I_{Si}$  and determine number of layers. Some values cannot be plotted (below), because the flakes are often smaller than the Raman laser spot causing  $I_{Si}$  to be artificially raised, and  $I_G/I_{Si}$  to not lie on the graph.



Comparison of sonication times.

## Future Work

Intercalation at higher energies and/or for longer may help to improve LPI, although continuing to break the flakes laterally as hours of sonication increase may pose problems of de-intercalation of very small flakes. To assess this problem a machine could be used to stir the dispersion at high temperatures without further sonication and lateral breakup of flakes.

To improve coverage of a substrate, either a higher concentration of graphene in the dispersion is needed, or more coats of spray. A high enough density of flakes will allow for a continuous electrical channel across a sample.

Once electrical channels have been created, electrical characteristics can be measured by creating a transistor-like structure, with which charge transport parameters such as the mobility of electrons, the magnetic field and temperature dependence of the resistance can be measured.

- References:
- [1] Novoselov, K., 2011. Nobel Lecture: Graphene: Materials in the Flatland. *Reviews of Modern Physics*, 83(3), pp.837–849. Available at: <http://link.ittaps.org/doi/10.1103/RevModPhys.83.837>.
  - [2] Hernandez, Y. et al., 2008. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3(9), pp.563–8. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/18772919> [Accessed July 12, 2012].
  - [3] Khrapach, I. et al., 2012. Novel highly conductive and transparent graphene-based conductors. *Advanced materials* (Deerfield Beach, Fla.), 24(21), pp.2844–9. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22535615> [Accessed July 13, 2012].
  - [4] W. Worster, M. Mu, M. Craciun