A modified Langmuir Schaefer method for the creation of functional thin films
Gengler, Régis

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2010

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter 4
Graphite exfoliation and deposition using the Langmuir Schaefer Approach

4.1 Short introduction

As described in the previous chapter, graphene was discovered half a decade ago and proved the existence of a two-dimensional system which becomes stable as a result of three-dimensional (3D) corrugation. It appeared very quickly that this exceptional material had truly outstanding electronic, mechanical, thermal and optical properties. Consequently a broad range of applications appeared as the graphene science speedily moved forward. Since then, a lot of effort has been devoted not only to the study of graphene but also to its fabrication. Here we report on a chemical approach based on the exfoliation of graphene (without oxidation) and deposition of the produced material using a Langmuir Schaefer (LS) approach. The results presented here are preliminary but meant to be compared with the graphene oxide presented in chapter 3 of this thesis. The attention will be focussed on successful transfer of unfunctionalized graphene to a substrate at an air-water interface as afforded by the LS method. An introduction to the chemistry of exfoliation is given hereafter.

4.2 Why exfoliated graphene?

While we discussed in chapter 3 and its appendix mainly the ambipolar behaviour, structural properties and the coverage analysis concerning reduced graphene oxide, this section is dedicated to the chemical preparation of graphene without oxidation (listed in the right part of our roadmap to graphene, scheme A3-2). This study was motivated by the need of a reliable chemical method for the creation and deposition of pure graphene in order to hopefully increase the quality in term of conductivity (i.e. transport).
Recent research efforts showed that a very effective method for the exfoliation of graphite is afforded by the use of organic solvents such as N-Methylpyrrolidone (NMP), N,N-Dimethylacetamide (DMA), g-butyrolactone (GBL) and 1,3-dimethyl-2-imidazolidinone (DMEU) and was proposed by Hernandez et al.\textsuperscript{1} This exfoliation takes place due to the solvent-graphene interaction energy. In fact, this process works for solvents which have an interaction energy with graphene that is equal to the graphene-graphene interaction energy\textsuperscript{2,3,4} resulting in a minimal energy cost to overcome the van der Waals forces between the graphene sheets. High quality graphene is produced in this way but the very low concentration of single layer graphene in the dispersion (0.01 mg ml\textsuperscript{-1})\textsuperscript{1} is a drawback. Some of the best TEM images using the solvent exfoliation route are displayed in figure 4-1 where one can distinguish monolayer graphene with sizes in the range of 0.5-1 \(\mu\)m. Among the proposed solvents NMP seems to yield the best results since one can clearly see graphene single layers in the corresponding TEM images. Fig 4-1h displays a histogram of the number of layers per sheet for the exfoliation of graphite in NMP which is peaked between 1 and 4 layers. An alternative route, still based on NMP but avoiding the sonication step to afford bigger flakes, was proposed by Vallés et al.\textsuperscript{5} Inspired by carbon nanotube (CNT)

Figure 4-1 Electron microscopy of graphite and graphene. (a) SEM image of sieved, pristine graphite (scale bar: 500 mm). (b) SEM image of sediment after centrifugation (scale bar: 25 mm). (c–e) Bright-field TEM images of monolayer graphene flakes deposited from GBL (c) DMEU (d) and NMP (e), respectively, (scale bars: 500 nm). (f, g) Bright-field TEM images of a folded graphene sheet and multilayer graphene, both deposited from NMP (scale bars: 500 nm). (h) Histogram of the number of visual observations of flakes as a function of the number of monolayers per flake for NMP dispersions. Images and graph reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnology, Y. Hernandez et al. \textsuperscript{1}, Copyright 2008.
processing technology, the authors showed that the exposure of graphite to a ternary potassium salt K (THF) x C 24 (THF) tetrahydrofurane, x ) 1-3) in NMP leads to stable exfoliation of graphite. As depicted in scheme 4-1, an alkali metal graphite intercalation compound is formed, which thanks to its charge, helps the exfoliation of graphite in NMP and leads to a stable dispersion of negatively charge graphene in NMP mixed with the alkaline salt.

As expected for this mild exfoliation method, yields drastically improved flake size as compared to the results reported in figures 4-1. Very recently Bourlinos et al. presented an approach following the idea of Hernandez et al. for the exfoliation of graphite with the help of solvents with a surface energy that matches the graphene-graphene interaction energy. Some of the solvents of this approach belong to a peculiar class of perfluorinated aromatic molecules and include hexafluorobenzene (C₆F₆), octafluorotoluene (C₆F₅CF₃), pentafluorobenzonitrile (C₆F₅CN), and pentafluoropyridine (C₅F₅N). Aside from the aromatic compounds

Scheme 4-1 Representation of the potassium salt K(THF) x C 24 (THF) tetrahydrofurane, x ) 1-3) driven exfoliation of graphite in NMP. Scheme reprinted with permission from C. Vallés et al. Copyright 2008 American Chemical Society.

Figure 4-2 (Top) Colloidal dispersions obtained after liquid-phase exfoliation of graphite using the perfluorinated aromatic solvents below. (Bottom) TEM images of some pentafluorobenzonitrile-etched thin sheets. The SAED pattern is included as inset. Images reprinted with the permission from AB. Bourlinos et al. Copyright 2009 Wiley-VCH.
Boulinos et al.\textsuperscript{7} also found that some non-aromatic solvents tested successfully for dispersing graphite, namely ethyl acetate, vinyl acetate, methyl chloroacetate, 2-methoxyethyl ether acetylacetone, and N-tetramethylmethylenediamine, which all exhibited remarkable colloidal stabilities and concentrations of 0.2-0.3 mg ml\textsuperscript{-1}. Examples of the dispersions and TEM images are presented in figure 4-2. Uniform dark dispersions testify to the absence of aggregation, while single to 2-3 layer thick graphene with flake size is in the order of few micrometers were observed by TEM. Lotya et al.\textsuperscript{10} proposed a liquid phase exfoliation of graphene which does not require oxidation or high temperature, avoids expensive solvents and is even, according to the author, safe and user friendly. Here graphite was dispersed in surfactant-water solutions in a manner similar to surfactant aided CNT dispersion.\textsuperscript{11-15} The dispersed graphitic/graphene flakes are stabilized against re-aggregation by Coulomb repulsion between the adsorbed surfactant molecules. Electrical measurements on such flakes show a conductivity of 35 S/m, a low value attributed to the presence of residual surfactant molecules which are difficult to remove even after several washing treatments. After annealing at 250\degree C, as expected the conductivity rose to 1500 S/m (the sheet resistance fell from 920 K\Omega to 22.5 K\Omega) while optical measurements demonstrated that the transparency did not vary throughout the processing. However, this conductivity value is still far from those resulting after the reduction of graphene oxide, which vary from 7200 S/m \textsuperscript{16} to 10000 S/m \textsuperscript{17} and also significantly lower than the conductivity of graphene derived from exfoliation in NMP (6500 S/m).\textsuperscript{77} Nevertheless, HRTEM with atomic resolution reproduced in figure 4-3(a) shows the monolayers to be well graphitized and largely defect free. The authors observed large flakes made of monolayers and bilayers but also reaggregation of thin layers. Selected area electron diffraction images reveal the hexagonal lattice of graphene and from the analysis of images like that reproduced in Figure 4-3(b), one can deduce from the number of lines at the edge of the flake that it is a three layer graphite sheet \textsuperscript{18}. The relative amount of the multilayer structures is illustrated in the histogram of the number of layers per flake for dispersions from original sieved graphite and from recycled sediment shown in figure 4-3 (the very large flakes are ignored in this histogram); from this histogram one deduces that \textasciitilde 43\% of flakes have less than 5 layers and about \textasciitilde 3\% of the flakes were monolayer graphene. While this value is considerably smaller than that observed for graphene/solvent dispersions, working in aqueous systems has its own advantages. In general, the majority of these few-layer flakes had lateral dimensions of \textasciitilde 1 \mu m. Though these results do not compete with the top quality of the reduced graphene oxide, we believe that today’s research is at the beginning and much more can be expected from such an approach. Characterization of the electrical properties would be of great help to learn more about the true quality of the prepared material and it is obvious that efforts are still needed to conserve larger flake sizes in this kind of approach.
4.3 Deposition attempt of not-oxidized graphene

As already described in the previous chapter, we developed a technique for the controlled deposition of single layer graphene on arbitrary substrates. The preparation method very similar to this previous system (i.e. graphene oxide-ODA functionalized) is summarized in Scheme 4-2. As we just reviewed in the previous paragraph regarding the exfoliation without oxidation, it was demonstrated that graphite can be exfoliated and turned soluble through chemical treatment. In opposition to the previously demonstrated method (Clay or GO-chapters 2 and 3), in the present case ultra pure Millipore 18 MΩ was used as a subphase for the Langmuir–Schaefer deposition (while mixing of small amounts of clay or GO were used previously). Whereas one would commonly inject long chain molecule at the
air-water interface to form a monolayer or trigger an hybridization, we used here pure graphene as the surface active agent. As in a common LB experiment the solvent was allowed to evaporate and the layer was compressed to a desired pressure (= packing of the floating material) prior to deposition (Scheme 4-2). The study of the stability of the material floating at air-water interface was performed following a procedure very similar to the one applied to clay and GO and describe hereafter.

We used as injected material, graphene chemically exfoliated and suspended/solubilised in two solvents (2-methoxyethyl ether and pyridine-technical data can be found in appendix of this chapter). A significant part of the research efforts was dedicated to find out which solvents were suitable for the LS approach and having good exfoliation properties as well as to determining the right parameters for the stabilization and deposition of such material.

Scheme 4-2 – Representation of the injection of graphene at the air-water interface of the LB trough and evaporation of the carrier solvent (A). Compression of the floating graphene layer (B)

In the quest to understand the properties of a new surface active agent at the air water interface, the first measurements to perform are isotherms where one compresses the area between the barriers (while the temperature is kept constant) and studies the surface tension behaviour when applying this external stimulus. As a reminder, if a material injected between the barriers is not amphiphilic or sufficiently hydrophobic, it will not be able to “float” at the air water interface and will therefore not create any film. In this case the injected material will simply set down at the bottom of the trough and accordingly no change of the surface properties of the water will be observed (no change of the surface tension). Conversely, any floating material will give rise to a change in surface pressure when compressed sufficiently to act on the pressure sensor, or if sprayed on the water surface in large quantities. Any rise in pressure is therefore associated with the presence of floating material - in our case graphene.
4.4 Isotherms of 2-methoxyethyl ether

As mentioned above two solvents were investigated for what concerns their suitability for exfoliation and LS deposition. A first set of experiments was performed on 2-methoxyethyl ether exfoliated graphene. The material and methods were as described by Bourlinos et al., the material was actually provided by Bourlinos, who also confirmed by TEM measurements that single layer graphene was present and stable in the carrier solvent. Our task was then to try to study and deposit the exfoliated graphene. The graph of figure 4-4 summarizes this effort: it presents isotherms recorded during various compression and decompression cycles of 2-methoxyethyl ether exfoliated graphene sprayed over the LB interface and equilibrated for 20 min. Various injection volumes were considered while the concentration of graphene in the solvent was kept constant. It can be observed that even for 100 µl of 2-methoxyethyl ether containing graphene, a rise in surface tension can be observed, and that a larger injection volume leads to an increased surface tension. Furthermore changes in the isotherm shape as a function of compression cycle (compression-decompression-recompression of the same surface active agent).

Figure 4-4 Comparison between the isotherms made with different amounts of solution. Compression decompression and recompression for volumes of 100 µl to 500 µl.
revealed instability of the formed layer. Since no isotherms of pure 2-methoxyethyl ether were performed it was not clear whether this instability came from an extremely slow solvent evaporation or was due to the instability of the graphene itself (further data clarified this point).

AFM micrographs of the deposited layer on SiO$_2$ showed a very poor quality with extremely low coverage and the protocol proved not easily reproducible. This convinced us to investigate a different graphene-solvent system.

### 4.5 Pyridine-graphene

The second solvent used was pure pyridine, also chosen for its ability to exfoliate graphene as discussed in Bourlinos et al.\textsuperscript{7} although a full study of this system has not been reported yet. Since the chemistry of graphene is still an emerging field, a general understanding of the broad range of applicable solvents for the exfoliation and their respective yields is still underway. However, theoretical calculations of the surface energy of given solvents defined the range of potential candidates\textsuperscript{7} and pyridine is one of them. Experimentally graphene-pyridine (GP) was prepared through the exfoliation of graphite in pyridine by a 170 W sonication for 1 h. A cartoon of the exfoliation process is depicted in Scheme 4-3, where in (i) one can see pyridine molecules (representative for the solvent) and few layer graphite (representative of the starting material). As sonication is applied, from ii) to iii), pyridine finds its way into the graphite stack and pushes the sheets apart, until

![Scheme 4-3 Schematic representation of the pyridine induced exfoliation of graphene.](image)
at the stage iv) the intercalated pyridine has completely de-stacked the graphite into no longer interacting, freestanding graphene sheets. This cartoon idealizes the process and unfortunately the yield of exfoliation is not 100%. In fact, in order to preserve as large sheets of graphene as possible, one needs to compromise between long sonication times which push up the yield of completely exfoliated layers but produces smaller flake sizes, and short sonication times leading to a higher amount of not completely exfoliated multilayers but larger flakes.

Different starting concentrations of graphite in pyridine were chosen. A photograph of the 3 solutions directly after the sonication is shown in figure 4-5(I). The highly concentrated solution on the left shows a very dark coloration, and going from left to right, the lower the graphite concentration the lighter the solution appears. We can conclude from this observation that the graphitic material which was initially in powder form has now been at least partially exfoliated and rendered dispersible. The extent of the exfoliation cannot be judged for those photographs. In time part of the suspended material migrates to the bottom under the action of gravity as shown in the Fig 4-5 (II), which presents photograph of the same 3 vials was taken 5 days after sonication. One can indeed observe a dark precipitate but more importantly a greyish supernatant indicating that some exfoliated material stays ultimately suspended/in solution. The stability of the material was checked over dramatically longer period of time (of several months) and proven stable. Five days after sonication, the supernatant was separated from the precipitate by siphoning it.

Figure 4-5 Optical photographs of various synthesis stages of the graphene-pyridine for different starting concentrations of graphite in pyridine, namely 0.5 mg/ml, 0.2 mg/ml and 0.05 mg/ml: (I) the dispersions right after sonication, (II) after 5 days during which suspended material precipitated to the bottom of the vial and (III) after the supernatant was separated from the precipitate.
the properties of the pure solvent at the air-water interface. They were therefore performed for pure pyridine. A summary of the study of the stability measurements of pyridene layers is depicted on figure 4-6; the different curves correspond to different injected volumes which were allowed to stabilize for 10 min and subsequently compressed. One can see that for the smallest volume (150 µl) a complete compression did not lead to any rise in surface tension. A first compression of the layer formed after injection of 300 µl (named compression 1 in the graph) resulted in a short increase in surface pressure while the compression 2, corresponding recompression following the cycle of the first compression and decompression, shows an even shorter increase (green curve in Figure 4-6). This supports the hypothesis that the solvent is soluble/volatile enough to not lead to the formation of any stable solid layer at the interface. Whatever the injected volume, a relatively short waiting time will result in a complete evaporation/solubilisation, although of course a longer evaporation/solubilisation times will be needed for a larger volume. Bearing in mind this property of pyridine, the next logic step was to inject GP at the air water interface, and to test the surface agent property of the mixture now containing pure graphene (supposedly hydrophobic-see definition of polarity in the introduction chapter). Figure 4-6 (right) displays the isotherms of two volumes of a given concentration of GP (0.5-0.05 mg/ml). One immediately notices that the compression leads to a dramatically increased rise of the surface off to yield the dispersion displayed in the last photograph (III) of figure 4-5 and used for the LS experiment. Similarly to the 2-methoxyethyl ether case, a study pressure at the air water interface than that observed for an equivalent volume of pure pyridine (figure 4-6): for 200 µl and 300 µl of GP supernatant, the surface

Figure 4-6 (Left) Isotherms of pure pyridine collected after 10 min stabilization time subsequent to spraying different volumes onto the water surface of a LB trough. (Right) Isotherms of Graphene-pyridine collected after 10 min stabilization time subsequent to spraying different volumes of the supernatant from the exfoliation process onto the water surface of a LB trough (for details see text).
pressure reaches values of 7 mNm\(^{-1}\) and 14.5 mNm\(^{-1}\), respectively. This difference in behaviour clearly testifies to the successful formation of a stable graphene layer at the air water interface. To the best of our knowledge those are the first results of this kind. Few research groups have achieved a stabilization and deposition of graphene oxide but none ever achieved stabilization of unfunctionalized graphene. However, as we shall describe below, although the first step of stabilization was achieved, realizing a successful well controlled deposition of this graphene layer is not a trivial task.

### 4.6 Deposition on various substrates

When compressing classical LB films to pressures usually of 10 mN m\(^{-1}\), the molecules floating between the barriers form a stable 2D solid film and deposition can be performed. Depending on the nature of the film and the structure one wants to construct as well as the substrate type, one can consider to deposit following the 2 modes described in the introduction, namely vertical dipping of the substrate, called LB deposition,\(^{19}\) and horizontal dipping called LS deposition.\(^{20}\) For this

![Figure 4-7 Tapping mode AFM micrographs of a selected region of graphene-pyridine deposited on SiO\(_2\). The same region is viewed topographically (top left) and in phase contrast (top right), corresponding plane corrected (bottom left) and flooded (bottom right) images are also shown to emphasis the hills created by graphene.](image-url)
Graphite exfoliation and deposition using the Langmuir Schaefer Approach.

study we opted for the latter (like for ODA functionalized graphene oxide previously discussed in chapter 3 of this thesis).

Depositions were performed at various applied surface pressures in order to verify the quality of the graphene packing and its controllability. The deposited films were characterized by atomic force (AFM) and scanning electron (SEM) microscopies. While ODA functionalized graphene oxide (see chapter 3) showed a very high coverage due to a high transfer ratio, it is not clear why for the graphene exfoliated with pyridine a deposition at the same pressure leads to a very different result as shown in Figure 4-7.

In fact, Figure 4-7 shows the AFM images of one of the most promising results: GP deposited at 20 mN/m of surface pressure and assisted with a bubbling effect (discussed below). In both the top left and top right panels, which present the topography and phase contrast of GP deposited on SiO$_2$, respectively, only isolated flakes having lateral sizes that range form 0.5 to 2 µm can be identified. The debris observable on top and next to the flakes (white spots) might originate either from post deposition contamination or leftover material from the deposition process itself. Height measurements on these flakes, either by recording step edge profiles or by establishing height histograms, reveal a flake thickness of 0.6 nm±0.2 nm which is in accordance with the literature for single layer flakes deposited on SiO$_2$ (REF). The images in the bottom panels of the Figure 4-7 have received some further treatment in order to flatten the image (left) or to increase the visual contrast between the graphene an the substrate (right).

Further characterisation with SEM allowed to visualize the sample on a larger scale. In figure 4-8 SEM micrographs providing a detailed view of a typical region which presents both types of deposited material are reproduced. The right panel is an enlarged image of a selected part of the left one (highlighted with a white rectangle). These images, in accordance with AFM, show solid like elements (light grey) that appear to be single layer graphene. In several locations within the field of view, darker contrast is observed, presumably corresponding to bi- and few layer graphite. These very thin layers are always found in the vicinity of tens of micron large elements giving a very dark contrast, which we suspect to be also graphitic material. Another valuable piece of information comes from the coverage of the substrate. While at the surface pressure applied in the LB for the deposition (20 mN/m) one would expect a solid like coverage of most of the surface, the SEM micrograph reveals that the major part of the surface is uncovered, or covered by unresolvable nanometric elements. Even in the selected area of figure 4-8 one finds a coverage of around 50% for the bigger elements (>0.5 µm of lateral size) while ~10% of the area is covered by ~100 nm-sized material.

Two hypotheses can explain this surprising result: a wide size distribution of single layer graphene or a very poor transfer ratio. In the first scenario, one could imagine that the prolonged sonication that affords the 0.5-1 µm single layer graphene flakes, could also be responsible for the creation of a significant amount of few nanometer (1-20 nm) sized debris of graphene surrounded by pyridine (or not).
Once injected with the rest of the GP exfoliated material, such debris, which is by nature hydrophobic, will float on the air-water interface. This effect would indeed affect the surface pressure and truly create a film not visible with the probing methods we used. Only STM could prove this hypothesis. Following this line of thought, an improved of the deposition yield producing densely packed, reasonably sized (>1 um) graphene flakes on the chosen substrate, would require a purification which eliminates all undesired small graphene/graphitic material. Such a selection could be achieved through centrifugation.

A second hypothesis, consistent with the AFM and SEM observations, could be that the transfer ratio/yield is very low. Although having perfectly hydrophobic surface, the floating material (i.e. graphene) could lack of “sticking affinity”, the graphene would then be well packed at the air-water interface but would hardly attach to any type of substrate. In fact, no surfactants are employed here, while the surfactant most of the time acts as a clue binding a material to the substrate. This could clearly be seen especially well when processing graphene and graphene oxide to make devices as described in Chapter 3 of this thesis, where we noticed that loosing graphene obtained from microcleavage was quite common while the surfactant coated graphene oxide never detached from the surface. However, a careful study of the surface energy of the pyrene covered graphene, SiO$_2$ and SAM/gold should be carried out to prove that no surfactants are needed to create an interaction between the Langmuir film and the substrate. Exploring the validity of one or the other proposed hypotheses is still to be done. We also studied the stability of the Langmuir film in time. In an ideal case, once a surface active agent is stable at the air-water interface, if well below its boiling point, it should stay at the interface for an infinite amount of time. Real life scenarios are slightly different of course but most of the commonly used surfactants like the fatty acid-long chain molecule C16+, can survive at the air water interface when packed in a liquid or solid like state for days. Unlike the extremely stable DODA-clay system discussed in chapter 2 (isobar for several

Figure 4-8 SEM image of the graphene pyridine.
days) and the less but still reasonable stable ODA-GO system discussed in chapter 3 of this thesis, the stability of the GP air-water interface is quite poor. When we stabilized a very extended area (large amount of molecules at the interface) stabilized at a given pressure, the packed system survived only for few hours. We believe the stability is connected to the hydrophobic character of the species. When a Langmuir film is built up of solely highly amphiphilic surfactants it is extremely stable, while the hybrid clay surfactant system is a bit less stable due to the clay pulling down the surfactant. The graphene pyridine system on the other hand is permanently in the risk of drowning. To counteract this tendency, we tried to get as much graphene to the surface as possible by applying a trick proposed by Cote et al. very recently.\textsuperscript{21} The ingenious idea consists of the application of a stream of gas bubbled through the water to catch the material in dispersion - Cote et al. used gaseous water for that purpose. Random collisions between individual bubbles and graphene anchor the latter and drive it towards the surface simply through buoyancy.

Applying this trick to our GP system by bubbling N\textsubscript{2} or Ar through the subphase for 10-20 min before stabilization, improved the layer quality. In fact, the results of this manipulation are the ones displayed in figure 4-8. Unfortunately the improvement in the deposition yield could not be verified at larger scale. The figure 4-9 shows the tapping mode AFM images of G-pyridine prepared by a 6 min sonicating time and deposited (from the supernatant of the GP) at a surface pressure of 28 mNm\textsuperscript{-1}. One can observe a medium coverage of the substrate surface, topographic profile showed that the flakes are ~4-6nm thick. From those observations, one understands the crucial role played by the sonication time, indeed more flakes are observed but they are not fully exfoliated. A detailed study of the sonication vs population and flake dimension is still to be done.

![Figure 4-9 Tapping mode AFM micrographs of a selected regions of few layer graphene-pyridine deposited on SiO\textsubscript{2}. GP sonicated for 6 min.](image-url)
4.7 Conclusion

We showed that the synthesis, but mainly the deposition of single layer not oxidized graphene was possible; as for GO the method affords single layer graphene on arbitrary substrates without size limitation and under ambient conditions. The controllability, coverage and single to multilayer ratio still need to be optimized. Efforts should be driven towards a better size/thickness selection of the flakes prior to injection. Investigation of the sticking properties of graphene for various substrates has still to be done to increase the transfer ratio.

4.8 References

Graphite exfoliation and deposition using the Langmuir Schaefer Approach.


(19) Blodgett, K. B. Journal of the American Chemical Society 1934, 56, 495.

(20) Langmuir, I.; Schaefer, V. J. Journal of the American Chemical Society 1938, 60, 1351-1360.

(21) Kim, J.; Cote, L. J.; Kim, F.; Yuan, W.; Shull, K. R.; Huang, J. Journal of the American Chemical Society 2010, 0.
Appendix 4
Description of pyridine and 2-methoxyethyl ether

4.8.1 Pyridine
Molecular structure:

<table>
<thead>
<tr>
<th>Linear Formula: C₅H₅N</th>
<th>Molecular Weight: 79.10</th>
</tr>
</thead>
</table>

bp 115 °C(lit.)
mp −42 °C(lit.)
density 0.978 g/mL at 25 °C(lit.)
©Sigma Aldrich

4.8.2 2-methoxyethyl ether
Molecular Structure:

<table>
<thead>
<tr>
<th>Molecular Formula C₆H₁₄O₃</th>
<th>Molecular Weight 134.17</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Density</th>
<th>0.937</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>-64 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>162 °C</td>
</tr>
</tbody>
</table>