Scanning Electronic Microscopy for Analysis of the Effects of Surfactants on De-Wrinkling and Dispersion of Graphene

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Abstract—Graphene was dispersed using a tip sonicator and the effect of surfactants were analysed. Sodium Dodecyl Sulphate (SDS) and Polyvinyl Alcohol (PVA) were compared to observe whether or not they had any effect on any de-wrinkling, and secondly whether they aided to achieve better dispersions. There is a huge demand for wrinkle free graphene as this will greatly increase its usefulness in various engineering applications. A comprehensive literature on de-wrinkling graphene has been discussed. Low magnification Scanning Electronic Microscopy (SEM) was conducted to assess the quality of graphene de-wrinkling. The utilization of the PVA has significant effect on de-wrinkling whereas SDS had minimal effect on the de-wrinkling of graphene.

Keywords—De-wrinkling, dispersion, graphene, scanning electron microscopy.

I. INTRODUCTION

SINCE 2004, graphene has risen to the top of the scientific and engineering domains. Its unique properties have sparked interest in many different research organisations, industries and governments. But despite this, it has yet to reach its full potential and still requires significant amount of research to be done. The super material is formed by carbon atoms joined by sp-2 bonds in a hexagonal pattern, but the real defining feature is that the material is only one atom layer thick. Graphene has the highest known tensile stiffness, is very brittle but is also very ductile [1]. These are very strange properties to have in tandem as they are contradicting and hence very interesting, not only for graphene by its self but also for the use of graphene in making composite materials [2]. Although these are very impressive traits for a material to have, arguably the most interesting of all is graphene's ability to conduct electricity [3]. This makes it a prime candidate to take over from silicone as the material used for computer chips, which could cause rise to a new generation of faster computers [4]. With more research it may be possible to create almost whole circuit boards made of solely graphene, by introducing other particles such as oxygen into local areas of the graphene, changing the electrical and mechanical properties of specific local areas to achieve the full capabilities

of a circuit board [4]. There is hope of using graphene in super capacitors which one day could be used in hybrid vehicles, laptops and mobile phones [5]. Thin graphene sheet is transparent and this combined with its other properties is an excellent choice as an optically transparent conductor which can and is being used to create flexible liquid crystal displays [6].

Andre Geim first used the scotch tape method to create single layer graphene flakes which were subsequently mounted on Silicone (Si) wafers making them visible through an optical microscope [7]. This discovery has led to significant research in a very small amount of time in the area of graphene. The majority of the work has developed around using graphene for electrical components because the material has shown carrier mobility in excess of 15000 cm2V-1 S-1 even in ambient conditions [7]. Other application for graphene in electronics includes transistors. Using thin film metals for use as transistors has always been an appealing theory but the fall down occurs as they are proven to be thermodynamically unstable. On the contrary, thin film graphene, in its de-wrinkled form is a stable materials and a comprehensive study was conducted by [8] for the use of graphene in field-effect transistors (FET).

Research carried out by [9] showed a broad scope of graphene's electrical properties. Graphene samples were obtained using micromechanical cleavage and the transferred to Si substrates. The key aspect of this experiment was to observe whether graphene had the same form of noise as that found in carbon nanotubes. During this experiment it was observed that the gate voltage was variable for different samples and in some cases changed in the same sample. It was found that this was caused by the trapped charges in the SiO2 substrate which are sensitive to temperature and environmental changes. The Nano-ribbon (confined) samples were then tested for carrier mobility. It was found that the mobility was ten times smaller than that of unconfined graphene. This also indicated that graphene can only be effectively used when it is in its de-wrinkled form.

In order to achieve large quantities of graphene needed for making compound materials, chemical conversion of graphite to graphene-oxide is the most viable method. After this process, the graphene sheets are oxygenated and still need to be chemically reduced to create the graphene sheets that are to be used. The process of manipulating the graphene-oxide, which is usually suspended in aqueous media, was compared to the suspension in organic solvents by [10]. This suspension

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was also to facilitate preparation for use in composite materials as that would be the next step in an industrial environment. There was also a suspension of graphene-oxide in water carried out in the exact same way as the organic solvents so that they could be compared to the currently used method. The results found that there were a few organic solvents that showed longer term stability in the dispersions than the water did. It was also observed that water, Dimethylformamide (DMF) and N-Methyl-2-pyrrolidone (NMP) had the smallest amounts of precipitate forming after a few days which showed that they had the best dispersing ability. The problem with some of these solvents is that they are quite hazardous, this poses a health and safety risk which would be advantageous to avoid if the method was incorporated into an industrial scale. The cost of environmental protection could render the process uneconomic. This may also cause problems in the case of equipment preservation. Many of the solvents used in the prior research were corrosive and hence when using equipment such as a tip sonicator, they would not be viable. Another technique to stabilize the dispersion of graphene in suspension is through the use or surface acting agents (surfactants), which subsequently allows the water to be used as the suspension liquid. In a recent work by [11], the surfactant sodium cholate was tested to find the effects that it would have on the stability of the specimens and especially how the graphene concentration could be increased. It was found that using the relatively low power bath sonicator created higher concentration dispersions compared to previous results using the tip sonicator, although it was mentioned that with the honing of the process, for the tip sonicator, this may vary. Transmission Electron Microscopy (TEM) was conducted to measure the number of layers per flake created a flaw in the experiment as the smaller flakes could have been missed. The study showed that the use of right surface acting agent could yield dispersions with quality that rivals that of using DMF or NMP solvents. The use of surfactants requires further study as to which is the best to use and also as a process that could be used for industrial mass production.

The synthesis of graphene is far from perfect, but increasing amounts of research are being conducted to make the process viable for future mass production. At the moment, graphene sheets have many wrinkles and some are as a result of the compressive stress caused during cooling by the difference in thermal expansion coefficients between graphene and metals [12]. These are sometime referred as stress-induced wrinkles. The most promising method of creating graphene seems to be the Chemical Vapour Deposition (CVD). This method allows for relatively large amounts of single/few layer graphene sheets to be created [13]. But this process has inherent problems as research has shown strong correlations between the wrinkles formed during growth of graphene in the CVD process and the morphology of the substrate used [14]. The use of images from SEM microscopes and Auger electron spectroscopy AES to compare the substrate morphology (wrinkles) was used in both studies by [14] and [15]. These wrinkles found in all graphene sheets whatever the method

used to create them, can lead to de-lamination [15] from the material on which the graphene is mounted. For electrical products, the wrinkles create a massive product variance as the wrinkles cause a change in conductivity from sheet to sheet and in extreme cases even in different local areas of the same sample [15]. This is a massive drawback as of yet, due to the fact that using Graphene sheets in a product with this variance would lead to each product having different specifications.

Currently, the practical uses of graphene are relatively because there are problems in creating graphene based samples that are useable and consistent. Therefore the de-wrinkling of graphene is an important issue. To fully realise graphene potential, key work must be carried out into removing the wrinkles prior to its positioning or dispersion in the product. There is already a fair amount of work completed in the area of dispersion for use in composites [10], [11], [16]-[18] but there seems to be a gap in the research when it comes to removing the wrinkles in the graphene using ultrasonication. The work that has been accomplished so far has not assessed the effects of de-wrinkling by the sonication and any differences caused by the surfactants.

This work has concentrated on a pre-emptive view and has tried to reduce the wrinkles created during synthesis of commercially supplied graphene powder. The current research of using surfactants to create graphene concentrated stable solutions will be analysed. At the moment only a few specific surfactants have been studied and hence there is scope for improvement by testing different ones. By comparing the dispersions achieved, the most viable way to create stable dispersions can be found. The concentration of surfactant and sonication time will be carefully monitored to produce the greatest results. Using chloroform with SDS would have been an option, but in water it creates a corrosive acid which would harm the tip of the sonicator. Therefore, in this study, non-hazardous mixtures will be placed into the high power tip sonicator in order to try and remove the wrinkles in the graphene sheets. In this part of the experiment, the key aspect will be the sonication time and the pattern in which it is sonicated, whether it is an on-off or a constant process. This pattern will have to be monitored closely not only for the results when trying to de-wrinkle but because in other studies it has shown that sonication can cause the graphene flakes to be cut into smaller flakes which may pose as a disadvantage after sonication.

II. Experimental Details

Selection of solvent and surfactant was the most critical step in this research. It was reported by [10] that graphene oxide can be dispersed very effectively in DMF, NMP, THF and ethylene glycol. These dispersions possessed long term stability when dispersed even three weeks after sonication. Apart from these solvents, water was tested alongside for comparison by [10]. The results for the water just after sonication and three weeks after were very similar to the solvents mentioned prior and hence it could be justified to use just the water. Arguably the main factor when choosing the

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solvent was the protection of the tip of the sonicator. The tip sonicator also came with a warning that very low surface tension liquids should not be used as a solvent as it could damage the tip sonicator. Therefore with the relatively similar results in the dispersion affect and the risk of damage to the machine it was decided that water was the best choice of solvent for this work. Similarly, there were many different choices when choosing surfactants. There are four different types of surfactants, i.e. Anionic, Cationic, Zwitterionic (amphoteric) and non-ionic surfactants. Anionic having a negatively charged head, Cationic having a positively charged head, Zwitterionic Having both a positively and negatively charged head and non-ionic having no charge at the head. Sodium Dodecyl Sulphate (SDS) [18] was chosen as an anionic surfactant for this work and polyvinyl alcohol (PVA) [19] was used as a non-ionic surfactant.

SDS (ACS reagent ≥99.0%) and PVA (average Mw=85,000-124,000 and 87-89% hydrolysed) and graphene nanopowder were supplied by Sigma-Aldrich, UK. For all samples, a glass beaker was filled with 100ml of de-ionised water at room temperature. Different surfactants were added at various concentrations. At this point the samples were treated differently to achieve solutions, as stated below. Once a solution was achieved and returned to room temperature, 0.0025g of graphene was placed into the solution with care taken to avoid any graphene sticking to the sides of the beaker. The graphene was weighed on a Denver high-sensitivity instrument scale. A Sonics Vibra-cell VCX 750 tip sonicator with a solid standard probe was used. Samples were sonicated for 5 minutes (10 seconds on and 5 seconds off) at 50% amplitude. The apparatus was set up in the fume cupboard. The tip of the sonicator was then placed in the centre of the beaker with the bottom aligned with the 50ml beaker marking. Once the sample had been sonicated it was removed from the fume cupboard and a micropipette tip was used to extract the sample. This was done by marking a distance of 20 mm on the micropipette tip, placing it into the centre of the beaker level with the 50ml line and extracting the sample up to the mark. This was then placed onto a sample mount with a sticker ready for use in the Scanning Electronic Microscope (SEM, FEI), labelled and left to dry (Fig. 1). The same procedure was carried out with the beaker and the mixer.

Five samples were produced in this work. Sample I was produced with no surfactant. Sample II was produced with 0.025 g of SDS. This was stirred by hand until all the SDS had dissolved. Sample III was produced with 1 g of SDS and in the same manner like sample II. Sample IV was produced with 1 g of 0.025 g of PVA. This was hand stirred and then placed into a vacuum oven. The PVA-water mixture was heated until all the PVA had dissolved. During heating the mixture was stirred at each 20°C increase in temperature. Once fully dissolved the solution was taken out of the oven and allowed to cool down to room temperature. Sample V was produced with 1 g of PVA and in the same manner like sample IV.

Fig. 1 De-wrinkled graphene sample collection prior to drying

III. Results and Discussion

SEM analysis of raw powdered graphene is shown in Fig. 2. Fig. 2 (a) shows the arrangement of raw graphene. It is clearly visible that there are many graphene sheets clustered together and highly wrinkled. This is detrimental for its use in composite materials as there is a need for the graphene to be evenly spread in the matrix. The work highlighted in [20] shows the importance for the dispersion of the material for use in Nano-composites and outlines some different ways of achieving this. The need for the stable dispersions is very high but its importance should be coupled with the de-wrinkling.

Fig. 2 (b) shows a few layer thick sample of graphene. The lighter areas of the image show where the graphene is wrinkled and as a result is crumpled. These are the areas that the sonication process should reduce. The area, in the middle, is very transparent and has no bright white sections. This indicates that there are very limited wrinkles here. There are only very small areas in these unsonicated samples which have such good quality transparency. It should be noted that although these de-wrinkled areas occur in graphene before sonication there are very few in proportion to those sheets which are highly wrinkled. Therefore images such as this are not a representative of graphene on the whole before sonication.

To compare the effect of surfactant on the de-wrinkling process, representative images at the 1000x and at representative areas were taken (Fig. 3). Firstly the dispersion is assessed by the distance between the individual graphene sheets. The greater the distance, the better the dispersion achieved. Next is the de-wrinkling affect, as stated before, the areas of highly wrinkled graphene appear bright white and the unwrinkled areas appear transparent. Therefore the sample with the more un-wrinkled graphene will have a higher proportion of sheets that appear transparent with less bright white areas witnessed.

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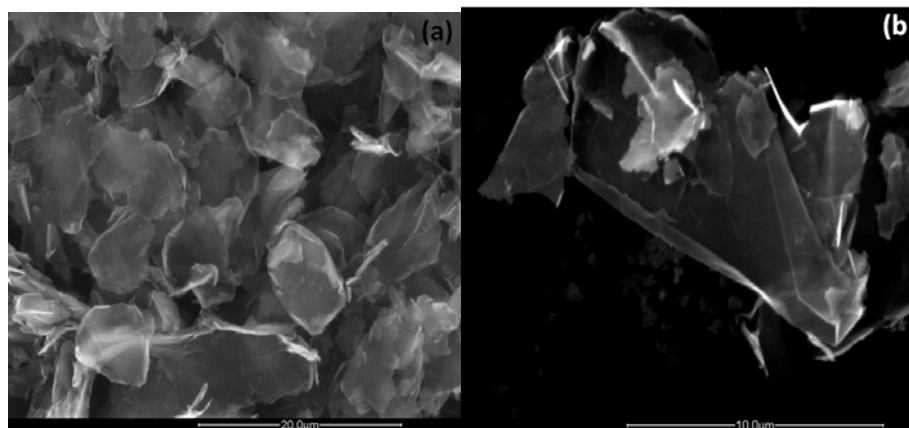Vol:9, No:6, 2015

Fig. 2 SEM images of raw graphene powder before de-wrinkling process
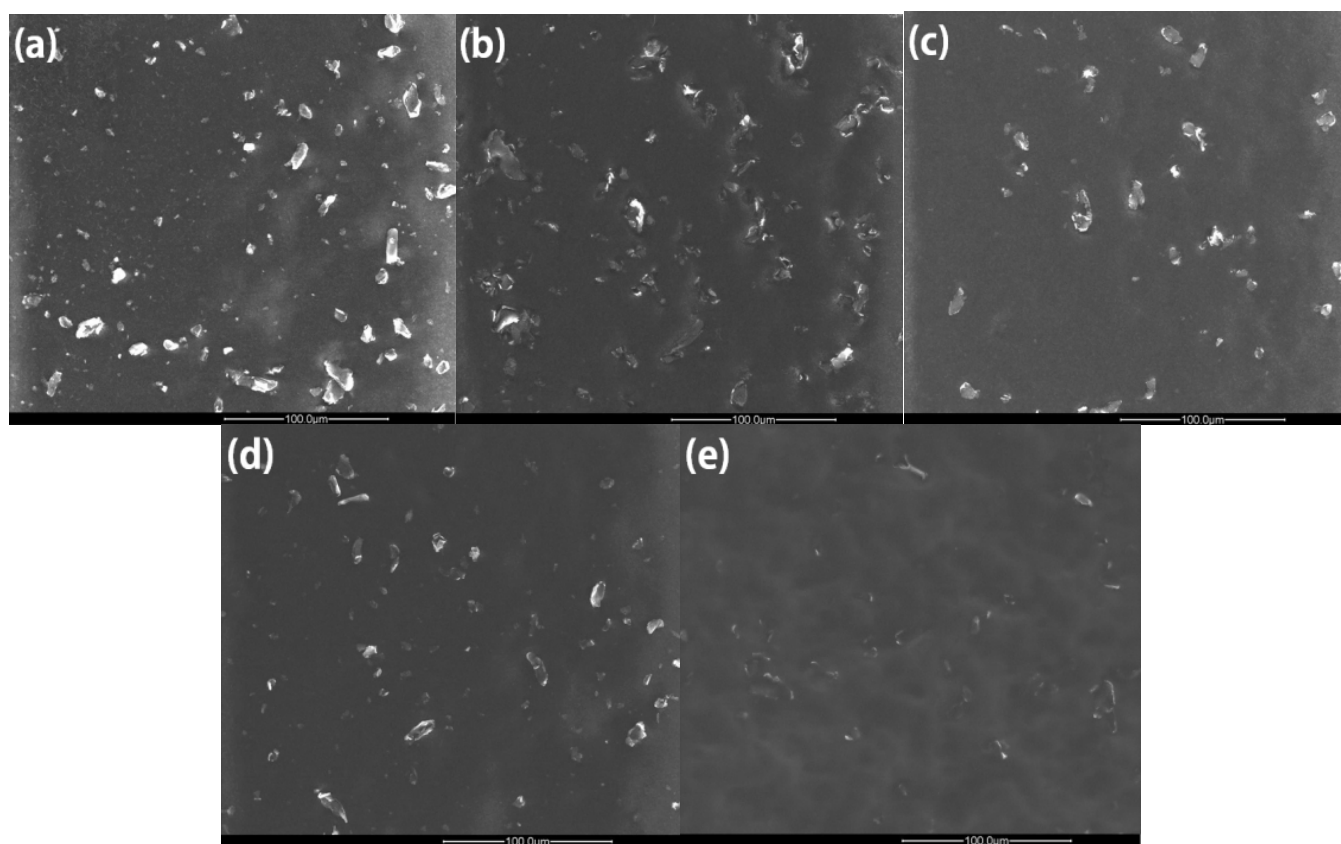

Fig. 3 SEM images of graphene before and after de-wrinkling process. (a) Sample I, no surfactant; (b) Sample II, 0.025 g of SDS; (c) Sample III, 1 g of SDS; (d) Sample IV, 0.025 g of PVA; and (e) Sample V, 1 g of PVA

Fig. 3 (a) confirms that graphene was not dispersed or de-wrinkled in de-ionized water. This can be seen as there are many graphene sheets close together. The quality of de-wrinkling is poor, concluded from the fact that there are many white patches observed from the low magnification analysis. In Fig. 3 (a), there seems to be some unwrinkled graphene sheet, as a result of high power tip sonication, but it does not seem to be consistent, as there are some very white patches. Fig. 3 (b) shows that good dispersion was achieved as there are very few graphene sheets present in the image. This is due to the general spacing between each sheet being increased meaning that only a few graphene sheets fit into the area that the image covers. As compared to Fig. 3 (a), lesser white patches can be observed as well. The majority of the graphene that can be observed in this image are transparent compared to Fig. 3 (a). When concentration of SDS solution was increased, it can be observed from Fig. 3 (c) that there was detrimental effect on the dispersion and de-wrinkling. Therefore, we can conclude that low concentration of SDS solution caused some de-wrinkling and dispersion as compared to de-ionised water solution.

From the analysis of Figs. 3 (d) and (e), it is clear that the PVA solution has achieved the best de-wrinkling and dispersion as compared to other samples. There are substantial amounts of small graphene sheets that are very transparent and of very light grey color. There are still some bright white areas indicating wrinkled or agglomerated graphene, but as a whole, there is a very high proportion that is unwrinkled. The central left side of Fig. 3 (e) has many transparent graphene sheets. From the analysis of these images, it's concluded that the material is highly unwrinkled and dispersed.

IV. Conclusion

There is a huge demand for wrinkle free graphene as this will greatly increase its usefulness in various engineering applications. A comprehensive literature on de-wrinkling graphene has been discussed to explain the importance of wrinkle free graphene. Low concentration of SDS solution showed visual evidence of minimal de-wrinkling and some dispersion. High concentration of PVA solution significantly improve dispersion and de-wrinkling as confirmed from the low magnification SEM analysis. It can also be concluded that the technique used in this work can be employed for quick dispersion and de-wrinkling analysis or to check the effectiveness of surfactants or solvents for de-agglomeration graphene. Further work would be aimed around honing the concentration of PVA in the solution to increase the de-wrinkling effect.

Acknowledgment

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