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## **Lateral Size Selection of Surfactant-Stabilised Graphene Flakes using Size Exclusion Chromatography**

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Abstract: Aqueous dispersions of graphene, stabilised by a surfactant, have been separated according to lateral flake size using size exclusion chromatography. Transition electron microscopy was used to characterise the flake size as a function of fraction number. While the stock dispersion had a mean lateral flake size of 0.6  $\mu\text{m}$ , the separated fractions displayed clear size separation, with the second and fourteenth fractions displaying mean sizes of  $\sim 1.2$  and  $\sim 0.5$  microns respectively. Raman spectroscopy shows the flake D:G intensity ratio to scale inversely with the flake size indicating that any defects present are associated with flake edges rather than basal plane defects.

## Introduction

Due to its unique mechanical and electrical properties, graphene has recently generated intense interest among researchers.<sup>1</sup> While much of this work has been carried out on micromechanically cleaved samples, many future applications will require high throughput processing techniques<sup>2</sup>. Large scale exfoliation of graphene in the liquid phase is now a well-established technique with two main processes existing: Oxidation of graphite with subsequent exfoliation to give graphene oxide<sup>3, 4</sup> and exfoliation of graphite in solvents<sup>5, 6</sup> or surfactant solutions<sup>7, 8</sup> to give dispersed pristine graphene.

While Graphene oxide dispersions have proved to be very useful in areas such as graphene-polymer composite processing<sup>3</sup> and the formation of thin graphene films,<sup>9</sup> some significant disadvantages remain. GO is a poor electrical conductor<sup>10</sup> due to the disruption of its  $\pi$  orbital structure on oxidation. While these oxides can be removed, for example by thermal reduction,<sup>11</sup> such processes do not completely heal the structural defects introduced during the oxidation process.<sup>10</sup> Exfoliation of graphite in organic solvents or surfactant solutions yields dispersions of pristine graphene<sup>6, 8</sup> giving it the potential to be very useful in a wide range of applications. This method however suffers from one critical disadvantage. The flakes produced have a significant spread in both lateral flake size and number of layers that has so far proved difficult to control through adjustment of processing conditions. While some work has been done to separate dispersed flakes according to number of layers<sup>7</sup>, relatively little progress has been made on separation by lateral size.<sup>12, 13</sup> We note that the lateral flake size can be very important when considering applications such as polymer reinforcement.<sup>14, 15</sup>

Size Exclusion Chromatography is a well-established chromatographic method for separating particles according to their size as they pass through porous gel filtration medium packed tightly into a column.<sup>16</sup> This medium consists of porous spherical particles made of a chemically inert and physically stable material. As a sample moves through the column, particles diffuse and out of these pores. Smaller particles have more available volume to diffuse into and hence have a retention volume. This means that larger particles leave the column first followed by smaller particles in order of their size. By collecting samples based on their elution time, separation based on particle size can be achieved. One significant advantage of this

technique is that it has been studied for over 50 years which means that methodologies to increase resolution and throughput are well understood.

In this work we demonstrate the separation of surfactant exfoliated graphene flakes according to their lateral dimensions using size exclusion chromatography. We use Raman spectroscopy and transmission electron microscopy to confirm size selection.

### Experimental procedure

A graphene stock dispersion was prepared by adding graphite powder (Aldrich) at initial concentration  $C_G=20\text{mgmL}^{-1}$  to sodium cholate solution  $C_{SC}=0.3\text{mgmL}^{-1}$  as described previously.<sup>17</sup> Ultra sonication was carried out using a high powered sonic tip (Sonics VX-750 ultrasonic processor) for approximately 8 hours. The dispersion was left to sit overnight and then centrifuged (Hettich Mickro 22R) at 500 rpm for 45 mins to remove large aggregates. The dispersion was then placed in a rotary evaporator to remove 50% of the water present and hence double its concentration. The volume of the glass column was measured to be ~50 mL. By using the known density of controlled pore glass (CPG, Purchased from Millipore, product No. CPG3000B, mean pore diameter 300 nm) we calculated the mass required to fill the column. The CPG was then added to a sodium cholate surfactant solution (0.3mg/mL). The CPG/surfactant mixture was then packed tightly into the glass column. The stock dispersion was mixed with ethylene glycol at a ratio of 3:1 to increase the density of the dispersion. A syringe was used to add 3 mL of the resulting mixture to the column just above the top of the CPG mixture, the tap was opened and surfactant solution added to the top of the column. Each fraction was collected every 3mL of dispersion.

### Results and Discussion

After the dispersion was passed through the column we obtained several fractions of varying concentration as can be seen from the inset in figure 1. Optical absorption measurements (taking  $\epsilon_{660\text{nm}}=6600\text{Lg}^{-1}\text{m}^{-1}$ )<sup>17</sup> on these fractions showed the concentration to increase dramatically over the first few fractions peaking around fraction 4 or 5 before falling smoothly (figure 1). The first 14 fractions were kept for characterisation as they contained 84% of initial material.

We have used TEM to characterize a range of fractions as well as the stock dispersion. Samples for TEM analysis were prepared by drop-casting dispersion onto holey carbon grids (400 mesh). Bright-field TEM images were taken with a JEOL 2100, operated at 200 kV. Figure 2a shows a sample image of an exfoliated graphene flake. Each fraction predominantly contained few layer flakes such as this one with a range of aspect ratios (length/width) present (mean aspect ratio close to 2). Figure 2b shows a wide field TEM image of deposited flakes of the type used to generate lateral flake length statistics for each fraction. As can be seen from these statistics (figure 2c), there is a gradual shift in the size distribution, as we go from higher to lower fraction numbers. The average flake length decreased from  $\sim 1.2\mu\text{m}$  for fraction 2 to  $\sim 0.5\mu\text{m}$  for fraction 14 as shown in figure 3a. We note that the mean flake length for fraction 2 is approximately twice that of the original stock dispersion. We note that while there is a clear shift in mean lateral flake size with fraction number, the size distributions are rather broad. This is due to the relatively low resolution of our column, which can be improved by increasing the column size relative to the dispersion volume. Although the lateral flake size varied with fraction number, the average number of layers per flake appeared roughly invariant.

We can further characterise these fractions using Raman spectroscopy. We prepared thin graphene films from each fraction by vacuum filtration onto porous mixed cellulose ester membranes (MF-Millipore mixed cellulose ester membrane, 25 nm, 47 mm diameter). These films could then be transferred to glass<sup>17</sup> and analysed using Raman Spectroscopy (633nm, Horiba Jobin Yvon LabRAM-HR). Representative spectra for three fractions are shown in figure 3b as well as the graphite powder.

In Raman spectroscopy, graphitic materials are generally characterised by D, G, and 2D bands around  $1350\text{ cm}^{-1}$ ,  $1580\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$  respectively.<sup>18</sup> The D band is particularly interesting in this case as the defect content is indicated by the intensity of the D band relative to the G band.<sup>19</sup> We note that all spectra have D bands significantly larger than that of the starting powder, indicating that processing induces defects. Similarly, the growth of the shoulder at  $1615\text{ cm}^{-1}$  also indicates defect creation.<sup>20</sup> Figure 3b shows the mean D/G band ratio ( $\langle I_D/I_G \rangle$ ) as a function of fraction number and clearly shows the steady increase in  $\langle I_D/I_G \rangle$  relative to the starting graphite as the fraction number is increased and the flake size decreases. We

also note that the change in the 2D band for graphene films compared to the bulk graphite is indicative of exfoliation<sup>18</sup>.

Defects in graphene are divided into two main types: body defects such as point defects on the basal plane and edge defects. It is important to distinguish between the contributions of these defect types. The introduction of edge defects is known to occur during processing as sonication cuts the initially large crystallites up into smaller flakes.<sup>21</sup> These smaller flakes have more edges per unit mass resulting in an increase in the population of edge defects. If the variation in  $\langle I_D/I_G \rangle$  with fraction is solely due to flake size effects (i.e. changes in the population of edge defects), the ratio of the D to G band must be related to the average flake length<sup>17, 22</sup> such that

$$\langle I_D / I_G \rangle = (I_D / I_G)_{\text{Powder}} + k / \langle L \rangle$$

where  $k$  is a constant. By plotting  $\langle I_D/I_G \rangle$  versus  $1/\langle L \rangle$  in figure 4 we see that these quantities scale linearly with an intercept very close to  $(I_D/I_G)_{\text{Powder}}$  and a value of  $k=0.65$ . This is significantly higher than that observed for solvent exfoliated graphene<sup>21, 22</sup> but agrees well with what has previously been observed for surfactant exfoliated graphene.<sup>17</sup> This gives a strong indication that this increase in D band intensity is due to edge effects and not increased number of basal plane defects.

## Conclusion

To summarise, using size selection column chromatography we have successfully separated typical aqueous graphene dispersion into several fractions according to their average lateral flake size. We have confirmed this separation by means of TEM analysis of the dispersions themselves and Raman spectroscopy of thin films cast from these fractions. Effectively, this process has allowed us to double the average flake size of our dispersion through the removal of smaller flakes.

Although initial results are promising, some applications such as the use of graphene as a reinforcing material will require average flake sizes larger than those reported in this work.<sup>14</sup> We hope to achieve this through two approaches. The first is to increase the population of large flakes in our initial stock dispersion through re-dispersing sediment as outlined in previous work.<sup>23</sup> The second is to increase the resolution of our column in order to be better able to isolate this population of large flakes. This can be done by increasing the column size relative to the volume of dispersion passed through it and hence can be achieved both by increasing initial

concentration of stock dispersion as well as the volume of the column itself. All these options will be investigated in future work. In addition, we will extend this approach to surfactant exfoliated inorganic layered compounds such as BN, and MnO<sub>2</sub>.<sup>24</sup>

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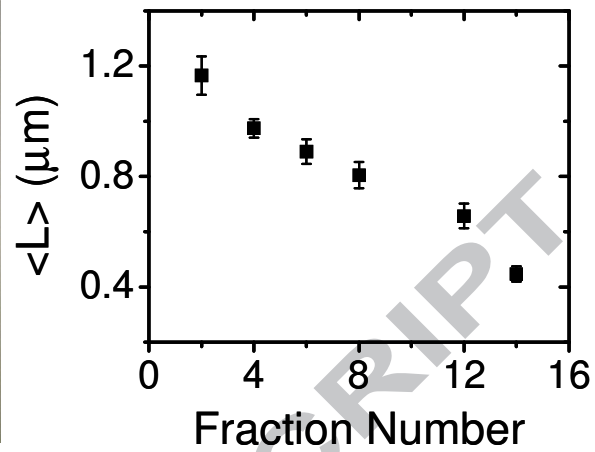
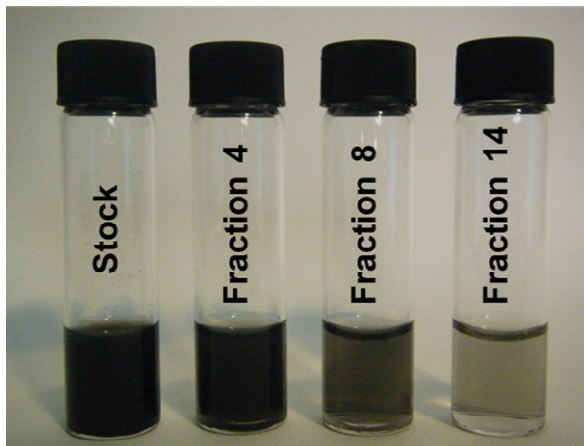
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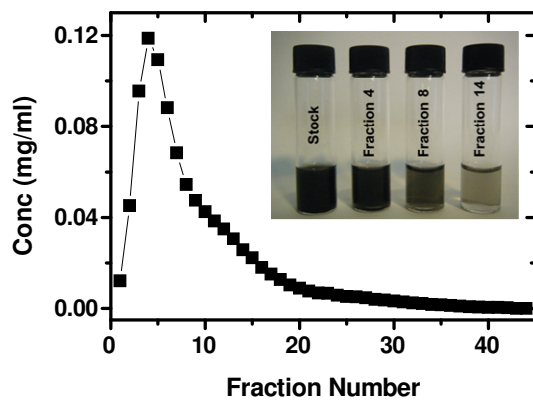
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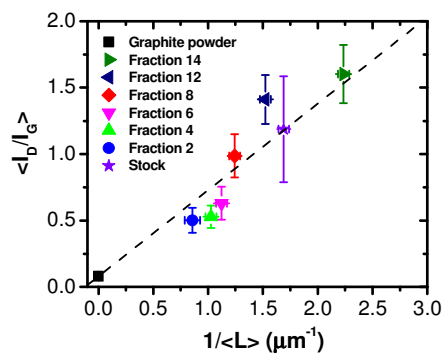
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## Highlights

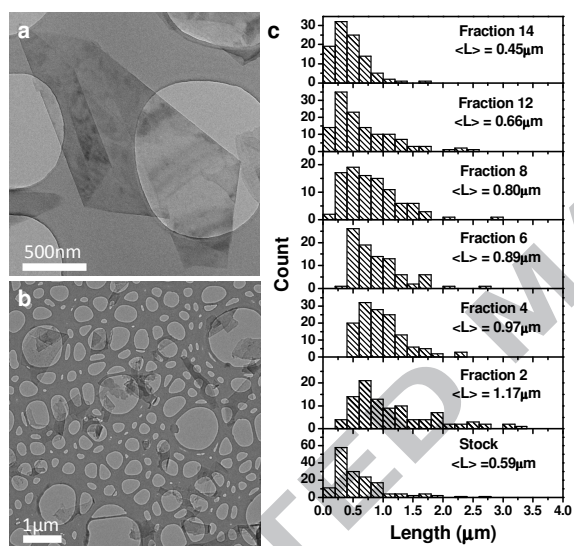
- Aqueous dispersions of surfactant stabilised Graphene were passed through a size exclusion chromatography column.
- The resulting fractions were drop cast onto grids and flake sizes measured using Transmission Electron Microscopy.
- Thin Films were vacuum filtered from these fractions and examined using Raman Spectroscopy.
- The First fraction showed an increase in average flake size from that of the stock by a factor of 2.
- The flake D:G intensity ratio scales inversely with flake size showing defects to be edge related rather than basal plane.



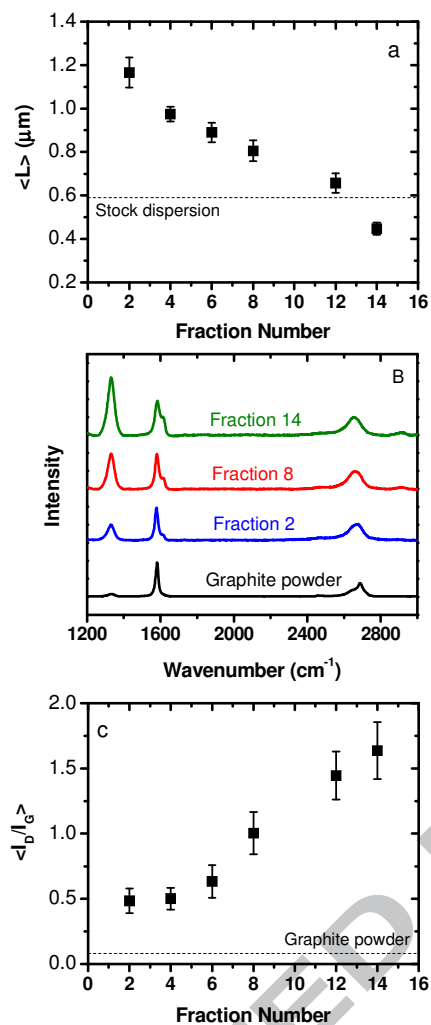
**Fig. 1** Concentration of dispersion as a function of fraction number. Inset shows a photograph of selected fractions before characterisation.



**Fig. 4** D band to G band ratio plotted as a function of  $1/\langle L \rangle$



**Fig. 2** (a) TEM image of typical graphene flake found in dispersion. (b) Wide field TEM image of graphene flakes used to generate statistics. (c) Histogram of flake size distributions for different fractions as well as stock dispersion.



**Fig. 3** (a) Average flake length as a function of fraction number. The mean flake size measured for the stock dispersion is shown by the dashed line. (b) Representative Raman spectra of films filtered from various fractions as well as that of graphite powder. (c) Average D band to G band ratio as a function of fraction number. The D/G ratio measured for the graphite powder is shown by the dashed line.