

Measuring Synthesis Yield in Graphene Oxide Synthesis by Modified Hummers Method

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Running head: Measuring GO synthesis yield

Synthesis of graphene oxide by modified Hummers method and measuring the synthesis yield were investigated. Based on the results, a comprehensive method to measure graphene oxide synthesis yield was proposed which will allow comparison of future literature results. Also changes are proposed to the exfoliation procedure to improve the yield of the modified Hummers synthesis. With the proposed method, systematic error of the concentration measurement was calculated to be $\pm 0.08 \times 10^{-3} \text{ gmL}^{-1}$. Additionally changes proposed to the graphene oxide exfoliation process can improve the synthesis yield up to 70 %.

1. Introduction

Quantifying the graphene oxide (GO) synthesis by Hummers method^[1] or its derivatives including a mechanical exfoliation step^[2] has expanded in the recent years. Studies have been conducted to quantify the effect of synthesis parameters such as ultrasonic exfoliation, on the size of graphene oxide platelets^[3-6], Yield of graphene oxide^[5-9] and the oxidation process^[10]. In the case of graphene oxide synthesis yield, a detailed measurement method has been reported only in few exceptions^[6, 11] but in majority of publication it has not been reported^[5, 7, 8, 9, 12]. In studies where method has not been reported, the reported conversion/yield rates can be misleading since mass of graphite oxide is different to pristine graphite^[13], and additionally because the yield of the synthesis is low in absolute mass and prone to be substantially changed by measurement error.

As above discussed, literature holds very few accounts of detailed concentration measurements of synthesized graphene oxide suspension. Problem of measuring the mass seems trivial at first glance but the challenges lay in the structure of graphene oxide. The important interconnected reasons for difficulties include: 1. Graphene oxide can hold up to 25 wt. % of

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adsorbed water and 2. The graphene oxide starts to decompose at temperature around 373 K, which makes it difficult to completely remove water from the graphene oxide [2, 11, 13]. In their study, Fan et al. [11] introduced a detailed description of the calculation of the graphene oxide suspension concentration which is particularly interesting. In this study we will review Fan's concentration measurement procedure and kindly propose improvements to it, to make it more useful and accurate. This would help to improve the comparability of future studies which present results on graphene oxide concentration in suspensions or measure for example mass balance of graphene oxide composites. To do this we introduce a comprehensive method to analyse systematic error for the suspension concentration and synthesis yield measurements.

2. Experimental Section

2.1 Materials and Graphene Oxide Synthesis

Graphite oxide was synthesized using the modified Hummers method described by Fan et al. [11]. Some liberties were taken by using a different type of precursor graphite powder (Synthetic, APS 7-11 μm , 99 % purity, Alfa Aesar), dialysis in a dialysis tubing (12 - 14 kDa, SpectraPor 4, Spectrum laboratories Inc.) for 6 days according to the instructions of the manufacturer and using a modified ultrasonic treatment with a high power ultrasonic probe (13 mm diameter probe, maximum amplitude 114 μm , 20 kHz, VCX 750 W, Sonics Inc.). All suspensions were treated with ultrasound in 250 mL batches as recommended by the probe manufacturer. To exfoliate graphite oxide, synthesized and dialyzed suspension (with 0.5 g of precursor graphite) was first diluted with ion exchanged water (to a total volume of 250 mL). Mixture was first sonicated for 10 min with 80 % of maximum amplitude (A). Then the mixture was diluted with additional ion exchanged water (250 mL) and the following sonications were carried out in 250 mL batches, one after another: 10 min 50 % A, 10 min 30 % A, 10 min 20 % A and 10 min 20 % A. In total the suspension was scanned with different amplitudes of ultrasound for 50 min. Sonication procedure was divided into shorter sections to avoid excessive heating of the mixture. Finally the sonicated suspension was centrifuged

for 20 min with 3900 rpm to remove any larger or unreacted particles after which the brown supernatant colloidal suspension was pipetted into a flask.

The same synthesis was performed also with 1.5 g of precursor graphite (other synthesis parameters scaled up accordingly) to verify results. Also a batch with decreased sonication time (10 min 80 % A and 10 min 30 % A) was prepared to study its effect on graphene oxide yield.

2.2 Measuring the synthesis yield

Yield of the synthesis was measured using the process suggested by Fan et al. ^[11] with modifications introduced here and discussed further in chapter 3 where the systematic error of the process is analysed. Shortly: a 2 mL glass vial was heated in vacuum (2.5 mbar) for 24 hours at 60 °C and weighed immediately. Then 20 mL of graphene oxide suspension was measured using a 20 ml laboratory injection syringe and heated in the 2 mL glass vial few drops at a time at 80 °C in normal atmosphere to remove most of the water from the suspension. Next the vial and graphene oxide was heated in 60 °C in vacuum (2.5 mbar) for 24 hours to further remove water then weighed immediately. Vacuum furnace was pressurized using nitrogen gas.

2.3 Characterization of the Synthesized Graphene Oxide

The graphene oxide platelet thicknesses were measured with an atomic force microscope (AFM). For AFM characterization, the synthesized graphene oxide suspension was further diluted by adding one drop of suspension in to 50 mL of ion exchanged water. A drop of diluted suspension was then added on a cleaved mica substrate (1 x 1 cm, Agar scientific) and left to dry in an exicator for 24 hours. Measurements were done using an atomic force microscope (AFM, Nanoscope E AFM/STM, Veeco Instruments Inc.) with a pyramidal probe and a 200 µm long triangular silicon nitride cantilever with a spring constant of 0.12 Nm⁻¹. Measurements were performed in contact mode. Cylindricity and tilt of the mica substrate was corrected in the AFM images using the Veeco Vision software tools.

Lateral size distribution was measured using dynamic light scattering (DLS). For DLS characterization, few drops of synthesized suspension were diluted into 20 ml of ion-exchanged

water. Resulting suspension was mixed and few drops were pipetted into a plastic measurement cuvette. Measurements were done using a DLS equipment (ZetaSizer Nano ZS, 25 °C, scattering angle 173°) and results were averaged from 3 different measurements (11 measuring runs for 10 seconds each per each measurement).

3. Results and Discussion

Concentration of the obtained graphene oxide suspension was first measured using the procedure suggested by Fan et al. ^[11]. The results indicated that the yield had increased over 1.5 times compared to what they had reported. This raised a need to analyse and lower the systematic measurement error to see if the difference was due to measurement error of graphene oxide dry mass or due to the modified synthesis. As stated earlier, it is highly probable that it is too difficult to remove all water from the graphene oxide without decomposing it ^[2]. Therefore obtaining the virgin mass of graphene oxide by drying is difficult. The best target would be to use a standard method (such as proposed by Fan et al.) of measuring the dry weight to obtain comparable results for example when calculating mass balance for composites containing graphene oxide.

3.1 Method to Measure Graphene Oxide Synthesis Yield and Suspension Concentration

In the evaluation of the systematic measurement error, sources of error were identified and modified to lower systematic error to an acceptable level. We identified three independent systematic error sources. **First**, results indicate that error in the mass measurement results is highly influenced by the glass container volume used in the measurement since measurements are done in the magnitude of milligrams. As well known, the container walls adsorb water in atmospheric conditions and the amount of water is proportional to the surface area of the container. When a vessel is heated, most of the moisture can be removed but the adsorption begins again immediately as the vessel cools down. Therefore small vessels of 2 - 3 mL are recommended for measurements, which will yield significantly smaller error in weight measurements even if they are allowed to cool down before weighing. Additionally 20 - 40 mL of suspension is recommended to use per measurement since then the mass of the dried graphene oxide is then proportionally large enough to overcome the error

caused by vessel water adsorption. 20 - 40 mL can be dried in the 2-3 mL vessel few drops at a time. 2 ml vessel was weighed to give a maximum error of $\pm 0.5 \times 10^{-3}$ g. **Secondly**, we found that although accuracy of the used scales is estimated by the manufacturers to be around $\pm 0.1 \times 10^{-3}$ g, which is sufficient for the purpose, the difference in measured mass between two different scales can be as high as $\pm 1.0 \times 10^{-3}$ g. This has to be taken into account when comparing the results. **Thirdly**, an error occurs from measuring the volume of the suspension. We used 20 mL laboratory injection syringes in which the maximum error was estimated to be ± 0.1 mL. When changed into equivalent mass of graphene oxide, in the best yield scenario of our synthesis (1.00×10^{-3} gmL⁻¹), volume measurement error yields a mass error of $\pm 0.1 \times 10^{-3}$ g. In total, systematic concentration measurement error was calculated to be $\pm 0.08 \times 10^{-3}$ gmL⁻¹ for 20 mL of dried and weighed graphene oxide suspension. **Table 1** summarizes the systematic error analysis and the calculated systematic error for mass measurements. Proportionally the error decreases further if the suspension volume (total mass of graphene oxide) is increased. Further on, to obtain random error, mass measurements should be conducted at least three times to the same suspension batch.

Measured graphene oxide suspension concentrations, synthesis yield and used synthesis parameters of current study and selected literature results are summarized in **Table 2**. Since dilution during the synthesis can vary, concentrations are normalized. Normalization of results was done on basis of 500 mL dilution for 0.5 g of precursor graphite (1000 mL for 1.0 g etc...). Results indicate that lowering the graphite precursor particle size and modifying the ultrasonic treatment can increase the synthesis yield up to 70 %.

3.2 AFM Characterization of the Synthesized Graphene Oxide

Atomic force microscope (AFM) measurements were conducted to verify the physical dimensions and thickness of the synthesized graphene oxide platelets.

Numerous platelets of graphene oxide were easily detected in contact mode AFM. Example AFM image of a graphene oxide platelet is shown in **Figure 1**. It was chosen to show a single and double layer configuration in a single platelet indicating that exfoliation is not entirely perfect in all

of the platelets, although found only in one platelet in this test. Thickness of most of the measured platelets were found to be of roughly 1 nm and individual platelets with thickness significantly less than 1 nm were not found, leading to a conclusion that single layer graphene oxide platelets were successfully obtained in the synthesis. Line profiles of graphene oxide platelets in the AFM images were measured to confirm the thickness of the layers. Line profiles of the chosen graphene oxide platelet are shown in **Figure 2**. Thickness of individual graphene sheets are known to have van der Waals thickness of 0.34 nm, but the graphene oxide sheet thickness increases due to addition of surface groups. Contact mode AFM can yield a high background noise to the measurement data and careful sample preparation and image processing is required to successfully interpret the data.

3.3 DLS characterization of Graphene oxide Lateral Size

Dynamic light scattering (DLS) results indicate that highest fraction of platelets are approximately 800 nm in width, although suspension exhibits a wide size distribution. Results of DLS measurements are summarized in **Figure 3**. Also a population of platelets below 100 nm exists. The measurement is based on the assumption that the largest detected diameters represent the true platelet sizes. This is backed by the fast decline of signal after 800 nm. Size distribution at lower diameter than 800 nm could arise also from platelets positioned against the laser beam so that the full diameter is not obtained, therefore DLS results below the largest diameters can be largely ignored excluding the peak around 100 nm. DLS results are well in line with the AFM characterization results.

4. Conclusions

A comprehensive method was proposed to evaluate the systematic error in graphene oxide synthesis yield measurement, which was calculated to give a sufficiently small error of $\pm 0.08 \times 10^{-3} \text{ gmL}^{-1}$. Current results indicate that using a precursor graphite powder with smaller average particle size and that changing the ultrasonic treatment parameters can increase the yield of graphene oxide synthesis by up to 70 % (in gmL^{-1}), which was confirmed by the new measurement method. Current results suggest that synthetic graphite can also result in a high synthesis yield ^[5], if sonication

process is modified. Difference in time efficiency of proposed process (50 min) and references ^[5] and ^[6] (up to 12 hours) can be attributed to major differences in the used ultrasonic process, power and equipment.

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References

- [1] W. S. Hummers, R. E. Offeman, "Preparation of graphitic oxide" *American Chemical Society* **1958**, 80, 1339-1340
- [2] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia et al. "Synthesis of graphene based nanosheets via chemical reduction of exfoliated graphite oxide" *Carbon* **2007**, 45, 1558-1565.
- [3] J. Jia, C-M. Kan, X. Lin, X. Shen, J-K. Kim "Effects of processing and material parameters on synthesis of monolayer ultralarge graphene oxide sheets" *Carbon* **2014**, 77, 244-254
- [4] L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang, Y. Chen, "Size-controlled synthesis of graphene oxide sheets on a large scale using chemical exfoliation" *Carbon* **2009**, 3365-3380
- [5] C. Botas, A. M. Pérez-Mas, P. Álvarez, R. Santamaría, M. Granda, C. Blanco et al. "Optimization of the size and yield of graphene oxide sheets in the exfoliation step" *Carbon* **2013**, 63, 562-592
- [6] U. Sierra, P. Álvarez, R. Santamaría, M. Granda, C. Blanco, R. Menéndez, "A multi-step exfoliation approach to maintain the lateral size of graphene oxide sheets" *Carbon* **2014**, 80, 830-832
- [7] J. Chen, B. Yao, C. Li, G. Shi, "An improved Hummers method for eco-friendly synthesis of graphene oxide" *Carbon* **2013**, 64, 225-229
- [8] T-T. Wu, J-M. Ting, "Preparation and characteristics of graphene oxide and its thin films" *Surface and Coatings Technology* **2013**, 231, 487-491

- [9] N. M. Huang, H. N. Lim, C. H. Chia, M. A. Yarmo, M. R. Muhamad, "Simple room-temperature preparation of high-yield large-area graphene oxide" *International Journal of Nanomedicine* **2011**, 6, 3443-3448
- [10] A. Esmacili, M.H. Entezari, "Facile and fast synthesis of graphene oxide nanosheets via bath ultrasonic irradiation" *Journal of Colloid and Interface Science* **2014**, 432, 19-25
- [11] Y. Fan, W. Jiang, A. Kawasaki "Highly conductive few-layer graphene/Al₂O₃ nanocomposites with tunable charge carrier type" *Adv. Funct. Mater.* **2012**, 22, 3882-3889.
- [12] Z. Luo, Y. Lu, L. A. Somers, A. T. C. Johnson, "High yield preparation of macroscopic graphene oxide membranes" *Journal of American Chemical Society* **2009**, 131, NO. 3, 898-899
- [13] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff "The chemistry of graphene oxide" *Chem. Soc. Rev.* **2010**, 39, 228-240