Determination of the lateral size and thickness of solution-processed graphene flakes

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Determination of the lateral size and thickness of solution-processed graphene flakes

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Abstract. We present a method to determine the lateral size distribution of solution–processed graphene via direct image analysis techniques. Initially transmission electron microscopy (TEM) and optical microscopy (OM) were correlated and used to provide a reliable benchmark. A rapid, automated OM method was then developed to obtain the distribution from thousands of flakes, avoiding statistical uncertainties and providing high accuracy. Dynamic light scattering (DLS) was further employed to develop an in-situ method to derive the number particle size distribution (PSD) for a dispersion, with a deviation lower than *22%* in the sub-micron regime. Methods for determining flake thickness are also discussed.

1. Introduction

Graphene has gained enormous interest since its unique properties and practical isolation were demonstrated under ambient conditions [1]. While potential applications are still being discussed, developing a practicable scalable production process is a key obstacle. Solution-processed exfoliation methods are one of the most promising approaches to achieve large-scale graphene production. However these methods do not yet produce completely exfoliated graphene [2]. To monitor and optimize the graphene production process, a fast, standardized and reliable characterization protocol for large-scale solution-processed graphene is therefore desirable for both industry and academia.

The lateral size of graphene flakes is one of the most important factors affecting properties as variation in size and geometry causes a change in ratio between edge and bulk structures, resulting in spatial confinement in specific dimensions that alters the electrical and mechanical behaviour [3]. Even though characterization techniques have constantly improved, methods to obtain the lateral size distribution of solution-processed graphene are still limited owing to the difficulties in visualizing the ultra-thin nano-flakes and the fact that many of the properties of graphene are, de facto, still unknown.

Here, we demonstrate methodologies to determine the lateral size distribution for solution-processed graphene. The lateral dimension distribution was measured via direct imaging using two microscopy techniques (TEM and OM) and via a fast, but less direct technique based on DLS. Approximations, errors and deviations are calculated and discussed.

2. Experimental

The graphene sample used was synthesized by milling graphite powder in ionic liquids (2Dtech™ Aquagraph series). The graphene sample was dispersed in isopropyl alcohol (IPA) at a concentration estimated to be *1.65 ± 0.21(g/ml)*. A 300-second sonication (40 kHz, 80W) process was applied prior to each experiment to overcome any serious agglomeration. The resulting suspension was drop cast onto holey carbon grids and SiO_2/Si substrates (*284.1 ± 0.75 (nm*) thick) for TEM and OM, respectively. A

graphene suspension, size-fractionated by sedimentation, was used for DLS study. This was characterized in standard quartz cuvette cells without any need for sample deposition.

TEM was initially carried out to determine the lateral dimension and size distribution of the flakes. Owing to the precision of the TEM measurement, the lateral size distribution was then used as a benchmark for further experiments. Flake thickness was estimated by the Mean Grey Value Ratio (MGVR) method which is based on normalised TEM Bright Field image contrast [4]. Direct imaging of folded graphene edges and low-loss electron energy loss spectroscopy (EELS) were used to provide complementary information for MGVR measurements. In addition, an image technique was developed so that the flake lateral size distribution could be obtained rapidly via quantification of several OM images. To develop an in-situ characterisation technique, DLS was performed to obtain the lateral size distribution of dispersed flakes. Although no precise or reliable parameters for graphene flakes dispersed in IPA exist in the literature, approximate optical parameters were used to perform the DLS analysis.

TEM measurements were conducted using an FEI Titan^3 Themis 300 S/TEM operated at 80 kV, which is below the threshold for knock-on damage [5]. TEM magnifications of 55,000 x and 295,000 x were used for the development of MGVR and folded edge methods respectively. EELS measurements were recorded in diffraction mode from an area of ca. 100nm in diameter. Use of STEM could improve the spatial resolution of such measurements in the future. An Olympus BX51 series reflection light microscope was employed for OM, using a 100x objective lens (N.A. = 0.95) and 163 ms exposure time; white balance and RGB ratio were optimised by the pre-installed AxioVision software. A Malvern Zetasizer Nano ZS series was employed for DLS using standard quartz cuvette cells. The sample was equilibrated to *25°C* for *120* seconds prior each measurement. The viscosity of IPA was set to be *2.32 cP* at *25°C*. Using a *633 nm* laser and by operating in backscatter mode (*173°* scattering angle), the particle size can be detected using optimized beam-positioning. Different material refractive indices (RI) and absorption coefficients (α) between graphene and graphite were used to derive number particle distributions (PSDs). Parameters of: (1) 1nm thick graphene *($RI_{graphene}$ = 2.225;α_{1nm} = 3%)* and (2) 3nm thick graphite *($RI_{graphite}$ = 1.942; α_{3nm}= 10%)* were employed [6]. Each of the PSDs were the average of 3 measurements. Image data was processed by Fiji or GMS 3. The Scipy package and OriginPro were used for data analysis and visualisation.

3. **Results**

3.1 Imaging techniques

Graphene flakes are often aggregated or partially folded, complicating images and making them hard to quantify. Example TEM images are shown in fig. 1 (a) and (b); lateral flake size measurements are illustrated by the yellow lines (Feret diameter). To further quantify TEM images, the Mean Grey Value Ratio (MGVR) method was used. Precise flake thicknesses were first estimated by (002) lattice imaging at folded flake edges and corresponding MGVR values were determined by $MGVR = \mu_s/\mu_v$, where μ_s is the MGV of the flake and μ_v is the MGV of the neighbouring vacuum region (figure 2(a)). A linear correlation between the MGVR and the flake thickness is shown in figure 2 (b). Using the following empirical expression, the number of graphene layers (n) can be estimated by:

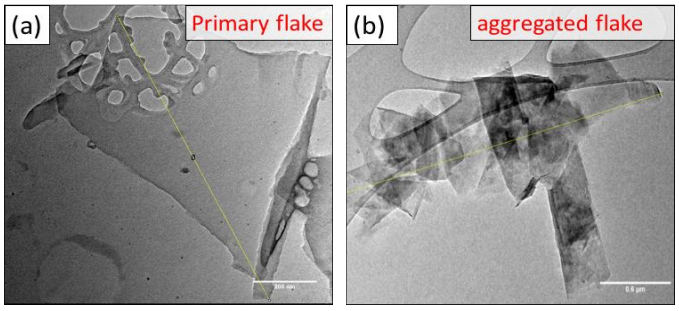

Figure 1. Bright field TEM image of graphene (a) primary flake and (b) aggregated flake. Size measurements are illustrated by yellow lines (Feret diameter)

$$n = MGVR - (1.0358 \pm 0.017)/(-0.012 \pm 0.001) \quad (1)$$

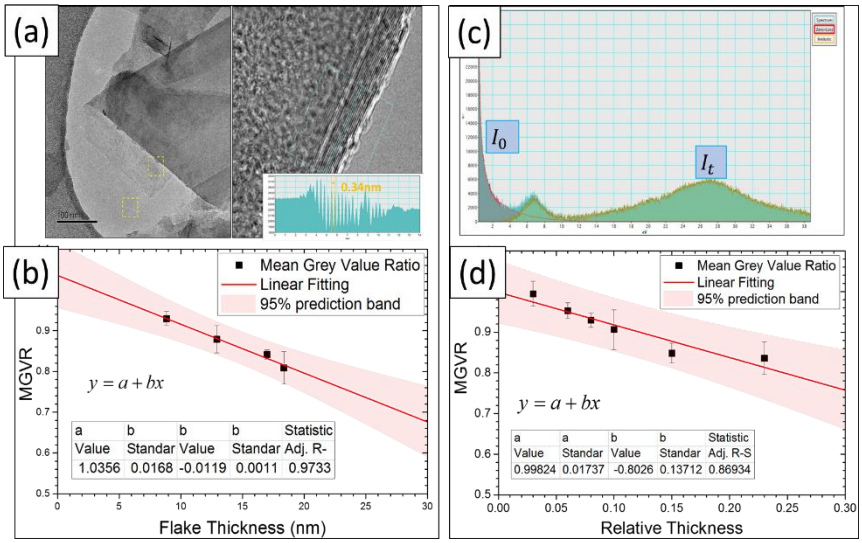

Figure 2. Flake thickness estimation by TEM. (a) and (b): comparison folded edge and MGVR method. (c) Low-Loss EELS spectrum and (d) comparison of relative thickness derived by MGVR and low-loss EELS

This relationship was further supported by calculating the relative thickness (t/λ) from the low-loss EELS spectrum. The relative thickness was calculated using $(t/\lambda) = \log(I_t/I_0)$. t and λ are the absolute thickness of sample and the electron inelastic mean free path in nm; I_t and I_0 are the integrated areas under the entire low-loss spectrum and the zero-loss peak respectively (figure 2(c)). Correlation between the MGVR and the relative thickness is shown in figure 2(d).

The distribution of lateral flake sizes was obtained by analysis of TEM images and showed mean sizes of $< D > = 0.619 \pm 0.32\mu m$ and $< D > = 1.236 \pm 0.43\mu m$ for primary and aggregated flakes, respectively (figure 3(c)). A similar bimodal distribution was obtained from OM. Using the variation of RGB contrast versus flake thickness, flakes of interest can be identified by a computer algorithm (figures. 3(a) and (b)). The size distribution was then derived via analysis of *6572* thin graphene flakes (blue spots) from several OM images, giving a mean *lateral size of* $< D > = 0.776 \pm 0.345\mu m$. As seen in Figure 3(c), the distribution was fitted by two Gaussians, exhibiting only *0.9 %* and *0.5 %* mean size differences from the distribution of primary and aggregated flakes derived by TEM. Owing to the increased sampling of flakes, a smoother distribution was obtained from OM as compared to TEM.

To gain insight into flake thicknesses, Eq.1 was used to estimate the thicknesses of primary and aggregated flakes as *37 ± 13 layers (MGVR = 0.884 ± 0.097)* and *76 ± 29 layers (MGVR=0.725 ± 0.191)* respectively. Although flake thicknesses are difficult

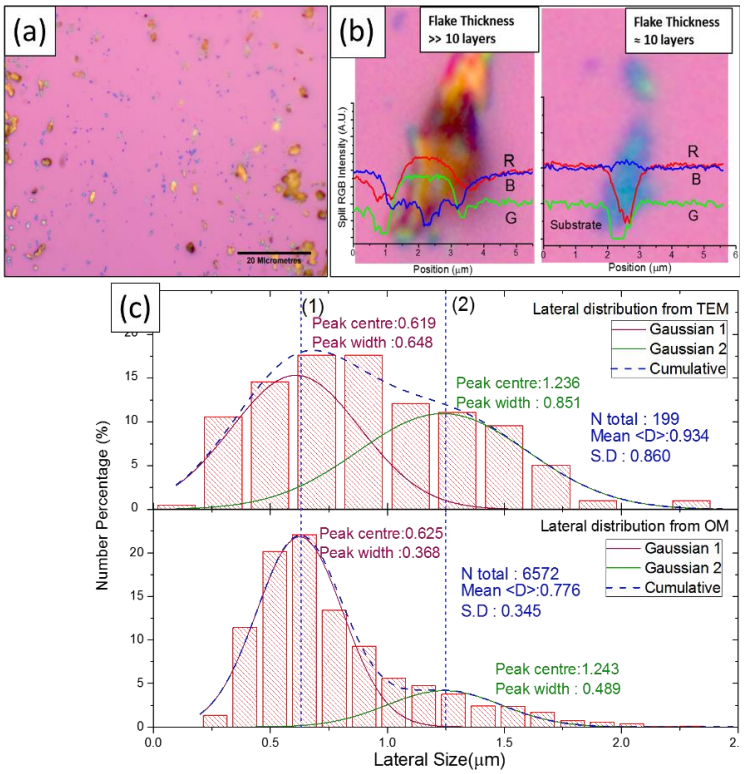

Figure 3. The lateral size distribution obtained by image analysis techniques: (a) an example of OM image. (b) Split RGB images of thick and thin graphene flakes. (c) Comparison of lateral size distributions obtained by TEM (above) and OM (below)

to determine precisely from the MGVR method, it is evident that flake aggregation is preferable vertically rather than horizontally. Determination of flake thickness by OM is even more difficult; even though it has been reported that flakes >>10 layers appear yellow/brown and flakes ~10 layers appear blue/purple on such SiO_2/Si substrates [7], inadequate colour resolution makes thickness estimation by OM highly imprecise.

3.2 Dynamic Light Scattering (DLS)

In DLS, the lateral flake PSD is highly influenced by sample concentration. Thus, the suspensions were size-fractionated to minimize uncertainty. In figure 4, the peak position of number PSD (Xc) from DLS was plotted versus the mean lateral flake diameter measured by OM (labelled as $< D >$). The Xc values using selected optical parameters are close to each other and scale linearly with $< D >$ on the log-log plot. This means the Xc is correlated to < D > by a power exponent. As in reference [8], the data was fitted using $Xc = a < D >^{b}$, where the exponent $b = 1.594 \pm 0.12$ and $a = 0.018 \pm 0.015$. Using the data in figure 4, we can write:

$$< D > = (12.433 \pm 4.33) Xc^{(0.627 \pm 0.05)} \quad (2)$$

For each of the size fractionated samples, DLS and OM results deviate by less than *22%* for flake sizes *< 1000 (nm)*, with results from DLS being consistently larger. The expression can provide an alternative approach for determining graphene lateral size distribution from DLS number PSD with a similar precision to direct imaging techniques in the sub-micrometre region. However, weaknesses of this approach arise from the effects of sample concentration, whereby the signal is too low to detect when the absorbance is *< 0.001(m^{-1})*. Also, though the deviations between DLS and OM are small in sub-micron region, it increases significantly for flake sizes *> 1000 nm*.

4. Conclusions:

We present a simple and rapid method to estimate the lateral size distribution of flakes of solution-processed graphene which is highly important for its applications. Using imaging and image analysis, good correspondence was found between precise measurements made by TEM and automated image analysis of OM images. Flake thickness was also estimated by MGVR of TEM images, which is difficult to achieve by OM. Results from DLS were then compared to the OM measurements, suggesting that DLS could provide a rapid screening for graphene lateral size distribution.

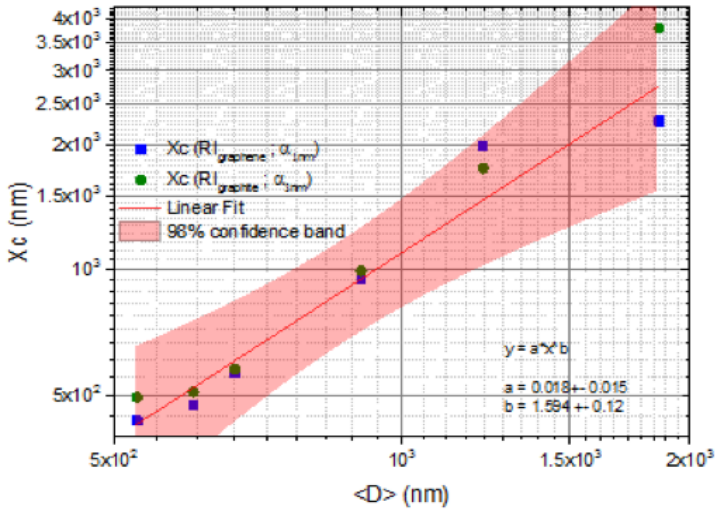

Figure 4. Plot of number PSD peak centre (Xc) versus flake mean lateral size < D >. The red line is the fitted power law dependence of Xc with < D >

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