Chemical Exfoliation of graphene and other 2D-materials

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Abstract

Graphene has been described as a ‘miracle material’ and since its isolation in 2004 there have been thousands of reports of its exceptional properties and the wide range of applications it could be incorporated into.

This thesis focuses on several topics; the first being the liquid exfoliation of graphite using ‘surfactant’ like 1 – pyrenesulfonic acid sodium salt (1-PSA), this dispersion was produced using the sonication method and it was found the single-layer yield was ~ 20%. A graphene paper was produced using this dispersion and a second was produced from sonication of graphite in N-Methyl-2-pyrrolidone (NMP). The second paper was produced as a reference as it has been well characterised in previous studies. X-ray Photoelectron Spectroscopy (XPS) was performed on both papers to check no graphene oxide or graphene derivative had been produced. It was found there was a ~ 14% residual of 1-PSA molecules present in the 1-PSA based paper, compared to ~ 8% residual NMP in the corresponding paper.

The second topic covers the transfer of anodic bonding graphene samples in solution. This technique allows deposition of mostly single and few-layer graphene flakes onto a glass substrate. The transfer method we adopted was to use cellulose acetate butyrate (CAB) in ethyl acetate, which forms a film, encapsulating the flakes on the substrate. These films can then be dissolved in ethyl acetate. Although, we had promising results at the beginning of this study, it was concluded that the graphene flakes were embedded in the CAB films and the cellulose could not be removed.

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1. Introduction

1.1 Carbon

Forming a diverse range of materials, carbon can be classed as an extraordinary element. This is a result of the s and p-orbitals of carbon being able to hybridise into sp-, sp²- and sp³- bonds. For example, diamond is a 3-dimensional (3D) solid made up of sp³ bonded carbons in a tetrahedral shape; whereas graphite is made up of 2-dimensional (2D) sheets containing sp² bonded carbons. Bonding can affect the properties of these materials; diamond is an insulator whereas graphite can conduct electricity.

Hybridisation is not the only parameter that can determine the properties of a material, dimensionality is also important. [1] Carbon can form a number of inorganic allotropes with different dimensionality; graphite (3D), fullerenes (0D), nanotubes (1D) and the most recently discovered: graphene (2D). [2-9] Graphene is a single layer of sp² hybridised carbon atoms packed into a hexagonal lattice. A trigonal planar structure is observed due to the s, p(x) and p(y) orbitals forming σ-bonds, 142 pm in length. The p(z) orbitals of neighbouring carbon atoms interact forming a π-band, which makes up the delocalised network of electrons. Graphene is the basic building block of all other graphitic material [8] (Figure 1). The sheets can be stacked into layers forming 3D graphite, with an interlayer spacing of 0.335nm, held together by weak Van der Waals forces. Spherically arranged carbon atoms make up fullerene; where some of the hexagonal lattices are replaced by pentagons, which give them their curvature. This spherical arrangement produces discrete energy levels so that fullerenes can be seen as 0D materials. [2] Rolling up sheets produces 1D nanotubes; they have outstanding properties which strongly depend on the direction the graphene sheet is rolled to form the tube, this can make them either metallic or semiconducting in nature and will also possess different optical transition energies which make them interesting for various applications. [1]
Dimensionality strongly affects the properties of a material. Graphene and graphite have the same planar structure and hybridisation. However, they have very different optical, electronic and mechanical properties.

1.2 Graphene electronic structure
The band structure of graphene was originally stated by P. R. Wallace in 1948, to be semi-metallic[10]. We now know graphene is a semimetal/zero bandgap semiconductor (Figure 2). The crystal lattice of graphene contains two sublattices containing atoms A and B, which make up the unit cell (Figure 2a).
Going from real space to reciprocal space, the Brillouin zone is also hexagonal, the centre is the Γ point and the non-equivalent corners are the K and K' points, where there is high symmetry, also called Dirac points. The K and K' points are inequivalent as they relate to the atoms A and B in the unit cell. By overlapping two graphene sublattices, two energy bands are formed; the valence band (bottom cone) and conduction band (top cone) which only meet at the six Dirac points at the corners of the Brillouin zone. This crystal structure produces a linear electronic band structure at the K and K' Dirac points at low energy. The Fermi energy, $E_F$, lies at the Dirac point. At low energy, the energy of the electronic states varies linearly with momentum of the charge carriers. Thus, quasiparticles in graphene exhibit a linear dispersion relation:

$$E = \pm \hbar v_F \sqrt{Kx^2 + Ky^2}$$

Where $v_F$ is Fermi velocity $\sim 10^6$ m/s, Kx and Ky are components of the momentum in the direction x and y (Figure 2c inset). [12]

Conventional semiconductors show a parabolic conduction and valence band, which are separated by a small gap (1-2 eV). e.g. silicon [8] (Figure 3).
In this case, the electrons are described using the Schrödinger equation. However in graphene the linear dispersion between energy and momentum means the electrons within graphene maintain a constant speed and are described using the Dirac equation, as they behave as massless relativistic particles. [8, 13, 14]

1.3 Graphene properties

1.3.1 Electronic properties
Graphene’s linear energy dispersion at low energies (near the 6 corners of the Brillouin zone) gives electrons their zero-effective mass, meaning they travel at a constant speed, equal to $10^6$ m/s. Thus, the graphene charge mobility is essentially independent of temperature, $T$, and is limited only by defect scattering. [14]

If graphene is placed in a device configuration, i.e. it is contacted with a source, drain and gate voltage, $V_g$, then graphene will show an ambipolar electric field; the charge carriers can be tuned between electrons and holes [15] (Figure 4).
There is a potential of obtaining high mobilities at room temperature (R.T.) due to the independence of mobility between 10 and 100K. [15]

Mobility remains high even at high carrier densities, resulting in the electrons travelling through a sheet with negligible electrical resistivity, i.e. the electrons can travel micrometres in length before hitting other atoms or defects in the structure and being scattered. [16] This is called ballistic transport.

Graphene also shows exotic properties when it is immersed in magnetic fields. [17]

1.3.2 Optical properties
For a single atomic layer, graphene has an unexpectedly high absorbance (~2.3%) of visible light. [14] The fraction of visible light it absorbs is attributed to its unique electronic structure that features electron and hole canonical bands which meet at the Dirac point. [18] The Dirac Fermions’ high frequency conductivity is constant from the Infra-red (IR) region through to the visible range. The rest of the light is transmitted through graphene, i.e. graphene is essentially transparent when deposited on a substrate, and thus it is particularly challenging to locate graphene flakes among thicker flakes. The type of substrate used to deposit graphene can
make a difference to its optical visibility. Oxidised silicon is a popular choice and it has been shown that an oxide layer of 90/300 nm, on top of silicon, shows maximum optical enhancement of graphene (~12%). i.e. even a single layer of graphene on an oxidised silicon substrate can give enough contrast for it to be spotted under an optical microscope. [19, 20] The oxide layer causes light interference with the incident and reflected light, enhancing the visibility of graphene on the substrate. [21, 19] Figure 5 shows an optical picture of a graphene flake composed of multiple layers and the corresponding Raman spectrum of the different layers. A darker colour is consistent with thicker layers; however, once above 10 layers this trend does not continue. [21]

![Optical picture and Raman spectra](image)

**Figure 5** - Left: Optical picture of large flake consisting of 1, 2, 3 and 6 layers of graphene. Right: the corresponding Raman spectra of the layers.

### 1.3.3 Mechanical properties
Graphene has recently been shown to be the strongest material ever. [22] The mechanical properties have been extensively studied, specifically the breaking strength of free standing monolayer graphene using the experimental setup described in figure 6. [14, 22, 23] An AFM tip is used to indent free standing graphene. [22]
Defect free graphene has been found to have a Young’s modulus of 1.0 TPa and an average fracture strength of 130 KPa. Compared to diamond which has a Young’s modulus of 900 GPa. Graphene can also be stretched up to 20% more than any other crystal known to man. [22]

1.4 Graphene applications
Owing to graphene’s unique properties, there are many potential applications of this material, such as use in; transistors, gas detectors, sensors, solar cells and transparent conductive electrodes. A short description of the possible applications is given below.

i) Field Effect Transistor (FET)
The unique band structure and high carrier mobility of graphene make it an ideal material to be used in integrated circuits. The electrons and holes can be continuously tuned to change the E_F. The mobility of graphene deposited on a silicon substrate has been found to be 1 order of magnitude above that of silicon, which is currently being used in FETs. [15] Higher mobilities have been achieved by depositing graphene on other substrates, such as hexagonal boron nitride (h-BN) or by making it suspended. [24] To make a good transistor, a material needs a high on/off ratio, which cannot be achieved in graphene as it is gapless, so it is unsuitable for use in transistors. [25] Several methods are being investigated in order to open a gap in graphene without affecting its charge mobility significantly. For example, graphene is cut into small strips to form nano-ribbons. Due to
quantum confinement, a gap will open. The size of the gap depends on the width of the ribbon [26]. Another option consists of using bilayer graphene, in which a gap can be opened through application of a top or bottom gate [27]. There are currently many methods being explored on the opening of band gaps in graphene.

ii) Transparent conductive electrodes
High electrical conductivity, carrier mobility and optical transmittance in the visible region make it a promising material for use in transparent conductive films. Transparent conductive electrodes made with graphene can be a viable route to replacing Indium-Tin Oxide (ITO) electrodes. ITO has been widely used as an electrode material because it shows high conductivity and good transmittance. [28] Yet, there are several drawbacks to ITO, the first being the limited availability of indium on Earth, increasing the price of producing the material. ITO’s poor flexibility prevents it from being used in flexible electronics. Also, the reflection of light from a single sheet is ~10%, which can rapidly rise if sheets of ITO are stacked on top of one another, diminishing their role in applications that will operate in bright light. [29] Graphene’s mechanical strength gives it an advantage over the brittle and fragile ITO films.

iii) Gas detectors and sensors
Conventional gas detectors are assessed on their high sensitivity and low production costs. Graphene’s surface can adsorb gas molecules, which act as electron donors/acceptors, changing graphene’s electrical conductivity. The 2D structure leaves the entire surface exposed to adsorbents. It is highly conductive and charge concentration is very sensitive to charge carriers, i.e. a few extra electrons can cause a notable change in its electronic properties. Few crystal defects allow graphene to have low excess noise caused by thermal switching. These properties allow graphene to detect changes in local concentration through maximisation of the signal-to-noise ratio. The high sensitivity of graphene has been demonstrated when it was shown that this material can detect adsorption of individual gas molecules. [30]
iv) **Batteries**
Lithium (Li) ion batteries have, thus far, been used in power sources for portable electronics; however, higher density electrodes are needed for advanced application electronics. Li ion batteries use a lithium cobalt oxide (LiCoO$_2$) cathode and a graphite anode. Although, the performance of these devices depends on the physical and chemical properties of the anode/cathode material, there is limited improvement that can be achieved due to the provisions, such as; high potential, structural stability and that it must contain Li. The use of graphene in the process has shown stage 1 intercalation can be achieved with Li ions; this involves the Li ions being intercalated between each and every graphene layer. The large surface area-to-volume ratio graphene has, suggests Li can bind to both sides of a graphene sheet and also at the edges of the sheet. With its high conductivity, graphene could be a potential material for use in reversible lithium storage capacity. [31]

1.5 **Graphene: Production routes**
In order to explore the potential applications of graphene, we must first find a method able to achieve high yield and high quality graphene flakes. Obtaining a large area is useful in certain applications, such as electronics, where the sheets can be easily manipulated and processed into devices.

i) **Micromechanical cleavage**
The micromechanical cleavage of graphite has been the first method used to isolate graphene. This was first established by researchers in Manchester using scotch tape to repeatedly cleave graphite until only a single layer was left. This became known as the ‘scotch tape’ method [25]. The material produced using this method is characterised by the highest mobility, showing that micro-mechanical exfoliation gives very high quality graphene flakes which are free of any defects. Although this technique is simple and cheap, the flakes are not obtained in high yield and the method is very time consuming, as most of the flakes produced are thick or few-layer sheets. This is not a scalable route that could be employed in industrial processes.
ii) Anodic bonding
A recent method of producing high quality single layer flakes has been reported using the anodic bonding technique. [32, 33] This technique is usually used to bond borosilicate glass and Si wafers but can be used to bond graphene flakes to glass. A high T and high electrostatic field is applied perpendicular to the layers. (Figure 7) Upon heating, the Na₂O impurities in glass decompose into Na⁺ and O²⁻ ions, Na⁺ has a higher mobility as it is lighter and so at a certain charge polarity the Na⁺ ions will move to the back contact leaving a concentrated charge of O²⁻ ions at the glass surface. [34] These O²⁻ ions produce a strong electric field at the surface allowing bonding to occur between graphene flakes and the glass.

![Figure 7 - Anodic bonding experimental setup](image)

This method allows quick and cheap production of graphene layers at a high yield. Yet, the high T utilised in this setup can damage the flakes. It has been found that the best parameters for this deposition are a voltage range of between 0.5 and 2kV and a T of ~ 200°C for deposition times of 10-20 minutes. As charges are used as part of the bonding process, the graphene flakes can be doped. [32]

There are many advantages and disadvantages to using micromechanical cleavage and anodic bonding to produce graphene flakes. Table 1 shows a comparison of the techniques.
Table 1 - Comparison of micromechanical cleavage and anodic bonding techniques used to produce graphene flakes.

<table>
<thead>
<tr>
<th>Production method</th>
<th>Yield</th>
<th>Average lateral size of flakes</th>
<th>Doping</th>
</tr>
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<tbody>
<tr>
<td>Micromechanical cleavage</td>
<td>v. low</td>
<td>1 mm</td>
<td>N/A</td>
</tr>
<tr>
<td>Anodic bonding</td>
<td>High</td>
<td>20 µm</td>
<td>p-type</td>
</tr>
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</table>

iii) Chemical vapour deposition (CVD)

The concept of combining carbon with other materials and then dissociating it was first proposed in 1896. [35] The first graphene layers were grown on nickel (Ni) where researchers found the formation of the carbon film on the metal substrate was down to diffusion and segregation of carbon impurities. [35, 36]

When graphene was discovered, this method was re-visited, to grow single layer graphene on metals. [35] Growing graphene films on Ni and copper (Cu) has been popular, but non uniform films form when using Ni. [36, 37] Single and few layer flakes form over different regions of the substrate. Conversely, polycrystalline Cu has been used to deposit high quality, single layer graphene covering a large area, up to 95% of the Cu surface is covered in single layers. [35] Although this technique is suitable to cover a large area, there are still some challenges to overcome: i) due to the growth process, graphene is poly-crystalline, i.e. there are grain boundaries, which strongly affect the electronic properties of graphene. The grain size can be controlled but this requires a careful control of the deposition parameters. Thus, it may take years before the process is optimised. ii) graphene is grown on a technologically relevant substrate. Transfer of the graphene can be achieved by coating it in a protective polymer, i.e. PMMA, and then etching away the Cu film by using FeCl₃ in HCl/ H₂O, for example. [35]
iv) Chemical exfoliation of graphite

This method is very attractive because, in principle, a high yield is obtainable, which is suitable for processing in solution. The goal is to separate the layers of graphite. This can be obtained in a number of different ways: some methods are based on chemical modification of graphite (e.g. graphene oxide), followed by separation; others are based on directly intercalating small molecules between the layers (e.g. liquid-phase exfoliation). Every method has its own advantages and disadvantages. In general, if one wants to keep the outstanding properties of graphene, then an exfoliation method based on non-covalent interactions should be selected.

In our group, we have recently developed a method on exfoliation of graphite using non-covalent and reversible interactions between graphene and small polyaromatic molecules, such as pyrene derivatives. These molecules can be seen as nanographene units, since they are characterised by an aromatic core, allowing \( \pi-\pi \) interaction with graphene.

In this chapter, I will describe the liquid-phase exfoliation method and I will focus on separation using polyaromatic molecules. One of the goals of the project is to study the interaction between graphene and these molecules in order to achieve a hybrid graphene-based material, where the molecules are arranged in a well-defined structure on the graphene surface.

Liquid phase exfoliation

There are two types of liquid exfoliation currently being explored, exfoliation in organic solvents and exfoliation in aqueous solutions. In the latter case, water alone cannot exfoliate graphite, so the addition of surfactants or other small molecules is necessary.

To exfoliate graphite in a solvent, the enthalpy of mixing \( \Delta H_{\text{mix}} \) has to be zero (or small) for the exfoliation to occur. The \( \Delta H_{\text{mix}} \) can be expressed as:

\[
\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} = \frac{2}{T_{\text{fليك}}} (\delta_G - \delta_{\text{sol}})^2 \varphi
\]
Where:

\[ \delta_i = \text{square root of the surface energy of the phase} \]

\[ T_{\text{flake}} = \text{flake thickness} \]

\[ \phi = \text{graphene volume fraction} \]

Enthalpy of mixing is dependent on the balance of graphene and solvent surface energies. It has been found that the minimal energy cost of exfoliation is for solvents whose surface energy matches that of graphene. The researchers showed for graphene dispersed in a good solvent, \( \Delta H_{\text{mix}} \) is close to zero and the solvent-graphene interactions are Van der Waals rather than covalent. It has been shown that a solvent with a surface tension in the region of 40-50 mJ/ m\(^2\) is needed to achieve efficient exfoliation. Thus, N-Methyl-2-pyrrolidone (NMP) and Dimethylformamide (DMF) have been selected as good solvents for exfoliation. For example, graphene dispersions of concentrations up to \( \sim 1.2 \) mg/ mL in NMP have been reported with a monolayer yield of 4% wt. This method relies on long sonication times of up to 400 hours of suspensions. [38, 39] 2.21 mg/ mL in NMP is the highest concentration obtained through this method. [40] The average lateral size of the flakes is related to the sonication time of the sample; longer sonication times result in smaller flake size. The main disadvantage of using this method is the toxicity and high boiling point of the solvent involved. Organic solvents can be toxic, expensive and difficult to remove once exfoliation has occurred.

A safer, more desirable solvent to process in is water; this is not toxic and cheaper than organic solvents. However, it is known that the surface tension of water is too high to exfoliate graphite alone, so the use of surfactants is essential to lower the surface tension and allow it to exfoliate graphite and for the single layers to be stable in solution. The use of surfactants in exfoliating graphite has been demonstrated [41]. However a low yield of graphene has been obtained, 0.05 mg/ mL, furthermore, it is difficult to wash away the surfactants.

Recently, there have been several reports on the investigation of exfoliating graphite through non-covalent interactions with polyaromatic hydrocarbons. [42-
Polyaromatic molecules have an aromatic core, which allow them to physisorb on the hydrophobic surface of graphene and also intercalate between layers in graphite, through π-π stacking. The functional groups attached to the polyaromatic hydrocarbons separate the layers and also stabilise the graphene sheets in water.

Controlling the arrangement of molecules, by supramolecular interactions, could produce a hybrid graphene material, which combines the outstanding properties of graphene with the tuneability of organic molecules. In our group, we worked with 1-pyrenesulfonic acid sodium salt (1-PSA) (figure 8) to exfoliate graphite due to its solubility in water and its ability to have π-π interactions with the graphene surface. We obtained a rather efficient exfoliation of graphite: the final suspension contained ~20% single layers and ~70% few graphene layers (<7). However, we observed that the suspension contained an excess of molecules and also aggregates, due to the amphilic nature of pyrene. Thus, we could not achieve a well-controlled arrangement of the molecules on graphene. On the other side, we observed that by using a more soluble pyrene derivative such as 1,3,6,8-pyrenetetrasulfonic acid tetra sodium salt hydrate (TPA), the exfoliation efficiency is poor, due to the smaller number of molecules interacting with graphene. Thus, both exfoliation and controlled assembly of the molecules in solution seem not to be possible. One way to overcome this problem would be to avoid the exfoliation process, i.e. to transfer the molecules on single-layers already in solution. We investigated if it is possible to transfer the flakes deposited on the glass substrate by anodic bonding in solution. Note that this technique can be easily scaled. We explored different liquid-phase exfoliation based methods and investigated the possibility of transferring the flakes using pyrene derivatives in order to try to improve the assembly of the molecules on the flakes.
1.6 2D layered materials

Transition metal dichalcogenides (TMDs) are a form of 2D-layered material. TMDs consist of hexagonal layers of metal atoms (M) sandwiched between two layers of chalogen atoms (X) with a MX2 stoichiometry. [48] Bonding between the atoms in the layers is covalent but the layers are held together by weak Van der Waals forces. [49, 50] Coordination geometry plays a role in determining whether a particular material is metallic, such as NbSe2, semi-metallic or semi-conducting, such as MoS2, WS2, MoSe2 and MoTe2. [51, 52] Hence these materials could be useful in a wide area of electronics. [48]

In bulk crystalline, Mo is in the (IV) oxidation state and has six sulfide ligands in trigonal prismatic coordination geometry. (Figure 9)

![Diagram of MoS2 coordination geometry](image)

**Figure 9 - General coordination geometry of MoX2 compounds**

MoX2 compounds are indirect band gap semiconductors with band gaps of 1.29, 1.10 and 1.10 eV for MoS2, MoSe2 and MoTe2 respectively. Studies have shown that going from bulk to single layer MoS2, it becomes a direct band gap semiconductor. [53] All the MoX2 compounds mentioned above have optical band gaps that match with the solar spectrum therefore they could have potential applications in photovoltaics and photocatalytic systems. [49]
1.7 Aims and objectives

Graphene papers:

i) Develop and optimise a liquid phase exfoliation process of graphite which produces mostly single and few layer graphene flakes.

Anodic bonding samples:

i) Establish a method to transfer anodic bonded graphene flakes in solution

ii) Create a technique which will allow a controlled deposition of 1-PSA molecules onto graphene flakes, in order to functionalise graphene.

Transition metal dichalogenides:

i) Improve and optimise the solvent and liquid phase exfoliation process using 1-PSA molecules to yield mostly single and few layer flakes of these 2D-layered materials
2. Experimental and Characterisation

2.1 Graphene papers preparation
We produced two graphene papers, one with our method, and the other with the traditional method, based on NMP (Section 1.5), which we used as a reference, since this type of dispersion and laminate is very well characterised in literature. [54]

i) Our method: we selected 1-pyrene sulfonic acid sodium salt (1-PSA) as a “surfactant” to exfoliate graphite.

The dispersion is prepared in the following way: 1-PSA in de-ionised (DI) water (10 mL, 0.1 mg/mL) was mixed with graphite flakes (30 mg) and sonicated in an ultrasonic bath for 80 minutes. This dispersion was centrifuged for 20 minutes at 1000 rpm to remove unexfoliated graphite flakes. Dispersion is re-filled with DI water then undergoes a washing process. The dispersion is centrifuged for 20 minutes at 12000 rpm, the top layer is discarded as it will contain a lot of free 1-PSA molecule. Dispersion is re-filled with DI water and sonicated for 1 minute to re-disperse the graphene flakes. This washing process is repeated three times. Dispersion is then centrifuged for 20 minutes at 1000 rpm to remove any residual graphite. Under these conditions, we know that the dispersion contains ~20% single-layers, with average size of ~400 nm. 100 mL of this dispersion is passed through a vacuum filtration system with an aluminium membrane of pore size 0.2 µm (Figure 10).
ii) NMP-based method: Graphite flakes (400 mg) were added to NMP (120 mL), this mixture was sonicated for 72 hours. Unexfoliated graphite was removed by centrifuging the dispersion for 40 minutes at 1500 rpm. The resulting suspension was then centrifuged for 20 minutes at 12000 rpm, the top layer was collected and 60 mL was filtered by a syringe pump through an aluminium membrane. Under these conditions, we know that the dispersion contains 50% single-layers, with average size of 10-50 nm.

Raman and X-ray photoelectron spectroscopy (XPS) measurements were performed on both papers.

2.2 Transfer of Anodic bonded samples in suspension
A new method to make a high yield and high quality graphene flakes was reported recently. [32] This method makes use of the anodic bonding technique, (see section 1.5.ii) allowing deposition of large graphene flakes onto a glass substrate. Thicker flakes are few, amongst largely single/ few-layer flakes, which have an average lateral size of 20 - 30 μm. These flakes have been transferred to different substrates
using the wedging method. [55] Transfer to a different substrate (Si/SiO₂) has been successful using a solution of cellulose acetate butyrate (CAB) in ethyl acetate. A method of transferring the flakes in solution needed to be developed, there were several methods that could be employed to tackle this and keep the single layers stable in solution.

i) **Transfer based on solvent and sonication**
As described in Section 1.5.iv, for graphene monolayers to be stable in a solvent, the surface tensions of graphene and the solvent need to match. We wanted to use solvents that were relatively safe and whose boiling points were not too high. Therefore, we chose ethanol (EtOH) and isopropanol (IPA).

We used the following process: we placed anodic bonded graphene samples deposited on glass in EtOH/ IPA, we sonicated the samples for 3 hours and we centrifuged for 20 minutes at 12000 rpm to collect the graphene flakes at the bottom of the tube. The top layer was discarded and the bottom layer was drop cast onto Si/SiO₂ substrate for Raman spectroscopy.

i) **Transfer with Cellulose acetate butyrate (CAB)**
This method has been used with success to transfer graphene to different substrates [55]. It has been shown that this method also works for graphene deposited by anodic bonding on glass. The flakes can be easily transferred from glass to another glass or silicon substrate (Figure 11)
This method works in the following way: a solution of CAB in ethyl acetate (10 µL, 30 mg/ mL) is dropped onto the flakes on the glass slide. This is allowed to dry so that CAB forms a solid film and it encapsulates the graphene flakes. The glass slide with the CAB film is immersed in water, which lifts the CAB with the flakes off the glass. The graphene-encapsulated film is then re-deposited on a new substrate. Finally, the solid CAB film is dissolved in ethyl acetate.

We decided to modify this method and try to dissolve the CAB directly in water: we added ethyl acetate and we centrifuged for 20 minutes at 12000 rpm. The top layer is discarded, as it will contain residual CAB, and the bottom layer is dropped onto a Si/SiO₂ substrate.

We used different processing parameters in order to optimise the process. Table 2 shows the different parameters changed in this experiment.

![Graphene and Glass](image1.png)

**Figure 11** - a) optical picture of as deposited graphene on a glass substrate. b) optical picture of same graphene sheet transferred onto new glass slide. c) optical picture of second as deposited graphene on a glass substrate. d) optical picture taken after transferred onto Si/ SiO₂ substrate
2.3 Transition metal dichalogenides

Previous work has exfoliated various 2D-layered materials in a range of organic solvents using the sonication method. Studies have shown the production of mono- and few-layer nanosheets of MoS$_2$, WS$_2$ and BN. Typical lateral sizes of sheets obtained were between 50 and 5000 nm. It was also shown that no distortions were present in the robust films produced from the exfoliation process. [48] It was found that one of the best solvents for exfoliation was NMP, as this has a high boiling point and hence very difficult to remove, we tried two different methods to exfoliate the materials; MoSe$_2$ and MoTe$_2$. Firstly, we tried exfoliation in low boiling point organic solvents as these will be easier to remove than NMP. Our second route was to use 1-PSA molecules as a surfactant and exfoliate the materials in water.

### Table 2 - Table to show different parameters changed while transferring anodic bonding flakes

<table>
<thead>
<tr>
<th>Sample</th>
<th>CAB concentration (mg/mL)</th>
<th>Amount of CAB dropped on glass slides (μL)</th>
<th>Glass substrate after transfer</th>
<th>Ultracentrifugation power (rpm) and time (minutes)</th>
<th>Sonication time (hours)</th>
<th>Washing time (hours)</th>
<th>Flakes present after drop casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>10</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>N/A</td>
<td>N/A</td>
<td>N</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>8</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>N/A</td>
<td>N/A</td>
<td>N</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>N/A</td>
<td>N/A</td>
<td>Y</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>8</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>N/A</td>
<td>N/A</td>
<td>Y</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>8</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>1</td>
<td>N/A</td>
<td>Y</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>9</td>
<td>3</td>
<td>Y</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>9</td>
<td>Overnight</td>
<td>Y</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>24</td>
<td>3</td>
<td>Y</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>24</td>
<td>Overnight</td>
<td>Y</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>48</td>
<td>3</td>
<td>Y</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>48</td>
<td>Overnight</td>
<td>Y</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>72</td>
<td>3</td>
<td>Y</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>5</td>
<td>Clean</td>
<td>12000 + 20</td>
<td>72</td>
<td>Overnight</td>
<td>Y</td>
</tr>
</tbody>
</table>
2.3.1 Solvent sonication method
MoSe$_2$/MoTe$_2$ (10 mg) was sonicated in IPA (10 mL) for 3 hours and also 24 hours. MoSe$_2$/MoTe$_2$ (10 mg) was sonicated in DMF (10 mL) for 3 hours and also 24 hours. The resulting suspensions were centrifuged at 1000 rpm for 20 minutes to remove any residual material that had not been exfoliated. The suspension was then dropped onto a Si/ SiO$_2$ substrate.

2.3.2 1-PSA method
MoSe$_2$ (10 mg) was added to 1-PSA (aq.) solution (10 mL, 3 mg/ mL) and sonicated for 48 hours. The resulting solution was centrifuged at 1000 rpm to collect and discard any unexfoliated material. The resulting suspension was dropped onto a Si/ SiO$_2$ substrate.

MoTe$_2$ (10 mg) was added to 1-PSA (aq.) solution (10 mL, 4 mg/ mL) and sonicated for 48 hours. The resulting solution was centrifuged at 1000 rpm to collect and discard any unexfoliated material. The resulting suspension was dropped onto a Si/ SiO$_2$ substrate.

2.4 Characterisation
Several techniques were used to characterise the material produced: Raman Spectroscopy, Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). Raman spectroscopy is a very flexible, non-destructive technique, which can be applied to the material in suspension, on the single flake deposited on a substrate and on graphene laminates. This technique is used to identify graphene and to obtain a rough estimate of the thickness distribution. AFM is used to get the lateral size and morphology of the flakes. Note that due to the presence of molecules /surfactant residuals, AFM is not reliable in determining the thickness of the flakes. XPS has been used mainly on laminates in order to investigate the presence of any C-O groups, which can be attributed to oxidation during the exfoliation. The applied techniques are described in more detail below.
2.4.1 Raman spectroscopy
Theoretical background

Raman spectroscopy relies on light scattering, which is fast, sensitive and non-destructive. It has become a standard technique used to look at crystals and semiconductors. [56] When light hits a surface, it is reflected, transmitted, absorbed or scattered. When absorbed, the photons interact with matter and transfer their energy to the system. Scattering involves interaction of matter with the incident light as well as the scattered light, which makes it weaker than absorption as it involves two interactions of photons with matter. Scattering can be elastic or inelastic, corresponding to Rayleigh and Raman scattering, respectively, elastic scattering occurs when the incident and the scattered light have the same energy, whereas inelastic scattering occur when the incident and scattered light have different energies. Raman spectroscopy analyses the inelastic scattered light, produced by the interaction of light with atomic vibrations in a crystal. [56] Atomic vibrations in a material are called phonons and these change the energy of the scattered light, compared to the incident light.

One can describe the Raman scattering process in terms of light-phonon interactions. However, this type of interaction is very weak, in contrast to electron–phonon interactions. [56] In a semiconductor, a photon which possesses energy larger than that of the bandgap can excite electrons from the valence band into the conduction band. This excited electron can interact with crystal vibrations leading to absorption or emission of a phonon. Thus we need to take into account the electrons in the atoms of a crystal. The microscopic description describes the inelastic scattering as a 3-step process:

i. An electron in its initial state is excited by an incoming photon with energy, $\omega_1$.

ii. The electron interacts with a phonon, of energy $\omega_{ph}$, due to electron–phonon coupling.

iii. Emission of a photon, with energy $\omega_2$, and the electron returns to its ground state.
The energy of the emitted photon can be calculated taking into account that energy must be conserved in the process using the following formula:

\[ \omega_1 = \omega_2 + \omega_{ph} \]

\[ k_1 = k_2 + q_{ph} \]

Here, \( k_1 \) and \( k_2 \) are the corresponding wave vectors of the incoming and outgoing photons and \( q_{ph} \) is the phonon energy, respectively. From energy conservation, we can have two possible forms of Raman light observed; Stokes scattering will occur when \( \omega_1 > \omega_2 \) and anti-Stokes scattering is when \( \omega_2 > \omega_1 \). Stokes scattering has a higher intensity than anti-Stokes, hence we will refer to Stokes scattering.

Momentum also needs to be conserved and this determines which phonon we can probe. Phonons can retain the same energy whilst exhibiting different wave vectors, which are determined by:

\[ |k_i| = \frac{2\pi}{\lambda} \]

This is usually \( 10^{-3} \text{ Å}^{-1} \) when using a 514 nm laser wavelength (\( \lambda \)). The extension of a Brillouin zone is of the order 1Å\(^{-1} \), therefore \( k_1 \sim k_2 \sim 0 \). This denotes that Raman spectroscopy can only probe phonons with \( q_{ph} \approx 0 \) i.e. phonons near or at the \( \Gamma \) point.

Scattering can involve more than one phonon, in the case of two phonons, \( a \) and \( b \), momentum conservation requires the sum of the wave vectors, \( q_a + q_b \), to be 0. So, in a second order process every phonon can be probed. If an electron scatters with two identical phonons, \( a = b \), this is called overtone and when these electronic transitions match with real electronic states, the Raman scattering process is resonant.

**Phonons**

Six phonon branches are present in graphene due to the two atom unit cell with three being optical branches (O) and the remaining three being acoustic branches (A). One pair, consisting of one O and one A, are out-of-plane (o) and the rest are in-plane (i). These in-plane phonons can be longitudinal (L) or transverse (T) to the...
A-B crystal, depending on their direction with respect to the nearest two neighbouring atoms. [58] LO and iTO, labelled in figure 12, are the most prominent branches in graphene and are degenerate at the Γ point, therefore they correspond to the $E_{2g}$ and give rise to the G-peak seen in the Raman spectrum of graphite and graphene. [59] At the Γ and K points the energy of the highest optical phonons lowers, this is shown by the red lines in figure 12, these falls in energy correspond to Kohn anomalies. [60] Kohn anomalies arise when there is strong electron-phonon coupling, which is reliant on the shape of the Fermi surface. Kohn anomalies only occur for phonon wave vectors $q$, hence with two electronic states $k_1$ and $K_2$ that can be $k_2 = k_1 + q$. With only K and K' points comprising the graphene Fermi surface, this results in either:

i. $k_1 = k_2 = K$ therefore $q = 0$ (Γ point) 
ii. $k_1 = K$ and $k_2 = K'$ therefore $q = K$ (K point)

Hence, Kohn anomalies are observed at the Γ and K points. Though this changes for doped graphene as the Fermi surface for pristine graphene is degenerate but when doped the Fermi surface changes shape. This leads to the Kohn anomaly moving away from the Γ and K points, i.e. it affects different phonons. Consequently, the Raman spectrum will be highly sensitive to doping in graphene.

![Phonon Band Structure of Graphene](image)

Figure 12 - Phonon band structure of graphene derived from DFT calculations. The LO, LA and iTO phonon are displayed. The Kohn anomalies at Γ and K are emphasised by red lines. Adapted from [61].
Raman spectrum of graphene

Graphitic materials show similar peaks in their Raman spectra; the G and 2D peaks, which lie at ~1580 cm\(^{-1}\) and ~2700 cm\(^{-1}\) respectively (Figure 13). The G-peak arises from stretching of the sp\(^2\) pairs, [62] and it corresponds to the phonon at the Γ point of the Brillouin zone (q=0). The D-peak results from the breathing mode of the 6 atom rings and involves the phonons at the K point. [59] The 2D-peak is an overtone, generated by a second order process, so it does not require any defect to be activated. In this case, momentum conservation is satisfied by two phonons with opposite wavevectors (±q). The first order of the 2D peak is called the D-peak and it is not visible in the Raman spectrum because it cannot satisfy momentum conservation. However, this peak appears every time disorder is introduced in the crystal lattice; the defect provides the missing momentum. This peak lies at ~1350 cm\(^{-1}\).

Figure 13 - Raman spectrum of monolayer graphene

The Raman scattering process only applies to the G-peak as it is associated with a phonon at the centre of the Brillouin zone (q=0). (Figure 14) The D and 2D peaks involve an exchange of momentum and so the electron – phonon scattering cannot be described by a vertical intraband transition.
For a low energy dispersion curve of graphene we have two inequivalent Dirac cones centred at the K and K’ points (figure 14). The Raman scattering process is:

i. The incident photon excites an electron, which jumps from a real electronic state to another real electronic state. An electron-hole pair is created and is the first resonant process. This step is shown with the blue arrow in figure 14.

ii. The excited electron interacts with a phonon, with a certain wave vector, and there is an exchange of momentum, q. The 2D-peak is usually associated with phonons that have a large wave vector as they lie close to the edge of the Brillouin zone. Momentum exchange, q, is therefore close to K since the K and K’ points are separated by K. Thus, the electron is scattered to an electronic state in a different Dirac cone (intervalley scattering). This process is shown by the dotted line labelled q in figure 14.

iii. The hole also interacts with a phonon of equal and opposite momentum, -q, and also undergoes intervalley scattering. The phonon has the opposite momentum due to momentum conservation. This process is shown by the dotted line labelled –q in figure 14.

iv. The electron hole couple recombine with the emission of a photon of light. [63]

The D peak is activated by a similar process, where the scattering with a defect is replaced with the scattering with one of the phonons.
Owing to the intervalley scattering process the 2D-peak is sensitive to changes in the electronic band structure as the phonon probed strongly depends on the electronic structure. Every change in the electronic dispersion will produce changes in the phonon wave vector associated with the 2D-peak. The 2D peak changes its shape because the electronic structure is strongly sensitive to the number of layers. In graphene, the electronic structure is linear, as described in Chapter 1, in this case the 2D-peak is a single and sharp peak. For bilayer, the electronic structure changes: whether a bilayer graphene flake is Bernal stacked (AB) or not, greatly influences its electronic properties. Bernal stacked graphene layers show a 2D-peak composed of four bands and the characteristic graphite peak is also a sharp peak but with a prominent shoulder. Above 5-7 layers the changes in the electronic structure are too small, so that the 2D peaks of a flake containing more than 7 layers and of a thick graphite flake are basically indistinguishable. (Figure 15) This explains why Raman spectroscopy is currently the most used technique to identify graphene. [59, 64-68]

![Figure 15 - Evolution of the 2D peak from graphite to graphene](image)

**Effect of doping**

An excess charge on graphene can move the Fermi energy away from the Γ point. In the case of excess charges (n-doping) the Fermi energy will move up and with depletion of charges (p-doping) the Fermi energy will move down. Electrical doping
in graphene can change the charge concentration, this can easily be done using a gate voltage; in this case a Si/ SiO$_2$ substrate can be used as a back gate. Raman spectroscopy can monitor doping; charge transfer will produce varying bond lengths and phonon frequencies, which produce changes in the Raman spectrum. In graphene’s spectrum, these changes are significant:

i. G peak upshifts with increasing doping. Full Width at Half Maximum (FWHM) of G-peak decreases with increasing doping, this saturates at high doping.

ii. 2D position changes depending on type of charges, n-doping downshifts peak and p-doping upshifts peak.

iii. Intensity ratio of 2D and G-peaks I(2D)/ I(G) decreases for increasing doping.

Thus, Raman spectroscopy can distinguish between n- and p- doping in graphene. [69-71]

Effect of defects

A defect in graphene is classed as something that breaks the symmetry of the lattice. Several types of defects can be present; edges, grain boundaries, vacancies, intercalated atoms, also changes in carbon hybridisation state, e.g. from sp$^2$ to sp$^3$. The nature and quantity of defects strongly depend on the production method; defects can also affect the properties of graphene.

Raman spectroscopy can probe disorder through defect-activated features, including the D and D’ peaks which lie at $\sim$1350 cm$^{-1}$ and $\sim$1620 cm$^{-1}$ respectively. Graphene that is produced through micro mechanical exfoliation often does not have enough structural defects for the D and D’ peaks to be Raman active, so these peaks are only seen at the edges. Edges activate the D and D’ peaks because they break the translational symmetry of the crystal. It has been seen that the defect activated peaks arise when moving from the centre of a pristine graphene sample to the edges. [72]
Raman spectroscopy: Experimental setup

The Raman system we currently use is a Witec alpha 300 spectrometer, equipped with 488, 514.5 and 633 nm excitation lines (figure 16). The laser light is delivered through a single-mode optical fibre in an optical microscope, the Raman scattered light is collected using the same objective and is focussed into a multi-mode fibre, which detects the beam to the spectrometer with a CCD camera. There are different ways to collect a Raman spectrum, such as; single spectrum at a selected area on the sample. Since the microscope is equipped with a piezoelectric stage, line scans can also be collected along a certain line of a sample and Raman mapping can also be done by collecting a Raman spectrum at every point of a selected area. The Raman spectrometer is equipped with 2 gratings: 600 g/ mm, which we use to take a broad scan from 0 – 3000 cm\(^{-1}\) and 1800 g/ mm which is used to take a higher resolution scan of a narrower window than 600 g/ mm.

**Figure 16 - Picture of Raman system**
2.4.2 Atomic force microscopy (AFM)
AFM can directly image any surface, using a laser beam deflection system. It consists of a tip (on the end of a cantilever) which is brought into proximity of the sample being measured, leading to forces between the tip and the sample that deflect the cantilever from the sample. Deflection is measured using a laser beam reflecting to a detector. AFM is a viable route to identify graphene, but it has a very low throughput and in practice it would be impossible to find crystals by randomly scanning surfaces. [73] Also, it has been shown that single layer graphene on Si/SiO$_2$ substrate has had heights of 0.8 – 1.2 nm, which is considerably larger than the theoretical 0.33nm value of the height of single layer graphene, probably due to adsorbates on the surface. [25] Hence, AFM can only distinguish between 1 and 2 layers if the flake is folded. [64]

2.4.3 X-ray Photoelectron Spectroscopy (XPS)
XPS is a surface analysis technique, where X-rays are used to irradiate a material, emitting photoelectrons from the surface of the sample. An electron energy analyser determines the binding energy of the emitted photoelectrons. From these measurements, the elemental identity, chemical state and quantity of an element can be determined.

The XPS measurements have been performed by our collaborators in Belgium.

3. Results and discussion
In the first part of this chapter I will focus on the method developed in our group (based on 1-PSA) to exfoliate graphite (Appendix 1). I have produced graphene laminates with the dispersions and I have characterised them using Raman spectroscopy. I have compared our laminates with the ones produced by standard NMP-based dispersions.

In the second part of this chapter I will focus on a problem we observed by exfoliating graphite in 1-PSA, i.e. we do not get controlled assembly of the molecules on graphene. Thus, it is difficult to achieve exfoliation and controlled functionalisation at the same time. Due to this, we decided to try transferring single
layer flakes produced by anodic bonding in suspension and then add the molecules in order to functionalise the graphene flakes in suspension. I will show that it is possible to transfer the flakes from the substrate, but it is very difficult to detect them in suspension, probably because they re-aggregate or because they are removed after centrifugation.

In the third part of this chapter I will present some preliminary results I have obtained about the exfoliation of graphene analogues. These materials are interesting because they often have complementary properties to graphene. For example, single layer Boron Nitride is an insulator, while single layer Molybdenum Disulphide (MoS$_2$) is a semiconductor with a gap of ~2 eV. Those materials can be re-assembled together to form hetero-structures, which combine the properties of all of them [74].

**3.1 Graphene papers**
Polyaromatic hydrocarbons (PAHs) are lipophilic; they have a higher solubility in oil than in water. They can be functionalised with different groups including hydroxyls, carboxylic acids and sulfonic acid groups. The functional groups contribute to the solubility of the polyaromatic hydrocarbons. We chose a pyrene derivative as it is soluble in a variety of solvents including water. [42, 43, 45, 75-77]

There have been several studies which have used PAH derivatives (TPA, 9-anthracene carboxylic acid and 1-pyrenecarboxylic acid) to exfoliate graphite in various solvents including methanol. These studies have had successful exfoliation using supramolecular interactions but have done so in an uncontrolled way. Using 1-PSA we aim to fully control the position and orientation of the molecules on the graphene surface.

**3.1.2 XPS results**

Figure 17 shows the data for the 1-PSA based paper. The survey spectrum shows the presence of C (93.6%), O (4.9%), N (0.7%) and S (0.8%). From the sulfur value we can estimate the residual 1-PSA in the paper, 0.8% sulfur is present and for every 1 sulfur atom there are 16 C atoms, thus, 12.8% of the C signal is present due to 1-PSA. The high oxygen content is attributed to the oxygen atoms in the sulfonic
group. No large peaks between 286 and 288 eV corresponding to C-O and C=O
groups were observed, confirming no graphene oxide was produced. Residual C-O
and C=O is ~3%, assigned to slight oxidation or presence of contaminants.

Graphite, PSA powder and PSA graphene paper spectra were all recorded in the C1s
spectrum. The residual PSA was estimated to be 14%, fitting well with survey
spectrum results, from the area under the peak.

Figure 18 shows the XPS data for the NMP based paper. The survey spectrum shows
the presence of C (96.4%), O (2.1%) and N (1.0%). The nitrogen content comes from
the NMP and as a result, 1.0% of the O content is from NMP. This shows an 8.7%
residual NMP in the paper. The rest of the oxygen content is possibly due to
contamination. The N peak has a binding energy of ~400 eV, which matches with
the binding energy of NMP. The C1s spectrum shows the different C environments
in NMP.
Figure 18 - XPS results of NMP-based graphene paper. Left: survey spectrum and right: C1S spectrum

3.1.3 Raman spectroscopy results

Figure 19 shows the typical Raman spectrum for both PSA-based paper and the NMP-based paper.

Figure 19 - Comparison of Raman spectra of 1-PSA-/ NMP- based graphene papers.
There are two main differences in the spectra:

i) The intensity of the D-peaks: the NMP-paper shows higher D-peak intensity. In this case, the D-peak is assigned to the small size of the flakes. One should note that the dispersion was sonicated for 72 hours, whereas we sonicated the 1-PSA dispersion for 80 minutes, In the case of the PSA-paper, however, the D-peak can have a further contribution. Polyaromatic hydrocarbons are known to show a D-peak in their Raman spectrum. [1, 47] So, we expect some form of contribution to the D-peak from the 1-PSA molecules. This has been confirmed by looking at the evolution of the Raman spectrum of an exfoliated graphene flake covered with a layer of 1-PSA molecules: as soon as the power increases the D-peak changes in shape and position. This corresponds to desorption and degradation of the molecules since no D-peak is observed in pristine graphene measured under the same conditions. [12]

ii) The second difference is in the shape of the 2D-peaks; in NMP this is a single sharp peak, indicating the presence of an array of randomly stacked layers. In contrast, the 2D-peak for PSA is composed of two components; the smaller one relates to the same position as the 2D-peak in NMP and the second lying at a higher wavenumber. The structured shape of the 2D-peak in the 1-PSA graphene paper can be attributed to the different flake thickness distribution in solution, i.e. our method produces mostly few-layer graphene.

3.2 Anodic bonding samples
A method of transferring the flakes in solution needed to be developed, there were several methods that could be employed to tackle this and keep the single layers stable in solution. (See section 2.2) We first needed to check whether transfer had occurred, this was simply done by checking the slide before and after the transfer to confirm whether the flakes were present. If the glass substrate is clean, we know transfer has occurred and then we can drop the suspension onto a Si substrate and search for the flakes in suspension using Raman spectroscopy.

We used different methods to transfer the flakes produced by anodic bonding from the glass substrate into solution. First, we have to check that the flakes have been
transferred: this can easily be done by looking at the glass substrate, after the chemical processing, under the optical microscope. The glass has to appear clean and empty; note that graphene is almost transparent on glass. However, our microscope is equipped with a function which enhances the visibility of graphene on the substrate; a monochromatic filter. A 1 channel image is generated from a 3 channel image; this increases the optical visibility of the flakes on the substrate.

After checking the substrate, we need to investigate if the flakes are in suspension and if they are stable in it (i.e. they do not re-aggregate). This can be done by depositing a drop on a silicon substrate covered with an oxide layer. As explained in Section 1.3.2, this substrate enhances the visibility of graphene under the optical microscope. We then look at what is left on the substrate under the optical microscope. The flakes selected in this way are then measured by Raman spectroscopy for identification.

Note that there are several challenges we have to overcome:
- we work at very low concentration, so spotting the flakes on the substrate could be difficult;
- the flakes could be transferred in suspension, but they can be removed during the processing, for example after centrifugation;
- a lot of solvent or residual molecules can be observed, as is the case of 1-PSA based suspensions (Section 1.5.iv).

I will show that most of these challenges cannot be solved. Improvement on the transfer may be obtained by scaling up the anodic bonding technique in order to work with large amounts of material.

3.2.1 Transfer based on solvent and sonication
Figure 20 shows the optical microscope pictures of the substrate with the EtOH dispersion drop cast onto it. The substrate was left in EtOH overnight to remove the residual solvent.
Removal of the flakes from the glass substrate was confirmed by optical pictures taken before and after the transfer process. However, the flakes could not be located on the Si/SiO$_2$ substrate; they may have been covered by the large amount of solvent on the substrate, or they could have been removed during centrifugation.

Figure 21 shows optical pictures of the Si/SiO$_2$ substrate after drop casting of IPA dispersion, which was also left in IPA overnight. There is also a lot of residual IPA on the substrate, however, not as much as with EtOH.

In this case, flakes were found on the substrate and the typical Raman spectrum is shown in figure 22. The Raman spectrum shows the flakes to be bilayer or few layer
flakes, confirmed by fitting of the peak to show it is composed of two components and cannot be attributed to a single layer flake. The defect activated D-peak is also present, which is attributed to edge effects due to the small size of the flakes seen in the optical pictures.

Figure 22 - Raman spectrum of flakes found in IPA dispersion

In conclusion, this method can be used to transfer the flakes, but we observed a relatively large amount of solvent left in suspension.
3.2.2 Transfer with Cellulose acetate butyrate (CAB)

We first looked at the effect of the concentration of CAB and the amount of solution dropped to cover the flakes. Initially, we started with a CAB concentration of 30 mg/ mL and dropped 10 µL on the glass slide. However, there was a lot of residual CAB visible on the Si/SiO₂ substrate. Thus, we reduced the amount of CAB to 8 µL as it was thought this would reduce residual CAB. However, this made little difference, the substrate is completely covered with CAB and no flakes can be observed. (Figure 23)

![Image](image.jpg)

**Figure 23 - Optical pictures of Si/SiO₂ substrate once 10 µL (left) and 8 µL (right) of CAB solution was dropped.**

We found out that the minimum amount that could be dropped to cover the entire region on the glass substrate by encapsulating graphene was 5 µL. We then looked at reducing the concentration of CAB used, which was initially 30 mg/ mL. This concentration was reduced to 10 mg/ mL, which resulted in the samples looking cleaner and the flakes were visible through the cellulose (Figure 24).
We measured the Raman spectrum of the flakes shown in Figure 24 (right). From the shape of the 2D peak this flake is likely a large bilayer or trilayer. It is, however, covered in cellulose, as shown by the presence of small peaks between the D- and G-peak. They are coming from the cellulose, which we measured separately. 5 mg/mL was found to be the smallest concentration which could be used, any less then the CAB would not form a film strong enough to transfer flakes.

Since one of the biggest difficulties in dealing with this method is related to the relatively small amount of flakes deposited by anodic bonding, we decided to increase the amount of flakes by sonicating the suspension. It is well know that sonication reduces the size of the flakes. Thus, we looked at different sonication times, after centrifugation (Table 2). In order to remove the residual CAB, we also introduced some washing steps: a drop of suspension is deposited on the silicon substrate, and then the sample is washed in ethyl acetate to remove as much CAB as possible.

The first sample was left in ethyl acetate for 3 hours and sonicated for 9 hours, (figure 25a) the residual CAB is considerably reduced; although, from the average flake size before transfer, the flake size does not seem to be reduced. The Raman spectrum of the corresponding flake, (figure 25b) shows the flake to be a few-layer
flake or maybe graphitic, this is seen from the shape of the 2D peak, it has a sharp peak at a higher wavenumber and also a shoulder lying at lower wavenumber. Washing the sample overnight in ethyl acetate significantly reduced the CAB left on the substrate, (figure 25c,d).

We then looked at the sonication times to reduce the size of the flakes; we sonicated the samples, while still in suspension, for 24, 48 and 72 hours (Figure 26). We could not see any appreciable change in the size of the flakes and most of the flakes are thick, as observed by the colour contrast of the flakes and by Raman spectroscopy. Figure 26 a and c show the clearly thick flakes found in the
suspension and figure 26 b and d show the corresponding Raman spectra for the flakes, it is clear these are thick flakes as a shoulder can be seen on the 2D-peak.

![Optical picture and Raman spectrum images](image)

**Figure 26** - a) optical picture and b) Raman spectrum of sample sonicated for 24 hours. c) optical picture and d) Raman spectrum of sample sonicated for 72 hours. Red X marks where flakes were found.

Although, some flakes were found that were relatively free of CAB, it was found that the majority of flakes were irreversibly encapsulated in the CAB film and the cellulose could not be removed. (Figure 27).

In conclusion, this method can be used to transfer graphene from the substrate in solution. However, the flakes are covered by CAB, which cannot be completely removed.
Figure 27 - Optical pictures and typical Raman spectrum of flakes encapsulated in CAB film. Red X marks where flakes were found.
3.3 Transition metal dichalogenides (TMDs)

Solvent sonication results

AFM was used to determine flake thickness, as the single layer height of MoTe$_2$ and MoSe$_2$ were known to be 5.29Å and 4.90Å respectively. Figure 28 shows the AFM images obtained of sonicating MoTe$_2$ in IPA for 3 and 24 hours then drop casting these suspensions onto a Si/ SiO$_2$ substrate.

![AFM image of MoTe$_2$ sonicated for 3 hours (left) and 24 hours (right).](image)

With a 3 hour sonication time, the average height of the flakes was ~ 400-500nm and this was significantly improved when the sample was sonicated for 24 hours, where the thickness appeared to be ~ 100-150 nm.

Figure 29 shows the AFM images of MoSe$_2$ sonicated for 3 and 24 hours.

![AFM images of MoSe$_2$ in IPA sonicated for 3 hours (left) and 24 hours (right)](image)
AFM images show that after a 3-hour sonication, the flakes were approximately 400-500 nm in height and this reduced to 100-130 nm when sonication time was increased to 24 hours.

There was also residual solvent left on these samples. It was concluded that very long sonication times, 72+ hours, would be needed to achieve mono- or few-layer flakes. The longer the sonication time the smaller the lateral size of the flakes, this would result in the flakes being so small they would not be able to be measured by Raman spectroscopy. We then moved onto the 1-PSA method.

1-PSA results

To optimise the parameters of the exfoliation of MoSe$_2$ and MoTe$_2$, we started with the same method used for graphene exfoliation. The initial sonication time used was 80 minutes in accordance with graphene suspensions; it became clear that a short sonication time was insufficient to exfoliate the materials, as after sonication the materials were still at the bottom of the sample vial. So, the sonication time was periodically increased up to 48 hours. Next, we looked at 1-PSA concentration, initially; we used 0.1 mg/mL. Although, it originally seemed the materials had been exfoliated, when left to stand, the suspensions were not stable and the materials re-aggregated. The concentration of 1-PSA was periodically increased until it was found that 3 mg/mL (for MoSe$_2$) and 4 mg/mL (for MoTe$_2$) were sufficient to produce stable suspensions. (Figure 30)
To remove residual 1-PSA molecules from the suspensions, they were washed. The suspensions were centrifuged at 1000 rpm to remove any unexfoliated material and then centrifuged at 12,000 rpm to collect the exfoliated material, the top layer was decanted and the vial refilled with de-ionised water and put in the centrifuge again at 12,000 rpm. However, even after just one washing step the samples become unstable. Raman spectroscopy measurements were performed on the unwashed samples [Figure 31], the spectra show characteristic peaks associated with MoSe$_2$ and MoTe$_2$ in stacked crystals. [78]
The peaks observed in stacked crystals of MoSe$_2$ include 242 cm$^{-1}$ and 286 cm$^{-1}$; we observe the peaks at 239 cm$^{-1}$ and 284 cm$^{-1}$. It is well known that peaks can shift a few wavenumbers on exfoliation. For MoTe$_2$, the characteristic peaks are detected at 168 cm$^{-1}$ and 243 cm$^{-1}$; the only peak we observe is one at 233 cm$^{-1}$. [78] The Raman spectra of the materials can also give information about residual 1-PSA molecules since they show fluorescence in their spectra. The spectra do not show considerable fluorescence and hence we can conclude there is not too much free 1-PSA molecules in solution.

Figure 31 - Left: Raman spectrum of MoSe$_2$. Right: Raman spectrum of MoTe$_2$
6. Conclusions and future work

In the first part of this report we investigated the supramolecular interactions between graphene and 1-PSA, comparing exfoliation efficiency of 1-PSA to that of NMP. NMP dispersions have been characterised very well and the single layer yield is known. We produced graphene papers from these dispersions and through XPS showed that no graphene oxide or derivative of graphene had been produced. Residual 1-PSA was estimated to be around 13% which was more than the residual NMP present in the corresponding paper. Raman spectroscopy determined the PSA-based paper had less than a 50% monolayer yield of flakes and the size of flakes was much larger than the size of flakes in the NMP dispersions. The aim of this project was to achieve a hybrid graphene material with a controlled amount of 1-PSA molecules on the surface of graphene. This could not be achieved through sonication in the 1-PSA solution; another possible way to achieve this is using pristine graphene samples and adding the molecules using drop casting or dip coating. Both will allow us to drop a specific amount and concentration of molecules onto the flakes. We can investigate washing steps, if necessary, to obtain the desired amount of molecules on graphene. However, obtaining a high yield and quality of single layer flakes cannot be achieved using the micro mechanical cleavage method. This is explored in the next part of the report.

In the second part of this report we showed results on a transfer method being developed for anodic bonding graphene samples. Transfer of flakes by simple sonication in a solvent left behind too much residual solvent and when washed in the solvent, only a small amount of residual solvent could be removed. The next method involved using CAB as it is a coating polymer that forms a film around the flakes, thus encapsulating them. Many parameters were changed in this experiment and it was found that washing samples in ethyl acetate once they had been dropped onto a Si/SiO₂ substrate, helped in removing some cellulose. However, a plateau was reached and it was concluded that the majority of flakes were encapsulated in the CAB and it could not be removed. If the anodic bonding technique is scaled up and we can deposit graphene flakes on a glass substrate with an area of 1 cm² then this process could become more efficient. We are currently...
working with a very small concentration of flakes which make it hard to find the flakes on the substrate, if we were to have a larger area of flakes then this might result in a small proportion of the flakes embedded in the cellulose and the rest free and stable in solution.

Exfoliation of other 2D-layered materials has been started and could be looked at in more detail; a comparative study using different pyrene derivatives can be undertaken to better understand the interactions occurring between graphene and the pyrene derivatives. These molecules may have more functional groups which will give the molecule a more polar character. Molecular aggregation also needs to be studied, which depends on interaction between the molecules, solvent and graphene. Thus, self-assembly behaviour will be different with different molecules. Self-assembly can be investigated with AFM and Raman spectroscopy studies, these techniques can also give information on any charge transfer or defects that may occur with the molecules being used.

There are many other 2D-layered materials which could be looked at; topological insulators, such as Bi$_2$Te$_3$/Bi$_2$Se$_3$ could be looked at. Exfoliating MoS$_2$ has shown that the indirect band gap of the bulk material transforms into a direct band gap for few-layer flakes. [48] A change in the electronic properties of exfoliated Bi$_2$Te$_3$ and Bi$_2$Se$_3$ is also expected to occur. This is certainly a topic that could be investigated.

Raman characterisation of the bulk 2D materials has been reported [79] However, for most of them the single layer spectra have not been reported. Going from bulk to single layer can produce changes in the electronic properties of a material. This can be reflected in a change of the Raman spectrum. This could be further confirmed using AFM, as the theoretical height of a single layer of this material can be found in literature. Future plans for this work could aim at using a combination of Raman spectroscopy and AFM in order to study the evolution of the Raman spectrum of the new 2D materials from bulk to single-layers. There are several challenges involved: first of all the optical visibility of the new 2D material is not known- they could be transparent, and a different substrate from the Si/SiO$_2$ may need to be used in order to enhance the colour contrast of the new material.
Second, in certain materials the Raman process is not resonant (for example, h-BN, which has a large gap above 5eV). This makes the Raman spectrum a lot less sensitive to changes in the electronic structure. Finally, it is well known that these new 2D materials do not have a good thermal and chemical stability. Thus, it will be essential to investigate the effect of defects, ambient air, oxygen and temperature by Raman spectroscopy. This type of analysis could be difficult in these materials, where the analogue of the D-peak may not exist, i.e. the Raman spectrum does not show any peak related to defects.

Carbon nanotubes (CNT) have been extensively studied, since their discovery, for many possible applications, such as in biological systems. One piece of research has shown functionalising CNT’s with amino groups to be successful. [80] This study could extend to graphene and it could also be functionalised with amino groups. XPS could be used to confirm the functionalisation has taken place as it should show a peak corresponding to C-N bond. Infra-red (IR) spectroscopy could also show N-H stretches from the sample. If this is successful, then there could be scope to functionalise graphene with amino acids. This could further lead to peptide self-assembly on graphene sheets. Peptides have incredible self-assembling properties, in which they construct themselves into ordered nanostructures; this can allow specific modifications to be introduced during the assembly process. Peptides also show resistance to extreme conditions, such as high and low temperature. [81]

Specific surfactant-like peptides can also undergo self-assembly, they are soluble in water and could potentially be used to decorate the surface of graphene in water. Made up of a hydrophilic head group and a tail made up of hydrophobic amino acids. [82] Charged surfactant-like peptides have also been reported. [83] For example, positively charged peptides have been described, consisting of a cationic hydrophilic head made up from lysine or histidine.

Thus, graphene surface could be functionalised with amine groups, amino acids and hopefully peptides. From this, peptide nucleic acids (PNA) can be decorated onto the graphene surface, which has been achieved with CNT. DNA was shown to attach to the PNA–CNT hybrid from sequence specific PNA-DNA base pairing, rather than
nonspecific interactions. This recognition property could be exploited in biosensors. [84]
A simple method for graphene production based on exfoliation of graphite in water using 1-pyrenesulfonic acid sodium salt

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1. Introduction

Graphene, a single-layer of graphite, has become one of the most exciting topics of research because of its outstanding optical, electronic, and mechanical properties [1,2]. In particular, its optical transmittance (~99%) combined with high mobility makes graphene a perfect material for transparent conductive electrodes [3-5]. Few-layers thick graphene (less than ten layers) are being investigated with equal interest to monolayer graphene [6-8]. However, reliable production of single- and few-layers graphene samples in high quality and yield is still a challenge.

Liquid-phase exfoliation is a mass-scalable approach for the production of graphene [9-11]. However, this requires the use of organic solvents, which are expensive, toxic, difficult to remove and can cause environmental issues. Thus, an alternative chemical approach, which allows processability without affecting the intrinsic properties of graphene and makes use of "green" solvents such as water, is urgently required, in particular for life science applications.

The high surface energy of water does not allow dispersion and exfoliation of graphite in this solvent. Graphene can be produced in aqueous surfactant solutions [12]. However, the yield of the dispersed graphene flakes is low (~10%) and
surfactants are difficult to remove [12]. A few recent works [13-17] report on the exfoliation of graphene through non-covalent interactions between graphene and pyrene derivatives, which can be seen as “nano-graphene units”. The aromatic core of the molecule allows its intercalation and physiosorption on the hydrophobic surface of graphene through π-π interactions, while appropriate functional groups attached to the molecule allows the electrostatic stabilization of graphene in the solvent. Pyrene, as it is, is not soluble in water. Different groups can be attached to pyrene to tune its solubility such as sulfophonic groups [SO3H] [13,15,18], carboxylic acid groups [COOH] [14] or more complex groups generating aromatic amphiphiles [17]. The nature and number of the functional groups is very important because the molecule must have a good affinity with the solvent, i.e. it needs to get sufficiently dissolved, but at the same time, the solvent has to allow hydrophobic interactions between graphene and the core of the molecule [14]. Thus, the easiest solution is to use a mixed solvent such as methanol and water: the first allows dispersion of the molecule in the solvent, while the second allows interactions between the molecule and graphene [13,14]. An overview of the most recent works is reported in Table 1.

In this work we investigate the use of 1-pyrenesulfonic acid sodium salt (Py-1SO3H) to achieve exfoliation of graphene by using only water. The sulfonic group of this molecule improves the affinity of the molecule in the solvent, while at the same time hydrophobic interactions between graphene and the molecule are allowed. To the best of our knowledge, the use of Py-1SO3H for exfoliation of graphene has been reported only in the work of Jang et al. [13]. In this case, a mixed solvent was used. Furthermore, graphene was produced by using supercritical fluid exfoliation, which requires high temperature and pressure, while Py-1SO3H was used to achieve non-covalent modification of graphene during exfoliation. Because of the complexity of this method, it is not possible to really get information on the role of Py-1SO3H as compared with the use of the solvent alone on the exfoliation mechanism and how this compares with the use of other pyrene derivatives.

In this work we aim at investigating the direct exfoliation of graphene in water using Py-1SO3H by using a combination of microscopic and spectroscopic techniques. In particular, we present an extensive Raman analysis of the material in suspension. A careful analysis of the Raman spectrum is very important since it is used to quantify the yield of single layers and to investigate the interaction between the molecules and graphene.

2. Experimental section

2.1. Material preparation

The schematic of the exfoliation process is shown in Fig. 1. The Py-1SO3H yellowish solution was prepared by dissolving 1 mg of Py-1SO3H powder (Sigma-Aldrich, > 99.0%, 4HPLC) in 10 mL of distilled water. The dispersion was produced by sonication (Bionick UK 1020 bath sonicator) 30 mg of graphene flakes (Bran Fell UK, Grade 99.5) with 10 mL of as-prepared Py-1SO3H solution. After 80 min sonication, the large cluster of non-exfoliated graphene can be removed by mild centrifugation at 1000 rpm for 20 min. The dispersion was then refluidized with water and centrifuged at 12,000 rpm for 20 min for three times in order to wash the excess Py-1SO3H.

After washing, the graphene-based materials collected at

| Table 1 - List of the works reporting production of graphene by chemical exfoliation of graphene with pyrene, as compared with our work. Details of the exfoliation process, the yield obtained and the Raman spectrum have been included such as the shape of the 2D peak and the presence of the D peak. |
|---|---|---|---|
| Ref. | Molecule | Exfoliation process and yield | Raman Spectrum |
| [13] | Py-1SO3H | Bath sonicator, mixed solvent | In most cases the 2D peak is not a single peak |
| [14] | Py-COOH | Bath sonicator, mixed solvent | D peak is not shown, but D' is visible |
| [15] | Py-4SO3H | Single layers and bilayers | D peak: yes |
| [16] | Py-NH2, Py-4SO3H | Bath sonicator, water | 2D peak not shown |
| [17] | Amorphophlic-Py | Bath sonicator, mixed solvent | Single 2D peak |
| This work | Py-1SO3H | Bath sonicator, water | D peak: yes |
the bottom of the micro-centrifuge tubes were re-sonicated in water for 1 min. In the last step, the final dispersion was obtained after further removing the residual graphite flakes by mild centrifugation at 1000 rpm for 20 min. The resulting dispersion is gray and stable over months, Fig. 1B. Graphene laminates, Fig. 1C, were prepared by vacuum filtering 300 ml of dispersion on an alumina membrane (pores size of 0.2 μm). The film drying was carried out in air at room temperature for 3 days. The concentration of dispersion remaining after centrifugation is ~0.04 mg ml⁻¹, calculated using an extinction coefficient \( \epsilon_{230} = 24600 \text{ g}^{-1} \text{ cm}^{-1} \).

Suspensions obtained by chemical exfoliation with organic solvents (1-Methyl-2-pyrrolidone, NMP) were also produced by following the recipe published in previous work [8,9]. We sonicated the dispersion for 3 days in order to achieve a high yield of single-layer graphene (~90%) [8]. This type of suspensions has been already well characterized in previous works [8,9], so we simply use them as reference in order to compare the quality of the dispersions obtained with Py-15O.

2.2. Characterization

A Perkin-Elmer 1-700 UV-vis-NIR spectrophotometer was used to perform UV-vis spectroscopy of the dispersion. Fluorescence measurements were obtained by using a Spex Fluorolog II, equipped with a 450 Watt Xenon lamp.

The prepared dispersion was drop coated on a SiO₂/Si substrate for Atomic Force Microscopy (AFM) and Raman Spectroscopy characterization. A Nanoscope III a, operating in tapping mode was used. A Witec alpha300 Raman spectrometer, equipped with 488, 514.5 and 633 nm excitation lines and a piezoelectric stage for Raman mapping, was used.

The Raman peaks were fitted with Lorentzian lines. The laser power on the sample was below 1 mW in order to avoid damage of graphene and desorption of the molecules.

The flakes were also deposited by pipetting a few milliliters of the dispersion onto holey carbon mesh grid for Transmission Electron Microscopy (TEM) analysis. An FEI Tecnai F20 with 200 kV accelerating voltage was used.

The graphene laminates have been analyzed by Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). A Thermo Scientific X-ray XPS was used with pass energy of 50 eV. The spot size on the sample is ~400 μm. The XPS measurements were done on a vacuum filtered laminated (~2 μm thickness, see Fig. 1C) that had been dried at room temperature for 2 weeks before the measurements.

3. Results and discussion

3.1. Flakes in suspension

Fig. 2 shows the absorption spectra of the Py-15O solution (bottom) and the Py-15O/graphene dispersion (top). The spectrum of Py-15O solution shows the characteristic peaks between 200 and 400 nm [20]. Compared to the absorption spectrum of Py-15O, the baseline of the absorption of the graphene-based dispersion absorbs over the whole frequency range, as it is expected for graphene dispersions [14]. The original peaks of the Py-15O solution are still visible, but they are broader: this is fingerprint of the π→π* interaction between Py-15O and graphene, as observed when single-walled carbon nanotubes were dispersed by pyrene molecules [20,21]. Collectively, these observations confirm the presence of both pyrene and graphene, i.e., the molecules interact with the graphene sheets through π→π* interaction, thus exfoliating...
and stabilizing graphene in water. Fluorescence measurements further confirm this result: the inset in Fig. 2 shows a strong decrease of the fluorescence after 1.5 h sonication. This is fingerprint of interaction between the molecules and graphene [22,23]. This type of charge transfer interaction is of great importance for the design of optoelectronic composite materials. In the case of composite materials based on graphene oxide, the nanographene molecules anchor on the functional groups on the basal plane causing the fluorescence to be fully quenched [24]. Note that in our case the fluorescence is not completely quenched. This means that there is an excess of molecules in solution. Indeed, we did try to perform Raman spectroscopy directly on the dispersion, but the Raman signal was completely hidden by a strong fluorescence background.

3.2. Flakes on the substrate

Raman spectroscopy is a powerful probe for characterizing graphene [25]. A typical Raman spectrum of monolayer graphene shows two main features [25]: the G peak, corresponding to the Eg phonon mode at the Brillouin zone center, at ~1580 cm$^{-1}$ and 2D peak, which is activated by two-phonon interband assisted Raman scattering at ~2700 cm$^{-1}$. The 2D peak can be used to identify graphene [26]: the 2D peak is a single and sharp peak in the case of monolayer graphene, while in multilayer graphene, the 2D peak is composed by four bands. Graphite shows a broad and up-shifted 2D peak, which in first approximation can be fitted with two peaks. The 2D peak shape quickly evolves with the number of layers, so that the 2D band of a sample containing more than 8-10 layers is hardly distinguishable from that of bulk graphite [26]. In case of disorder, defect-activated features appear in the Raman spectrum: the D peak, first order of the 2D peak, which lies at ~1350 cm$^{-1}$, and the D' peak, which appears at ~1620 cm$^{-1}$ [27]. It is common for pristine graphene not to have enough structural defects for the D and D' peaks to be Raman active so that they can only be seen at the edges [26,28].

In order to have a good statistics of the composition of the material obtained, Raman spectroscopy was performed on a large amount of flakes (~130) deposited on a silicon substrate. We selected only flakes large enough to be observed under the optical microscope. Fig. 3 shows the typical Raman spectra measured on our flakes. The spectra show common features of graphene, such as the G and 2D peaks. However, D and D' peaks are also visible. A small peak at about 1245 cm$^{-1}$ also appears. Fig. 3. This is attributed to pyrene aggregates, since this peak has been observed in pyrene crystals [29]. Re-aggregation is driven by the amphiphilic nature of the molecules. Furthermore, a small fluorescence background is also visible in the Raman spectrum, indicating that the flakes are covered by a layer of molecules. Note that graphene is able to quench the fluorescence from the molecules due to charge transfer [30]. However, charge transfer happens only if the molecules are close enough to the surface of graphene [31]. In our case, since the fluorescence background is not completely quenched, we do expect to find a relatively thick layer of molecules on graphene.

Fig. 3 shows that the shape of the 2D peak strongly changes: this reflects the different thickness composition of the flakes. Based on the shape of the 2D peak, we can make an attempt to derive the amount of graphene in solution. We found that ~18% of the flakes are single layers, ~60% are few-layer graphene flakes (<7 layers) and 4% are thick flakes. We used the same method to test stability against re-aggregation over longer time. We repeated the statistics on the same dispersions, which stand undisturbed for 8 months. About 130 flakes were checked. We found that the aged dispersion is composed by ~22% single layers, ~61% few graphene layers (<7) and ~17% thick flakes. Thus, no appreciable difference is observed in the composition of the flakes after 8 months, demonstrating a good degree of stability. Note that these numbers need to be treated with care since the composition of the flakes on the substrate may not correspond exactly to the composition of the flakes in suspension. However, they offer a rough idea on the exfoliation efficiency.

Note that both relative intensity and position of the 2D peak...
cannot be used to identify graphene because they change with doping [31] and defects [32]. In contrast to mechanically exfoliated graphene, here we are dealing with flakes produced by chemical exfoliation, so we do expect doping and disorder to produce changes in Raman spectrum. For example, we do expect a shift and a decrease in the intensity of the 2D peak caused by doping from water (rather than from the molecules themselves) [33].

Furthermore, the Raman spectra show defects-activated features, indicating the presence of some form of disorder. Note that generally, in graphene dispersion the presence of a 2D peak is related to edges: for instance, NMP-based dispersions of graphene flakes with typical size of 10-20 nm show a strong D peak which is not correlated with structural defects, but edges [38]. The similar effect could explain the D peak observed in our Raman spectrum. However, we observed the D peak to appear on both thin and thick layers and its intensity to strongly change from flake to flake. In addition to it, we did not observe any dependence on the intensity of the D peak with the sonication time: for increasing processing time, the size of the flakes should decrease, giving a higher D peak. We attribute the D peak to the presence of Py-15SO$_2$ molecule on graphene: since the molecules are nano-graphenes, once they are deposited on graphene, they break the symmetry of the basal plane, thus activating the D peak [35]. The intensity of the D peak will depend on the number of molecules and their configuration. This is in agreement with previous results obtained with other pyrene derivatives, where a D peak is always visible in the Raman spectrum, no matter the lateral size of the flakes [34, 16, 17], although its origin is not discussed. In order to investigate this idea, we selected two graphene flakes obtained by micro-mechanical exfoliation. 2 µL of Py-15SO$_2$ solution at 0.1 mg/mL were deposited on one of the flakes by drop casting. Then, we measured the Raman spectrum on both flakes with increasing laser power. It is expected that Py-15SO$_2$ will be desorbed at a certain laser power. Fig. 4 shows the evolution of the Raman spectrum of Py-15SO$_2$/graphene with increasing laser power. At low power a strong fluorescence background is observed. However, the Raman features of graphene are visible, including a tiny D peak. For increasing laser power, the fluorescence disappears while the D peak is very weak. This probably corresponds to desorption of most of the molecules on the flake. Note that no strong variations in the G and 2D peaks width or position are observed. Above 3.5 mW of laser power the Raman spectrum strongly changes: a strong and broad D peak appears, indicating thermal degradation of the molecules-based film. Note that the D peak position does not correspond to the initial D peak position observed at low power. In the case of pristine graphene (i.e., without Py-15SO$_2$), no changes have been observed [13 – 7 mW], where a tiny D peak appears. Thus, particular attention has to be paid to the laser power in the Raman measurements of hybrid-graphene materials obtained with this method.

Because of the molecules residual on the flakes, AFM is not able to provide reliable information on the thickness distribution. A large amount of flakes (~62) were measured, but the smallest thickness was ~5 nm, well above 0.33 nm (theoretical thickness of a supported single-layer graphene), as expected. AFM also shows that the average lateral size of the flakes is 200-400 nm (Fig. 5). A few large flakes can also be found in the dispersion. These large flakes can be used to perform both Raman mapping and AFM on the same sample and thus compare the results obtained by the two techniques. Fig. 6a shows the AFM image of a large size flake. In addition the flake shows a folded part (in the dotted rectangle), useful to derive information on the distance between the layers. This figure shows that there are some small clusters on the flakes, visible also on the substrate. A few large
clusters are also visible. Fig. 6B shows that the thickness of the flake is about 5 nm and the distance between the two layers is again 5 nm. Fig. 6C shows the Raman spectrum measured in the center of the flake with a laser power of 0.7 mW; a few (2–3) layers 2D shape is observed. Note the presence of the pyrene peak at ~1245 cm⁻¹, the fluorescence background and a small D peak. Since the flake is rather large, we do not expect edges to contribute to the D peak. This has been further confirmed by Raman mapping of the intensity ratio between the D and G peak, ID/IG, in the flake. Fig. 6D shows that the maximum ID/IG is observed at the edges. However, far from the edges, ID/IG is not null and it is not uniform over the flake. This further confirms that the D peak cannot be entirely assigned to edges and disorder, but needs to be related to the amount and distribution of the molecules. Since we know that the molecules can be easily desorbed by laser heating (Fig. 4), we performed several Raman measurements in the center of the flake till we saw the fluorescence background disappearing. We then took a high resolution AFM image in the treated area, Fig. 6A. The topography image shows that the flake is covered by a rather uniform molecules film and a few clusters. However, the treated area (in the circle) seems rather clean—only several small clusters of ~20 nm in size are visible. The topography profile in Fig. 6F, corresponding to the line in Fig. 6E, shows that the thickness of the flake after laser treatment is ~1 nm, which would correspond to ~3 graphene layers, in good agreement with Raman spectroscopy. Note that the real thickness of the flake could be even smaller due to the presence of the molecules on the bottom side of the flake, in contact with the substrate. We have tried to remove this molecules film by washing the sample: we inserted 300 mL of water for 60 h and refilled the container with fresh water every 12 h. We then re-measured the same flakes after washing. We found that the excess molecules get removed further with each wash but a limit is reached at the 3rd or 4th wash, in agreement with Ref. [14]. Thus, the molecules cannot be completely removed. Plasma etching could be used, but this could damage the flakes.

Since the presence of free-molecules and aggregates can affect the efficiency of the exfoliation, we then prepared some dispersions with different concentration of Py-ISO₂ (0.05 mg/mL, 0.1 mg/mL, and 5 mg/mL). At low concentration (0.05 mg/mL) the dispersion is mostly composed by thick flakes, as observed by optical microscopy and Raman spectroscopy. As expected, by using high concentration (5 mg/mL), a large amount of molecules residual did not allow Raman measurement because the signal was hidden by a strong fluorescence. This lets us to conclude that a relatively large amount of Py-ISO₂ is needed to achieve exfoliation. However, this concentration is probably close to higher to the critical concentration needed for the formation of small aggregates. This is also similar to what observed with surfactants, where a concentration very close to the critical micelles concentration is needed to achieve successful dispersion of graphite [22].

Finally, TEM analysis was performed to further characterize our dispersion. Fig. 7. TEM shows a large quantity of flakes...
with lateral size of ~200–400 nm, in agreement with AFM (Fig. 5). Most of the flakes are characterized by folded and wrinkled area, such as in Fig. 7A and C. This can further affect the thickness measured by AFM and contribute to the D peak intensity. In particular, by looking at the folded edges, the flake in Fig. 7A seems to be a large bilayer graphene folded on itself. The color contrast of the suspended part of this flake corresponds indeed to 3-4 layers. Some of the flakes are composed by many and disordered layers, which may indicate that these flakes are formed by re-aggregation during deposition on the TEM grid. Note that the TEM analysis is usually based on the color contrast of graphene. However, our flakes are covered with a large amount of molecules and this may cause a change in the contrast. This is for example visible in the thick layer in Fig. 7B, which is characterized by a non-uniform color, probably related to an inhomogeneous film of molecules.

3.3. Graphene laminates

XPS was performed in order to check that no graphene oxide or related version of derivate graphene are present in our dispersion as well as to obtain the percentage of residual Py-150 or after washing. Fig. 8A shows the survey spectrum recorded on the PSA-based graphene films. This reveals the presence of oxygen, nitrogen and sulfur with respective concentrations of 4.9, 0.7 and 0.8 at%. Using the latter value, we can estimate that ~13% of the carbon signal is coming from the Py-150 molecule. The relatively high oxygen content is explained by the presence of SO3 groups from the Py-150 molecule with a possible contribution from atmospheric adsorbates. These adsorbates are also probably contributing to the nitrogen peak too.

The carbon 1s spectrum of the Py-150 based graphene film is presented in Fig. 8B. No large peak between 286 and 288 eV corresponding to C-O and C=O groups [34], is observed showing that our material does not contain graphene oxide. The C1s line is, on the contrary, very similar to the graphite signal with a slightly larger full width at half maximum (0.77 eV instead of 0.65 eV in graphite) which can be explained by the presence of the Py-150 molecules. The carbon 1s peak of the Py-150 based graphene film was fitted using the pristine graphite signal, the Py-150 powder signal and some residual C-O and CO bonds (~3%). Both graphite and
nants and/or to a very slight oxidation. XPS measurements thus reveal that our method produces graphene films free from graphene oxide. We further estimate that around 13-14% of the carbon content in the film is coming from Py-ISO, molecules.

We also prepared NMP-based graphene laminate as described in Ref. [18]. The concentration of single-layer is expected to be ~50% [18]. Thus, we compared the Raman spectrum of this laminate with the one obtained from our Py-ISO/graphene dispersion. Fig. 9: first we can note a huge D peak in NMP-based graphene film (the Raman spectra have been normalized to the G peak intensity). This is related to the different size of the flakes: sonication for 3 days strongly reduces the size of the flakes, compared to 30 min sonication of our method. A clear difference is visible in the shape of the 2D peak: this is a single and relatively sharp peak in NMP-based graphene, paper, indicating the presence of randomly stacked graphene flakes. In contrast, the 2D peak of the Py-ISO based graphene paper is composed by two components: one smaller, corresponding to the one observed in NMP-based laminate, and one lying to higher wavenumbers. This reflects the thickness composition previously found by analyzing the flakes deposited on the substrate (Section 3.2).

3.4. Discussion

We found that by using our method, based on ultrasoundication with Py-ISO, it is possible to achieve stable graphene suspensions directly in water. It is now interesting to compare our results with previous works in order to achieve a further understanding of the exfoliation mechanism. In particular, it is interesting to compare exfoliation obtained with Py-ISO and with Py-4SO. The difference between these two molecules is given only by the number of sulphonic groups. The presence of 4 sulphonic groups strongly improves the solubility of Py-4SO in water. Thus, one would expect better exfoliation efficiency from Py-4SO, as compared to Py-ISO.

![Graphene Raman spectra](image)

Fig. 9 – Raman spectra of Py-ISO based graphene film (bottom) and NMP based graphene film (top).

However, our results disagree with this expectation: Fig. 10 shows the suspensions obtained with Py-ISO, and Py-4SO, in the case of Py-4SO the exfoliation yield is very small, as observed from the color of the suspension (almost transparent). On the other side, Dong et al. [15] and Zhang et al. [16] obtained a large yield of single-layers by using sonication with Py-4SO, directly in water, Table 1. However, the Raman spectra of the material obtained by the two groups is very different: Dong et al. observed a clear splitting of the G peak [15], while Zhang et al. observed a very weak Raman spectrum, dominated by defect-activated peaks [16], Table 1. Thus, there is a large discrepancy in the results obtained by chemical exfoliation with Py-4SO in water. This clearly shows that more studies on exfoliation of graphene by using pyrene derivatives are needed to get a deep understanding of the exfoliation mechanism. In particular, a detailed comparison of suspensions obtained with the same method, but using different pyrene derivatives, would be very useful to understand the effect of the number and nature of the functional groups on the exfoliation mechanism. This knowledge can be then used to optimize the yield of monolayers.

4. Summary

We have developed a simple method to produce graphene suspensions by using non-covalent interaction with Py-ISO using only water as solvent. We used a combination of different microscopy and spectroscopy techniques to study the material obtained. We have shown that exfoliation of graphene directly in water is quick, non-destructive and rather efficient. Our suspensions are produced in water with the help of low-cost and commercial molecules. Furthermore, since protein and other biological objects can be easily attached to pyrene, the suspension can be used as inks for printable nano-based electrochemical sensors.

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